

DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**EFFECTS OF FILLER TYPE AND
MORPHOLOGY ON THERMOPLASTIC
NANOCOMPOSITES: THERMAL, ELECTRICAL
AND MECHANICAL PROPERTIES**

by
Tuba EVGİN

March, 2020
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MORPHOLOGY ON THERMOPLASTIC
NANOCOMPOSITES: THERMAL, ELECTRICAL
AND MECHANICAL PROPERTIES**

**A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of Dokuz Eylül University
In Partial Fulfillment of the Requirements for the Degree of Doctor of
Philosophy in Mechanical Engineering, Energy Program**

**by
Tuba EVGİN**

**March, 2020
İZMİR**

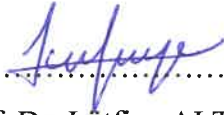
Ph. D. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled “EFFECTS OF FILLER TYPE AND MORPHOLOGY ON THERMOPLASTIC NANOCOMPOSITES: THERMAL, ELECTRICAL AND MECHANICAL PROPERTIES” completed by TUBA EVGİN under supervision of ASSOC. PROF. DR. ALPASLAN TURGUT and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy.

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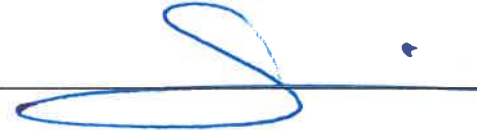

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EFFECTS OF FILLER TYPE AND MORPHOLOGY ON THERMOPLASTIC NANOCOMPOSITES: THERMAL, ELECTRICAL AND MECHANICAL PROPERTIES

ABSTRACT

In recent years, polymer nanocomposites reinforced by carbon-based nanofillers, especially multiwall carbon nanotubes (MWCNTs) and graphene nanoplatelets (GnPs), have received increasing attention due to their potentials as tailored materials with improved properties. Many studies have been reported that these nanocomposites exhibit better enhancement in thermal, electrical, and mechanical properties compared the nanocomposites with other filler materials. However, the dispersion of carbon-based nanofillers within the polymers is the bottleneck impeding their applications and the performance of the nanocomposites including them. The incorporation of hybrid nanofillers into polymer matrix is the easiest method to overcome this problem.

The main objective of this thesis is to investigate the effects of synergic, weight ratio and size of carbon-based nanofillers on the thermal, electrical, and mechanical properties. For this purpose, two different dimensions of MWCNTs and three different dimensions of GnPs were used to investigate the size effect on the high-density polyethylene (HDPE)-based nanocomposites properties. All samples were prepared by using melt mixing, followed by compression molding. To better understand size and synergic effects, first, the size effect of carbon-based nanofillers on the properties of nanocomposites including MWCNTs or GnPs alone were investigated. Then, MWCNTs and GnPs exhibiting the best performance were simultaneously added into the matrix to investigate the synergic effect between nanofillers. Finally, these properties of the hybrid nanocomposites including GnPs and CNTs with different sizes were investigated experimentally to determine optimum filler weight ratio and size which maximally enhance certain properties.

Keywords: Polymer nanocomposites, carbon-based nanofillers, thermal conductivity, electrical conductivity, mechanical properties, thermal properties

DOLGU MADDESİ TİPİ VE MORFOLOJİSİNİN, TERMOPLASTİK NANOKOMPOZİTLERE ETKİLERİ: ISIL, ELEKTRİKSEL VE MEKANİK ÖZELLİKLER

ÖZ

Son yıllarda, iyileştirilmiş özelliklere sahip malzeme olabilme potansiyelleri nedeniyle karbon-bazlı katkı maddeleri, özellikle karbon nanotüp (KNT) ve grafen nano plakalar (GnP), ile güçlendirilmiş polimer nanokompozitler artan ilgi görmektedir. Diğer katkı maddeli kompozitlerle karşılaştırıldığında, bu kompozitler ısı, elektriksel ve mekanik özelliklerde daha iyi bir artış göstermektedir. Fakat, karbon-bazlı katkı maddelerinin polimerlerdeki dağılımı, uygulamalarını ve onları içeren nanokompozitlerin performansını kısıtlayan bir engeldir. Bu sorunu çözmek için en basit yöntem hibrit katkı maddelerinin polimer matrise eklenmesidir.

Bu tezin temel amacı, karbon bazlı katkı maddelerinin sinerjik etkisinin, ağırlık oranının ve boyutunun ısı, elektriksel ve mekanik özellikler üzerine etkilerini incelemektir. Bu amaçla, katkı maddesinin boyutunun yüksek yoğunluklu polietilen (YYPE)-bazlı nanokompozitlerin özellikleri üzerine etkisinin incelenmesi için, farklı en-boy oranına sahip iki tip KNT ve farklı boyutlara sahip üç tip GnP kullanılmıştır. Tüm numuneler eriyik harmanlama yöntemi ve ardından kalıp sıkıştırma yöntemi kullanılarak hazırlanmıştır. Boyut ve sinerjik etkisini daha iyi anlamak için, ilk olarak, sadece KNT veya GnP içeren nanokompozitlerin özellikleri üzerine karbon-bazlı katkı maddelerinin boyut etkisi araştırılmıştır. Daha sonra, katkı maddeleri arasındaki sinerjik etkiyi araştırmak için en iyi performansı gösteren KNT ve GnP aynı anda matrise eklenmiştir. Son olarak, bu özellikleri en iyi şekilde artıran katkı maddelerinin optimum dolgu ağırlık oranını ve boyutunu belirlemek için farklı boyutlarda GnP'ler ve KNT'ler içeren hibrit nanokompozitlerin özellikleri deneysel olarak incelenmiştir.

Anahtar Kelimeler: Polimer nanokompozitler, karbon-bazlı katkı maddeleri, ısı iletkenlik, elektriksel iletkenlik, mekanik özellikler, ısı özellikler

CONTENTS

	Page
Ph. D. THESIS EXAMINATION RESULT FORM	ii
ACKNOWLEDGEMENT	iii
ABSTRACT.....	v
ÖZ	vi
LIST OF FIGURES	xii
LIST OF TABLES	xvii
 CHAPTER ONE - INTRODUCTION	 1
1.1 Introduction	1
1.2 Motivation of the Thesis.....	11
1.3 Objectives of the Thesis	13
1.3 Organization of the Dissertation.....	14
 CHAPTER TWO - BACKGROUND.....	 16
2.1 Polymers.....	16
2.2 Properties of Polymers	17
2.2.1 Electrical Conductivity of Polymers.....	18
2.2.2 Thermal Conductivity of Polymers	22
2.2.2.1 Thermal Conductivity in Crystalline Structure.....	23
2.2.2.2 Thermal Conductivity in Amorphous Structure	25
2.2.2.3 Thermal Conductivity in Polymer	26
2.2.3 Mechanical Properties of Polymers	36
2.2.4 Thermal Properties of Polymers	41
2.3 Polymer Nanocomposites.....	44
2.3.1 Carbon-Based Materials	47
2.3.1.1 Graphene	51
2.3.1.2 Carbon nanotubes.....	54
2.4 Methods for the Preparation of Polymer Nanocomposite	56
2.4.1 In-Situ Polymerization.....	57

2.4.2 Solution Mixing	58
2.4.3 Melt Mixing	59
2.5 Properties of Polymer Nanocomposites	61
2.5.1 Electrical Conductivity of Polymer Nanocomposites	61
2.5.1.1 AC Conductivity of Polymer Nanocomposite	64
2.5.1.2 DC Conductivity of Polymer Nanocomposite	68
2.5.2 Thermal Conductivity of Polymer Nanocomposite	71
2.5.3 Mechanical Properties of Polymer Nanocomposites	81
2.5.4 Thermal Properties in Polymer Nanocomposites	82
CHAPTER THREE - LITERATURE REVIEW	85
3.1 Polymer Nanocomposites with MWCNTs	85
3.2 Polymer Nanocomposites with GnPs	104
3.3 Hybrid Polymer Nanocomposites	118
CHAPTER FOUR - MATERIALS & METHODS	133
4.1 Materials	133
4.1.1 High Density Polyethylene	133
4.1.2 Multiwall Carbon Nanotubes (MWCNTs)	133
4.1.3 Graphene Nanoplatelets (GnPs)	134
4.2 Preparation of Nanocomposites	136
4.3 Measurement Methods	136
4.3.1 Characterization	136
4.3.2 Electrical Conductivity Measurement	137
4.3.3 Measurements of Mechanical Properties	137
4.3.4 Volumetric Heat Capacity Determination	138
4.3.4.1 Density Measurement	138
4.3.4.2 Specific Heat Capacity Measurement	140
4.3.4.3 Calculation of Volumetric Heat Capacity	141
4.3.5 Thermal Diffusivity Measurements	143
4.3.5.1 The Photothermal Radiometry (PTR) for the HDPE/MWCNTs Nanocomposites	143

4.3.5.2 The Photothermal Radiometry (PTR) for the HDPE/GnPs and Hybrid Nanocomposites	145
4.3.6 Thermal Analysis	146
CHAPTER FIVE - HDPE/MWCNTS NANOCOMPOSITES	147
5.1 Abstract	147
5.2 Introduction	147
5.3 Materials and Methods	151
5.4 Results and discussion.....	151
5.4.1 Characterization	151
5.4.1.1 XPS Results of HDPE/MWCNTs Nanocomposites	151
5.4.1.2 XRD Results of HDPE/MWCNTs Nanocomposites	153
5.4.1.3 FTIR Results of HDPE/MWCNTs Nanocomposites.....	154
5.4.1.4 Morphological Results of HDPE/MWCNTs Nanocomposites.....	155
5.4.2 Electrical Conductivity	157
5.4.3 Thermal conductivity	161
5.4.4 Mechanical Properties	163
5.4.5 Thermal Properties.....	165
5.4.5.1 DSC Results of HDPE/MWCNTs nanocomposites	165
5.4.5.2 TGA Results of HDPE/MWCNTs nanocomposites	166
5.5 Conclusions	169
CHAPTER SIX - HDPE/GNPS NANOCOMPOSITES.....	171
6.1 Abstract	171
6.2 Introduction	171
6.3 Materials and Methods	173
6.4 Results and Discussion	173
6.4.1 Characterization	173
6.4.1.1 XPS Results of HDPE/GnPs Nanocomposites	173
6.4.1.2 XRD Results of HDPE/GnPs Nanocomposites	175
6.4.1.3 FTIR Results of HDPE/GnPs Nanocomposites.....	176
6.4.1.4 Morphological Results of the HDPE/GnPs nanocomposites.....	177

6.4.2 Electrical Conductivity	179
6.4.3 Thermal conductivity	184
6.4.4 Mechanical Properties	186
6.4.5 Thermal Properties.....	189
6.4.5.1 DSC Results	189
6.4.5.2 TGA Results.....	189
6.5 Conclusion.....	192
CHAPTER SEVEN - HYBRID NANOCOMPOSITES.....	194
7.1 Abstract	194
7.2 Introduction	196
7.3 Materials and Methods	201
7.4 Results and Discussion.....	201
7.4.1 Characterization.....	202
7.4.1.1 XRD Results of Hybrid Nanocomposites	202
7.4.1.2 FTIR Results of Hybrid Nanocomposites.....	204
7.4.1.3 Morphological Results	206
7.4.2 Electrical Conductivity	213
7.4.2.1 Comparison of electrical properties of the HDPE/GnPs and HDPE/MWCNTs nanocomposites	214
7.4.2.2 The Electrical conductivity of the HDPE/G2 (11.70 wt.)/M12 nanocomposites.....	216
7.4.2.3 The Electrical conductivity of the HDPE-based hybrid nanocomposites.....	220
7.4.3 Thermal conductivity.....	233
7.4.3.1 Comparison of thermal conductivity of the HDPE/GnPs and HDPE/MWCNTs nanocomposites	235
7.4.3.2 The thermal conductivity of the HDPE/G2 (11.70 wt.)/M12 nanocomposites.....	237
7.4.3.3 The thermal conductivity of the hybrid nanocomposites.....	240
7.4.4 Mechanical Properties	252

7.4.4.1 Comparison of mechanical properties of the HDPE/GnPs and HDPE/MWCNTs nanocomposites	252
7.4.4.2 The mechanical properties of the HDPE/G2 (11.70 wt.%)/M12 nanocomposites.....	255
7.4.4.3 The mechanical properties of the hybrid nanocomposites.....	257
7.4.5 Thermal Properties.....	265
7.4.5.1 DSC Results	265
7.4.5.2 TGA Results.....	271
7.5 Conclusion.....	277
CHAPTER EIGHT - CONCLUSIONS & RECOMMENDATIONS	283
REFERENCES.....	294
APPENDICES	328

LIST OF FIGURES

	Page
Figure 2.1 Electrical conductivity and resistivity of materials	21
Figure 2.2 Schematic representation of the band theory of electronic conduction: a) insulators; b) semi-conductors and c) conducting materials. The hatched bands are allowed bands, the cross hatched bands are occupied	21
Figure 2.3 Thermal conduction in matter by collision of particles	23
Figure 2.4 Thermal conductivity mechanism in a crystalline material	24
Figure 2.5 Thermal conductivity mechanism in an amorphous material	24
Figure 2.6 Schematic comparison by the Newton pendulum of thermal conductivity in a) crystalline materials and b) polymers	25
Figure 2.7 a) Representation of lattice by spring-mass system, b) non-vibrating atom and c) phonon generation by lattice vibration	26
Figure 2.8 Schematic symbol of phonon	27
Figure 2.9 The mechanism of thermal conduction in amorphous polymers. Different atoms in the molecules of polymer are shown by different size and color	27
Figure 2.10 Phonon scattering modes of a) phonon-phonon scattering, b) phonon-impurity scattering and c) phonon-boundary scattering.....	28
Figure 2.11 Phonon scattering in crystalline materials, because of different defects	29
Figure 2.12 The mean free paths of phonon because of different scattering modes..	31
Figure 2.13 The structure of a) a polymer includes crystalline and amorphous domains, b) of a polymer chain	34
Figure 2.14 The Stress-strain curves of three types of polymers.....	38
Figure 2.15 The stress-strain curve of 6,6-nylon, a typical thermoplastic	39
Figure 2.16 Necks are not stable in amorphous polymers, since local alignment strengthens the necked region and decreases its rate of deformation	40
Figure 2.17 DSC thermogram of a polymer.....	43
Figure 2. 18 General considerations for the production of nanocomposite with high properties.....	46

Figure 2.19 Different carbon allotropes and derived structures.....	49
Figure 2.20 Thermal conductivity of carbon allotropes.....	50
Figure 2.21 Graphene chemical structure and its important physical properties (The black dots represent carbon atoms)	53
Figure 2.22 Schematic of the GnPs preparation beginning from natural graphite. The typical black powder obtained after liquid phase exfoliation and solvent evaporation is constituted by a mixture of single and few layer graphene and nanostructured graphite	53
Figure 2.23 a) the structural types of CNTs and the carbon network orientation in zigzag (n, 0) and armchair (n, n); b) SWCNT, DWCNT and MWCNTs	55
Figure 2.24 Tunneling and hopping transport of charge carriers	63
Figure 2.25 a) Schematic of the percolation theory in the polymer b) the electrical conductivity of polymer nanocomposites vs. the filler concentration	69
Figure 2.26 Illustration of the percolation threshold based on the aspect ratio of the filler materials(Jouni et al., 2017)	70
Figure 2.27 Schematic representation of thermal conductivity at filler-matrix interface	74
Figure 2.28 Thermal conduction mechanism in polymer/crystalline nanofiller with a) a continuous nanofiller network, and b) a discontinuous nanofiller network. The green balls represent crystalline nanofiller; other balls represent polymer atoms	76
Figure 2.29 Schematic diagram which explains the low thermal conductivity of polymer nanocomposites reinforced by MWCNTs	81
Figure 4.1. SEM images of a) M12 and b) M58 MWCNTs	134
Figure 4.2 SEM images of a) G1 b) G2 and c) G3	135
Figure 4.3 Experimental results of density vs. filler fractions for HDPE/MWCNTs nanocomposites	139
Figure 4.4 Experimental results of density vs. filler fractions for HDPE/GnPs nanocomposites	140
Figure 4.5 Experimental results of density vs. filler fractions for HDPE/MWCNTs nanocomposites	142

Figure 4.6 Experimental results of density vs. filler fractions for HDPE/GnPs nanocomposites	142
Figure 4.7 Photothermal radiometry set up in front-detection configuration (FD-PTR)	144
Figure 5.1 XPS survey spectra for M12 and M58	152
Figure 5.2 C1s high-resolution spectra for M12 and M58.....	152
Figure 5.3 XRD patterns of the a) M12 b) M58 c) HDPE d) HDPE/M12 nanocomposites (18.74 wt.%) and e) HDPE/M58 nanocomposites (18.74 wt.%)	154
Figure 5.4 FTIR results of the a) M12 b) M58 c) HDPE d) HDPE/M12 nanocomposites (18.74 wt.%) and e) HDPE/M58 nanocomposites (18.74 wt.%)	155
Figure 5.5 TEM micrographs showing the HDPE/MWCNT nanocomposites containing 11.70 wt. % of M12 (a, b) and 11.70 wt. % of M58 at lower (a, c) and higher (b, d) magnifications	156
Figure 5.6 AC conductivity vs. frequency for HDPE/M12 nanocomposites at various concentrations of MWCNTs	158
Figure 5.7 AC conductivity vs. frequency for HDPE/M58 nanocomposites at various concentrations of MWCNTs	158
Figure 5.8 The AC conductivity at 0.1 Hz vs. vol.% of MWCNTs for the HDPE/M12 and HDPE/M58 nanocomposites.	160
Figure 5.9 Experimental results of thermal conductivity of HDPE/MWCNT samples as a function of the weight fraction.....	162
Figure 6.1 XPS survey spectra for G1, G2, and G3	174
Figure 6.2 C1s high-resolution spectra for G1, G2, and G3	174
Figure 6.3 XRD pattern of a) G1, b) G2, c) G3, d) HDPE, e) HDPE/26.81 wt.% G1, HDPE/26.81 wt.% G2 and HDPE/26.81 wt.% G3 nanocomposites....	176
Figure 6.4 FTIR spectroscopy of a) G1, b) G2, c) G3, d) HDPE, e) HDPE/26.81 wt.% G1, HDPE/26.81 wt.% and HDPE/26.81 wt.% G3 nanocomposites....	177
Figure 6.5 SEM image of HDPE/G1 nanocomposite with 11.70 wt.%.....	178
Figure 6.6 SEM image of HDPE/G2 nanocomposite with 11.70 wt.%.....	179
Figure 6.7 SEM image of HDPE/G3 nanocomposite with 11.70 wt.%.....	179
Figure 6.8 AC conductivity vs. frequency for the HDPE/G1 nanocomposites	180

Figure 6.9 AC conductivity vs. frequency for the HDPE/G2 nanocomposites	181
Figure 6.10 AC conductivity vs. frequency for the HDPE/G3 nanocomposites	181
Figure 6.11 Electrical conductivity vs. vol.% of GnPs for the HDPE/GnPs nanocomposites	183
Figure 6.12 Thermal conductivity values of HDPE-based nanocomposites with G1, G2, and G3 fillers	185
Figure 7.1 XRD patterns of the a) HDPE/G2 (11.70 wt.)/M12 (0 wt.%) and b) a) HDPE/G2 (11.70 wt.)/M12 (4 wt.%) nanocomposites	203
Figure 7.2 XRD patterns of the a)HDPE/G1/M12, b)HDPE/G2/M12, c)HDPE/G3/M12, d)HDPE/G1/M58 e)HDPE/G3/M12, f)HDPE/G2/M58 HDPE/G3/M58 nanocomposites (5wt.%) containing GnPs/MWCNTs of 1/4 weight ratio.....	204
Figure 7.3 FTIR results of the a) HDPE/G2 (11.70 wt.%), b) HDPE/G2 (11.70 wt.)/M12 (0.97 wt.%) c) HDPE/G2 (11.70 wt.)/M12 (3.82 wt.%) and d) HDPE/G2 (15.82 wt.%) nanocomposites	205
Figure 7.4 FTIR results of the a)HDPE/G1/M12, b)HDPE/G2/M12, c)HDPE/G3/M58, d)HDPE/G1/M58 e)HDPE/G3/M12, f)HDPE/G2/M58 HDPE/G3/M58 nanocomposites (5wt.%) containing GnPs/MWCNTs of 1/4 weight ratio	206
Figure 7.5 SEM image of the HDPE/G2 (11.70 wt.)/M12 (3.82 wt.%) nanocomposites (50 000 ×)	207
Figure 7.6 SEM image of the HDPE/G1/M12 nanocomposites with 1/4 weight ratio of GnPs/MWCNTs (5wt.%) (10 000 ×)	208
Figure 7.7 SEM image of the HDPE/G2/M12 nanocomposites with 1/4 weight ratio of GnPs/MWCNTs (5wt.%) (10 000 ×)	209
Figure 7.8 SEM image of the HDPE/G3/M12 nanocomposites with 1/4 weight ratio of GnPs/MWCNTs (5wt.%) (10 000 ×)	210
Figure 7.9 SEM image of the HDPE/G1/M58 nanocomposites with 1/4 weight ratio of GnPs/MWCNTs (5wt.%) (10 000 ×)	211
Figure 7.10 SEM image of the HDPE/G2/M58 nanocomposites with 1/4 weight ratio of GnPs/MWCNTs (5wt.%) (10 000 ×)	211

Figure 7.11 SEM image of the HDPE/G3/M58 nanocomposites with 1/4 weight ratio of GnPs/MWCNTs (5wt.%) (10 000 ×)	212
Figure 7.12 Relative electrical conductivity vs. wt.% of filler fraction for the HDPE/MWCNTs and HDPE/GnPs nanocomposites.....	216
Figure 7.13 AC conductivity vs. frequency for HDPE/G2 (11.70 wt.%)/M12 (3.82 wt.%) nanocomposites	216
Figure 7.14 Electrical conductivity vs. wt.% of MWCNTs for the HDPE/G2 (11.70 wt.%)/M12 nanocomposites.....	218
Figure 7.15 AC conductivity vs. frequency for HDPE/G1/M12 nanocomposites (5 wt.%)	221
Figure 7.16 AC conductivity vs. frequency for HDPE/G2/M12 nanocomposites (5 wt.%)	222
Figure 7.17 AC conductivity vs. frequency for HDPE/G3/M12 nanocomposites (5 wt.%)	223
Figure 7.18 AC conductivity vs. frequency for HDPE/G1/M58 nanocomposites (5 wt.%)	223
Figure 7.19 AC conductivity vs. frequency for HDPE/G2/M58 nanocomposites (5 wt.%)	225
Figure 7.20 AC conductivity vs. frequency for HDPE/G3/M58 nanocomposites (5 wt.%)	225
Figure 7.21 Electrical conductivity vs. GnPs/MWCNTs ratio for the hybrid nanocomposites.	227
Figure 7.22 Relative thermal conductivity vs. wt.% of filler fraction for the HDPE based nanocomposites	235
Figure 7.23 Thermal conductivity vs. wt.% of MWCNTs for the HDPE/G2 (11.70 wt.%)/M12 nanocomposites.....	237
Figure 7.24 The synergic efficiency [<i>f</i>] of G2 and M12 vs. wt.% of MWCNTs for the HDPE/G2 (11.70 wt.%)/M12 nanocomposites	240
Figure 7.25 Thermal conductivity of the hybrid nanocomposites	241
Figure 7.26 The comparison of the synergic efficiency [<i>f</i>] of GnPs and MWCNTs on the thermal conductivity in the hybrid nanocomposites	249
Figure 7.27 Relative Young's Modulus of the HDPE-based nanocomposites	253

LIST OF TABLES

	Page
Table 1.1 Studies on the aspect ratio and dimension (diameter or length) of MWCNTs on the final properties of polymer nanocomposites	5
Table 1.2 Studies on the aspect ratio and dimension (lateral size or thickness) of GnPs on the final properties of polymer nanocomposites	6
Table 1.3 Studies on the properties of hybrid polymer nanocomposites with GnPs and MWCNTs on the final properties of hybrid nanocomposites	10
Table 2.1 Electrical conductivity of some polymers.....	22
Table 2.2 Thermal conductivity of some polymers	36
Table 2.3 Mechanical properties of some polymers	37
Table 2.4 Thermal conductivity of widely used filler materials	47
Table 2.5 Physical properties of various types of carbon-based nanomaterials	50
Table 2.6 Properties of graphene	52
Table 3.1 Studies on the aspect ratio and dimension (diameter or length) of MWCNTs on the final properties of polymer nanocomposites	90
Table 3.2 Studies on the aspect ratio and dimension (lateral size or thickness) of graphene derivatives on the final properties of polymer nanocomposites .	107
Table 3.3 Studies on the properties of hybrid nanocomposites	121
Table 4.1 Properties of MWCNTs used for composites preparation	133
Table 4.2 The size of GnPs used in this study	134
Table 5.1 Results of MWCNTs XPS analysis	152
Table 5.2 The curve fitting results of electrical conductivity for $p > p_c$ of HDPE-based nanocomposites with two different MWCNTs.....	160
Table 5.3 Results of mechanical conductivity for the HDPE/M12 and HDPE/M58 nanocomposites	164
Table 5.4 DSC data of the HDPE/MWCNTs nanocomposites.....	168
Table 5.5 The results of TGA analysis for the HDPE/MWCNTs nanocomposites.	168
Table 6.1 Apparent surface chemical composition of GnPs as determined by XPS	175
Table 6.2 Young's Modulus of HDPE/GnPs nanocomposites (MPa).....	187
Table 6.3 Tensile Strength of HDPE/ GnPs nanocomposites (MPa).....	187

Table 6.4 Elongation of HDPE/ GnPs nanocomposites (%).....	187
Table 6.5 DSC results of HDPE/GnPs nanocomposites	191
Table 6.6 The results of TGA analysis for the HDPE/GnPs nanocomposites	191
Table 7.2 Mechanical properties of HDPE/G2 (11.70 wt.%) /M12 nanocomposites.....	255
Table 7.3 Young's Modulus of hybrid nanocomposites	257
Table 7.4 Tensile strength (MPa) of hybrid nanocomposites	261
Table 7.5 Elongation (%) of hybrid nanocomposites.....	261
Table 7.6 DSC results of HDPE/G2 (11.70 wt.%) /M12 nanocomposites	268
Table 7.7 DSC results of HDPE/G2 /M12 and HDPE/G2/M58 nanocomposites ...	269
Table 7.8 T_m [°C] results of hybrid nanocomposites.....	269
Table 7.9 T_c [°C] results of hybrid nanocomposites	269
Table 7.10 ΔH_f [J/g] results of hybrid nanocomposites	270
Table 7.11 X_c [%] results of hybrid nanocomposites.....	270
Table 7.12 TGA results of HDPE/G2 (11.70 wt.%) /M12 nanocomposites.....	272
Table 7.13 $T_{5\%}$ [°C] results of hybrid nanocomposites	276
Table 7.14 $T_{50\%}$ [°C] results of hybrid nanocomposites.....	276
Table 7.15 T_{deg} [°C] results of hybrid nanocomposites.....	276
Table 7.16 Residual Mass [%] results of hybrid nanocomposites	276

CHAPTER ONE

INTRODUCTION

1.1 Introduction

In recent years, the polymers have been widely used in many applications due to their low density, electrical insulative properties, high corrosion resistance, better mechanical properties, low cost, ease of processing and design (Huang, Qian, & Yang, 2018; Liu, Ullah, Kuo, & Cai, 2019; Mehra, Mu, Ji, & Zhu, 2019). In addition, many studies have been performed to replace metal and ceramic materials with polymer-based materials (Kim et al., 2018). However, the polymeric materials have limitations in their application fields due to inherently low thermal and electrical conductivities. The reason is that, the rapid improvements in technological applications demands to better performance in material properties (Liu et al., 2019). For example, rapid developments of the integrated circuits in electronics, aeronautics and aerospace are always accompanied by the heat diffusion issue, impacting instrument life and service efficiency (Zhang et al., 2019). When the demands in faster, smaller, lighter and denser intensify, the heat dissipation in the electronic products is becoming progressively significant (Lee, Park, Kim, Lee, & Yoon, 2006; Nilagiri Balasubramanian & Ramesh, 2018; Shtein, Nadiv, Buzaglo, Kahil, & Regev, 2015; Z. Xu et al., 2019). It is expected that the high conductive materials can be used for solving the issues of heat dissipation in the electronic products. However, the thermal conductivity of polymers is in the range of 0.1-0.6 W/mK and these values are far away from meeting the industrial demands (Huang et al., 2018; Nilagiri Balasubramanian & Ramesh, 2018; Zhang et al., 2019).

It is well-known that the thermal conductivity of a polymer is greatly based on its morphology. When the amorphous domains seem to be dominant in the polymer, a low thermal conductivity value is observed because vibrational modes in polymer tend to be localized. Therefore, thermal conductivity can be expected to improve by enhancing the alignment of polymer chains (Huang et al., 2018). The polymer chains orientation should be enhanced and the amount of oriented and ordered domains in

bulk polymers should be increased to improve the thermal conductivity (Chen et al., 2016). As a result, enhancing chain alignment and crystallinity of polymer generally improves the thermal conductivity of polymers. In the literature, numerous studies have been conducted for aligning the polymer chains to improve thermal conductivity, e.g., electrospinning, mechanical stretching, and nanoscale templating. Although arranging the regularity of molecule can enhance the thermal conductivity of a polymer, the influence is quite limited and this method is quite complicated (Huang et al., 2018).

Adding high thermal conductive nanofiller materials into polymers is the most economical, promising, efficient and the easiest method to enhance the thermal conductivity of polymers (Zhang et al., 2019). Aside from the thermal conductivity enhancement, the polymer nanocomposites are also popular due to their great ability and versatility to be incorporated into multifunctional properties (Mehra et al., 2019). In addition, the applications of polymer nanocomposites are notably promising in the fields of medicine, packing materials, automobiles, microelectronic, flexible electronics, bioelectronics, sensory, aerospace, optical integrated circuits, light emitting diodes/field effect transistors/actuators, membranes, hydrogen storage, consumer goods, drug delivery, adhesives, heat exchangers coatings, shielding of electromagnetic radiation, absorption of radar waves and solar cells (Billah, 2019; Hashim, 2019; Mehra et al., 2019; Zhang et al., 2019).

Among the filler materials, the metallic fillers show the highest thermal conductivity enhancement, however, they have heavy mass and costly. The ceramic fillers exhibit none of these disadvantages, yet their thermal conductivities are low. In recent years, it is considered that the carbon-based nanofiller materials are promising candidates as nanofiller materials because of their superior thermal conductivity, low weight, easy processing, low cost and high corrosion resistance. (Kim et al., 2018; Mondal & Khastgir, 2019; Safdari & Al-haik, 2018; Zhang et al., 2019). In addition, recent studies have shown that the thermal conductivity of the polymer nanocomposites with the carbon-based nanofillers are relatively higher than those of metal and ceramic filler materials (Kim et al., 2018; Zhang et al., 2019).

As a pioneer work, the Toyota research group was discovered the first polymer nanocomposites in early 1990s and Ajayan, Stephan, Colliex, & Trauth (1994) reported the first polymer nanocomposite including carbon-based material (Safdari & Al-haik, 2018). Up to date, numerous have been carried out on the properties of the polymer nanocomposites including carbon-based nanofillers and numerous reviews have been published on the properties of these nanocomposites (Al Sheheri et al., 2019; Cataldi, Athanassiou, & Bayer, 2018; Chen et al., 2016; Han & Fina, 2011; Huang et al., 2018; Kim et al., 2018; Kumar, Sharma, & Dixit, 2019b; Liu et al., 2019; Mohan, Lau, Hui, & Bhattacharyya, 2018; Noh, Kim, Ku, Khil, & Kim, 2016; Safdari & Al-haik, 2018; Szeluga, Kumanek, & Trzebicka, 2015; Zhang et al., 2017).

Numerous studies have been reported that the properties of polymer nanocomposites are affected by several variables with various characters of nanofiller such as dimensions, shape, size, content, degree of dispersion and orientation, and the interaction between the polymer matrix and nanofillers, type, intrinsic properties of the matrix and nanofillers, processing method and conditions (Billah, 2019; Szeluga et al., 2015; Yinhang Zhang et al., 2019). Especially, the determination of thermal conductivity is complex, since it is influenced by several factors such as nanofiller dispersion, nanofiller structure, intrinsic thermal conductivities of polymer and nanofiller, the network of nanofiller, and the interfacial thermal conductance (Billah, 2019; Szeluga et al., 2015; Xu et al., 2019; Zhang et al., 2019).

The allotropes of carbon are fullerenes, carbon nanotubes (CNTs), graphene and diamond. It is known that each allotropic forms of carbon exhibits a distinct and different range of the physical properties (Al Sheheri et al., 2019). Therefore, the enhancement of properties is different for the polymer nanocomposites with different nanofillers (Safdari & Al-haik, 2018). For example, while CNTs exhibit a better performance for improving the thermal and electrical conductivities of polymers (Namasivayam & Shapter, 2017; Safdari & Al-haik, 2018), graphene exhibits certain additional benefits such as possessing higher gas permeation resistance and lower

production cost due to their platelet structure as compared to the other types of carbon nanofillers (Safdari & Al-haik, 2018).

Among carbon nanofiller materials, CNTs have attracted increasing interest both in basic research and industry due to their excellent thermal (thermal conductivity of ~15-3000 W/mK), mechanical (Young's modulus of ~1TPa, yield strength of 20-100 GPa) and electrical properties (electrical conductivity of 10^3 - 10^7 S/m), low density, low melt flow viscosity, and high aspect ratio (Cha et al., 2016; Jouni, Djurado, Massardier, & Boiteux, 2017; Kaseem, Hamad, & Ko, 2016; Li, Zhang, Liang, & Li, 2018). Several review papers (Al-Saleh & Sundararaj, 2011; Al Sheheri et al., 2019; Chen, Liu, Gao, & Xu, 2018; Han & Fina, 2011; Hong et al., 2015; Mittal, Dhand, Rhee, Park, & Lee, 2015) summarize many studies on remarkable mechanical, electrical, thermal, rheological and morphological properties of polymer/CNTs nanocomposites. Although the aspect ratio or the dimension of Multiwall carbon nanotubes (MWCNTs) is known to be one of the most important parameters to control the final properties of nanocomposites, published studies on the influence of the MWCNTs dimension on these properties are very limited. In Table 1.1, the studies in which different polymer matrix are used such as thermosets and thermoplastics.

One drawback of using CNTs as nanofillers is the high fabrication cost of CNTs. Moreover, it is known that the large-scale fabrication of CNTs is still very difficult (Szeluga et al., 2015). However, the mass production of graphene is solved, and the costs of graphene is acceptable for the commercial applications. Thus, the graphene can be considered as suitable a nanofiller to replace CNTs (Liu et al., 2019).

Table 1.1 Studies on the aspect ratio and dimension (diameter or length) of MWCNTs on the final properties of polymer nanocomposites

Authors	Year	Matrix	Matrix type
Dubnikova et al.	2010	Polypropylene (PP)	thermoplastics
Morcom, Atkinson, & Simon	2010	HDPE	thermoplastics
Abbasi, Al-Juhani, Ul-Hamid, & Hussein	2011	low density polyethylene (LDPE)	thermoplastics
Castillo et al.	2011	polycarbonate (PC)	thermoplastics
Park & Youn	2012	acrylonitrile butadiene styrene (ABS)	thermoplastics
Rahaman, Thomas, Hussein, & De	2013	LDPE	thermoplastics
Guo et al.	2014	PC	thermoplastics
Lin et al.	2017	PP	thermoplastics
Cruz & Son	2018	PC	thermoplastics
Ayatollahi, Shadlou, Shokrieh, & Chitsazadeh	2011	Epoxy	thermosets
Russ, Rahatekar, Koziol, Farmer, & Peng	2013	Epoxy	thermosets
Wang et al	2013	bismaleimide (BMI)	thermosets
Ciecierska, Boczkowska, Kurzydowski, Rosca, & Van Hoa	2013	Epoxy	thermosets
Zhang, Li, Liu, & Peng	2016	Epoxy	thermosets
Chen & Yan	2018	Epoxy	thermosets
Chen, Yan, Song, & Xu	2018	Epoxy	thermosets
Mu, Teblum, Figiel, Nessim, & McNally	2018	Poly(methyl methacrylate) (PMMA)	transparent thermoplastic
Dang et al.	2011	polypropylene and copolymer of ethylene–propylene–diene monomer (TPE)	thermoplastic elastomers
Shehzad et al.	2013	TPE	thermoplastic elastomers
Costa et al.	2014	styrene-butadiene-styrene (SBS)	thermoplastic elastomers
Su & Miao	2014	poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP)	thermoplastic elastomers

Graphene has a single atom thick structure of sp^2 -hybridized carbon atoms in a hexagonal arrangement. The usage of graphene is of great interest due to its large specific surface area, 2D structural and superior inherent properties such as thermal conductivity (1000-5000 W/mK (Huang et al., 2018)), electrical conductivity (6000 S/cm (Zakaria, Abdul Kudus, Md. Akil, & Mohd Thirmizir, 2017)) mechanical properties (Young's modulus of 1 TPa and tensile strength of 130 GPa (Paszkiewicz et al., 2014)). However, the mass production of graphene with high quality at low-cost has been the most important challenge by available production technology (Jun, Um, Jiang, & Yu, 2018). Thus, GnPs, formed by several graphene layers bonded together by Van der Waals force, are a potential alternative to graphene which exhibit approximately all above mentioned properties at low-cost (Imran, Lou, & Shivakumar, 2018; Jun et al., 2018).

Table 1.2 Studies on the aspect ratio and dimension (lateral size or thickness) of GnPs on the final properties of polymer nanocomposites

Authors	Year	Matrix	Matrix type
Jiang & Drzal	2012	HDPE	thermoplastics
Tarani et al.	2016	HDPE	thermoplastics
Kim & Son	2016	PC	thermoplastics
Liang, Du, Tsui, & Tang	2016	PP	thermoplastics
Tarani et al.	2017	HDPE	thermoplastics
Imran et al.	2018	PP	thermoplastics
Liang	2018	PP	thermoplastics
Jun et al.	2018	PP	thermoplastics
Chatterjee et al.	2012	Epoxy	thermosets
Shtein et al.	2015	Epoxy	thermosets
Ravindran et al.	2018	Epoxy	thermosets

A great number of studies have been performed on the nanocomposites with graphene or its derivatives. They show that the properties of the nanocomposites depend on several factors such as polymer type, morphology, intrinsic properties, the size and defect level of filler material, production method, interface between filler and the polymer (Bakir, Meyer, Sutrisno, Economy, & Jasiuk, 2018; Chaudhry & Mittal,

2013; Kim et al., 2018). Although, the size of GnPs is one of the most important factors, limited studies have been carried out on the size effect of GnPs on the properties of nanocomposites with various matrix, shown in Table 1.2.

Although many advantages of CNTs and GnPs, their original forms can not completely be applied for the development of polymer nanocomposites due to the agglomeration issue between nanofillers because of the strong intermolecular interactions between them, such as π - π interactions and van der Waals forces. The agglomeration influence later leads to uneven dispersion, decreasing the aspect ratio of the nanofillers. The agglomeration affects the physicochemical properties of nanofillers, resulting in deteriorating the properties of the carbon-based nanofillers (Mansor, Fadzullah, Masripan, Omar, & Akop, 2019; Othman & Wilkinson, 2019; Szeluga et al., 2015). As summary, the poor dispersion degree of carbon-based nanofillers deteriorate the overall efficiency of polymer nanocomposites (Kumar et al., 2019b).

A lot of studies have been focused on the effort to enhance the dispersion of carbon-based nanofillers in the polymer matrix with a purpose to break down their the agglomeration, bundles or stacks by applying several methods such as intensive tip sonication, high shear forces and/or mixing nanofillers with surfactants. They include a lot of additional processes, being both inefficient and time-consuming for the industrial processing. Moreover, dispersing the agglomerated in the polymer matrices leads to increase the mixture viscosity, adversely influencing the nanocomposites processing. In order to minimize the dispersion problem, chemical functionalization of nanofillers is generally carried out to provide good dispersion in the polymer matrix (Othman & Wilkinson, 2019). Nevertheless, the functionalization process may lead to decrease the intrinsic properties of carbon nanofillers.

In addition, especially, the reported thermal conductivity values of the nanocomposites reinforced by carbon-based nanofillers are still much lower than the required and theoretical values. In other words, despite high difference ($\sim 10^4$) between the thermal conductivity of matrix and nanofillers, the thermal conductivity of

polymer nanocomposites with carbon-based nanofillers exhibits modest enhancements (generally between 0.1 and 30 W/mK) (Safdari & Al-haik, 2018). Generally, their thermal conductivities have been reported to be near the lower boundary of mixtures rule. The main reasons of this are the strong phonon scattering at the polymer/nanofiller interface and nonideal nanofiller dispersion (Kim et al., 2018; Safdari & Al-haik, 2018; Shi & Zhu, 2020; Zhang et al., 2019). The heat transfer throughout the polymer nanocomposites is restricted by the phonon modulus mismatch and weak bonding between the carbon-based nanofillers (Shi & Zhu, 2020).

As mentioned above, it is proven that the functionalization is effective method to improve dispersion of nanofiller within the polymer and to increase the thermal conductivity by reducing the interfacial resistance between the polymer matrix and nanofiller. There is controversial issue whether the functionalization can enhance thermal conductivities of the polymer nanocomposites. This query arises from the balance that the functionalization causes more defects, increasing the possibility of phonon scattering, therefore reduces the thermal conductivity (Zhang et al., 2019).

Another bottleneck for the carbon-based polymer nanocomposites is the necessary of relatively high nanofillers loading to achieve the desired properties of polymer nanocomposites. Because of high nanofiller content, the polymer losses the intrinsic properties such as ease of fabrication, good mechanical properties. After a certain content of nanofillers, thermal conductivity raises, however at the cost of the mechanical properties (Huang et al., 2018; Mehra et al., 2019). For example, the incorporation of high filler concentration (> 15 wt.%) can increase thermal conductivity of the polymer nanocomposites, however, leads to a drastic decrease in the mechanical properties. It is known that the content of nanofillers should be low and the dispersion of nanofillers should be well. Because, the higher the nanofiller loading, the higher the possibility of porosity; also high viscosity matrix cannot be distributed between the nanofillers and causes the formation of void (Nilagiri Balasubramanian & Ramesh, 2018; Szeluga et al., 2015). Additionally, the high nanofiller content also contributes significantly to the polymer weight. It is also significant to own a cost-effective material. As is known, many of carbon-based

nanofiller, such as CNTs and graphene, are expensive and considerably increase the cost of polymer nanocomposites (Mehra et al., 2019).

Considering the disadvantages of functionalization, the incorporation of hybrid carbon nanofillers into the polymers is one of the easiest methods to solve previous stated problems. It is known that the primary purpose of adding the hybrid nanofillers into the polymer matrix is to achieve materials with a high thermal and/or electrical conductivity without the breakdown of the mechanical properties or potentially with an enhancement in the mechanical properties.

The different aspect ratios and geometric shapes as well as distinct dispersion characteristics of hybrid nanofillers present a unique synergy, causing the improved conductivity of polymer nanocomposites. The addition of two geometrically different fillers, such as GNPs with CNTs, may first induce a decrease in the total filler content in consequence of forming a co-supporting network of them. At relatively low contents of nanofillers, the regular global conducting pathways are formed by these layers and network structures of nanofillers. That is, the polymer nanocomposites also induce good mechanical properties (Szeluga et al., 2015).

There have been many of studies on the hybrid nanocomposites with GNPs and MWCNTs based on a wide variety of polymers, which have been reported in the literature. These studies are summarized in Table 1.3. As mentioned previously, the strategy of hybrid nanofillers with different aspect ratios and dimensions has revealed that to provide effectiveness in achieving the enhanced properties of polymer nanocomposites (Al Sheheri et al., 2019). The simultaneous incorporation of GNPs and CNTs may demonstrate advantageous in affecting the ultimate properties of polymer nanocomposites due to their synergic effect (Kumar et al., 2019b). In literature, various studies have shown that the polymer nanocomposites with hybrid nanofillers exhibit a better performance than those incorporated with single nanofillers (Mehra et al., 2019; Xu et al., 2019). For example, in hybrid system, CNTs act as a bridge between the adjacent graphene sheets to accelerate the phonon, hole and

electron transport, thus improving the thermally and electrically conductive performance (Zhang et al., 2019).

Table 1.3 Studies on the properties of hybrid polymer nanocomposites with GnPs and MWCNTs on the final properties of hybrid nanocomposites

Authors	Year	Matrix	Matrix type
Wegrzyn, Galindo, Benedito, & Gimenez	2015	PP	thermoplastics
Al-Saleh	2015	PP	thermoplastics
Maiti & Khatua	2016	PC	thermoplastics
Yu, Choi, Kim, & Kim	2016	PC	thermoplastics
Kumar, Mahmoodi, TabkhPaz, Park, & Jin	2017	PC	thermoplastics
Dul, Pegoretti, & Fambri	2018	ABS	thermoplastics
Wang et al.	2018	HDPE	thermoplastics
Paszkievicz et al.	2018	LDPE	thermoplastics
Yang et al.	2011	epoxy	thermosets
Chatterjee et al.	2012	epoxy	thermosets
Li, Dichiaro, & Bai	2013	epoxy	thermosets
Yue, Pircheraghi, Monemian, & Manas-Zloczower	2014	epoxy	thermosets
Khurram, Rakha, Zhou, Shafi, & Munir	2015	epoxy	thermosets
Ghaleb, Mariatti, & Ariff	2017	epoxy	thermosets
Moosa, A, Abdul, Kubba, & Raad	2017	epoxy	thermosets
Kranauskaitė et al.	2018	epoxy	thermosets
Han, Meng, Araby, Liu, & Demiral	2019	epoxy	thermosets
Jen & Huang	2019	epoxy	thermosets
Xiao et al.	2016	poly(vinylidene fluoride) (PVDF)	thermoplastic fluoropolymer
Lin et al.	2016	polyvinyl alcohol (PVA)	water-soluble synthetic polymer.

1.2 Motivation of the Thesis

There have been numerous papers published on GnPs and CNTs as single nanofillers, a scarcity of literature on the production of polymer nanocomposites with GnPs and CNTs as co-applications, altering their category from the nanocomposites to the hybrid nanocomposites, is recognized. Most of the studies in recent years conclude that by a hybrid combination of carbon-based nanofillers and through a mechanism displayed, even greater property improvements can be achieved (Safdari & Al-haik, 2018). Many studies on the hybrid nanocomposites has been clearly reported a synergic effect, however, some studies have been reported a negative or no synergy. Consequently, the subject of synergic effect of hybrid nanocomposites has still been discussed.

The applications of these nanocomposites have been still in preliminary stage. The hybrid nanocomposites must be systematically studied in terms of both experimental problems and theoretical questions. Within the combination of study in fields of material science, physics and chemistry, it is likely that promising hybrid nanocomposites will find a broad spectrum application areas in the near future (Szeluga et al., 2015).

The selection and pairing of the nanofillers can be crucial to obtain the desired properties with the improved performance, as mention by Mehra et al. (2019) and Xu et al. (2019). In addition, Billah (2019) and Szeluga et al. (2015) claimed that one of the main parameters in hybrid nanocomposites design is the weight ratio of hybrid nanofillers that has a direct important control on the overall performance of a sample being related to synergic effect. In other words, it is found that the relative ratio and geometry of filler in the filler mixture have significantly influence on the final properties of the hybrid nanocomposites, despite the fact that the mechanisms responsible for the synergetic effects have not been yet understood (Szeluga et al., 2015; Yuan, Pedrazzoli, Pircheraghi, & Manas-Zloczower, 2017). For example, some studies have shown that the mechanical properties of the polymer nanocomposites can be enhanced under certain GnPs/MWCNTs ratios (Jen & Huang, 2019). However, a

lot of studies are still required to understand the relationship between the weight ratio and geometric properties of carbon-based hybrid nanofillers like as dimensionality and size.

Moreover, the optimum weight ratio and concentration of hybrid fillers may not always be providing the maximum enhancement in the desired property, as other properties may be deteriorated. It should be also noted that the optimal concentration ratio of hybrid fillers not always ensure a maximum thermal conductivity, whereas a much higher concentration of fillers may destroy the synergic effect of hybrid fillers. It is still difficult that the optimum weight ratio is determined except by the experiments. Additionally, it is still a question to fully understand how to change the influence resulted from hybrid nanofillers (Huang et al., 2018).

Additionally, the important progress has been made in improving the properties of polymers and polymer nanocomposites in recent years, however, there is still much more studies required to be conducted, given the technical significant of polymer nanocomposites. Although adding carbon-based nanofillers into a polymer can enhance the properties, producing polymer nanocomposites with desired properties is still a challenge due to some well-known difficulties such as large thermal contact resistance and dispersion problem (Huang et al., 2018).

It is known that there are many studies on the properties of the polymer nanocomposites with MWCNTs or GnPs in the literature. Experimental data on the properties of polymer nanocomposites with GnPs or CNTs have been still intensively collected since their properties are still not adequately understood, while there is a great number of potential applications. In despite of the intensive studies, the knowledge of the correlation between the structure of carbon-based nanofillers and the properties of polymer nanocomposites are also still insufficient, especially, the effect of different nanofiller structures on the properties of the final polymer nanocomposites. Moreover, making a comparison of GnPs and MWCNTs in terms of their performance is hard because the processing method and/or conditions, filler size, filler compositions and measurement techniques vary commonly from case to case and they are significant

factors in obtaining the final properties of the polymer nanocomposites (Han et al., 2019).

As a result, there are many lacks in the polymer nanocomposites, especially hybrid nanocomposites. Numerous studies are required (i) to understand how several factors influence on the properties of hybrid nanocomposites or polymer nanocomposites, and (ii) to determine the optimum conditions for achieving the desired properties.

1.3 Objectives of the Thesis

Considering the shortcomings in the hybrid and polymer nanocomposites, the objectives of this thesis are:

- 1- To investigate synergic effect of two different dimensional carbon-based nanomaterials on the morphological, thermal, electrical, and mechanical properties of hybrid nanocomposites.
- 2- to systematically research the hybrid nanocomposites with different filler sizes at different weight ratios of GnPs/MWCNTs to highlight the size and synergic effects on these properties.
- 3- to clearly interpret the effects of synergic, size and weight ratio of GnPs and MWCNTs, and to make comparison between the performance of GnPs and MWCNTs on the property enhancements of polymer nanocomposites, the properties of HDPE-based nanocomposites with GnPs or MWCNTs alone are investigated.
- 4- to understand the role of the concentration and the aspect ratio of the filler in determining the final properties of the HDPE/MWCNTs nanocomposites.
- 5- to investigate how the previous mentioned properties of HDPE-based nanocomposites are correlated with the size of GnPs in terms of both thickness and lateral size.

1.3 Organization of the Dissertation

The thesis is divided into eight chapters.

Chapter 1: A short introduction to polymer nanocomposites is given. Also, the motivation and objectives of this thesis are proposed.

Chapter 2: Background information about the thesis subject is given. This chapter gives a general overview of polymer, polymer nanocomposites, thermal conductivity, electrical conductivity, and mechanical properties.

Chapter 3: A brief literature review on the polymer nanocomposites is presented. There are various studies in the literature on the polymer nanocomposites including MWCNTs, GnPs and hybrid nanofillers (GnPs+MWCNTs).

Chapter 4: Materials and Methods are detailed in this chapter.

Chapter 5: The size effect of MWCNTs on the thermal, electrical, and mechanical properties of HDPE-based nanocomposites at various filler concentration are discussed. This chapter is dedicated to the published two articles.

Chapter 6: The size effect of GnPs on the thermal, electrical, and mechanical properties of HDPE-based nanocomposites at various filler concentration are discussed. This chapter is dedicated to the published one article.

Chapter 7: The synergic effect, weight ratio effect and size effect of GnPs and MWCNTS on the thermal, electrical, and mechanical properties of HDPE-based hybrid nanocomposites at various filler concentration are discussed. First, the synergic effect on the morphological, electrical,

thermal, and mechanical properties of the HDPE-based hybrid nanocomposites with MWCNTs and GNPs giving the best enhancement are investigated. For this purpose, based on the results of the previous chapter, while fixing the GNPs loading at a certain value for all composites, the MWCNTs content is made variable. Secondly, the morphological, electrical, thermal and mechanical properties of the HDPE-based hybrid nanocomposites including a total amount of 5 wt% carbon-based nano fillers with different sizes have been investigated experimentally to determine optimum filler weight ratio and size which maximally enhance certain these properties and application possibility.

Chapter 8: This chapter presents the concluding remarks of the thesis.

CHAPTER TWO

BACKGROUND

2.1 Polymers

A polymer is a long chain macromolecule made up of many repeating units linked together by covalent bonds. This repeat unit is called as monomer. If a polymer including one type of monomer, it is known as homopolymer; if a polymer is made of two or more different monomers is named copolymer. Polymers can be classified in several ways based on some special considerations. The classification of polymers based on some considerations are given below:

- 1) Classification based on source: Natural polymers (proteins), Semi-synthetic polymers (cellulose nitrate) and synthetic polymers (plastic).
- 2) Classification based on polymerization mechanism: condensation polymers (Polysulfone) and addition polymers (Polyethylene).
- 3) Classification based on structure: linear polymers, branched polymers, and network polymers.
- 4) Classification based on properties: thermosets polymers (epoxy), thermoplastics polymers (polyethylene), elastomers (vulcanized rubber).

Although there are several classifications of polymers, generally polymers are classified in two group depending on whether the polymers can be softened, melted, and reshaped by the application of pressure and heat. These polymers are named as “thermoplastics” The other classification pertains to compounds decomposing before these polymers can be shaped or melted. These materials are called “thermosets” (Carraher, 2017).

Thermoplastics consist of the long chains formed by joining together monomers; they typically act in a ductile fashion. The chains may or may not possess the branches and individual chains are intertwined. Relatively weak van der Waals bonds occur between the atoms of various chains. This is like a few trees tangled up together. The

tress may or may not possess the branches and each tree is on its own and not contacted with another. The application of a tensile stress can untangle the chains in the thermoplastics. When heating, they soften and melt. Thermoplastics can be processed into shapes by heating to high temperatures and they are recycled easily (Askeland, 2009). Polyethylene and polystyrene are common examples of the thermoplastics (Swallowe, 1999).

The thermosetting polymers are of long molecules chains (branched or linear) cross-linked strongly to another for the formation of 3D network structures. Thermosetting or network polymers are similar to a bunch of strings knotted to another in many places and not just tangled up. Each string may possess other side strings which is attached to it. They are usually stronger, however more brittle, than thermoplastics. When heating, they do not melt, however start to degradation. Thermosetting cannot be easily reprocessed after the cross-linking reaction has happened and thus recycling is difficult (Askeland, 2009). The most well-known thermoset is epoxy.

Regardless of polymer classification, polymers are widely used in many applications due to their diverse functionality, excellent chemical stability, low water absorption, easy processing, reproducibility, light weight and low cost (Chen et al., 2016; Huang et al., 2018; Mittal et al., 2015). Although their superior properties, their low conductivity limits in their some application such as electronic packaging, heat exchangers (Huang et al., 2018).

2.2 Properties of Polymers

Polymer properties not only depend on the polymer chemical nature, but also on such factors; distribution of lengths of polymer chain, the distribution and extent of crystallinity, amount, and nature of additives, such as reinforcing agents, fillers, and plasticizers, etc. These factors affect mainly all properties of polymers such as electrical properties, thermal properties, mechanical properties, softening point, biological response, flammability, hardness, chemical stability, dyeability, moisture

retention, weatherability, flex life, comfort and appearance (Carraher, 2017). Some properties are explained as following.

2.2.1 Electrical Conductivity of Polymers

The electrical behavior of materials is governed by several basic relationships. As an electrical potential difference is applied to a solid, an electric current flow through it. According to Ohm's law (Sperling, 2005; Taherian, 2019) (Eq. 2.1):

$$V = IR \quad (2.1)$$

where V refers to voltage (volts, V), I is the current (amperes or amps, A) and R refer to the resistance of materials to the current flow. Nevertheless, some of materials does not obey the law of Ohm. The resistance should be emphasized to not only be a material property, but also depend on the shape and dimension of materials. However, the conductivity (σ) and resistivity (ρ) does not depend on the appearance specifications. Thus, the conductivity or resistivity of various materials can be stated to be comparable. The relation between conductivity, resistivity and resistance is given by following equation (Eq. (2.2)) (Taherian, 2019):

$$R = \frac{\rho l}{A} = \frac{l}{\sigma A} \quad (2.2)$$

A refers to the cross-sectional area (cm^2) and l is the length or resist of resistor. ρ (ohm.cm or $\Omega\text{.cm}$) is the inverse of σ (S/cm). Resistivity is the micro-structure sensitive property and based on materials specification. Any twist or distortion in the materials' crystal structure can reduce the electrical conductivity (Taherian, 2019).

The wasted electrical power P (with the unit of watts, W) because of the current flow through a resistance is expressed (Eq. 2.3) (Taherian, 2019):

$$P = VI = RI^2 \quad (2.3)$$

These electrical losses are known as Joule heating losses. The Ohm's law can be rewritten in second form (Taherian, 2019):

$$\frac{I}{A} = \sigma \frac{V}{L} \quad (2.4)$$

The current density J (A/cm²) and electrical field E (V/cm) are replaced instead of I/A and V/L , deriving Eq. (2.5) (Taherian, 2019):

$$J = \sigma E \quad (2.5)$$

In current, density can be defined in another state (Eq. (2.6)) (Taherian, 2019):

$$J = nq\bar{v} \quad (2.6)$$

n refers to the number of charge carriers (carriers/cm³), q is the charge on each carrier (1.6×10^{-19} °C), and v refers to the average drift velocity (cm/s). By combining the above Eq. (2.5) , it can be followed (Eq. (2.7)) (Taherian, 2019):

$$\sigma = nq \frac{\bar{v}}{E} \quad (2.7)$$

Drift in the electrical conductivity is similar to atoms' diffusion in the metals, with this difference that diffusion happens as a result of concentration and temperature, nonetheless, the drift happens as a result of applied magnetics or electrical field. The conduction may happen as a consequence of drift, diffusion or both, based on type of material, however the drift is the main mechanism in the metals' electrical conduction. The carriers' mobility μ (cm²/Vs), which in the case of semiconductors is the mobility of holes and electron, and in case of metals is the mobility of electrons is defined as Eq. (2.8) (Taherian, 2019):

$$\mu = \frac{\bar{v}}{E} \quad (2.8)$$

It can be concluded that (Taherian, 2019):

$$\sigma = nq\mu \quad (2.9)$$

This means that the charge carries' number in the material and their mobility (or ease of movement) can control the electrical conductivity, which is based on the type of material. In metals and carbon, because of high electrons' number on the electronic cloud, the mobility is detrimental for the electrical conductivity, while for insulators and semiconductors because of low density of carriers or electrons, the number of carries is more significant than mobility (Taherian, 2019).

The electrical conductivity and resistivity of materials are shown in Figure 2.1. One can see that the range of electrical conductivity is 25 orders of magnitude. According to electrical property, materials can be classified to three groups: insulator, semiconductor and conductor (Rahaman, 2019). Materials with the electrical conductivity lower than 10^{-12} S/cm are considered as dielectric or insulator. Materials with conductivity in the range of 10^{-12} S/cm and 10^3 S/cm are considered as semiconductors. Materials with conductivity higher than 10^3 S/cm or resistivity lower than 10^{-3} Ω .cm, considered as conductors (Fischer, 2009; Taherian, 2019). The band theory shown in Figure 2.2 explains the difference between three categories. The dashed lines in Figure 2.2 show the energy as a function of electron distances to atomic nuclei. The crosshatched bands are occupied bands. The hatched bands are allowed but not occupied. For conductive materials, as seen in Figure 2.2 (c), the highest energy level with electrons is not fully filled. Furthermore, this band can overlap adjacent atoms. In others, the highest filled bands refer to the matching atoms. The energy bands overlapping adjacent atoms are in the ground state unoccupied. If the distance between the unoccupied and filled bands is small, as semiconductors (Figure 2.2 (b)), the electrons easily take up some energy (for example, thermal energy) and jump to the conducting band. If the distance is very large, as insulators (Figure 2.2 (a)), the electrons cannot jump to the conducting band (Van Krevelen & Te Nijenhuis, 2009).

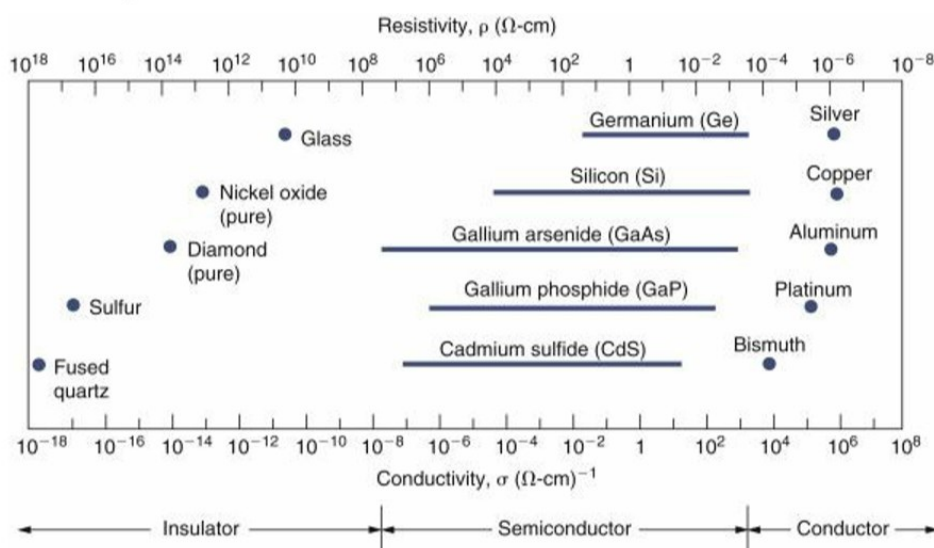


Figure 2.1 Electrical conductivity and resistivity of materials (Fischer, 2009)

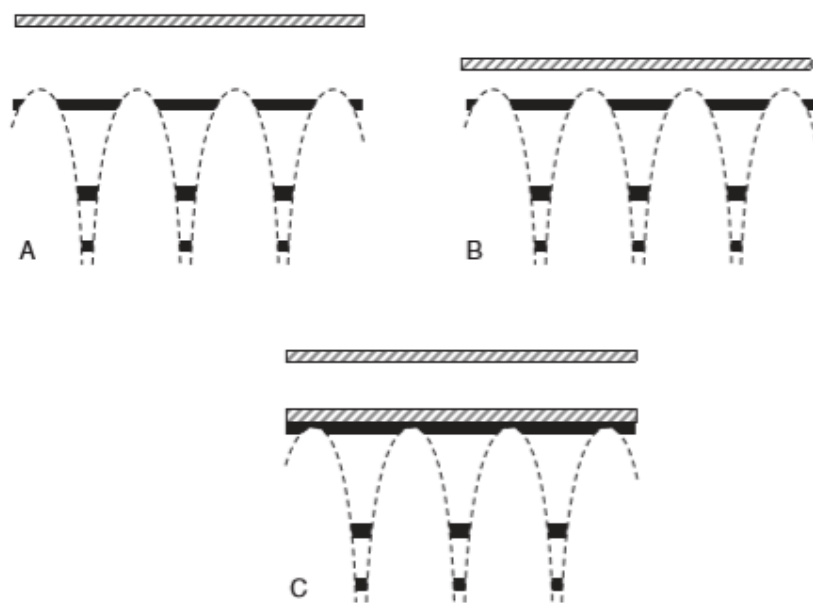


Figure 2.2 Schematic representation of the band theory of electronic conduction: a) insulators; b) semi-conductors and c) conducting materials. The hatched bands are allowed bands, the cross hatched bands are occupied (Van Krevelen & Te Nijenhuis, 2009)

To better comprehend the electronic properties of polymer by the band structure concept and the means of electrical theory, the degree of periodicity or order of the atoms is required to be known, since it is known that only strongly interaction and ordered atoms or molecules cause wide and distinct electron bands. The order degree

in the polymers is based on the simplicity of molecular structure or on the molecules' length. Some of structural parameters may be affected by specific heat treatments (Hummel, 1993).

Generally, polymers are insulators and their electrical resistance too high. It is known that the polymers generally consist of the covalent bond. In this bond, the common electrons between two elements are fixed and they cannot move at all, since the angle and directionality of the common bond vary by any movement of the atoms and electron, which thereby fails the bond. From the perspective of band model, in polymers, the band gap energy is much larger. These are the reasons for the low electrical conductivity of polymers (Taherian, 2019). In addition, their conductivity likely arise partially from the existence of ionic impurities, the mobility of ionic impurities is restricted by the high viscosity of medium (Van Krevelen & Te Nijenhuis, 2009). The electrical conductivity of some polymers is given in Table 2.1.

Table 2.1 Electrical conductivity of some polymers (Tavman & Evgin, 2018)

Polymers	Electrical Conductivity (S/cm)
High density polyethylene (HDPE)	1.00×10^{-18}
Low density polyethylene (LDPE)	1.00×10^{-19}
Poly (ethylene vinyl acetate) (EVA)	1.99×10^{-14}
Polymethylmethacrylate (PMMA)	1.00×10^{-16}
Polycarbonate (PC)	5.00×10^{-15}
Epoxy	1.00×10^{-17}
Polyvinyl chloride (PVC)	1.00×10^{-16}
Polypropylene (PP)	1.00×10^{-14}

2.2.2 Thermal Conductivity of Polymers

Heat transfer is defined as the transport of energy from one place to another place of different temperature by the heat carriers. Heat transfer can occur by conduction, convection, or radiation. In gasses, energy can be transported either by an overall drift of the molecules in a special direction (advection) or by random molecular motion (diffusion). In a liquid phase, advection and diffusion of molecules can carry energy. The main heat transfer in solid materials can occur by thermal conduction (Han &

Fina, 2011). In terms of a main perspective, as seen in Figure 2.3, the thermal conduction can correspond to the transport of vibration energy of a particle to adjacent particles without any matter motion, fundamentally by collision (Burger et al., 2016). Phonons, photons or electrons transfer energy in solids (Han & Fina, 2011).

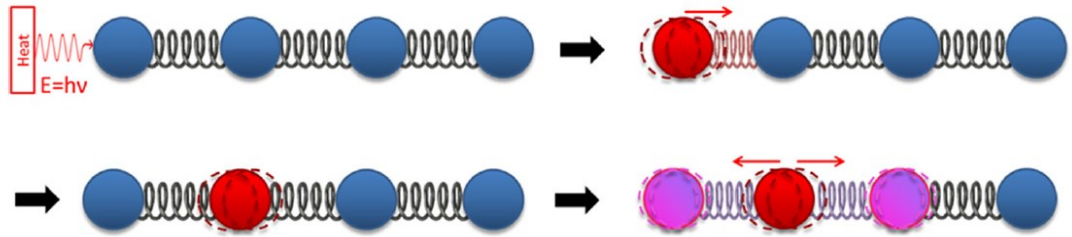


Figure 2.3 Thermal conduction in matter by collision of particles (Burger et al., 2016)

From a main view of quantum theory, the definition of thermal conductivity is the ability to transfer a vibration energy of atoms to its adjacent atoms basically by collision without shifting the matter to achieve thermal equilibrium (Zhang et al., 2019). In most polymers, phonons, quantized vibration modes of vibration taking place in a rigid crystal lattice, are the main mechanism of heat conduction, because the free movement of electrons is not possible. (Han & Fina, 2011).

2.2.2.1 Thermal Conductivity in Crystalline Structure

Highly crystalline materials, such as silicon, metals, graphene, diamond etc., are the most thermal conducting materials. The thermal conduction mechanism in a crystalline material are shown in Figure 2.4 to explain the main aspects of thermal conduction. This approach to the mechanism of thermal conduction by an ordered, perfectly crystalline and rigid sample is greatly simplified, however still helps to visualize the phenomenon (Burger et al., 2016):

- a) First, thermal energy is passed to the surface atoms of sample.
- b) The surface atoms gain vibrational energy.
- c) Then, the energy of surface atoms transport to the adjacent atoms at the same speed, as in a wave (modeled here in red lines).

- d) Thermal energy diffuses in the sample.
- e) Thermal energy diffuses with a general vibrational mode (or a phonon) to all crystal.
- f) As the heat reaches the opposite surface of the sample, then it is relatively transported by conduction or radiation to the surroundings (Burger et al., 2016).

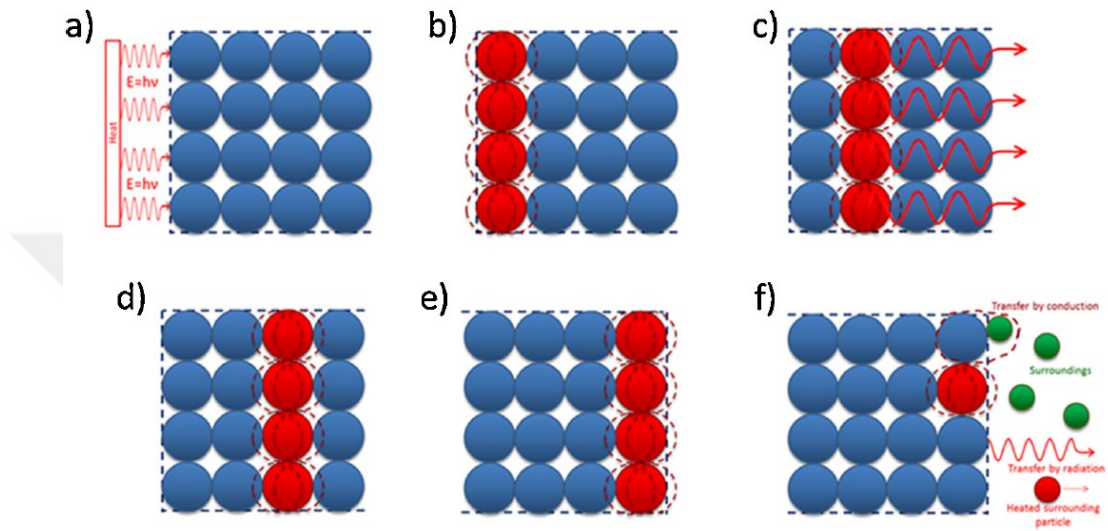


Figure 2.4 Thermal conductivity mechanism in a crystalline material (Burger et al., 2016)

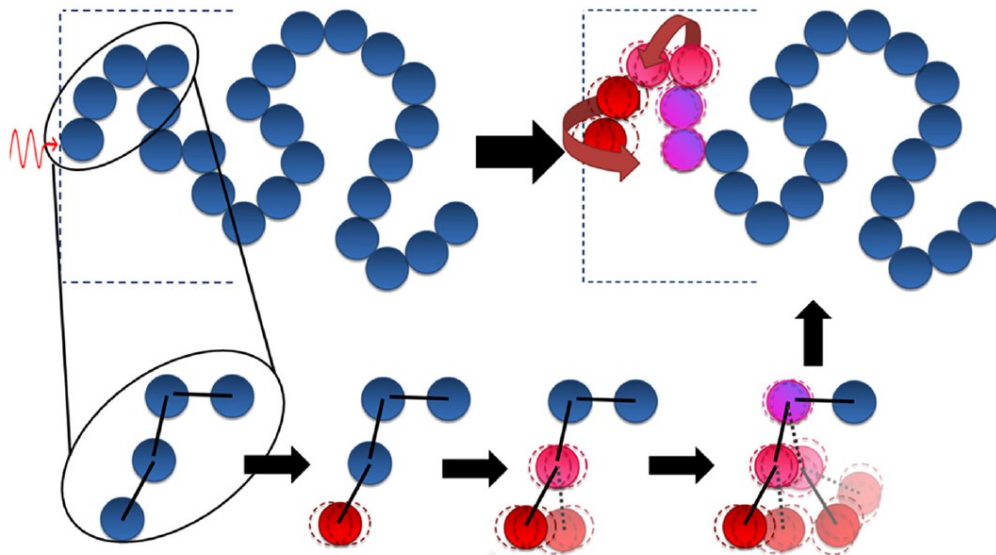


Figure 2.5 Thermal conductivity mechanism in an amorphous material (Burger et al., 2016)

2.2.2.2 Thermal Conductivity in Amorphous Structure

In Figure 2.5, the disordered and amorphous structure are represented (no compact lattice, as before). First, heat reaches a surface atom or monomer, schematically the nearest the heat source. Later, heat is transported to adjacent atom, after that the next one and so on. Heat will not progress a wave as in the crystal (Figure 2.4), however will diffuse very slowly in a polymer, which leads to disordered rotations and vibrations of all atoms of polymer around their equilibrium position, scattered to adjacent chains.

Summary, the thermal conductive mechanisms for the crystalline and amorphous material are quite different. Figure 2.6 show a schematic comparison with Newton pendulum between a crystal material (metal) and an amorphous material (polymer), as a function of their structure. Indeed, while a crystalline material can be symbolized by a classic ordered pendulum, an amorphous polymer can be symbolized a disordered Newton pendulum. Figure 2.6 more precisely shows the vibration aspect of particles in two structures. While an ordered structure (crystalline structure) will quickly diffuse the initial vibration to the opposite face, the initial kinetic energy is mostly spread into the atoms of the disordered structure (polymer), leading to vibrations of each ball (Burger et al., 2016).

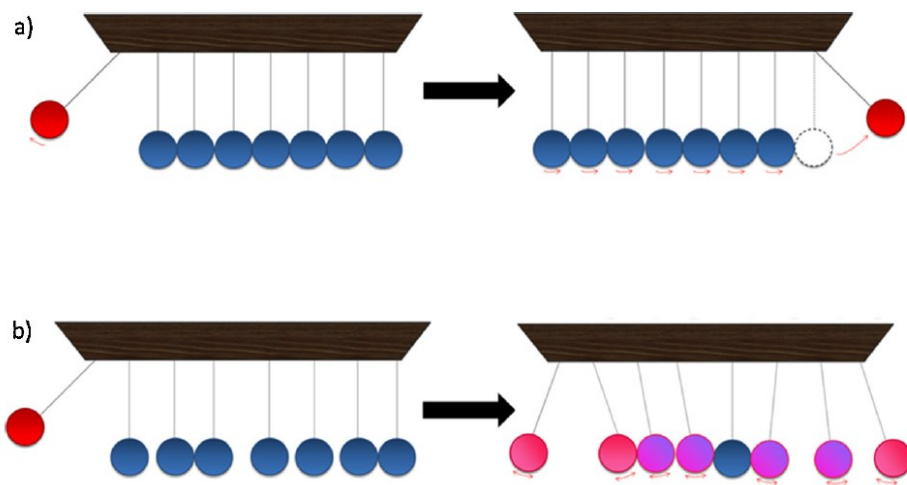


Figure 2.6 Schematic comparison by the Newton pendulum of thermal conductivity in a) crystalline materials and b) polymers (Burger et al., 2016)

2.2.2.3 Thermal Conductivity in Polymer

Acoustic phonons, along with charge carriers (such as holes and electrons), may transport heat in solids. And the thermal conductivity can be written as a summation of $k=k_e+k_p$, where k_e and k_p are the electron and phonon contributions, respectively (Mehra et al., 2018, 2019). In metals, the contribution from electrons extremely preponderates the contribution from phonons, while the phonons contribution dominates the thermal conductivity of insulator and semiconductors. The dominant heat conduction mechanism for many of polymers is by phonons (Chen et al., 2016). As mentioned above, the definition of phonon is the quanta of lattice vibration energy, realizing heat diffusion through the lattice vibration in the material (Zhang et al., 2019).

2.2.2.3.1 Lattice Vibration and Phonon. In a material, if there is the lack of the electron transport, the heat occurs through phonon and lattice vibration. The lattice of material can be considered as a mass and spring system (Figure 2.7 (a)). When a material is exposed to heat, an atom of material vibrates. The origin of phonon is caused by this vibration. In other word, the phonons are produced by the lattice vibration, as seen in Figure 2.7 (b) and (c). Heat transfers from one point to another through heat carrying known as phonons (quantified energy of atomic lattice vibration).

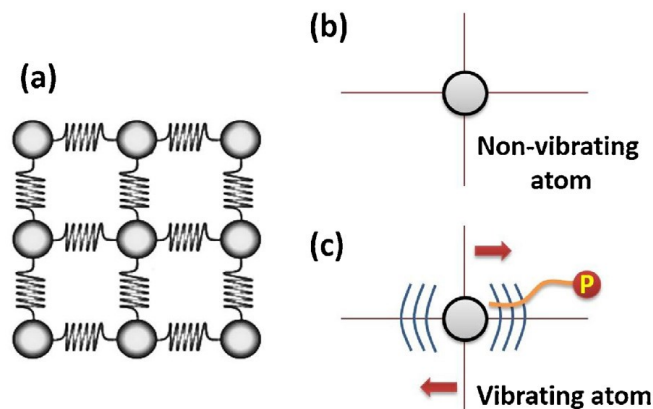


Figure 2.7 a) Representation of lattice by spring-mass system, b) non-vibrating atom and c) phonon generation by lattice vibration (Mehra et al., 2018)

To understand well the phonon concept, Mehra et al., (2018) showed a schematic presentation of a phonon (Figure 2.8). Two properties of phonon were captured, a circle with P (head) demonstrated the phonon particle nature, the wave nature of phonon was shown by tail (Mehra et al., 2018).



Figure 2.8 Schematic symbol of phonon (Mehra et al., 2018)

2.2.2.3.2 Thermal Conductivity in Polymers. As mentioned early, the thermal transport in a polymer is occurred by phonons. Figure 2.9 shows the thermal transfer process in a polymer occurred by phonons. (Zhang et al., 2019). It is known that the better phonon transport in polymer, the higher ability to conduct heat and thus the better thermal conductivity. If non-metals restrict the phonon transport, it will cause low thermal conductivity. All reasons, contributing to the poor phonon transport, is scattering in the material. Phonon scattering is defined as phenomena causing change in the energy, momentum or direction of the phonon (Mehra et al., 2018). On other word, phonons are not transported as a single common wave along the crystal anymore (Burger et al., 2016).

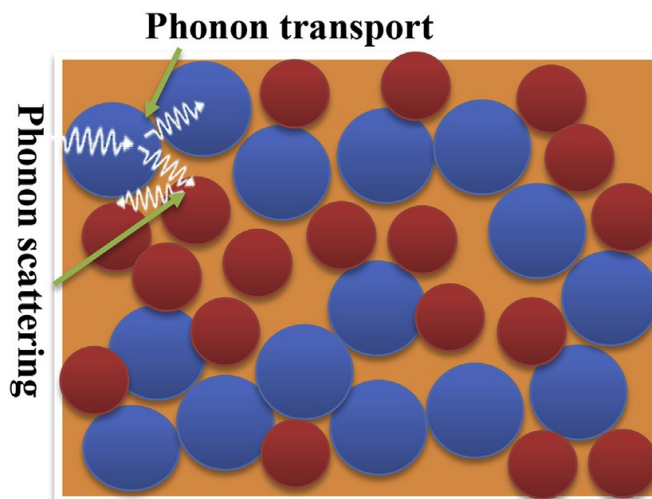


Figure 2.9 The mechanism of thermal conduction in amorphous polymers. Different atoms in the molecules of polymer are shown by different size and color (Zhang et al., 2019)

In a polymer, the phonon scattering can be divided into three types: 1- phonon-phonon scattering, 2- phonon-impurity scattering and 3- phonon-boundary scattering (Figure 2.10) (Burger et al., 2016; Mehra et al., 2018). As it is known, the lattice atoms will vibrate to transport the thermal energy during the heat transfer by conduction. In ideal situation, all atoms have harmonically vibrations, i.e. they vibrate together at the same frequency. Indeed, different normal modes and frequency exist in a material, in the other word; atoms will exhibit the anharmonic vibrations. The mechanisms of phonon-phonon scattering inevitably cause some thermal resistance sources in a material, however even more scattering phenomena make contribution to reducing thermal conductivity, for example, phonon-phonon scattering, phonon-electron scattering, electron-defect scattering and others (Burger et al., 2016). Based on momentum and energy conservation, the phonon-phonon collision can be classed into two main types: normal (N) and Umklapp (U) processes. During phonon scattering, both momentum and energy are conserved in Normal process, while energy is only preserved in Umklapp process (Mehra et al., 2018).

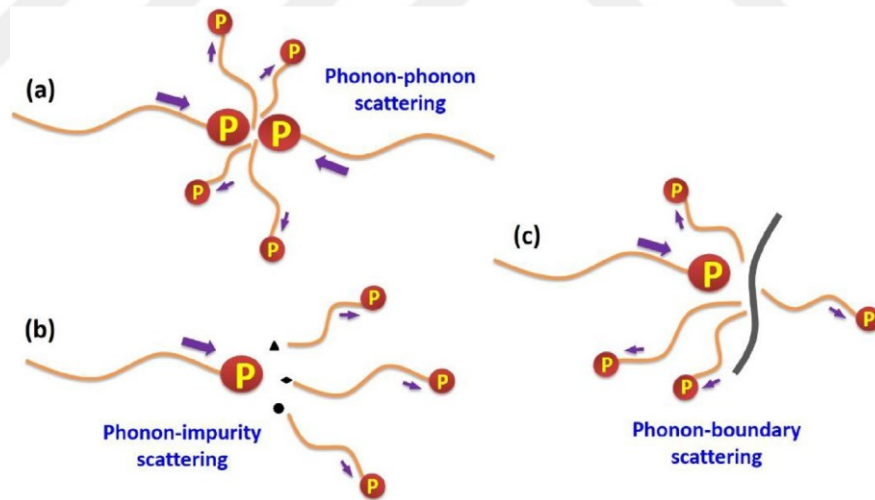


Figure 2.10 Phonon scattering modes of a) phonon-phonon scattering, b) phonon-impurity scattering and c) phonon-boundary scattering (Mehra et al., 2018)

As it is mentioned above, the lattice vibration is thought of a mass/spring system, the changes in the mass or spring constant during the propagation of phonon will influence the thermal transport. The spring constant can be changed by the impurities, resulting in changing the phonon energy. There are various types of imperfection in

the lattice such as dislocations, vacancy and point defect. It is known that impurities in a material can cause the phonon scattering and have negative effect on the transport of phonon (Mehra et al., 2018). When there are imperfections in the lattice, phonon scattering is occurred because of difference in the mass/spring constant at such imperfections (Mehra et al., 2018). Because, it is known that a defect or an impurity in a crystalline structure act as a barrier to the phonon transport. As shown in Figure 2.10, the phonon-impurity scattering can be easily be imagined in imperfect crystal (Burger et al., 2016). Although, the phonon-boundary and phonon-impurity scattering are type of elastic scattering and they cause no change in the phonon frequency, even a small amount of impurity seems to have a significant effect on thermal conductivity (Mehra et al., 2018).

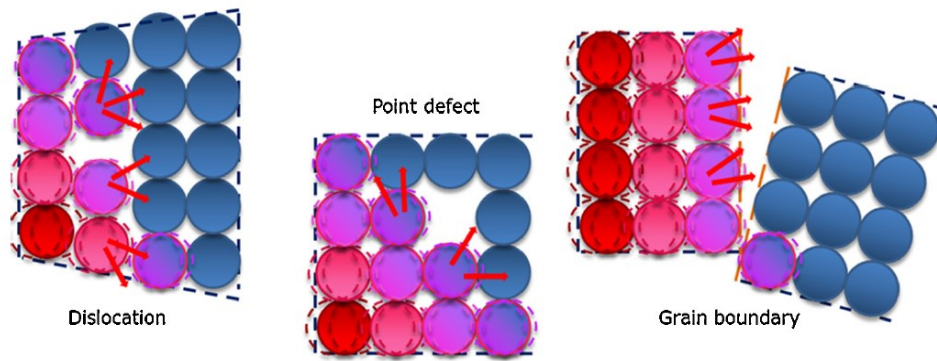


Figure 2.11 Phonon scattering in crystalline materials, because of different defects (Burger et al., 2016)

It is known that the phonon-boundary scattering is based on the geometry of sample and it is unavoidable (Burger et al., 2016). Two kinds of phonon-boundary scattering can occur when the phonon gets close to boundary: 1- specular phonon-boundary scattering: the phonon reflection from boundary is specular in nature 2-difuse phonon-boundary scattering: the phonon is scattered at different angles. These two types of phonon-boundary scattering lead to important bottlenecks in heat transfer through the interfaces. When the phonon transport across the crystal boundaries, phonon gets scattered and the effective phonon mean free path is influenced by this scattering. The most important effect of phonon-boundary scattering is observed at the low temperature, where the phonon mean free path is longest (Mehra et al., 2018).

In principal, a pure harmonic solid has infinite thermal conductivity. This reason is that phonons are the quantum eigenstates of the atomic system in the purely harmonic picture of the lattice vibrations. Hence, the phonons can propagate without dissipation. However, solids actually possess a finite thermal conductivity due to the phonon dissipation occurring by the phonon scattering (Chernatynskiy, Clarke, & Phillpot, 2012). The thermal conductivity can be theoretically predicted using Debye equation (Eq. (2.10)). As the phonons are treated as pseudo-particles through a solid, the Debye equation is an expression produced from a basic kinetic theory:

$$k = \frac{1}{3} \int c_v(\omega) v(\omega) L(\omega) d(\omega) \quad (2.10)$$

where c_v shows the heat capacity at constant volume, v is the velocity of the phonons, L is the phonon mean free path—the characteristic length before the phonon gets scattered (Chernatynskiy, Clarke, & Phillpot, 2012; Mehra et al., 2018).

The definition of specific heat is the ability of sample to store heat. Aside from the storage capacity, it is can be used to understand the rate of heating and cooling ability of the sample. This heat can be stored in the free conduction electrons and lattice vibrations form in any material. As mentioned above, due to the lack of electrons in majority of the polymers, the lattice vibrations or phonons play a dominant role. Mathematically, specific heat can be determined as partial derivate of the phonons' total energy, with reference to the temperature at a constant volume. The specific heat values vary with temperature and take different forms in various temperature regimes (Mehra et al., 2019).

The definition of mean free path is the distance transferred by the phonon before it is scattered, and three main scatterings influence on the mean free path: 1- There can be phonon- impurity scattering due to change mass/spring constant when a phonon comes across an impurity in host medium. The impurity-phonon scattering is elastic in nature. 2- Anharmonicity of chemical bond leads to the inelastic phonon–phonon scattering. 3- A phonon experiences a phonon-boundary when encountering a boundary. The mean free path of phonon approaches the lattice dimension at

nanoscale, and the phonon is fairly different. It is critical that the phonon scattering is controlled, thus the mean free path of materials can be larger. The effective phonon mean free path, L_{eff} , can be determined by the following equation (Eq. (2.11)) based on Matthiessen's rule (Mehra et al., 2018):

$$\frac{1}{L_{eff}} = \frac{1}{L_{ph}} + \frac{1}{L_b} + \frac{1}{L_{im}} \quad (2.11)$$

Where L_{ph} is the mean free path of phonon–phonon scattering process, L_b is the mean free path of phonon–boundary scattering process, L_{im} is the mean free path of phonon–impurity scattering process.

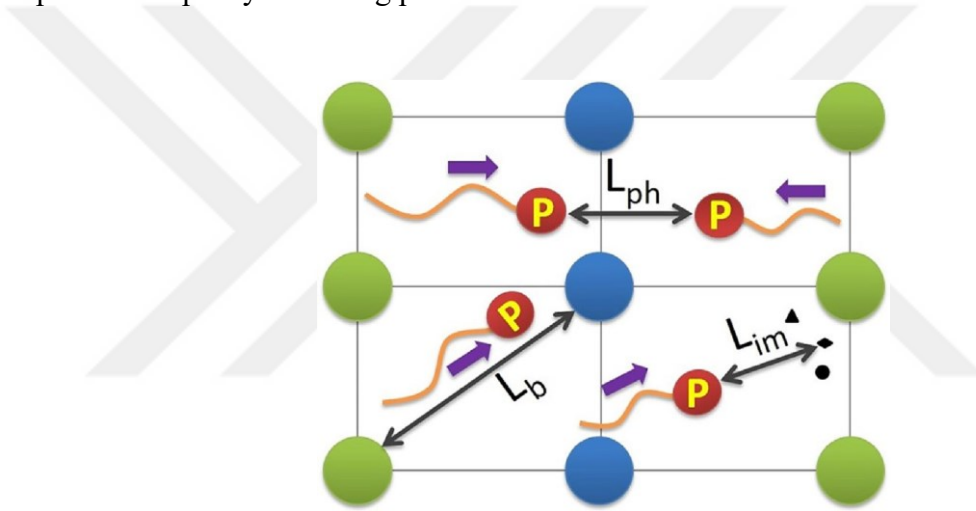


Figure 2.12 The mean free paths of phonon because of different scattering modes (Mehra et al., 2018)

According to Eq. (2.11), one of three scattering processes leading to the shortest mean free path will have a dominating effect overall other. Figure 2.12 shows the mean free path of the phonon because of different scattering processes. The maximum phonon scattered is usually experienced at the boundary or interfaces. At low temperature and for the long-wavelength phonons, the boundary scattering process is dominant. The boundary scattering can be observed at grain boundaries or filler-matrix interface and reduces the mean free path of phonon. Due to phonon scattering, the presence of imperfection and impurities in the crystal lattice affects detrimentally on the heat conduction. The vacancies and interstitial sites possess significant effect on the phonon transport (Mehra et al., 2018).

For phonon transport with little phonon scattering, an efficient path is provided by single polymer chain. The thermal conductivities of polymer nanofiber and single polymer chain is higher than that of their bulk polymers because of efficient phonon transport. Thus, at individual chain level, polymers such as Teflon, polyethylene (PE), so on, have high potential to accomplish high thermal conductivity (Mehra et al., 2018). For most of the polymers, both phonon group velocity and heat capacity of the bulk polymers are approximately equal to that of the individual chains. Thus, the reason for the large difference between the thermal conductivity of single chains and the bulk polymers is the mean free path of phonon. The mean free path of phonon in a transverse direction is very smaller than along a chain, because the vibrations of lattice relative to secondary bonds are more inharmonic than those related to covalent bonds. Polymer chains in a bulk polymer are in the condition of twisted random orientation and inter molecular weak coupling, mostly through van der Waals forces. These causes that the average mean free path of phonon for bulk polymer is very smaller than the phonon mean free path of a single polymer chain (Chen et al., 2016). As a result, in polymers, strong covalent bonds are responsible for intra-chain molecular interaction; weak van der Waals forces are responsible inter-chain molecular interaction. And both of them make a contribution to the phonon transport in different ways (Mehra et al., 2018). Moreover, the inherent defects (entanglements, voids, impurities and polymer chain ends, etc.) in bulk polymer lead to further decrease the mean free path of phonon and thermal conductivity of bulk polymer (Chen et al., 2016).

The thermal conduction mechanism in amorphous polymer nanocomposites quietly differs from that of crystalline particles. In polymers, due to the irregular atom arrangement, the phonon cannot transport in a straight wave, which leads to disordered vibrations and rotations of phonons around their equilibrium position (Kim et al., 2018).

The thermal conductivity of polymer mainly depends on the orientation of polymer chain and the transports of thermal energy effectively throughout the polymer chain. Crystalline polymers have highly ordered polymer chain segments with very low defect and therefore, show less phonon scattering and high thermal conductivity.

Amorphous polymers exhibit more low thermal conductivity because the mean free path of phonon is small constant because of the phonon scattering at many defects. It is reported that the thermal conductivity of semi-crystalline polymers increases with crystallinity (Namasivayam & Shapter, 2017).

Indeed, most of crystalline polymers are the semi-crystalline structures and they consist of amorphous and crystalline domains. As seen in Figure 2.13 (a), the polymer chains are periodically aligned in the crystalline domains, while they are entangled randomly in the amorphous domains (Huang et al., 2018). The crystalline degree of the system indicates the relative volumes of two domains. In semi crystalline polymer, the crystalline and amorphous regions make contribution to the thermal conductivity in various ways. In general, the heat conduction capacity in the crystalline domain is higher than in the amorphous domain. As it is known, the arrangement of chain is more intense in the crystalline region than in the amorphous region. The regions in which individual chains are extended provide higher thermal conductivity, which can be monitored in both the aligned polymer region and crystalline region. Because of the stiff covalent bonding, these regions of extended individual polymer chains behave as effective heat conductors throughout the chain axis. Nevertheless, in real systems, both the aligned and crystalline regions of polymer interact with one another, and so the phonon scattering happens. For the propagation of vibrational waves, different curvatures and random orientation in single polymer chain cause a tortuous path. The effective mean free path of the amorphous polymer is short due to occurring the phonon scattering at a great number of regions, and it causes the low thermal conductivity. This can be named as structural scattering meaning that the bends and different disordered structures limit the phonon propagation. And the mean free path of phonon is decreased to the length of several monomers by structural scattering. The heat conduction behavior of the amorphous polymer is similar to that of the amorphous material. The thermal conductivity of amorphous polymers is low due to the irregular structure of the amorphous polymers (Mehra et al., 2018).

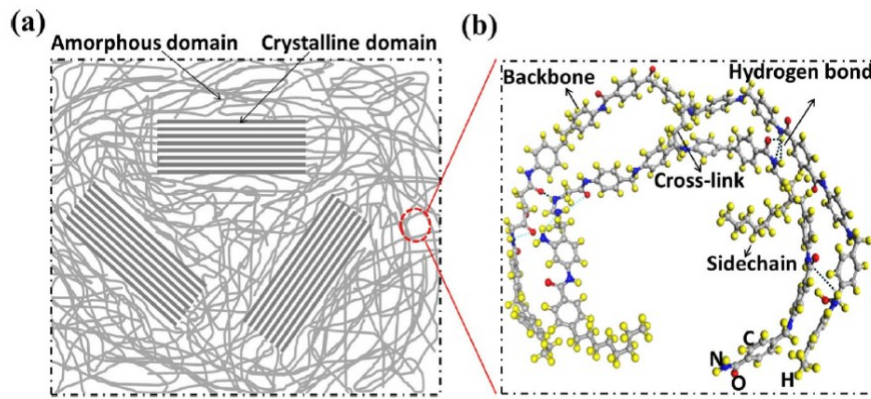


Figure 2.13 The structure of a) a polymer includes crystalline and amorphous domains, b) of a polymer chain (Huang et al., 2018)

As mentioned previously, enhancing the polymer chain alignment can enhance the thermal conductivity of polymers. Apart from the alignment of polymer chains, the inter-chain coupling and the chain structure which consists of sidechain and backbone bonds effect on the thermal conductivity. As seen in Figure 2.13 (b), the functional groups which branches out of the backbones are named as sidechains. The thermal conductivity and vibrational dynamics are expected to vary when various kinds of sidechains are introduced, because the polymer chains topology is changed by sidechains. It is found that thermal conductivity of polymer chain decreases with introducing sidechains. A great number of sidechains and a higher length of sidechains cause lower thermal conductivity due to increase in the phonon scattering. The thermal conductivity of bulk polymers is decreased by sidechains because of decrease in the crystallinity as sidechains are introduced (Huang et al., 2018).

Crystallinity is known to be a significant physical factor on the thermal conductivity (Burger et al., 2016; Kim et al., 2018). Actually, revealed the relationship between the crystallinity and thermal conductivity is difficult in the experimental results. This is because the crystallinity can be influenced by many key factors such as bond strength, temperature, defects, molecular weight, processing conditions, and so on (Kim et al., 2018).

As previously mentioned, in a crystalline material, the existence of a defect, any discontinuity or an interface of in the crystalline will lead to drastically reduce the

thermal conductivity. And, this thermal conductivity decrease at component interface is generally named as “Kapitza resistance”, which quantifies this “thermal resistance”. The Kapitza resistance theory also explains that even with an interface in which atoms of two ideal consistent perfectly keep in touch with each other and are perfectly ordered, there will be a thermal resistance because of the variation between the normal modes of vibration. The more defects exist in the crystalline structure, the lower thermal conductivity of the crystal, because defects cause the phonon scattering such as phonons are diffracted, reflected or refracted, which decrease the mean free path and this decrease thermal conductivity (Burger et al., 2016). In other words, the presence of interfacial thermal resistance in the polymer nanocomposites can cause the backscattering of heat carriers, e.g. phonons, holes and electrons, this varying the thermal conducting pathways and reducing the efficiency of thermal conductivity enhancement (Kim et al., 2018).

The molecular weight (M_w) has effect on the thermal conductivity of polymers. As mentioned early, the various thermal pathways nature in the polymer chains can be provided by short and long polymer chains. It is presumed that long polymers chains provide long thermal pathways, and thus phonon can transport more effectively. In addition, the thermal conductivity of branched polymers is lower than that of the linear polymers as keeping the same M_w . Because the branched polymers show more resistance to the phonon transport than the linear ones. A polymer chain having less branching, good linearity and elastic modulus provides better thermal phonon transport; however a polymer chain with low elastic modulus and more branching can cause the phonon scattering because of side chain vibration (Mehra et al., 2018).

In general, larger stiffness of angular bending and bond stretching causes a higher thermal conductivity. The presence of double $-C=C-$ bond having sp^2 hybridization leads to higher thermal conductivity because of two reasons: 1- the bonding energy of $-C-C-$ bond having sp^3 hybridization is 2.8 times lower than that of $-C=C-$ bond, 2- Delocalized conjugated π -bond is formed by consecutive sp^2 bond. The atoms in conjugated π -bond are constrained by this bond to be in the same atomic plane.

Consequently, the segmental rotation stiffness is increased by the conjugated π -bond (Huang et al., 2018).

The thermal conductivity of most polymers is in the range of 0.1-0.6 W/mK (Table 2.2). In general, polymers have low thermal conductivity because of its feeble atomic interactions, very complex crystal structure, lower atomic density and eventually larger level of anharmonicity in the molecular vibrations limits the phonon transport (Mondal & Khastgir, 2019). And the factors influencing the thermal conductivity of polymers are explained above.

Table 2.2 Thermal conductivity of some polymers (Chen et al., 2016; Han & Fina, 2011)

Polymers	Thermal conductivity (W/mK)
HDPE	0.33-0.53
LDPE	0.30-0.34
EVA	0.35
PMMA	0.16-0.25
PC	0.19-0.21
Epoxy	0.17-0.21
ABS	0.15–0.33
PVC	0.13–0.29
PVDF	0.19
PVDC	0.13
PP	0.11–0.17

2.2.3 Mechanical Properties of Polymers

It is difficult that the polymers are categorized as certain types of materials, such as a viscous liquid or a glassy solid. Because the mechanical properties of polymers depend on the testing conditions, e.g. temperature, amount of strain and the rate of load application. A polymer can display all properties of a brittle, glassy solid or a viscous liquid or an elastic rubber according as the time scale and temperature of measurement. In general, polymers are viscoelastic materials, a common term emphasizing the intermediate position of polymers between elastic solids and viscous liquids. At high frequencies or low temperatures of measurement, a polymer may behave like a glass

with 1-10 GPa of Young's modulus and it will flow or break at strains higher than 5%. At low frequencies or high temperatures, the same polymer may behave like a rubber with Young's modulus of 1-10 MPa, which withstands high extensions (about 100 %) without the persistent deformation. At still higher temperatures, the persistent deformation happens under load, and the polymer act as a highly viscous liquid. In an intermediate frequency and intermediate range, generally named as the glass transition range, the polymer is neither rubber nor glassy-like. It indicates an intermediate modulus; it is viscoelastic, and it may dissipate a significant energy amount on being strained (Ward & Sweeney, 2012).

As mentioned previously, the polymers exhibit viscoelastic behavior. This behavior not only mean a superposition of independent elastic and viscous forces, but also it contains a new phenomenon which is known as “anelasticity”, at which both forces become coupled. It is clear in the observation that some deformation, in spite of being reversible, needs a specific time to be established as applied a load. The contributions of viscous flow, anelasticity and elasticity to all mechanical response of polymer have various weights for various polymers. Especially, they highly change with temperature (Strobl, 1996).

Table 2.3 Mechanical properties of some polymers (Fischer, 2009)

Polymers	Young's modulus [GPa]	Yield strength [MPa]	Density [g/cm ³]
HDPE	0.56	30	0.96
LDPE	0.18	11	0.91
PMMA	2.80	70	1.20
PC	2.30	68	1.20-1.30
Epoxy	2.10-5.50	60	1.20-1.40
ABS	2.50	50	1.20
PVC	2.00	25	1.20
PP	1.30	35	0.90

Polymers are known to uniquely respond to the applied stresses which reflects the nature of their molecular structure and chemical bond. Mechanical properties of some polymers are given in Table 2.3 (Fischer, 2009). High Young's modulus values show that the sample is rigid and resistant to stretching and elongation. The polymer

deformations may contain two parts: reversible and irreversible part. Generally, the behavior of all polymers is Hookean before yield point. The reversible elongation before the yield point, named as the elastic range, mainly results from stretching and bending of covalent bonds in the backbone of polymer. Also, the beneficial part of the stress-strain curve may contain some of recoverable uncoiling of the polymer chains. After yield point, the irreversible slippage of polymer chains is the main mechanism. As mentioned above, the behavior of polymers exhibits time and temperature dependence. Therefore, the range of stress-strain behavior is more complicated and change with polymers, as seen in Figure 2.14 (Carraher, 2017).

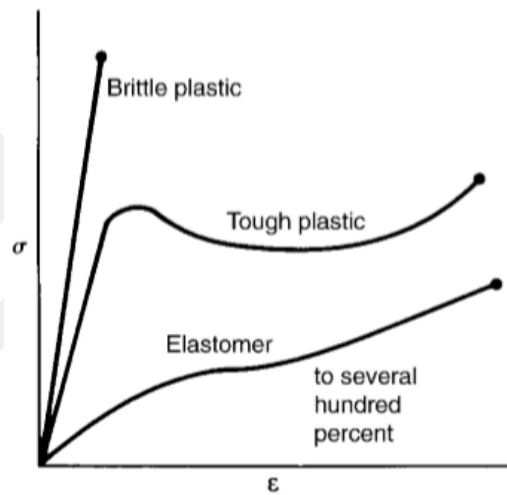


Figure 2.14 The Stress-strain curves of three types of polymers (Sperling, 2005)

For brittle polymer, the stress-strain curve is linear up to fracture at almost 1-2 % of elongation. The typical stresses at break for these polymers are almost 6×10^7 Pa. Polystyrene is an example for this type of polymers. For tough plastic, an example is polyethylene. As seen in Figure 2.14, the Young's modulus of this polymers is lower than that of glassy, brittle polymer. Generally, tough polymer shows a yield point, which is followed by the extensive elongation at about constant stress. This is named as the plastic flow region and it is obviously a nonlinear viscoelasticity region. In this range, Stresses are generally in the range of $2-5 \times 10^7$ Pa. In plastic flow region, the extension at constant stress is called as cold drawing. At last, the polymer strain hardens and then ruptures. Most of tough polymers break at nearly 50 % of elongation. For the rubber elasticity, the state equation governs here, with the peculiar

nonlinear curve of elastomer. For elastomer, the elongation may be several hundred percent (Sperling, 2005).

It is known that the commercially polymers are generally classified as thermoplastic and thermoset. Therefore, the mechanical behavior of both groups has been studied carefully. Thermosets are greatly cross-linked polymer chains forming 3D network structure. Since the chains cannot slide or rotate, these polymers have good hardness, stiffness, and strength. However, they also possess a high glass temperature, impact properties and poor ductility. In terms of a tensile test, the behavior of these polymers is the similar to that of brittle metal or a ceramic (Askeland, 2009).

Most thermoplastics (solid and molten) present a Non-Newtonian and viscoelastic behavior. Non-behavior is that the strain and stress are nonlinearly related for most part of the stress-strain curve. The viscoelastic behavior means that the deformation of both elastic and plastic (viscous) occurs as applying an external force to a thermoplastic polymer. The mechanical behavior is tightly related to the way in which the chains of polymer move relative to other under load. Deformation is known to be more complex in thermoplastics and the deformation process is based on both the rate and time at which the load is applied. Figure 2.15 shows an example for stress-strain curve of thermoplastic (Askeland, 2009).

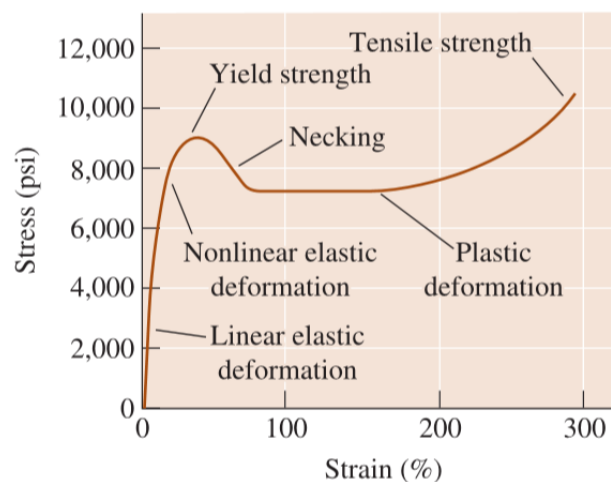


Figure 2.15 The stress-strain curve of 6,6-nylon, a typical thermoplastic (Askeland, 2009)

In the thermoplastics, the elastic deformation is the results of two mechanisms. An applied stress leads to the covalent bonds in the chain to distort and stretch, which allows the chains to elastically elongate. When removing the stress, recovery from this distortion is nearly instantaneous. This behavior likes as that ceramics and metals, also deforming elastically by the stretching of ionic, covalent, or metallic bonds. However, additionally, all segments of polymer chains may be deformed; as removing the stress, the segment come back to the original positions of segments only for a space-mostly hours or even moths. This time-dependent (viscoelastic) behavior maybe make contribution to some of non-linear elastic behavior (Askeland, 2009).

The amorphous thermoplastic polymers distort plastically, as the stress surpasses the yield strength. In contrast to the deformation in metals, the plastic deformation is not as a result of the dislocation movement. Instead, the chains rotate, slide, stretch and disentangle under load for causing the permanent deformation. This phenomenon can explain the drop in the stress above the yield point. Firstly, the chains may be greatly intertwined and tangled. As the stress is enough high, the chains start to straighten and untangle. Necking also happens, which permits the continued sliding of chains at a lower stress. Finally, however, the chains are nearly parallel and near each other; stronger van der Waals between the more closely aligned chains needs greater stresses to carry through the deformation and fracture process (Figure 2.16) (Askeland, 2009).

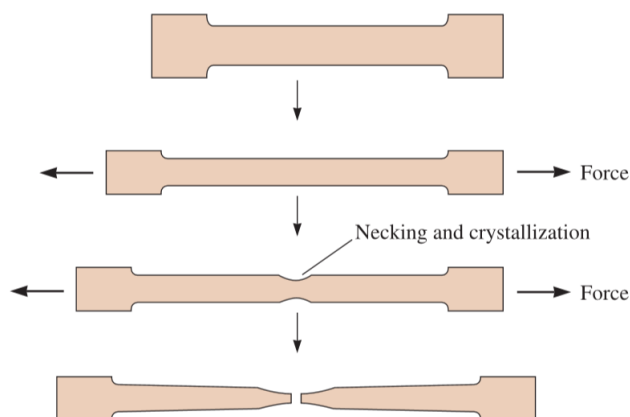


Figure 2.16 Necks are not stable in amorphous polymers, since local alignment strengthens the necked region and decreases its rate of deformation (Askeland, 2009)

2.2.4 Thermal Properties of Polymers

Crystallization in polymers is the topic of academic interest, as it is known that polymers exhibit a diversity of structures at various length scales, such as lamella, the unit-cell and spherulites. The polymers' crystallization results in various morphologies, which are based on the existence of other constituents and the crystallization conditions. Crystallization is commonly observed for numerous polymers having the structural regularity. The polymers' crystallization process includes two steps, named as nucleation and growth. When the nucleation happens spontaneously, because of only supercooling and where no second phase or other nuclei exist, this nucleation is called as homogenous nucleation. As the nucleation is induced in the existence of any other second phase, e.g. a foreign surface or particle, this type of nucleation is known as heterogeneous nucleation. The nucleation, growth and development kinetics of these crystalline structures has the main and pragmatic interest. The polymer crystallization kinetics is controlled by several inherent factors including chain flexibility, chain defects, molecular weight, and stereo-regularity. Also, the crystallization process is influenced by the experimental conditions such as stress, nucleating agents, pressure and temperature (Mittal, 2010).

It is known that the mechanical properties of materials strongly depend on the crystallinity. For example, the Young' modulus and yield stress of amorphous material is lower than that of the crystalline composite, therefore the mechanical properties of semi-crystalline polymer will change with the ratio of amorphous to crystalline material. Since the crystallinity strongly influences the mechanical properties, it is attractive to control the polymer crystallinity. This can be carried out to a particular extent by the appropriate heat treatments. Slow cooling and annealing will give much better crystalline content than a rapid quench. Notwithstanding, in most of products, the imposed strain and cooling rate will differ highly from one place to other in the molding, and thus the large differences in the crystallinity may be observed in the material. Especially, this problem will be highest for thick samples (Swallowe, 1999).

It is known that the morphology of molecular controls all properties and the crystallization mechanisms determine the molecular morphology. These mechanisms are made inferences from the detailed researches on the crystallization kinetics. To examine the kinetics correctly, the knowledge of crystallization thermodynamics or equilibrium requirements is necessary. Even though this knowledge is significant, and it can be provided theoretically, the real equilibrium state of crystalline polymer is seldom achieved. This well-known case is because of the kinetic factor included in the crystallization from melt causing the creation of relatively little crystallites with accompanying large interfacial free energies. It is difficult that crystallites which include the extended chains achieve (Mark, 2004).

The thermal properties of material can be determined by the differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA). While DSC gives the melting, crystallization temperature, specific heat as well as heat of fusion, TGA gives the thermal stability behavior of materials. As increasing temperature, the temperature is sufficient to overcome the forces existing the polymer crystalline portion which allows a breaking up of the crystalline portion. This temperature is named as “crystalline transition temperature (T_c)”. In general, T_c has direct relation with melting point or “melt transition temperature (T_m)” (Figure 2.17). T_m is temperature range at which the whole or total polymer chain mobility forms (Carraher, 2017). The area under the peak presented in Figure 2.17 gives the heat of fusion (ΔH_f). The polymer chemical structure controls the actual values of entropy and enthalpy of fusion. The most significant intramolecular and inter structural characteristics contain bond flexibility, structural regularity, interchain attraction and close packing ability. The high melting points generally depend on close packing capability, highly regular structures, strong interchain attraction, rigid molecules or various of these factors combined (Sperling, 2005). When the temperature continues to increase, enough energy is available to overcome the main bonds which hold polymer together, thus the polymer degrades at the “degradation (decomposition) temperature (T_{deg})” (Carraher, 2017).

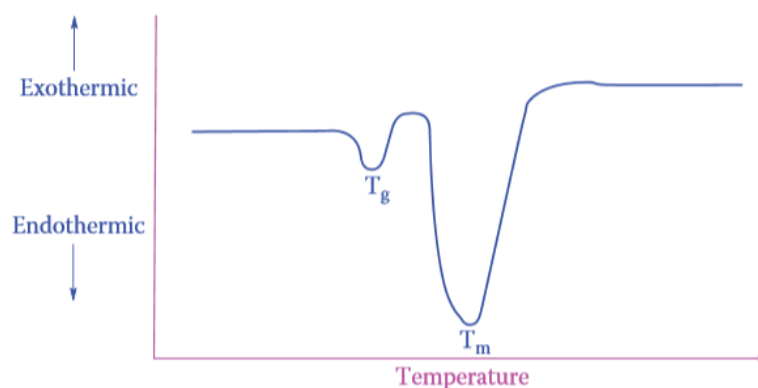


Figure 2.17 DSC thermogram of a polymer (Carraher, 2017)

A suitable understanding of thermal degradation process of a certain polymer is a significant stage in the thermal stabilization of polymer. The polymer degradation process itself is a complicated procedure including many chemical reactions in the solid material as well as the physical processes which simultaneously occur during heating and cause the formation of solid and gaseous products. The polymer degradation starts at weak sites such as side chain groups or unstable end and it is followed by processes as the chain stripping at higher temperatures, β -scission, hydrogen transfer and main chain random scission. Additionally, consecutive reactions such as radical recombination, crosslinking, condensation, and cyclization happen simultaneously (Mittal, 2010).

As mention above, thermal decomposition of polymers takes place via various possible mechanisms, e.g., side group elimination, depolymerisation and random scission. Side group elimination includes the elimination of molecules or atoms from the polymer chain backbone, by separating an unsaturated chain. Random scission happens by the generation of free radicals in a polymer, causing the fragmentation of the polymer molecules into smaller molecules with dissimilar lengths of chain (Jineesh & Mohapatra, 2019)

A good understanding of the polymers' thermal stability is thus highly significant to (Mittal, 2010):

- enhance a rational technology for the fabrication of polymer;

- produce fire-safe polymeric materials;
- provide the use of polymers, practically at high temperatures;
- improve new technologies for effective energy management;
- perform the thermal recycling of waste polymers (Mittal, 2010).

2.3 Polymer Nanocomposites

Polymers are used commonly in wide range of applications due to their properties, however, their low thermal conductivity limits their applications in some fields. Because, with the miniaturization, functionalization and integration of electronics, the thermal dissipation becomes an important problem to be solved and thermal management is important to the lifetime, reliability and performance of the electronic devices. (Chen et al., 2016). So, the enhancement of their thermal conductivity is a challenging problem for the application area of polymers and this subject have increased interested in recent years. As it is clearly seen in the previous part of this chapter, to increase thermal conductivity, the polymer chains orientation should be enhanced and the amount of oriented and ordered domains in bulk polymers should be increased (Chen et al., 2016). Enhancing chain alignment and crystallinity of polymer generally improves the thermal conductivity of polymers (Huang et al., 2018). In addition, the other effective method to improve the thermal conductivity of polymer is cross-linking to occur chemical bond (Huang et al., 2018). Although arranging the regularity of molecule can improve the thermal conductivity of polymer, the influence is quite limited. Addition of thermally conductive filler into polymer matrix is the most common, practical and acceptable method to improve thermal conductivity (Huang et al., 2018; Zhang et al., 2019).

In the field of polymer science, one of the popular progressions is on the polymer nanocomposites (Bayan & Mtech, 2020). The definition of polymer nanocomposites may be a mixture of two or more components, where the continuous phase (matrix) is a polymer and the dispersed phase possess at least one dimension smaller than 100 nm (Szeluga et al., 2015). One aim of the materials science is to enhance the nanocomposites with better electrical and thermal properties and higher mechanical

strength while decreasing the weight and ensuring high resistance against external factors (Szeluga et al., 2015). It is known that in general, the nanofillers are used in many application due to their superior thermal and mechanical properties that are largely due to their large surface area to volume ratio (Hussein, Abd-Elnaiem, Asafa, & Jaafar, 2018).

Compared to conventional micrometer-sized fillers, at the same filler concentration, nanofiller achieve a better enhancement in the properties (Safdari & Al-haik, 2018). In addition, the polymer nanocomposites progressively take place of more conventional composites because of their highly enhanced properties and ease of manufacturing and processability. Indeed, due to the enhancements at low filler concentrations, the polymer nanocomposites are excellent candidates for application in high-performance structural composites, such as those in production of automotive, sports facility, aircraft, marina and spacecraft composites (Araby et al., 2015).

It is known that the excellent combination of a polymer and nanofiller leads to not only changes in morphological and structure properties of materials but also physicochemical variations. These ones can be adjusted considerably by the choice of proper polymer and nanofiller (Bayan & Mtech, 2020). In addition, as seen in Figure 2.18, obtaining the polymer nanocomposites with high properties needs careful design of following segments:

- 1- The formation of conductive and strong nanofiller network,
- 2- Suitable polymer matrix, and
- 3- Good interface between matrix and nanofillers.

In specific terms, forming effective interconnected networks is nearly associated with the selection of nanofiller type, directly controlling the geometric shape of network structure. Distribution and dispersion of two fundamental issues for the formation of conducting networks. Uniform distribution and good dispersion of nanofillers are beneficial for forming interconnected networks. However, incomparably designed non-uniform distribution and specific extent of the agglomeration can also achieve interesting segregated structures with superior properties, based on the polymer matrix type. Also, the interface between the matrix and nanofiller is a critical key factor in

affecting the properties of bulk nanocomposite. Generally, comprehensive consideration of the polymer matrix, contents, and types of nanofillers, interfacial behavior and production method that influence dispersion quality should be paid attention to design the polymer nanocomposites with excellent properties. However, the large cluster of aggregates mostly cause defects and bad interfacial interaction to the matrix and reduce the mechanical properties of samples. For example, based on the reported studies in the literature, CNTs loading in the matrix is generally controlled below 10 wt.% because of the important increase in the viscosity, leading the poor inferior quality and processability of final polymer nanocomposites. Content, integrity, dispersion and purity of nanofillers as well as the types of polymer are all considered to be the main factors of affecting the properties of the polymer nanocomposites (Li et al., 2019).

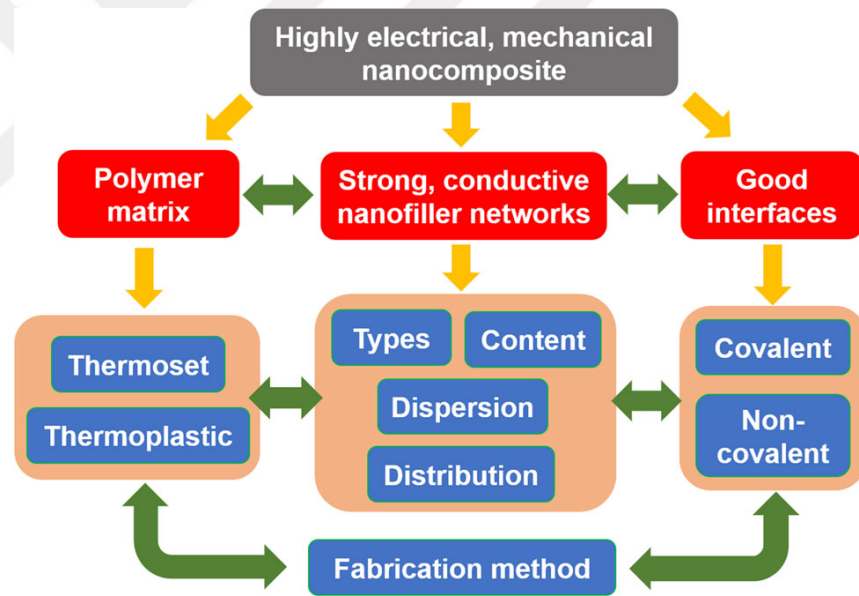


Figure 2. 18 General considerations for the production of nanocomposite with high properties (Li et al., 2019)

Especially, the thermal conductivity is the most significant thermal property needing to be considered for the new polymer nanocomposite product. It is known that the thermal conductivity of nanofiller materials is one of the significant factors influencing the thermal conductivity of polymer nanocomposites. Table 2.4 shows the thermal conductivity of some nanofillers used the over past decades. To enhance the polymers' conductivity, it is considered that metals are ideal candidates because of

their high electrical and thermal conductivity. Numerous studies have been conducted on the influence of different metal powders on thermal properties such as diffusivity, conductivity, and specific heat of various polymer categories. The addition of metallic particles into polymers leads to increase in the thermal conductivity and simultaneously in density of polymer nanocomposites, thus limiting the use of metal powders for the light-weight applications. However, carbon-based materials seem to be promising candidates as nanofillers because of their high conductivity and low density (Agrawal & Satapathy, 2015).

Table 2.4 Thermal conductivity of widely used filler materials (Chen et al. 2016; Zhang et al. 2019)

Fillers	Category	Thermal conductivity [W/mK]
Silver	Metal	427
Aluminum	Metal	234
Copper	Metal	400
Aluminum nitride	Ceramics	>230
Boron nitride	Ceramics	200-300
Aluminum oxide	Ceramics	30
Graphene	Carbon-based	2000-6000
Carbon nanotubes	Carbon-based	1000-4000
Diamond	Carbon-based	2966

2.3.1 Carbon-Based Materials

Carbon-based nanomaterials are fundamentally nanomaterials where carbon is the only or main constituting element (Bayan & Mtech, 2020). As compared to other filler materials, carbon based materials such as carbon nanotubes (CNTs), graphene are promising filler materials due to their intrinsic properties such as superior electrical properties, high thermal conductivity, high mechanical properties and high aspect ratio, and unique graphitized plane structure (Mittal et al., 2015; Safdari and Al-haik, 2018). These properties is attributed to the unique structure of carbon-based materials which offers strong surface interaction and large surface to volume ratio (Safdari & Al-haik, 2018).

It is known that the sixth element in the periodic table is carbon and it belongs to the group IV. The atomic number and electronic configuration of carbon are 6 and $1s^2 2s^2 2p^2$, respectively. As a result, the carbon atom has four valence electrons which are different hybridized in sp , sp^2 and sp^3 forms. In group IV, just carbon can create $\pi-\pi$ multiple bonds such as $C=C$, $C=N$, $C=S$ and $C=O$. The carbon strongly tends to occur the long homoatomic structures. These structures of carbon are due to the sp^2 and sp^3 bonded carbon atoms. In the nature, the carbon occurs in several allotropic forms such as diamond, graphite, and coal. Synthetically, the carbon is produced in various allotropic forms such as carbon black, carbon nanotubes, synthetic graphite, carbon fibers and synthetic diamond, so on, having many applications (Khan, Kausar, & Ullah, 2016).

As stated above, carbon-based nanomaterials do not only consist of graphene, CNTs and GnP. Several other types of carbon-based nanomaterials have been explored and successfully defined (Figure 2.19). The allotropes of carbon exist in different shapes 0D to 2D and in different sizes from micro sizes to nano sizes (Noh et al., 2016) and each carbon allotrope has a diverse range and distinct of physical properties. Interestingly, all carbon allotropes are quite stable under the environmental conditions (Al Sheheri et al., 2019). For example, graphene nanoribbons can be produced by unzipping carbon atoms throughout an axial direction. Another type of carbon-based nanomaterials is carbon nanofibers (CNFs) (with micrometer length and nm to micrometer diameter) having excellent electrical, chemical, and mechanical properties. Expanded graphite (EG) is layered structure with a little increase in the interlayer spacing with reference to the natural graphite, having thin platelets (3080) stacked loosely (Safdari & Al-haik, 2018).

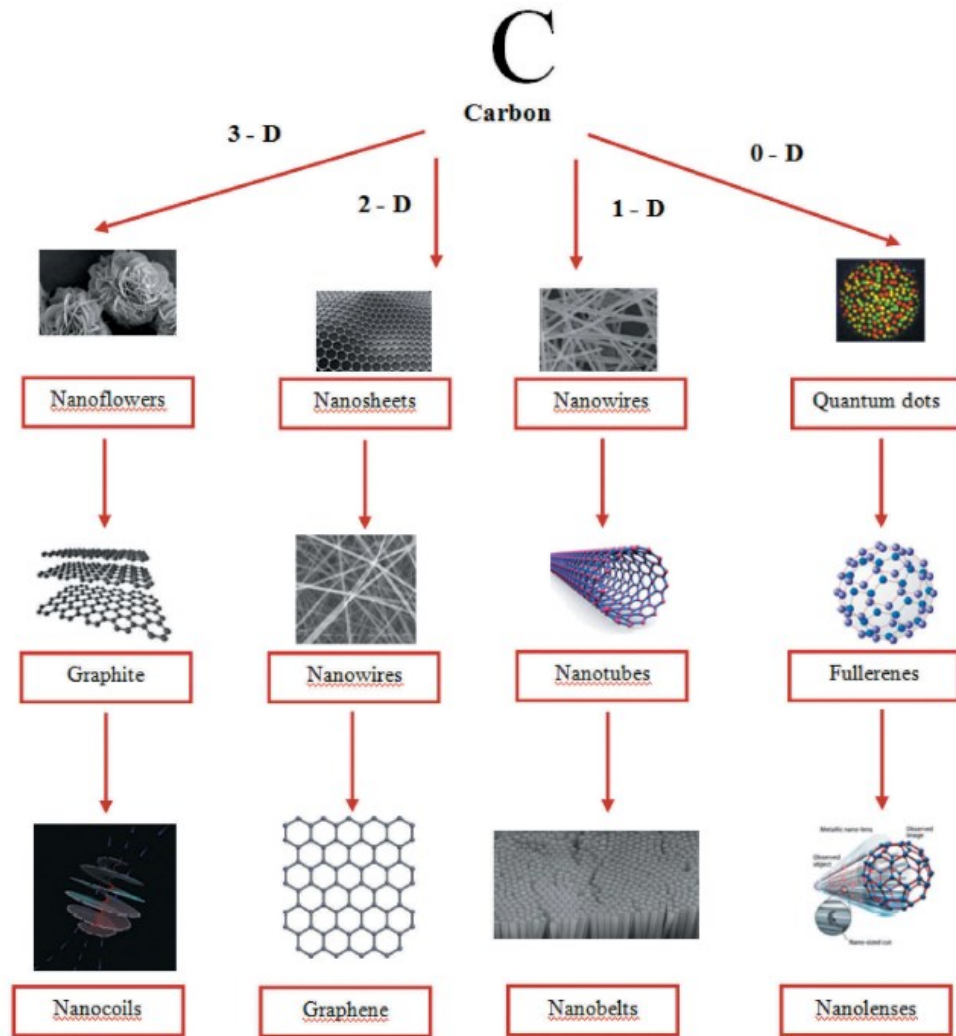


Figure 2.19 Different carbon allotropes and derived structures (Guo et al., 2019)

As compared with the pure polymers, almost all of the studies show enhancement in the properties of obtained polymer nanocomposites due to intrinsic properties of carbon-based materials (Safdari & Al-haik, 2018). However, the property enhancement for the polymer nanocomposites including different carbon-based materials is different due to various structure and properties of carbon-based materials. For example, as seen in Figure 2.20 and Table 2.5, thermal conductivity of carbon allotropes is a wide range from 0.01 W/mK for amorphous carbon to 6000 W/mK for graphene. Generally, the phonons dominate the heat conduction in the carbon nanofillers; however, some carbon-based materials, for example graphite, act as metals. Strong covalent bonding with sp^2 hybridization of carbon atoms in the material

causes effective phonons transport by lattice vibrations (Mehra et al., 2019; Noh et al., 2016).

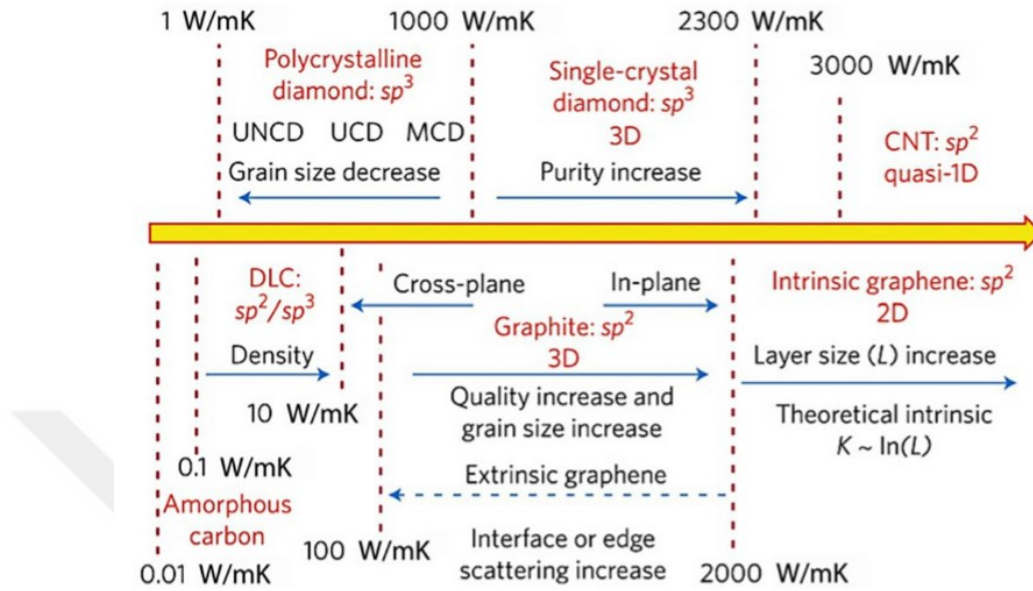


Figure 2.20 Thermal conductivity of carbon allotropes (Mehra et al., 2019)

Table 2.5 Physical properties of various types of carbon-based nanomaterials (Mittal et al., 2015)

Property	Fullerene	SWCNT	MWCNT	Graphite	Diamond
Density [g/cm ³]	1.7	0.8	1.8	1.9-2.3	3.5
Thermal conductivity [W/mK]	0.4	6000	2000	298 ^p , 2.2 ^c	900-2320
Thermal stability in air [°C]	~600	>600	>600	450-650	<600
Thermal expansion coefficient [K ⁻¹]	6.2×10 ⁻⁵	Negligible	Negligible	-1×10 ^{-6p} , 2.9×10 ⁻⁵	1-3×10 ⁻⁶
Electrical conductivity [S/cm]	10 ⁻⁵	10 ² -10 ⁶	10 ³ -10 ⁵	4000 ^p , 3.3 ^c	10 ⁻² -10 ⁻¹⁵
Electron mobility [cm ² /Vs]	0.5-6	~10 ⁵	10 ⁴ -10 ⁵	2.0×10 ⁴	1800

c: c-axis; p: in-plane

The property enhancement of nanocomposites is different depending on the use of carbon-based materials. Therefore, among the carbon nanofillers with three geometrically different types, i.e. particles, tubes, and platelet, CNTs and graphene are the most popular and attractive candidates as the use of nanofillers to enhance the properties of polymers due to their excellent intrinsic properties.

2.3.1.1 Graphene

Graphene was discovered by Andre Geim and Kostya Novoselov at Manchester university in 2004 and they won a Nobel Prize Award in Physics in 2010 for the discovery of graphene (Khan et al., 2016). A graphene is basically defined as two-dimensional material (layer) with one atom thickness. Graphene is defined as a two dimensional single-atom-thick sheet of sp^2 hybridization carbon atoms tightly packed in a the honeycomb crystal lattice (Jouni et al., 2017; Khan et al., 2016; Kumar et al., 2017). In addition, graphene is known to be the fundamental structural unit of other carbon allotropes such as 3-D graphite, 1-D CNTs and 0-D fullerenes (Khan et al., 2016) and graphene derivatives have been classified based on total oxygen content, layer numbers of the sheet, chemical modifications and orientation (Kumar et al., 2019b)

Graphene have significant attention in the physics, chemistry, the communities of materials science and biology because of its excellent properties (Safdari & Al-haik, 2018; Szeluga et al., 2015). However, its intrinsic properties are based on its structural perfection, influenced strongly by preparation methods (Du & Cheng, 2012). Its properties are given in Table 2.6 (Khan et al., 2016). Graphene is lightweight, transparent, 100 times stronger than steel, very thin, a good thermal and electrical conductor. Furthermore, graphene is the thinnest material in the World and strongest as measured. The electrical conductivity of graphene is 6×10^5 S/m which is not influenced by the chirality as in CNTs. Moreover, these properties associated with its impermeability to gases and high specific surface area ($2630 \text{ m}^2/\text{g}$) demonstrate the excellent graphene derivatives potential as filler materials to enhance the polymer nanocomposites properties (Garzón & Palza, 2014; Safdari & Al-haik, 2018).

Graphene with the integrated crystalline structures theoretically introduce superior physical and chemical performance for its polymer nanocomposites (Figure 2.21). Graphene and its nanostructures can be formed from the exfoliation of expanded graphite. Indeed, there is not appeared graphene with ideal crystalline in the nature, and defect are inevitably formed during the preparation process. Relevant to thermal conductivity, the existence of defects leads to various vibration modes for the phonon

transport, resulting in scattering phonons and charge carriers, reducing the length of ballistic transport path and influencing the mobility of carrier and thermal conduction (Zhang et al., 2019). According to actual atomic layer numbers, the lattice dynamic - phonon- property of multi-layer graphene and GnPs may differ from single-layer graphene, which result in a lower intrinsic thermal conductivity value (from 3000 down to 10 W/mK) (Su, Li, & Weng, 2018). For example, experimental thermal conductivity of single-layered graphene layer in is 3000-5000 W/mK in in-plane, however 6 W/mK in cross-plane because of the weak inter-plane van der Waals forces (Kumar, Sharma, & Dixit, 2019a). In addition to difference in thermal conductivity, the strength of graphene and its derivates can considerably change due to the presence of vacancy and Stone-Wales defects (Kumar et al., 2019b).

Table 2.6 Properties of graphene (Khan et al., 2016)

Properties	
Thermal conductivity [W/mK]	3000-5000
Electrical conductivity [S/cm]	6000-7200
Charge carrier mobility [1/Vs]	2×10^5
Tensile strength [GPa]	130
Young's modulus [TPa]	1
Optical transmittance [%]	97.7

Although, the superior properties of graphene, at high concentration, the addition of graphene into the polymer matrix is difficult due to its large surface area (Chen et al., 2016). Considerable Van der Waals force and strong π - π interactions between single graphene layers seem due to large ratio of surface to thickness of graphene layers and it leads to the stacks and/or agglomerates formation (Szeluga et al., 2015). Additionally, the high cost of graphene is other anxiety which may restrict the potential industrial applications. Nevertheless, as compared with another carbon-based nanomaterials, graphene is highly thermally conductive, relatively cheap, abundant, and has many application areas (Chen et al., 2016).

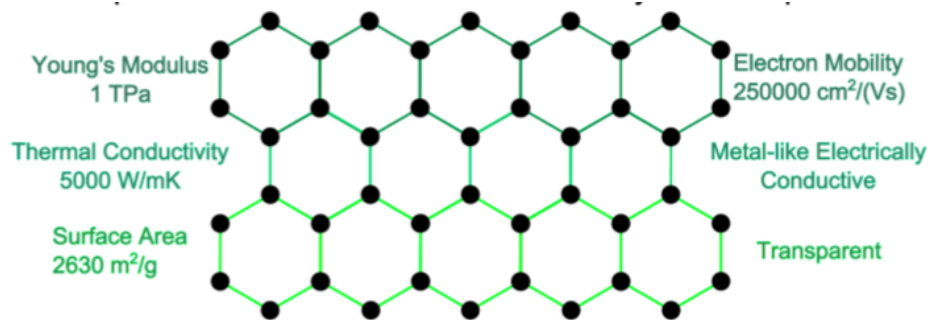


Figure 2.21 Graphene chemical structure and its important physical properties (The black dots represent carbon atoms) (Cataldi et al., 2018)

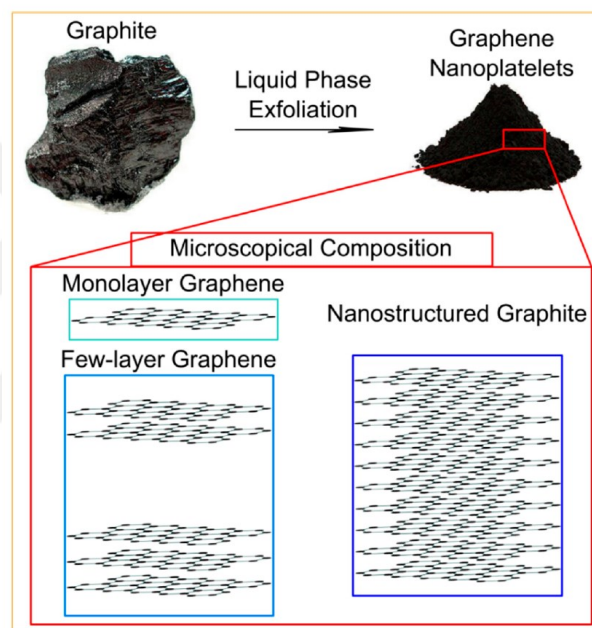


Figure 2.22 Schematic of the GNPs preparation beginning from natural graphite. The typical black powder obtained after liquid phase exfoliation and solvent evaporation is constituted by a mixture of single and few layer graphene and nanostructured graphite (Cataldi et al., 2018)

The mass production of pure graphene has not yet achieved. There is still a lack of a large-scale fabrication methods isolating 2D crystals with same superior performance as that needed to fabricate the samples manufactured in research laboratories. The main restraints are the high sale cost and low manufacturing rates. However, GNPs combine low cost and large-scale fabrication with important physical properties. GNPs are comprised of single and few graphene sheet mixed with thicker graphite (Figure 2.22); therefore GNPs are structurally between graphite and graphene

(Cataldi et al., 2018). Due to low cost and properties of GnPs, it has increasing interest in industrial and scientific areas.

Graphene Nanoplatelets

Graphene platelets (GnPs) consists of few graphene layers (2-5 sheets with thickness >5 nm) having a very low degree of oxidation (Araby et al., 2015; Safdari & Al-haik, 2018). GnPs represents a variety of dimensions (lateral size up to $16\text{ }\mu\text{m}$, thickness: 2-10 nm) based on manufacturing method. It is known that the GnPs properties are similar to the graphene properties. GnPs can display superior mechanical properties (Modulus of Young: 208-650 GPa) and high thermal conductivity (10^3 S/m) (Safdari and Al-haik, 2018). Due to the unique graphitized plane structure, high in-plane conductivity and more importantly the low production cost, GnPs exhibit promise to the enhancement of the polymer nanocomposites (Araby et al., 2015; Mittal et al., 2015). GnPs planar structure can provide a 2-D path for the phonon transport and the high surface area of GnPs provides a high interface surfaces area with the polymer matrix so long as preventing the stacking of graphene layers, resulting in desirable enhancements of functional and mechanical properties for the polymers as reported. Notwithstanding, it is a difficult challenge to generate a considerable reinforcing effect at low filler concentration by melt mixing (Araby et al., 2015).

2.3.1.2 Carbon nanotubes

CNTs can be basically defined as a cylinder rolled from a single graphene layer and is terminated at both ends by hemispheres of fullerenes (Szeluga et al., 2015) . The CNT structure is composed of enrolled graphene layer, being a planar-hexagonal arrangement of carbon atoms distributed in a honeycomb lattice. A typical CNTs have few nanometers in the diameter and several micrometer in the length (Khan et al., 2016). CNTs are classified based on the carbon layers number in the sidewalls of CNTs: a) Single-walled CNTs (SWCNTs), b) double-walled CNTs (DWCNTs) and c) Multi-walled CNTs (MWCNTs) (Figure 2.23) (Szeluga et al., 2015). SWCNTs is defined as a single graphene layer is rolled-up into a cylinder. Stack graphene layers

are rolled-up into the concentric cylinders with 0.34 interlayer spacing, named as MWCNTs (Khan et al., 2016; Jouni et al., 2017). MWCNTs can be considered as resulting from the wrapping of several graphene sheets. DWCNTs is a special type of MWCNTs, consisting of two concentric cylinder of graphene (Jouni et al., 2017).

The carbon atoms in CNTs are bound to each other via the covalent bond in a sp^2 configuration (Jouni et al., 2017). The CNTs can display different chirality based on how the graphene layers are rolled-up (wrapped). And the chirality is described by the chirality (or circumferential) vector as given in Eq. (2.12):

$$C_h = n\vec{a}_1 + m\vec{a}_2 \quad (2.12)$$

where n and m refer to the direction coefficients of unit vectors and basic vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ of the hexagonal lattice (Jouni et al., 2017). Based on the atomic arrangement of CNTs, the SWCNTs and MWCNTs structures may be zigzag ($n=0$ or $m=0$), chiral (any other combination of n and m) and armchair ($n=m$) (Jouni et al., 2017; Khan et al., 2016).

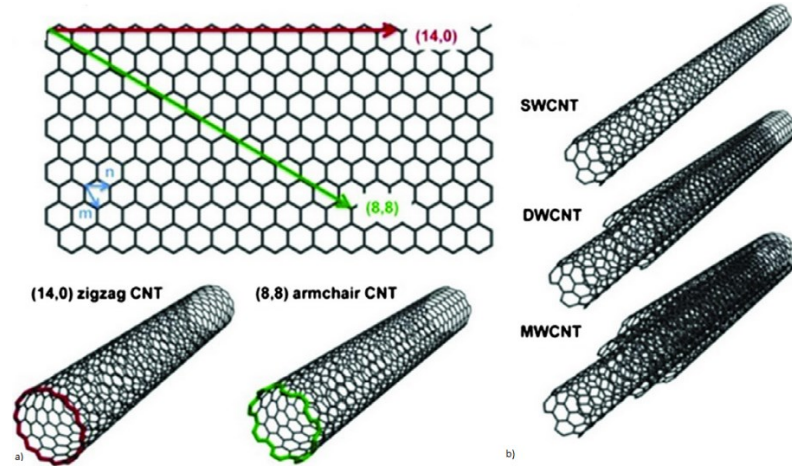


Figure 2.23 a) the structural types of CNTs and the carbon network orientation in zigzag ($n, 0$) and armchair (n, n); (b) SWCNT, DWCNT and MWCNTs (Szeluga et al., 2015)

The morphology, diameter, and size of CNTs have strongly influence on its properties. Additionally, the chirality highly effects on the CNTs physical properties, especially on the characteristics of electronic transport. CNTs can be semiconducting

or metallic based on its atomic arrangement (Jouni et al., 2017; Khan et al., 2016; Mittal et al., 2015). The intricacies involved in the fabrication process cause unwanted defects, e.g. open caps, vacancy and Stone-Wales and these defects have a strong effect on the properties of CNTs (Kumar et al., 2019b).

SWCNTs are very light (density ranging from 1.3 to 1.5 g/cm³) and small (diameter in the range of 0.8-2 nm) and exhibit superior mechanical (tensile strength: 10-52 GPa and Young's modulus: 0.32-1.47 GPa), thermal (thermal conductivity >6000 W/mK) and electrical (a low band-gap semi to metallic conductor with conductivity in order of 10⁶ S/m) based on the chirality) properties. Furthermore, SWCNTs demonstrate the negative thermal expansion coefficient. MWCNTs (density: 1.8-2.0 g/cm³ and diameter: 5-20 nm however pass over several to hundreds of nm) also indicate the similar excellent properties (Tensile strength: 11-63 GPa, Young's modulus 0.27-0.95 TPa and can transport the electrical currents up to 10⁹ A/cm²), expect that MWCNTs always show the metallic conductivity (Safdari & Al-haik, 2018). The thermal conductivity of MWCNTs is in a wide range from 15 to 3000 W/mK (Jouni et al., 2017). It is assumed that thermal conductivity of CNTs occurs through a phonon conduction mechanism as other nonmetallic materials (Namasivayam & Shapter, 2017). As previously mentioned, there are four valence electrons per a carbon atom. Three of these valence electrons (2s, 2p_x and 2p_y) are in the sp² hybridization to occur σ bonds with neighbors. The other electron (2p_z) is participated in a π -bond which is perpendicularly oriented to the plane of graphene. For this reason, the π electrons move freely in the plane of carbon atoms. The experimental electrical conductivity of MWCNTs is in the range of 1×10³-2×10⁷ S/cm (Jouni et al., 2017).

2.4 Methods for the Preparation of Polymer Nanocomposite

It is known that the bulk properties of polymer nanocomposites are strongly based on the structure which are formed throughout the preparation processing step (Han & Fina, 2011). To optimize and tailor the properties of nanocomposites, it is required to disperse nanofiller homogeneously with strong adhesion and interaction between the polymer and nanofillers (Mittal et al., 2015). For instance, to achieve the effective

continuous thermal conductive network, optimum preparation conditions (pressure, temperature, extruding speed, solvent, etc.) should be determined (Mehra et al., 2018). For example, due to the flexibility and high aspect ratio of carbon-based materials, preparation methods can make them wrinkle, fold and buckle, and as a result, change their properties. Moreover, by changing the level of distribution and dispersion of nanofillers, the preparation method also indirectly changes the bulk properties of polymer nanocomposites (Safdari & Al-haik, 2018). The preparation techniques and conditions can greatly influence on its capabilities to drive thermal phonons. Therefore, similar materials can exhibit various thermal conductivity properties based on the selected preparation method (Mehra et al., 2018). In the literature, several preparation methods available to fabricate the polymer nanocomposites based on either thermoplastic and thermoset matrix (Zdenko Spitalsky, Tasis, Papagelis, & Galiotis, 2010). In addition, the choice of preparation method and conditions (e.g. mixing speed, temperature, duration, type of used solvent, etc.) are at least relatively related to the nanofiller type (Safdari & Al-haik, 2018). Some of the preparation methods are discussed briefly in the following.

2.4.1 In-Situ Polymerization

In-Situ polymerization is a chemical encapsulation method where polymerization takes place in the continuous phase, rather than on both sides of the interface between the nanofiller and monomer or prepolymer. The nanofiller is swollen and dispersed in a proper prepolymer or monomer in this method. The suitably dispersed nanofiller is then added to the continuous phase throughout the polymerization process to fabricate the polymer nanocomposite. As compared to the solution mixing, the better level of nanofiller dispersion in the matrix is achieved by this method. Because the nanofiller is incorporated before or throughout the polymerization reaction, it can easily join in the cross-linking process or the reaction, which forge the strong nanofiller-polymer reaction. Moreover, low viscosity of the prepolymer or monomer helps in suitable dispersion of nanofiller in the system (Bayan & Mtech, 2020). The in-situ polymerization including different chemical reactions to induce the covalent bonds between nanofillers and polymer, helping the improvement of interfacial and

mechanical properties of polymer nanocomposites (Kim et al., 2018). Generally, the polymer nanocomposites fabricated by in-situ polymerization exhibit better electrical properties, thermomechanical and flame-retardant at lower content of nanofiller (Safdari & Al-haik, 2018). Moreover, in-situ polymerization method allows the fabrication of polymer nanocomposites with high carbon loading, diluted by other methods (Rahaman, 2019).

Summary, the fundamental advantages of this method is summarized on two points:

- 1- It creates a strong interaction between the polymer matrix and nanofillers, which causes facilitating the stress transfer bringing about a rapid creation of uniform nanofiller dispersion in the matrix.
- 2- It supplies excellent miscibility for high content of nanofillers in the polymers (Guo et al., 2019).

Although these advantages of this method, it is generally accompanied by increment in the blend viscosity causing a restriction of loading fraction and operation. Furthermore, this method happens in the existence of solvents and thus another critical problem is removing the solvent. Because of this, in-situ polymerization method raises the necessity for extra purification steps for removing applied solvent (Guo et al., 2019).

2.4.2 Solution Mixing

Solution mixing is one of the most generally used methods for fabricating the polymer nanocomposites. For all solution processing method, the general protocol contains three main steps: the dispersion of nanofiller in a suitable liquid medium by sonication and/or vigorous stirring, mixing the nanofiller dispersion within a polymer solution at a certain temperature and controlled the solvent evaporation with or without vacuum conditions step (Han & Fina, 2011; Safdari & Al-haik, 2018; Spitalsky et al., 2010). In this method, the degree of the nanofiller dispersion in the matrix is based on the interactions among the solvent molecules, nanofiller and polymer (Bayan & Mtech, 2020). In addition, generally, the most effective dispersion of nanofiller throughout

the first step is achieved by the tip sonication or bath (Spitalsky et al., 2010). However, it is difficult to disperse the carbon-based materials, such as GnPs, graphene and CNTs, in the solvent through using a simple mechanical stirring. It should be considered that too much power can decrease the nanofiller aspect ratio and thus lead to change in its properties. Besides, the dispersant and chemical functionalization is always needed to achieve better dispersion of nanofillers and more stable suspension of nanofillers. Using surfactants is another strategy to avoid agglomeration and promote dispersion of nanofillers (Kumar, Kalia, & Swart, 2017; Safdari & Al-haik, 2018). However, the chemical functionalization of carbon-based materials through oxidation in a high acidic medium can introduce oxygenated groups on the nanofiller surface to enhance the dispersion of nanofiller, however it generally damages the electrical properties of carbon-based nanofillers (Kumar et al., 2017).

The disadvantages of solution mixing are toxicity, finding a common solvent, nanofiller aggregation and difficulty in solvent removal (Safdari & Al-haik, 2018). Removing solvent is a time-consuming step and leads to re-agglomeration of nanofillers during drying process (Kim et al., 2018).

2.4.3 Melt Mixing

The melt mixing is much valuable technique for the preparation of polymer nanocomposites. The melt mixing is complied with the present industrial processes and it is also practical for the polymers which are not favorable for solution mixing or in situ polymerization method because of their insolubility in common solvents (Bayan & Mtech, 2020; Spitalsky et al., 2010). In other word, the melt mixing is convenient and economical method with environmental benefits, rapid production, and low cost. Melt mixing can employ high shear forces and temperatures to disperse the nanofiller materials into the polymers by traditional melt mixing equipment such as internal mixer, extruder and two-roll mill (Kumar et al., 2017).

Based on the results of studies in the literature, the processing parameters (e.g. time, temperature, speed, time) strongly influence on the dispersion of nanofillers and

properties of samples. In addition to processing conditions, the design of the screw profiles plays a key role for the dispersion of nanofillers. During compounding, the control of shear-stress and mixing time is much more significant to disperse nanofiller in the polymer and avoid the detriment of polymer and nanofiller themselves. Excessive mixing time and very high shear-stresses cause the decrement in the nanofiller aspect ratio during processing owing to the breakage of nanofillers. Therefore, the melt mixing processes should be optimized to balance the dispersion states and the nanofiller breakage for obtaining the desirable properties of polymer nanocomposites (Kumar et al., 2017). The processing temperature is about 20 °C greater than the melting temperature of polymers (Rahaman, 2019).

The melt mixing is widely used for the thermoplastic polymers. The thermoplastic semi crystalline polymers soften when heated above their melting point. Generally, melt processing includes the blending of polymer melt with nanofiller by the application of intense shear forces. Melt mixing uses high shear forces and temperature to disperse nanofillers in a thermoplastic polymer, which uses the conventional equipment for the industrial preparation processing. Based on the final shape/morphology of nanocomposites, the bulk samples can then be prepared by several techniques (Han & Fina, 2011; Jabeen, Kausar, Muhammad, Gul, & Farooq, 2015; Spitalsky et al., 2010).

As compared with other methods, the melt mixing allows for high nanofiller loadings, however it is usually less efficient in achieving better dispersion of nanofillers in the polymer matrix. For melt mixing, one of the main challenges is its poor effectiveness in disentangling initially agglomerated industrial-grade carbon nanomaterials (Safdari & Al-haik, 2018) .

It is noted that the interaction of polymer/nanofiller and the polymer molecular weight are two remarkable factors in this method. For instance, to provide the good graphene dispersion in the polymers, it is needed to increase the interaction of polymer-nanofiller and decrease the molecular weight of polymer. Else, the high

entropy in polymer nanocomposites with high molecular weight will prohibit the nanofiller dispersion (Liu et al., 2019)

Summary, the main disadvantages of melt mixing are that:

- 1- the preparation of polymer nanocomposites with higher nanofiller loadings becomes difficult because of the viscosity increment,
- 2- as compared to other methods, the distribution of nanofillers in the matrix is relatively poor, and
- 3- the possibility of nanofiller aggregation throughout the mixing step is high because of using heavy shear forces inducing more damage and defect graphene layers (Guo et al., 2019)

2.5 Properties of Polymer Nanocomposites

2.5.1 Electrical Conductivity of Polymer Nanocomposites

Polymer nanocomposites provide an outstanding potential to fabricate electrically conducting materials through adding electrically conductive nanofillers (e.g. conductive metal oxides, graphene, CNTs) into polymer matrix. The electrically conductive polymer nanocomposites are beneficial for wide application range which includes conductive films, antistatic coatings, electrical appliances, conductive adhesives, packaging and electronics (Jafar Mazumder, Sheardown, & Al-Ahmed, 2019).

Electrostatic dissipation (EDS) and electromagnetic interference (EMI) shielding are two main applications of electrically conductive polymer nanocomposites. For these applications, the moderate values of electrical conductivity (σ) are required ($\sigma > 10^{-2}$ S/cm for IME and $\sigma = 10^{-6}$ - 10^{-2} S/cm for EDS). EMI shielding is significant for protecting the electronic devices, which can both emit and be sensitive to stray the emissions of electromagnetic. The EMI shielding enclosures are especially important for portable electronic systems such as pagers, cell phones and laptops. The nanocomposites with carbon-based materials are promising candidates for antistatic,

EMI and EDS applications, being important across a lot of industries such as electronic, automotive, and aerospace. Moreover, the electrically conductive nanocomposites is candidate for the novel applications such as actuators, printable circuit wiring, biological and chemical sensors, variable resistors, transparent and flexible plastic electronics and photovoltaic (Mutiso & Winey, 2015).

It is known that the change in the electrical conductivity with the increase in the nanofiller loadings can be clarified by the percolation theory. It suggests that the transition from an insulating material to a conducting material at certain loading of the conductivity nanofiller materials (percolation threshold) where they occur a continuous conductive network in the polymer matrix. The percolation thresholds defined as the minimum content of nanofiller materials where the electrical conductivity of the polymer nanocomposites is abruptly increased. In the other words, below percolation threshold, a small enhancement in the electrical conductivity of the samples can be due to a small number of charges carries through the nanocomposites without a continuous conducting pathway. The electrical conductivity increases rapidly at the percolation threshold, this can be attributed to the creation of a continuous conducting pathways in the samples. Beyond the percolation threshold, the conductivity exhibits a marginal increase with the further addition of the filler materials (Špitalský et al., 2015).

In addition, for polymer nanocomposites with carbon-based nanofillers, two mechanisms of electrical conductivity, conductive network and electron tunneling (hopping), complement each other (Kim, Lee, Song, & Lee, 2019). Generally, the electrical conductivity of the polymer nanocomposites enhances by direct contact among the conductive nanofiller materials and tunneling or hopping through the matrix material which separates the adjacent conductive nanofiller materials. At certain nanofillers' loading, the inter-particle gap among the conductive nanofillers is small enough to touch or come close to each other and creates a continuous conductive network structure in the polymer matrix. Therefore, the effect of the contact or tunneling improves and the continuous conductive network is improved in the polymer matrix (Gogotsi, 2006; Maiti & Khatua, 2016).

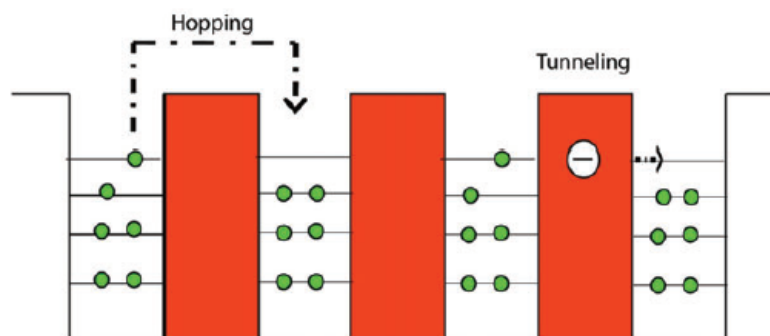


Figure 2.24 Tunneling and hopping transport of charge carriers (Jouni et al., 2017)

As stated previously, the polymer nanocomposite generally comprised of insulation polymer matrix and conducting nanofillers. In the nanocomposites, electrons do not only transfer in the nanofillers themselves, but also require transferring from one nanofiller to other one. Hence, the energy barriers are highly possible to exist between the nanofillers and the electrons require to pass through these barriers by the quantum mechanics tunneling, “tunneling resistance”. The tunneling resistance is based on the temperature. Additionally, this resistance exponentially depends on the distance of interfillers (the gap width) (Kumar et al., 2017). Actually, two sources of the resistance to the current flow are available in a percolation network of nanofillers. While one of them is the intrinsic filler resistance, the other one is the resistance of polymer layer between two nanofiller materials; therefore, the total resistance is the sum of the resistances because of the tunneling resistance of polymer layer and their direct contact resistance. The contact resistance of filler materials and tunneling resistance are decreased with increasing the filler concentration. Decrease of tunneling resistance displays that the thickness of polymer layer between the nanofiller materials is decreasing and thus the tunneling of electron occurs easier across the insulator barrier (Khurram et al., 2015).

The conductive networks in polymer nanocomposites cannot always be considered as ideal percolation networks, since conducting networks do not only include an infinite resistor (polymer) and conductors (conductive nanofillers). In the polymer nanocomposites, the current (charge carriers) transfer along the interconnected

conducting nanofiller network in the matrix. Therefore, the formation of conductive network with high quality plays a significant role in the production of the polymer nanocomposites with excellent electrical properties. Generally, good conducting network requires nanofillers for interconnecting firmly and obtaining 3D continuous distribution in the matrix. Hence, the control of nanofiller network morphology is too critical to tune the electrical properties of polymer nanocomposites. As mentioned previously, the fabrication method and conditions of polymer nanocomposites can considerably tailor the morphology of these network structures and highly influence the percolation behaviors of polymer nanocomposites (Kumar et al., 2017).

It is known that the carbon-based materials are anisotropic conductors. As the addition of them into a polymer matrix, the electrical properties of polymer nanocomposites are isotropic and as mention previously, they follow the percolation behavior in a specific range. Above percolation threshold, the contents of adding nanofillers boost the electrical conductivity to an asymptotic range. The highest electrical conductivity values which are achieved in this range change for different combinations of polymer and nanofiller (typically 10^{-7} - 10^1 S/cm). In addition, the electrical conductivity of polymer nanocomposites is characterized in DC and AC regimes (Safdari & Al-haik, 2018)

2.5.1.1 AC Conductivity of Polymer Nanocomposite

The frequency of the electromagnetic/electric field influences the AC conductivity (σ_{AC}) of polymer nanocomposites. It is found that the AC conductivity increases with increasing the frequency of electric field. With increasing the frequency, the charge carriers/electrons in the nanocomposite get energies, which increase the tunneling/hopping of charge carriers/electrons resulting in the increment of electrical conductivity. Nevertheless, the nature of difference in the electrical conductivity with the frequency is based on the polymer types, types, and content of nanofiller. The pure polymers, insulating polymers, show a strong frequency-dependent behavior. When increasing the nanofiller loading in the polymer matrix, this frequency-dependency decreases. At above a certain nanofiller content, the polymer nanocomposites display

a frequency-independent behavior, and the AC conductivity is equal to DC conductivity of polymer nanocomposites (Rahaman, 2019).

As briefly mentioned above, when considering the AC conductivity results of polymer nanocomposites, generally, it is clear that the frequency-dependence of the electrical conductivity displays three different distinct behaviors, related to different dissipating effects. In first behavior, up to a certain concentration (percolation threshold) for each filler materials, the AC conductivity obeys the universal dielectric response law, the conductivity increases linearly with increasing frequency in a logarithmic scale. This is characteristic of a capacitive behavior (Špitalský, Georga, Krontiras, & Galiotis, 2010). This behavior is because there is no sufficient formation of continuous conductive networks within the polymer nanocomposites. The electron conduction in the polymer matrix is because of electron hopping from one conducting site to other one. With increasing the frequency, the electrons obtain energies, this leads to increase the hopping tendency of them. Furthermore, some trapped electrons cannot hop from one conducting site to other conducting site. Consequently, there is a wide difference in the AC conductivity in the low and high frequency and the conductivity becomes more frequency dependent (Ram, Khastgir, & Rahaman, 2019).

In the other behavior, when the content of filler materials is almost in the percolation transition region where both the isolated filler materials and a gradually formation of conductive networks exist, the AC conductivity remains at a constant value (independent of frequency) up to a critical frequency, above which the AC conductivity increases almost linearly with increasing frequency, i.e. it follows the universal dielectric response law. When the filler loading increases gradually, this critical frequency extends to higher frequency. This indicates that an expanding conductive network is gradually created throughout the polymer composites (Špitalský, Krontiras, Georga, & Galiotis, 2009).

This type of behavior of the AC conductivity of the nanocomposites can be explained by the electron hopping and tunneling mechanisms. It is known that the electrical conductivity of the polymer nanocomposites is in direct proportion to the

rate of electron hopping and tunneling. The conductivity pathways in the nanocomposites increase with increase of nanofiller concentration which causes an increment in the rate of the electron hopping or tunneling. To achieve an important electrical conductivity, the electron tunneling pathways' aggregate population must take part above the percolation threshold. Below the critical frequency, the AC conductivity of any dielectric material can be expressed by following Eq. (2.13):

$$\sigma_{AC} = \sigma_{DC} + \omega \varepsilon'' \quad (2.13)$$

Where σ_{DC} is DC conductivity, ω signifies angular frequency ($\omega \approx 2\pi f$) and ε'' displays dielectric loss factor. It is seen in Eq. 2.4 that, the AC conductivity's value of a dielectric materials under the frequency is combination of two constituent. The first one displays the DC conductivity arising from the electronic or ionic conductivity. Nevertheless, the second constituent is based on the degree of dipoles (permanent and induced) polarization and accumulated interfacial charges, known as Maxwell-Wagner-Sillars (MWS) effect. Below critical frequency (at low frequency), the influence of interfacial polarization becomes more important when the dipoles/induced dipoles get sufficient time to orient themselves with the direction of applied electric field (relaxation phenomena) and thereby, the AC conductivity for a conductive material essentially displays the DC conductivity. Above critical frequency (at high frequency), the influence of polarization becomes unimportant when the dipoles get less relaxation time to orient themselves in the direction of applied electric field. Above critical frequency, the applied AC electric field (periodic alternation) leads to the radical decrease of the accumulation of the space charge and the dipoles dispersion in the applied field direction decreasing the polarization value. Therefore, the AC conductivity is strongly based on the charge particles' excitation and the electrons' flow through the continuous conducting pathway in the phase of matrix. Moreover, it can be supposed that above the critical frequency, the excited electrons' hopping through thin polymer layer gets easier, which adds to the electrical conductivity existing at low frequency in the polymer nanocomposites (Maiti & Khatua, 2016).

In final behavior, beyond the percolation threshold, the AC conductivity remains almost at a constant value in the whole frequency range. This behavior corresponds to that of a conductor. The plateau electrical conductivity is considered as DC conductivity (Špitalský et al., 2010). It can be explained that at above percolation threshold, the electrical conduction process in the nanocomposites is much less by electron hopping and mostly dominated by the particle-particle contact. For this reason, there is a small difference in the AC conductivity between the low and high frequency regions and the AC conductivity is almost independent of frequency. As is known, at any particular frequency, before percolation the AC conductivity increases sharply with increasing the content of the filler materials, while a moderate increase is observed beyond percolation threshold. This is because, the conductive network is not formed before the percolation threshold, and however, at and above the percolation threshold, the conductive networks are formed and the AC conductivity is independent of frequency, so the AC conductivity becomes DC conductivity. The continuous conductive networks can be formed by the geometric arrangement of the conductive filler materials which have the distance of inter-particle equal to or less than 10 nm. The electrons can easily jump this gap. As mentioned before, below the percolation threshold, the value of DC conductivity is similar that of the neat matrix ($\sigma_{DC} \sim 0$), the conductivity is dependent of frequency and obeys a power law (Ram et al., 2019).

As mentioned above, the total AC conductivity is expressed by the following expression (2.14) (Barrau, Demont, Peigney, Laurent, & Lacabanne, 2003):

$$\sigma = \sigma(0) + \sigma_{AC}(\omega) = \sigma_{DC} + A\omega^s \quad (2.14)$$

where σ_{DC} is dc conductivity (at $\omega \rightarrow 0$) or the independent-frequency conductivity, A and ω refer to a constant dependent on temperature T and the angular frequency, respectively, s is exponent depending on both temperature and temperature with 0-1 value range. This ω^s is characteristic for the transfer in the disordered systems and shows the frequency response of the conductivity in the polymer nanocomposites. Jonscher named this kind of behavior as “the universal dynamic response (UDR)” due to a wide variety of materials which show such behavior. The DC conductivity is

predicted the plateau value of AC conductivity in the AC conductivity-frequency plot. For each nanocomposite, there exists a critical frequency (Barrau et al., 2003; Logakis et al., 2009). At low frequencies, the random diffusion of the charge carriers, via activated hopping, leads to a frequency-independent conductivity (Tsonos, 2019).

2.5.1.2 DC Conductivity of Polymer Nanocomposite

The electrical conductivity behavior of the polymer nanocomposites is explained by the percolation theory. Figure 2.25 shows the illustration of the percolation pathway in a polymer matrix. The elementary sites, which are represented by the colored line, refer to the filler materials in the polymer matrix. The possibility of forming a percolation pathway which is responsible for the transition from insulator to conductor is based on the concentration of filler material. This transition happens for a critical filler material concentration (p_c), named as percolation threshold. The filler materials are dispersed homogenously and not get in touch with each other at low concentration. This expounds the existence of an insulating phase. As increasing the concentration of filler materials, the possibility of coming into direct contact between the filler materials slowly increases until the concentration of filler materials reaches a critical concentration where the electrical conductivity of the polymer nanocomposite rapidly increases several orders of magnitude. Above the percolation threshold, the electrical conductivity variation gets more limited and changes as a function of volumetric concentration of the filler materials by the following power law (Eq. (2.15)) (Jouni et al., 2017; Mittal et al., 2015):

$$\sigma \sim (p - p_c)^t \quad (2.15)$$

where p refers to the volume fraction of filler materials, p_c is the value of percolation threshold and t refers to an exponent of which the numerical value is related to the percolating network dimensionality.

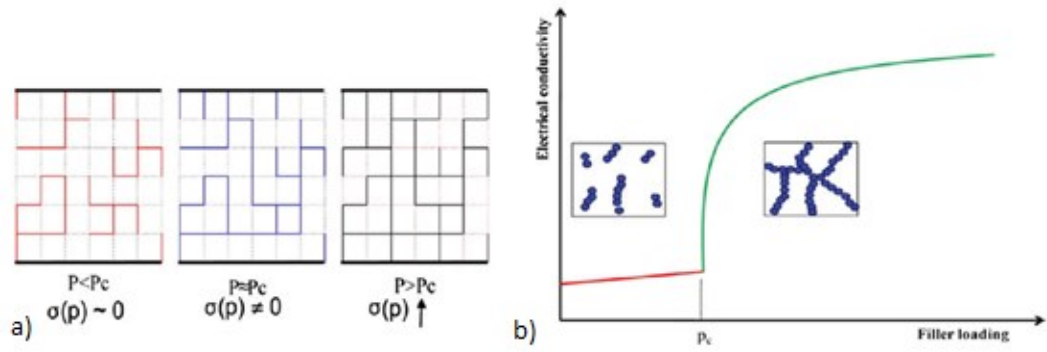


Figure 2.25 (a) Schematic of the percolation theory in the polymer (b) the electrical conductivity of polymer nanocomposites vs. the filler concentration (Jouni et al., 2017)

In the literature, there is a wide distribution of the results of the percolation threshold and maximum electrical conductivity of the polymer nanocomposites for the same type of filler materials and the same polymer matrix. Electrical properties are affected by different factors such as alignment, dispersion, aspect ratio, processing, functionalization, polymer type and filler type (Mittal et al., 2015; Mutiso & Winey, 2015). For example, the percolation threshold of polymer nanocomposites with GNPs is generally higher than that with MWCNTs. In addition, the percolation threshold changes according to the matrix type. Generally, a lower viscosity polymer leads to lower percolation threshold because of better dispersion properties (Safdari & Al-haik, 2018). It demonstrates that the maximum electrical conductivity and percolation threshold are not completely determined by the polymer nanocomposite composition, however the production method of the polymer nanocomposites is significant factor (Jouni et al., 2017).

Especially, the nanofiller dispersion, alignment and aspect ratio are three fundamental factors influencing the electrical percolation threshold. When the quality of nanofiller dispersion and the nanofiller aspect ratio increase, the lower amount of nanofillers is needed to enhance electrical conductivities (Gogotsi, 2006). As seen in Figure 2.26, the percolation threshold for high aspect ratio of the filler materials is inversely proportional to their aspect ratio. The theoretical percolation threshold value can be predicted by an excluded volume approach (Jouni et al., 2017).

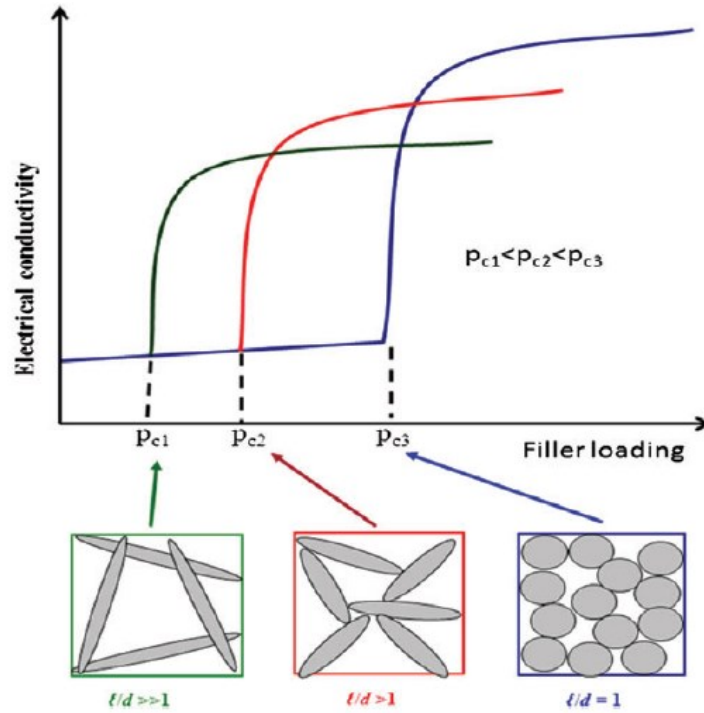


Figure 2.26 Illustration of the percolation threshold based on the aspect ratio of the filler materials (Jouni et al., 2017)

The aspect ratio of nanofillers has significant effect on the electrical properties of polymer nanocomposites. Generally, with increasing aspect ratio of nanofillers, the electrical conductivity of polymer nanocomposites increases, and the percolation threshold decreases. The number of contacts as well as the average distance between nanofillers reduces with increase of their aspect ratio. Thus, the electron flows by hopping is facilitated when decreasing both the numbers of contacts and average distance among the nanofillers, which result in greater electrical conductivity of polymer nanocomposites reinforced by nanofiller with higher aspect ratio. The alignment/orientation of nanofiller meaning anisotropic nanofillers highly influences the percolation threshold and electrical conductivity of polymer nanocomposites. In literature, it is reported that the alignment of anisotropic nanofillers cause the lower contacts between the nanofillers which results in the damage of conducting networks. As a result, the electrical conductivity of polymer nanocomposites is greatly decreased. As the alignment of nanofiller is slightly anisotropic or isotropic in nature in the polymers, the low electrical percolation threshold is achieved (Rahaman, 2019).

2.5.2 Thermal Conductivity of Polymer Nanocomposite

For the polymer nanocomposites, the electrical conductivity increases dramatically at a certain nanofiller loading because of the electrons tunneling effect in compliance with the percolation theory. Whereas, the thermal conductivity increases linearly with nanofiller content. This means that the mechanisms of thermal and electrical conduction are disparate (Noh et al., 2016). The electrical conductivity needs networks with neighboring nanofillers, separated by thin polymer layers with the distances below the electron tunneling and/or hopping distance (assumed to about 2-8 nm). Only the creation of an electrical network at the concentration of percolation threshold varies the electrical properties from insulating to electrically conductive. However, the thermal conductivity needs the phonon transport between neighboring nanofillers. Therefore, the trends in the improvement of thermal conductivity and electrical properties with nanofiller loading is very different for the polymer nanocomposites (Krause, Rzeczkowski, & Pötschke, 2019).

Phonons or atomic vibration dominates the thermal conductivity of polymer nanocomposites (Chen & Yan, 2018). It is recognized that several parameters play a significant role in the thermal conductivity performance of polymer nanocomposites, containing dispersion, aspect ratio, dimension, purity, distribution and alignment of nanofillers, interfacial resistance (Chen & Yan, 2018; Han & Fina, 2011)

As stated previously, in polymer materials, heat conduction is by the elastic vibrations of lattice. The addition of thermally conductive nanofillers improves the rate of heat transfer by creating a thermal conductive pathway. At low nanofiller contents, the boundary and dispersion of nanofillers are significant factor to enhance thermal conductivity. However, it is known that the thermal conductive pathways created by the nanofillers mainly govern the thermal conductivity of polymer nanocomposites. Thus, designed thermal conductive pathway and minimal the thermal interfacial resistance between the matrix and nanofiller are one of the significant key factors for maximizing the thermal conductivity (Vadivelu, Kumar, & Joshi, 2016).

Phonon scattering happens throughout the phonon transport, it consists of the phonon-phonon scattering and phonon-interface scattering which is caused by impurities defect and the like in the amorphous phase, which result in producing the interfacial thermal resistance. The interfacial resistance is also named Kapitza resistance and it demonstrates the heat barriers to the flow of heat transfer related to two different quantum states spectra of two material phases. The presence of the interfacial thermal resistance in polymer nanocomposites can cause the backscattering of heat carriers such as holes, phonons, and electrons. Hence, it changes thermal conductivity paths and reduces the efficiency of thermal conductivity (Zhang et al., 2019).

Even though the dispersion of the nanofiller is good, the phonon scattering is unavoidable because of the contact thermal resistance at the interface of nanofillers and the interfacial thermal resistance at the matrix and the nanofiller interface, this is the main reason of the low nanocomposite thermal conductivity (Kim et al., 2018; Kim et al., 2019). To effectively improve the thermal conductivity of polymer nanocomposites, understanding the thermal interfacial resistance between the matrix and nanofillers is very important. Low thermal resistance to heat flow at the interface is technologically significant for many applications for which polymer nanocomposites with high heat dissipation capability is needed (Chen & Han, 2019). Figure 2.27 can show what happens at the interface between the polymer matrix and crystalline nanofiller during the thermal conduction. In a particular amount of time (t), it is considered that the thermal energy is theoretically diffused to other face of the nanofiller during heat transport by the conduction along crystalline nanofillers. Throughout thermal conduction in the polymer chain, at the same time amount (t), traveled distance by heat is shorter than the length of equivalent path through the nanofiller. In other words, the thermal conductivity of polymer is much smaller than that of nanofiller (Burger et al., 2016).

A strong phonon scattering is caused by the large interfaces (i.e., long distances between the polymer matrix and nanofiller). The reason of phonon scattering in the materials is mostly the interfacial resistances resulting from acoustic mismatch at

matrix-filler interfacial (Burger et al., 2016). The interfacial thermal resistance can be categorized in two ways:

- 1- by thermal boundary resistance which originates from the mismatch in vibrational harmonics of energy carriers (i.e. phonon spectra) and/or the flow of electronic energy carriers between materials, and
- 2- by thermal contact resistance which is due to the mismatches in the surface conditions of two solids (Chen et al., 2016).

Boundary scattering is based on the characteristic length of sample. Thermal transfer in a material deviates as the mean free path of phonon is comparable to the material characteristic length. At the interface region, phonons can be observed either scattering diffusively and specularly. In nanocomposites, the interface of matrix-nanofiller is one of the basic reasons for the high phonon scattering because of an acoustic mismatch, resulting in the reduction in the effective thermal conductivity of polymer nanocomposite. The interface acts as a transition area in which the properties vary locally and serve as a center of phonon scattering (Mehra et al., 2019). In the region of interface, the properties of nanocomposites are different from that of bulk. The addition of nanofiller leads to a change in the property of the polymer matrix around the nanofiller. This causes the improvement of the interfacial layer, offering thermal resistance for the phonon flow. This flow, aside from phonon scattering, also affects thermal conductivity, permittivity, crystallinity, crosslink density and glass transition temperature of the polymer nanocomposites. In polymer nanocomposites, the interfacial resistance effect is more pronounced because of the high increase in the matrix-filler area (Mehra et al., 2018, 2019).

The main barrier for efficient heat transport is the interface of polymer nanocomposites. Heat loss takes place as heat transfers across the interface, the main region for phonon scattering. The characteristics of phonon transport vary at interfaces in bulk compared to the nanoscale region. When the size of the particle reduces to the nanometer scale, the interface can cause considerable phonon scattering. The interphase is an essential key factor for thermal conductance. Because it is an intrinsic interface property hindering the heat flow which is caused by sudden changes in the structure of polymers

and variation in properties at matrix/filler interface from the bulk. Enough interface bonding between the matrix and nanofiller is completely beneficial to reduce the thermal interfacial resistance. This resistance is a barrier to heat flow reducing the benefit of the incorporation of high conductive nanofiller. This is one of essential reasons why the thermal conductivity of nanofiller doesn't proportionally translate into polymer nanocomposite (Mehra et al., 2018).

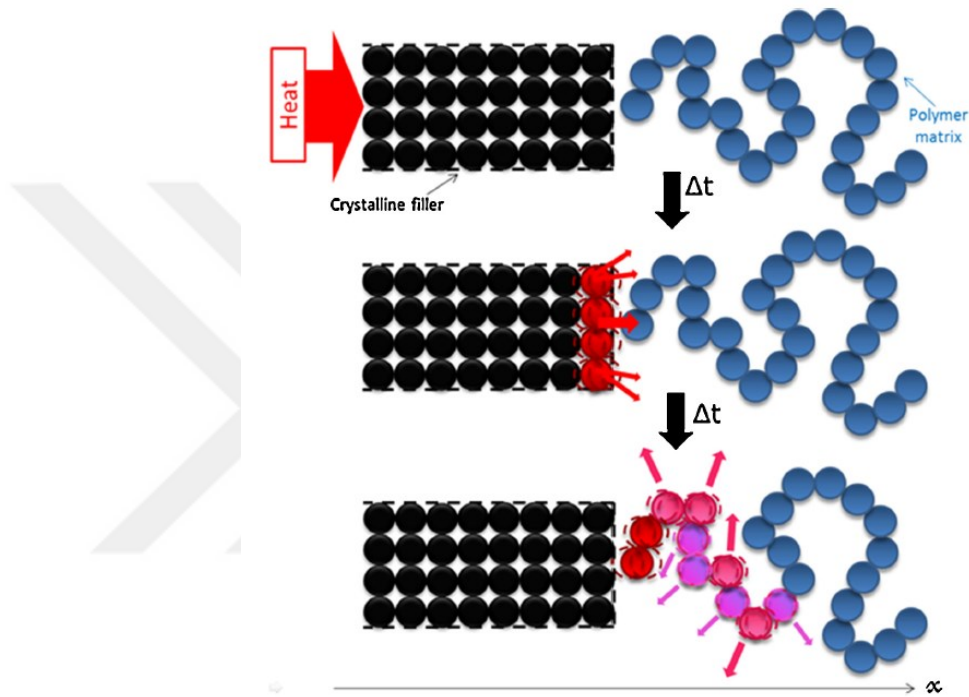


Figure 2.27 Schematic representation of thermal conductivity at filler-matrix interface (Burger et al., 2016)

Phonon transport along the phase interface is theoretically based on the vibration frequencies of two phases forming the interface, and the mismatches of vibration frequency due to the existence of the interfacial thermal barriers lead to phonon scattering. As is known, the imperfective physical contact between two phases, resulting in the heat loss, leads to the interfacial thermal resistance. When two different or similar filler materials keep in touch and create a junction, merely small part of real surface area is contained because of the roughness and non-planarity of the contact surface; this leads to the contact thermal resistance. Meanwhile, at the junction, the heat transport can just take place along the real contact area (Kim et al., 2018).

In addition to the interfacial thermal resistance, the tendency of aggregation of nanofillers can also restrict the enhancement of thermal conductivity. To prevent the aggregation of nanofillers, in past few decades, several methods are developed to enhance the distribution of nanofillers including special preparation, surface functionalization and addition dispersant techniques. The dispersion of nanofillers can be improved by the chemical functionalization of nanofillers, however, the covalent functionalization can damage the nanofiller structure and therefore sometimes even decreasing its thermal conductivity. Simultaneously achieving low aggregation and strong matrix-nanofiller coupling is still challenge. Surface functionalization for preventing the aggregations of nanofillers generally causes a weak matrix and nanofiller coupling, which makes it difficult to obtain high thermal conductivity. In addition to functionalization and surface treatment, another choice is dispersant to suppress the nanofiller aggregation. Some special processing methods can also enhance the nanofiller distribution. The orientation of high aspect ratio nanofiller is another critical key factor which determines the thermal conductivity of polymer nanocomposites (Huang et al., 2018).

Phonons in the thermal conduction are scattered at the contact area of nanofillers due to contact resistance and at the interface between the matrix and nanofiller because of the interfacial thermal resistance. Thus, the effective formation of 3D heat conduction pathways within the polymer matrix is as significant as the properties of matrix and nanofiller (Noh et al., 2016). As seen in Figure 2.28 (a), in case of nanofiller network, it can accelerate the flow of heat to transport along the integrated and continuous nanofiller network with less phonon scattering. Figure 2.28 (b) shows that in discontinuous network, great number of phonon scattering will occur at the matrix/nanofiller interface due to acoustic mismatch which occurs in various atoms. Largely, the optimization of the nanofiller dispersion and structure (containing the aspect ratio and size) can improve the thermal conductivity through arranging the nanofiller for the formation of a thermally conducting network in the matrix (Zhang et al., 2019).

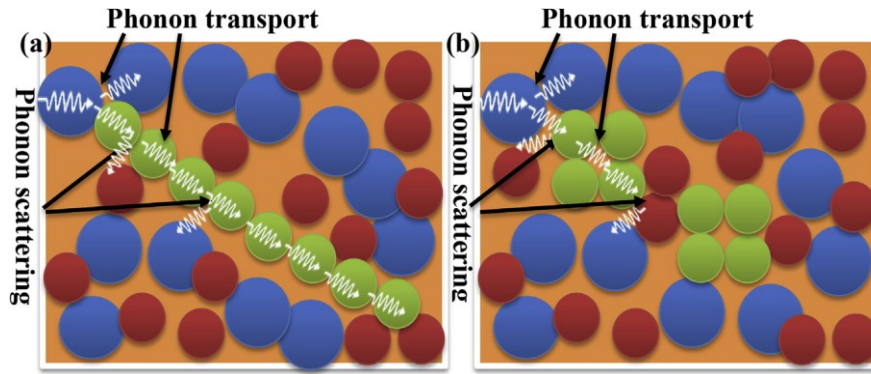


Figure 2.28 Thermal conduction mechanism in polymer/crystalline nanofiller with a) a continuous nanofiller network, and b) a discontinuous nanofiller network. The green balls represent crystalline nanofiller; other balls represent polymer atoms (Zhang et al., 2019)

The thermal conductivity of polymer nanocomposites is clearly improved with increase in the size of nanofillers. When the polymer nanocomposites reinforced by smaller nanofillers, the interface between nanofillers and matrix dramatically increases, which results in increment of the interfacial thermal resistance at interfaces and phonon scattering. It is reported that the contact resistance owing to imperfect contact among the nanofillers also leads to phonon scattering. On the contrary, in terms of thermal conductivity, for example, as comparing graphite and GnPs, GnPs are about 3-5 times smaller than graphite, however thermal conductivity of polymer nanocomposites with GnPs is nearly 17% higher than that with graphite. This means that the size of nanofiller is not only key factor for thermal conductivity of polymer nanocomposites (Noh et al., 2016).

The size of nanofillers can mainly influence the thermal conductivity of samples by affecting the contact area between the matrix and nanofillers and shortening the mean free path of the energy carries in a polymer nanocomposite with reinforced by randomly distributed nanofillers. In brief, as any inter-nanofiller networks are not created, the high interfacial thermal resistance and aggregation of nanofillers pay a key role in the thermal conductivity of nanocomposites. To decrease the interfacial thermal resistance, the functionalization and surface treatment of nanofillers are commonly implemented (Huang et al., 2018).

As it is well known, the larger filler materials are more efficient at producing thermally conductive polymer nanocomposites, the reason is that the interfacial area of the polymer matrix and filler material is highly decreased, this decreases the interfacial thermal resistance and it is beneficial for the phonon transfer. Increasing the direct contacts of filler materials can be a good method to enhance the polymer composite thermal conductivity, which causes the thermal percolation behavior. This is because the phonon scattering, and heat loss caused by the contact thermal resistance is smaller than those due to the interfacial thermal resistance. In addition, concurrently adding thermally conductive filler materials with different shapes and sizes induces the direct contacts of the filler materials; this leads to synergic enhancement of the thermal conductivity (Kim et al., 2018).

As explained previously, heat rapidly diffuses along the crystalline filler, however the polymer significantly slows it. As it is known, the high thermal conductivity of filler materials can be only benefited through the filler. That is to say, the longer the filler, the higher the thermal conductivity of the polymer nanocomposites in the direction of filler (anisotropic property). Hence, the aspect ratio of filler materials is a significant key factor to consider.

Generally, the thermal conductivity of polymer nanocomposites increases non-linearly with increasing the nanofiller loading. Up to 35 vol. % of nanofillers, the thermally conductivity enhance moderately and only at high concentration of nanofillers, a high enhancement in thermal conductivity can be observed. This means that the effective thermally conducting pathways begin to be created at high nanofiller content because of nanofiller to nanofiller connections. It is known that high amount of nanofiller can cause the polymer nanocomposite to have poor processability, to be brittle and results in a high cost. The low viscosity is desired for the nanocomposite preparation process. However, the high nanofiller content will normally lead to a considerable increase in the nanocomposites viscosity and make it more difficult for the polymer nanocomposites to be fabricated by conventional polymer preparation methods. The increase of viscosity fundamentally results from the interfacial friction between polymer and nanofillers, and nanofillers. Most of low-cost nanofillers possess

irregular shapes with several corners and edges and can lead to important friction throughout compounding and mixing. At the high nanofiller loading, the irregular shape can result in increase of viscosity. Other nanofiller characteristics such as low flowability, rough surface, breakability, aggregation, will be improper for the nanocomposite processing and may harm of the polymer nanocomposites. Polymer nanocomposites reinforced by nanofillers with low aspect ratio show a lower thermal conductivity even at high concentrations of nanofillers. As compared to nanofiller with other shapes, 1D nanofillers, such as tubes, fibers, wires, or rods, are expected to considerably enhance the thermal conductivity of nanocomposites. Because, for the high aspect ratio nanofiller, it is easier to form a long thermal conducting pathway through the longitudinal direction of 1D nanofillers in the polymer nanocomposites. For them, thermal conductivity in perpendicular direction is much lower than that in the longitudinal direction (Chen et al., 2016).

The requirement of large nanofiller loading is one of the bottlenecks for the improvement of high thermal conducting material. Because of high filler content, the polymers loss their intrinsic properties, e.g. ease of fabrication, good mechanical properties and so forth. Above a certain content of nanofillers, the thermal conductivity enhances, however at the cost of mechanical properties. In addition, high nanofiller content leads to a large increase in the weight of polymer and this is significant to obtain a cost efficient material (Mehra et al., 2019).

Additionally, the mean free path in the polymers is very small, nearly few angstroms, because of phonon scattering from a large number of defects, fundamentally the interfaces of the crystalline and amorphous region, therefore the contribution of mean free path to thermal conductivity is much low. Because of the chain line structure of polymer, the heat capacity contribution occurs by two forms: a) acoustics vibration or lattice vibrations, and b) characteristics vibrations from the repeating unit internal motion because the electrons free movement is impossible here. At low temperature, the lattice vibrations have the main contribution in the thermal conductivity of nanocomposites. The side groups contribution to thermal conductivity only comes at temperature above 100 K. This is the reason behind the net increase in

the thermal conductivity with increasing temperature. As mentioned above, the basic mechanism of thermal conductivity is the phonon transport and because of this, the mean free path of the phonon transport is the main requirement. A certain nanofiller with larger length is considered to have higher mean free path of phonon than that of having lower length. For example, it is found that the phonon mean free path for MWCNTs is 500 nm and the phonon mean free path for SWCNTs is even higher. Therefore, the size and shape of nanofiller play important key parameters in controlling thermal conductivity. For example, at a certain temperature, the thermal conductivity of MWCNTs increase with increasing the tube length (Mondal & Khastgir, 2019).

The mechanism of thermal conduction in polymer nanocomposites is complicated. The existing theories, e.g. phonon scattering, cannot explain it sufficiently. The obtained experimental results are generally much lower or lower than the theoretical values due to nonideal dispersion of nanofiller and unpredictable interfacial thermal resistance between the nanofiller and matrix (Zhang et al., 2019).

Structural defects in the nanofillers lead to scattering, diffraction, reflections, or refraction of phonons, interfering with the free movement and decreasing the thermal conductivity. Discontinuities and defects in the crystallinity can strongly deteriorate its thermal conductivity and this can explain fact that the experimental thermal conductivity results are lower than theoretical and expected values. Since there is no totally defect-free and pure nanofiller. For example, the defects of CNTs found up to now contain for types: bonding defects such as dislocations and vacancies, rehybridization with sp^3 and sp^2 , topological structure with non-hexagonal carbon, and other elemental doping (Kim et al., 2018).

When comparing the nanofillers, up to now, the thermal conductivity of polymer nanocomposites with metallic or ceramic fillers is still higher than that with GnPs or MWCNTs. This can be explained by two possible reasons (Huang et al., 2018):

- 1- The quality of individual GnPs and MWCNTs used in polymer nanocomposites can differ from those prepared for individual characterization of thermal

properties. MWCNTs generally have some defects decreasing the effective thermal conductivity of MWCNTs, such as doping or vacancy defects, Stone-Wales defects and intertube junction. In addition to its intrinsic defects, the waviness, kinks, and twists which are formed in MWCNTs can also decrease its aspect ratio, and results in a lower thermal conductivity of polymer nanocomposites than expected. Similarly, the waviness of GnP leads to decrease in the thermal conductivity. To remove such defects in GnP and MWCNTs, surface modification methods are improved to change the defect density and morphology, such as plasma and acid treatment.

- 2- The interfacial thermal resistance across the polymer matrix and nanofiller can mainly decrease the benefits of the nanofillers with high thermal conductivity. As the nanofiller loading is low and a filler network is not created, the high interface thermal resistance generally causes a low thermal conductivity. Moreover, the polymer molecules wrap around GnP or MWCNTs, this can induce shape and strain variation and therefore decrease their thermal conductivity. Although increasing nanofiller loading to create a thermal conductive network can considerably improve thermal conductivity, a high nanofiller loading can compromise other significant properties of polymer, e.g. electrical, mechanical and optical properties (Huang et al., 2018).

Even though the carbon-based filler materials have the highest inherent thermal conductivity, in contrast with expected, the reported thermal conductivity of polymer nanocomposites with carbon-based materials is close to the lower boundary of mixtures law. The reasons for this are size-dependent thermal conductivity of the nanofillers, difficulty in increasing the content of nanofillers and considerable weak-coupling-induced interfacial thermal resistance between the nanofillers and their interfaces with polymers (Xu, Chen, Zhou, & Li, 2018). Different dispersion methods have been improved to obtain homogenous dispersion of carbon nanofillers, such as an in-situ polymerization method dependent on ring-opening polymerizable oligoesters. Nevertheless, even if well-dispersion of nanofiller is achieved, phonon scattering because of the contact thermal resistance at the nanofiller-nanofiller interface and the interfacial thermal resistance at the matrix-nanofiller interface is

inevitable and this is basic reason of low thermal conductivity of polymer nanocomposites, as seen in Figure 2.29. At high nanofiller loading, the interfacial thermal resistance can be overcome by the formation of a contacted 3D conductive network among the nanofillers (Kim et al., 2018).

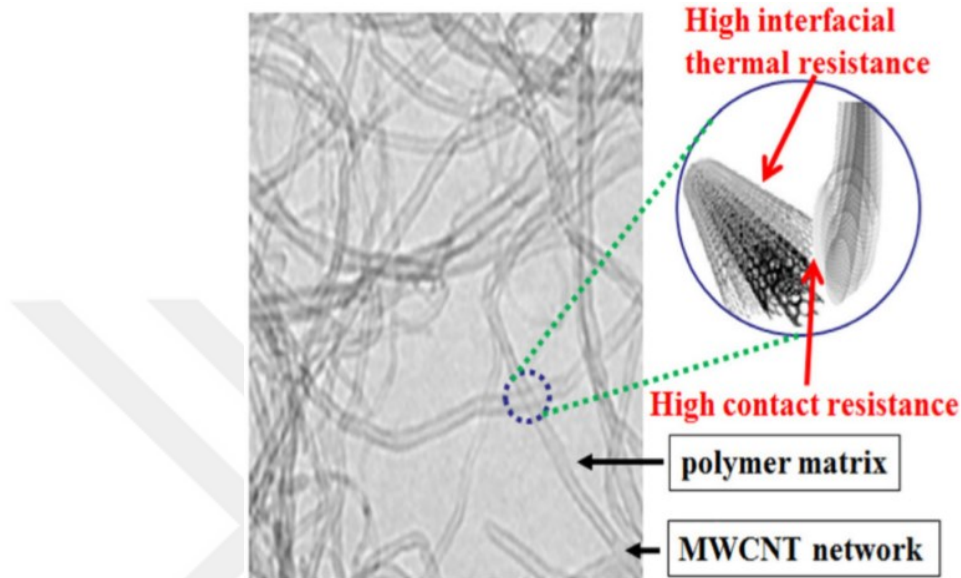


Figure 2.29 Schematic diagram which explains the low thermal conductivity of polymer nanocomposites reinforced by MWCNTs (Kim et al., 2018)

2.5.3 Mechanical Properties of Polymer Nanocomposites

The enhancement in the mechanical performances of the polymer nanocomposites is mainly owing to nanosize dimensions of nanofiller and to the strong nanofiller-polymer interactions which may influence the load transfer efficiency between the matrix and nanofillers. As a homogenous dispersion is obtained in the nanoscale size, the stiffness of nanocomposites is enhanced by a considerable factor over the pure matrix stiffness. Notwithstanding, nonlinear mechanical properties, e.g. impact strength, tensile strength, or elongation at break, usually reduce beyond a certain proportion of nanofillers. The dispersion of nanofillers in the matrix has significant effect on these properties. The distribution of nanofillers in the matrix is based on several factors (type of matrix and nanofiller, processing conditions, nanofiller loading, nanofiller treatment, etc.) (Mittal, 2010).

Even though the Young's modulus of nanocomposites increases with nanofiller loading, this increase is higher at low filler loading. This shows that the nanofillers are better exfoliated and/or dispersed. For nanocomposites, the reinforcing effect is lower at the high nanofiller loading due to the part of nanofillers that are partially exfoliated or dispersed and stacked or aggregated. The ultimate mechanical properties of polymer nanocomposites are strongly dependent of their microstructures, governed by the dispersion and/or exfoliation of nanofillers in the polymer matrix (Mittal, 2010).

The mechanical properties of polymer nanocomposites are mainly based on the dispersion of nanofillers and dispersion is based on matrix and alignment of nanofillers and interfacial interaction. The interfacial adhesion at the molecular level optimizes the interface in polymer nanocomposites. In general, the nanofiller content also influences the mechanical properties and the addition of nanofiller into the polymer matrix leads to enhance the mechanical properties of nanocomposites due to their intrinsic mechanical properties. The modulus and strength of polymer nanocomposites increase with the alignment, dispersion and loading of nanofillers. As compared with that of isolated nanofillers, the nanofiller agglomeration decreases the aspect ratio and Young's modulus. In terms of geometric consideration, the random orientation and alignment of nanofillers change the several properties of polymer nanocomposites (Jabeen et al., 2015).

2.5.4 Thermal Properties in Polymer Nanocomposites

The properties of polymer nanocomposites strongly depend on the morphology formed throughout their fabrication. In terms of semi-crystalline polymers, this is more significant when the crystallization of polymers occurs during fabrication. A data of crystallization process, and the influence of nanofillers on the polymer nanocomposite crystallization behavior, is thus vital to obtain an understanding of property-structure relationship in the nanocomposites. The existence of a second phase either inorganic nanofiller, a polymer or low-molecular weight compound has a significant influence on the polymer crystallization. In polymer nanocomposites, the second phase dimensions are similar to the chain dimensions (Mittal, 2010).

The thermal stability of polymers can be enhanced by addition of nanofillers. The major reasons for thermal stability enhancement of the polymer nanocomposites are given below:

- 1- One of the major reasons is the barrier effect of nanofillers to the mass and heat transfer. Nanofillers behave as thermal barrier, preventing the polymer matrix from the degradation because of heat.
- 2- Nanofillers behave as a barricade to the mass transfer decreases the diffusion of the gaseous products obtained from the degradation's initial stage of the matrix.
- 3- The interphase of polymer and nanofillers decreases the polymers' molecular mobility and this causes better thermal stability.
- 4- Trapping of free radicals obtained during the polymer degradation.
- 5- Combined chemical and physical mechanisms improve the thermal stability of nanocomposites.
- 6- Nanofillers can absorb the volatile decomposition product either chemically or physically to improve the thermal stability of nanocomposites (Jineesh & Mohapatra, 2019).

In case of polymer nanocomposites, the mechanisms of thermal stabilization are based on the nanocomposite structure, interfacial interaction of nanofiller and matrix and morphological properties of polymer. The structure itself is influenced by several factors, such as the fabrication method, miscibility of the components, nanofiller loading (Mittal, 2010).

Up to now, the mechanisms which relate to the enhancement of thermal stability of nanocomposites are not wholly understood. Studies have not yet shown a specific mechanism. When elucidated, the eventual mechanism will be probably to include both chemical and physical processes. The variation in the chemical reactions throughout the thermal decomposition of a polymer is a particular effect which is characteristic for each nanofiller/polymer system. Nevertheless, it may also result in important variations in the thermal stability which are higher than caused by the physical shielding alone (Mittal, 2010).

To date, various mechanisms of thermal stability improvement have been considered for CNTs. Based on the literature, the mass loss retardation in the inert atmosphere is probably to result from a physical adsorption influence of the polymer molecules onto the surface of MWCNTs, or the absorption of free radicals occurred throughout the polymer degradation by the activated carbon surface. Another influence related to carbon-based nanofillers is a restriction of the polymer molecules mobility. This decreases the tension induced by the thermal excitation of the C–O–C bond and causes an improvement of thermal stability. Even though CNTs do not suggest an intercalation phenomenon, the stabilizing influences of CNTs may be rationalized similar to the influence of layered nanofillers, in regard to a barrier effect. Therefore, CNTs and aggregates of CNTs will restrict the diffusion of the decomposition products from the polymer bulk to the gas phase, an influence that is particularly evident in an inert atmosphere and it is characterized through a shift in the onset decomposition temperature. Also, the carbon nanoparticles may have an accelerating effect at the start of the polymer degradation, practically under the oxidative conditions, even though this effect is attributed to the remaining traces of inorganic elements, e.g. Co, Al and Fe. Interestingly, notwithstanding this effect can be observed for the carbon-based nanofillers, the existence of metal elements cannot be detected (Jineesh & Mohapatra, 2019; Mittal, 2010; Rahaman, 2019).

In addition, free radicals formed during the polymer degradation may be absorbed/entrapped by MWCNTs which also causes the development in the polymer stability. The physical absorption leads to a decrease in the polymer volatilization without influencing the onset decomposition temperature. In addition, the effective GnPs addition can increase the thermal degradation temperature of polymers up to 10-100 °C. Interaction with polymer and graphene will hinder the chain movement of macromolecules near the GnPs surface and causes better thermal stability (Jineesh & Mohapatra, 2019).

CHAPTER THREE

LITERATURE REVIEW

3.1 Polymer Nanocomposites with MWCNTs

The excellent thermal, electrical, and mechanical properties, low density and high aspect ratio of 1D fiber-like structure of CNTs make them extremely attractive as nanofiller material in the polymer nanocomposites. Up to now, numerous studies have been performed particular aspects of property enhancement of various polymer nanocomposites reinforced by CNTs and these studies have been discussed in many reviews. Generally, the addition of MWCNTs into polymer matrix leads to enhancement in the thermal, electrical, and mechanical properties of nanocomposites. Based on the obtained results in the literature, the properties of polymer nanocomposites reinforced by MWCNTs depends on several factors: the fabrication method of nanocomposites, types, concentration, dimension and dispersion of CNTs, choice and nature of the matrix, and interfacial interaction between CNTs-CNTs or CNTs-matrix (Bauhofer & Kovacs, 2009; Dubnikova et al., 2010; Kaseem et al., 2016; Patti, Russo, Acierno, & Acierno, 2016; Spitalsky et al., 2010).

Although hundreds of scientific publications have been reported on the properties of polymer nanocomposites with MWCNTs, there are limited number of studies on the aspect ratio effect of MWCNTs on the property enhancement of nanocomposites. Table 3.1 shows a comprehensive collection of studies on this subject. As seen in Table 3.1, in the literature, the influence of the MWCNTs dimension has been generally discussed with three parameters: aspect ratio, length and diameter.

To the best of authors' knowledge, the effect of MWCNTs dimensionality on the properties of nanocomposites has still been a controversial topic (up to now, there has been no clear consensus on the effect of MWCNTs dimensionality on the properties of nanocomposites containing MWCNTs). As seen in Table 3.1, Russ et al. (2013), Zhang et al. (2016), Chen & Yan (2018) and Chen, Yan, et al. (2018) claimed that the higher aspect ratio results in higher thermal conductivity. Ciecierska et al. (2013),

Jang, Yang, Khil, Kim, & Kim (2019) and Wang et al., (2013) claimed that the thermal conductivity of polymer nanocomposites increases with increasing the length of CNTs.

Several groups (Castillo et al., 2011; Zhang, Li, Liu, Peng, & Ieee, 2016) claimed that the percolation threshold of nanocomposites decreases with the increase of MWCNTs aspect ratio. In addition, the difference in the electrical conductivity is found to be insignificant for all nanocomposites. However, Guo et al. (2013) observed two tendencies: 1- The percolation threshold values of nanocomposites decrease with increasing the aspect ratio of MWCNTs for MWCNTs with low aspect ratios. This could be attributed to the conductive network theory for low aspect ratio of MWCTNs. This theory alleges that the MWCNTs with higher aspect ratio can form the conductive network in the lower content. 2- The percolation threshold of a nanocomposite is independent of the initial aspect ratio of MWCNTs at high aspect ratios of MWCNTs (higher than 300). This could be related to the fact that MWCNTs with higher aspect ratio are broken much more easily during the mixing process and the aspect ratios of MWCNTs in nanocomposites were almost the same. Additionally, the electrical conductivity of nanocomposites with high aspect ratio of MWCNTs were not changed with the increase of aspect ratio. However, the electrical conductivity of these nanocomposites was still remarkably higher than that of nanocomposites with low aspect ratio of MWCNTs. Another study conducted by Rahaman et al. (2013), the DC electrical resistivity of the nanocomposite decreases by increasing the aspect ratio of MWCNTs due to the decrement in the average distance among MWCNTs is reduced. The electron flow by hopping becomes easier when the average distance among MWCNTs, so the nanocomposites including higher aspect ratio of MWCNTs showed lower electrical resistivity. Ayatollahi et al. (2011) reported that the electrical conductivity of nanocomposites reinforced with MWCNTs is commonly increased by increasing the aspect ratio of MWCNTs. Excluded volume approach may elucidate this behavior. They claimed that the percolation threshold theory can be considered in two various ways: (i) the percolation threshold for various amounts of the filler at a fixed aspect ratio of the filler and (ii) the percolation threshold for various aspect ratios at a fixed amount of the filler.

Dang et al. (2011), Sethi et al. (2017), Shehzad et al. (2014, 2013) claimed that the length and diameter of MWCNTs were more realistic parameters than aspect ratio of MWCNTs in order to investigate the dimension effect of MWCNTs on the electrical properties. Practically, Dang et al. (2011) and Shehzad et al. (2014) pointed out that the percolation threshold of nanocomposites has a non-monotonic and fluctuating relationship with the aspect ratio of MWCNTs. For a better prediction and explanation the percolation threshold, Dang et al. (2011) proposed a percolation threshold the aspect ratio (d , l) theory divided two sections: the first one is diameter-dependent section, i.e., the aspect ratio (d) and the other is length-dependent section, i.e., the aspect ratio (l). Sethi et al., (2017) alleged that the length of MWCNTs are proportional to the electrical properties, such as percolation threshold and electrical resistivity, where it is not dependent on the aspect ratio of MWCNTs. The lowest percolation threshold and electrical resistivity were observed for nanocomposites with the longest MWCNTs. As reported by Dubnikova et al. (2010) nanocomposites with long and large diameter MWCNTs showed high electrical conductivity and the lowest value of percolation threshold. The increment in MWCNTs aspect ratio due to the decrease in diameter reduces the efficiency of MWCNTs. This reduction could be explained by decrement in the effective aspect ratio because of the high entanglement and flexibility of thin MWCNTs. It is significant to remark that the selection of optimum length and diameter of MWCNTs was the correct approach to achieve the maximum enhancement in the properties of nanocomposites. Wang et al. (2013) found that the decrease in the diameter and length of MWCNTs resulted in reduction in the electrical conductivity of nanocomposites. Structures of MWCNTs have an influence on the electrical conductivity of nanocomposites in two ways: (i) thicker and longer MWCNTs establish a more effective electron conduction network through individual MWCNTs and (ii) larger diameter MWCNTs lead to a denser structure, thus the tunneling distance of MWCNTs is reduced.

Lin et al. (2017), Su & Miao (2014), Yang, Jang, Eem, & Kim (2017) alleged that the length of MWCNTs affect the electrical properties significantly and the nanocomposites with a longer MWCNTs exhibited a higher electrical conductivity and lower percolation threshold. As pointed out in the study of Yang et al. (2017), the

percolation threshold point of nanocomposites with both MWCNTs are almost identical but the electrical conductivity of nanocomposites with long MWCNTs are slightly higher when it is compared to that of nanocomposites with short MWCNTs. This was explained by the weakened tunneling effect of the short MWCNTs. The similar results for electrical conductivity were reported in Lin et al. (2017). Higher improvement in the electrical conductivity is observed for the nanocomposites including the long MWCNTs. The reason for this may be the entanglement of long MWCNTs and more effective conductive network to enhance the electrical conductivity.

Several groups (Guo, Zhou, & Lv (2013), Wang et al., (2013)) claimed that the mechanical properties increase insignificantly by the increase in the aspect ratio. However, the opposite findings were also reported by researchers (Abbasi et al., 2011; Ayatollahi et al., 2011; Castillo & Grady, 2012; Lin et al., 2017; Sethi et al., 2017; Su & Miao, 2014). They claimed that the aspect ratio/length of MWCNTs have significant effect on the mechanical properties of nanocomposites. Guo et al. (2013) observed an insignificant change in the modulus and tensile strength of nanocomposites depending on the aspect ratio (length) of MWCNTs. As pointed out in Wang et al. (2013), the length of MWCNTs does not show a clear relation with Young's modulus and the tensile strength of nanocomposites. The mechanical properties of nanocomposites remain almost same by increase in the length MWCNTs. They explained that the aspect ratio of MWCNTs does not considerably change by increasing lengths of MWCNTs due to their high diameter. Lin et al. (2017) claimed that the short length MWCNTs shows a better enhancement in the mechanical properties due to better MWCNTs dispersion. In contrast, Su & Miao (2014) alleged that nanocomposites with longer MWCNTs exhibits more favorable mechanical properties. Ayatollahi et al. (2011) reported that both Young's modulus and tensile strength of nanocomposites increase by increasing the aspect ratio of MWCNTs. Sethi et al. (2017) asserted that the elastic modulus of nanocomposites is linearly depended on the aspect ratio of MWCNTs, not on their length. Abbasi et al. (2011) reported that the aspect ratio of MWCNTs has effect on the mechanical properties of nanocomposites, expect for elongation. The use of high aspect ratio MWCNTs enhances MWCNTs dispersion and

as a result, provide enhancement in the most of the mechanical properties of nanocomposites. Castillo et al. (2011) observed that the strains at break and tensile strengths are more sensitive to the various types of MWCNTs. Besides, it is noted that, the Young's modulus does not significantly change depending on the type of MWCNTs.



Table 3.1 Studies on the aspect ratio and dimension (diameter or length) of MWCNTs on the final properties of polymer nanocomposites

Reference	Matrix	d (nm)	L (μm)	AR (L/d)	Content	Fabrication Method	Results
Dubnikova et al., 2010	PP	<10 40-60 40-60	5-15 1-2 5-15	500-1500 20-40 100-300	0.1–5 vol.% (0.2–10 wt.%)	Melt mixing Compression Molding	-The enhancement in the straightness and dispersion state of MWCNTs in the matrix as well as the improvement of their efficiency as conducting and reinforcing nanofillers can be obtained through the choice of optimal MWCNTs sizes (diameter and length). -The results of both mechanical and electrical properties of nanocomposites indicate the maximum effectivity for the MWCNTs with large diameter and long length. -When the length of MWCNTs is the same, the increment in the aspect ratio of MWCNTs through diameter reduction decreases their efficiency owing to the great entanglement and flexibility of thin MWCNTs, which causes decrease in the effective aspect ratio. -The nanocomposites reinforced based the long large diameter MWCNTs display the lowest percolation threshold and highest electrical properties. -In terms of mechanical properties, MWCNTs with same length, but different diameter shows the similar reinforcing efficiency due to drastic decrease in the effective aspect ratio of MWCNTs with smaller diameter.

Table 3.1 continues

Reference	Matrix	d (nm)	L (μm)	AR (L/d)	Content	Fabrication Method	Results
Morcom et al., 2010	HDPE	50.0 $\pm$ 2.0 10.4 $\pm$ 0.3	15.0 $\pm$ 2.0 0.7 $\pm$ 0.1	300 67	5 wt.%	Melt mixing Injection molding	-The MWCNTs with high aspect ratio give more effective enhancement in the mechanical properties of nanocomposites.
Dang et al., 2011	thermoplastic elastomer (TPE)	20-40 10-30 20-40 10-30	1-2 1-2 5-15 5-15	62 116 437 833	-	Melt mixing Compression Molding	-There is a nonmonotonic relation between the aspect ratio of nanofiller and percolation threshold. -To predict the percolation threshold of samples, mathematically determined nominal aspect ratio of MWCNTs is unclear parameter. -In terms of percolation thresholds, the MWCNTs dimensions (length and diameter) is required to be take into consideration as individual parameter rather as the combined parameter of aspect ratio. - To better explain and predict the percolation threshold in the nanocomposites, aspect ratio function must be divided two functions: length dependent part and diameter dependent part. -As compared to MWCNTs with the same length, any diameter dependent increment in the aspect ratio of MWCNTs has inverse proportion with the percolation threshold. -By keeping the diameter constant, an increase in the length of MWCNTs leads to increment of aspect ratio, resulting in decrease in the percolation threshold.

Table 3.1 continues

Reference	Matrix	d (nm)	L (μm)	AR (L/d)	Content	Fabrication Method	Results																		
Abbasi et al., 2011	LDPE	30-50	10-20	375	0.5, 2, 5 wt. %	Melt mixing	-The use of high aspect ratio MWCNTs generally enhances the dispersion of MWCNTs and as a result, enhance the mechanical properties except for the elongation at break. -The high aspect ratio MWCNTs promote nucleation because of its great surface area per tube. -The aspect ratio of MWCNTs does not indicate influence of the crystallization onset. -For all loadings, the MWCNTs with high aspect ratio exhibit higher crystallinity than low aspect ratio ones.																		
		30-50	0.5-2.0	31		Compression molding		Castillo et al., 2011	PC	7.8	0.735	94	0.25-3.0 wt. %	Melt mixing	-The percolation thresholds of nanocomposites with different MWCNTs are between 0.28 and 0.60 wt. %. -The polymer nanocomposites reinforced by MWCNTs with high aspect ratios exhibit lower percolation threshold. -There are no considerable variations in the Young's modulus of the nanocomposites as a function of aspect ratio. -The tensile strengths and strain at break are more sensitive to the various aspect ratio of MWCNTs. -Except for the MWCNTs with highest aspect ratio, all other MWCNTs give the same enhancement in the electrical conductivity.	10.5	0.770	73	Compression	10	1.341	134	molding	10.5	0.727
Castillo et al., 2011	PC	7.8	0.735	94	0.25-3.0 wt. %	Melt mixing	-The percolation thresholds of nanocomposites with different MWCNTs are between 0.28 and 0.60 wt. %. -The polymer nanocomposites reinforced by MWCNTs with high aspect ratios exhibit lower percolation threshold. -There are no considerable variations in the Young's modulus of the nanocomposites as a function of aspect ratio. -The tensile strengths and strain at break are more sensitive to the various aspect ratio of MWCNTs. -Except for the MWCNTs with highest aspect ratio, all other MWCNTs give the same enhancement in the electrical conductivity.																		
		10.5	0.770	73		Compression																			
		10	1.341	134		molding																			
		10.5	0.727	69																					
		6	0.332	55																					

Table 3.1 continues

Reference	Matrix	d (nm)	L (μm)	AR (L/d)	Content	Fabrication Method	Results
Castillo et al. , 2011	PC	7.8 10.5 10 10.5 6	0.735 0.770 1.341 0.727 0.332	94 73 134 69 55	0.25-3.0 wt. %	Melt mixing Compression molding	The nanocomposites with the highest aspect ratio MWCNTs achieve higher electrical conductivity than others.
Ayatollahi et al., 2011	Epoxy	20-30 30-40 40-50 50-60	10-30 10-30 10-30 10-30	1000 715 555 455	0.1,0.5 and 1wt. %	Solution Mixing Casted Molding	-The properties of nanocomposites indicate high dependent on the dimensions of nanofiller. -The electrical conductivity and mechanical properties of nanocomposites generally increase with increasing the aspect ratio MWCNTs. -For 0.5 wt. % of MWCNTs loading, the critical aspect ratio is about 500 for the electrical conductivity.
Rahaman et al., 2013	LDPE	30-50 30-50 20-30	0.5-2 10-20 10-30	31 375 800		Melt mixing	-The higher aspect ratio of MWCNTs the higher electrical conductivity of nanocomposites

Table 3.1 continues

Reference	Matrix	d (nm)	L (μm)	AR (L/d)	Content	Fabrication Method	Results
Russ et al., 2013	Epoxy	100 100	50 5	500 50 - Sonication-induced scission	0.1, 0.2, 0.5 and 1wt.%	Melt mixing Injection molding	-Electrical and thermal conductivity of nanocomposites are shown to strongly depend on the aspect ratio of MWCNTs. -The percolation threshold of nanocomposites with long or short aspect ratio is at below 0.1 wt.%. -The nanocomposites with long MWCNTs exhibit higher electrical conductivity than ones with short MWCNTs. -These differences can be explained by increment in the conduct resistance because of increase in the number of connections needed by shorter MWCNTs for the formation of a percolation network.
Wang et al., 2013	BMI	38 58 60 68 69	650 800 900 1100 1300	17105 13793 15000 16176 18841	35 wt.%	Spray winding Cured Molding	-Longer MWCNTs result in greater electrical and thermal conductivity of nanocomposites. - Mechanical properties do not present the MWCNTs length dependency and it seems that the mechanical properties are governed by the aspect ratio of MWCNTs. -At the millimeter scale, the longer MWCNTs with larger diameter cause more effective long-distance electron and phonon conductions, which results in greater electrical and thermal conductivity in the polymer nanocomposites. - Up to a certain length of MWCNTs, the thermal conductivity of nanocomposites increases with the increase of MWCNTs length.

Table 3.1 continues

Reference	Matrix	d (nm)	L (μm)	AR (L/d)	Content	Fabrication Method	Results
Wang et al., 2013	BMI	38	650	17105	35 wt.%	Spray winding	- Up to a certain length of MWCNTs, the thermal conductivity of nanocomposites increases with the increase of MWCNTs length.
		58	800	13793		Cured Molding	However, after this value, the further increase of MWCNTs length does not enhance the thermal conductivity, which reaches a saturation level.
		60	900	15000			-MWCNTs with longer and thicker can form a more effective thermal conductive pathways, allowing the transfer of phonons with longer wavelengths.
		68	1100	16176			-It is more probably that MWCNTs with higher diameter create a compact and rigid structure, and thus decrease the thermal contact resistance at polymer-MWCNTs and intertube interfaces.
		69	1300	18841			-The structures of MWCNTs may influence the electrical conductivity of polymer nanocomposites in two ways: - thicker and longer MWCNTs provide more efficient electron conduction pathway through the individual MWCNTs, as the the mechanism of thermal conduction - larger diameter MWCNTs support more contact structures and thus, tunneling distance between MWCNTs reduces.

Table 3.1 continues

Reference	Matrix	d (nm)	L (μm)	AR (L/d)	Content	Fabrication Method	Results
Ciecierska et al., 2013	Epoxy	9.5 9.5	1 1.5	105 158	0.5, 1, 2 and 5 wt.%	Melt mixing Cured molding	-The thermal properties of polymer nanocomposites are dependent on the length of MWCNTs. -The diffusivity of samples increases with increasing the length of nanocomposites, longer MWCNTs form a thermal percolated network much easier than shorter MWCNTs. -The dispersion of MWCNTs in the matrix is uniform independent of their length. -The length of MWCNTs has no important effect on the degradation temperature.
Guo et al., 2014	PC	7.8 9.9 9.5	0.74 3.1 4.5	94 313 474		Melt mixing Solution mixing Compression molding	-Electrical conductivity and percolation threshold of polymer nanocomposites are independent of aspect ratio of MWCNTs for high aspect ratios, however the electrical conductivity of samples is still greater than that of nanocomposites with MWCNTs aspect ratio of about 100. -The melt mixing leads to decrease in the length of MWCNTs due to the broken of MWCNTs. -For lower aspect ratio values (<300 for this study), the percolation threshold decreases with increasing the aspect ratio of MWCNTs.

Table 3.1 continues

Reference	Matrix	d (nm)	L (μm)	AR (L/d)	Content	Fabrication Method	Results
Guo et al., 2014	PC	7.8 9.9 9.5	0.74 3.1 4.5	94 313 474		Melt mixing Solution mixing Compression molding	-While the nanocomposites reinforced by MWCNTs with low aspect ratio do not exhibit clear change in the Young's modulus with MWCNTs loading, the nanocomposites with high aspect ratio MWCNTs show slightly increment with MWCNTs loading.
Costa et al., 2014	SBS	13-16 9.5	1-10 1.5	38 158	0-8 wt.%	Solution mixing Cured molding	-The aspect ratio of MWCNTs have a slight effect on the thermal stability of nanocomposites. -MWCNTs with high aspect ratio give much better enhancement in the electrical properties, it exhibits lower percolation threshold and higher electrical conductivity.
Su & Miao, 2014	PVDF-HFP	10-50 60-100 10-20	100-1000 5-15 1-2	18333 125 100	0-3.5 wt.%	Solution mixing Compression molding	-The mechanical properties polymer nanocomposites with longer MWCNTs is higher than that with shorter MWCNTs due to more even distribution of longer ones. -The electrical conductivity and percolation threshold are strongly influenced by the dimension of MWCNTs. -The nanocomposites with longer MWCNTs exhibit lower percolation threshold and higher electrical conductivity than ones with lower MWCNTs because of better distribution of MWCNTs.

Table 3.1 continues

Reference	Matrix	d (nm)	L (μm)	AR (L/d)	Content	Fabrication Method	Results
Zhang et al., 2016	Epoxy	10-20 10-20	20-30 0.5-2	1000-3000 25-2000	0.03-0.5 wt. %	Solution mixing Cured Molding	-The increase of aspect ratio leads to decrease in the percolation threshold and increase in the electrical and thermal conductivity.
Lin et al., 2017	PP	5-10 5-20	<5 5-20	667 1000	0.5, 1, 2, 4 and 8 wt. %	Melt mixing Injection molding	-The properties of polymer nanocomposites are significantly influenced by the MWCNTs length. -The length of MWCNTs does not have effect on the percolation threshold and up to the percolation threshold, the electrical conductivity of nanocomposites slightly changes with the length of MWCNTs. After this value, the long MWCNTs give much better performance in the electrical conductivity. -Short MWCNTs exhibit better dispersion within the polymer matrix and thus, they contribute to better mechanical properties. -The polymer nanocomposites with short MWCNTs show higher degree of crystallinity. -The properties of polymer nanocomposites can be adjusted by the use of MWCNTs with different lengths and this is benefit for the application in the diverse products.

Table 3.1 continues

Reference	Matrix	d (nm)	L (μm)	AR (L/d)	Content	Fabrication Method	Results
Chen & Yan, 2018	Epoxy	50 50	40 4	800 80- Sonication- induced scission		Melt mixing Injection molding	-The aspect ratio of MWCNTs is a significant key factor to determine the physical properties of nanocomposites. -The enhancement in the physical properties of samples can be interpreted in the way of MWCNTs networks. -For both MWCNTs with different aspect ratio, it found that the electrical percolation threshold is below 0.1 wt.%. -The electrical conductivity of the nanocomposites with high aspect ratio MWCNTs is three orders of magnitude higher than that of the nanocomposites with low aspect ratio ones. -The thermal conductivity of nanocomposites increases with increasing aspect ratio of MWCNTs.
Chen, Yan, et al., 2018	Epoxy	50 50	40 4	800 80- Sonication- induced scission		Melt mixing Injection molding	-The aspect ratio of MWCNTs is a significant key factor for the enhancement in physical properties of the polymer nanocomposites. -The electrical and thermal conductivity of nanocomposites are strongly dependent on the aspect ratio of MWCNTs. -In contrast to moderate increase in the thermal conductivity, electrical conductivity of nanocomposites shows the orders of magnitude improvement at the much more MWCNTs loading. -Under two values of aspect ratio, the electrical percolation of the polymer nanocomposites is at below 0.1 wt.%.

Table 3.1 continues

Reference	Matrix	d (nm)	L (μm)	AR (L/d)	Content	Fabrication Method	Results
Chen, Yan, et al., 2018	Epoxy	50 50	40 4	800 80- Sonication- induced scission		Melt mixing Injection molding	-High aspect ratios of MWCNTs tend to decrease the percolation threshold. -The nanocomposites reinforced by MWCNTs with high aspect ratio exhibit higher electrical and thermal conductivity than ones with low aspect ratio MWCNTs. -When the aspect ratio of MWCNTs is high, there are much more contact between the matrix and MWCNTs, facilitating the creation of thermally and electrically conductive pathways within the matrix.
Mu et al., 2018	PMMA	-	300 700 1500 1800 2300 3700 5000	60000 140000 214286 257143 255556 370000 500000	0.15 wt. %	Melt mixing Injection molding	-All nanocomposites do not show any enhancement in the thermal stability with increasing the length of MWCNTs due to very low MWCNTs loading. -The Young's modulus of the nanocomposites does not changed with the increase of MWCNTs length. Only, the nanocomposite with the longest MWCNTs exhibits enhancement in the Young's modulus.

Table 3.1 continues

Reference	Matrix	d (nm)	L (μm)	AR (L/d)	Content	Fabrication Method	Results
Cruz & Son, 2018	PC	12.5	25	2000	1, 2, 3	Melt mixing	-MWCNTs with high aspect ratio give much better enhancement in the electrical conductivity. In other word, the high amount of low aspect ratio MWCNTs is required to reach the same electrical conductivity with nanocomposites reinforced by high aspect ratio ones.
		12.5	100	8000	and 4	Injection	
		12.5	200	1600	wt. %	molding Compression Molding	
Jang et al., 2019	polyamide 6 (PA6)	7-10 7-10	10-50 100-200	3529 17647	1, 3, 5, 7 and 10 wt. %	Melt mixing Compression Molding	-Based on the results of FTIR and Raman spectra, the defect levels and surface chemistry of both MWCNTs are almost the same, two types of MWCNTs only differ in terms of dispersion degree and length. -For all loadings, short MWCNTs exhibit more uniform dispersion into the matrix than long ones. -As the MWCNTs are homogenously dispersed, the length of MWCNTs mainly affects the tensile properties. However, when the formation of aggregation increases with the increase of MWCNTs loading, the dispersion of MWCNTs into the polymer matrix becomes a predominant effect factor. -For two types of MWCNTs, the electrical percolation is at 1 wt. % and above this concentration, the length of MWCNTs does not significant effect on the electrical conductivity of nanocomposites.

Table 3.1 continues

Reference	Matrix	d (nm)	L (μm)	AR (L/d)	Content	Fabrication Method	Results
Jang et al., 2019	polyamide 6 (PA6)	7-10 7-10	10-50 100-200	3529 17647	1, 3, 5, 7 and 10 wt. %	Melt mixing Compression Molding	-At low MWCNTs loading, MWCNTs exhibit a homogenous dispersion without any aggregation irrespective of MWCNTs length, thus one can see that the length of MWCNTs dominates the variation in the mechanical properties and long MWCNTs give much better enhancement in the tensile properties due to high efficiency of force transfer. -The content of MWCNTs at which both Young's modulus and tensile strength achieved the maximum values is strongly based on the length of MWCNTs. -For all MWCNTs, the occurrence of aggregation increases with increase in MWCNTs loading, however the formation of aggregation starts at various MWCNTs loading depending on the length of MWCNTs. -At MWCNTs loading, the nanocomposites with short MWCNTs indicated much better mechanical properties than the nanocomposites with long MWCNTs because of better dispersion. -Long MWCNTs give much better improvement in the thermal conductivity compared to short ones. -The dispersion of MWCNTs is not a significant key factor for the thermal conductivity.

Table 3.1 continues

Reference	Matrix	d (nm)	L (μm)	AR (L/d)	Content	Fabrication Method	Results
Qian et al., 2019	Ethylene- α -octene block copolymer (OBC)	≤ 8	10-30	2500	0-15 vol.%	Melt mixing	-The high aspect ratio MWCNTs are beneficial for MWCNTs dispersion into the matrix and enhancing mechanical properties of nanocomposites. - High aspect ratio MWCNTs tend to create the network structure, However, the formation of electrical networks is weakened by the occurrence of agglomerates. -The low aspect ratio MWCNTs tend to align and straighten as stiff fibers, they are difficult to create network locally, which exhibit poor conductivity. -Generally, the percolation threshold of nanocomposites reduces with increasing aspect ratio. However, for MWCNTs with same length but different length, both higher aspect ratios exhibit the same percolation threshold and however, the electrical conductivity increase with aspect ratio. In addition, for MWCNTs with the same diameter and different length, the nanocomposites reinforced by MWCNTs with the highest aspect ratio indicate higher percolation threshold than ones with high aspect ratio. This is explained by the formation of agglomerates.
		10-20	10-30	1300		Compression	
		30-50	10-30	375		Molding	
		10-20	20-100	4000			
		10-20	10-30	1300			
		10-20	0.5-2	80			

3.2 Polymer Nanocomposites with GnPs

The discovery and research of graphene have been more attractive area of interest to many researchers in the field of polymer nanocomposites because of its excellent properties. Numerous studies that are performed on nanocomposites with graphene or its derivatives have shown that the graphene-polymer nanocomposites confer desired engineering properties and the properties of nanocomposites depend on several factors such as polymer type, the morphology, intrinsic properties, size and defect level of the filler material, production method, the interface between filler and polymer, etc. (Bakir et al., 2018; Chaudhry & Mittal, 2013; Kim et al., 2018). Although the size of GnPs is one of the most important factors, only a few studies have investigated the size effect of GnPs on the properties of nanocomposites with various matrices. These studies are summarized in Table 3.2.

Jiang & Drzal (2012) claimed that the percolation threshold values of the HDPE based nanocomposites were almost the same regardless of the GnPs size. However, the HDPE/GnPs with larger size showed a slightly lower in-plane electrical conductivity, while the nanocomposites with smaller one exhibited a slightly lower through electrical conductivity due to structure of GnPs and dispersion level. Imran et al. (2018) mentioned that no change was observed in the percolation threshold of the nanocomposites and a slight difference in the electrical conductivity in terms of GnPs size. Jun et al. (2018) reported that the percolation threshold of the nanocomposites decreased and the electrical conductivity of the PP based nanocomposites increased with increasing the lateral size of GnPs. Ravindran et al. (2018) mentioned that GnPs having larger surface area and size were favorable filler to enhance of the electrical conductivity of the Epoxy based nanocomposites.

Liang et al. (2016) reported that the PP/GnPs nanocomposites with the smaller lateral size had a higher Young's modulus. They claimed that the stiffness of the polymer composites would increase with increase in the inclusions number as the filler materials dispersed homogenously in the matrix materials. Under the same volume fraction of filler materials, the smaller partial size led to the more number of the

particles. Jun et al. (2018) claimed that the GnPs with a small size showed a more significant enhancement in the mechanical properties of the nanocomposites because of the increased surface areas which accelerated the efficient stress transfer between the polymer matrix and filler materials. In addition, the increased filler surface areas achieved a higher hindrance to the propagation of crack resulting in an enhance strength. Consequently, a significant reinforcement could be provided with the small-size GnPs could be ascribed to the combined effects of less agglomeration, better dispersion, and the original filler morphology retention within the matrix.

The results of Xu et al. (2019) show that the influence of GnPs diameter on the thermal conductivity changes with the fraction of GnPs loading. At low GnPs loading (6 wt.%), GnPs with larger diameter and moderate distribution is beneficial to obtain a higher thermal conductivity. At higher GnPs loading (6, 12 wt.%), the thermal conductivity decreases with the increment of GnPs diameter due to larger thickness and worse distribution. The increase of interface results in the serious phonon scattering and thus decrease in the thermal conductivity. Jiang & Drzal (2012) claimed that up to 5 vol.% of GnPs, the diameter of GnPs has a slight effect on the thermal conductivity of nanocomposites. After this concentration of GnPs, GnPs with higher diameter exhibit much better performance in the thermal conductivity than the ones with smaller diameter. This can be explained that GnPs with larger diameter have much more aspect ratio than other, and they can contact each other easily to form conductive network causing lower contact resistance and greater thermal conductivity. Chatterjee et al. (2012) claimed that the higher lateral size of GnPs, the higher thermal conductivity of nanocomposites. Because, the effective heat transport in GnPs is mainly due to phonons diffusion, a homogenous dispersion and network of GnPs in the matrix contributes to increase in the thermal conductivity of nanocomposites. Shtein et al. (2015) claimed that the high thermal conductivity of nanocomposites is achieved by GnPs with low defect densities and large lateral sizes. Tarani et al. (2017) reported that large aspect ratio of GnPs enables the creation of a good interface between polymer and GnPs, and thus it leads to an increase in thermal conductivity of polymer nanocomposites. Kim, Bae, Yu, & Kim (2016) asserted that GnPs with larger lateral size show a higher enhancement in the thermal conductivity. One reason is that

it can more easily contact with each other to occur conductive network in the nanocomposites, resulting in the lower interfacial thermal resistance and higher thermal conductivity. Another reason is that a small lateral size and thickness of GnPs lead to larger interface with the polymer matrix and increase the phonon scattering at the matrix-bonded interface, resulting in a lower thermal conductivity of nanocomposites.



Table 3.2 Studies on the aspect ratio and dimension (lateral size or thickness) of graphene derivatives on the final properties of polymer nanocomposites

Reference	Matrix	d (μm)	t (nm)	AR (d/t)	Content	Fabrication Method	Results
Jiang & Drzal, 2012	HDPE	1 15	10 10	100 150	1, 3, 5, 10 and 15 vol.%	Melt mixing Injection molding	-At low GnP's loading (up to 5 vol.%), the diameter of GnP's does not have significant effect on the thermal conductivity. After this concentration, the thermal conductivity of nanocomposites with large diameter is higher than that of ones with small diameter due to higher aspect ratio. GnP's with large diameter can contact with each other more easily and thus, it is beneficial for the formation of the thermally conductive network causing lower thermal contact resistance and greater thermal conductivity. -The diameter of GnP's does not lead to change in the electrical percolation threshold of nanocomposites. -When GnP's loading exceeds the electrical percolation threshold, the in-plane electrical resistivity of nanocomposites with larger diameter GnP's is lower than that of the nanocomposites with smaller diameter GnP's, i.e., the GnP's with larger diameter exhibit much better performance in the enhancement of electrical conductivity. However, in terms of the through plane electrical conductivity, the nanocomposites with small diameter GnP's is more electrically conductive at this content of GnP's.

Table 3.2 continues

Reference	Matrix	d (μm)	t (nm)	AR (d/t)	Content	Fabrication Method	Results
Jiang & Drzal, 2012	HDPE	1 15	10 10	100 150	1, 3, 5, 10 and 15 vol.%	Melt mixing Injection molding	-When comparing the through-plane resistivity with the in-plane resistivity, except for small diameter GnPs at highest content of GnPs, both types of nanocomposites exhibit greater in-plane electrical conductivity due to the platelet structure and anisotropic property of GnPs. For highest GnPs loading, the nanocomposites with small diameter GnPs exhibit almost the same in-plane and through plane electrical conductivity.
Chatterjee et al., 2012	Epoxy	5 25	$\sim$ 6-10 $\sim$ 6-10	625 3125	0.1, 0.5, 1 and 2 wt.%	Melt mixing Curled molding	-Bigger GnPs display an enhancement of more than double compared with smaller GnPs.
Shtein et al., 2015	Epoxy	10 $\pm$ 7 19 $\pm$ 9 20 $\pm$ 7 34 $\pm$ 20 2 $\pm$ 1	5-20 9-20 15-100 >100 5-20	725 $\pm$ 125 1255 $\pm$ 145 568 $\pm$ 298 340 $\pm$ 200 175 $\pm$ 25	0-25 vol.%	Solution mixing Compression molding	-The lateral dimension of GnPs has a strong effect on the thermal conductivity. -Phonon scattering is widespread in the nanocomposites reinforced by GnPs with smaller lateral dimensions, because these composites have greater interface densities. -The lowest thermal conductivity enhancement is exhibited by GnPs with the smallest diameter and low thickness, results from small lateral dimension, high defect density and impurities of this GnPs.

Table 3.2 continues

Reference	Matrix	d (μm)	t (nm)	AR (d/t)	Content	Fabrication Method	Results
Kim & Son, 2016	PC	<2	<3	667	5, 10, 15	Melt mixing	-The dimensions (lateral size and thickness) of GnPs is one of the most significant physical factors which are related to the thermal conductivity of nanocomposites. -It is found that the dispersion of GnPs is uniform irrespective of GnPs types. Therefore, the influence of GnPs dispersion on the thermal conductivity of nanocomposites is minimized. -Based on the results of XPS and FTIR analyses, All GnPs types exhibit the similar surface-chemical properties. The influence of the properties of their interface with the polymer matrix on the thermal conductivity is negligible. -Raman analyses show that -A larger thickness and lateral size of GnPs raise the possibility of the matrix bonded interfaces which are decreased, resulting in an efficiency enhancement in the thermal conductivity and the ability of heat dissipation of the polymer nanocomposites. -A comparison of thermal conductivity between the nanocomposites reinforced by GnPs with the same lateral size but different thickness shows that the nanocomposites with thinner GnPs exhibit lower thermal conductivity than samples with thicker ones.
		5	6-8	714	and 20	Compression	
		15	6-8	2143	wt. %	molding	
		25	6-8	3571			
		5	15	333			

Table 3.2 continues

Reference	Matrix	d (μm)	t (nm)	AR (d/t)	Content	Fabrication Method	Results
Kim & Son, 2016	PC	<2 5 15 25 5	<3 6-8 6-8 6-8 15	667 714 2143 3571 333	5, 10, 15 and 20 wt.%	Melt mixing Compression molding	-GnPs with larger lateral size and thickness show less phonon scattering at matrix-bonded interface. -As compared to GnPs with the same thickness, the thermal conductivity of nanocomposites increasing with the increment of their lateral size. -The nanocomposites exhibit a lower enhancement in the thermal conductivity in the bulk direction than in the in-plane direction because of forming thermally conducting pathways in the polymer nanocomposites with the increase of GnPs loading.
Liang et al., 2016	PP	<10 0.5-20 10-50	≤ 5 5-25 3.4-7	200 673 5769	0.1, 0.2, 0.3, 0.4 and 0.5 wt.%.	Melt mixing Injection molding	-Under the same content of GnPs, the Yong's modulus of the nanocomposites increases with the decrement in the lateral size of GnPs.
Tarani et al., 2017	HDPE	5 15 25	-	-	0, 0.5, 1, 2.5, 3 and 5 wt.%	Melt mixing	-Summing up the effect of nanofiller size on the thermal properties of matrix, GnPs with higher diameter have more influence. -The nanocomposites with the highest diameter GnPs increase more thermal stability than others. Because, GnPs with higher aspect ratio create a nanofiller network and restrict, even more, the polymer molecule movements.

Table 3.2 continues

Reference	Matrix	d (μm)	t (nm)	AR (d/t)	Content	Fabrication Method	Results
Tarani et al., 2017	HDPE	5 15 25	-	-	0, 0.5, 1, 2.5, 3 and 5 wt. %	Melt mixing	-The initial degradation and maximum mass loss temperatures increase with the increment of GnPs diameter. -When the same GnPs loadings, the GnPs with higher diameter are obviously more efficiency to enhance the thermal conductivity of nanocomposites than GnPs with smaller diameter. i.e., the large aspect ratio of GnPs facilitate the creation of a good interface between the matrix and nanofillers, playing a key role in achieving thermal conductivity in polymer nanocomposites. -The phonon transport is enabled from the random bridge of higher diameter GnPs pathways and lower aspect area of smaller diameter GnPs leads to more phonon scattering at the interfaces.
He, Zhang, Xiao, Hong, & Lai, 2017	PP	~8 ~40 ~100 ~40 ~8	~100 ~100 ~100 ~30 ~5	~80 ~400 ~1000 ~1300 ~1600	3, 6, 7, 9, 12 and 15 wt. %	Melt mixing Compression molding	-GnPs with larger diameter and smaller thickness are better suited to form an electrically conductive network. -The electrical conductivity of nanocomposites is influenced by the aspect ratio of GnPs when GnPs loadings exceeds the percolation threshold. -At near the percolation threshold, the diameter and dispersion of GnPs have strong influence on the electrical conductivity.

Table 3.2 continues

Reference	Matrix	d (μm)	t (nm)	AR (d/t)	Content	Fabrication Method	Results
He et al., 2017	PP	~8 ~40 ~100 ~40 ~8	~100 ~100 ~100 ~30 ~5	~80 ~400 ~1000 ~1300 ~1600	3, 6, 7, 9, 12 and 15 wt.%	Melt mixing Compression molding	-The incorporation of GnPs into the matrix leads to increase in the melting temperature. -While the thickness of GnPs have a slight effect on the melting temperature, it increases with decreasing the diameter of GnPs. -The electrical conductivity of nanocomposites with lowest aspect ratio GnPs is similar to that of pure polymer. This means that the addition of this GnPs can neither facilitate forming the conductive network nor improve the electrical conductivity of nanocomposites. -As compared GnPs with same thickness but different diameter, the electrical conductivity of nanocomposites considerably increases with the increase of the diameter. This can be explained that their diameter plays a significant role in forming the conductive network. -As compared GnPs with the same diameter but different length, the thickness is significant to enhance the electrical conductivity of nanocomposites. -A larger diameter GnPs facilitates the creation of electrical conductivity network and thinner GnPs can accelerate the electronic movement between the GnPs layers.

Table 3.2 continues

Reference	Matrix	d (μm)	t (nm)	AR (d/t)	Content	Fabrication Method	Results
He et al, 2017	PP	~8 ~40 ~100 ~40 ~8	~100 ~100 ~100 ~30 ~5	~80 ~400 ~1000 ~1300 ~1600	3, 6, 7, 9, 12 and 15 wt.%	Melt mixing Compression molding	-GnPs with highest aspect ratio (small diameter and smallest thickness) show the highest electrical conductivity enhancement because of its perfect dispersion, which is useful to either form a conductive network or facilitate electron tunneling. -GnPs with small diameter and smaller thickness exhibit better dispersion in the polymer matrix. -For low GnPs loading, GnPs with moderate diameter and appropriate dispersion are more beneficial to create an electrically conductive network and make easy electron conduction. -The optimal electrical conductivity is achieved by the perfectly dispersed GnPs and the electrical conductivity of nanocomposites is dependent of the aspect ratio of GnPs for high GnPs loading.
Liang, 2018	PP	<10 0.5-20 10-50	≤ 5 5-25 3.4-7	200 673 5769	0.1, 0.2, 0.3, 0.4 and 0.5 wt.%.	Melt mixing Injection molding	-Under the same content of GnPs, the Yong's modulus of the nanocomposites increases with the decrement in the lateral size of GnPs. However, the difference in Young's modulus between three types of nanocomposites is small.

Table 3.2 continues

Reference	Matrix	d (μm)	t (nm)	AR (d/t)	Content	Fabrication Method	Results
Liang, 2018	PP	<10 0.5-20 10-50	≤ 5 5-25 3.4-7	200 673 5769	0.1, 0.2, 0.3, 0.4 and 0.5 wt.%. 	Melt mixing Injection molding	-At the same GnPs loadings, the nanocomposites with lowest lateral size GnPs exhibit clearly higher tensile strength than other ones. The difference in the tensile strength of other two types nanocomposites is close to each other. Tensile strength of nanocomposites depends on the interfacial adhesion between the polymer matrix and nanofiller. The larger interfacial area between them the higher tensile strength and this area increases with the increase in specific surface area of GnPs. -The elongation at break of the nanocomposites with the largest lateral size GnPs is lower than the others. And the difference in the tensile elongation at break between other types of nanocomposites is small.
Jun et al., 2018	PP	>150 >25 >5 >2	~ 15 $\sim 6-8$ $\sim 6-8$ ~ 5	10000 3571 714 400	0-20 wt.%. 	Melt mixing Injection molding	-The properties of nanocomposites are strongly influenced by the physical property of GnPs. -The introduction of small-sized GnPs (smaller than $25 \mu\text{m}$) into polymer leads to better enhancement in the thermal stability of nanocomposites due to better GnPs distribution with less aggregation.

Table 3.2 continues

Reference	Matrix	d (μm)	t (nm)	AR (d/t)	Content	Fabrication Method	Results
Jun et al., 2018	PP	>150 >25 >5 >2	~15 ~6-8 ~6-8 ~5	10000 3571 714 400	0-20 wt.%	Melt mixing Injection molding	-The highest enhancement in the mechanical properties is achieved by the nanocomposites with small-sized GnPs. The explained that the small-sized GnPs can obtain a better degree of dispersion with less aggregation. -Large-sized GnPs are useful to achieve the lowest percolation threshold and thus for purposes concerning the electrical conductivity. -The percolation threshold of nanocomposites decreases with increasing the size of GnPs. -The higher GnPs size, the lower percolation threshold value of nanocomposites. -After a certain GnPs loading, GnPs with largest size does not show the best performance in the electrical conductivity enhancement. This can be explained by poor dispersion state caused by its agglomeration. The lateral size of GnPs and number of dispersed particles per unit volume are decreased result from this agglomeration.

Table 3.2 continues

Reference	Matrix	d (μm)	t (nm)	AR (d/t)	Content	Fabrication Method	Results
Jun et al., 2018	PP	>150 >25 >5 >2	~15 ~6-8 ~6-8 ~5	10000 3571 714 400	0-20 wt.%	Melt mixing Injection molding	-The use of the smallest size GnPs exhibits the highest effectiveness in the tensile strength reinforcement because of the original morphology retention and a high dispersion degree with less agglomeration in the polymer nanocomposites.
Xu et al., 2019	PP	~100 ~40 ~8	<100 <30 <5	~1000 ~1300 ~1600	6, 9, 12 wt.%	Melt mixing Compression molding	-GnPs with lowest diameter show the highest crystallinity values. Since, its larger surface area provides more area for higher nucleation efficiency. -At high GnPs loadings, the thermal conductivity of nanocomposites decreases with increasing diameter. The poor performance of GnPs with largest diameter is attributed to poor distribution and high thickness of this GnPs. This is not useful for the interface property between the matrix and GnPs. - The existence of large amounts of interfaces lead to serious phonon scattering, and thus the lowest thermal conductivity. -At low content of GnPs, the GnPs with lowest diameter exhibit lower thermal conductivity. This may be that GnPs cannot touch each other and their distribution is still very narrow to create complete thermal conductive pathways.

Table 3.2 continues

Reference	Matrix	d (μm)	t (nm)	AR (d/t)	Content	Fabrication Method	Results
Xu et al., 2019	PP	~100 ~40 ~8	<100 <30 <5	~1000 ~1300 ~1600	6, 9, 12 wt. %	Melt mixing Compression molding	-The nanocomposites with high aspect ratio GnPs (large lateral size and thickness) indicates agglomeration and unevenly distribution of GnPs in the matrix. Therefore, these nanocomposites have the lowest thermal conductivity. - Two types of GnPs with smaller thickness show good dispersibility and uniform distribution, resulting in higher thermal conductivity. -Microstructure which is created by various type of GnPs play a significant role in enhancing of the thermal properties of nanocomposites.

3.3 Hybrid Polymer Nanocomposites

The dispersion of nanofillers in the polymer matrix is the key challenge in the polymer nanocomposites preparation. Other key challenge is the formation of good interfacial interaction between the polymer and nanofiller (Jabeen et al., 2015). Especially, due to strong surface interactions, the carbon-based filler materials tend to aggregate into ropes and bundles. Dispersing and disentangling the carbon-based materials in the polymer matrix are one of the main problems in using these materials as fillers. It is known that the effective properties of the final polymer nanocomposites strongly depend on the state of the distribution and dispersion of the carbon-based materials in the polymer matrix. Removing the amorphous carbon and metallic impurities from these filler materials is another problem in the use of them (Safdari & Al-haik, 2018). As is known, favorable dispersion of the nanofiller materials in the polymer matrix is necessary to utilize their superior properties (Chatterjee et al., 2012; Al-Saleh, 2015). To solve the agglomeration problems, some studies suggested that the addition of CNTs in the polymer/graphene nanocomposites enhances the carbon filler dispersion. The clear synergic influence on enhancing the hybrid nanofillers dispersion rapidly increases interest to research the carbon-based hybrid nanocomposites (Jen & Huang, 2019).

To achieve better property enhancements, more than one type of carbon-based nanofillers with different dimensions can be used to fabricate polymer nanocomposites such as 0D atomic clusters (e.g. fullerenes, nano-carbon black), 1D rod-like nanofiller (e.g. CNTs, carbon fiber) and 2D platelet-like nanofiller (e.g. graphene, GnPs) (V. Kumar et al., 2017). Using two geometrically different nanofiller materials, such as MWCNTs and GnPs or expanded graphite (EG) and carbon black (CB) or CB and carbon nanofibers (CNFs), could provide the formation of a co-supporting network of the two nano filler materials and so a reduction in the amount of total filler materials (Szeluga et al., 2015; Zhang et al., 2018). These network and layered structures of filler materials create uniform global conductive pathways in the polymer nanocomposites at relatively low concentration of filler materials. Hereby, these polymer

nanocomposites also exhibit good mechanical properties. It is known that the main objective of carbon-based polymer nanocomposite preparation is to create material with a high thermal and/or electrical conductivity without destroying the mechanical properties or possibility with an enhancement in the mechanical properties (Szeluga et al., 2015).

When adding 2-D GnPs and 1-D MWCNTs simultaneously, they can form 3-D structures. It is known that the tortuous and long MWCNTs can act as a bridge between the adjacent GnPs layer and prevent their aggregation, which result in increasing the contact surface area between the polymer matrix and GnPs/MWCNTs structures. In the 3-D hybrid architectures, MWCNTs which behave as chelating arms entangle with the polymer chain to ensure stronger interaction between the polymer matrix and GnPs/MWCNTs minimizing the aggregation of nanofillers. As a result, the 3-D MWCNT/GnPs hybrid nanofillers show the highest influence in the improvement of thermal conductivity and mechanical properties among the individual graphene-based materials and MWCNTs (Al-Saleh, 2015c; Araby et al., 2015; Moosa et al., 2017; Szeluga et al., 2015; Yang et al., 2011). In other words, MWCNTs work additional to GnPs by creating the conductive network, in which MWCNTs behave as long nanocables to transfer stress and electrons while GnPs act as inter relationship sites between MWCNTs creating the local conductive network (Araby et al., 2015). The clear synergic effect on enhancing the dispersion of the hybrid (GnPs+MWCNTs) nanofiller materials makes them attractive to research the hybrid polymer nanocomposites increases rapidly (Jen & Huang, 2019). In comparison to single GnPs and MWCNTs, the contact geometry varies from 0D point contact to 1D linear contact, resulting in the increase of contact area in the hybrid nanofillers. Large contact area leads to increase the pathways for the phonon transport and reduce the interfacial resistance in the hybrid nanofillers. Thus, the synergic effects of GnPs and MWCNTs have profound influences on the properties of nanocomposites (Yang et al., 2011).

In the literature, the various studies on the hybrid nanocomposites with GnPs and MWCNTs are reported on a wide variety of polymers. Table 3.3 shows a comprehensive collection of published studies in this field. As seen in Table 3.3, while

some studies have reported the synergic effect between GnP_s and MWCNTs in enhancing properties, others have not observed any distinct synergic effect.



Table 3.3 Studies on the properties of hybrid nanocomposites

Reference	Matrix	MWCNTs		Content	GnPs		Content	Total Content GnPs/MWCNTs ratio	Fabrication method	Results
		d (nm)	L (μm)		d (μm)	t (nm)				
Yang et al., 2011	epoxy	20	1-25	-	100	1-15	-	1 wt% 0.9/0.1	Solution Mixing	-The higher thermal conductivity and mechanical properties of hybrid nanocomposites exhibit synergic effect between GnPs and MWCNTs. -Hybrid nanocomposites exhibit more elastic and flexible behavior throughout loading compared to the nanocomposites of individual GnPs or MWCNTs. -The improvement in thermal conductivity and tensile properties suggests that MWCNTs have a significant key role in the enhancement of the compatibility and dispersion of GnPs in the matrix.
Chatterjee et al. , 2012	epoxy	10-20	1	-	25	6-10	-	0.5 wt.% 1/3, 1/5, 1/9, 3/1, 5/1, 9/1	Melt Mixing Mold casted	-The ratio of GnPs/MWCNTs is an interesting factor importantly effecting the properties of nanocomposites. -The combination of GnPs with larger surface area and MWCNTs with high aspect ratio contributed to the synergic effect of the hybrid samples. -The synergic effect between GnPs and MWCNTs is observed except for the GnPs/MWCNTs ratios of 1/3 and 3/1.

Table 3.3 continues

Reference	Matrix	MWCNTs		Content	GnPs		Content	Total Content GnPs/MWCNTs ratio	Fabrication method	Results
		d (nm)	L (μm)		d (μm)	t (nm)				
Chatterjee et al. , 2012	epoxy	10-20	1	-	25	6-10	-	0.5 wt.% 1/3, 1/5, 1/9, 3/1, 5/1, 9/1	Melt Mixing Mold casted	-The 1/9 ratio of GnPs/MWCNTs is the most appropriate combination for the improvement of mechanical properties.
Huang, Zhi, & Jiang, 2012	epoxy	30-50	10-20	-	5	20	-	10, 20, 30, 40, 50 vol.% 1/1	Solution mixing Curing under a high press	-Hybrid nanofiller shows an effective synergic improvement in the thermal conductivity of polymer nanocomposites. -Synergic effect is more noticeable at the high nanofiller content. -The efficiency of thermal conductivity increases up to 40 vol.% of hybrid nanofiller, and then decreases with the further increase of nanofiller loading. -When the total hybrid loading is lower than 20 vol.% (30 wt.), any synergic effect is not observed. -There is no synergic effect of GnPs and MWCNTs on enhancing the electrical conductivity.

Table 3.3 continues

Reference	Matrix	MWCNTs		Content	GnPs		Content	Total Content GnPs/MWCNTs ratio	Fabrication method	Results
		<i>d</i> (nm)	<i>L</i> (μm)		<i>d</i> (μm)	<i>t</i> (nm)				
Li et al., 2013	epoxy		10-15	-	3-4	30	-	0.5 wt. %	Solution mixing Curing under atmospheric press	-There is a distinct synergic effect of GnPs and MWCNTs in enhancing the mechanical properties.
Yue et al., 2014	epoxy	13	>1	-	4-5	<1	-	0.8 - 4 wt. % 0/10, 8/2, 6/4, 4/6, 2/8, 10/0	Solution mixing Cured mold	-With the 2/8 ratio of GnPs/MWCNTs, the hybrid nanocomposites exhibit a remarkable increase in the thermal conductivity at lower total nanofiller loading. -The combination of GnPs and MWCNTs in ratio 2/8 decreases the electrical percolation for the nanocomposites.
Jeong & An, 2014	epoxy	10-15	100	-	-	-	-	5 wt. % 9/1, 7/3, 5/5, 3/7	Film-casting Thermal-curing	-The electrical resistivity of hybrid nanocomposites decreases with increasing the MWCNTs loading in the amount of mixed carbon nanofillers due to its bridge effect among GnPs layers.
Araby et al., 2015	EPDM	8-25	0.75	2.8 vol% - 5 wt%					Melt mixing Compression molding	-A remarkable synergic effect between GnPs and MWCNTs may provide a guideline for the design and fabrication of nanocomposites.

Table 3.3 continues

Reference	Matrix	MWCNTs		Content	GnPs		Content	Total Content GnPs/MWCNTs ratio	Fabrication method	Results
		<i>d</i> (nm)	<i>L</i> (μm)		<i>d</i> (μm)	<i>t</i> (nm)				
Wegrzyn, Galindo, et al., 2015	PP	9.5	1.5	0.5, 1 wt.%	5	5-8	0.5, 1 wt.%	-	Masterbatch dilution/mixing approach Compression molding	-It is observed that electrical conductivity of hybrid nanocomposites enhances up to an order of magnitude when the content of each nanofillers increases from 0.5 wt.% to 1 wt.%. -Unequal content of both nanofiller leads to reduce in the electrical conductivity of samples. -While MWCNTs are more responsible the increase of electrical properties for increasing electrical properties, GnPs are more efficient in enhancing thermomechanical properties.
Al-Saleh, 2015a	PP	9.5	1.5	1 wt.%	5	7	0-20 wt.%	5 vol% 5/0, 4/1, 3/2, 2/3, 1/4, 0/5	Melt mixing Compression molding	- The electrical conductivity of hybrid nanocomposites is higher than that with GnPs alone. - The electrical conductivity and Young's modulus of hybrid nanocomposites increases with MWCNTs in total nanofiller content. - No synergic effect owing to the use of hybrid nanofiller is observed.

Table 3.3 continues

Reference	Matrix	MWCNTs		Content	GnPs		Content	Total Content GnPs/MWCNTs ratio	Fabrication method	Results
		d (nm)	L (μm)		d (μm)	t (nm)				
Lin et al., 2016	PVA	10-30	5-20	-	-	50- 100	-	1.5 wt.% 1.5/0, 1.25/0.25, 1/0.5, 0.75/0.75, 0.5/1, 0.25/1.25, 0/1.5	Melt mixing Solution mixing	-The incorporation of MWCNTs provides the PVA-based nanocomposite reinforced by GnPs with better synergy which can improve the electrical conductivity, thermal stability, and tensile properties of nanocomposites. - For all properties, the solution mixing outperforms the melt mixing. -The hybrid nanocomposites with GnPs/MWCNTs ratio of 0.25/1.25 wt% exhibit the optimal tensile strength and thermal stability for both preparation method.
Xiao et al., 2016	PVDF	>50	10-30	2 wt.% 0-20 wt.%	5-7	-	0-20 wt.% 2 wt.%	-	Solution mixing + Melt mixing Compression molding	-The addition of MWCNTs in to the PDVF/GnPs nanocomposites highly promotes the creation of the nanofiller hybrid network structure. And this is very various from the scenario that the addition of GnPs in to the PDVF/MWCNTs nanocomposites -GnPs and MWCNTs show superior nucleation influences for PDVF crystallization. However, the difference of PDVF crystallinity is little.

Table 3.3 continues

Reference	Matrix	MWCNTs		Content	GnPs		Content	Total Content GnPs/MWCNTs ratio	Fabrication method	Results
		d (nm)	L (μm)		d (μm)	t (nm)				
Xiao et al., 2016	PVDF	>50	10-30	2 wt.% 0-20 wt. %	5-7	-	0-20 wt. % 2 wt. %	-	Solution mixing + Melt mixing Compression molding	-Thermal conductivity enhancement is mainly based on the formation of the nanofillers network structure in the nanocomposites. -The incorporation of 1D MWCNTs into the polymer nanocomposites with 2D GnPs indicates higher synergic effects compared to the scenario that the addition 2D GnPs into the polymer nanocomposites with 1D MWCNTs. -The hybrid nanocomposites show better thermal and electrical conductivity compared with the nanocomposites with single nanofiller. -Especially, the PVDF/ MWCNTs/ GnPs nanocomposites exhibit superior thermal and electrical conductivity and they have high potential application as the heat management materials.
Kumar et al., 2017	PC	10-15	1-10	1 wt. %	5 25	6 6	1 wt. %	-	Melt mixing Injection molding	-The hybrid nanocomposite exhibits the highest thermal conductivity. In other words, there is a distinct a synergic effect on the thermal conductivity.

Table 3.3 continues

Reference	Matrix	MWCNTs		Content	GnPs		Content	Total Content GnPs/MWCNTs ratio	Fabrication method	Results
		d (nm)	L (μm)		d (μm)	t (nm)				
Ghaleb et al., 2017	epoxy	6.2 $\pm$ 0.5	5-50	-	15	5-10	-	0.5 vol.% 0.4/0.1, 0.3/0.2, 0.25/0.25, 0.2/0.3, 0.1/0.4	Solution mixing	-The tensile modulus and strength considerably increase with increasing MWCNTs content in the total nanofiller loading. -The electrical conductivity of hybrid nanocomposites improves consistently with the increase of MWCNTs loading in 5 vol% of total hybrid nanofiller content. -The highest improvement in the tensile properties and electrical conductivity of hybrid nanocomposites is acquired by GnPs/MWCNTs ratio of 0.1/0.4. -When the GnPs/MWCNTs ratios are 0.2/0.3 and 0.1/0.4, the hybrid nanocomposites exhibit synergic effect for electrical and tensile properties.
Moosa et al., 2017	epoxy	8-15	50	-	1	2	-	0.5 wt.% 0/10, 1/9, 2.5/7.5, 5/5, 7.5/2.5, 9/1, 10/0	Melt mixing	-It is found that the best enhancements in the mechanical properties is observed at two weight ratios of GNPs/ MWNTs (5/5) and (9/1).

Table 3.3 continues

Reference	Matrix	MWCNTs		Content	GnPs		Content	Total Content GnPs/MWCNTs ratio	Fabrication method	Results
		d (nm)	L (μm)		d (μm)	t (nm)				
Wang et al., 2018	HDPE	8-15	30-50	0.5 wt.%		3-5	0.5, 1, 3 wt.%		Melt mixing Compression molding	-When GnPs and MWCNTs are incorporated simultaneously, the synergic effect of GnPs and MWCNTs are produced in electrical conductivity and tensile strength.
Paszkiewicz et al. , 2018	LDPE	9.5	1.5	-	5-10	5-10	-	20wt.% masterbatch 3, 5 and 20 wt.% 1/3, 1/1	Melt mixing Compression molding Injection molding	-There is not a distinct synergic effect of GnPs and MWCNTs on the electrical and thermal properties of nanocomposites. However, a synergic effect on the mechanical properties is observed. -In hybrid system, while the hybrid nanocomposites with 1/3 weight ratio of GnPs/MWCNTs exhibit better enhancement of thermal and electrical conductivity, the samples with 1/1 weight ratio show higher values of Young's modulus and tensile strength.

Table 3.3 continues

Reference	Matrix	MWCNTs		Content	GnPs		Content	Total Content GnPs/MWCNTs ratio	Fabrication method	Results
		d (nm)	L (μm)		d (μm)	t (nm)				
Kranauskaitė et al. , 2018	epoxy	10	0.1-10	-	20-50	-	-	0.3 wt.% 1/5, 1/2, 1/1, 2/1, 5/1	Solution mixing	- Simultaneously adding GnPs and MWCNTs does not have influence of the percolative behavior of MWCNTs, however enhance the overall electrical performances. -The highest value of electrical conductivity is achieved by the nanocomposites with 1/5 weight ratio of GnPs/MWCNTs.
Zhang et al., 2018	PMMA	30-50	10-20	-	5-10	3-10	-	2 wt.% 2/0, 1/1, 0/2 3 wt.% 3/0, 2/1, 1.5/1.5, 1/2, 0/3	Solution mixing Compression molding	-GnPs and MWCNTs demonstrate a clear synergic effect in enhancing the mechanical performance. -the hybrid nanocomposites exhibit better dispersion state and stronger nanofiller-polymer interaction than the samples with a single nanofiller. -The electrical conductivity of hybrid nanocomposites lies between the nanocomposites with only MWCNTs or GnPs. i.e., there is no evident synergic effect of GnPs and MWCNTs in effecting the electrical conductivity.

Table 3.3 continues

Reference	Matrix	MWCNTs		Content	GnPs		Content	Total Content GnPs/MWCNTs ratio	Fabrication method	Results
		d (nm)	L (μm)		d (μm)	t (nm)				
Jen & Huang, 2019	epoxy	10	2	-	-	3	-	0.4 wt.% 0/10, 1/9, 3/7, 5/5, 7/3, 9/1, 10/0	Solution mixing	-The synergic effect of GnPs and MWCNTs is clear for the enhancement of electrical conductivity and thermomechanical properties. -While the hybrid nanocomposites with GnPs/MWCNTs weight ratio of 9/1 exhibits the most apparent improvement of thermomechanical properties, ones with GnPs/MWCNTs weight ratio of 1/9 indicates remarkable enhancement in the electrical conductivity. -The hybrid nanofiller does not have any influence on the thermal stability.
Krause et al., 2019	epoxy	10	1.3	2.5 vol.%, 5 vol.%	5	6-8	2.5 vol.%, 5 vol.%	-	Melt mixing Compression molded	- GnPs and MWCNTs are more responsible for enhancing thermal and electrical conductivity, respectively. - The combination of GnPs and MWCNTs exhibits the synergic effect on the thermal and electrical conductivity.

Table 3.3 continues

Reference	Matrix	MWCNTs		Content	GnPs		Content	Total Content GnPs/MWCNTs ratio	Fabrication method	Results
		d (nm)	L (μm)		d (μm)	t (nm)				
Caradonna, Badini, Padovano, & Pietroluongo, 2019	epoxy	9.5	1.5	0.1, 0.05 wt.%	15	6-8	0-5 wt.%	-	Melt mixing	-While the hybrid nanofillers with different aspect ratio show a synergic effect, which results in a significant enhancement of electrical properties, only a little influence on the thermal conductivity is observed.
Joseph, Munda, John, Sidpara, & Paul, 2019	PMMA PVC	5-20	1-10	2.5, 5, 10 wt.%	10-20	3-6	17.5, 15, 10 wt.%	20wt.%	Solvent casting technique	-The synergic effect on electrical conductivity is observed for only the hybrid nanocomposites with 1/1 weight ratio of GnPs and MWCNTs.
Chen, Liu, & Yan, 2019	epoxy	30-80	10	-	5-10	4-20	-	8 wt.% 95:5-5:95	Solution mixing	-There exists a synergic effect of GnPs and MWCNTs on the thermal conductivity. -Only at low nanofiller content, the unique structure of hybrid fillers provides functional advantages in terms of thermal conductivity. -The optimum weight ratio of GnPs and MWCNTs is 80/20 for enhancing thermal conductivity. -Thermal conductivity of hybrid nanocomposites increase with increasing of total hybrid nanofiller loading up to a certain value, then decreases.

Table 3.3 continues

Reference	Matrix	MWCNTs		Content	GnPs		Content	Total Content GnPs/MWCNTs ratio	Fabrication method	Results
		d (nm)	L (μm)		d (μm)	t (nm)				
Chen et al., 2019	epoxy	30-80	10	-	5-10	4-20	-	8 wt.% 90:10-10:90	Solution mixing	-There is a distinct synergic effect of GnPs and MWCNTs on the thermal conductivity of polymer nanocomposites. -The low nanofiller content is needed to exploit the benefits obtained from the matchless structure of hybrid nanofillers. -The maximum thermal conductivity is achieved by the GnPs/MWCNTs of 80/20. -The hybrid nanocomposite with 20/80 weight ratio of GnPs and MWCNTs exhibits the highest electrical conductivity. - The electrical and thermal conductivity of hybrid nanocomposites increase with increasing GnPs loading in total hybrid nanofiller content until a certain level of GnPs. After these critical GnPs/MWCNTs weight ratios, the thermal and electrical conductivity decrease. -In this study, the optimum weight ratio for electrical conductivity contrasts to it for thermal conductivity.

CHAPTER FOUR

MATERIALS & METHODS

In this chapter, the general description of the used materials, nanocomposites fabrication methods and different characterization techniques were discussed in sufficient detail. Section 4.1 describes the used materials in this thesis. Section 4.2 describes the method for preparing the nanocomposites. Section 4.3 describes the various characterization methods such as X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning/transmission electron microscopy (SEM/TEM), broadband dielectric spectroscopy, the photothermal radiometry (PTR), tensile tests, modulated differential scanning calorimeter (MDSC) and thermal gravimetric analysis (TGA).

4.1 Materials

4.1.1 High Density Polyethylene

The HDPE (LITEN FB 75) was purchased from Unipetrol (Czech Republic). Its density and melt flow index are 948 kg/cm^3 and 0.45 g/10 min ($190 \text{ }^\circ\text{C}/5 \text{ kg}$) respectively.

4.1.2 Multiwall Carbon Nanotubes (MWCNTs)

Two different aspect ratios (L/d) (500-3000 and 200-400) of MWCNTs were used, which were supplied by Grafen Chemical Industries Co. (Turkey). The MWCNTs with aspect ratios of 500-3000 and 200-400 are indicated as M12 and M58, respectively. The SEM (Philips XL 30S FEG) micrographs of their structures are given in Figure 4.1 and for each type of MWCNT dimensions and densities are given in Table 4.1.

Table 4.1 Properties of MWCNTs used for composites preparation

MWCNTs Type	$d \text{ (nm)}^a$	$L \text{ (}\mu\text{m)}^a$	AR (L/d)	Surface area (SA) (m^2/g)
M12	10-20	10-30	500-3000	200
M58	>50	10-20	200-400	40

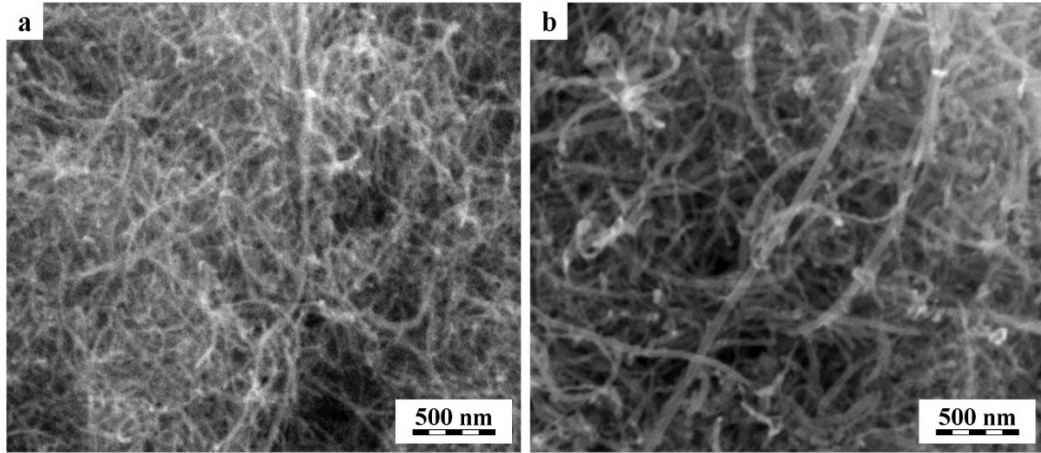


Figure 4.1. SEM images of a) M12 and b) M58 MWCNTs

4.1.3 Graphene Nanoplatelets (GnPs)

Three different sizes of GnPs with trademark iGP ($\sim 5 \mu\text{m}$), iGP ($\sim 44 \mu\text{m}$) and iGP2 which were provided by Grafen Chemical Industries Co. (Turkey) were used as filler materials to investigate the size effect of GnPs on the properties of the HDPE/GnPs nanocomposites. The GnPs with trademark iGP ($\sim 5 \mu\text{m}$), iGP ($\sim 44 \mu\text{m}$) and iGP2 were indicated as G1, G2 and G3, respectively. The size of GnPs is given in Table 4.2 and SEM (Philips XL 30S FEG) micrographs of each GnPs are presented in Figure 4.2.

Table 4.2 The size of GnPs used in this study

GnPs Type	d (μm)	t (nm)	AR (d/t)	Surface area (SA) (m^2/g)
G1	~ 5	50-100	50-100	13
G2	~ 44	50-100	440-880	40
G3	~ 5	5-8	635-1000	20-150

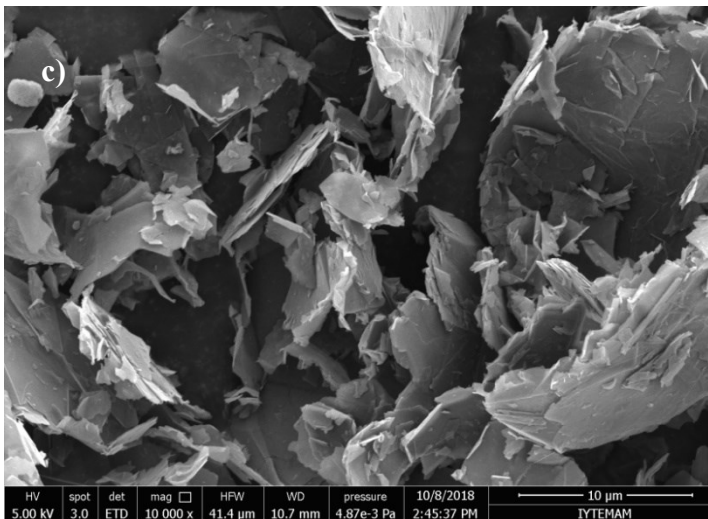
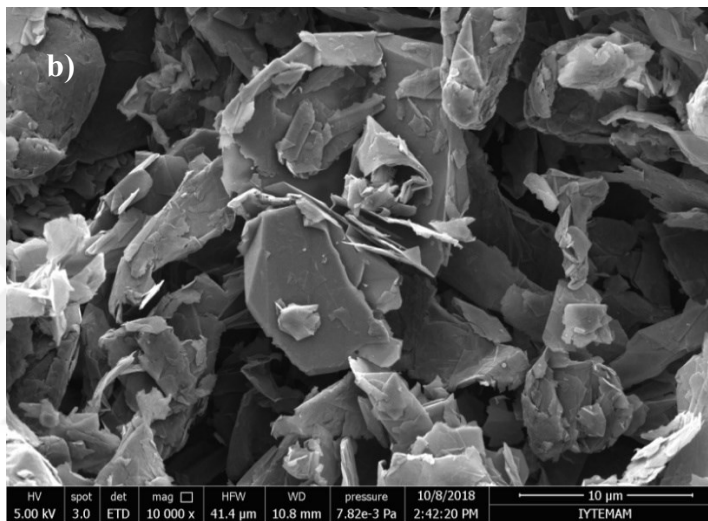
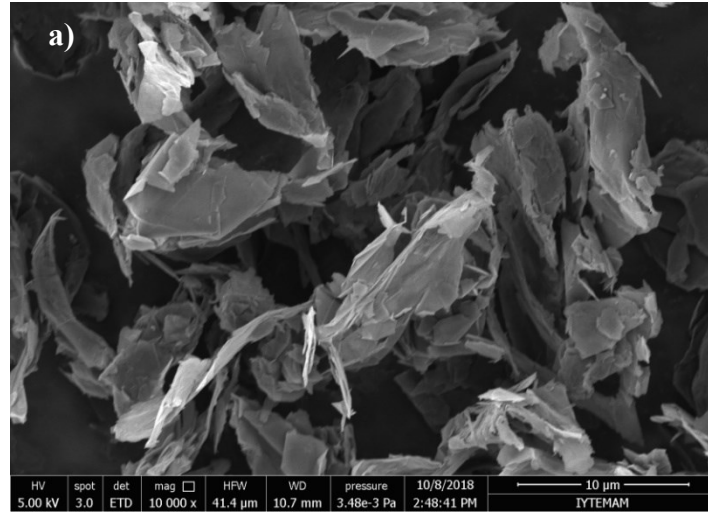


Figure 4.2 SEM images of a) G1 b) G2 and c) G3

4.2 Preparation of Nanocomposites

Within the scope of this thesis, different amounts of MWCNTs (≤ 18.74 wt.%), GNPs (≤ 26.81 wt%) and combination (11.70 wt% GNPs with ≤ 4 wt % M12 and 5 wt% with different GNPs/MWCNTs weight ratio) of fillers were incorporated into the HDPE matrix. The considered GNPs/MWCNTs weight ratios in the sample preparation were 0/5, 1/4, 2/3, 3/2, 4/1 and 5/0. The samples with the nanofiller weight ratios of 5/0 and 0/5 represent the HDPE matrix of the samples, reinforced with GNPs and MWCNTs alone, respectively. All nanocomposites were prepared by a melt mixing in a Brabender with a 30 mL chamber (Brabender Plasticorder, PLE 331 internal, Germany) at 160 °C and a rotor speed of 60 rpm for 15 min. All filler materials were used without any treatment and a pure HDPE sample was fabricated by melt mixing as a standard reference using the same conditions.

The samples with 1 mm thickness in a sheet form for mechanical property measurements were prepared by compression molding at 180 °C without pressure for 2 min and under 50 kPa of Pressure for 3 min using a hot press (ABB GTR208, Fontune, The Netherlands). All samples were cut to a dog-bone shape with a gauge length of 30 mm, a width of 4 mm and a thickness of 1 mm by the Pneumatic Press (APK 4L, Tinius Olsen LTD, USA). The samples for the electrical conductivity testing were prepared as disks with a diameter of 20 mm and a thickness of 0.5 mm by compression molding as mentioned above.

4.3 Measurement Methods

4.3.1 Characterization

The surfaces of filler materials were characterized by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha X-ray, UK). X-ray diffraction (XRD, Philips X'Pert Pro) analyses were conducted to identify the overall crystallinity and the phase structures of the nanocomposites. The XRD patterns were recorded in the range of 5–85° with a scanning speed of 0.03°/s. Fourier transform infrared

spectroscopy (FTIR) measurements of samples were carried out in Thermo-Scientific iS10 infrared spectrometer in the range of 4000–650 cm^{-1} at room temperature. The morphology was examined using scanning electron microscopy (SEM, Philips XL 30S FEG electron microscope). The microstructures of nanocomposites were examined at a cryo-fractured surface in liquid nitrogen after coating with a thin layer of gold. The dispersion of MWCNTs in the HDPE/MWCNTs composites was visualized by means of transmission electron microscopy (TEM, Tecnai G2 Spirit Twin 12, FEI). Ultrathin sections for TEM microscopy (thickness approx. 60 nm) were prepared by cryo-ultramicrotomy (ultramicrotome with a cryo-attachment: Ultracut UCT, Leica), and the sample and knife temperatures during cutting were $-90\text{ }^{\circ}\text{C}$ and $-50\text{ }^{\circ}\text{C}$, respectively. All samples were observed with bright field imaging at an accelerating voltage of 120 kV.

4.3.2 Electrical Conductivity Measurement

Broadband dielectric spectroscopy (BDS) measurements were conducted by a Novocontrol Concept 40 instrument with an Alpha dielectric spectrometer supplied by Novocontrol Technologies GmbH (Germany). The BDS-1200 parallel-plate capacitor with two gold-plated electrodes was used as a test cell for the samples and provided by Novocontrol Technologies. The diameter and thickness of samples were 20 mm and 0.5 mm, respectively. All measurements were carried out in the 0.1 Hz – 1 MHz frequency range at room temperature.

4.3.3 Measurements of Mechanical Properties

The tensile tests were conducted by using an Instron 4301 tensile test machine (UK) at a crosshead speed of 10 mm/min at room temperature, according to ASTM D638. The samples were cut in dog-bone shape with thickness of 1 mm, a width of 4 mm and a gauge length of 30 mm by the Pneumatic Press (APK 4L, Tinius Olsen LTD). The mean values of seven tests were reported for each sample.

4.3.4 Volumetric Heat Capacity Determination

4.3.4.1 Density Measurement

The density (ρ) values of HDPE/MWCNTs and other nanocomposites were determined by weighing the composites in water and in air with a Mettler H15 balance having a resolution of 10^{-4} g and a MatsuHaku Electronic Densimeter GP-300E, respectively. Referring to the buoyant *force of Archimedes'* principle, one can determine the volume of the samples. For the density of the composite, the mixture law gives:

$$\rho = \varphi_{vol}\rho_f + (1 - \varphi_{vol})\rho_m = \rho_m + (\rho_f - \rho_m)\varphi_{vol} \quad (4.1)$$

where, ρ_m and ρ_f are the density of matrix and filler materials, respectively. However, the volume fraction of fillers (φ_{vol}) is not known from the sample preparation procedure, as the exact density of filler materials is not known a priori. Thus, one way to determine the density values for each component is plotting the linear correlation of the specific volume V_S of the polymer composites *versus* the filler mass fraction φ_{wt} (known from sample preparation procedure) (Tlili et al., 2010):

$$V_S = \varphi_{wt}V_{Sf} + (1 - \varphi_{wt})V_{Sm} = \frac{\varphi_{wt}}{\rho_f} + \frac{1-\varphi_{wt}}{\rho_m} = \frac{1}{\rho} \quad (4.2)$$

where V_{Sm} and V_{Sf} refer to the specific volumes of matrix and filler, respectively. The experimental data were fitted with the linear Eq. (4.2) to determine V_{Sm} and V_{Sf} values. Their reciprocals yield $\rho_m=960.4$ kg/m³ for pure HDPE while for pure MWCNTs, $\rho_f=1911.3$ kg/m³ for M12 and $\rho_f=2060.6$ kg/m³ for M58 and for pure GnPs, $\rho_f=2193.0$ kg/m³ for G1, $\rho_f=2113.7$ kg/m³ for G2 and $\rho_f=1835.0$ kg/m³ for G3. The average value of $\rho_f=1986$ kg/m³ for M12 and M58 and $\rho_f=2047$ kg/m³ for G1, G2 and G3 will be used in the following calculations.

From Eqs. (4.1) and (4.2), the following expression is obtained for ϕ_{vol} :

$$\phi_{vol} = \frac{1}{1 + \left(\frac{1}{\phi_{wt}} - 1\right) \left(\frac{\rho_f}{\rho_m}\right)} \quad (4.3)$$

Thus, the ϕ_{vol} fractions were calculated using ϕ_{wt} and the densities of pure constituents. Then by fitting the measured densities (Figure 4.3 and 4.4) with Eq. (4.1), the following fit equations were obtained:

$$\rho = (946.4\phi_{vol} + 964.9)kg/m^3 \text{ for M12} \quad (4.4)$$

$$\rho = (1095.7\phi_{vol} + 964.9)kg/m^3 \text{ for M58} \quad (4.5)$$

$$\rho = (1237.2\phi_{vol} + 955.8)kg/m^3 \text{ for G1} \quad (4.6)$$

$$\rho = (1157.9\phi_{vol} + 955.8)kg/m^3 \text{ for G2} \quad (4.7)$$

$$\rho = (879.2\phi_{vol} + 955.8)kg/m^3 \text{ for G3} \quad (4.8)$$

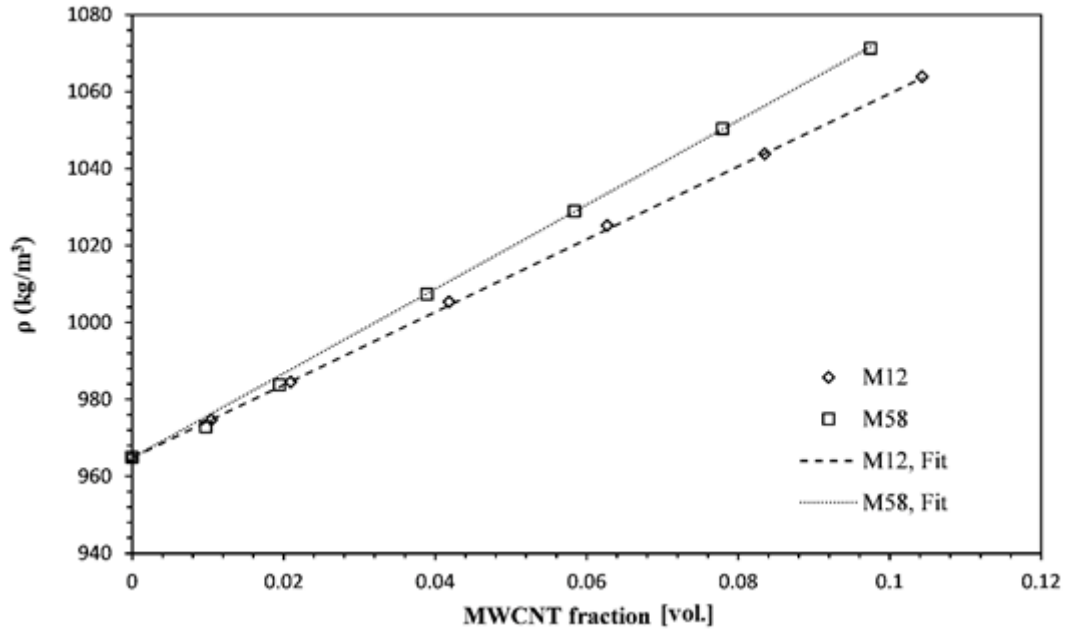


Figure 4.3 Experimental results of density vs. filler fractions for HDPE/MWCNTs nanocomposites. The linear fits correspond to Eqs. (4.4 and 4.5)

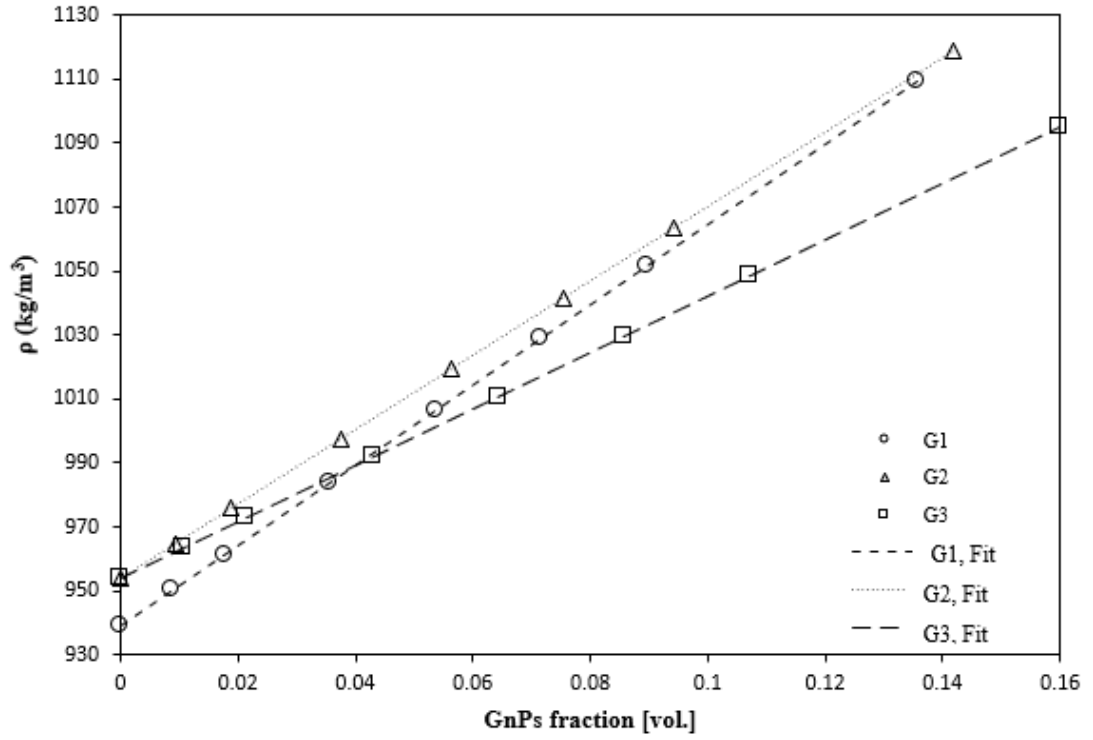


Figure 4.4 Experimental results of density vs. filler fractions for HDPE/GnPs nanocomposites. The linear fits correspond to Eqs. (4.6-8)

4.3.4.2 Specific Heat Capacity Measurement

The specific heat of HDPE/MWCNTs and other nanocomposites was determined by a differential scanning calorimeter (Perkin Elmer, Diamond DSC) and a modulated differential scanning calorimeter (Q200 series MDSC, TA instruments, USA), respectively. The mixture law for c_p of nanocomposites writes:

$$c_p = \varphi_{wt}c_{pf} + (1 - \varphi_{wt})c_{pm} = c_{pm} + (c_{pf} - c_{pm})\varphi_{wt} \quad (4.9)$$

where c_{pf} and c_{pm} corresponding to the specific heat capacity of filler and matrix, respectively. The fit of the average of MWCNTs and GnPs experimental data of Figure 4.5 and 4.6 is given by the following equation:

$$c_p = (-1052.4\varphi_{wt} + 1832.9) \text{ J/kgK for MWCNTs} \quad (4.10)$$

$$c_p = (-1077\varphi_{wt} + 1833.1) \text{ J/kgK for GnPs} \quad (4.11)$$

For $\phi_{wt}=0$, Eqs. (4.10-1) yields $c_{pm}=1832.9$ J/kgK for pure HDPE and for $\phi_{wt}=1$, $c_{pf}=780.5$ J/kgK for pure MWCNTs and $c_{pf}=756.1$ J/kgK for pure GnPs.

3.4.4.3 Calculation of Volumetric Heat Capacity

The volumetric heat capacity $C=\rho c_p$ as a function of ϕ_{vol} is predicted by the mixture law:

for HDPE/MWCNTs nanocomposites:

$$C = \phi_{vol}C_f + (1 - \phi_{vol})C_m = (-219\phi_{vol} + 1.769)10^6 J/m^3K \quad (4.12)$$

for HDPE/GnPs nanocomposites:

$$C = \phi_{vol}C_f + (1 - \phi_{vol})C_m = (-168\phi_{vol} + 1.769)10^6 J/m^3K \quad (4.12)$$

where C_f and C_m refer to the filler and the matrix, respectively and were calculated by using the above mentioned values for the pure components (with the average MWCNTs density of $\rho_f=1986$ kg/m³ and with the average GnPs density of $\rho_f=2047$ kg/m³ and). c_p and ρ show opposite variations and compensate each other. Therefore, C is rather constant and within the researched range of nanofiller fraction, it decreases only by 1.5%. Consequently, the thermal diffusivity α and the thermal conductivity $k=C\alpha$ have very similar evolutions with filler fraction.

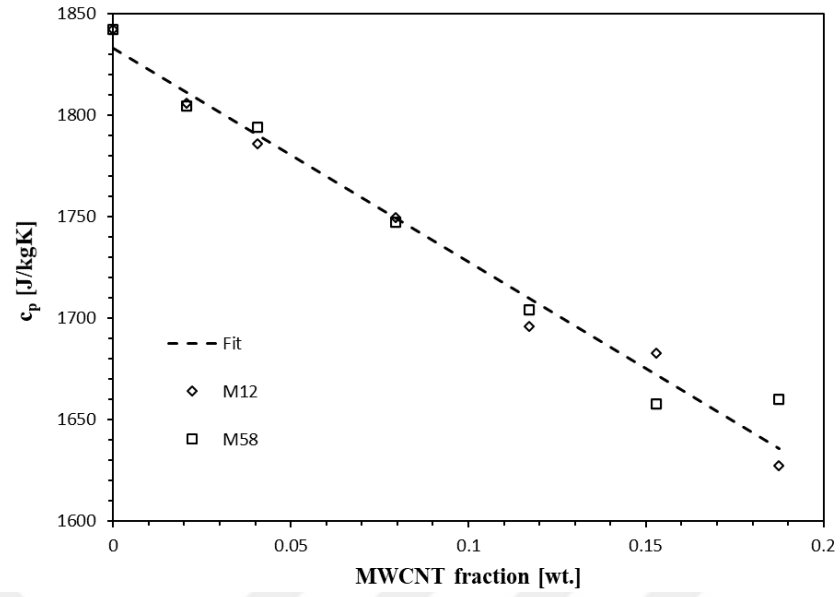


Figure 4.5 Experimental results of density vs. filler fractions for HDPE/MWCNTs nanocomposites. The linear fits correspond to Eq. (4.10)

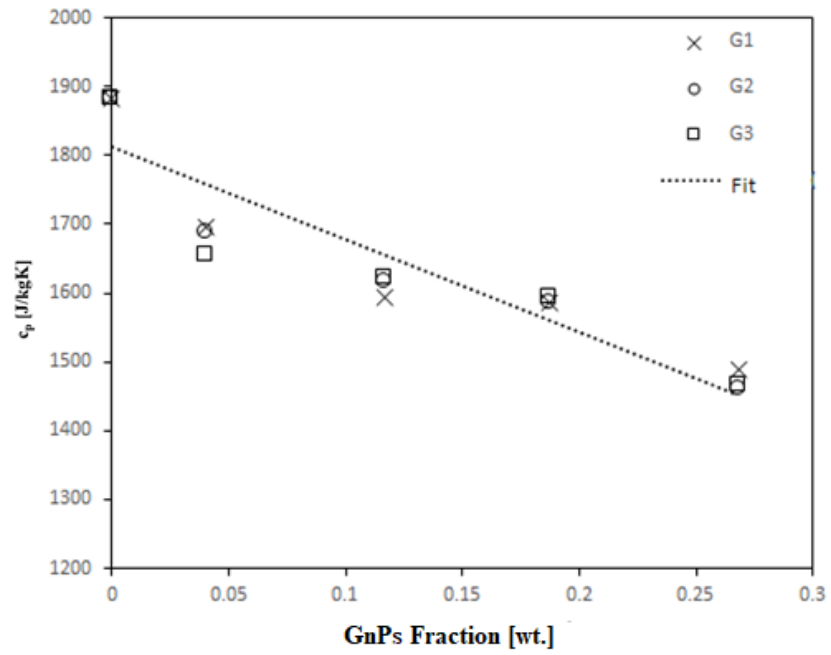


Figure 4.6 Experimental results of density vs. filler fractions for HDPE/GnPs nanocomposites. The linear fits correspond to Eq. (4.11)

4.3.5 Thermal Diffusivity Measurements

4.3.5.1 The Photothermal Radiometry (PTR) for the HDPE/MWCNTs Nanocomposites

PTR method for thermophysical characterization of materials is based on the change of the blackbody IR radiation induced by a change in temperature following absorption of pulsed or periodically modulated laser radiation (Li, Tabil, Oguocha, & Panigrahi, 2008). The PTR signal was generated using a diode-pumped solid state (DPSS) laser having 245 mW of power at 532 nm. The laser beam was intensity modulated by means of an acousto-optical modulator (AOM) in the frequency range $f=0.1$ Hz to 100 kHz. Two Au-coated, parabolic off-axis mirrors captured the emitted IR radiation from the sample surface, focusing it on a photovoltaic liquid-nitrogen cooled HgCdTe detector type KMPV11-1 (Kolmar Technologies) with a sensor diameter of 1 mm. The detector was provided with a Ge filter to block the visible radiation of the pump laser beam. The signal S (containing amplitude A and phase φ) of the detector was fed to a low noise preamplifier and then to a lock-in amplifier type Stanford 830 DSP.

In view of PTR measurements, the sample slab with optimal thickness of $L=0.2-0.5$ mm was attached to an annular sample holder, which kept both faces of the central part of the sample with a diameter greater than 1 cm, exposed to ambient air. One-dimensional (1D) heat flow across the sample was achieved with a flat top beam shaper which expanded and homogenized the laser beam. A uniform beam profile with a diameter of 8 mm was projected to the center of the sample surface. 1D condition was fulfilled since the lateral irradiated zone was larger than the spot seen by the detector and then the sample thickness. The detection of surface temperature can be made at the irradiated face (front detection configuration, FD) or at the rear face (back detection configuration, BD) (Chirtoc et al., 2012). FD-PTR was chosen in this study to measure in a contactless way the surface temperature of the sample, Figure 4.3.

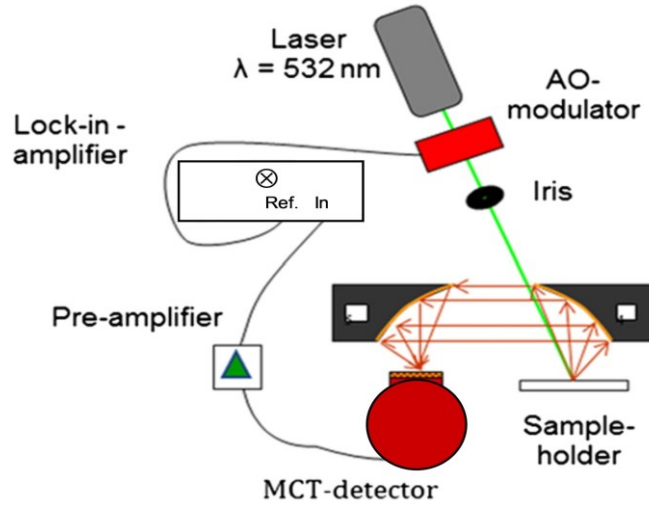


Figure 4.7 Photothermal radiometry set up in front-detection configuration (FD-PTR) (Evgin et al., 2016)

Carbon-filled polymer composites are favorable materials for PTR measurements because they easily fulfill the requirement of being opaque for the excitation irradiation and in the IR range. They also have a good IR emissivity and hence the generated PTR signal is reasonably high. If the heat losses to the ambient air are neglected, the expression of PTR signal of an opaque slab is given in the 1D approximation by (Chirtoc et al., 2012; Chirtoc, 2010):

$$S = \frac{1-i}{\sqrt{2\pi f} e} \frac{1 + \exp[-2(1+i)L/\mu]}{1 - \exp[-2(1+i)L/\mu]} \quad (4.1)$$

where $\mu = [\alpha/(\pi f)]^{1/2}$ is the thermal diffusion length in the material and $e = (Ck)^{1/2}$ is the thermal effusivity. This signal was normalized to the transfer function of the set up measured with a photodiode, in order to cancel the frequency dependence of electronic instruments. The thermal diffusivity contained in μ was determined as a fit parameter of amplitude and phase frequency spectra taken around the thermally thin/thick transition where $L/\mu \approx 1$. In practice, the respective transition frequency was situated between 0.1 and 10 Hz. FD- and BD-PTR spectra obtained for HDPE/EG (expanded graphite) nanocomposites are shown in (Chirtoc et al., 2012).

4.3.5.2 The Photothermal Radiometry (PTR) for the HDPE/GnPs and Hybrid Nanocomposites

The thermal diffusivity of the samples were measured by photothermal radiometry technique (PTR) which is a non-destructive characterization method based on the detection of the infrared (IR) signal, called photothermal signal (PS), emitted after a change of the sample's temperature (Almond & Patel, 1996; Horne, Ban, Mandelis, & Matvienko, 2012). The heating is achieved by a frequency modulated laser beam (DPSS, Dream Lasers Technol. Co., model SDL-532-300T) with 300 mW at 532 nm wavelength and a diameter of 0.6 mm at 1/e. The IR radiations linked to the fast conversion of a fraction of the absorbed optical energy into heat, are collected by a suitable optic (Au-coated mirrors Edmund Optics) and focused into an IR photodetector (HgCdTe photoconductive detector Kolmar Technologies, KMPV 11-1-J1/DC). Afterwards, a heterodyne lock-in amplifier (Stanford Research Systems SR865) outputs the amplitude and phase of the detector electrical signal proportional to the variation of the sample temperature which depends on its thermophysical properties. A more detailed description of the used setup can be found elsewhere (Horny, Chirtoc, Fleming, Hamaoui, & Ban, 2016). Using this PTR setup, different kind of materials (nanocomposites (Evgin et al., 2016), organic (Reisdorffer et al., 2014; Trefon-Radziejewska et al., 2019, 2017), irradiated (Jensen et al., 2013), metal-semiconductor couples (Hamaoui et al., 2018; Horny, Chirtoc, et al., 2016) can be thermally characterized in order to find their thermophysical properties like the thermal diffusivity, thermal effusivity and many others. One should note that at lower frequencies, the measurements are subject to 3D effect and necessitate a change of the laser beam shape. i.e., at low frequencies a flat top (FT) optics regrouping a diffuser/ a beam shaper (ED1-C20, Ø1" 20 ° Circle Pattern Diffuser, Thorlabs) and two lenses (one to collect the large diffused beam, and another to converge it on the sample) are used. Using this configuration, the shape of the heating spot is circular, and the illumination is uniform on the sample's surface. The heating is therefore considered one dimensional, and a 1D thermal characterization of the thermally thick HDPE samples has been applied by analyzing the amplitude and phase of the PTR signal using a 1D quadrupole based model (Fuente, Mendioroz, Apiñaniz, & Salazar, 2012;

Maillet, Andre, Batsale, Degiovanni, & Moyne, 2000). This modelling was used by a Gauss-Newton algorithm to simultaneously adjust the experimental amplitude and phase of the PTR signal analyzed by the lock-in amplifier in order to extract the thermal diffusivity and the optical absorption coefficient of the studied samples.

4.3.6 Thermal Analysis

The melting and crystallization properties of the nanocomposites and the pure HDPE were investigated by using a modulated differential scanning calorimeter (Q200 series MDSC, TA instruments, USA) under a nitrogen atmosphere. The samples were cooled quickly to -10 °C and equilibrated at this temperature for 1 min. Then, the samples were heated up to 200 °C at 10 °C/min to remove the thermal history, held for 1 min at 200 °C, and thereafter cooled to -10 °C at the same rate to study the crystallization behavior of the samples. Next, the samples were held for 3 min and then the second heating was performed in the MDSC mode with a scanning rate of 5 °C/min, a modulating period (P) of 100 s and a temperature-oscillation amplitude of 1.326 °C to study the melting behavior. The HDPE crystallinity in the polymer nanocomposites was determined by:

$$X_c = \frac{\Delta H}{\Delta H_0(1-\varphi)} \times 100 \quad (4.2)$$

where $\Delta H_0=293$ J/g is the enthalpy of fusion for 100 % crystallinity of HDPE (McNally et al., 2005), ΔH is the enthalpy of fusion for the samples and φ is the weight fraction of the filler.

Thermogravimetric analysis (TGA) of the samples was performed using a Q500 system from TA Company, USA. TGA was carried out at a heating rate of 10 °C/min from room temperature to 700 °C under a nitrogen atmosphere.

CHAPTER FIVE

HDPE/MWCNTS NANOCOMPOSITES

5.1 Abstract

The effects of the aspect ratio and the addition of MWCNTs on the morphological, electrical, mechanical, and thermal properties of HDPE-based nanocomposites are investigated. The aspect ratios of two types of MWCNT fillers are in the range of 200-400 and 500-3000 (mainly due to different tube diameter). Composite samples were prepared by melt mixing up to weight fraction of 19% filler content, followed by a compression molding. The results show that the composites containing MWCNTs with higher aspect ratio have higher thermal conductivities than the ones with lower aspect ratio. For 19 wt% of MWCNTs concentration, the respective thermal conductivity increases are 97% and 67%, respectively. In terms of thermal conductivity enhancement, the results indicate that MWCNTs with higher aspect ratio provide three- to four-fold larger enhancement than the ones with lower aspect ratio, at low filler concentrations. The results demonstrate that the addition of MWCNTs enhances the electrical, mechanical, and thermal properties of the HDPE/MWCNTs nanocomposites. The HDPE nanocomposites with higher aspect ratio MWCNTs demonstrated a slightly better enhancement in the morphological and electrical properties than the other ones with lower aspect ratio MWCNTs. Additionally, Young's modulus and the thermal stability increased with increasing aspect ratio of MWCNTs.

5.2 Introduction

Polymer materials have many advantages over metals and ceramics. They are widely used in many industrial applications such as aerospace, electronics, heat exchangers, circuit boards, corrosion resistant coatings, light emitting devices, electronics protection thanks to their low density, easy processing, better anti corrosion and mechanical properties (Chen et al., 2015; Chirtoc et al., 2012). Nonetheless, their lower thermal conductivity than that of ceramics and metals, is a major problem. In

new miniaturized electronic and optoelectronic systems, where the polymers are widely used, thermal management has become an increasingly important factor. The components of these devices have gradually become faster and denser so that the heat generated by them needs to be removed effectively (Shtein et al., 2015). Due to inherently low k , the polymeric materials have limitations in their application fields. To overcome this situation, much research has been devoted to enhance their k values (Han & Fina, 2011). One route to achieve this is to add conductive filler materials to polymer matrices (Chirtoc et al., 2012; Gardea & Lagoudas, 2014; Tlili et al., 2010).

Among the filler materials, carbon nanotubes (CNTs) have attracted considerable interest both in industry and in basic research since Iijima (1991) discovered this carbon structure in 1991, due to their excellent thermal (thermal conductivity of $\sim 15\text{--}3000\text{ W/mK}$), mechanical (Young's modulus of $\sim 1\text{TPa}$, yield strength of $20\text{--}100\text{ GPa}$) and electrical properties (electrical conductivity of $10^3\text{--}10^7\text{ S/m}$), low density, low melt flow viscosity, and high aspect ratio (Cha et al., 2016; Jouni et al., 2017; Kaseem et al., 2016; Li et al., 2018). CNTs are used in many different applications such as hydrogen storage, nanoelectronics, nano devices, biosensors, and catalyst support (Spitalsky, Krontiras, Georga, & Galiotis, 2009). Many studies suggested that CNTs are optimal reinforcing fillers for polymer nanocomposites in many applications due to the combination of their superior properties.

The enhancement in the properties of polymer nanocomposites with CNTs depends on several factors such as the processing method of nanocomposites, types, content, dimension and dispersion of CNTs, choice and nature of the matrix, and interfacial interaction between CNTs-CNTs or CNTs-matrix (Bauhofer & Kovacs, 2009; Dubnikova et al., 2010; Kaseem et al., 2016; Patti et al., 2016). Although the aspect ratio or the dimension of MWCNTs is known to be one of the most important parameters to control the final properties of nanocomposites, published studies on the influence of the MWCNTs dimension on these properties are only few. There are limited studies that were carried out by using different polymer matrix types: thermosets, thermoplastic elastomers, and thermoplastics (Table 1.1). In these studies, some groups studied both mechanical and electrical properties, while some groups

studied only electrical or mechanical properties. In the available literature, the effect of the MWCNTs dimension has been generally discussed with three parameters: aspect, length, and diameter. The aspect ratio effect can be studied at constant diameter by changing the length (Abbasi et al., 2011; Russ et al., 2013; Zhang et al., 2016), at constant length by changing the diameter (Ayatollahi et al., 2011; Shehzad et al., 2016) or some combination of two (Costa et al., 2014; Dang et al., 2011; Dubnikova et al., 2010; Guo et al., 2014; Park & Youn, 2012; Rahaman et al., 2013; Shehzad et al., 2013). However, interpretation of the results was made mostly in terms of aspect ratio.

Several review papers (Al-Saleh & Sundararaj, 2011; Han & Fina, 2011; Hong et al., 2015; Ma, Siddiqui, Marom, & Kim, 2010; Mittal et al., 2015; Nam, Jeong, & Kil, 2016) summarize the studies on remarkable mechanical, electrical, thermal, rheological and morphological properties of polymer/CNTs nanocomposites. However, studies on thermal conductivity are limited (El-Brolossy & Ibrahim, 2014; Gojny et al., 2006; Hong & Tai, 2008; J Kim, Hong, Kwak, & Seo, 2009; Kim, Kim, Lee, Park, & Kang, 2006; King et al., 2010; Kwon, Kwon, Kim, Lee, & Seo, 2013; Moisala, Li, Kinloch, & Windle, 2006; Park et al., 2012; Raja, Ryu, & Shanmugharaj, 2013; Safdari & Al-Haik, 2013; Sanada, Tada, & Shindo, 2009; Song & Youn, 2005; Theravalappil et al., 2014). Besides, these studies contain scattered experimental data. Some reports claim that even for low amounts of CNTs, by the addition of 1.5 wt.% (Song & Youn, 2005), 2 vol.% (Kwon et al., 2013) or 4 wt.% (Hong & Tai, 2008) in polymer based composites the thermal conductivity enhancement reaches 111%, 272% and 1352%, respectively. On the other hand, for similar concentration (5 wt.%) of MWCNTs, Safdari & Al-Haik (2013) reported only 14% thermal conductivity enhancement of epoxy based composite. Also, Theravalappil et al. (2014) achieved similar enhancement to that of Song & Youn (2005) at 35 wt.% concentration. All these studies indicate that various factors play a significant role in the thermal conductivity enhancement, such as the type of polymer and CNTs, the aspect ratio, diameter, distribution, alignment and dispersion of CNTs, the thermal resistance and functionalization (surface treatment) of polymer/CNT interface. The topic is still attractive since the effects of these factors on nanocomposites properties are not yet fully understood.

Although it is mentioned by Han & Fina (2011) that the aspect ratio AR , length l and outer diameter d are the key parameters to characterize CNTs and it is emphasized that these parameters directly affect the effective thermal conductivity k of polymer/CNT composites, systematic studies were rarely reported (Ciecierska et al., 2013; Russ et al., 2013). Russ et al. (2013) investigated the thermal conductivity of epoxy/MWCNTs composites produced by shear mixing and containing short and long CNTs having $AR=50$ and 500. The respective thermal conductivity enhancement was found to be 21% and 75% at 1 wt.% filler concentration leading to the conclusion that higher aspect ratio results in higher thermal conductivity. Ciecierska et al. (2013) investigated the effects of CNTs length and surface functionalization on thermal diffusivity of epoxy/CNTs composites. Three types of CNTs ($d=9.5$ nm) were used: non-modified ones with 1 μm and 1.5 μm lengths and CNTs modified by amino groups having 1 μm in length. Samples were prepared by three roll mill in the range of 1 to 5 wt% of MWCNTs contents. The thermal diffusivity of samples increased with the weight fraction (up to 1.6-fold and 1.8-fold) and with the length of CNTs (1 μm and 1.5 μm , respectively).

HDPE is one of the most popular thermoplastic materials as a matrix for preparing composite materials. Many studies on electrical and mechanical properties of HDPE/CNT composites are present in literature, but studies on thermal conductivity are scarce. Chen, He, Du, Pei, & Guo (2009) found that thermal conductivity of composites prepared by melt-blending increases sharply (by almost 30%) up to 3.35 vol.% of MWCNTs and then the increasing rate slows down reaching 80% increase at 11 vol.% filler content. Kim et al. (2009) prepared HDPE/MWCNT by *in situ* metallocene polymerization. They found 58% thermal conductivity increment at 12 wt% filler content. However, to the best of the authors' knowledge, none of these studies investigates the effect of aspect ratio on thermal conductivity of HDPE/MWCNTs composite and therefore, this will be the aim of this study. To the best of our knowledge, there is no study carried out on the effect of the aspect ratio of MWCNTs on the morphological, electrical, mechanical, and thermal properties of the HDPE/MWCNTs nanocomposites in the literature. This study aims to understand the

role of the concentration and the aspect of the filler in determining the previously mentioned properties of the HDPE-based nanocomposites. In this study, two different aspect ratios of MWCNTs, which have different diameter but the similar length, have been incorporated into HDPE matrix by a melt mixing, followed by compression molding. The relationship between the morphological, electrical, mechanical, and thermal properties of the HDPE-based nanocomposites and the aspect ratio of MWCNTs has been investigated.

5.3 Materials and Methods

Details about the used materials, production and characterization methods were explained in Chapter 4.

5.4 Results and discussion

5.4.1 Characterization

5.4.1.1 XPS Results of HDPE/MWCNTs Nanocomposites

The first step of the study was the investigation of the surface properties of both types of MWCNTs, which can be important to understand the differences in composites properties. The XPS results of M12 ($d=10\text{-}20\text{ nm}$, $L=10\text{-}20\text{ }\mu\text{m}$, $AR=200\text{-}400$) and M58 ($d>50\text{ nm}$, $L=10\text{-}20\text{ }\mu\text{m}$, $AR=500\text{-}3000$) are given in Table 5.1 and shown in Figures 5.1 and 5.2. Only carbon (C1s at ca. 285 eV) and a small amount of oxygen (O1s at ca. 533 eV) were detected. C1s at ca. 284.6 eV with a clear asymmetry towards the higher binding energies is typical for sp^2 carbon. The presence of delocalized π electrons (conduction electrons) available for shake-up-like events following the core electron photoemission also resulted in the broad peak at ca. 291 eV (labeled $\pi - \pi^*$ in Figure 5.2) [Avantage software 5.9902, XPS knowledge database (UK:ThermoFisher Scientific)]. The C1s signals as well as the apparent surface chemical compositions of M12 and M58 are almost the same. It can be concluded that the surface of M58 is slightly more oxidized, but it will not significantly influence the

nanocomposite properties when mixing with HDPE compared with the M12 filled composites.

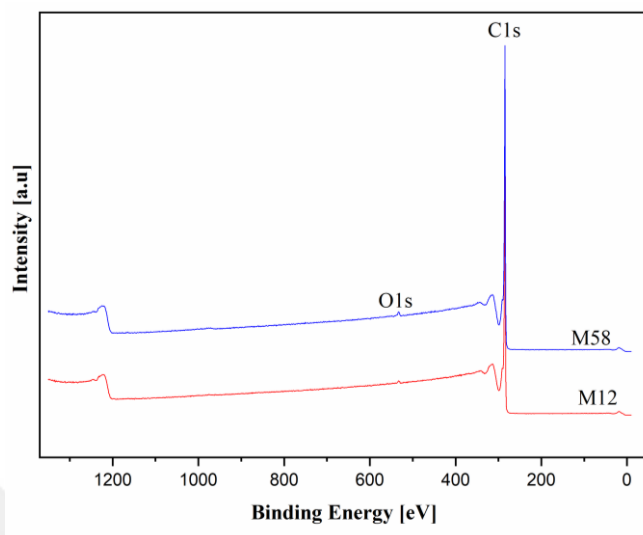


Figure 5.1 XPS survey spectra for M12 and M58

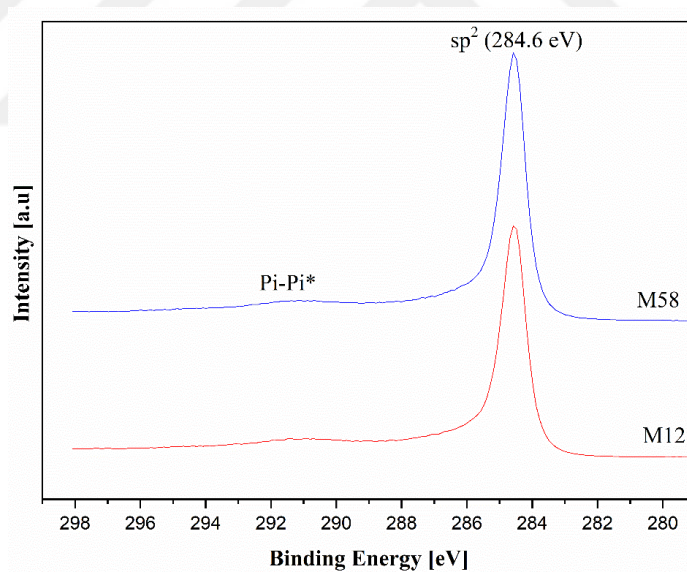


Figure 5.2 C1s high-resolution spectra for M12 and M58

Table 5.1 Results of MWCNTs XPS analysis

Sample	Surface chemical composition [at.%]	
	C1s	O1s
M12	99.50	0.50
M58	99.30	0.70

5.4.1.2 XRD Results of HDPE/MWCNTs Nanocomposites

The XRD patterns of pure M12, M58, HDPE and HDPE-based nanocomposites are demonstrated in Figure 5.3 and Figures 5A.1-2 in the Appendixes. The XRD patterns of the two MWCNTs types have almost the same reflection peaks at approximately $2\theta=25.85^\circ$ and 42.67° , corresponding to (002) and (100) carbon reflection planes, respectively. A sharp peak observed at $2\theta=25.85^\circ$ is a characteristic reflection peak for pure MWCNTs. It can be found that the aspect ratio of MWCNTs does not lead to a significant difference in the crystalline structure of MWCNTs. HDPE is known to be a semi-crystalline polymer (Linares et al., 2008). Pure HDPE shows a dominant reflection peak at $2\theta=21.42^\circ$ followed by a less dominant peak at $2\theta=23.45^\circ$, which can be attributed to the (110) and (200) reflection planes of the polyethylene orthorhombic phase, respectively (Linares et al., 2008). In addition to these peaks, pure HDPE shows two weak reflection peaks at $2\theta=29.94^\circ$ and 36.11° , corresponding to the (210) and (020) reflection planes, respectively (Chouit et al., 2014).

Compared to pure HDPE, the XRD patterns of the HDPE/M12 and HDPE/M58 nanocomposites indicates an extra reflection peak at approximately $2\theta=25.9^\circ$, which can be attributed to the (002) reflection plane from the structure of the graphitic layer, because of the addition of MWCNTs (Wang et al., 2018). It can be clearly observed that the characteristic peaks for HDPE do not change after the incorporation of MWCNTs. This means that the incorporation of MWCNTs does not influence the original crystal structure of the HDPE matrix because there is no interaction or reaction between HDPE and MWCNTs (Linares et al., 2008). Additionally, it is clear in Figure 5.3 that the aspect ratio of MWCNTs does not considerably affect the reflection peaks of the nanocomposites.

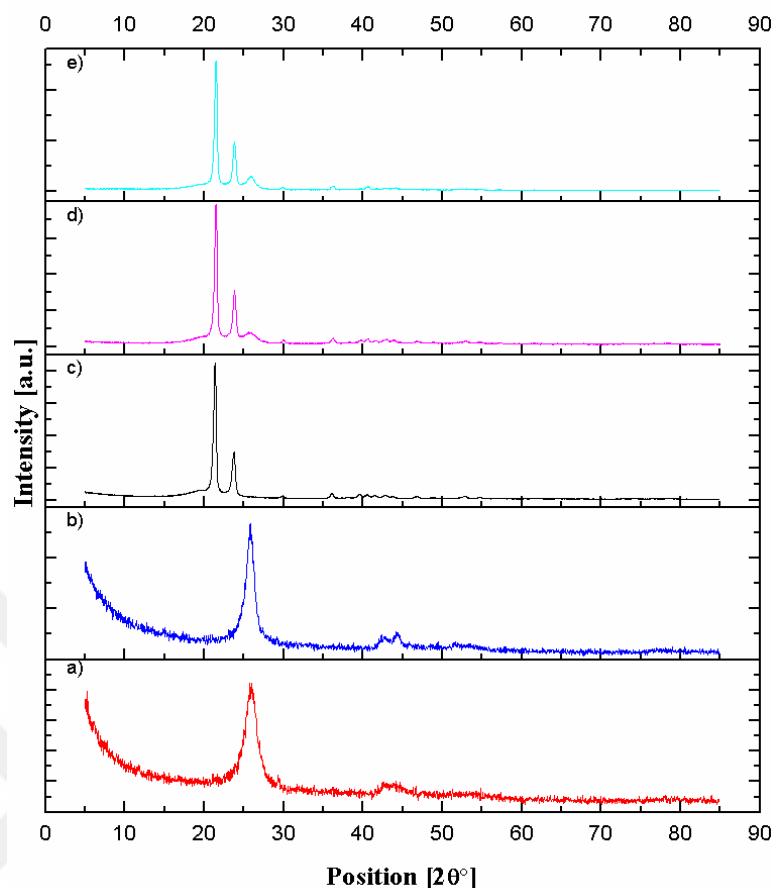


Figure 5.3 XRD patterns of the a) M12 b) M58 c) HDPE d) HDPE/M12 nanocomposites (18.74 wt.%) and e) HDPE/M58 nanocomposites (18.74 wt.%)

5.4.1.3 FTIR Results of HDPE/MWCNTs Nanocomposites

The FTIR results are shown in Figure 5.4 and Figures 5A.3-4. The spectrum of HDPE shows two strong peaks at 2914.99 cm^{-1} , 2867.40 cm^{-1} and four weak peaks at 1472.49 cm^{-1} , 1461.94 cm^{-1} , 730.05 cm^{-1} and 718.74 cm^{-1} . The peaks at $\sim 2914\text{ cm}^{-1}$ and $\sim 2847\text{ cm}^{-1}$ can be assigned to Alkyl (C-H) stretch vibrations. The peaks at wavenumbers of $\sim 1471\text{ cm}^{-1}$ and $\sim 1462\text{ cm}^{-1}$ can be related to $-\text{CH}_3$. The spectrums demonstrated at absorption peaks at $\sim 730\text{ cm}^{-1}$ and $\sim 718\text{ cm}^{-1}$ can be attributed to aromatic C-H bending. As seen in Figure 3.4, both pure MWCNTs do not display any peak assigning to functional groups on the surface MWCNTs (Cha et al., 2016). The curves of HDPE and HDPE/MWCNTs nanocomposites have almost the same absorption peaks. However, the peaks at wave numbers of $\sim 2914\text{ cm}^{-1}$, $\sim 1471\text{ cm}^{-1}$ and $\sim 730\text{ cm}^{-1}$ are invisible at high volume concentration of MWCNTs. It can be said

that the aspect ratio and the content of MWCNTs do not cause any change in the characteristic peaks of HDPE matrix identifiable in the spectra of FTIR. These results are confirmed with the previous studies conducted by Costa et al., (2014) and Yang et al., (2017).

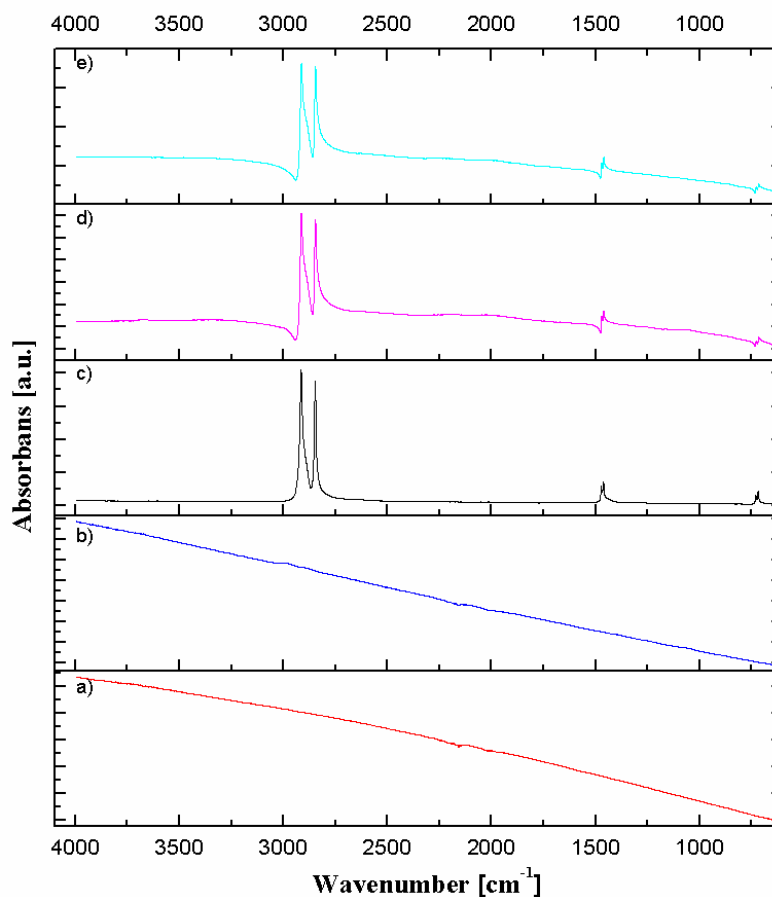


Figure 5.4 FTIR results of the a) M12 b) M58 c) HDPE d) HDPE/M12 nanocomposites (18.74 wt.%) and e) HDPE/M58 nanocomposites (18.74 wt.%)

5.4.1.4 Morphological Results of HDPE/MWCNTs Nanocomposites

The dispersion of MWCNTs within the HDPE was not clearly observed by using SEM due to their structures. Therefore, the dispersion of MWCNTs in HDPE was observed by TEM at two different magnifications. The TEM micrographs of the HDPE-based nanocomposites with different types of MWCNTs at a weight fraction of 11.70 wt.% are displayed in Figure 5.5. In all TEM micrographs of the HDPE/MWCNT nanocomposites, the MWCNTs appeared darker than the polymer

matrix due to the diffraction contrast. As expected, MWCNTs were randomly dispersed in the HDPE matrix and two different dispersion types were observed: separately dispersed and clustered (Li et al., 2013). The clustered form is known to occur due to the strong nanotube-nanotube interaction (Mutiso & Winey, 2015). The low magnification micrographs (Figures 5.5a and 5.5c) confirmed that the overall dispersion of the nanotubes was quite homogeneous. Both individual nanotubes and their clusters were well fixed within the polymer matrix, which enveloped them tightly without any observable voids. The high magnification micrographs (Figures 5.5b and 5.5d) also showed the entangled form of MWCNTs. Careful comparison of all TEM micrographs suggested that the difference between the two types of MWCNTs was small concerning their dispersion in the HDPE matrix. The size of nanotube agglomerates, the amount of agglomerates with respect to individual nanotubes, and the amount of entanglements were comparable. The nanotubes with a higher aspect ratio exhibited slightly better dispersion.

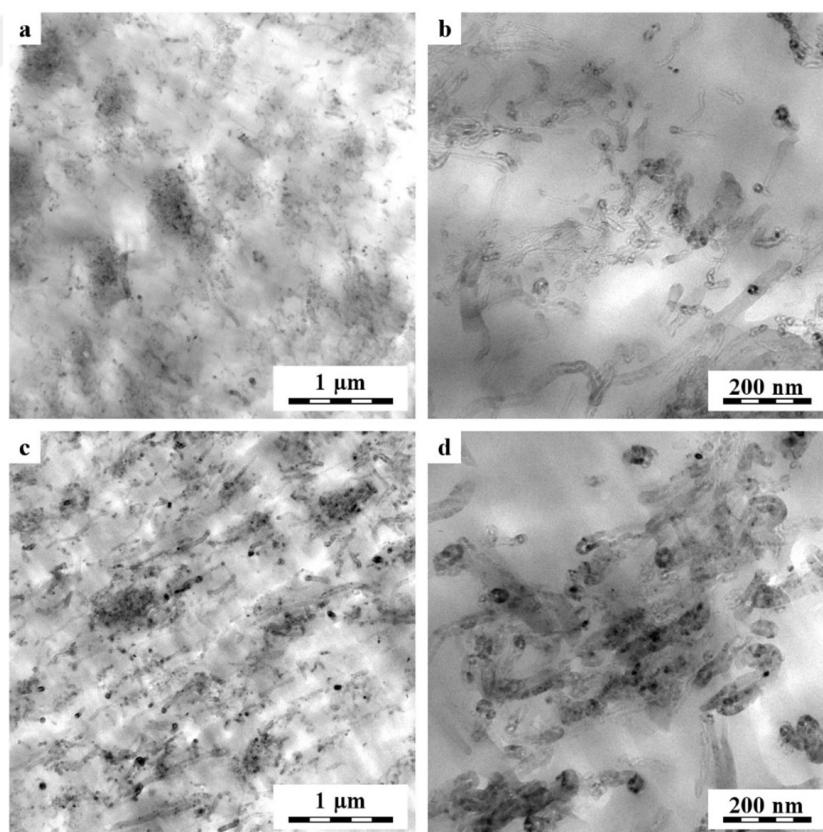


Figure 5.5 TEM micrographs showing the HDPE/MWCNT nanocomposites containing 11.70 wt. % of M12 (a, b) and 11.70 wt. % of M58 at lower (a, c) and higher (b, d) magnifications

5.4.2 Electrical Conductivity

All electrical conductivity measurements of the samples were performed at room temperature. The AC conductivity (σ_{AC}) for the HDPE/M12 and HDPE/M58 nanocomposites as a function of frequency are shown in Figures 5.6 and 5.7, respectively. The values for pure HDPE are also included for a better comparison. As expected, the conductivities of all nanocomposites increase with the MWCNT loading. It is caused by the formation of conductive pathways between the conductive filler particles, as the number of conductive pathways increases with increasing amount of the filler.

Nevertheless, as seen in Figures 5.6 and 5.7, the nanocomposites have different behaviors. In the case of the HDPE/M12 nanocomposites, the electrical conductivity gradually increases with increasing the concentration of MWCNTs, while in the case of the HDPE/M58 nanocomposite, a significant increase of 10 orders of magnitude in the conductivity is observed in the range of 1.42 and 1.95 vol.% of the filler. The pure HDPE and the HDPE/M12 nanocomposites with the filler below 1.22 vol.% or the HDPE/M58 nanocomposites with the filler below 1.95 vol.% have a characteristic dielectric behavior when the AC conductivity increases linearly with the frequency. This behavior is typical for insulating materials. It may be because the MWCNTs are isolated in the HDPE matrix and the isolated MWCNTs behave as nanocapacitors. For higher concentrations of the filler, the dependence of AC conductivity on the frequency indicates two different dielectric behaviors. At approximately the percolation threshold, the electrical conductivity became independent of the frequency due to the gradual MWCNT conductive network formation up to the critical frequency, when nanocapacitor behavior is dominant. This critical frequency is shifted to higher frequencies with increasing number of the conductive pathways (increasing volume fraction of the conductive filler) until it entirely disappears and the conductivity of the polymer nanocomposites became independent of the frequency, i.e.,-fully conductive. The reason is that MWCNTs formed 3D conductive networks along the whole nanocomposites.

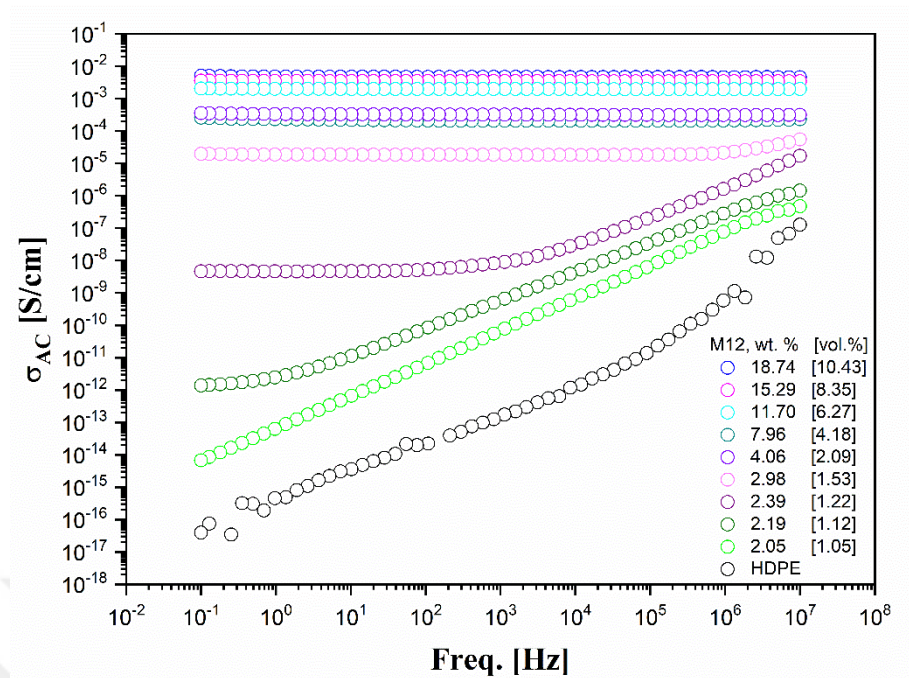


Figure 5.6 AC conductivity vs. frequency for HDPE/M12 nanocomposites at various concentrations of MWCNTs

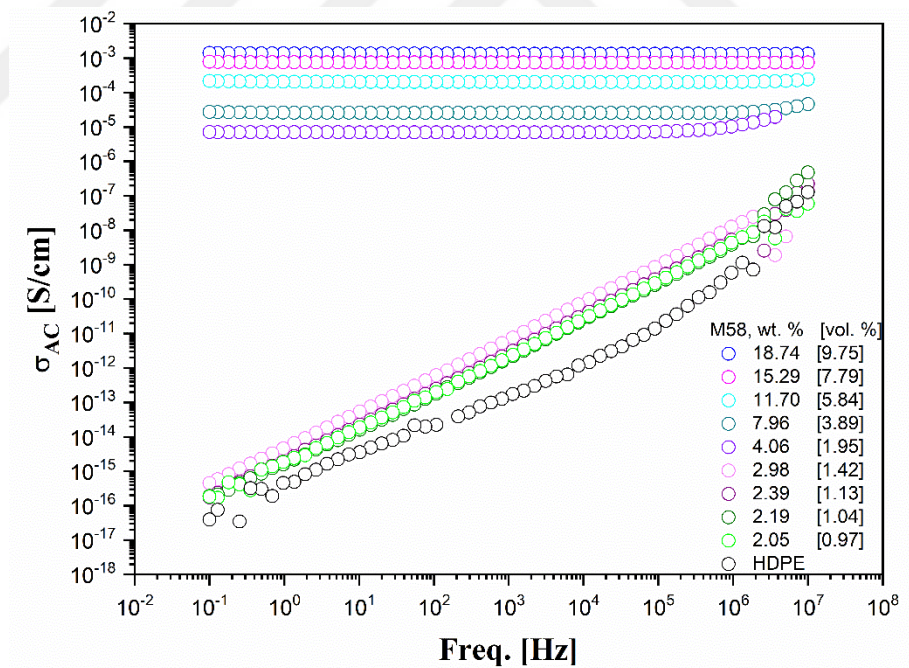


Figure 5.7 AC conductivity vs. frequency for HDPE/M58 nanocomposites at various concentrations of MWCNTs

The variation in the AC conductivity at 0.1 Hz for pure HDPE and the HDPE/MWCNTs nanocomposites as a function of MWCNTs volume fraction is

shown in Figure 5.8. It is clear that the HDPE-based nanocomposites with both types of MWCNTs display a nonlinear (polynomial) increase in the electrical conductivity with increasing MWCNT content. The conductivity of pure HDPE is approximately 4×10^{-17} S/cm, which means that HDPE is an electrical insulating material. The abrupt and significant increase in the electrical conductivity of nanocomposites occurring in a very narrow range of concentration at approximately the critical filler content is named as the percolation threshold, characterizing the percolation behavior. The electrical conductivities of the nanocomposites below the percolation threshold are almost on the same order as the polymeric matrix. The reason is that the HDPE molecules wraps the MWCNTs and obtains an electrical insulating HDPE layer among the MWCNTs. This layer increases the distance between individual MWCNTs, which results in the harder tunneling of electrons from MWCNTs to MWCNTs. The direct contact among MWCNTs cannot happen because of this layer (Kim et al., 2009). As expected, an increase in the electrical conductivity is observed with increasing MWCNT contents because of the increase in conductive pathways and the elimination of the isolation layers of the pure polymer matrix.

As mentioned above, the electrical conductivity of nanocomposites is generally described by the percolation theory and the percolation threshold of nanocomposites can be determined by fitting the experimental data using power law function (Castillo et al., 2011):

$$\sigma = \sigma_0(p - p_c)^t \quad p > p_c \quad (5.1)$$

where p is the volume fraction of MWCNTs, p_c refers to the percolation threshold value, σ_0 is a constant and t is the critical exponent. σ_0 is dependent on the conductivity of the filler, contact resistance of the filler and topology of the network and t is based on the dimensionality of the system (Mutiso & Winey, 2015). The best fit data for σ_0 , p_c and t are listed in Table 5.2. The determined percolation threshold of the HDPE/M12 nanocomposites is 1.22 vol.% (2.23 wt.%), while this value is calculated to be 1.43 vol.% (2.81 wt.%) for the HDPE/M58 nanocomposites. The values of t for the HDPE/M12 and HDPE/M58 nanocomposites are approximately 1.51 and 1.93,

respectively. The universal value of t is between 1.6 and 2 for 3D systems and approximately 1.33 in 2D systems (Bauhofer & Kovacs, 2009). The variations in these values may be attributed to the difference in dispersion, ARs and filler networks in the matrix (Shehzad et al., 2016). σ_0 was determined as 0.16 S/cm for the HDPE/M12 nanocomposites and 0.11 S/cm for the HDPE/M58 nanocomposites. It means that the electrical conductivities are almost the same for both types of MWCNTs, but the electrical conductivity values of the HDPE/M12 nanocomposites are slightly higher than that of the HDPE/M58 nanocomposites at the same filler concentrations. The maximum electrical conductivities of the samples for the maximum concentration of MWCNTs are 5.08×10^{-3} S/cm and 1.42×10^{-3} S/cm for the HDPE/M12 and HDPE/M58 nanocomposites, respectively.

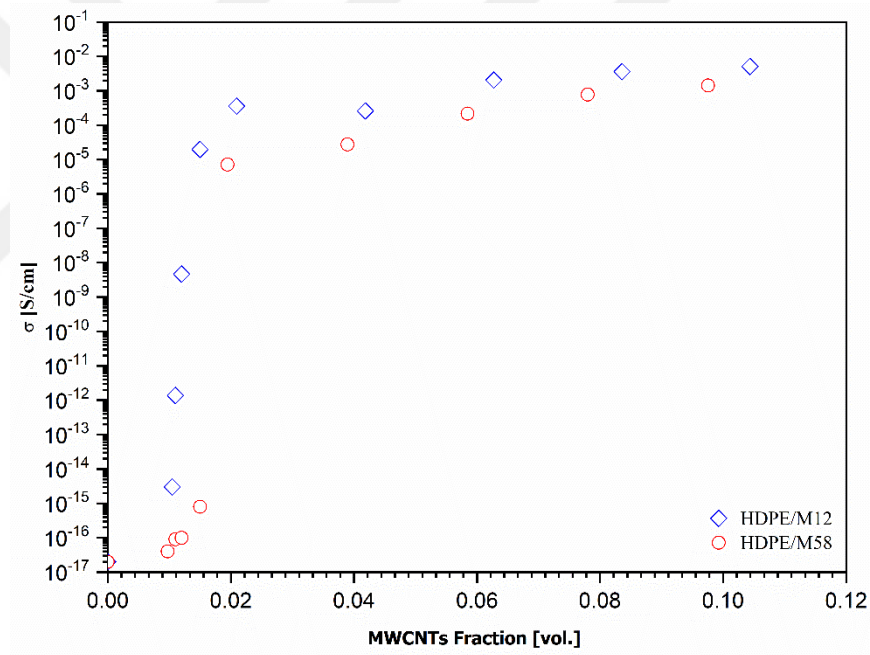


Figure 5.8 The AC conductivity at 0.1 Hz vs. vol.% of MWCNTs for the HDPE/M12 and HDPE/M58 nanocomposites.

Table 5.2 The curve fitting results of electrical conductivity for $p > p_c$ of HDPE-based nanocomposites with two different MWCNTs.

Sample	σ_0 [S/cm]	p_c [vol.%]	t
M12	0.16	1.22	1.51
M58	0.11	1.42	1.93

The nanocomposites with higher aspect ratios of MWCNTs demonstrate a slightly better enhancement in electrical properties. The reason is that the higher aspect ratio of MWCNTs may show a more uniform distribution with less agglomeration and entanglement, resulting in increasing MWCNTs-MWCNTs contact and forming a more effective electrical network.

5.4.3 Thermal conductivity

The experimental thermal conductivity of composite samples was obtained from the following relationship:

$$k = \alpha C \quad (5.2)$$

with the thermal diffusivity α determined as explained in Chapter 4. Our effective thermal conductivity results as function of MWCNTs concentration are given in Figure 5.9. The value $k_m=0.386 \text{ Wm}^{-1}\text{K}^{-1}$ is obtained for pure HDPE and it is in good agreement with the literature ((Ye, Shentu, & Weng, 2006), ($k_m=0.390 \text{ W/mK}$)). To the upper bound of the investigated interval at 18.74 wt.% of filler content, the maximum thermal conductivity value is 0.76 W/mK for HDPE/M12 and 0.63 W/mK for HDPE/M58, corresponding to an increase of 97% and 63%, respectively, relative to neat HDPE.

Experimental thermal conductivities could be fitted by using the model of Nan, Birringer, Clarke, & Gleiter (1997). This model takes into account the size and the orientation of the filler as well as the thermal boundary resistance between matrix and filler. The diameter of MWCNTs are known ($d = 12 \text{ nm}$ for M12 and $d = 58 \text{ nm}$ for M58) and it is assumed that thermal boundary resistance between MWCNTs and HDPE is the same than the one of EG/HDPE interface ($R_{th} = 2.1 \cdot 10^{-7} \text{ W/mK}$) found in Chirtoc et al., (2012). The thermal conductivity of the matrix is known ($k_m = 0.386 \text{ W/mK}$) and the one of the fillers is assumed to be $k_f = 300 \text{ W/mK}$. With these values for the diameter of MWCNTs and R_{th} , the parameter of adjustment is only the length of the MWCNTs which has a strong effect on the effective thermal conductivity. The

fitted length are $L_{M12} = 0.75 \mu\text{m}$ and $L_{M58} = 1.08 \mu\text{m}$ and lead to the conclusion that MWCNTs are broken during the process, as demonstrated by Lizundia et al. (2012). They effectively found by TEM micrographs that length of MWCNTs could be divided up to a factor ten and more. This mechanical effect on the length of MWCNTs during the process has been rarely demonstrated in the literature. The second conclusion concern also the length of MWCNTs. Data given by the supplier shown that M12 has longer size than M58. However, after the process, M58 shows a length 25% higher than M12. It can be concluded that MWCNTs with small diameter are less resistant to mechanical stresses.

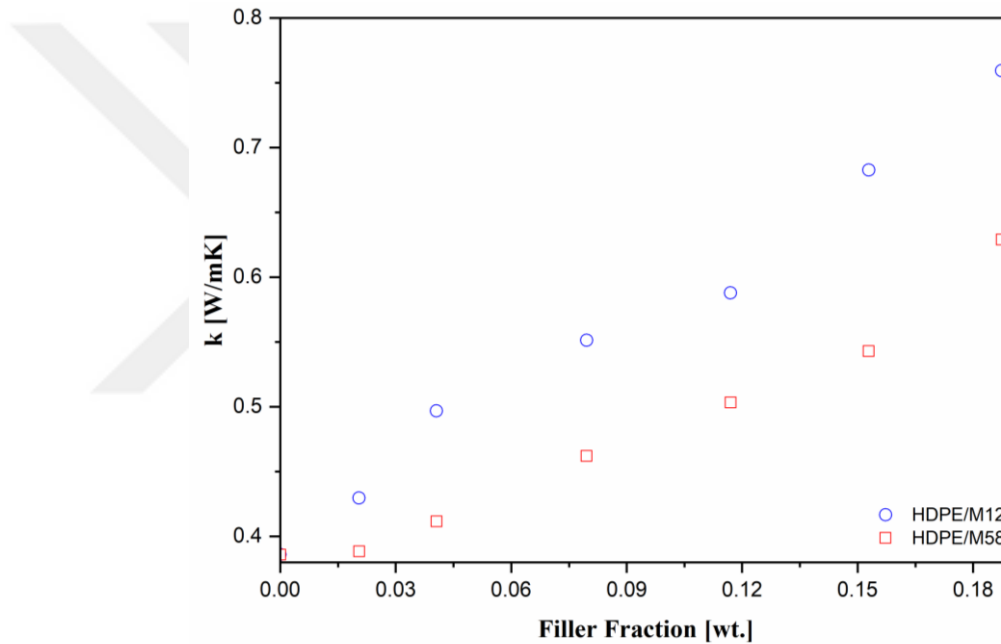


Figure 5.9 Experimental results of thermal conductivity of HDPE/MWCNT samples as a function of the weight fraction

As mentioned before, thermal conductivity data on HDPE based MWNCTs nanocomposites are limited in the literature. Since the study of Chen et al. (2009) did not mention the dimensions of the fillers, we compare our results with those of Kim et al. (2009). As one can see, there is good agreement with HDPE/M12 sample series which contains CNTs with similar aspect ratio, as distinct from the HDPE/M58 series which is situated lower due to lower aspect ratio of the fillers. Moreover, at low filler

concentrations, MWCNTs with higher aspect ratio (M12) provide three to four-fold higher thermal conductivity enhancement (k/k_m-1) than the shorter ones (M58).

The explanation at microscopic scale for these observations is that higher aspect ratio of MWCNTs favors the creation of a percolated network enabling the passage of phonons over longer distance without transitions from particle to particle, as mentioned by Gojny et al. (2006). In addition, in a network made up by shorter filaments, the required number of contacts per unit distance increases exponentially and so does the number of interfacial thermal resistances that scatter the phonon-mediated heat transport, as reported by Russ et al. (2013). Thus, our results confirm the previous limited studies (Ciecierska et al., 2013; Russ et al., 2013) which reported on the effect of aspect ratio on thermal conductivity and thermal diffusivity of polymer based MWCNTs composites.

Also, the comparison of present results with our previous data on HDPE based nanocomposites with expanded graphite (EG) fillers (Chirtoc et al., 2012), shows that EG fillers give better thermal conductivity enhancement than MWCNTs. This could be due to higher surface area, lower interface resistance and more rigid structure of EG as compared to MWCNTs fillers, as mentioned by Safdari & Al-Haik (2013). It is also along the line of the report by Xie, Liu, & Li (2008) which demonstrates that graphene nanosheets are more effective in conductivity enhancement than carbon nanotubes.

5.4.4 Mechanical Properties

The mechanical properties of polymer nanocomposites are considerably important for industrial applications. The dependencies of the mechanical properties on filler contents for the HDPE-based nanocomposites reinforced with MWCNTs were demonstrated in Table 5.3.

Young's moduli of the HDPE/M12 and HDPE/M58 nanocomposites increase regularly with the increase in the filler content. In other words, the addition of MWCNTs leads to an increase in Young's modulus of the nanocomposites due to the

higher Young's modulus of MWCNTs compared to pure HDPE. Young's modulus of the nanocomposites increases from 882.89 MPa for pure HDPE to 1699.18 MPa for the HDPE/M12 nanocomposites and 1456.65 MPa for HDPE/M58 nanocomposites with increasing MWCNTs contents from 0 to 18.74 wt.%. These improvements correspond to approximately 93% and 65% for the HDPE/M12 and HDPE/M58 nanocomposites, respectively. It is clear that this increase is more pronounced for the HDPE/M12 nanocomposites relative to the HDPE/M58 nanocomposites. From these results, it can be concluded that Young's modulus is dependent on the aspect ratio of MWCNTs and MWCNTs with a higher aspect ratio achieved a higher Young's modulus value.

Table 5.3 Results of mechanical conductivity for the HDPE/M12 and HDPE/M58 nanocomposites

Weight Fraction [wt. %]	Young's Modulus [MPa]		Tensile Strength [MPa]		Elongation at Break [%]	
	HDPE/M12	HDPE/M58	HDPE/M12	HDPE/M58	HDPE/M12	HDPE/M58
0.00	882.89±47.55	882.89±47.55	37.46±1.11	37.46±1.11	1202.21±37.60	1202.21±37.60
2.05	993.68±42.26	893.23±20.77	26.62±0.54	25.14±3.07	10.08±0.19	374.16±564.06
4.06	1063.83±35.16	1013.97±41.13	26.44±0.21	24.91±0.68	9.28±0.27	9.08±0.28
7.96	1397.10±54.10	1112.33±56.52	27.64±0.45	25.64±0.63	8.40±0.11	8.43±0.48
11.70	1341.02±107.13	1173.06±105.32	27.86±0.67	26.56±0.39	7.82±0.26	8.00±0.20
15.29	1584.86±62.63	1456.37±75.14	29.00±0.39	28.53±0.55	7.95±0.09	7.88±0.14
18.74	1699.18±97.49	1456.53±121.23	30.21±0.51	29.08±0.82	7.43±0.22	7.12±0.29

The tensile strength of the nanocomposites with both types of MWCNTs rapidly decreases at the preliminary stage (up to 1 vol.%), and then increases with increasing volume fraction of MWCNTs. As seen in Table 5.3, pure HDPE has the highest tensile strength compared to all HDPE-based nanocomposites at different loadings. While the tensile strength of pure HDPE is approximately 37.46 MPa, with the incorporation of MWCNTs of 18.74 wt.% into the HDPE matrix, the mean tensile strengths of the HDPE/M12 and HDPE/M58 nanocomposites are 30.21 and 29.08 MPa, respectively. It can be certainly observed that these values are below the value of pure HDPE despite the increase in the filler contents. These values correspond to a decrease of 19.4% for the HDPE/M12 nanocomposites and 22.4% for the HDPE/M58 nanocomposites at the maximum concentration of MWCNTs, compared to pure HDPE. It is known that the aggregation of MWCNTs can deteriorate the MWCNT reinforcing effect, resulting in

a decrease in the tensile strength of nanocomposites. Homogenous dispersion of MWCNTs leads to effective load transfer from the matrix to MWCNTs, causing an enhancement in mechanical properties at higher contents of MWCNTs (Singh et al., 2013). The first rapid decrease may be attributed to poor dispersion and a weak interfacial interaction between MWCNTs and the matrix (Sever et al., 2013).

The elongation of HDPE-based nanocomposites decreases with the incorporation of MWCNTs because of the decrease in the nanocomposites' molecular mobility (Altay et al., 2018). The addition of MWCNTs into the HDPE matrix results in the degradation in the elongation of the nanocomposites. The initial mean value of elongation for pure HDPE is 1202% and the elongation of the nanocomposites decreases to 7.4% for HDPE/M12 and 7.1% for HDPE/M58 upon the addition of 18.74 wt.% of MWCNTs into the HDPE matrix. Finally, it can be concluded that the aspect ratio of MWCNTs does not have significant effects on the tensile strength and the elongation of the nanocomposites, while Young's modulus increased with increasing aspect ratio of MWCNTs.

5.4.5 Thermal Properties

5.4.5.1 DSC Results of HDPE/MWCNTs nanocomposites

The melting temperatures (T_m), crystallization temperatures (T_c), heat of fusions (ΔH_f) and crystallinity (X_c) of pure HDPE and the HDPE-based nanocomposites with M12 and M58 are listed in Table 5.4. It can be seen that the melting temperature is in the range of 129.74 - 132.80 °C for all measured samples. These results obviously demonstrate that there is a slight effect of the loading of MWCNTs on the melting temperatures. The crystallization temperature increases while the heat of fusion decreases with increasing content of MWCNTs. The crystallization temperature of pure HDPE is 116.30°C. The increase in crystallization temperature is approximately 5°C for the HDPE nanocomposites with 18.74 wt.% of MWCNTs because of the MWCNT nucleation effect. The results show that the heat of fusion of the HDPE/M12 and HDPE/M58 nanocomposites decrease by approximately 20% to the minimum

value with the MWCNTs content of 18.74 wt.%. It is clear that the crystallinity does not change much. It is observed that the melting temperature, crystallization temperature, heat of fusion and crystallinity of the studied nanocomposites do not depend on the AR, because these values are almost the same for all carbon-based materials.

5.4.5.2 TGA Results of HDPE/MWCNTs nanocomposites

The thermogravimetric curves of the HDPE/M12 and HDPE/M58 nanocomposites are shown in Figures 5A.5 and 5A.6. in the Appendixes, respectively. The effect of MWCNTs on the thermal stability of HDPE is detected using the temperatures related to $T_{5\%}$ (5% weight loss), $T_{50\%}$ (50% weight loss), T_{deg} (maximum weight loss). Their values and residue at 700 °C are listed in Table 5.5.

The results of MWCNTs thermal treatment demonstrate that there is no considerable mass change throughout the entire temperature range. This means that MWCNTs are not degraded until 700 °C (Cha et al., 2016; Costa et al., 2014) and MWCNTs are known to remain stable up to 1000 °C (Costa et al., 2014). However, the HDPE matrix is absolutely degraded at 700 °C. It can be clearly observed that the thermal decomposition behavior of all nanocomposites is similar to that of pure HDPE. These curves indicate the single-stage decomposition temperature. The decomposition of pure HDPE starts at ~400 °C and finishes at ~500 °C. The weight loss of 5% ($T_{5\%}$) for pure HDPE occurs at ~440.80 °C. Although the nanocomposites reinforced with MWCNTs reveal similar thermal degradation behavior to that of pure HDPE, the degradation temperature is higher than that of pure HDPE. $T_{5\%}$ increases with increasing MWCNTs content for the two types of MWCNTs. The $T_{5\%}$ value for the HDPE/M12 nanocomposite with 18.74wt.% of MWCNTs is shifted by approximately 30 °C to higher temperature up to 470.34°C while the value of $T_{5\%}$ increases with the incorporation of M58 by approximately 25 °C to 466.11 °C. $T_{50\%}$ for pure HDPE is ~474 °C. These values have remarkably increased up to values of ~495 °C and ~491 °C for the HDPE/M12 and HDPE/M58 nanocomposites, respectively for the

maximum concentration of MWCNTs, which represents a significant improvement in thermal stability at high temperatures.

It is observed from Figures 5A.5 and 5A.6 that all the samples follow a similar trend during the thermal treatment. The HDPE/MWCNT nanocomposites have a higher thermal stability than pure HDPE. The maximum decomposition temperature (T_{deg}) of pure HDPE is approximately 479 °C. For T_{deg} , an average temperature increase is obtained of 12-16 °C for the HDPE/M12 nanocomposites and nearly 14 °C for HDPE/M58 nanocomposites. While the increase in T_{deg} for HDPE/M58 nanocomposites is independent of the MWCNTs content, T_{deg} increases with increasing concentration of MWCNTs for the HDPE/M12 nanocomposites. For both MWCNT types, the residual mass (%) increased with increase in MWCNT content because of the high thermal stability of MWCNTs. MWCNTs degraded by approximately 0.4 wt.% after the TGA analysis, whereas the HDPE matrix remained approximately 0.84 wt.%.

As seen from the results, the thermal stability of HDPE is significantly improved by the incorporation of MWCNTs. It is related to the barrier effect, good distribution of MWCNTs and the polymer-MWCNTs interaction. However, the results of the TGA analysis demonstrate that the thermal stability of the HDPE nanocomposites is improved by the increase in aspect ratio of MWCNTs, except for the residual mass. The nanocomposites with higher aspect ratios indicate a better enhancement in thermal stability. As mentioned above, the reason for this might be the better dispersion of M12 in the HDPE matrix.

Table 5.4 DSC data of the HDPE/MWCNTs nanocomposites

MWCNTs Fraction [wt.%]	T_m [$^{\circ}\text{C}$]		T_c [$^{\circ}\text{C}$]		ΔH_f [J/g]		X_c (%)	
	HDPE/M12	HDPE/M58	HDPE/M12	HDPE/M58	HDPE/M12	HDPE/M58	HDPE/M12	HDPE/M58
0.00	130.06	130.06	116.30	116.30	205.80	205.80	70.24	70.24
4.06	132.03	131.56	119.25	119.10	196.90	196.80	70.07	70.04
11.70	132.80	130.91	118.02	12.33	180.90	180.90	69.92	69.92
18.74	129.74	130.54	121.31	121.75	165.30	165.20	69.39	69.35

Table 5.5 The results of TGA analysis for the HDPE/MWCNTs nanocomposites

Sample	$T_{5\%}$ [$^{\circ}\text{C}$]	$T_{50\%}$ [$^{\circ}\text{C}$]	Residual Mass [%]	T_{deg} [$^{\circ}\text{C}$]
HDPE	440.80	474.46	0.84	478.79
MWCNTs	-	-	99.60	-
HDPE/M12_4.06 wt. %	464.32	487.98	4.32	490.90
HDPE/M12_11.70 wt. %	467.46	490.45	12.26	492.03
HDPE/M12_18.74 wt. %	470.34	495.24	18.92	495.03
HDPE/M58_4.06 wt. %	463.49	488.56	4.56	492.31
HDPE/M58_11.70 wt. %	466.98	490.97	12.13	491.88
HDPE/M58_18.74 wt. %	466.11	491.51	19.15	492.09

5.5 Conclusions

In this study, the influence of aspect ratio and concentration of MWCNTs on the thermal conductivity of HDPE based nanocomposites was experimentally investigated. The aspect ratios of the two types of fillers are in the range of 200-400 and 500-3000. Samples were prepared up to a weight fraction of 19%. From the experimental results we may conclude that:

- The morphological properties of MWCNTs, pure HDPE and the nanocomposites were determined by various approaches: XPS, TEM, and XRD analyses. The MWCNT surface properties do not show any remarkable change with respect to the aspect ratio. The atomic contents of carbon and oxygen are nearly the same. The TEM micrographs indicate just a small difference in the dispersion of MWCNTs in the HDPE matrix: the nanotubes with a higher aspect ratio showed a slightly better distribution in the polymeric matrix. The XRD results demonstrate that the aspect ratio effect of MWCNTs on the crystal and chemical structures of the HDPE/MWCNTs nanocomposites is negligible.
- The percolation threshold of the HDPE/M58 nanocomposites is 1.43vol.%, which is higher than that of the HDPE/M12 nanocomposites, 1.22 vol.%. At the highest MWCNTs contents, the electrical conductivity of the HDPE nanocomposites with M12 is found to be higher than that of the HDPE/M58 nanocomposites. The slight difference in percolation threshold and electrical conductivity of the two HDPE/MWCNTs nanocomposites could be attributed to the difference in aspect ratio of the two MWCNTs types. M12 having comparatively higher aspect ratio achieves a greater enhancement in the electrical properties. This outcome is in agreement with the TEM micrographs that indicate slightly better dispersion of M12 in the HDPE matrix.
- For both sample series, the effective thermal conductivity increases with the addition of MWCNTs. At the maximum of 10 vol% concentration, the thermal conductivity increase reaches 97% and 63% for the samples with high and low CNT aspect ratios, respectively. At low filler concentrations, the thermal conductivity enhancement (k/k_m-1) provided by composites with higher CNT

aspect ratio is three to four fold higher than that for lower aspect ratio. Compared to previous results, HDPE based MWCNTs composites were found to be thermally less conductive than HDPE/EG composites. MWCNTs with small diameter are less resistant to mechanical stresses.

- M12 gives a much better enhancement in Young's modulus of the prepared nanocomposites compared to M58, because MWCNTs with higher aspect ratios indicated a better distribution in the polymeric matrix compared to MWCNTs with lower aspect ratios. The changes in tensile strength and elongation are insignificant with the increase in aspect ratio.
- The decomposition temperature values of the nanocomposites increase with increasing contents and aspect ratio of MWCNTs. The values of the residual mass increase with the increase in MWCNTs contents, but they are independent of the MWCNT aspect ratio. Moreover, the melting temperature, crystallization temperature, heat of fusion and crystallinity of HDPE barely changed, regardless of the MWCNTs aspect ratio.

CHAPTER SIX

HDPE/GNPS NANOCOMPOSITES

6.1 Abstract

In this chapter, HDPE-based nanocomposites incorporating three different types of GnPs were fabricated to investigate the size effect of GnPs in terms of both lateral size and thickness on the morphological, thermal, electrical, and mechanical properties. The results show that the inclusion of GnPs enhances the thermal, electrical, and mechanical properties of HDPE-based nanocomposites regardless of GnPs size. Nevertheless, the most significant enhancement in the thermal and electrical conductivities and the lowest electrical percolation threshold are achieved with the use of larger lateral size GnPs. This could be attributed to the fact that the larger lateral size GnPs exhibit a better dispersion in the HDPE and form conductive pathways easily observed in scanning SEM images. Our results show that the lateral size of GnPs is a more regulating factor for the above-mentioned nanocomposite properties compared to their thickness. For a given lateral size, thinner GnPs show significantly higher electrical conductivity and lower percolation threshold than thicker ones. On the other hand, in terms of thermal conductivity, a remarkable amount of enhancement is observed only after a certain filler concentration. The results demonstrate that GnPs with smaller lateral size and larger thickness lead to lower enhancement in the mechanical properties of the samples due to poorer dispersion compared to the others used. In addition, the size of GnPs has no considerable effect on the melting and crystallization properties of the HDPE/GnPs nanocomposites.

6.2 Introduction

In recent years, electrically and thermally conductive polymer nanocomposites have attracted considerable attention because of their potential use in many industrial applications such as aerospace, electronics, packaging, automotive, sensors, batteries, anti-static, light emitting devices, and corrosion-resistant coatings (Chirtoc et al., 2012; Mohan et al., 2018). The addition of a conductive filler into the polymeric matrix

is one of the easiest methods to produce these nanocomposites. Among conductive filler materials, carbon-based materials are attractive since they show significant enhancement in the properties of the nanocomposites at relatively low filler concentrations compared to others (Chirtoc et al., 2012; Evgin et al., 2016; Kumar et al., 2019a). In particular, using graphene, a single-atom-thick structure of sp^2 -hybridized carbon atoms in a hexagonal arrangement, is of great interest due to its large specific surface area, 2D structure and superior inherent properties such as thermal conductivity (1000-5000 W/mK (Huang et al., 2018)), electrical conductivity (6000 S/cm (Zakaria et al., 2017)), and mechanical properties (Young's modulus of 1 TPa and tensile strength of 130 GPa (Paszkievicz et al., 2014)). However, the mass production of graphene with high-quality at a low cost is still challenging using available production technologies (Jun et al., 2018). GnPs, formed by several graphene layers bonded together by Van der Waals forces, are a potential alternative to graphene, since they exhibit interesting properties and their fabrication cost is lower (Imran et al., 2018; Jun et al., 2018).

Numerous studies performed on nanocomposites with graphene or its derivatives have shown that the properties of nanocomposites depend on several factors such as polymer type, morphology, intrinsic properties, size and defect level of the filler material, production method, interface between filler and polymer, and others (Bakir et al., 2018; Chaudhry & Mittal, 2013; Kim et al., 2018). Although the size of GnPs is one of the most important factors, only a few studies have investigated the size effect of GnPs on the properties of nanocomposites with various matrices (as seen in Table 1.2) such as HDPE, PP, epoxy and PC in the range of about 0.1 - 50 wt. %. However, to the best of our knowledge, there has been no study on how the morphological, thermal, electrical, and mechanical properties of HDPE-based nanocomposites are correlated with the size of GnPs in terms of both thickness and lateral size. Therefore, the objective of this chapter is to investigate the size effect of GnPs on the above-mentioned properties of HDPE-based nanocomposites. Considering the concentration of HDPE based nanocomposites with GnPs inclusions studied in the literature, the maximum concentration is up to 15 vol.%. Therefore, this study is carried out within the range of 0.92 - 13.92 vol.% (2.05 – 26.81 wt.%) of GnPs concentration.

6.3 Materials and Methods

Details about the used materials, production and characterization methods were explained in Chapter 4.

6.4 Results and Discussion

6.4.1 Characterization

6.4.1.1 XPS Results of HDPE/GnPs Nanocomposites

The XPS results of samples can give more information about GnPs chemical compositions. The XPS results of GnPs are shown in Figure 6.1-2 and given in Table 6.1. GnPs generally consist of a strong signal of carbon (C1s at ~ 284.6 eV) and a small amount of oxygen (O1s at ~ 531 - 534 eV). C1s peak centered at ~ 284.6 eV with an asymmetry towards the higher binding energies is characteristic for sp² carbon. The broad peak observed at ca. 291 eV (labeled Pi-Pi* in Figure 6.2) occur due to the existence of the delocalized π electrons (conduction electrons) available for shake-up-like events following the core electron photoemission [Avantage software 5.9904, XPS knowledge database (UK:ThermoFisher Scientific)].

In Table 6.1 is shown also deconvolution fit of the C1s and O1s signals. Besides graphitic carbon (sp² centered at ca 284.6 eV) also peaks of C-O (centered at ca 286.4 eV), C=O (287.4 eV) and OC=O (289.2 eV) groups were detected. These signals correspond to the O1s signals of C=O aromatic (C=O_{ar}, centered at ca 531.2 eV), C=O aliphatic (C=O_{al}, centered at ca 532.2 eV), C-O (at ca 533.5 eV) and O2C=O (at ca 535.8 eV) groups. The C1s signals of GnPs are approximately the same (Table 6.1, Figure 6.2). It is clear that G2 shows the highest atomic content of C1s (98.4 %) and the surface of G2 is the least oxidized. This less oxidization of G2 is nicely visible on the lower amount of carbonyls (C=O_{ar}) in the case of O1s signal. There is also small surface contamination in the case of G1, where on the surface is present 0.1 at.% of

Si2p at ca. 103.6 eV corresponding to siloxanes and 0.1 at.% of sodium (Na1s at ca. 1072.1 eV). In the case of G3 some contamination of sulphur is observed (0.3 at.%, s2p at ~ 164 -169 eV). The small differences in the surface chemical composition of GnPs will not affect the properties of HDPE-based nanocomposites.

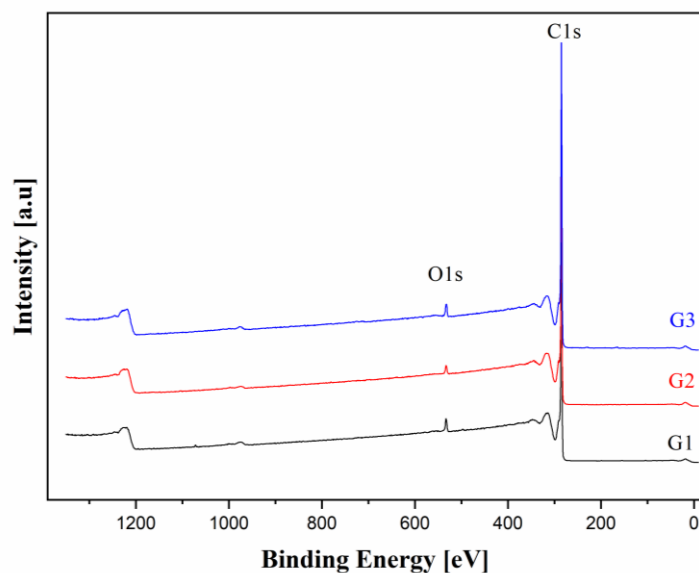


Figure 6.1 XPS survey spectra for G1, G2, and G3

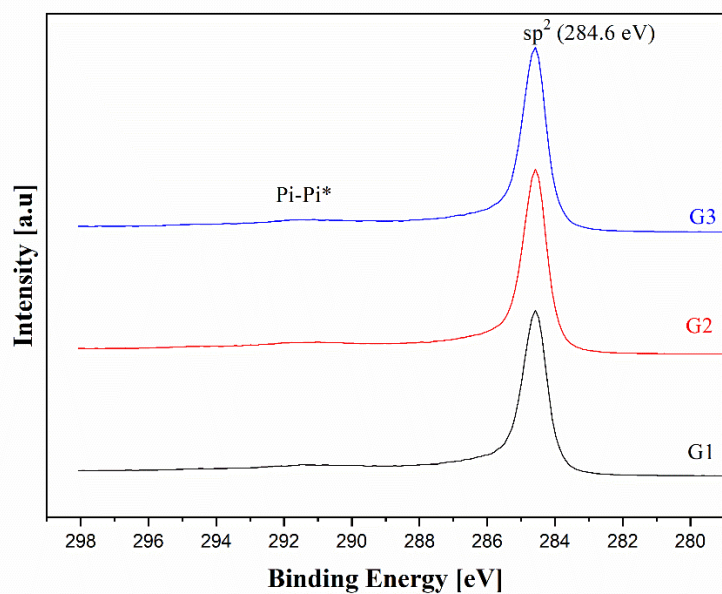


Figure 6.2 C1s high-resolution spectra for G1, G2, and G3

Table 6.1 Apparent surface chemical composition of GnPs as determined by XPS

Sample	Surface chemical composition [at.%]		
	C1s sp ² /sp ³ /C-O/C=O/OC=O/ π - π^*	O1s C=O _{ar} /C=O _{al} /C-O/O ₂ C=O	S2p/Na1s/Si2p
G1	97.2 66.5/21.0/2.2/1.1/0.4/5.9	2.6 0.7/1.0/0.7/0.2	-/0.1/0.1
G2	98.4 67.3/21.6/1.9/1.0/0.4/6.2	1.6 0.3/0.8/0.4/0.1	-/-/-
G3	97.3 65.1/21.8/2.1/1.4/0.6/6.3	2.4 0.8/0.8/0.7/0.1	0.3/-/-

6.4.1.2 XRD Results of HDPE/GnPs Nanocomposites

The crystalline structures of GnPs, HDPE and the HDPE/GnPs nanocomposites were studied and their XRD patterns are shown in Figure 6.3 and Figures A6.1-3 in the Appendixes. All types of GnPs show a sharp peak at 2θ of $\sim 26.5^\circ$ and a weak peak at 2θ of $\sim 54.6^\circ$, corresponding to the (002) and (004) carbon reflection, respectively. The size of GnPs does not cause a significant difference in the GnP crystalline structure. The sharp peak located at 2θ of $\sim 26.5^\circ$ is attributed to a characteristic peak of hexagonal GnPs with a d-spacing of 0.336. Two strong peaks centered at $2\theta=21.38^\circ$ and $2\theta=23.75^\circ$, corresponding to the (110) and (200) reflections of the HDPE orthorhombic phase, respectively, and two weakened peaks centered at $2\theta=29.93^\circ$ and 36.13° , corresponding to the (210) and (020) reflection planes, respectively, are clearly seen in the XRD pattern of the pure HDPE. Similar HDPE peaks were observed by Sever et al. (2013) and Wang et al. (2018). In the XRD patterns of the HDPE/GnPs nanocomposites, the intensities of the peaks at 2θ of $\sim 21.4^\circ$ and $\sim 23.8^\circ$ decrease with increasing the GnP loading, while the intensities of the peaks at 2θ of $\sim 26.5^\circ$ and $\sim 54.6^\circ$ increase. The XRD pattern for HDPE-based nanocomposites exhibits mixing of the peak appearing for the pure HDPE and GnPs. In the XRD patterns of the HDPE/GnPs nanocomposites, the intensities of the peaks at 2θ of $\sim 21.4^\circ$ and $\sim 23.8^\circ$ decrease with increasing the GnP loading, while the intensities of the peaks at 2θ of $\sim 26.5^\circ$ and $\sim 54.6^\circ$ increase. This is due to incorporation of GnPs particles in the HDPE matrix. It is observed that all the planes which display considerable peak growth with the existence of GnPs are in the general form of (00x) type, being crystallographically

in line with the GnPs (002) plane. It is indicated that GnPs may act as nucleation site and the nucleation starts around the GnPs (Jun et al., 2018). Figure 6.3 shows that the size of GnPs has a slight effect on the reflection peaks of the HDPE/GnPs nanocomposites, but it influences the peak's intensity.

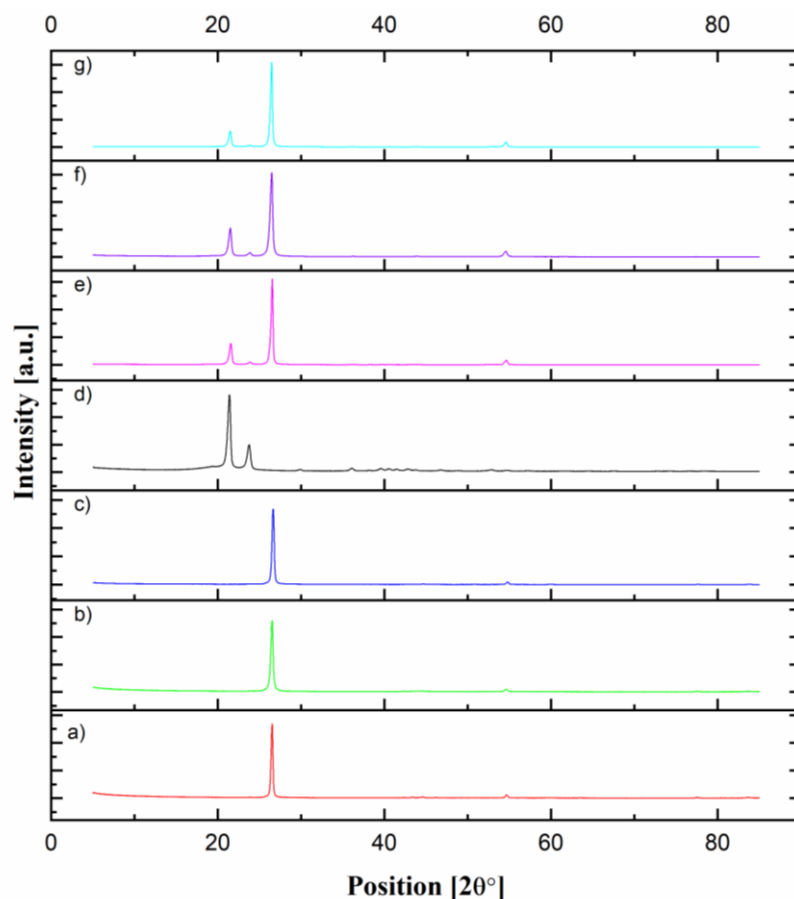


Figure 6.3 XRD pattern of a) G1, b) G2, c) G3, d) HDPE, e) HDPE/26.81 wt.% G1, HDPE/26.81 wt.% G2 and HDPE/26.81 wt.% G3 nanocomposites

6.4.1.3 FTIR Results of HDPE/GnPs Nanocomposites

Meanwhile, the results of FTIR analysis are shown in Figure 6.4 and Figure A6.4-11 in the Appendixes. The spectrum of HDPE shows two strong peaks at 2914.86 cm^{-1} , 2847.37 cm^{-1} and four weak peaks at 1472.59 cm^{-1} , 1462.11 cm^{-1} , 730.28 cm^{-1} and 718.84 cm^{-1} . The peaks at $\sim 2914\text{ cm}^{-1}$ and $\sim 2847\text{ cm}^{-1}$ are assigned to Alkyl (C-H) stretch vibrations. The peaks at wavenumbers of $\sim 1471\text{ cm}^{-1}$ and $\sim 1462\text{ cm}^{-1}$ are related to the $-\text{CH}_2$ group bending vibrations. The absorption peaks at $\sim 730\text{ cm}^{-1}$ and

$\sim 718\text{ cm}^{-1}$ are attributed to aromatic C-H bending. As seen in Figure 6.4, all GnPs do not display any peak assigning to functional groups on the surface of GnPs. The curves of HDPE and the HDPE/GnPs nanocomposites have almost the same absorption peaks. The size and content of GnPs cause no change in the characteristic peaks in the HDPE matrix.

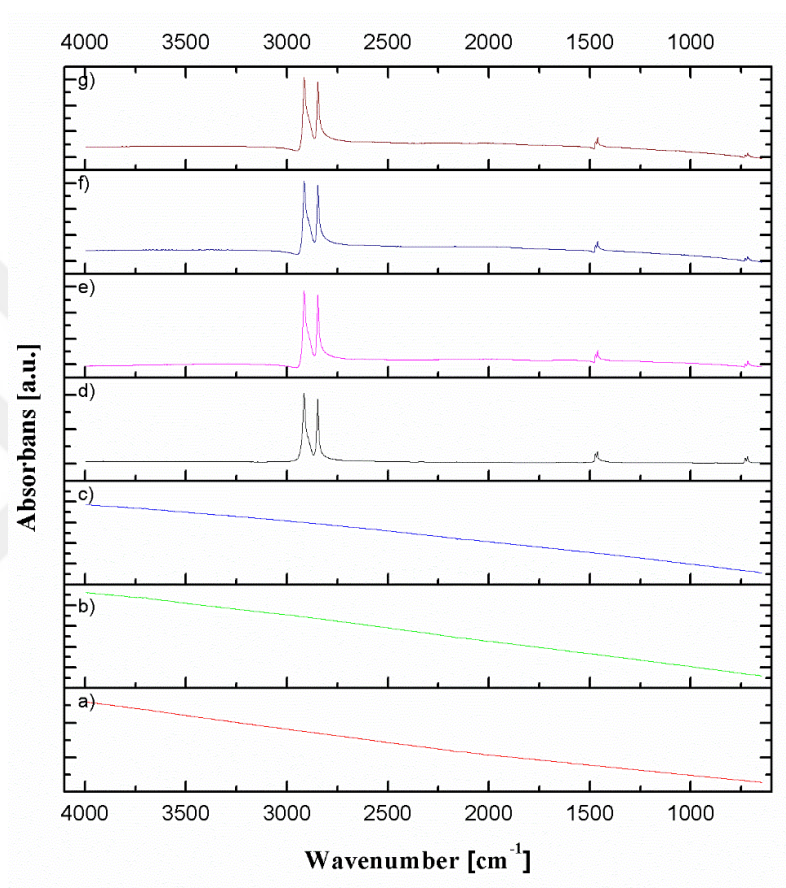


Figure 6.4 FTIR spectroscopy of a) G1, b) G2, c) G3, d) HDPE, e) HDPE/26.81 wt.% G1, HDPE/26.81 wt.% and HDPE/26.81 wt.% G3 nanocomposites

6.4.1.4 Morphological Results of the HDPE/GnPs nanocomposites

The SEM micrographs of each GnP and nanocomposites with 11.70 wt.% GnPs are presented in Figures 6.5-10. The aggregate forms of the GnPs are observed due to their high surface energy. Figure 4.2 indicates that the particles of G1, G2 and G3 include many sharp edges and are irregularly shaped. As shown in Figures 4.2 it can be

observed that the average lateral sizes of G1 and G2 are generally higher than that of G3, while G3 shows the lowest thickness.

Furthermore, SEM images of the cryo-fractured surface of the HDPE/GnPs nanocomposites with 11.70 wt.% GnPs are shown in Figures 6.5-7 to compare their structures. All types of GnPs are randomly and homogeneously distributed throughout the HDPE matrix where these layers separate the GnPs nanoflakes. Two different dispersions of GnPs in HDPE are observed: separately dispersed and aggregated. The observed aggregates of GnPs, especially G3, may be attributed to the large aspect ratio and high surface energy of GnPs. In particular, G1 nanoflakes are more isolated with each other while G2 nanoflakes are found to be in more contact with each other. It is obvious from Figures 6.8-10 that G2 can form filler networks more easily than G1 and G3. From this study it can be proposed that HDPE-based nanocomposites with G2 may show a greater number of the GnP pathways and consequently higher electrical and thermal conductivity values. Additionally, G3 is seen to have better dispersion when compared with G1 containing the HDPE nanocomposites.

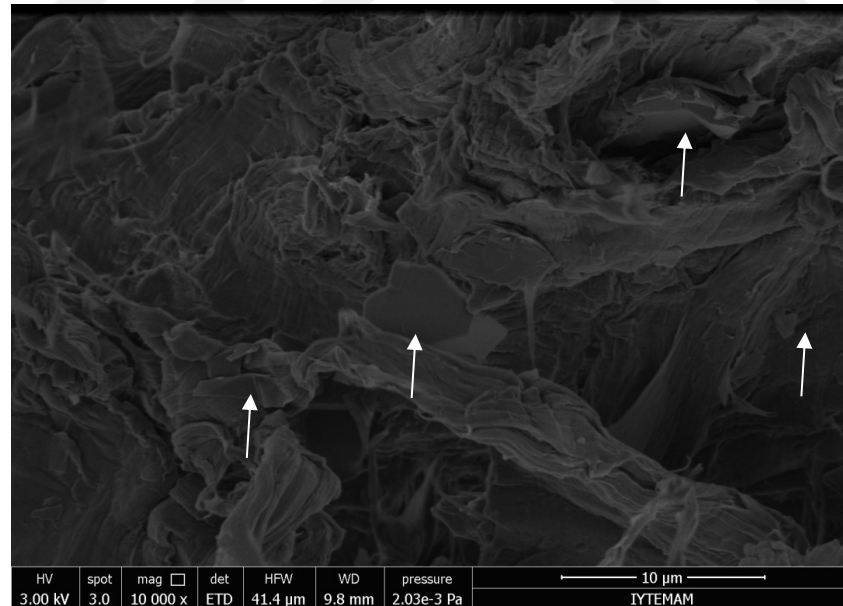


Figure 6.5 SEM image of HDPE/G1 nanocomposite with 11.70 wt.%

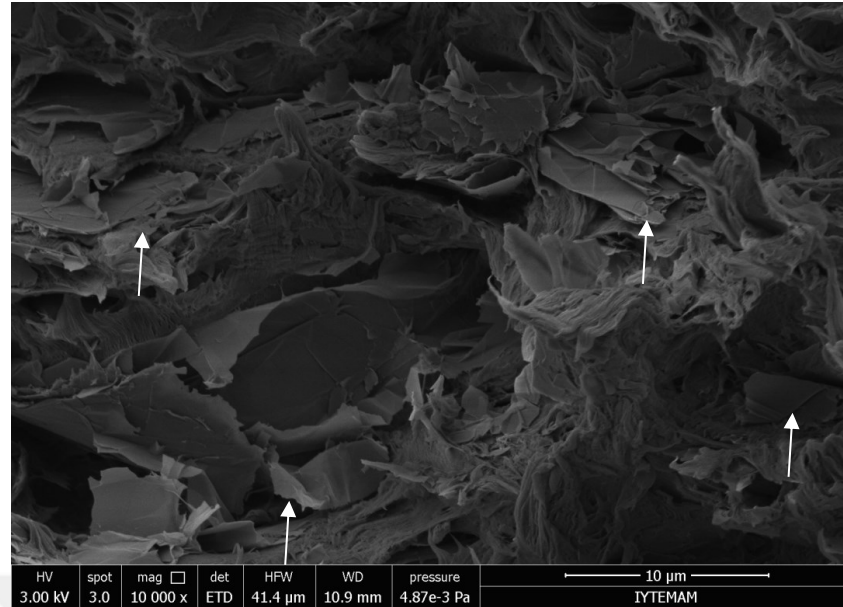


Figure 6.6 SEM image of HDPE/G2 nanocomposite with 11.70 wt.%

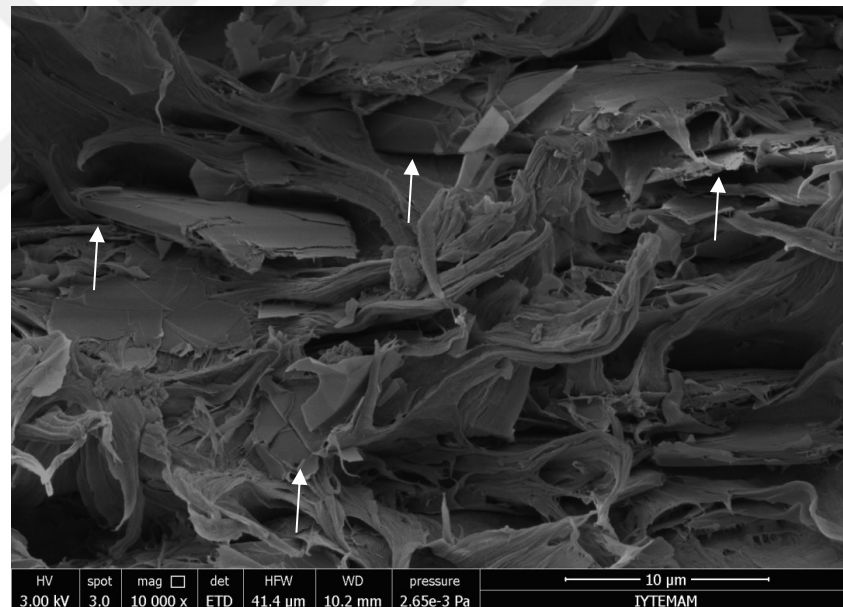


Figure 6.7 SEM image of HDPE/G3 nanocomposite with 11.70 wt.%

6.4.2 Electrical Conductivity

Figures 6.8-10 the AC conductivity (σ_{AC}) of all HDPE/GnP_s nanocomposites measured at room temperature as a function of frequency. Pure HDPE is an insulating material and has a characteristic dielectric behavior corresponding to a linear increase in the AC conductivity with increasing frequency (Jouni, Boiteux, & Massardier,

2013). The electrical conductivity of the nanocomposites increased with increasing amounts of GnPs. The reason for this increase may be that a greater number of electrons are conducted through the HDPE-GnPs interface because frequency facilitated the hopping of electrons (Ravindran et al., 2018). In the case of the HDPE/G1 nanocomposites, no significant enhancement in the electrical conductivity is observed. Figure 6.8 shows that the HDPE/G1 nanocomposites demonstrate the same linear behavior as the pure HDPE for all GnP concentration. Similar behavior is also exhibited by the HDPE/G2 and HDPE/G3 nanocomposites below a certain concentration, called the percolation threshold which defines the minimum filler concentration where the insulating material is converted to conductive or semi-conductive materials (Wypych, 2016).

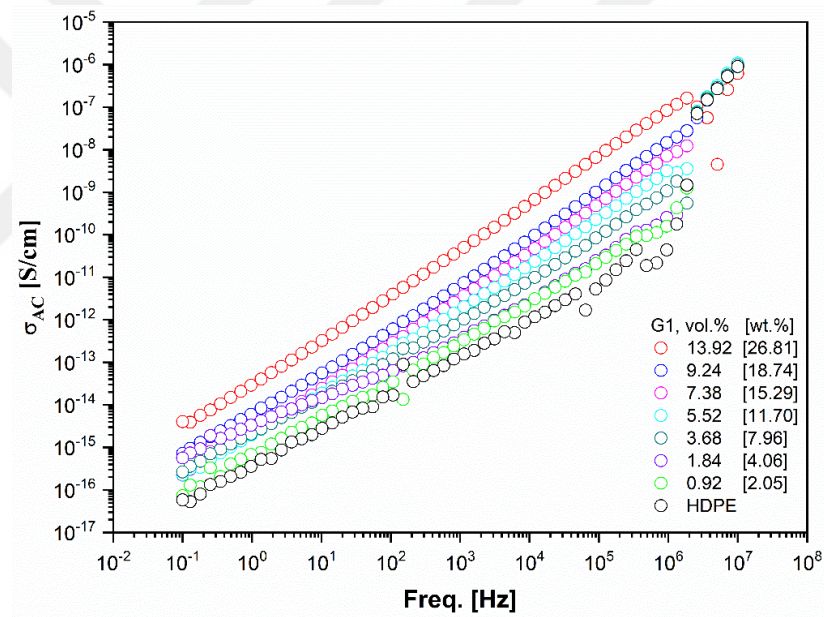


Figure 6.8 AC conductivity vs. frequency for the HDPE/G1 nanocomposites

Above the percolation threshold, the dependence of the electrical conductivity on the frequency shows two different parts: i) the conductivity does not depend on the frequency up to a critical value, ii) followed by a regime in which the conductivity is dependent on the frequency. The first part is linked to the transfer of charge carriers by direct contacts between the GnPs filler, while the second part reflects the conductivity due to hopping and tunneling of electrons between the adjacent particles (Al-Saleh & Abdul Jawad, 2016). It is apparent that the critical frequency shifts

towards higher frequencies and the AC conductivity increases with increasing GnP loading.

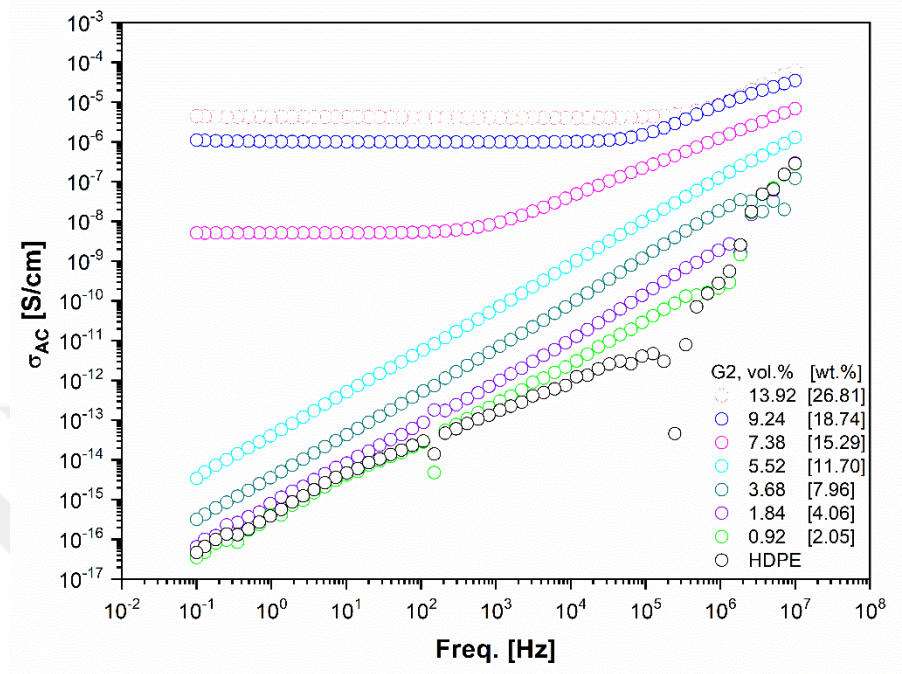


Figure 6.9 AC conductivity vs. frequency for the HDPE/G2 nanocomposites

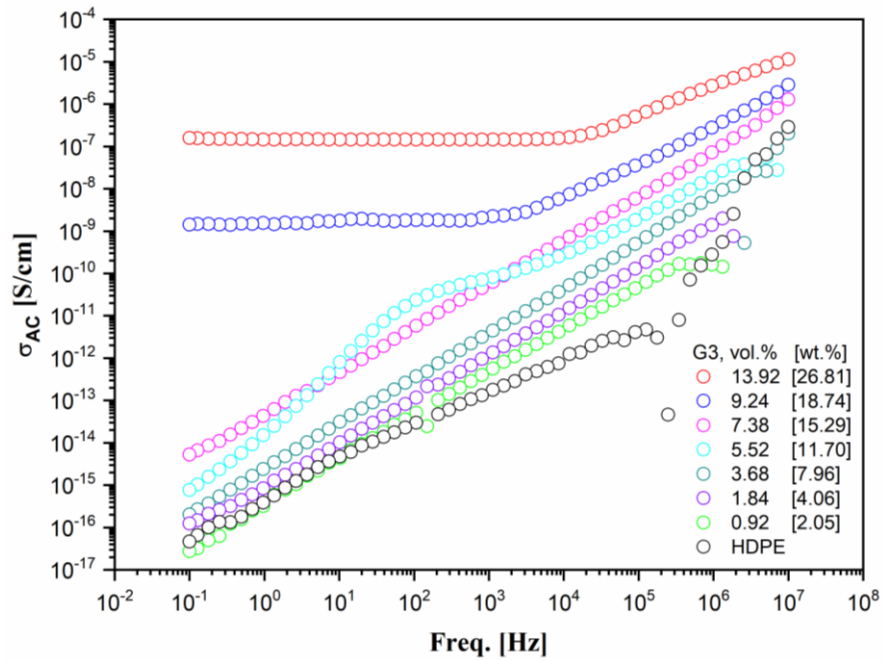


Figure 6.10 AC conductivity vs. frequency for the HDPE/G3 nanocomposites

Figure 6.11 shows the variation in the AC conductivity at 0.1 Hz for the pure HDPE and the HDPE/GnPs nanocomposites as a function of the GnPs content. The pure HDPE demonstrates a characteristic insulator material behavior with an electrical conductivity of 4.68×10^{-17} S/cm, which is typical for polymers. For all GnP loading, the HDPE/G1 nanocomposites are insulating, while it is clearly seen that at GnP concentrations higher than 11.70 wt.% (5.52 vol.%) for G2 and 15.29 wt.% (7.38 vol.%) for G3, the HDPE-based nanocomposites become conductive. The nanocomposites show the nonlinear increase in conductivity as a function of filler content. The HDPE/G2 and HDPE/G3 nanocomposites exhibit a characteristic S-shaped curves divided by three parts: insulating, transition and conducting (Mahmoud, 2011).

As seen in Figure 6.11, the electrical conductivity of the nanocomposites is approximately the same up to the percolation threshold for each type of the nanocomposite. As the GnP loading reaches this percolation threshold, there is an abrupt increase in the electrical conductivity because a conductive network is formed. The percolation threshold varies in terms of the sizes of GnPs, as mentioned by Bakir et al., (2018). The percolation thresholds of G2 and G3 are 11.70 wt.% (5.52 vol.%) and 15.29 wt.% (7.38 vol.%), respectively. However, the percolation threshold is not observed for HDPE/G1 nanocomposites. It should appear at higher concentrations. Nevertheless, with a filler concentration of 26.81 wt.% (13.92 vol.%), the electrical conductivity of the HDPE/G2 nanocomposite is approximately one order of magnitude higher than the that of the HDPE/G3 nanocomposites with the same filler content.

Furthermore, one of the most important parameters for the percolation threshold is the aspect ratio of the GnPs (Taherian, 2016). However, the aspect ratio is not the only important parameter. As described by Horny, Kanake, Chirtoc, & Tighzert (2016), for a given lateral size, an optimal thickness exists that gives the highest thermal conductivity. It could be assumed that it is also valid for electrical conductivity. Here the optimum value for thickness seems to be closer to 5-8 nm than 50-100 nm when comparing GnPs with the same lateral size (G1 and G3) because the lower percolation threshold is observed for G3 (Figure 6.11). It is worthwhile to mention that the

efficiency of G2 in enhancing the electrical conductivity of HDPE is even better than that of G1 and G3. Finally, compared to GnPs with the same thickness but different lateral sizes, GnPs with larger lateral sizes exhibit a lower percolation threshold and higher enhancement in the electrical conductivity, as they form a more easily conductive network and a better dispersion.

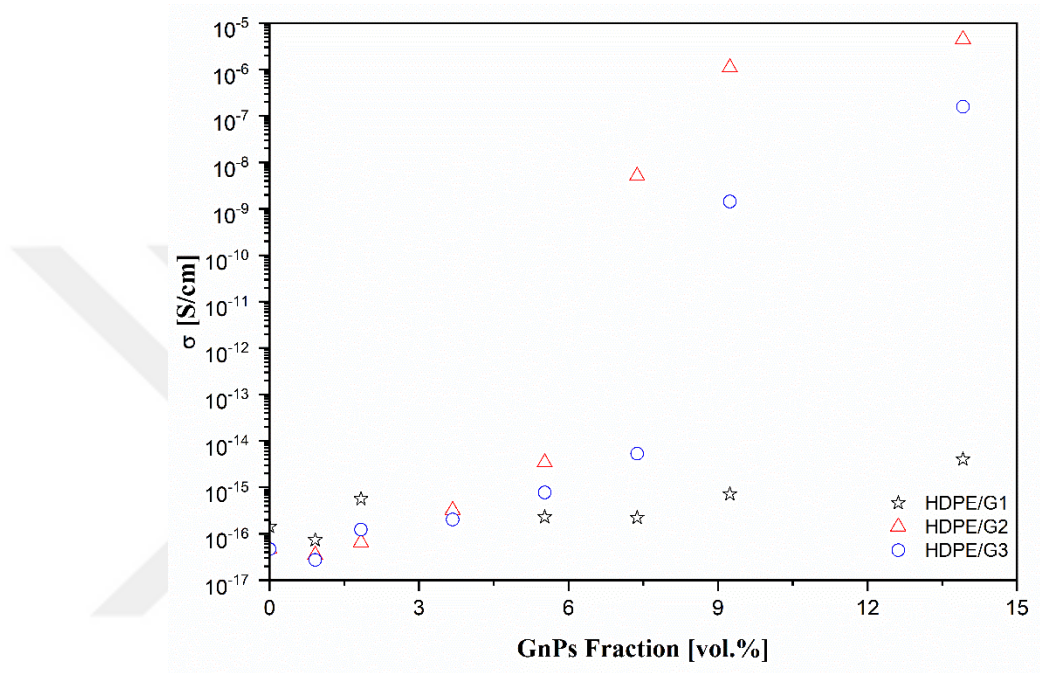


Figure 6.11 Electrical conductivity vs. vol.% of GnPs for the HDPE/GnPs nanocomposites

Our results are in agreement with those of Jun et al. (2018), who also found that the percolation threshold of the PP-based nanocomposites decreased with increasing lateral size of GnPs, while the thermal conductivity of samples increased. However, Imran et al. (2018) and Jiang & Drzal (2012) claimed that the percolation threshold values of the nanocomposites were almost the same regardless of the GnP size. Additionally, compared in terms of thickness, the nanocomposites with thicker GnPs have lower electrical conductivity due to poorer dispersion level, confirming the hypothesis of the existence of an optimum thickness for a given lateral size.

6.4.3 Thermal conductivity

The thermal diffusivity measurements were performed by the photothermal radiometry (PTR) method and the thermal conductivity ($k = \alpha\rho c_p$) of nanocomposites was calculated by combining the experimentally measured thermal diffusivity (α) data and the theoretical specific heat (c_p) and density (ρ) values. These theoretical values were determined by mixing law theory. c_{pm} and c_{pf} were taken as 1832.9 J/kgK (Evgin et al., 2016) and 700 J/kgK (Guan, Zhao, Wan, & Tang, 2018), respectively, and ρ_m and ρ_f were used as 964.9 kg/m³ (Evgin et al., 2016) and 2186.7 kg/m³ (Araby et al., 2014; Caradonna, Colucci, Giorcelli, Frache, & Badini, 2017; Potts, Dreyer, Bielawski, & Ruoff, 2011), respectively. The subscripts m and f refer to the matrix and filler material, respectively. The results of the relative thermal conductivity are given in Figure 6.12.

As a reference, the thermal conductivity of the pure HDPE is 0.386 W/mK (Evgin et al., 2016). In Figure 6.12, regardless of the GnP size, the thermal conductivity of nanocomposites increases linearly with the addition of GnPs due to the high thermal conductivity and large contact area of GnPs. No thermal percolation threshold is observed for all types of nanocomposites. The thermal conductivity enhancement is stronger in the HDPE-based nanocomposites with G2 than that with G1 and G3 at all GnP concentrations. For example, with GnPs content of 26.81 wt.% the thermal conductivity of the HDPE/G2 nanocomposite is 0.729 W/mK, while for the HDPE/G1 and HDPE/G3 nanocomposites, it is enhanced up to 0.521 W/mK and 0.625 W/mK, respectively. Therefore, G2 demonstrates a better enhancement of 89 % compared to pure HDPE, while G1 and G3 show improvement of 35 % and 62 %, respectively. Moreover, despite the high intrinsic thermal conductivity of GnPs, the thermal conductivities of the HDPE/GnPs nanocomposites increased moderately. The lower thermal conductivity enhancement than expected is mainly ascribed to the high interfacial thermal boundary resistance (TBR) between the HDPE matrix and GnPs fillers. It is known that the TBR, which is a physical parameter causes lower thermal conductivity by hindering phonon transfer between the HDPE matrix and GnPs fillers

(Kim et al., 2016; Pietrak & Winiewski, 2014; Shenogin, Xue, Ozisik, Keblinski, & Cahill, 2004).

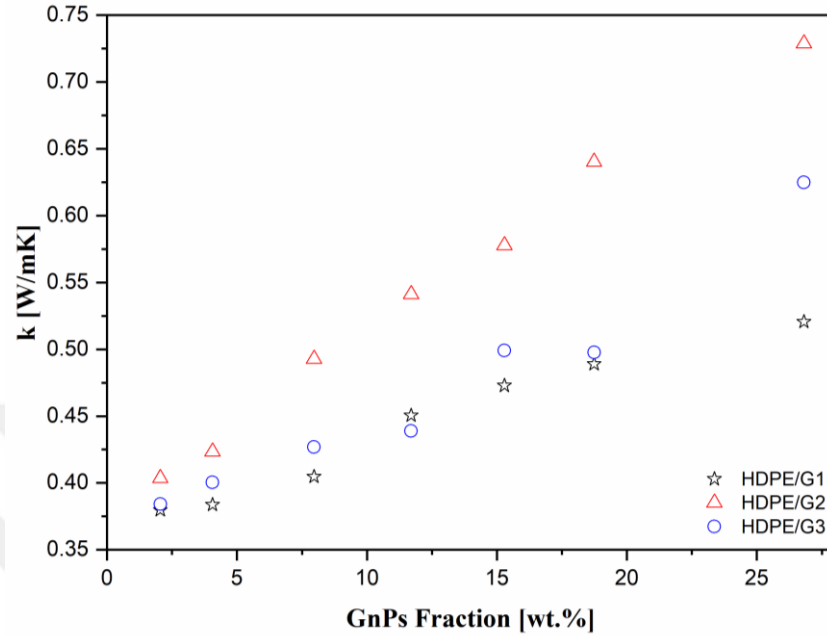


Figure 6.12 Thermal conductivity values of HDPE-based nanocomposites with G1, G2, and G3 fillers

Furthermore, GnPs with larger lateral sizes show a higher enhancement in the thermal conductivity. A similar lateral size effect of GnPs was also observed in (Chatterjee et al., 2012; Jiang & Drzal, 2012; Kim et al., 2016). One reason is that the fillers can more easily contact each other to create a more conductive network in the nanocomposites, resulting in a higher thermal conductivity (Jarosinski et al., 2017; Jiang & Drzal, 2012; Kim et al., 2016). Another reason is that a small lateral size increases the phonon scattering at the matrix-bonded interface, resulting in a lower thermal conductivity of nanocomposites (Kim et al., 2016). Additionally, for the same lateral size, G3 shows a slight enhancement of thermal conductivity compared to G1 (the enhancement becomes more effective for 13.92 vol.%). Based on the obtained results, it is suggested that, for a given lateral size, the maximum thermal conductivity is obtained at the optimum thickness of GnPs. For a fixed lateral size (5 μm), the optimum thickness is approximately 5-8 nm over 50-100 nm. The reason may be that thinner GnPs can couple well to the HDPE matrix and form a more effective thermal conductive network. However, Figure 6.12 displays that the thermal conductivity of

HDPE/G3 nanocomposites slightly decreased up to 2.05 wt.% of GnPs loading. The explanation is that G3 tends to aggregate, resulting in a decrease in the contact area between the HDPE and G3, as mentioned by Huang et al. (2018).

Subsequently, the enhancement in the thermal conductivity of the HDPE-based nanocomposites can be increased by optimizing the lateral size and thickness of GnPs at a fixed GnP concentration. Based on these results, the lateral size of GnPs is a more important parameter than the thickness of GnPs in terms of the thermal conductivity enhancement. The thermal conductivity of the nanocomposites with a larger lateral size can be further increased by forming a more effective thermal conductive pathway and reducing phonon scattering at the matrix-filler interface. In addition, to obtain the same thermal conductivity enhancement, larger amounts of thicker GnPs are required than thinner GnPs.

Consequently, as previously mentioned, it is clear that the highest enhancement in the electrical and thermal properties was achieved by the HDPE/G2 nanocomposites. The reason may be that G2 can establish a more effective conducting network and cause an increase in the filler contact. In addition, G2 with higher lateral size exhibits a better phonon diffusion mechanism along the conductive network.

6.4.4 Mechanical Properties

Following the electrical and thermal characterizations, Young's modulus of the pure HDPE and the HDPE/GnPs nanocomposites were given in Table 6.2. The Young's modulus of the nanocomposites increased with increasing GnP loading regardless of the GnP sizes. This may be due to the extraordinary Young's modulus of GnPs, their high aspect ratio, good dispersion and good interfacial adhesion between GnPs and HDPE, which restrict the polymer chain mobility under the load (Yasmin, Luo, & Daniel, 2006; Zakaria et al., 2017). The influence of GnP loadings increases the crosslink ratio and hinders the molecular motion of the matrix (Zakaria et al., 2017). When the GnP loading is 26.81 wt.%, the enhancements in Young's modulus of the HDPE/G1, HDPE/G2 and HDPE/G3 nanocomposites are 114.36 %, 168.21 %

and 184.58 %, respectively. The highest Young's modulus is achieved by the HDPE/G3 nanocomposites with an increment of up to 2.37 GPa. It can be seen that the Young's modulus value of the HDPE/G1 nanocomposites is the lowest, while the value of the Young's modulus of the HDPE/G3 nanocomposites is the highest.

Table 6.2 Young's Modulus of HDPE/GnPs nanocomposites (MPa)

GnPs Fraction [wt.%]	HDPE/G1	HDPE/G2	HDPE/G3
0.00	733.51±27.83	832.33±48.90	832.33±48.90
2.05	760.98±70.74	897.56±45.93	882.01±56.31
4.06	814.89±27.02	1018.75±63.17	1095.75±58.84
7.96	912.64±64.30	1204.32±41.75	1217.54±92.04
11.70	991.19±63.20	1465.32±82.19	1562.96±68.94
15.29	1205.86±86.52	1684.00±106.63	1819.77±46.70
18.74	1331.66±91.03	1891.91±64.85	1680.55±118.36
26.81	1572.34±163.98	2232.43±63.56	2368.63±278.40

Table 6.3 Tensile Strength of HDPE/ GnPs nanocomposites (MPa)

GnPs Fraction [wt.%]	HDPE/G1	HDPE/G2	HDPE/G3
0.00	34.61±1.32	34.96±2.01	34.96±2.01
2.05	35.70±1.27	33.93±2.06	28.41±2.76
4.06	34.97±0.70	28.78±2.18	29.53±0.70
7.96	28.92±1.46	29.52±0.74	30.92±0.28
11.70	28.53±0.28	30.80±0.74	32.28±0.55
15.29	29.24±0.76	33.57±0.45	33.78±0.64
18.74	30.16±0.30	34.82±0.57	32.99±0.53
26.81	32.42±0.35	37.57±1.03	35.25±0.16

Table 6.4 Elongation of HDPE/ GnPs nanocomposites (%)

GnPs Fraction [wt.%]	HDPE/G1	HDPE/G2	HDPE/G3
0.00	1656.40±137.38	1062.38±53.12	1062.38±53.12
2.05	1547.22±33.19	1031.54±49.37	527.95±486.35
4.06	1593.99±94.08	393.62±481.81	9.82±0.59
7.96	1189.83±86.65	9.31±0.32	9.96±0.85
11.70	10.49±0.29	9.02±0.52	7.27±0.50
15.29	9.53±0.33	8.94±0.11	6.46±0.31
18.74	8.71±0.30	6.00±0.23	6.30±0.30
26.81	7.50±0.24	5.65±0.24	5.05±0.30

The tensile strength of samples was given in Table 6.3. First, the tensile strength of the HDPE/G2 and HDPE/G3 nanocomposites decreases with increasing the GnP loading in the range of 0-2.05 wt.%, while the HDPE/G3 nanocomposites show a

decrement in the tensile strength in the range of 2.05-11.70 wt.% of GnPs. These decrements are approximately 18 % for the HDPE/G2 nanocomposites and 16 % for the HDPE/G3 nanocomposites for 2.05 wt.% of GnPs filler. Tensile strength depends on the filler content in a complex way (Mičušík, Omastová, Prokeš, & Krupa, 2006). The presence of filler can suppress the drawability of the polymer chains and increase the concentration of defects, what can then result in the decrease in tensile strength. On the other hand, the filler can reinforce the polymer matrix and this reinforcing effect is more obvious at higher concentrations (≥ 7 vol.%). The nonlinear behavior of tensile strength is then consequence of these effects. The tensile strength of the HDPE/G2 nanocomposites seems to be the highest among all HDPE/GnPs nanocomposites with 37.27 MPa and demonstrates an 8 % enhancement compared with the pure HDPE. On the other hand, the HDPE/G1 nanocomposite demonstrates a decrease of 6 % in the tensile strength, while the HDPE/G3 nanocomposite displays an increase of 1 % compared to the pure HDPE.

It is found that G3 with a smaller size and thickness (larger aspect ratio and surface area), shows an effective enhancement in the Young's modulus of nanocomposites owing to the fact that a larger surface area provides a more efficient stress transfer between GnPs and the HDPE matrix, while G2 with a larger size and thickness demonstrates an effective improvement in the tensile strength of nanocomposites because G2 achieves a better dispersion with less agglomeration as observed in the SEM images. According to the obtained results, the dispersion of GnPs in the HDPE matrix is a more important parameter for the tensile stress than others; however, the surface area of GnPs is a more critical factor. In the literature, a similar type of observation is made by Liang (2018), Liang et al. (2016) and Jun et al. (2018) where it was reported that GnPs with smaller lateral sizes are more favorable for enhancing the mechanical properties of PP-based nanocomposites.

6.4.5 Thermal Properties

6.4.5.1 DSC Results

The crystallization temperatures (T_c), melting temperatures (T_m), heat of fusions (ΔH_f) and crystallinity (X_c) of the pure HDPE and the HDPE/GnPs nanocomposites are given in Table 6.5. T_c for the pure HDPE is found to be equal to 116.30 °C whereas for all HDPE/GnPs nanocomposites, it increases by approximately 5 °C at 26.81 wt.% of GnPs content due to the nucleation effect of GnPs. It is clearly seen that T_m of all HDPE/GnPs nanocomposites ranges from 130.43 °C to 132.17 °C, which almost equals that of the pure HDPE (130.09 °C). For all samples, X_c first increases and then decreases with increasing the GnP content. This is due to a compromise between the nucleating and retarding effects of GnPs on the HDPE matrix, as mentioned by Jiang & Drzal (2012). It is clear that ΔH_f of all HDPE/GnPs nanocomposites decrease by approximately 25 % to the minimum value with 26.81 wt.% of GnPs loading. The crystallinity degree of the pure HDPE is ~70 % and increases up to ~71 % with 13.92 vol.% of G1 and G2 and up to ~72 % with 26.81 wt.% of G3. This increase is relatively inconsiderable considering the GnP content added to the HDPE matrix. These results clearly demonstrate that while there is a slight effect of the GnP loading on T_m and X_c , a significant effect on T_c and ΔH_f was observed. It can be observed that the size of GnPs induced little difference in these properties of the HDPE-based nanocomposites.

6.4.5.2 TGA Results

Meanwhile, the parameters of thermal stability predicted from TGA are given in Table 6.6 and TGA curves of the samples are shown in Figures 6A.12-15 in the Appendixes. Figures 6A.12-15 show that the pure HDPE and the three HDPE/GnPs nanocomposites all demonstrate a single-step thermal decomposition behavior between almost 440 °C and 500 °C, indicating that the increment of GnPs cannot affect the thermal decomposition behavior of the pure matrix. It is clear that the HDPE/GnP nanocomposites demonstrate better thermal stability than the pure HDPE. However, the thermal stability of the HDPE-based nanocomposites decreases at a low volume

fraction of GnPs. This may be due to agglomeration of GnPs in the polymer matrix (Jun et al., 2018). The agglomeration of GnPs may increase the molecular mobility and decrease the thermal stability of the polymer nanocomposites (Alam et al., 2019). Generally, the thermal stability of the nanocomposites is enhanced by increasing the content of GnPs for three GnPs with different sizes. This is attributed to the high thermal stability of the GnPs, the GnP shielding effect on the combustion gas diffusion into and out of the polymer during its thermal decomposition (Chatterjee et al., 2012), the barrier effect of GnPs, the removal of free radicals, which starts the polymer decomposition and uniform dispersion of GnPs (Jun et al., 2018).

Another reason is that the hindering influence of the GnP layers on the diffusion of small gaseous molecules along the HDPE-based nanocomposites (Aram, Ehsani, Khonakdar, & Abdollahi, 2018). Generally, $T_{5\%}$ (5 % weight loss of sample weight) is defined as the onset degradation temperature (Liang, 2018). $T_{5\%}$ of the pure HDPE is 440.77 °C, while this value increases to 461.05 °C, 459.45 °C and 457.16 °C, respectively, for the HDPE/G1, HDPE/G2 and HDPE/G3 nanocomposites. This shows that GnPs have a positive influence on the thermal stability of the HDPE-based nanocomposites (Aram et al., 2018). For three types of HDPE/GnP nanocomposites, T_{deg} (maximum weight loss) increases by approximately 11 °C compared to the pure HDPE matrix (478.79 °C). The addition of GnPs increases this temperature; however, the size and concentration of GnPs do not greatly influence T_{deg} . The residual mass of the HDPE-based nanocomposites increases with increasing GnP loading, which is attributed to the existence of a carbon net structure in the HDPE/GnP nanocomposites (Aram et al., 2018), because the initial thermal degradation temperature of GnPs is above 600 °C (Tarani et al., 2017). However, the size of GnPs do not have a significant effect on the $T_{50\%}$, T_{deg} and residual mass of the HDPE-based nanocomposites with GnPs, it only affects the $T_{5\%}$.

Table 6.5 DSC results of HDPE/GnPs nanocomposites

GNPs Fraction [wt.%]	T_m [°C]			T_c [°C]			ΔH_f [J/g]			X_c [%]		
	HDPE/G1	HDPE/G2	HDPE/G3	HDPE/G1	HDPE/G2	HDPE/G3	HDPE/G1	HDPE/G2	HDPE/G3	HDPE/G1	HDPE/G2	HDPE/G3
0.00	130.09	130.09	130.09	116.30	116.30	116.30	205.80	205.80	205.80	70.24	70.24	70.24
4.06	131.82	132.17	132.01	117.66	117.31	117.33	200.60	205.20	204.20	71.36	73.00	72.64
11.70	130.89	131.63	132.05	118.67	119.97	118.47	189.10	186.40	189.50	73.10	72.05	73.25
18.74	130.43	131.69	131.38	119.56	120.63	119.83	173.70	172.20	174.50	72.96	72.33	73.24
26.81	131.80	131.18	131.39	121.02	121.57	120.06	153.10	153.10	153.90	71.39	71.39	71.77

Table 6.6 The results of TGA analysis for the HDPE/GnPs nanocomposites

GNPs Fraction [wt.%]	$T_{5\%}$ [°C]			$T_{50\%}$ [°C]			T_{deg} [°C]			Residual Mass [%]		
	HDPE/G1	HDPE/G2	HDPE/G3	HDPE/G1	HDPE/G2	HDPE/G3	HDPE/G1	HDPE/G2	HDPE/G3	HDPE/G1	HDPE/G2	HDPE/G3
0.00	440.77	440.77	440.77	474.44	474.44	474.44	478.79	478.79	478.79	0.84	0.84	0.84
4.06	421.66	425.42	415.48	475.11	476.86	478.31	479.07	480.62	481.45	3.88	1.53	3.09
11.70	449.97	456.34	456.46	481.68	485.53	485.06	483.55	487.62	486.63	13.19	13.52	11.68
18.74	456.05	461.50	456.16	486.82	488.91	487.37	487.31	489.92	488.27	19.58	19.02	19.24
26.81	461.05	459.45	457.16	490.19	490.99	489.64	489.52	489.54	488.64	27.44	27.31	26.75

6.5 Conclusion

The HDPE-based nanocomposites with three types of GnPs (G1, G2 and G3) having different thicknesses and lateral sizes were prepared by a melt mixing and compression molding. The size effect of GnPs on the morphological, thermal, electrical, and mechanical properties of composites was studied. From the findings, we may conclude that;

- The small differences in the surface chemical composition of GnPs were detected by XPS, and the highest amount of oxygen was 2.6 at.% for G1.
- The findings from FTIR and XRD show that the addition and size of GnPs lead to a slight difference in the FTIR spectra of the nanocomposites compared to those of the pure HDPE, while the addition of GnPs affects the reflection peaks and peak intensity.
- Based on the SEM images, all GnPs show uniform and random dispersions in the HDPE matrix. In particular, G2 displays more GnP pathways, while G3 displays a worse distribution than the other two.
- The lateral size of GnPs is a more critical parameter for the thermal and electrical conductivity enhancement of nanocomposites than the thickness. Among all HDPE/GnPs nanocomposites, the thermal and electrical conductivities of the HDPE/G2 nanocomposites were the highest, with 0.729 W/mK and 4.46×10^{-6} S/cm, corresponding to ~89 % and ~11 orders of magnitude enhancement, respectively, compared to the pure HDPE.
- As examined in terms of the thickness, for a fixed lateral size, an optimum thickness is required to achieve the highest electrical and thermal conductivity.
- The percolation threshold varies significantly with the size of GnPs. G2 shows the lowest percolation threshold, and the nanocomposites with thinner GnPs exhibit lower percolation and higher electrical conductivity compared to those with thicker GnPs.
- G1 with a smaller lateral size and larger thickness (the lowest aspect ratio and surface area) shows the lowest enhancement in the Young's modulus and tensile strength due to worse distribution in the HDPE matrix and a less effective stress transfer between HDPE and GnPs.

- While a slight size effect of GnPs on the T_m , T_c , ΔH_f and X_c of the nanocomposites is observed, the addition of GnPs influences ΔH_f and T_c , however it does not affect T_m and X_c . In addition, the thermal stability of the nanocomposites increases with increasing GnP content, however, the size of GnPs only influences the $T_{5\%}$.

In summary, considering all the experimental measurements, G2 (larger lateral size) seems to be a more favorable type of GnPs to achieve the best enhancement in nanocomposite properties.



CHAPTER SEVEN

HYBRID NANOCOMPOSITES

7.1 Abstract

This chapter explains the synergic effect, weight ratio effect and size effect of GnPs and MWCNTs on the property enhancements of the HDPE-based nanocomposites. In order to obtain a better understanding of how the synergic effect of GnPs and MWCNTs on the property enhancement, first, the HDPE-based nanocomposites including GnPs and MWCNTs showing the best property developments were investigated. The results from Chapter 5 reveal that the MWCNTs with high aspect ratio (M12) exhibits better property enhancement of the nanocomposites than with low aspect ratio (M58). In addition, the results from Chapter 6 show that among three different dimensions of GnPs, the GnPs with highest later size (G2) demonstrate the best performance in enhancing the properties of HDPE-based polymer nanocomposites. Therefore, the various contents of M12 were added into the HDPE/G2 (11.70 wt.%) nanocomposites. Then, the HDPE-based hybrid nanocomposites including a total amount of 5 wt% carbon-based nano fillers were fabricated to determine optimum filler weight ratio and size which maximally enhance certain these properties and application possibility. The optimization of hybrid nanofillers combinations is done to synergistically enhance the properties using various types of GNPs and MWCNTs, and varied GnPs/MWCNTs (5/0, 4/1, 3/2, 2/3, 1/4 and 5/0). In order to study the size effect of GnPs and MWCNTs on the synergic effect of GnPs and MWCNTs, three types of GnPs, with varied lateral size and thickness, and two types of MWCNTs, with varied aspect ratio were utilized. In addition, to correctly interpret the synergic effect and size effect of hybrid nanofillers, the effect of used carbon-based nanofillers on the properties of HDPE-based nanocomposites were compared before commenting their synergic and size effects on the property enhancement.

The HDPE-based hybrid nanocomposites composed of 2D GnPs and 1D MWCNTs were manufactured by the melt mixing and compression molding method. The results

show that for the HDPE/G2(11.70 wt.)/M12 nanocomposites, there is no observed a distinct synergic effect on enhancing electrical properties, however the incorporation of M12 into the HDPE/G2(11.70 wt.%) nanocomposites cause increasing electrical conductivity and decreasing percolation threshold. For all types of HDPE-based hybrid nanocomposites, the electrical conductivity increases with increasing MWCNTs content in total nanofiller loading. In addition, the size and weight ratio of GnPs and MWCNTs has a strong effect on the electrical conductivity. The combinations of GnPs with large lateral size and MWCNTs with higher aspect ratio show the best enhancement of electrical conductivity. In terms of GnPs/MWCNTs weight ratio, although the highest electrical conductivity is achieved by 3/2 weight ratio of G3/M12, the best results are generally achieved by GnPs/MWCNTs weight ratio of 1/4.

The thermal conductivity of HDPE/G1(11.70 wt.)/M12 nanocomposites increases with the M12 content. The results indicate that there is a distinct synergic effect influencing thermal conductivity. The thermal conductivity of hybrid nanocomposites with 5 wt.% is influenced by the weight ratio of GnPs and MWCNTs and the sizes of GnPs and MWCNTs. For whole weight ratio, all hybrid nanocomposites exhibit a moderate thermal conductivity enhancement. In terms of thermal conductivity, three types of synergic effects, such as negative, positive and no synergic effect are observed. In case of hybrid nanocomposites with 5 wt.%, for all weight ratios, M12 is found be more beneficial than M58 to create conductive networks and obtain higher thermal and electrical conductivity values. The highest thermal conductivity (0.504 W/mK) is achieved by the HDPE/G2/M12 nanocomposites including 3/2 weight ratio for 5wt.% total filler content. The combination of GnPs with large diameter and MWCNTs with high aspect ratio is more effective to achieve greater thermal conductivity.

There is a distinct synergic effect between GnPs and MWCNTs in improving Young's modulus. However, the synergic effect of GnPs and MWCNTs on the tensile strength is observed for the hybrid nanocomposites with GnPs and M12. Additionally, there is no synergic effect in enhancing elongation. The weight ratio of GnPs and MWCNTs have non-linear effect on the Young's modulus, it does not lead to any

significant variation in the tensile strength and elongation. In addition, the size of GnPs and MWCNTs influences strongly on the Young's modulus, however slightly on tensile strength and elongation.

The coexistence of GnPs and MWCNTs leads to a slight or no variation in the crystallization behavior of the nanocomposites. In case of the HDPE/G2 (11.70 wt.%) / M12 nanocomposites and hybrid nanocomposites with 5 wt.% total nanofillers loading, the none of the thermal stability properties show any sing of synergic effect. However, their thermal stability increases with increasing MWCNTs content in the mixed.

7.2 Introduction

The polymer nanocomposites demonstrate a great potential in many applications due to their processability, better electrical and thermal conductivity (Zhang et al., 2018). However, as is known, to achieve high conductivities, the global aggregates of the networks and high filler contents of conductive particles are generally required. In addition, the incorporation of increasing amount of the filler materials improves the electrical and thermal conductivity of the nanocomposites by creating more conductive networks; however, the samples become porous and weak. It is clearly observed that the mechanical properties of the polymer nanocomposites reduce drastically at higher concentrations of the filler materials, generally higher than 15 wt.% (Szeluga et al., 2015). Additionally, high content of the filler materials increase the cost of polymer nanocomposites (Zhang et al., 2018). As a result, the low concentration and well-dispersion of the filler materials are necessary to obtain the desired properties. For this reason, there is an increasing interest on production of the carbon-based polymer nanocomposites with the aim of obtaining a low percolation threshold and high conductivity as well as maintaining the mechanical properties instead of the traditional conductive polymer composites with high filler loading (Szeluga et al., 2015).

As comparison of carbon-based filler materials, since the discovery of GnPs and MWCNTs, they have been attracted increasing attention as nanofiller material due to

their excellent properties. As mentioned in the previous chapter, the many studies in the literature have been reported that the addition of GnPs and MWCNTs enhance the properties of polymer nanocomposites, preparing polymer nanocomposites with desired properties is still a challenge due to some well-known difficulties. The main factors restrict the application of carbon-based polymer nanocomposites are:

- 1- the poor dispersion of the carbon-based nanofiller within the polymer matrix due to the van der Waals and π - π interaction, limiting the degree of realizing potential enhancements of the polymer nanocomposites,
- 2- the interface strength between the polymer matrix and nanofillers,
- 3- the high carbon-based materials costs. As is known, these are important parameters for the carbon-based polymer nanocomposite applications (Al-Saleh, 2015b, 2015a; Araby et al., 2015; Chatterjee et al., 2012; El Achaby & Qaiss, 2013; Yang et al., 2011).

As is known, favorable dispersion of the nanofiller materials in the polymer matrix is necessary to utilize the superior properties of properties (Chatterjee et al. 2012; Al-Saleh 2015) and the dispersion of GnPs and MWCNTs in the polymer matrix is an important challenges (Yuan et al., 2017). The several strategies, such as the use of hybrid nanofiller materials or the addition of surface-functionalized nanofiller material, have been suggested for the fabrication of polymer nanocomposites to further decrease undesired agglomerations and the filler loadings (Zhang et al., 2018).

The main objective of these strategies is to enhance the dispersion of carbon-based nanofillers in the polymer nanocomposites with maintaining their physical and electronic properties. Generally, the functionalization may lead to significant damage on the graphitic structure of the carbon-based nanofillers and loss of their intrinsic properties. Therefore, the use of hybrid nanofiller materials including two or more types of carbon-based nanomaterials with different geometries is one of the most effective methods. Using two geometrically different nanofiller materials, such as MWCNTs and GnPs, can provide the formation of a co-supporting network of the two nano filler materials and so a reduction in the amount of total filler materials (Szeluga

et al., 2015; Zhang et al., 2018). These network and layered structures of filler materials create uniform global conductive pathways in the polymer nanocomposites at relatively low concentration of filler materials. Hereby, these polymer nanocomposites also exhibit good mechanical properties as well as high electrical and thermal conductivity. (Szeluga et al., 2015).

When adding 2-D GnPs and 1-D MWCNTs simultaneously, they can form 3-D structures. It is known that the tortuous and long MWCNTs can act as a bridge between the adjacent GnPs layer and prevent their aggregation, which result in increasing the contact surface area between the polymer matrix and GnPs/MWCNTs structures. In the 3-D hybrid architectures, MWCNTs which behave as chelating arms entangle with the polymer chain to ensure stronger interaction between the polymer matrix and GnPs/MWCNTs minimizing the aggregation of nanofillers. As a result, the 3-D MWCNT/GnPs hybrid nanofillers show the highest influence in the improvement of thermal conductivity and mechanical properties among the individual graphene-based materials and MWCNTs (Al-Saleh, 2015c; Araby et al., 2015; Moosa et al., 2017; Szeluga et al., 2015; Yang et al., 2011). In other words, MWCNTs work additional to GnPs by creating the conductive network, in which MWCNTs behave as long nanocables to transfer stress and electrons while GnPs act as inter relationship sites between MWCNTs creating the local conductive network (Araby et al., 2015). The clear synergic effect on enhancing the dispersion of the hybrid (GnPs+MWCNTs) nanofiller materials makes them attractive to research the hybrid polymer nanocomposites increases rapidly (Jen & Huang, 2019).

In the literature, there are various studies on the hybrid nanocomposites with GnPs and MWCNTs reported based on a wide variety of polymers such as HDPE, LDPE, PC, PVDF, ABS, PVA and epoxy, etc. Table 1.3 in the Chapter One shows a comprehensive collection of published studies in this field.

Al-Saleh (2015a) studied on the microstructure, mechanical and thermal properties of the PP/GnPs/MWCNTs nanocomposites prepared by the melt mixing. They did not observe any synergic effect of hybrid nanofiller on the electrical conductivity.

However, they reported that the electrical conductivity of hybrid nanocomposites increased with the addition of MWCNTs. They claimed that this reason could be that MWCNTs bridge the gap between the adjacent GnPs. They showed that the PP/MWCNTs nanocomposites displayed better tensile strength and electrical conductivity as compared with the PP/GnPs/MWCNTs nanocomposites due to the better dispersion of MWCNTs and proper adhesion at the interface of PP/MWCNTs (Al-Saleh, 2015a).

Wegrzyn et al. (2015) investigated the morphology, thermal and electrical conductivity of the PP/GnPs/MWCNTs nanocomposites including various concentration of MWCNTs and GnPs that prepared by masterbatch dilution/mixing approach from the individual masterbatches PP/GnPs and PP/MWCNTs nanocomposites. They claimed that the melting enthalpy and melting point onset of the nanocomposites decreased linearly with addition of nanofiller materials and decrease in the thermal stability of the the PP/GnPs/MWCNTs nanocomposites exhibited. The synergic effect of GnPs/MWCNTs on the thermal properties of the nanocomposites was not observed. They explained that these reasons could be non-sufficient uniformity of nanofillers and decrease in the morphology effect with forming the hybrid system. They claimed that the enhancement of electrical properties could be related to the existence of two nanofillers with different geometry and to the possible existence of interconnected network of MWCNTs and GnPs. They observed a considerable decrease in the electrical conductivity when 1/1 ratio of GnPs/MWCNTs and this could be due to a statistical need of the existence of both nanofillers to obtain effective GnPs-MWCNTs bridging. They reported that except for this ratio, the electrical conductivity of nanocomposites increased with increase of MWCNTs loading in the amount of hybrid nanofillers, however, the electrical conductivity of the nanocomposites was lower than that of the nanocomposites with 1:1 ratio of GnPs/MWCNTs. They claimed that it appeared that 1-D MWCNTs was responsible for the formation of electrical charge paths inside the PP matrix. In addition, it was clear that the existence of a good distribution and interconnection of the agglomerates rather than an excellent MWCNTs network was necessary for higher the electrical conductivity (Wegrzyn, Galindo, et al., 2015).

Wang et al. (2018) studied on the synergic effect between GNPs and MWCNTs on the electrical and mechanical properties of antistatic HDPE-based nanocomposites. They claimed that the synergic effect rendered possible to considerably enhance the electrical properties by small amount addition of GNPs and MWCNTs and increased the probability of using GNPs in the industrial applications. In addition, the mechanical properties of composites slightly reduced due to the existence of unavoidable agglomerated MWCNTs and GNPs (Wang et al., 2018).

Paszkiewicz et al. (2018) reported that the electrical and thermal properties of the LDPE-based nanocomposites increased with increase in the concentration of the carbon-based nanofiller materials. Furthermore, the enhancement in the thermal stability and tensile properties was observed as the carbon-based nanofillers have been added into LDPE. However, they observed that the nanocomposites including only MWCNTs exhibit a greater enhancement in the electrical and thermal conductivity. They did not observe a synergetic effect when adding a mixture consist of two types of carbon-based nanofiller materials into LLPE matrix. However, the thermo-oxidative stability showed a considerable enhancement. The results of DSC analyses showed that the incorporation of less 10 wt.% of MWCNTs or MWCNTs+GNPs leads to no influence on the crystallization and melting temperatures (Paszkiewicz et al., 2018).

In summary, the literature includes many studies on the hybrid nanocomposites with carbon nanofillers. However, the subject of synergic effect of hybrid nanocomposites has still been discussed. Some of these studies exhibit the presence of the synergy mechanisms in the hybrid nanocomposites; however, others claim that there is no synergetic effect of hybrid nano fillers on the properties of the nanocomposites. In addition, it is known that the final properties of the hybrid nanocomposites may significantly depend on filler materials distribution, processing parameters, the concentrations, the particle geometry and structure of hybrid nanofillers, the interactions between the hybrid nanofillers, different crystallinity degree and ratios between MWCNTs and GNPs (Szeluga et al., 2015; Zhang et al., 2018). It is found that the relative ratio and geometry of filler in the filler mixture have

significantly influence on the final properties of the hybrid nanocomposites, despite of the fact that the mechanisms responsible for the synergetic effects have not been yet understood (Szeluga et al., 2015; Yuan et al., 2017). In addition, to the best of the authors' knowledge, none of these studies investigates the size effect of carbon-based nanofillers on the properties of the hybrid nanocomposites.

In view of all the shortcomings mentioned above, the aims of this chapter are to investigate synergic effect of two different dimensional carbon-based nanomaterials on the final properties of hybrid nanocomposites and to systematically research the synergic and size effect of carbon-based on the properties of hybrid nanocomposites at different weight ratios of GnPs/MWCNTs.

In this study, we used M12 as second filler materials for the HDPE/G2 nanocomposites prepared by melt mixing to investigate the synergic effect on the morphological, electrical, thermal and mechanical properties of the HDPE-based hybrid nanocomposites with MWCNTs and GnPs giving the best enhancement. Then, the morphological, electrical, thermal and mechanical properties of the HDPE-based hybrid nanocomposites including a total amount of 5 wt% carbon-based nano fillers with different sizes have been investigated experimentally to determine optimum filler weight ratio and size which enhance maximally these properties and application possibility.

7.3 Materials and Methods

Details about the used materials, production and characterization methods were explained in Chapter 4.

7.4 Results and Discussion

There have been many published studies on the properties of the polymer nanocomposites with MWCNTs or GnPs in the literature. However, making a comparison of GnPs and MWCNTs in terms of their performance is hard because the

processing method and/or conditions, filler size, filler compositions and measurement techniques vary commonly from case to case and they are significant factors in obtaining the final properties of the polymer nanocomposites (Han et al., 2019). Therefore, in this part, before interpreting the results of hybrid nanocomposites, the comparison between the HDPE/GnPs and HDPE/MWCNTs nanocomposites for each property were carried out in the terms of filler geometry to determine the best filler materials.

7.4.1 Characterization

7.4.1.1 XRD Results of Hybrid Nanocomposites

The XRD patterns of hybrid nanocomposites are given in Figure 7.1, 7.2 and Figures A7. 1-4 in the Appendix. As mentioned in the previous chapters, the XRD patterns of the pure HDPE show two sharp peaks displays at $2\theta=21.38^\circ$ and $2\theta=23.75^\circ$ and two weak at $2\theta=29.93^\circ$ and 36.13° , which are attributed to (110), (200), (210) and (020) reflection planes, respectively. As seen in Figure A7.1, while the pristine GnPs present a strong peak at $2\theta\sim 26.5^\circ$ and a week peak at $2\theta\sim 54.6^\circ$, corresponding to (002) and (004) carbon reflection, respectively, the pure MWCNTs demonstrate a two peaks at $2\theta=25.85^\circ$ and $2\theta=42.67^\circ$, which are attributed to (002) and (100) carbon reflection, respectively. It is known that a strong peak observed at $2\theta\sim 26^\circ$ is a characteristic peak for graphitic structure and as reported in the previous chapters, the size or aspect ratio of carbon-based structures does not have a significant influence of their crystalline structures. However, they only affect the peak intensity.

As seen in Figures 7.1 and 7.2, for all type of hybrid nanocomposites, it can be clearly observed that two sharp peaks and a weak peak appears at $2\theta\sim 21.4^\circ$, $2\theta\sim 26^\circ.4$ and $2\theta\sim 23^\circ.8$, respectively. After addition of MWCNTs and GnPs, two main characteristic peaks, which correspond to (110) and (200) reflection planes of the HDPE matrix, maintain almost the same. This shows that the adding GnPs and MWCNTS have not significant influence on the original crystal structure of the HDPE

matrix. The reason may be that there are no interactions and reactions among the matrix and filler materials. The similar behavior was observed by Wang et al. (2018).

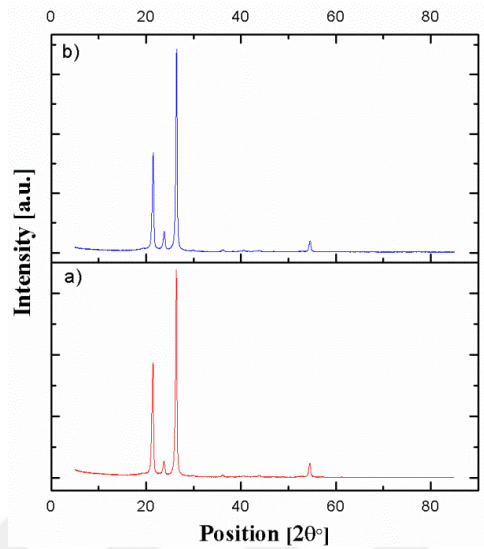


Figure 7.1 XRD patterns of the a) HDPE/G2 (11.70 wt.%)/M12 (0 wt.%) and b) a) HDPE/G2 (11.70 wt.%)/M12 (4 wt.%) nanocomposites

However, the intensity of peaks decreases compared to the pure HDPE, this can be explained that the crystallinity of HDPE may be influenced slightly by the presence of the carbon-based materials (Araby et al., 2015). As compared to the pure HDPE, the XRD patterns of the hybrid nanocomposites show a sharp extra peak at $2\theta \sim 26.4^\circ$, corresponding the (002) reflection plane from the structure of the graphitic layer, because of the addition of the carbon-based materials. However, if the total hybrid nanofiller loading including more GnPs, the peak at $2\theta \sim 54.5^\circ$ is more pronounced, if the total weight of hybrid nanofiller containing higher MWCNTs, the peak at $2\theta \sim 6.2^\circ$ is more distinct. It is clear from Figure 7.2 that the intensities of peaks which correspond to (002) and (004) crystal planes increase with increasing the amount of GnPs in the hybrid filler materials. One can seem that the type, size, and weight ratio of carbon-based nanofillers influence the diffraction intensity.

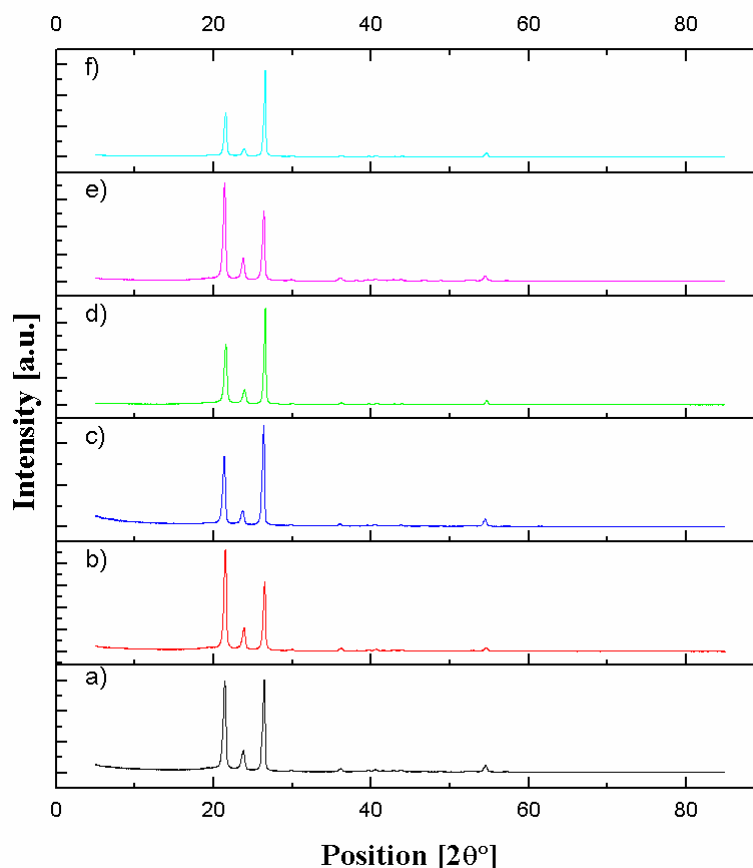


Figure 7.2 XRD patterns of the a)HDPE/G1/M12, b)HDPE/G2/M12, c)HDPE/G3/M12, d)HDPE/G1/M58 e)HDPE/G3/M12, f)HDPE/G2/M58 HDPE/G3/M58 nanocomposites (5wt.%) containing GnPs/MWCNTs of 1/4 weight ratio

7.4.1.2 FTIR Results of Hybrid Nanocomposites

The results of FTIR analysis for the hybrid nanocomposites are demonstrated in Figure 7.3, 7.4 and Figures A7.5-16 in Appendix. As mentioned in the previous chapters, the spectrum of the pure HDPE displays two strong peaks at 2914.86 cm^{-1} and 2847.37 cm^{-1} , corresponding to Alkyl (C-H) stretch vibrations and four weak peaks at 1472.59 cm^{-1} , 1462.11 cm^{-1} , 730.28 cm^{-1} and 718.84 cm^{-1} , assigning to the $-\text{CH}_2$ group binding vibrations (1472.59 cm^{-1} , 1462.11 cm^{-1}) and aromatic C-H bending (730.28 cm^{-1} and 718.84 cm^{-1}). However, GnPs and MWCNTs don't any peak corresponding to the functional groups on their surfaces. The spectrum of the hybrid nanocomposites is almost the same as that of the pure HDPE. It can clear from the results that the size, type and concentration of filler materials lead to insignificant

change in the characteristic peaks of the pure HDPE matrix. A slight change in the spectral pattern and intensity of these peaks may be attributed to the π - π interaction of the HDPE with GnP and MWCNTs.

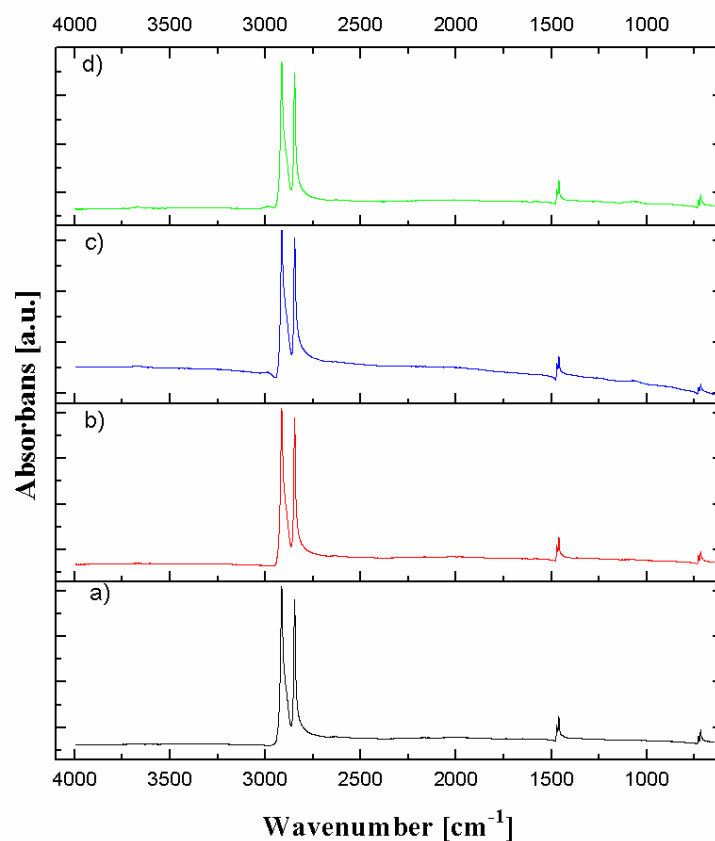


Figure 7.3 FTIR results of the a) HDPE/G2 (11.70 wt.%), b) HDPE/G2 (11.70 wt.%)/M12 (0.97 wt.%) c) HDPE/G2 (11.70 wt.%)/M12 (3.82 wt.%) and d) HDPE/G2 (15.82 wt.%) nanocomposites

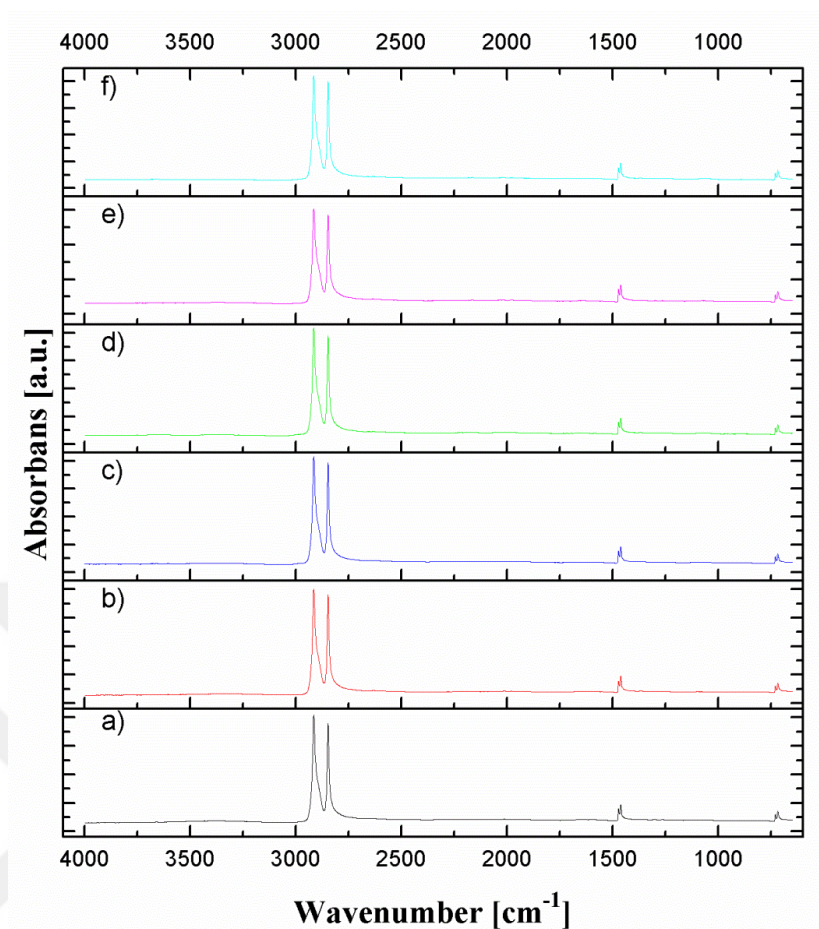


Figure 7.4 FTIR results of the a)HDPE/G1/M12, b)HDPE/G2/M12, c)HDPE/G3/M58, d)HDPE/G1/M58 e)HDPE/G3/M12, f)HDPE/G2/M58 HDPE/G3/M58 nanocomposites (5wt.%) containing GnPs/MWCNTs of 1/4 weight ratio

7.4.1.3 Morphological Results

To examine the effect of hybrid filler materials on the final properties of the polymer nanocomposites, the dispersion state of GnPs/MWCMTs hybrids with different weight ratios were initially studied. The dispersion of MWCNTs in HDPE was observed by SEM at two different magnifications. High magnification is used to clearly observe the networks and connection of GnPs and MWCNTs in the polymer nanocomposites and low magnification were used to make a clear observation of general dispersion of carbon-based nanofillers within the HDPE matrix.

7.4.1.3.1 Morphological Results of the HDPE/G2(11.70 wt. %)/M12 nanocomposites. Generally, in cases of hybrid polymer nanocomposites, 2-D GnPs and 1-D MWCNTs are connected with each other by forming a bridge network. For a better observation of this network, the SEM analysis was carried out for the HDPE/G2(11.70 wt. %)/M12 nanocomposites with maximum M12 loading (3.82 wt. %).

It is clearly seen in the SEM image with higher magnification (Figure 7.5) that MWCNTs can form a bridge between GnPs or/and the HDPE matrix and GnPs. Besides observing the formation of 3-D networks, there are observed voids/gaps in the polymer nanocomposites. SEM image with low magnification (Figure A7.17) shows that GnPs are randomly distributed within the HDPE matrix and it is difficult to clearly observe the MWCNTs particles due to the filamentous structure of HDPE.

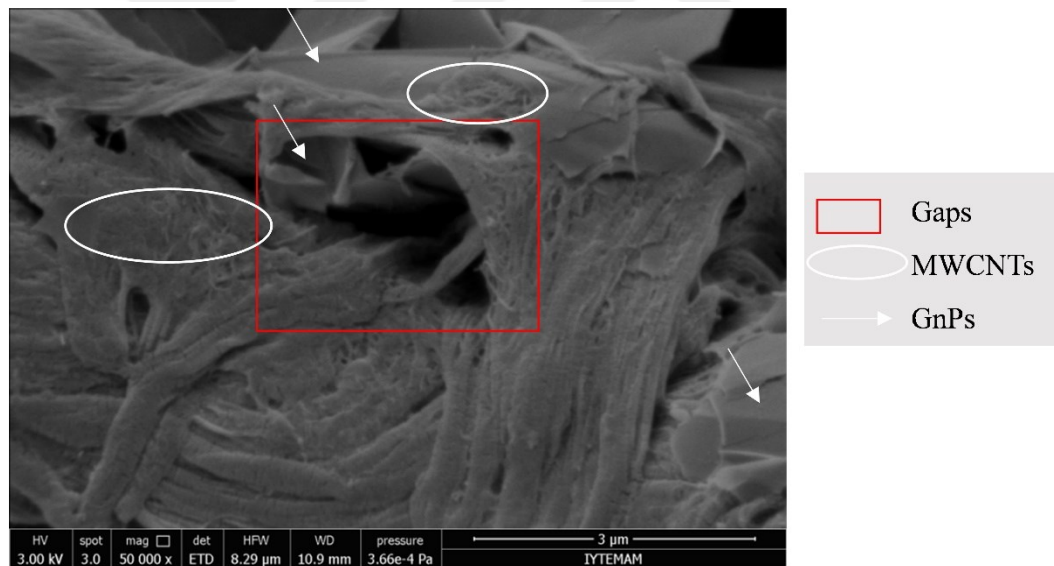


Figure 7.5 SEM image of the HDPE/G2 (11.70 wt. %)/M12 (3.82 wt. %) nanocomposites (50 000 ×)

7.4.1.3.1 Morphological results of the hybrid nanocomposites. As reported in the related parts of this chapter, the maximum electrical and thermal conductivity of hybrid nanocomposites are observed at 3/2 weight ratio of G3/M12 and of G2/M12, respectively. First, the dispersion of GnPs and MWCNTs in the HDPE matrix were investigated by SEM analysis. Generally, it is hard to obviously observe the MWCNTs. Therefore, the SEM analysis were carried out for the hybrid nanocomposites 1/4 weight ratio of GnPs/MWCNTs which general exhibit the best electrical conductivity enhancements.

High magnification SEM images of hybrid nanocomposites with 1/4 weight ratio of GnPs/MWCNTs are presented in Figures 7.6-11 and their SEM images with low magnification and the SEM images with two different magnifications of the hybrid nanocomposites with 3/2 of GnPs/MWCNTs ratio are shown in the Figures A7.17-35.

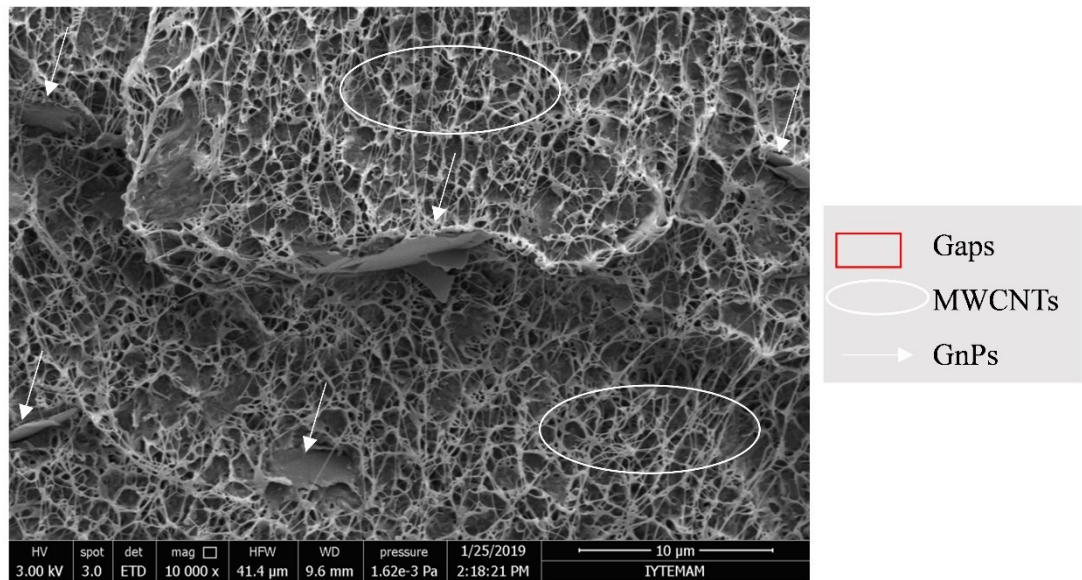


Figure 7.6 SEM image of the HDPE/G1/M12 nanocomposites with 1/4 weight ratio of GnPs/MWCNTs (5wt.%) (10 000 ×)

In case of the HDPE/G1/M12 nanocomposite, SEM micrographs with low (Figure A7.18) and high magnification (Figure 7.6) show that the MWCNTs can contact each other and form conducting networks. The GnPs is randomly dispersed and individually separated within the HDPE/M12 nanocomposites. It is clear that 2-D G1 and 1-D M12 can be contact with each other by forming a bridge network in the HDPE/G1/M12

nanocomposite with 1/4 weight ratio, indicating a good electrical conductivity. As seen in Figure A7.19, low magnification image shows that GnPs are separately and randomly distributed within the HDPE matrix and they cannot build up a full conducting pathway. It is difficult to obviously observe MWCNTs particles. They demonstrate the poor electrical conductivity of the HDPE/G1/M12 nanocomposites with 3/2 weight ratio. High magnification SEM image (Figure A7.20) displays that M12 aggregates can disperse between G1 particles.

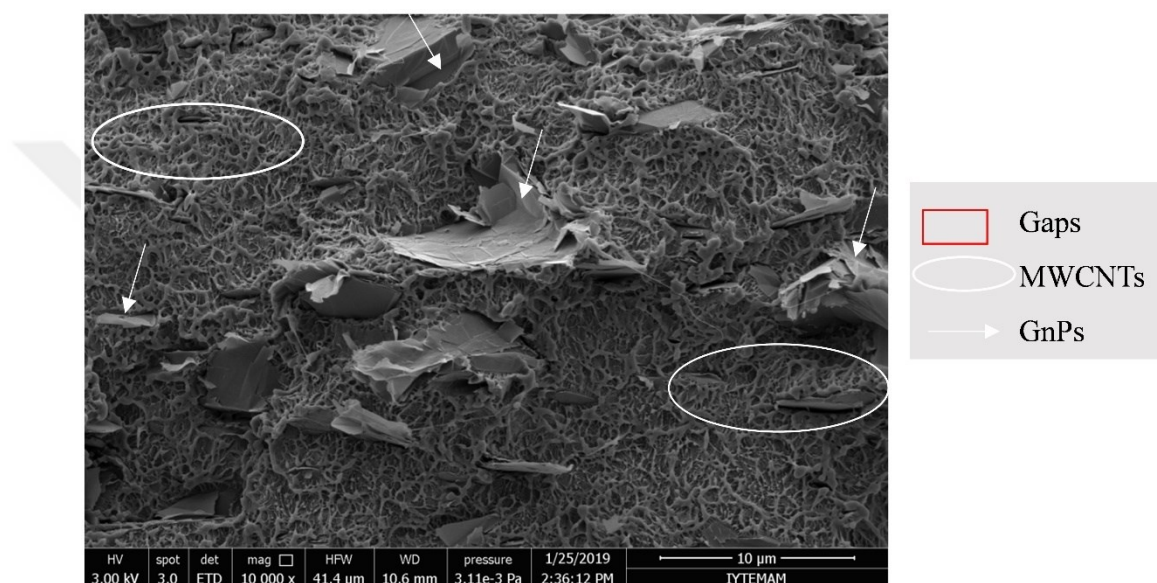


Figure 7.7 SEM image of the HDPE/G2/M12 nanocomposites with 1/4 weight ratio of GnPs/MWCNTs (5wt.%) (10 000 ×)

2-D GnPs and 1-D MWCNTs can connect with other by forming a bridge pathway in the HDPE/G2/M12 nanocomposite with 4/1 weight ratio, as seen Figure 7.7 and Figure A7.21 in Appendix. In other word, G2 and M12 can form an effective 3-D conducting network architecture. The HDPE/G2/M12 nanocomposite shows a reasonably dispersion of GnPs and MWCNTs in the HDPE matrix. It is found that there is a better compatibility and adhesion between the HDPE matrix and fillers. One can clearly see that the presence of both G2 and M12 particles, which indicates the excellent conductivity of the sample. However, in Figure A7.22, for the HDPE/G2/M12 nanocomposite with 3/2 weight ratio of GnPs/MWCNTs, the existence of both GnPs and MWCNTs cannot be clearly observed in the low

magnification SEM image. High magnification SEM image (Figure A7.23) indicates that some MWCNTs aggregate disperses between the HDPE matrix and HDPE.

In cases of the HDPE/G3/M12 nanocomposites (Figure 7.8 and Figure A7.24 in Appendix), MWCNTs can form effective conductive pathways. MWCNTs can bridge between GnPs layers. It is clearly seen that the carbon-based nanofillers cannot continuously dispersed, which are divided into HDPE-rich and filler-rich regions. For the HDPE/G3/M12 nanocomposites with 3/2 weight ratio of GnPs/MWCNTs, the 3-D conductive networks are observed in the low magnification (Figure A7.25). MWCNTs can behave as cheating arms to enhance the adhesion between the HDPE matrix and GnPs layers. High magnification image (Figure A7.26) shows that some M12 can disperse on the surface of G3 particles and some M12 aggregates can disperse between GnPs layers and/or HDPE matrix and GnPs.



Figure 7.8 SEM image of the HDPE/G3/M12 nanocomposites with 1/4 weight ratio of GnPs/MWCNTs (5wt.%) (10 000 ×)

In case of the HDPE/G1/M58 nanocomposites, the SEM observations (Figure 7.9 and Figure A7.27) are similar to that of the HDPE/G1/M12 nanocomposites. However, in Figure 7.9, small gaps are observed between G1 and M58 particles and these gaps display poorer compatibility and adhesion between GnPs and MWCNTs or HDPE matrix as compared to the combination of G1 and M12. This can lead to lower

conductivity of the samples. It seems in Figure A7.28-29 that the isolated MWCNTs are embedded into the GnPs layers. In all SEM images, some of the GnPs seems to be wrinkled in the nanocomposites.

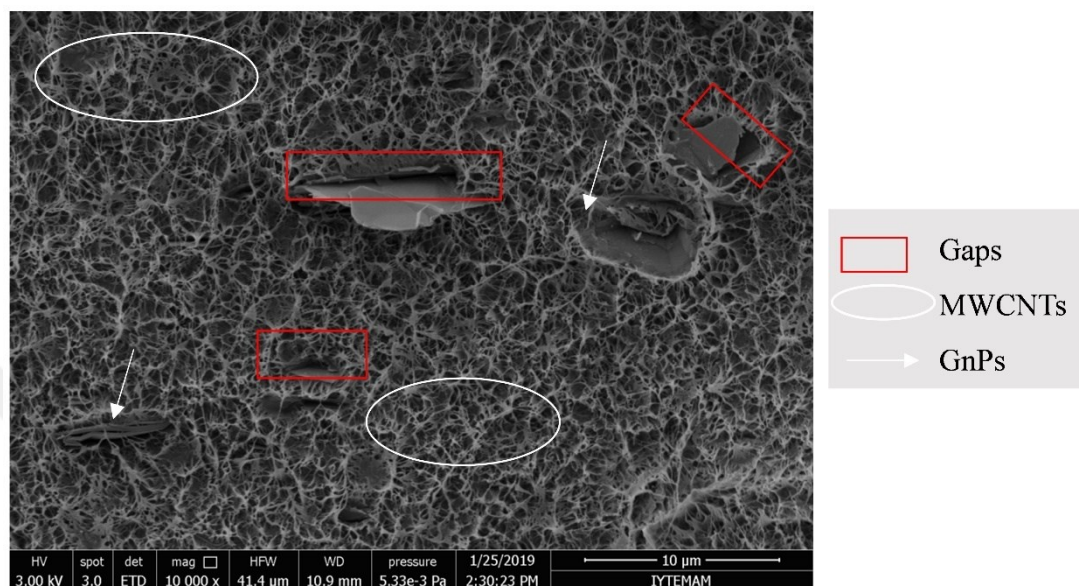


Figure 7.9 SEM image of the HDPE/G1/M58 nanocomposites with 1/4 weight ratio of GnPs/MWCNTs (5wt.%) (10 000 ×)

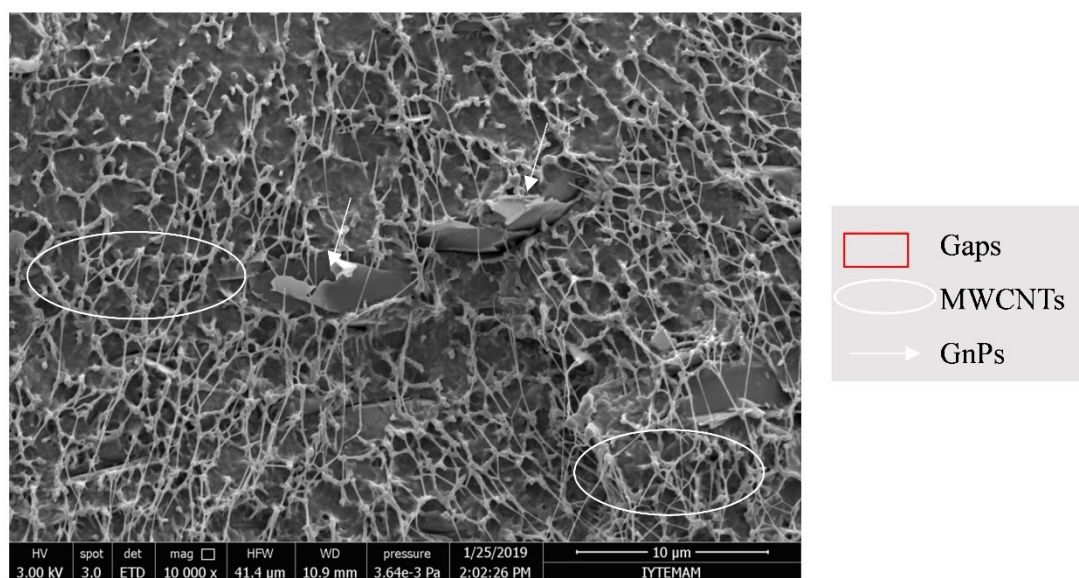


Figure 7.10 SEM image of the HDPE/G2/M58 nanocomposites with 1/4 weight ratio of GnPs/MWCNTs (5wt.%) (10 000 ×)

For HDPE/G2/M58 nanocomposite with 1/4 weight ratio of GnPs/MWCNTs (Figure 7.10 and Figure A7.30), it can be obviously observed the existence of both MWCNTs and GnPs. While MWCNTs can form a conductive network, GnPs can be randomly and separately dispersed throughout the HDPE matrix. Although these images confirm the formation of 3-D MWCNTs-GnPs-MWCNTs conducting network structure, SEM image with low magnification (Figure A7.30) displays additive-poor and additive rich regions. For HDPE/G2/M58 nanocomposite with 3/2 weight ratio of GnPs/MWCNTs, it is difficult to distinctly observe the MWCNTs and GnPs particle in the low magnification image (Figure A7.31), the agglomeration of GnPs and MWCNTs are observed in the high magnification image (Figure A7.32). It can be observed the GnPs-rich and MWCNTs-rich regions in the HDPE matrix. However, GnPs and MWCNTs aren't found to be interconnected each other in the HDPE matrix.

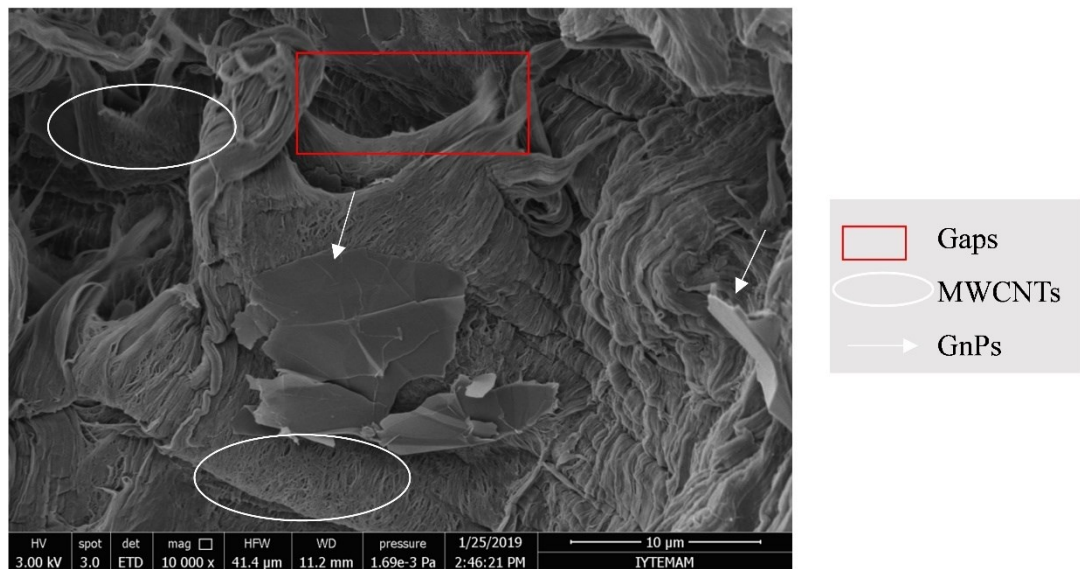


Figure 7.11 SEM image of the HDPE/G3/M58 nanocomposites with 1/4 weight ratio of GnPs/MWCNTs (5wt.%) (10 000 ×)

For the HDPE/G3/M58 nanocomposites with 1/4 weight ratio of GnPs/MWCNTs, low magnification image (Figure A7.33) displays the presence of both GnPs and MWCNTs in the nanocomposites, however, MWCNTs or GnPs can't contact each other and form a conductive network. High magnification image (Figure 7.11) show that some MWCNTs aggregates disperse between HDPE matrix and GnPs. Some MWCNTs –rich regions are observed in the nanocomposites. In cases of the

HDPE/G3/M58 nanocomposites with 3/2 weight ratio of GnPs/MWCNTs, it is difficult to clearly observe MWCNTs in the low magnification image (Figure A7.34) and GnPs are well dispersed in the HDPE matrix without forming any continuous conductive network structure. High magnification image (Figure A7.35) displays that some MWCNTs aggregates can disperse between the GnPs and matrix.

In conclusion, these findings display that:

1. Both GnPs and MWCNTs can be reasonably dispersed within HDPE matrix.
2. Generally, the GnPs are not excellent disk-shaped, they can be broken due to the melt mixing methods and lost their shapes.
3. Sometimes, in the low magnification, MWCNTs and/or GnPs cannot be clearly observed in the samples.
4. Generally, MWCNTs can contact each other and create a conductive network.
5. 2-D GnPs and 1-D MWCNTs can be contacted with each other by forming a bridge network in the hybrid nanocomposites. In other word, 3-D conductive network structure is generally formed.
6. It is clear that the dispersion of hybrid nanocomposites can be strongly based on the weight ratio of GnPs/MWCNTs, similar observation was made by (Ghaleb et al., 2017).
7. As the MWCNTs prevent aggregation of GnPs layers, GnPs improve the dispersion of MWCNTs.
8. The hybrid filler materials can increase contacting area between fillers and matrix.
9. The long MWCNTs can behave as cheating arms to improve adhesion between fillers and matrix.

7.4.2 Electrical Conductivity

The pure HDPE is an electrical insulating material with about 4×10^{-17} S/cm and exhibits a characteristic dielectric behavior corresponding to a linear increment in the

AC conductivity with the frequency. The HDPE-based nanocomposites exhibit a non-linear increase in the electrical conductivity with addition of carbon-based nanofillers and the electrical conductivity of nanocomposites is described by the percolation theory.

As it is known, the electrical conductivity of the polymer nanocomposites is influenced by the conductivity of matrix materials, type of filler materials, the properties of filler materials (such as surface area, length, diameter and conductivity), and the dispersion of the filler materials within the polymer matrix. In addition, the used preparation process and the matrix materials are the factors affecting the percolation threshold (Barrau et al., 2003). To determine the effect of MWCNTs and GnPs sizes on the synergic effect as well as to investigate their synergic effect on the properties of hybrid nanocomposites, as mentioned above, all parameters are the same during the preparation of the hybrid nanocomposites.

7.4.2.1 Comparison of electrical properties of the HDPE/GnPs and HDPE/MWCNTs nanocomposites

It can be seen in Figure 7.12 that the HDPE-based nanocomposites with MWCNTs exhibit considerably higher electrical conductivity and lower percolation threshold than that of the HDPE/GnPs nanocomposites. In the other word, MWCNTs have higher efficiency than that of GnPs in enhancing the electrical properties. As mentioned in the previous chapters, M12 exhibits the highest electrical conductivity among all carbon-based filler materials, while G2 shows best performance among GnPs nanofillers. The HDPE/M12 nanocomposite has the lowest percolation threshold value (1.43 vol%) with the electrical conductivity of 5.08×10^{-3} S/cm. For all filler concentration, MWCNTs give better electrical properties. For example, as a content of 18.74 wt. %, HDPE/M12 nanocomposite presents a conductivity value of 5.08×10^{-3} S/cm, which is almost 10^{13} orders of magnitude higher than the value of the HDPE/G1 nanocomposite (7.20×10^{-16} S/cm).

It is known that the intrinsic electrical conductivities of MWCNTs and GnPs are approximately similar. The difference can be attributed following (Al-Saleh, 2015a; Du et al., 2011):

- 1- It can be said that the morphology of filler materials can significantly influence on the electrical properties of the nanocomposites. It is clear that 1-D MWCNTs can form more stable and effective conductive network because of their structure.
- 2- GnPs aggregate more easily than MWCNTs because of the plane to plane contact area and larger surface area of GnPs.
- 3- The possible rolling, wrinkling, and crimping decrease the aspect ratio of GnPs.
- 4- There are several contact types between GNS in the polymer composite: edge to edge (parallel or cross), edge to plane and plane to plane; it is considered that the plane to plane contact was helpful for the electrical transport among these contact types; whereas the essential way in the electrical transport is the overlapping contact among CNTS which provided a high conductivity.
- 5- The contact resistance between the particles of GnPs may be higher than between the particles of MWCNTs.
- 6- It is difficult that GnPs with 2-D structures engaged each other in a conductive network than MWCNTs with 1-D structures. Thus, the GnPs/polymer composites have a very lower electrical conductivity than theoretically expected and higher percolation threshold than the MWCNT/polymer composite (Du et al., 2011).

Our observations are similar to those made by Martin-Gallego et al. (2013), Du et al. (2011), Paszkiewicz et al. (2018) and Dul et al. (2018). Martin-Gallego et al. (2013) reported that the morphology of filler materials can affect both the final properties and processing of the polymer nanocomposites. As comparing the HDPE/MWCNTs and HDPE/GnPs nanocomposites, the HDPE/MWCNTs nanocomposites indicate much lower percolation threshold and higher electrical conductivity than the HDPE/GnPs nanocomposites.

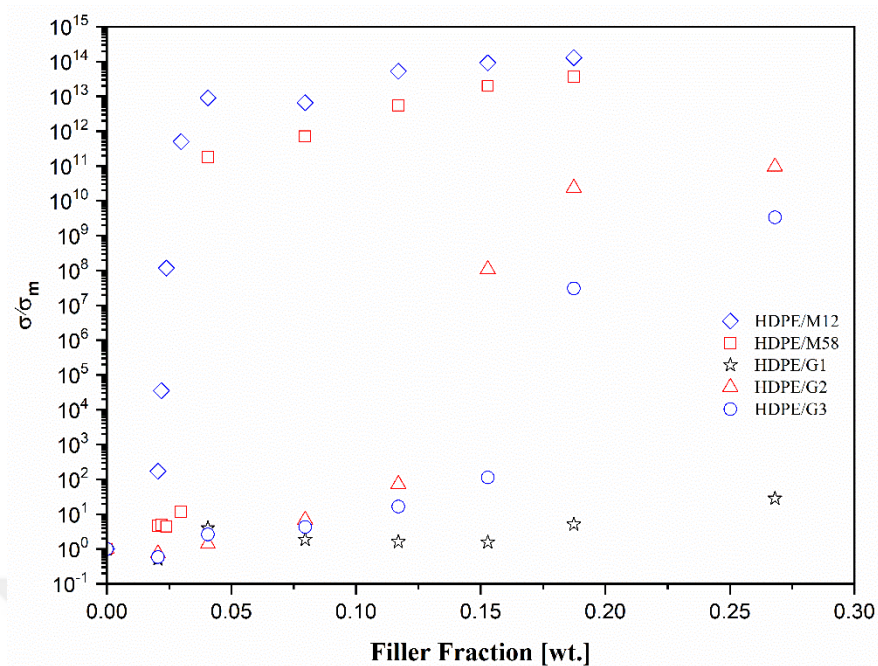


Figure 7.12 Relative electrical conductivity vs. wt.% of filler fraction for the HDPE/MWCNTs and HDPE/GnPs nanocomposites

7.4.2.2 The Electrical conductivity of the HDPE/G2 (11.70 wt.%)/M12 nanocomposites

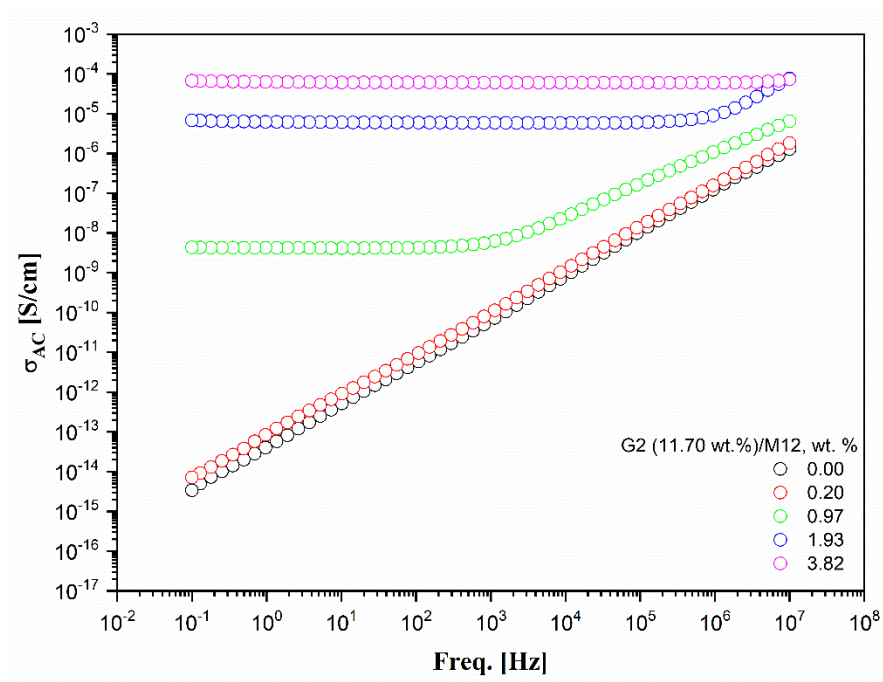


Figure 7.13 AC conductivity vs. frequency for HDPE/G2 (11.70 wt.%)/M12 (3.82 wt.%) nanocomposites

It is clear from Figure 7.13 that the AC conductivity depends on the frequency in whole range of frequency for 0 and 0.2 wt.% of MWCNTs loadings and this is a typical behavior for insulating materials. This behavior, which corresponds to a linear increase in the AC conductivity with increase in the frequency, is due to fact that many isolated MWCNTs behave as nanocapacitors (Mosnáčková et al., 2015).

When the hybrid nanocomposites including 0.97 or 1.93 wt.% of MWCNTs contents, up to a critical frequency, a frequency independent region of the AC conductivity is observed and the AC conductivity displays a significant increase at low frequency region, resulting in the onset of the formation of percolating structure (Khurram et al., 2015). This behavior of the AC conductivity of the polymer nanocomposites may be explained by electron hopping and tunneling mechanism. The electrical conductivity of the nanocomposites is directly proportionate to the rate of the electron hopping and tunneling. The conducting pathways of MWCNTs-GnPs-MWCNTs or GnPs-MWCNTs-GnPs in the HDPE/G2 (11.70 wt.%)/M12 increase with increase in the MWCNTs loading that causes an increment in the rate of electron hopping and/or tunneling (Maiti & Khatua, 2016). After the critical frequency, the AC conductivity increases with the increase of frequency. Frequency-independent region extends to higher frequency and the AC conductivity of the HDPE/G2 (11.70 wt.%)/M12 nanocomposites increase with increasing the MWCNTs loading.

For HDPE/G2 (11.70 wt.%)/M12 nanocomposites with 3.82 wt. % of MWCNTs, the AC conductivity is independent from the frequency. This may be explained by the formation of a full conductive network rather than a change in the concentration of the electric conductors (Szeluga et al., 2015). The addition of 3.82 wt.% M12 to the HDPE/G2 (11.70 wt.%) nanocomposite increases the AC conductivity from 3.41×10^{-15} to 6.76×10^{-5} S/cm.

It is known that the conductivity at $f=0.1$ Hz is taken for the DC conductivity. Figure 7.14 displays that the DC conductivity of the HDPE/G1(11.70 wt.%)/M12 nanocomposites with different concentration of M12 (0.20 wt.%, 0.97 wt.%, 1.93 wt.%)

and 3.82 wt.%). One can see that the electrical conductivity of hybrid nanocomposites increases with increase of M12 loadings. A polynomial increase in the conductivity is observed. The reasons of this increase may be that can be regarded as the conductivity evolution of the polymer nanocomposites and is due to an interconnected structure formation of filler materials. A high percentage of electrons are allowed to flow through the nanocomposites because of the formation of an interconnecting conductive pathway along the network of filler materials (Špitalský et al., 2009).

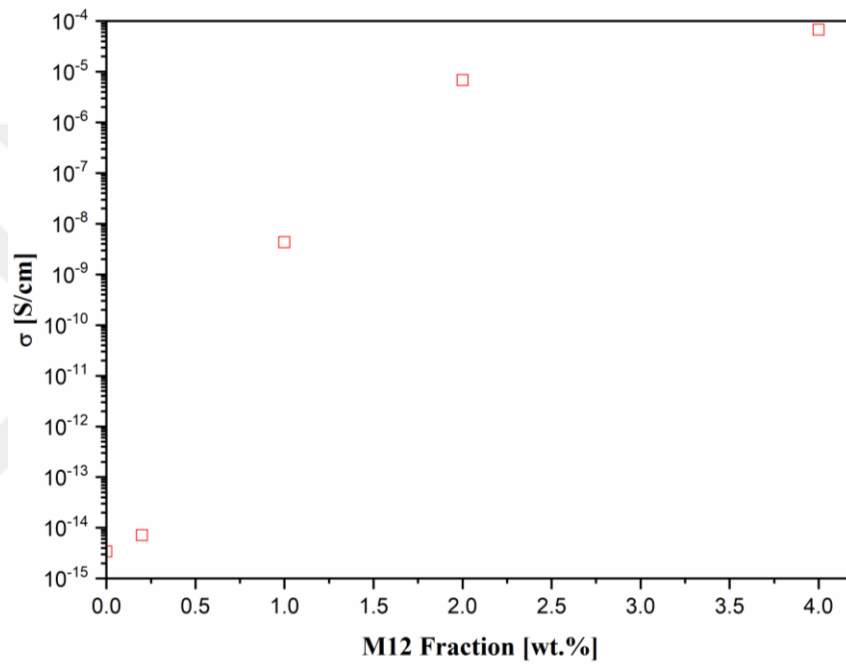


Figure 7.14 Electrical conductivity vs. wt.% of MWCNTs for the HDPE/G2 (11.70 wt.%)/M12 nanocomposites

When addition of 0.2 wt.% M12 into HDPE/GnPs nanocomposite, the DC conductivity of the hybrid nanocomposites is 7.13×10^{-15} S/cm. This value is nearly similar to the electrical conductivity value of the HDPE/GnPs nanocomposites with 11.70 wt.% loading of GnPs (3.41×10^{-15} S/cm) and two orders of magnitude higher than that of pure HDPE (5.84×10^{-17} S/cm). It is clear that the HDPE/G2 (11.70 wt.%)/M12 nanocomposites including 0.2 wt.% of M12 loading is still insulating. Because the electron tunneling gap is lower than the distance between adjacent filler materials and the continuous conducting network within the HDPE matrix is not formed (Al-Saleh, 2015a).

It can be seen that a significant increase in the electrical conductivity of nanocomposites is observed in the range of 0.20 and 0.97 wt.% of M12 loadings. The DC conductivity of HDPE/G2 (11.70 wt.%)/M12 nanocomposites further improves with increasing M12 loading in hybrid nanocomposites. The electrical conductivity of the HDPE/G2 (11.70 wt.%)/M12 nanocomposites is increased to 6.76×10^{-5} S/cm when addition of 3.82 wt.% of M12. This value is almost four orders of magnitude higher than that of the HDPE/G2 nanocomposite with the same total concentration (5.1×10^{-9} S/cm), however one order of magnitude lower than that of the HDPE/M12 nanocomposite. This shows that more continuous conducting pathways are formed in the HDPE matrix with increasing M12 loadings. Therefore, the electrical conductivity of the polymer nanocomposites is gradually increased with increase of M12 content in the polymer composites due to a π - π interaction throughout HDPE matrix and the formation of more GnPs-MWCNTs-GNPs conductive pathways, as seen in SEM images.

The percolation threshold for the HDPE/G2 (11.70 wt.%)/M12 nanocomposites is somewhere between 0.2 and 0.97 wt.% of M12 loadings, i.e it is between 11.90 and 12.67 wt.% of total hybrid filler materials. This value is at least 25 % lower than the percolation threshold of the HDPE/G2 nanocomposites.

The findings indicate that the conductivity of the HDPE/G2 (11.70 wt.%) nanocomposites with MWCNTs is not only several orders of magnitude higher than that of the HDPE/G2 (11.70 wt.%) nanocomposites, but also they percolate at lower filler concentration. As the addition of M12 material into the HDPE/G2 (11.70 wt.%) nanocomposites, which results in a hybrid nanocomposite, the space between the conductive filler materials is decreased creating a percolated structure with easy and reducing the electrical percolation threshold. This theory is defined as free volume theory and the final electrical conductivity of the hybrid nanocomposites is not based on the electrical conductivity of second filler material but its aspect ratio (Garzón & Palza, 2014). In the hybrid nanocomposites, MWCNTs are linked to GnPs and from

the conductive network at a much lower filler fraction. The reasons of this low filler loading are that (Araby et al., 2015; Jeong & An, 2014):

- 1- 1-D MWCNTs which are shortened by the melt mixing can promote GnPs dispersion in the HDPE matrix by increasing the viscosity of matrix leading to a higher shear stress degree and
- 2- a high aspect ratio of MWCNTs is favorable to form a co-supporting conductive pathways, in which MWCNTs behave as electrically conductive nanocables with GnPs serving as interconnections.
- 3- The number of the physical contacts between MWCNTs and GnPs increases with increasing the relative MWCNTs concentration in the mixed GnPs-MWCNTs and hereby the electric charges can transfer more effectively throughout the pathways of interconnected MWCNTs and GnPs for the HDPE-based nanocomposites.

Summary, a teamwork between 1-D MWCNTs with high aspect ratio and 2-D GnPs with great surface area forms a conductive network in the polymer nanocomposites

It is clearly seen that the addition of M12 into the HDPE/G1 (11.70 wt.%) nanocomposites leads to increase in the conductivity and decrease in the percolation threshold, however there is not observed any synergic effect between M12 and G2. This can be due to fact that M12 and G2 forms a less effective continuous conducting network that facilities the electron movements than only M12.

7.4.2.3 The Electrical conductivity of the HDPE-based hybrid nanocomposites

As seen in Figure 7.15, at 5 wt% of total filler content (GnPs+MWCNTs), the AC conductivity increases with increasing the ratio of MWCNTs in the total filler content. The AC conductivities of the nanocomposites with 5/0, 4/1 and 3/2 of GnPs/MWCNTs weight ratios show strongly dependence on the frequency in the range of 0.1-10⁷ Hz. The nanocomposites with 2/3 of GnPs/MWCNTs weight ratio demonstrates an AC conductivity of 3.22×10⁻⁷ S/cm, which is an enhancement of 7 orders of magnitude

over the AC conductivity of the nanocomposites with 3/2 of GnPs/MWCNTs weight ratio (1.03×10^{-14} S/cm).

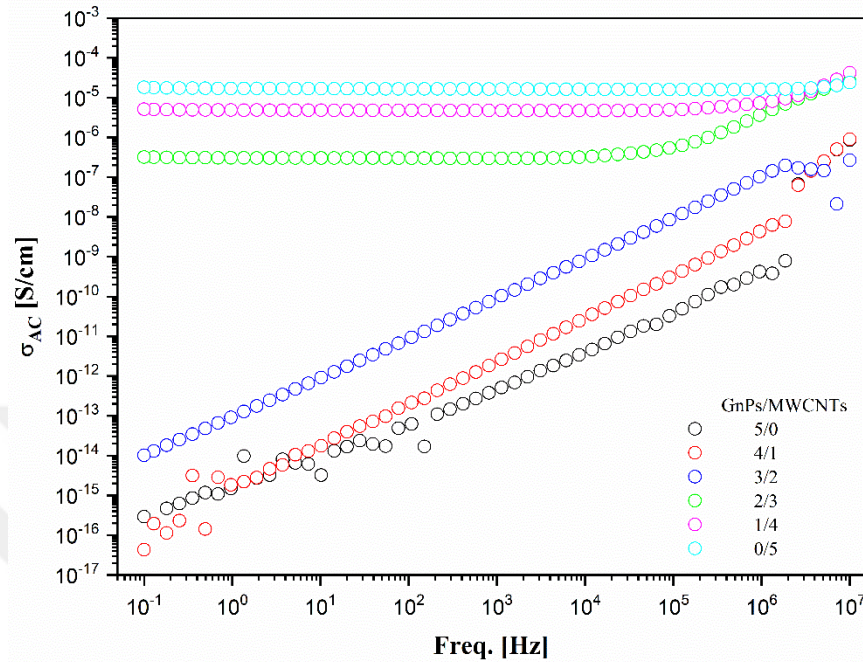


Figure 7.15 AC conductivity vs. frequency for HDPE/G1/M12 nanocomposites (5 wt.%)

The dependence of AC conductivity on the frequency for nanocomposites with GnPs/MWCNTs weight ratio of 1/4 and 2/3 shows two different behaviors: In the low frequency region (below the critical frequency), the AC conductivity does not change with increase in the frequency because of gradual formation of the conductive network. In the high frequency (above the critical frequency), the AC conductivity shows a nearly linear increase with increasing the frequency in a log-log scale. This critical frequency is broadened to higher frequency with increase in MWCNTs loading in total filler content. The AC conductivity for nanocomposites with GnPs/MWCNTs weight ratio of 5/0 is independent of the frequency.

Figure 7.16 displays the AC conductivity response of the HDPE/G2/M12 nanocomposites with different weight ratio of GnPs to MWCNTs as a function of frequency at the room temperature. The AC conductivity of the HDPE/G2/M12 nanocomposites with GnPs/MWCNTs weight ratios of 5/0, 4/1 and 3/2 represents a strong dependence on frequency. It increases with increasing the frequency. This

behavior is a characteristic of insulator. The electrical conductivity of these hybrid nanocomposites is close to that of the pure HDPE (1.42×10^{-16} S/cm). For the HDPE/G2/M12 nanocomposites with GnPs/MWCNTs weight ratio of 2/3, in the AC conductivity spectra, two distinct regions are observed; first one is the plateau region (the frequency independent region), the second one is dispersion region, in which the AC conductivity increases with increase in the frequency. For the HDPE/G2/M12 nanocomposites with GnPs/MWCNTs weight ratios of 1/4 and 0/5, the AC conductivity of samples becomes independent of frequency, i.e. –full conductive.

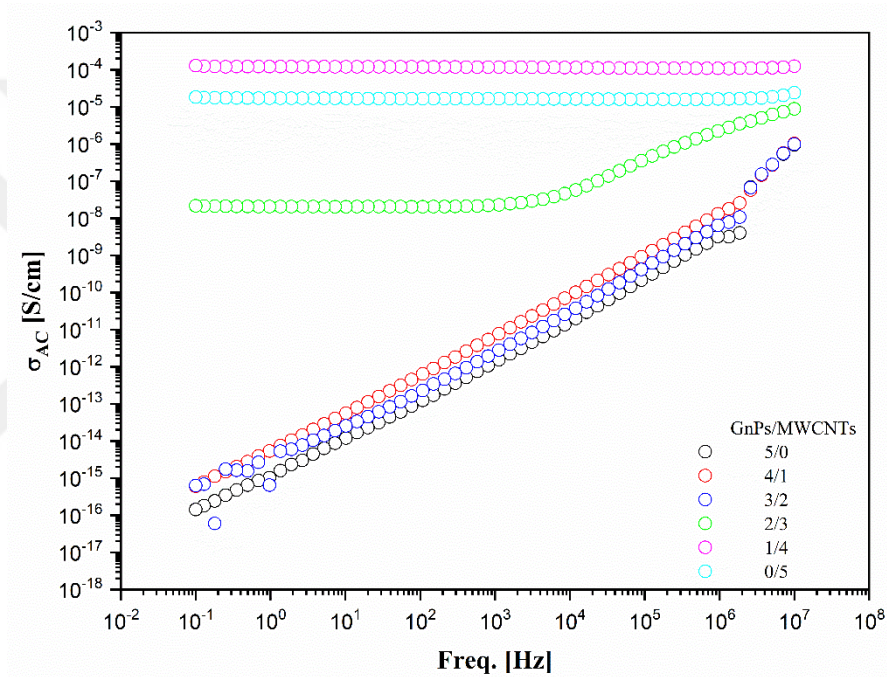


Figure 7.16 AC conductivity vs. frequency for HDPE/G2/M12 nanocomposites (5 wt.%)

As seen in Figure 7.17, the AC conductivity of the HDPE/G3/M12 nanocomposites with GnPs/MWCNTs weight ratios of 5/0 and 4/1 increases with increasing the frequency, i.e. they display the frequency-dependent conductivity. the AC conductivity of these nanocomposites remains at about the same level as the HDPE matrix ($\sim 10^{-16}$ S/cm). While the AC conductivity values of the HDPE/G3/M12 nanocomposites with GnPs/MWCNTs weight ratios of 2/3 and 0/5 are almost constant in the investigated frequency range. For the HDPE/G3/M12 nanocomposites with GnPs/MWCNTs weight ratios of 3/2 and 1/4, the AC conductivity shows two distinct regions: the low frequency region where the AC conductivity is found to be almost

constant at a value exhibiting frequency-independent and the high frequency region where the AC conductivity increases linearly with the frequency.

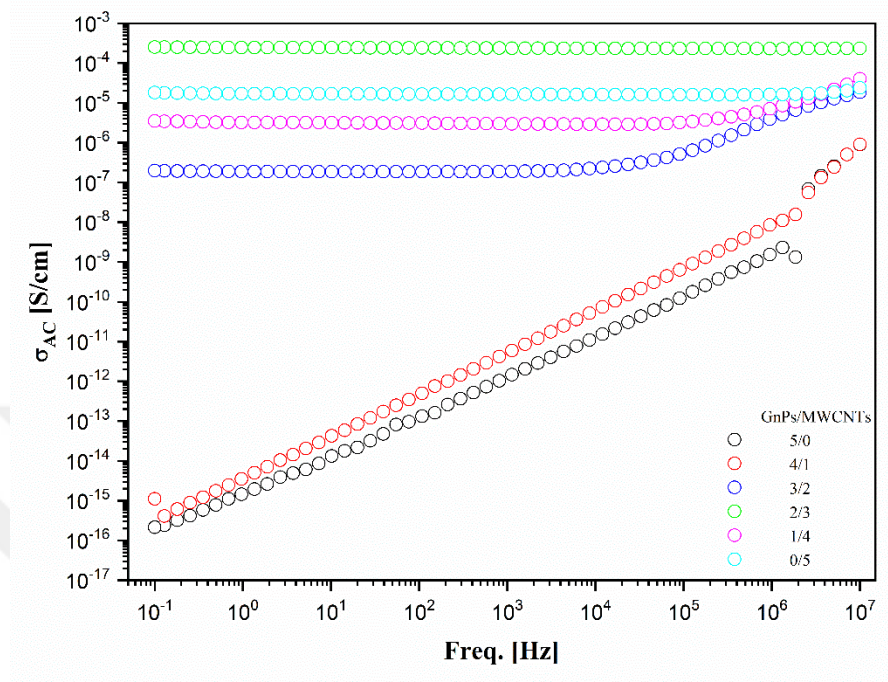


Figure 7.17 AC conductivity vs. frequency for HDPE/G3/M12 nanocomposites (5 wt.%)

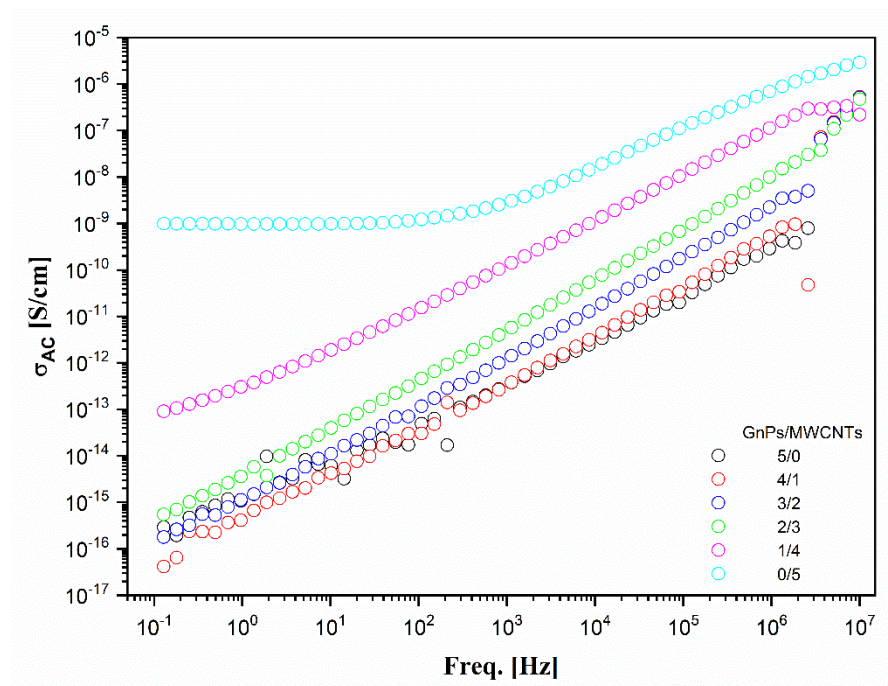


Figure 7.18 AC conductivity vs. frequency for HDPE/G1/M58 nanocomposites (5 wt.%)

It is clearly observed in the Figure 7.18 that expect for the HDPE/G1/M58 nanocomposite with GnPs/MWCNTs weight ratio of 0/5, the AC conductivity for the other the HDPE/G1/M58 nanocomposites follows a power law frequency dependence. They show a typical capacitor behavior. The HDPE/G1/M58 nanocomposite with GnPs/MWCNTs weight ratio of 1/4 increases AC conductivity almost 3 orders of magnitude, however the sample is still non-conductive. The AC conductivity of the HDPE/G1/M58 nanocomposite with GnPs/MWCNTs weight ratio of 0/5 exhibits two different behaviors, as mentioned above. Distinct regions indicate the presence of different dissipating influences and are typical for semiconductors.

In the case of HDPE/G2/M58 nanocomposites (Figure 7.19), the AC conductivity for the HDPE/G2/M58 nanocomposites with GnPs/MWCNTs weight ratios of 5/0, 4/1 and 3/2 is found to be in linear dependence with the frequency in the logarithmic scale, it is almost constant at a value for the HDPE/G2/M58 nanocomposites with GnPs/MWCNTs weight ratio of 1/4. There is a small fluctuation in the conductivity values for this sample in whole frequency range. This may be explained by a poor homogeneity of filler materials dispersion. It is clear that the AC conductivity of the HDPE/G2/M58 nanocomposites with GnPs/MWCNTs weight ratio of 1/4 is higher than that of the other nanocomposites. This nanocomposite achieves an AC conductivity of 5.19×10^{-7} S/cm. For the sample with weight ratio of 0/5, the AC conductivity is independent of the frequency below the critical frequency, after this value, it increases with increase in the frequency.

Figure 7.20 displays the AC conductivity response of the HDPE/G3/M58 nanocomposites with various GnPs/MWCNTs weight ratio as function of the frequency at room temperature. The samples with GnPs/MWCNTS weight ratio of 5/0 to 1/4 show a linear increase in the AC conductivity with the frequency on the logarithmic scale. However, the AC conductivity of the HDPE/G3/M58 nanocomposite with GnPs/MWCNTs weight ratio of 1/4 is about 2 orders of magnitude higher than that of others ($\sim 10^{-6}$ S/cm). Expect for the nanocomposite with GnPs/MWCNTS weight ratio of 0/5, others exhibit similar behavior as the pure HDPE. For the HDPE/G3/M58 nanocomposite with GnPs/MWCNTs weight ratio of 0/5, the

AC conductivity remains at a constant value up to a critical frequency, thereafter the AC conductivity increase with the frequency.

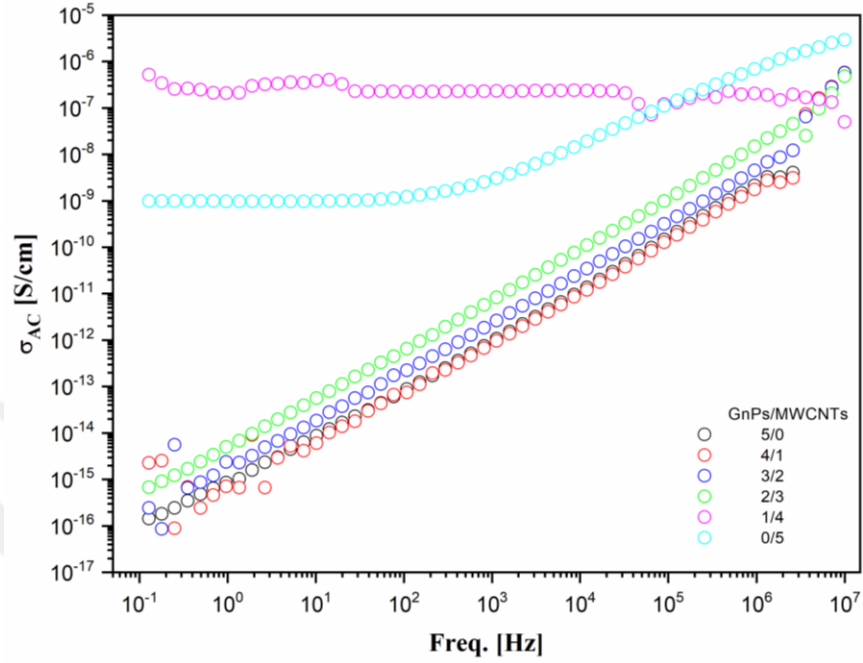


Figure 7.19 AC conductivity vs. frequency for HDPE/G2/M58 nanocomposites (5 wt.%)

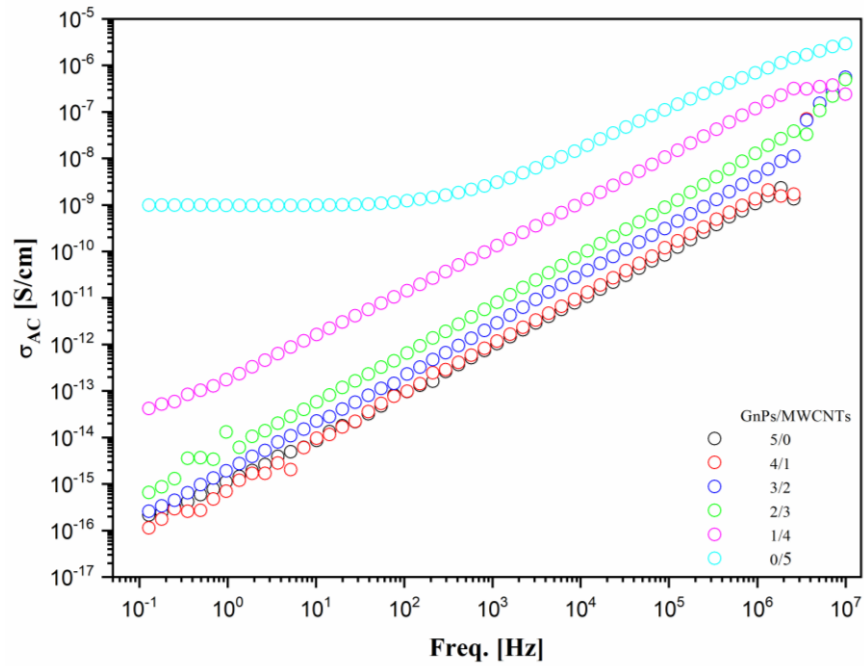


Figure 7.20 AC conductivity vs. frequency for HDPE/G3/M58 nanocomposites (5 wt.%)

Results can be summarized as follows:

- 1- for all HDPE/GnPs/MWCNTs nanocomposites with the GnPs/MWCNTs weight ratios of 5/0 and 4/1, the ac conductivity exhibits a linear increase with increasing the frequency in a log-log scale, i.e. they display the frequency-dependent conductivity, which is a typical dielectric response. In other words, the samples demonstrate similar behavior to that of the pure HDPE.
- 2- Except for the HDPE/G3/M12 nanocomposite, the samples with ratio of 3/2 GnPs/MWCNTs show similar behavior to that of the hybrid nanocomposites with the GnPs/MWCNTs weight ratios of 5/0 and 4/1. In addition, the HDPE/G1/M58 and HDPE/G3/M58 nanocomposites with ratio of 2/3 and 1/4, the HDPE/G2/M58 nanocomposite with ratio of 2/3 display the same behavior.
- 3- For the HDPE/G2/M12 nanocomposite with GnPs/MWCNTs weight ratio of 3/2, the HDPE/G1/M12 and HDPE/G2/M12 nanocomposites with GnPs/MWCNTs weight ratio of 2/3, the dependence of AC conductivity with the frequency is divided into two distinct regions: the AC conductivity remains almost a constant up to a critical frequency, thereafter increases with increasing the frequency. Similar behavior is also observed for the HDPE/G1/M12 and HDPE/G3/M12 nanocomposites with GnPs/MWCNTs weight ratio of 1/4 and all HDPE/GnPs/M58 nanocomposites with ratio of 0/5. This behavior is typical for semiconducting materials.
- 4- It is observed that the AC conductivity of HDPE/GnPs/M12 nanocomposites with the ratio of 0/5, the HDPE/G2/M12 and HDPE/G2/M58 nanocomposites with GnPs/MWCNTs weight ratio of 1/4 and the HDPE/G3/M12 nanocomposite with GnPs/MWCNTs weight ratio of 2/3 is frequency-independent over the whole frequency range.

As previously mentioned, the HDPE/GnPs nanocomposites are not conductive at 5 wt% of GnPs. The reason is that the distance between GnPs is larger than the gap of electron tunneling, and the continuous network of GnPs in the HDPE matrix is not formed. However, MWCNTs form an effective continuous conducting network within

the HDPE matrix at this concentration, the nanocomposites with them exhibits conductive behavior. Although all parameters are the same during the production of HDPE/M12, HDPE/M58, HDPE/G1, HDPE/G2 and HDPE/G3 nanocomposites, the electrical conductivity value is different, i.e. the order of enhancement in the electrical conductivity is HDPE/G1 < HDPE/G3 < HDPE/G2 < HDPE/M58 < HDPE/M12.

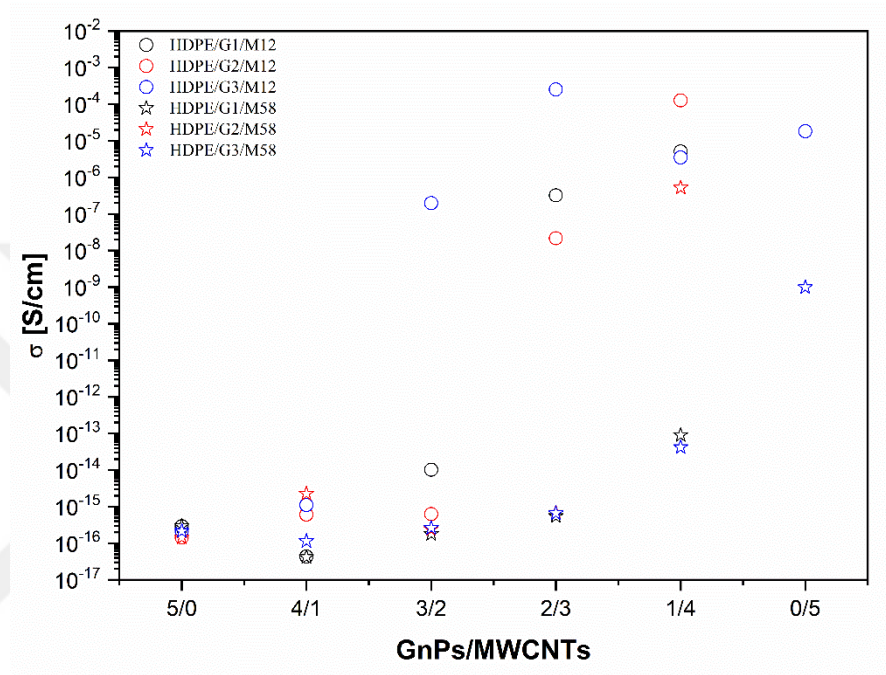


Figure 7.21 Electrical conductivity vs. GnPs/MWCNTs ratio for the hybrid nanocomposites.

When we evaluate the electrical conductivity of the hybrid nanocomposites of constant weight fraction (5 wt.%) but various GnPs/MWCNTs ratio (5/0-0/5), it is clear that the content of M12 increases the electrical conductivity of HDPE-based hybrid nanocomposites increases, however, the increase in M58 content in the hybrid nanocomposites generally exhibit a slight influence on the conductivity of the hybrid nanocomposites. In other words, M12 is proved to be more efficient in the increase of the electrical conductivity than M58. This increase may be explained by increase in the number of the physical contacts between GnPs and MWCNTs with increasing the MWCNTs loading in the total filler contents and hereby, the electric charges can flow more effectively by the pathways of the interconnected MWCNTs and GnPs for the hybrid nanocomposites with higher MWCNTs loading in the 5 wt.% of total filler content (Jeong & An, 2014).

Based on the data in Figure 7.21, it seems that the GnPs/MWCNTs ratio and size of filler materials in the hybrid nanocomposites play important roles in the electrical conductivity. The hybrid nanocomposites containing G3/M12 of 2/3 weight ratio exhibits the highest electrical conductivity of 2.54×10^{-4} S/cm, which is one-half order of magnitude higher than that of the HDPE/GnPs/M12 with 0/5 weight ratio (1.25×10^{-4} S/cm). The best enhancements in the electrical conductivity are found at two GnPs/MWCNTs ratio of 1/4 for the G2/M12 and G2/M58 nanocomposites and of 2/3 for the G3/M12 nanocomposites. The HDPE-based nanocomposite with 1/4 of G2/M58 weight ratio reaches the conductivity of 5.19×10^{-7} S/cm, which is more than ten orders of magnitude greater than those of the pure HDPE and HDPE-based nanocomposites with alone G2 and more than two orders of magnitude greater than that of HDPE/M12 nanocomposites. In addition, the enhancement in electrical conductivity of HDPE/G2/M12 nanocomposite with 1/4 of G2/M12 weight ratio is almost the same level as that of the hybrid nanocomposites containing G3/M12 of 2/3 weight ratio.

These enhancements in the electrical conductivity are ascribed to the synergic effect of the hybrid structure created between MWCNTs and GnPs. The electron transport along the HDPE matrix may be facilitated by the formation of interconnected hybrid network structure between MWCNTs and GnPs. MWCNTs can create conducting channels between GnPs, therefore decreasing gap between GnPs platelets facilitating the electron transport. The other reason may be improved dispersion and damage prevention of the MWCNTS in the existence of GnPs (Ghaleb et al., 2017; Xiao et al., 2016).

Another reason of increase can be the forming more efficient conductive networks because of combining 2D GnPs and 1D MWCNTs. The electrical transport in the hybrid nanocomposites can occur by

- 1) tunneling and hopping of electrons in the subsystem of MWCNTs,
- 2) tunneling and hopping of electrons in the subsystem of GnPs and
- 3) tunneling of electrons between the subsystems of GnPs and MWCNTs

Increase in the electrical conductivity with increasing the content of MWCNTs in the total nanofillers' concentration display that the second mechanism can be negligible as compared to the first and third mechanisms. So, the electrical conductivity in the hybrid nanocomposite increases due to better dispersion of MWCNTs and the tunneling of the electrons between GnPs and MWCNTs (Krauskaitė et al., 2018).

The electrical conductivity of the HDPE/G1/M12 nanocomposites is bounded between those of the HDPE/G1 and HDPE/M12 nanocomposites, i.e. there is no synergic effect of the M12 and G1. A similar observation is seen for the G1/M58 and G3/M58 nanocomposites. This reason may be the existence of a thick polymer layer on the surface of GnPs and MWCNTs. Because, it may increase the distance for direct contact between them and leads to an insulating layer in the barrier of tunneling for the transport of electric. The critical distance between GnPs and MWCNTs in the hybrid nanocomposites is not enough for efficient electron movements (Zhang et al., 2018). Wegrzyn, Ortega, Benedito, & Gimenez, (2015) claimed that the existence of a good dispersion and the interconnection of agglomerates rather than a perfect network of MWCNTs is required for a high conductivity.

The G1/M58, G2/M58 and G3/M58 nanocomposites with GnPs/MWCNTs weight ratios of 0/5, 4/1, 2/3 and 3/2 are insulators with electrical conductivity of $\sim 10^{-16}$ S/cm. As a GnPs/MWCNTs weight ratio of 1/4, the G1/M58 and G3/M58 nanocomposites show electrical conductivity values of 9.04×10^{-14} S/cm and 4.21×10^{-14} S/cm, respectively, which are almost two orders magnitude higher than that of the HDPE/GnPs nanocomposites. This may be explained that the addition of GnPs to the mixture leads to form the electrically inert bridges between M58 aggregates zones because of the graphitic structure of nanoplatelets. The electron hopping between M58 aggregates is hindered by these electrically inert bridges (Badakhsh et al., 2019)

As seen in Figure 7.21, generally the electrical conductivity of HDPE-based hybrid nanocomposites is lower than that of HDPE-based nanocomposites with MWCNTs. It is known that the synergic effect is generally accepted to be an effect which arises between two materials obtaining an effect higher than the sum of the individual effects

of them. Based on this definition, generally, the results in this study show no distinct synergic effect in effecting the electrical conductivity. The similar observation was made by (Al-Saleh, 2015a; Paszkiewicz et al., 2018; Wegrzyn, Galindo, et al., 2015)

The reason of this may be that the existence of a thick HDPE layer on the filler materials' surface may extent the distance for the direct contact between two filler materials and obtains an insulating layer in the tunneling barrier for the electrical transfer. The critical distance between filler materials in the HDPE-based nanocomposites is not enough for the efficient electron movements. Besides, high Schottky barriers at the connections of GnPs/MWCNTs as well as the significant difference in the electrical conductivities of HDPE-based nanocomposites with single filler materials ($\sigma_{\text{HDPE-MWCNTs}}/\sigma_{\text{HDPE-GnPs}} \sim 10^{10}$) may greatly hinder the potential synergic effect between GnPs and MWCNTs. It is observed that GnPs exhibits a much lower electrical conductivity enhancement than MWCNTs. The hopping electrons movement from MWCNTs to GnPs and GnPs to MWCNTs is seriously limited and therefore causes a less effective conductive pathway. Thus, MWCNTs and GnPs do not demonstrate clear synergic effect in improving the electrical conductivity of hybrid nanocomposites (Zhang et al., 2018).

It is clear from the findings that the GnPs/MWCNTs weight ratio and size of fillers in the mixed have a strong effect on the electrical properties. One can see that 1-D MWCNTs are mainly responsible for the formation of electrical charge pathway. Similar observation was reported by Wegrzyn, Ortega, et al. (2015).

As mention before, M12 exhibits higher enhancement in the electrical conductivity of HDPE-based nanocomposites than M58. The similar observation is made for the hybrid nanocomposites. M12 can form more effective conductive networks with GnPs than M58, i.e. the formation of continuous conducting pathways is more efficiently when combining GnPs and MWCNTs with higher aspect ratio. There is more number of the physical contact between GnPs and M12.

For three types of HDPE/GnPs/M12 nanocomposites, the content of M12 increases, the electrical conductivity of hybrid nanocomposites increases. It can be said that the MWCNTs can bridge the distance between GnPs. Although no synergic effect is observed between G1 and M12, the HDPE/G1/M12 nanocomposites with 1/4 of GnPs/MWCNTs weight ratio exhibit an electrical conductivity value of 5.12×10^{-6} S/cm, which is about 4 times lower than that of the HDPE/M12 nanocomposites (1.82×10^{-5} S/cm). This value is the same level as the value of the HDPE/G3/M12 nanocomposites. It can be seen from the findings that there is no distinct synergic effect between GnPs with small diameter and thicker thickness and M12 affecting the electrical conductivity. The reason may be the formation of less effective conductive network between G1 and M12. Notwithstanding, M12 among the carbon-based nanofillers and G2 among GnPs exhibit best performance in the electrical conductivity enhancement for the nanocomposites with single-carbon based filler, the HDPE/G3/M12 nanocomposite with GnPs/MWCNTs weight ratio of 2/3 achieves the highest electrical conductivity and these type of nanocomposites show the better improvement in the electrical conductivity for all GnPs/MWCNTs ratio, as compared to the others. In a summary, the combination of larger surface area of G2 and higher aspect ratio of M12 make contribution to the synergic effect of the HDPE-based hybrid nanocomposites, similar observation is made by Chatterjee et al. (2012) .

As compared in terms of GnPs, the size of GnPs has a slight effect on the electrical conductivity on the hybrid nanocomposites including M58. Except for the HDPE/GnPs/M58 nanocomposites with 1/4 of GnPs/MWCNTs weight ratio, GnPs and M58 cannot form a conductive network in the polymer matrix and physical contact between GnPs and MWCNTs. When the ratio of GnPs/MWCNTs weight ratio is 1/4, the HDPE/G1/M58 and HDPE/G3/M58 nanocomposites exhibit almost two orders of magnitude higher increase in the electrical conductivity than the GnPs/MWCNTs. This is may be explained by starting the formation of the continuous conductive pathways. It is clear that GnPs with the same diameter (G1 and G3) shows almost similar behavior and the same level enhancement.

The highest electrical conductivity value 5.19×10^{-7} S/cm is observed in the HDPE based nanocomposite with a filler loading of G2/M58 having 1/4 weight ratio, which is increase by nine and two orders of magnitude over that of the HDPE-based nanocomposites only with G2 and M58, respectively. This enhancement in the electrical conductivity is ascribed to the synergic effect of hybrid structure which is formed between G2 and M58 facilitating the electron transport along the nanocomposites. The results of this study display that, at 5 wt.% of total filler content, there is a distinct synergic effect between MWCNTs with lower aspect ratio and GnPs with the highest largest diameter influencing the electrical conductivity for a specific weight ratio of G2/M58 (1/4). Except for these nanocomposites, the electrical conductivity of all hybrid nanocomposites with M58 is almost similar to that of the insulating HDPE matrix.

As comparing hybrid nanocomposites with different filler ratios, although the electrical conductivity exhibits the maximum value when the weight ratio of G3 and M12 is 3/2, the best results are generally obtained for the HDPE-based hybrid nanocomposites with 1/4 weight ratio of GnPs to MWCNTs. In other words, these nanocomposites show the most apparent improvement of electrical conductivity. This can be explained by a statistical requirement of the existence of both GnPs and MWCNTs to provide effective GnPs-MWCNTs bridging (Wegrzyn, Ortega, et al., 2015). One reason may be that GnPs behave as a bridge connecting MWCNTs, which make it easier to create a full conducting network in the polymer nanocomposites. One other reason may be that the high aspect ratio of GnPs makes it hard for MWCNTs to bypass them and engage with other MWCNTs and in this way hinder the aggregation of MWCNTs. The another reason for this enhancement may be that the strong Van der Waals forces between MWCNTs and GnPs at the low curling degree raises the possibility of the formation of the conductive pathways (Szeluga et al., 2015). Jen and Huang 2019 observed this effect at the MWCNT/GnPs ratio of 1/9 and they claimed that it may be due to the bridging effect obtained by MWCNTs and large contact areas between GnPs. This ratio was found as 8/2 by Yue et al. 2014. They claimed that this improvement could be potentially due to easier formation of a conducting network because of the enhanced dispersion state of MWCNTs in the GnPs presence.

7.4.3 Thermal conductivity

It is mentioned in the earlier chapters that the thermal conductivity of the pure HDPE was measured as 0.386 W/mK and a general tendency is that the thermal conductivity of five types of nanocomposites increases with increasing filler loading. However, these enhancements are lower than expected due to the thermal interfacial resistance between filler/filler or/and the filler and the HDPE matrix. Utilizing the synergic effect of different carbon-based nanofiller is an effective strategy to improve the thermal conductivity of the HDPE-based nanocomposites.

As mentioned in chapter 4, the thermal diffusivity of samples is measured by PTR method and the experimental thermal conductivity of the samples were calculated from the following equation (Eq. (7.1)):

$$k = \alpha c_p \rho \quad (7.1)$$

where α is the thermal diffusivity (mm^2/s), c_p is the specific heat of materials and ρ is density (kg/m^3) of material. The thermal diffusivity, density and specific heat of samples were measured by using a photothermal radiometry, PTR, a Matsu Haku Electronic Densimeter and a differential scanning calorimeter (Perkin Elmer, Diamond DSC), respectively. Alternately, as is known, the specific heat and density can be predicted by the rule of mixtures. The mixture rule for c_p (Eq. (7.2)) and ρ (Eq. (7.3)) of the polymer nanocomposites can be written, respectively:

$$c_p = \sum \varphi_{wt,i} c_{p,i} \quad (7.2)$$

$$\rho = \sum \varphi_{vol,i} \rho_i \text{ or } \rho^{-1} = \sum \varphi_{wt,i} \rho_i^{-1} \quad (7.3)$$

where $\varphi_{wt,i}$ is the mass fraction of each components and $\varphi_{vol,i}$ is the volume fraction of components. The density and specific heat of composites determined in the Chapter 4.

It is known that the $\varphi_{vol,i}$ is determined by using the $\varphi_{wt,i}$ and the density of pure components. In hybrid nanocomposites, $\varphi_{wt,i}$ and ρ of each component are known, however the $\varphi_{vol,i}$ can not calculated by using the following equation (Eq. (7.4)):

$$\varphi_{vol} = [1 + (\varphi_{wt}^{-1} - 1)(\rho_f/\rho_m)]^{-1} \quad (7.4)$$

Because the hybrid nanocomposites include two nanofiller materials, and thus this equation includes two unknowns. Therefore, only the approximate volume fraction of nanofillers can be calculated. So, the density is calculated by the mixture rule in terms of φ_{wt} . In addition, for the polymer nanocomposites, the opposite variations of c_p and ρ compensate each other. Thus, the volumetric specific heat ($C = \rho c_p$) is almost constant. Thus, there is a direct relationship between the thermal conductivity and diffusivity.

It is known that, in the polymer nanocomposites, synergy refers to an interaction of components that ensure higher property improvement compared to the sum of the property improvement achieved by the individual components (Safdari & Al-haik, 2018; Szeluga et al., 2015). To better understand the change in the thermal conductivity of the hybrid nanocomposites, the synergic efficiency (f), representing the synergic effects of MWCNTs and GnPs on the thermal conductivity of hybrid nanocomposites, is suggested as follows (Eq. (7.7)) (Xiao et al., 2016):

$$f = \frac{k_{GnPs/MWCNTs} - k_{HDPE}}{(k_{GnPs} - k_{HDPE}) + (k_{MWCNTs} - k_{HDPE})} \quad (7.5)$$

Where $k_{GnPs/MWCNTs}$, k_{GnPs} and k_{MWCNTs} refer to the thermal conductivity of ternary HDPE/GnPs/MWCNTs nanocomposites, binary HDPE/GnPs and HDPE/MWCNTs nanocomposites, respectively. If the value of f is bigger than 1, the GnPs and MWCNTs show a synergic effect in enhancing the thermal conductivity of HDPE. Clearly, high value of f implies more probability to obtain high thermal conductivity (Xiao et al., 2016).

7.4.3.1 Comparison of thermal conductivity of the HDPE/GnPs and HDPE/MWCNTs nanocomposites

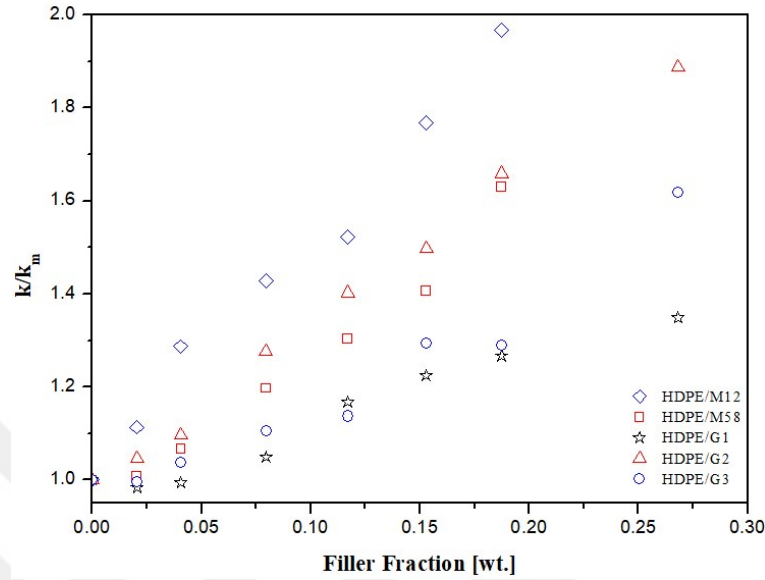


Figure 7.22 Relative thermal conductivity vs. wt.% of filler fraction for the HDPE based nanocomposites

It can be seen in Figure 7.22 that the thermal conductivity of all nanocomposites increases linearly with the inclusion of carbon-based nanofillers irrespective of filler's type. Based on the electrical and thermal conductivity results, M12 is proven to be the most effective as the conductive nanofiller among all our used carbon-based nanofiller materials. The thermal conductivity of the HDPE-based nanocomposites with G1 is increased by almost 27 %, which corresponds to the least enhancement in that of all HDPE-based nanocomposites. For instance, at 18.74 wt% of filler content, the thermal conductivity of the HDPE/M12 nanocomposite increases by almost 0.97-fold (0.759 W/mK), while the HDPE/G1 nanocomposite maximum increases by almost 0.27-fold (0.489 W/mK) compared with the pure HDPE (0.386 W/mK). However, G2 shows slightly higher enhancement in the thermal conductivity than M58. The HDPE/G2 nanocomposite containing 18.74 wt% filler loading demonstrates an increase of ~66% in thermal conductivity compared to the pure HDPE, while the HDPE/M58 nanocomposite displays slightly lower increase of ~63% at the same loading.

One can say that the type of carbon-based materials is not only key factor for thermal conductivity, but also the size of filler materials plays an important role in the thermal conductivity. It is known that the most promising carbon-based nanofiller material for the thermal property improvement is MWCNTs because the lowest interfacial area is offered by MWCNTs. The thermal properties of the polymer nanocomposites with MWCNTs primarily change by effective aspect ratio of MWCNTs embedded in the matrix. Generally, the thermal conductivity of the polymer nanocomposites with MWCNTs is much higher than that of the polymer nanocomposites with GnPs. As mention previously, GnPs increase the number of interfaces between the matrix and GnPs layers. And this leads to more phonon scattering, resulting in decrease in the thermal conductivity (D'hooge, Cardon, Wieme, Mys, & Duan, 2019).

The other reason of lower thermal conductivity enhancement may be that the lower aspect ratio of GnPs aggregation decreases the contact area between the HDPE matrix and GnPs, therefore, the severe scattering for the phonon transport is caused by the thicker HDPE layer on GnPs surface (Yang et al., 2011). However, the study displays that MWCNTs with higher aspect ratio perform better in the thermal conductivity compared to GnPs; while the HDPE nanocomposites containing GnPs with higher lateral size exhibit slightly higher increment than MWCNTs with lower aspect ratio. One seems that if the lateral size of GnPs is enough large, GnPs from more effective conductive filler than MWCNTs with lower aspect ratio.

As a result, in the literature, some of the studies claim that MWCNTs exhibit higher thermal conductivity enhancement than GnPs, however, the contradictory results are obtained in some of the studies. However, based on our results, when making the comparison between MWCNTs and GnPs, the size of carbon-based filler materials should be considered, because the thermal conductivity of nanocomposites considerably varies with the size of filler as well as the type of carbon-based nanofillers. In other word, the size of nanofiller should be taken in consideration when making a comparison of carbon-based nanocomposites in terms of the thermal conductivity.

7.4.3.2 The thermal conductivity of the HDPE/G2 (11.70 wt.%)/M12 nanocomposites

Figure 7.23 displays the variation of thermal conductivity of the HDPE/G2 (11.70 wt.%)/M12 nanocomposites with the addition of M12. The thermal diffusivity results are given in Figure A7.36. This is clearly shown that the thermal conductivity of the hybrid nanocomposites increases with increase in the M12 loadings due to the development of thermally conductive pathways for the transport of the phonons. The HDPE/G2 (11.70 wt.%)/M12 nanocomposites demonstrate a better enhancement in thermal conductivity as compared to the HDPE/G2 (11.70 wt.%) and the HDPE/M12 nanocomposites at the same filler loadings. The addition of 0.2 wt.% M12 to 11.70 wt.% G2 in HDPE leads to an increase from 0.514 W/mK (the HDPE/11.70 wt. G2 nanocomposite) to 0.615 W/mK, whereas the thermal conductivity of HDPE/M12 nanocomposite with 0.2 wt% is 0.390 W/mK, which is almost the level of the pure HDPE (0.386 W/mK). With an M12 loading of 3.82 wt.%, the thermal conductivity is increased up to 0.736 W/mK, corresponding to an enhancement of 90.7% compared to the neat HDPE, while the HDPE based nanocomposites with individual G2 and M12 shows an increase of 51.2% and 77.4%, respectively.

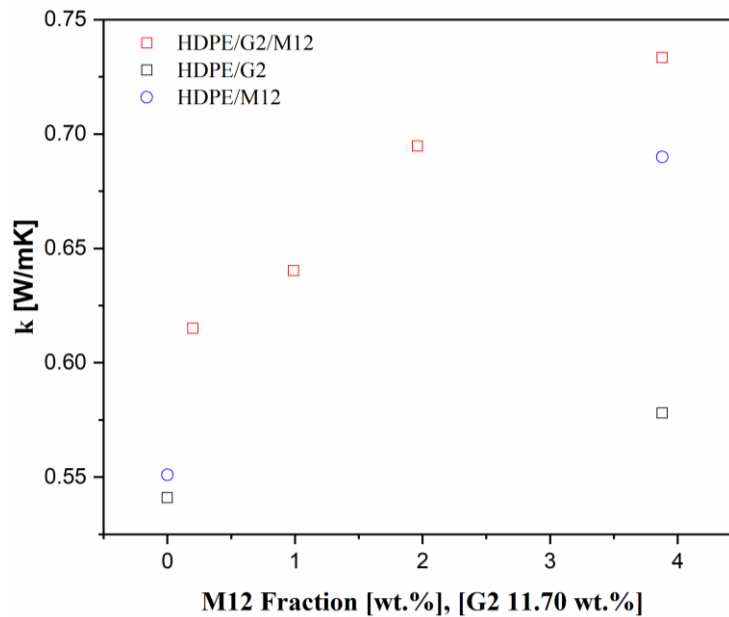


Figure 7.23 Thermal conductivity vs. wt.% of MWCNTs for the HDPE/G2 (11.70 wt.%)/M12 nanocomposites

It is clear from Figure 7.23 that M12 and G2 show the synergic effect in influencing the thermal conductivity. This may be explained by the formation of (3-D hybrid architectures) thermally interconnect conductive networks in the HDPE matrix as confirmed by SEM images. Another reason may be that M12 can effectively hinder the stacking between G2 layers and enhance the interfacial compatibility between the HDPE matrix and hybrid fillers. In other words, M12 acts as a bridge between G2 layers via π - π interaction between G2 and M12, facilitating the formation of 3-D thermal conductive network structure in the hybrid nanocomposites, and prevents the aggregation of G2, which includes the intrinsic high surface area of G2 to contact with the HDPE matrix, as reported by Yang et al., (2011), Guo et al., (2019) and Xiao et al., (2016). In addition, the 3-D architecture and interaction of the hybrid system contains: 1-the polymer/polymer network, 2- the HDPE/G2/M12 network, 3-G2/M12 interaction and G2/G2 interaction. The main reasons for obtained synergetic effect of G2 and M12 on the enhancement in the thermal properties of the HDPE-based composites may be attributed to these four factors (Yang et al., 2011).

Moreover, when increasing M12 loading, the distance between the filler materials can decrease, much more thermal chains can be created between the fillers; forming more thermal conductive network or pathway (Zakaria et al., 2017). The formation of more effective GnPs/MWCNTs hybrid network leads to decrease in the undesirable polymer/carbon-based nanofillers interfacial resistance influences.

In addition, other reason of the synergic effect may be that the contact geometry alters from 0D point contact to 1D linear contact, which increases the contact area within the hybrid nanofillers. The larger contact area leads to an increase in the pathway for the diffusion of phonon within the hybrid nanofillers and reduce in the thermal interfacial resistance. The uniform GnPs/MWCNTs have a great contact area with HDPE providing ease of heat flows and supporting the diffusion of phonon in their hybrid nanocomposites (Yang et al., 2011).

Krause, Rzeczkowski, & Pötschke, (2019) investigated the possible synergic effect of conductive networks of GnPs/MWCNTs on the thermal conductivity of PP-based hybrid nanocomposites prepared by melt mixing. They kept the total filler content at 7.5 vol%. They reported that the addition of 2.5 vol.% MWCNTs to 5 vol.% GnPs in PP causes an increase from 0.39 W/mK (PP/ 5 vol.% GnPs) to 0.5 W/mK (103 % of increase compared to the pure PP). They observed almost the same thermal conductivity value for the PP/ 7.5 vol.% GnPs nanocomposite. For PP/ 2.5 vol.% GnPs/5 vol.% MWCNTs nanocomposite, the thermal conductivity was determined as 0.46 W/mK, corresponding to 77 % of increase compared to the pure PP. They claimed from their results that the GnPs are more responsible to enhance the thermal conductivity. They found that there is a synergic effect of the GnPs/MWCNTs hybrid nanofillers for thermal conductivity. They reported that, to achieve high thermal conductivity, hybrid fillers with different aspect ratios and shapes are advantageous to create a combined conducting network (Krause et al., 2019).

Paszkiewicz et al. (2018) used GnPs with ~5–10 nm of thickness to produce the LDPE-based nanocomposites. They reported that the LDPE/MWCNTs nanocomposites show higher thermal conductivity than the LDPE/GnPs nanocomposites and the thermal conductivity values of the hybrid nanocomposites are between the LDPE-based nanocomposites with single nanofiller. They claimed that this may result from the mixture rule, and the synergic effect of hybrid nanofillers was not observed. They showed that the hybrid system of GnPs and MWCNTs does not lead to synergic improvement in the thermal and electrical conductivity due to the existence of a thin layer of the polymer matrix, preventing a direct contact between GnPs and MWCNTs and introducing a scattering layer for and phonons' transport as well as an insulating layer in the tunneling barrier for electrical transport. Although the proper dispersion is received, the enhancement in the thermal and electrical conductivity results from increasing the concentration of nanofillers, with no synergic effect (Paszkiewicz et al., 2018).

The f of the HDPE/G2 (11.70 wt.%) /M12 nanocomposites is illustrated in Figure 7.24. One can see that all samples show f higher than 1, obviously indicating the

synergic effect of G2 and M12 in enhancing the thermal conductivity of the nanocomposites. The f increases with the addition of M12 and the maximum value is observed at 1.93 wt.% M12 loading. However, the further addition of M12 causes a reduction of f . The similar observations was made by Xiao et al. (2016).

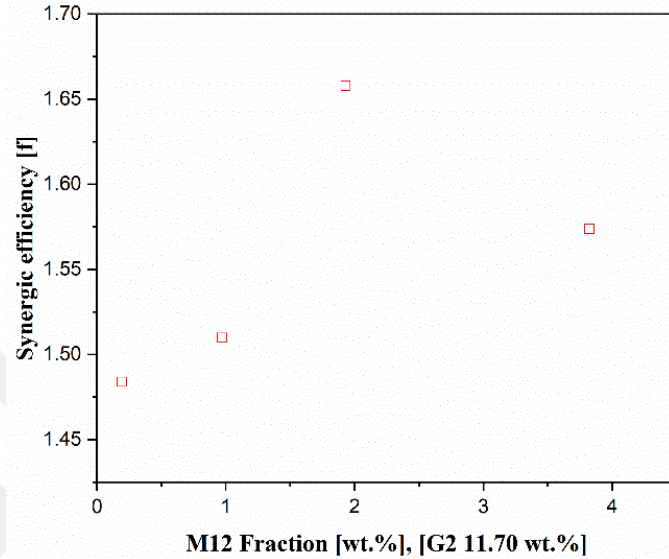


Figure 7.24 The synergic efficiency [f] of G2 and M12 vs. wt.% of MWCNTs for the HDPE/G2 (11.70 wt.%)/M12 nanocomposites

7.4.3.3 The thermal conductivity of the hybrid nanocomposites

As mentioned before, the trend of the thermal conductivity versus carbon-based nanofillers is similar, however, the magnitude of the thermal conductivity at any content of nanofillers is in the order as HDPE/M12 > HDPE/G2 > HDPE/M58 > HDPE/G3 > HDPE/G1. It is observed that the size of carbon-based nanofillers influence the thermal conductivity. To investigate the size effect on the synergic effect of hybrid nanofiller, at a constant filler concentration of 5 wt.%, two types of MWCNTs and three types of GnPs were used to produce hybrid nanocomposites with different weight ratio of GnPs/MWCNTs (5:0, 4:1, 3:2, 2:3, 1:4 and 5:0). The thermal diffusivity results of each hybrid nanocomposites are given in Figure A7.37. The effective thermal conductivity obtained from Eq. (7.3) is given in Figure 7.25.

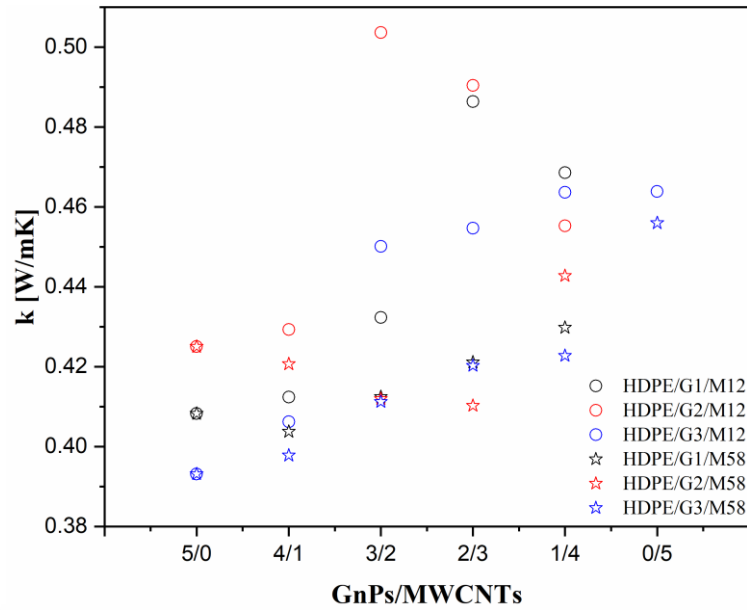


Figure 7.25 Thermal conductivity of the hybrid nanocomposites

It can be clearly observed from Figure 7.25 that the thermal conductivity of the HDPE-based hybrid nanocomposites only with MWCNTs is much higher than that of the nanocomposites only with GnPs. In case of the HDPE-based hybrid nanocomposites, it is expected that, in general, the thermal conductivity increases monotonically as the content of the more efficient MWCNTs increases, in concert with the mixture rule, as mentioned by (Yu et al., 2008). However, for some weight ratio of GnPs/MWCNTs, the carbon-based hybrid nanofillers outperform the performance of the single MWCNTs and GnPs and show a strong synergic effect.

In the hybrid nanocomposites, 1D-MWCNTs can form a bridge between the adjacent 2D-GnPs and provide the extra channels for the phonon bypassing the HDPE matrix. When compared with the individual MWCNTs or GnPs, the contact geometry changes from 0D point contact between the individual MWCNTs or GnPs along the filler network to 1D linear contact between MWCNTs and GnPs. This increases the probability of contact and the contact surface area within the carbon-based hybrid nanofillers. And, the large contact areas lead to decrease the thermal interface resistance between the HDPE matrix and carbon-based nanofillers. This may be thought as the main reason for the synergic effect of 1D and 2D carbon-based hybrid

nanofillers. (He et al., 2018; Su, Xiao, & Ren, 2013; Yu et al., 2008; Yuan et al., 2014; Zhang et al., 2017).

It is clearly observed that the sizes of GnPs and MWCNTs and their weight ratio have substantial influence on the thermal conductivity of hybrid nanocomposites. For all types of hybrid nanocomposites, the thermal conductivity displays only a marginal enhancement for all weight ratios of GnPs and MWCNTs. These results exhibit that by keeping total carbon-based nanofiller as 5 wt.%, the thermal conductivity of the hybrid nanocomposites displays considerable variation on varying the weight ratio of GnPs and MWCNTs in the hybrid nanocomposites.

As compared to the types of MWCNTs, for all weight ratio of GnPs/MWCNTs, MWCNTs with higher aspect ratio (M12) are found to be more effective (beneficial) than MWCNTs with lower aspect ratio (M58) to form thermally conductive networks and achieve higher thermal conductivity of the HDPE-based hybrid nanocomposites. This is to be expected, as mention in the chapter 5, M12 favors the formation of thermal conductive network which enables the transport of phonons over a longer distance without any transitions from the particle to the particle. Additionally, in a thermal conductive network formed by MWCNTs with lower aspect ratio, the needed number of contacts per unit distance exponentially increases, resulting in higher interfacial thermal resistance and phonon scattering.

In this study, it is reported that there are observed three different synergic effects of GnPs and MWCNTs: positive, negative and no synergic effect. The positive synergic effect of GnPs and MWCNTs is observed at the GnPs to MWCNTs weight ratios of 2/3 and 1/4 for the HDPE/G1/M12 nanocomposites and of 3/2 and 2/3 for the HDPE/G2/M12 nanocomposites. The negative synergic effect is observed in the HDPE/G1/M58 nanocomposite with 4/1 of GnPs/MWCNTs weight ratio and the HDPE/G2/M58 nanocomposite with 4/1, 3/2 and 2/3 of GnPs/MWCNTs weight ratios. No synergic effect is observed in the other nanocomposites. The HDPE/G2/M12 nanocomposite with 3/2 of GnPs/MWCNTs weight ratio exhibits the highest enhancement with a thermal conductivity of 0.504 W/mK, an increase of 30.47 % over

the pure HDPE (0.386 W/mK). At 5 wt.% total filler loading, the result of the HDPE/G3/MWCNTs nanocomposites with 5/0 weight ratio of GnPs/MWCNTs exhibits the lowest enhancement in the thermal conductivity of all hybrid nanocomposites (1.85 % increment).

At 5 wt.% of filler loading, compared to the thermal conductivity (0.408 W/mK, 5.75 % of increment) of the HDPE/G1 nanocomposites, the HDPE/M12 nanocomposite indicates higher thermal conductivity of 0.464 W/mK (20.17 % of increment). The synergic effect of G1 and M12 on the thermal conductivity is observed in the nanocomposites with 2/3 and 1/4 of GnPs/MWCNTs weight ratios. With 5 wt.% of G1/M12, the improvement of the thermal conductivity for the HDPE/G1/M12 nanocomposites with 1/4 of GnPs/MWCNTs weight ratio is 21.38%, compared with the 5.76 % and 20.17 % improvements corresponding to single G1 and M12.

For the HDPE/G1/M12 nanocomposites, the highest thermal conductivity 0.486 W/mK is observed in the hybrid nanocomposites with 2/3 of GnPs/MWCNTs weight ratio and it is increased by 4.7% and 19.12% over that of the HDPE-based nanocomposites containing only M12 and G1, respectively. This is may be more homogenous dispersion of nanofillers and the strong interfacial covalent bonds forming between G1/M12 and HDPE matrix (Kumar et al., 2019a).

Based on SEM results, the synergy can be mainly leaded to the formation of new continuous chains of GnPs and MWCNTs. M12 can bridge between the random dispersed G1 in HDPE matrix and form 3D thermally conductive pathways. In addition, the existence of MWCNTs inhibits the aggregation of G1. As mentioned in the SEM results of Chapter 4, G1 exhibits poor dispersion in the HDPE matrix. For the HDPE/G1/M12 nanocomposites with other GnPs/MWCNTs weight ratios, the thermal conductivity increases with increasing M12 loading, obeys the rule of mixtures. In case of the HDPE/G1/M12 nanocomposites, the synergic effect of G1 and M12 on the thermal conductivity in the HDPE nanocomposites is reported for 2/3 and 1/4 of GnPs/MWCNTs weight ratios, however the electrical conductivity doesn't indicate synergically improvement at other GnPs/MWCNTs weight ratios.

As mentioned above, while the results of the HDPE/M12 nanocomposites show the most enhancement in thermal conductivity of all HDPE-based nanocomposites, G2 exhibits the best enhancement among all types of GnPs. The HDPE-based nanocomposites prepared with 5 wt.% loading of the individual carbon fillers give 0.425 W/mK for the G2 reinforced nanocomposites and 0.464 W/mK for the M12 reinforced nanocomposite. In cases of the hybrid nanocomposites including G2 and M12, the thermal conductivity of samples indicates a strong dependence of the G2/M12 weight ratios at 5 wt.% hybrid nanofiller content. The thermal conductivity for the GnPs/MWCNTs weight ratios of 3/2 and 2/3 is observed to be greater than that of the HDPE-based nanocomposites with G2 and M12.

A better synergic effect is observed for the thermal conductivity measurements where the HDPE/G2/M12 hybrid nanocomposites with GnPs/MWCNTs weight ratio of 3/2 illustrates the highest increment of 30.47% compared to an increment of 10.10% and 20.17% with pure G2 and M12, respectively. In other words, the HDPE-based nanocomposites with G2/M12 weight ratio of 3/2 illustrate the most apparent improvement of thermal conductivity among the six different types of the hybrid nanocomposites. The thermal conductivity of this nanocomposite is reached up to 0.504 W/mK. In cases of the HDPE/G2/M12 nanocomposites with other GnPs/MWCNTs weight ratios, the thermal conductivity increases with increasing MWCNTs loading in the total carbon-based nanofillers content, however these values are between the those of the nanocomposites including G2 and M12 alone. These results show that, for these nanocomposites, there is no general distinct synergic effect between G2 and M12 influencing the thermal conductivity. The synergic effect in terms of the electrical conductivity is observed only at GnPs/MWCNTs weight ratio of 1/4.

Based on the images of SEM (Figure 7.7 and Figures A7.21-23), the combination of M12 and G2 leads to more uniform dispersion of nanofillers in the HDPE matrix and a more effective 3D thermally conductive network. The more uniform G2/M12 the larger contact area with the HDPE matrix. This permits ease of heat flows and promotes the phonon diffusion in hybrid nanocomposites. It is observed that the length

of M12 can behave as chelating arms to improve adhesion between the polymer matrix and 3-D hybrid nanofiller materials. In comparison with individual G2 and M12, the contact geometry changes from the point contact (0-D) to the linear contact (1-D), resulting in considerably increasing in the number of the contact area in the hybrid filler nanomaterials. The large contact areas have tendency to decrease the interfacial resistance between the filler materials and increase the pathway for the phonon transport in the hybrid nanocomposites. In brief, the improvement in the thermal conductivity proposes that M12 have a key role in the enhancement of the compatibility and dispersion of G2 within the HDPE matrix (He et al., 2018; Yang et al., 2011).

In case of the HDPE/G3/M12, the thermal conductivity increases with increasing the content of M12 in the total carbon-based nanofillers loading. The results indicate that there is no apparent synergic effect between G3 and M12 influencing the thermal conductivity, its enhancement only obeys the mixture rule. When the GnPs/MWCNTs weight ratio changes from 4/1 to 1/4, the thermal conductivity increase from 0.406 W/mK to 0.464 W/mK. This value is equal to the value of the HDPE-based nanocomposites including only M12 and almost 18% higher than that of HDPE/G3 nanocomposites.

SEM images reveal the existence of HDPE-rich and nanofillers-rich regions in the HDPE/G3/M12 nanocomposites. In addition, M12 bridges between G3 particles and forms thermal conductive network. However, it is observed in the images of SEM that M12 aggregates between GnPs layers and/or HDPE matrix and GnPs. The increase can most likely be due to the formation of thermal conductive network and bridge between the nanofiller. There is no synergic effect between G3 and M12, and this may be attributed not to form a continuous thermal conductive network. In other words, this may be due to the inadequate dispersion of nanofillers in the HDPE matrix. G3 and M12 particles or networks surrounded by HDPE matrix, the nanofillers cannot touch each other and therefore decrease of direct filler-filler phonon transfer. This leads to severe scattering for the transport of phonon and high thermal contact resistance inside the hybrid nanocomposites (He et al., 2018; Yang et al., 2011).

In addition, the presence of local aggregates of M12 causes increase of the interfacial thermal resistance between M12. The 0D point contact between M12 increases the degree of phonon scattering, preventing the transfer of heat (Xiao et al., 2016). The high energy loss during the heat transfer and a weak heat transfer network occur due to the large interfacial gaps between the matrix and agglomerates (Guo et al., 2019). However, as mentioned in the 5.2.2 section, the electrical conductivity increases with decreasing weight ratio of GnPs to MWCNTs, the distinct synergic effect of G3 and M12 is observed at 3/2 of G3/M12 weight ratio, i.e. among all HDPE-based hybrid nanocomposites, the electrical conductivity display the maximum value when the weight ratio of G3 to M12 is 3/2.

The thermal conductivity of the HDPE/G1/M58 nanocomposite with 5/0 weight ratio of GnPs/MWCNTs is 0.408 W/mK while this value is 0.456 W/mK for the HDPE/G1/M58 nanocomposite with 0/5 weight ratio of GnPs/MWCNTs. It is interesting to note that the thermal conductivity illustrates the minimum value when the weight ratio of G1 and M58 is 4/1. i.e., the nanocomposite demonstrates a lower thermal conductivity of 0.404 W/mK at 5 wt.% content of hybrid nanofillers with G1/M58 at their mass ratio of 4:1. Although the thermal conductivity is found to be enhanced by 4.60 % as compared to the pure HDPE, this value is 1% and 11.40 % lower than that of the nanocomposites with only G1 and M58, respectively, i.e., the thermal conductivity result indicates a presence of a negative hybrid effect. For the HDPE/G1/M58 nanocomposites with other GnPs/MWCNTs weight ratio, the thermal conductivity increases with increasing MWCNTs content in the total mixed carbon-filler materials, however this increase is marginal. The value of thermal conductivity at GnPs/MWCNTs weight ratio of 1/4 reaches up to 0.430 W/mK, a 5.39 % increase and 5.70 % decreased compared with the HDPE/G1 and HDPE/M58 nanocomposites, respectively. These results display that there is no synergic effect between G1 and M58 influencing the thermal conductivity.

As shown via SEM images in Figure 7.9 and Figures A7.27-29 the thermal conductive network is formed, however the small gaps are observed between G1 and M58 particles and the some GnPs seem to be wrinkled in the nanocomposites. These

gaps display poorer compatibility and adhesion between GnPs and MWCNTs or HDPE matrix. This can most likely be reason of lower thermal conductivities. In addition, it has been mentioned earlier that this is because G1 and M58 particles surrounded by the HDPE matrix cannot touch each other, resulting in high thermal contact resistance inside the hybrid nanocomposites, as reported by Yang et al. (2011) and Zhang et al. (2018). A similar behavior is observed in the electrical conductivity.

In case of the HDPE/G2/M58 nanocomposites, except for the hybrid sample with 1/4 weight ratio of GnPs/MWCNTs, the thermal conductivity presents a downward trend with increasing the amount of M58 in the total filler content. The lowest thermal conductivity value is reached up 0.410 W/mK at 2/3 weight ratio of G2/M58. These results show that generally there is a negative synergic effect between G2 and M58 influencing the thermal conductivity, i.e., the presence of a negative hybrid effect. This may be due to the inadequate dispersion of the combination of G2 and M58 in the HDPE matrix by melt mixing. In other words, the decrease in the thermal conductivity can be because of poor dispersion. SEM images confirm that 3-D thermally conducting network structure in the hybrid nanocomposites is lacking. One can observe that there are the G2-rich and M58-rich regions in the HDPE matrix. However, GnPs and MWCNTs aren't found to have interconnected each other in the HDPE matrix. It is clear that the HDPE-rich regions with low thermal conductivity lead to decrease the thermal conductivity. Additionally, it is known that the polymer matrix is a thermal barrier for the heat propagation, whereas the carbon-based materials conduct the heat faster (Kochetov, Andritsch, Morshuis, & Smit, 2010).

Among the HDPE/G2/M58 nanocomposites, at only 1/4 of GnPs weight ratio, the hybrid nanocomposite shows a thermal conductivity of 0.443 W/mK with increase about 14.70 % compared to the pure HDPE. This value is 1.04 % higher and 2.64 % lower than that of the HDPE/G2 and HDPE/M58 nanocomposites, respectively. Based on SEM images, while MWCNTs can form a conductive network, GnPs can be randomly and separately dispersed throughout the HDPE matrix. In addition, SEM images reveal the existence of agglomeration of GnPs randomly dispersed throughout the HDPE matrix. These agglomerations may lead to more phonon scattering. This

can be reason of lower thermal conductivity. In terms of electrical conductivity, the HDPE/G2/M58 nanocomposites exhibit a different behavior from the thermal conductivity. The electrical conductivity increases with increasing M58 content in the total nanofillers and the HDPE/G2/M58 nanocomposite with G2/M58 weight ratio of 1/4 shows apparent synergic effect between G2 and M58.

The thermal conductivity of the nanocomposites with only 5 wt.% G3 was measured to be 0.393 W/mK. For the HDPE-based nanocomposites containing mixed carbon nanofillers (G3/M58), the thermal conductivity increases moderately from 0.393 W/mK to 0.456 W/mK with increasing the relative M58 concentration in the 5 wt.% total mixed carbon fillers. The HDPE/G3/M58 nanocomposite with GnPs/MWCNTs weight ratio of 1/4 displays the thermal conductivity of 0.423 W/mK, which is 9.53 % and 7.63 % higher than those of the pure HDPE and HDPE/G3 nanocomposite, respectively, and 7.24 % lower than that of the HDPE/M58 nanocomposites. The thermal conductivity of the HDPE/G3/M58 nanocomposites is between those of the HDPE/G3 and HDPE/M58 nanocomposites, i.e. no synergic effect because of using carbon based nanofillers is obtained on the thermal conductivity. The similar behavior is observed in the electrical conductivity. Based on SEM images, G3 and M58 cannot form a conductive network or a bridge between G3 and M58. In the hybrid nanocomposites, M58-rich regions and some M58 aggregates are observed. The low thermal conductivity can be due to the inadequate dispersion of carbon-based nanofillers in the HDPE matrix.

It is mentioned earlier that we determined the synergic efficiency between the carbon-based nanofillers to better understand the variation in the thermal conductivity. Higher f shows the better synergic effect of GnPs and MWCNTs in the HDPE-based nanocomposites, i.e., if f is smaller than 1, the GnPs and MWCNTs do not indicate the synergic effect in enhancing the thermal conductivity of the HDPE-based nanocomposites in this condition, as mentioned by Bai, Jin, Yang, Qi, & Wang (2019).

The comparison of f of the hybrid nanocomposites is displayed in the Figure 7.26. It is clear that the synergic effect of GnPs and MWCNTs is dependent on

GnPs/MWCNTs weight ratio and size of GnPs and MWCNTs. The maximum f is 1.50, which is achieved by using the combination of G2 and M12 at their weight ratio of 3/2. Generally, the f value of our hybrid nanocomposites is less than 1, changing with the GnPs/MWCNTs weight ratio. This shows that, in general, there is not a distinct synergic effect between GnPs and MWCNTs. At weight ratio of 2/3 between the GnPs/MWCNTs, the HDPE/G1/M12 and HDPE/G2/M12 nanocomposites exhibit f value of 1.39 and 1.23, respectively. While the thermal conductivity of HDPE/G3/M12 nanocomposite with GnPs/MWCNTs weight ratio of 3/2 lies between those of HDPE/G3 and HDPE/ M12 nanocomposites, the f value is 1.04. This shows that two types of carbon-based nanofillers creates a thermally conductive network and this is sufficient to occur a synergic effect, however the synergic effect is not higher enough to achieve the thermal conductivity of the HDPE/ M12 nanocomposites. By contrast, the HDPE/G1/M12 nanocomposite with 1/4 weight ratio of GnPs/MWCNTs exhibits f of 0.97, however its thermal conductivity of 0.469 W/mK is almost %1.1 higher than that of the HDPE/M12 nanocomposite. One can say that the thermal conductivity is lower than the thermal conductivity predicted from mixture rule i.e., the effective synergic effect does not occur.

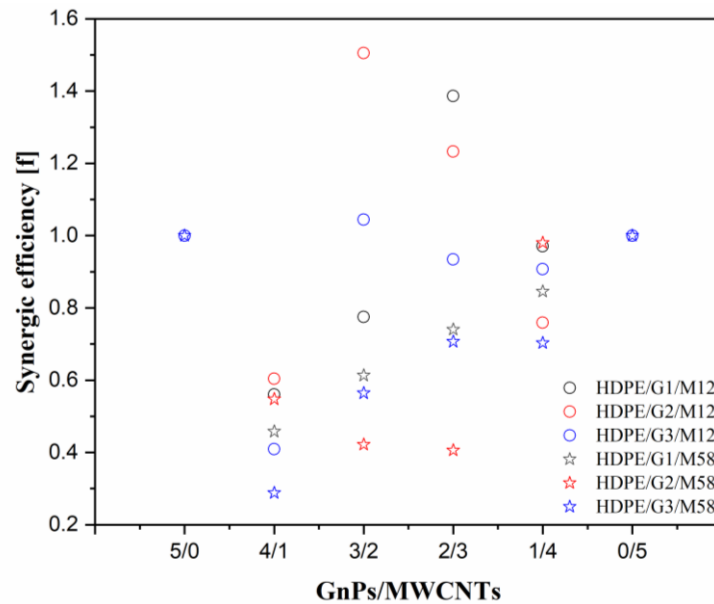


Figure 7.26 The comparison of the synergic efficiency $[f]$ of GnPs and MWCNTs on the thermal conductivity in the hybrid nanocomposites

As seen in Figure 7.26, the f values of resulting hybrid nanocomposites show a non-linear relation with types of carbon-based nanofillers and their weight ratio. Higher f is due to the bridge effect of MWCNTs on the adjacent GnPs, facilitating the formation of 3D thermal conductive network in the hybrid nanocomposites. The lower f than 1 is mainly attributed to the largely enhanced thermal conductivity of the nanocomposites with GnPs or MWCNTs and the role of MWCNTs or GnPs is weakened, as reported by Xiao et al., (2016).

To sum up briefly, in this study, the majority of hybrid system of GnPs and MWCNTs does not provide synergic improvement on the thermal conductivity, but only obeyed the mixture rule. This may be attributed to the existence of a thin polymer layer (few nm), preventing a direct contact between GnPs and MWCNTs and forming a scattering layer for the thermal transport. In addition, for some hybrid nanocomposites, SEM images reveal the existence of carbon-based nanofiller agglomerates randomly dispersed throughout the HDPE matrix. The presence of local agglomerates of nanofillers inevitably leads to increase in the thermal interfacial resistance between nanofillers. The 0D point contact between the nanofillers rises the degree of phonon scattering, preventing the heat transport (Xiao et al., 2016).

The synergic effect is depended on the filler content of hybrid nanofiller, and the similar observation is made by Caradonna et al. (2019), Huang et al. (2012) and Guo et al. (2019). In this study, the synergic effect is observed more clearly when the addition of M12 into the HDPE/G2 (11.80 wt.%) nanocomposites, compared to the HDPE-based nanocomposites with 5 wt.% of total carbon-based nanocomposites. At high GnPs concentration, when addition of MWCNTs into the HDPE/GnPs nanocomposites, 1D tube-like structure of MWCNTs is beneficial to create a more effective conductive network for the heat transport within the HDPE matrix (Szeluga et al., 2015). When decreasing the distance between the nanofillers, more thermal chains between the carbon-based nanofillers could be formed; which creates a thermal conductive network or pathway (Zakaria et al., 2017).

The weight ratio and of GnPs/MWCNTs are attractive factors importantly affecting the properties of the polymer nanocomposites, the similar results were observed by Chatterjee et al., (2012). By keeping the total carbon-based nanofiller materials as 5 wt.%, the thermal conductivity of hybrid nanocomposites exhibits considerable variation on varying the weight ratio of GnPs and MWCNTs in the hybrid nanocomposites. The synergic effect is observed at 2/3 and 1/4 weight ratios of GnPs/MWCNTs for the HDPE/G1/M12 nanocomposites, and at 3/2 and 2/3 weight ratios of GnPs/MWCNTs for the HDPE/G2/M12 nanocomposites.

The size of GnPs and MWCNTs has a significant effect on the synergic effect. The synergic effect is found to be the best for the HDPE-based nanocomposites with G2 and M12, followed by that with G1 and M12. The addition of M12 promotes the construction of a denser G2 network structure and a uniform dispersion in the HDPE matrix. Additionally, a general trend is that the thermal conductivity increases in all types of hybrid nanocomposites as the MWCNTs loading increases in the total fillers content.

In case of hybrid nanocomposites, under the same nanofiller fraction, the uprage of thermal conductivity brought by M12 is higher than M58. This can most likely be explained by the formation of more effective thermal conducting pathways as combining 1D MWCNTs having higher aspect ratio with 2D GnPs (Yue et al., 2014). Additionally, this may be due to better dispersion of M12 within the HDPE matrix.

For thermal conductivity, the selection of GnPs with a higher particle size (G2) seems be more effective to achieve a higher thermal conductivity of the HDPE-hybrid nanocomposites. In the hybrid nanocomposites, when two types of GnPs with the same diameter, G1 with thicker thickness exhibit outperform than G3 with thinner thickness. While G1 can form a more effective thermal conductive network with MWCNTs than G3.

In addition, although G2 and M58 exhibit the similar performance at enhancing the thermal conductivity in the HDPE-based nanocomposites with individual G2 and M58,

the combination of G2 and M58 displays negative synergic effect on the thermal conductivity of the HDPE/G2/M58 nanocomposites. It is greatly attributed to high thermal interfacial resistance between the polymer matrix and randomly dispersed carbon-based nanofillers. The randomly dispersed nanofillers cannot contact to each other well in the polymer matrix to greatly increase the interfacial thermal resistance, therefore displaying the lower thermal conductivity (Wu et al., 2017).

The hybrid carbon-based nanofillers have a very different effects on the thermal and electrical conductivity. The increase in thermal conductivity with the addition of MWCNTs into HDPE/GnPs nanocomposites is not dramatic as the increase of electrical conductivity. It is accepted that the different trends of variation in the electrical and thermal conductivity are primarily because of the different conducting mechanisms.

7.4.4 Mechanical Properties

The average Young's modulus, tensile strength and elongation of the pure HDPE are 816.24 MPa, 34.61 MPa and 1306.74 %, respectively. It is expected that the mechanical properties of the polymers enhance by adding MWCNTs and GnPs because of their excellent mechanical properties. It is known that the stiffness, shape, orientation and dispersion level of filler materials have effect on the Young's modulus of polymer nanocomposites. The content, geometry, dispersion level of filler materials and the interfacial adhesion of matrix/filler materials affect the tensile strength of polymer nanocomposites (Dul et al., 2018).

7.4.4.1 Comparison of mechanical properties of the HDPE/GnPs and HDPE/MWCNTs nanocomposites

As known, the mechanical reinforcement depends on two main factors:

- 1) the uniform dispersion of the nanofiller;
- 2) the strength of interfacial bonding between nanofiller and the matrix.

The GnPs and MWCNTs give different responses in the HDPE-based nanocomposites due to the contrast in their geometrical structure (Han et al., 2019). At low concentration, both MWCNTs and GnPs can disperse uniformly in the HDPE matrix. The 2-D plate-like structure of GnPs generally provide an advantage to have the strong interfacial bonding with the HDPE matrix compared to 1-D tube-like structure of MWCNTs. At high concentration, MWCNTs agglomerate and GnPs stack to each other which form the clusters.

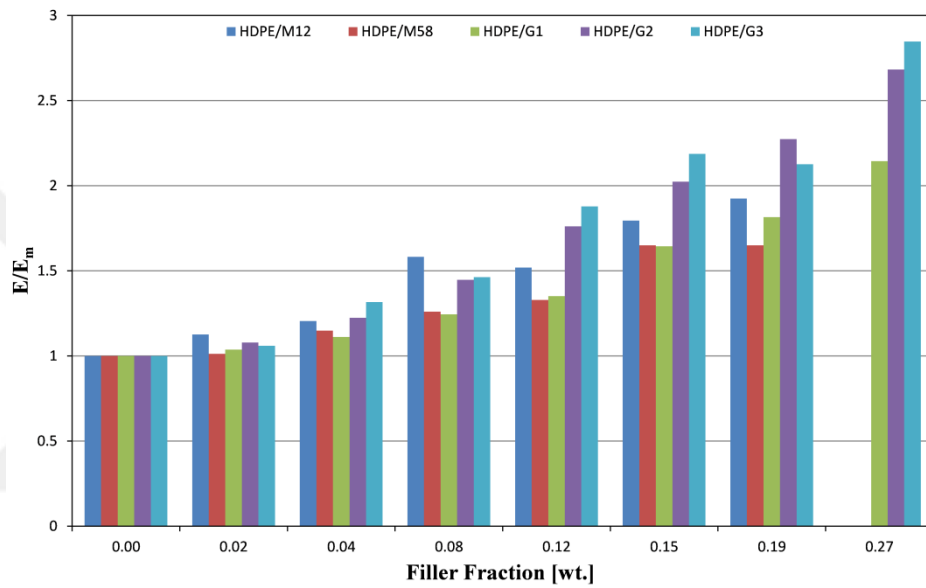


Figure 7.27 Relative Young's Modulus of the HDPE-based nanocomposites

As mentioned previously, the reinforcing effect of GnPs generally outperform that of MWCNTs. For example, the Young's modulus of the HDPE-based nanocomposites including 18.74 wt% of G2 is increased from 832.33 MPa to 1891.91 MPa (i.e., 127%) whereas in the case of 18.74 wt% of M58 a corresponding value is 1456.58 MPa. The highest enhancement is observed with the HDPE/G3 nanocomposites, boasting a 185 % improvement in the Young's modulus.

Based on the results in the present work, the dispersion of nanofiller materials is important key factor for efficient stress transfer as well as the geometry of nanofiller materials. It can be seen in Figure 7.27 that the Young's modulus of the HDPE/G1 nanocomposites is lower than that of the other types of the HDPE/GnPs and

HDPE/M12 nanocomposites and it is almost the same as that of the HDPE/M58 nanocomposites. It can be seen that G1 exhibits the poor reinforcement effect due to the agglomeration of GnPs layers which causes the weak interfacial interaction (Bisht, Dasgupta, & Lahiri, 2018).

In general, the polymer nanocomposites with GnPs show much better reinforcement performance compared to the polymer nanocomposites with MWCNTs. This may be attributed to several possible reasons, including:

- 1- The obtained results can be attributed to the geometric difference between MWCNTs and GnPs. This can be explained by the larger surface area of GnPs, increasing contact area with the HDPE matrix which maximizes the stress transport from the HDPE matrix to GnPs (Chatterjee et al., 2012). It is known that 2-D plate structure of GnPs provides larger interface than 1-D linear structure of MWCNTs. This ensures for better load transfer between the nanofiller and matrix, yielding better crack bridging and helping hinder pull-out (Cha, Kim, Ryu, & Hong, 2019; El Achaby & Qaiss, 2013).
- 2- the extremely small thickness of 2-D GnPs cause a wrinkled topography at the nanoscale, resulting in enhanced mechanical adhesion/interlocking in the polymer matrix-graphene layers interface (Bisht et al., 2018; El Achaby & Qaiss, 2013; Moosa et al., 2017).
- 3- the dispersion/distribution of GnPs in the polymer matrix is uniformly, whereas MWCNTs form some large aggregates in the HDPE-based nanocomposites,
- 4- the specific surface area of GnPs is higher than that of MWCNTs causing a substantial interphase zone around each graphene layer in the HDPE/GnPs nanocomposite, where the mobility of polymer chains was changed. However, it is less evident in the HDPE/MWCNTs nanocomposites because of 1-D linear contact in the HDPE/MWCNTs nanocomposites in opposition to the 2-D surface contact in the HDPE/GnPs nanocomposites. So, it is expected that the interfacial stress transfer in the HDPE/GnPs nanocomposites is more effective than in the HDPE/MWCNTs nanocomposites and

7.4.4.2 The mechanical properties of the HDPE/G2 (11.70 wt.%) /M12 nanocomposites

The mechanical properties of HDPE/G2 (11.70 wt.%) /M12 are given in Table 7.2. Young's modulus of the hybrid nanocomposites enhanced gradually with the addition of M12 at the same G2 loading in the ternary nanocomposites. Our observation is similar to one made by Che, Wu, Lin, Wang, & Fu, (2017). The HDPE/G2 (11.70 wt.%) /M12 nanocomposite containing 3.82 wt.% M12 content exhibits a 115 % increase, where the HDPE-based nanocomposites with G2 alone and M12 alone exhibit 102% and 79% increase, respectively, compared to the Young's modulus of a pure HDPE. In other words, the increments of Young's modulus of HDPE/G2 (11.70 wt.%) /M12 nanocomposites are higher than that of the HDPE/G2 and the HDPE/M12 nanocomposites at the same filler content.

Table 7.2 Mechanical properties of HDPE/G2 (11.70 wt.%) /M12 nanocomposites

MWCNTs Fraction [wt.%]	Young's Modulus (MPa)	Tensile Strength (MPa)	Elongation (%)
0.00	1263.56±72.43	30.61±0.62	9.02±0.52
0.20	1367.00±77.25	29.54±0.35	7.43±0.87
0.97	1496.23±95.08	31.19±0.79	7.48±1.10
1.93	1511.04±88.47	32.77±0.73	8.11±0.87
3.82	1581.03±90.47	33.53±0.39	8.71±0.83

Firstly, the addition of 0.2 wt.% M12 into the HDPE/G2 (11.70 wt.%) nanocomposites leads to a slight decrement in the tensile strength. However, this tensile strength reduction is unimportant, and this may be attributed to negligible nonuniform distribution of GnPs and MWCNTs in the HDPE matrix. Above this concentration of M12, the tensile strength of HDPE/G2 (11.70 wt.%) /M12 nanocomposite increases gradually by addition of M12 in the nanocomposites. At a total filler of 15.32 wt.%, while the tensile strength of the HDPE/G2 (11.70 wt.%) /M12 nanocomposite is 3.12 % lower than that of the pure HDPE, tensile strength of the HDPE/G2 and HDPE/M12 nanocomposite decreases by 3.98% and 22.58 % respectively.

The trend of elongation with the addition of G2 and M12 is similar to that of the tensile strength. The values of elongation of the HDPE/G2 (11.70 wt. %)/M12 nanocomposites are almost the same as that of the HDPE/G2 nanocomposites, but slightly higher than that of the HDPE/M12 nanocomposites. the synergic effect of GnPs and MWCNTs on the elongation is not discreble.

As considering the results (Table 5.2) a synergic effect on enhancing the mechanical properties is observed. The synergic effect of hybrid nanocomposites may be explained by four factors (Araby et al., 2015; Ghaleb et al., 2017; Guo et al., 2019; Yang et al., 2011) :

- 1- MWCNTs can construct GnPs to create the 3D hybrid structure, hindering the face to face agglomeration of GnPs. This provide a larger surface area, thus, which increases the contact area between the matrix and carbon-based nanofillers.
- 2- MWCNTs can behave as the extended tentacles for the 3D hybrid architectures, becoming entangled with the chain of polymer which results better interaction between the matrix and carbon-based nanofillers. In addition, producing more interfaces between the polymer matrix and nanofillers can promote load transfer from the matrix to nanofillers.
- 3- As is known, GnPs and MWCNTs are carbon-based nanofillers. Therefore, GnPs and MWCNTs are coherent through π - π interactions, which results in a synergic effect improving the mechanical performance.
- 4- The expanding contact area between the HDPE matrix and GnPs/MWCNTs results in the enhanced interfacial adhesion between the HDPE and reinforcements (Guo et al., 2019).

Our observations are similar to one made by Al-Saleh (2015a). The results of that study revealed that up to 20 wt. % of GnPs, the GnPs loading has almost no influence on the tensile strength of the PP/MWCNTs (1 wt. %)/GnPs nanocomposites. This could be attributed to the lack of proper adhesion at the interface of PP/GnPs. Al-Saleh (2015a) claimed that the used GnPs is almost the pure carbon, the lack of carboxyl and

hydroxyl groups at GnPs surface is responsible for the absence of interfacial interaction.

In other study, Wang et al. (2018) found that the tensile strength slightly decreased with addition of GnPs and MWCNTs. They reported that its maximum value is 22.93 MPa for the HDPE/GnPs (1wt.%)/MWCNTs (0.5 wt.%) nanocomposites. This value is almost the same as the value of the pure HDPE. They explained the reason of this reduction in tensile strength by the existence of unavoidable agglomerated carbon-based nanofillers (GnPs and MWCNTs) (Wang et al., 2018).

As is known, the Young's modulus of the nanocomposites is influenced by the nanofiller stiffness but also the orientation, dispersion, and shape of nanofillers. However, the tensile strength of nanocomposites is influenced by the various factors such as the matrix/nanofillers interface, the properties, amount, geometry of nanofillers and its dispersion level in the polymer matrix (Dul et al., 2018). At the same filler content, the addition of carbon-based nanofillers into the polymer matrix enhances the mechanical properties of the HDPE-based nanocomposites with direct dependence on the size and weight ratio of GnPs and MWCNTs (Zhang et al., 2018). Generally, the reinforcing effect of GnPs/MWCNTs outperforms that of the single GnPs or MWCNTs. The well-dispersed GnPs/MWCNTs in HDPE matrix provide a great number of 2D-1D interconnection for effective stress transferring as subjected to the tensile stress (Zhang et al., 2018).

7.4.4.3 The mechanical properties of the hybrid nanocomposites

Table 7.3 Young's Modulus of hybrid nanocomposites

GnPs/ MWCNTs	G1/M12	G2/M12	G3/M12	G1/M58	G2/M58	G3/M58
5\0	853.12±55.88	894.80±53.25	902.72±56.41	853.12±55.88	894.80±53.25	902.72±56.41
4\1	895.95±70.13	945.09±19.71	984.37±41.85	848.29±26.51	976.81±32.56	974.54±45.75
3\2	848.75±73.48	957.38±69.65	961.12±27.28	868.44±20.69	941.13±42.02	978.91±57.63
2\3	899.02±43.28	862.06±73.69	877.61±70.91	826.07±51.96	912.83±59.37	961.52±17.34
1\4	884.94±43.19	862.46±48.25	917.59±30.94	857.19±31.69	919.13±38.13	871.05±64.82
0\5	851.15±31.37	851.15±31.37	851.15±31.37	882.43±13.39	882.43±13.39	882.43±13.39

As seen in Tables 7.3, generally, the HDPE/GnPs/MWCNTs nanocomposites show better Young's modulus than HDPE/GnPs and HDPE/MWCNTs nanocomposites. The enhanced Young's modulus clearly indicates the synergetic effect. The rate of increment varies with the different weight ratio of GnPs/MWCNTs and size of GnPs and MWCNTs in the mixed. It is clear that the highest Young's modulus is achieved by the HDPE/G3/M12 nanocomposite with 4/1 weight ratio of GnPs/MWCNTs with an increment of up to 984.37 MPa, which corresponds to a 34.42 % increment compared with the pure HDPE. In addition, the lowest Young's modulus of the HDPE/GnPs/MWCNTs nanocomposites with 5 wt.% total nanofillers is 826.07 MPa, presenting an enhancement up to 12.62 % in comparison with the pure HDPE.

For all GnPs/MWCNTs weight ratios, except for 3/2, the coexistence of G1 and M12 displays a distinct synergic effect in enhancing the Young's modulus. The HDPE/G1/M12 nanocomposite with 3/2 weight ratio exhibits a Young's modulus value of 848.75 MPa, which is 1.09 % and 0.28 % lower than the values of HDPE/G1 and HDPE/M12 nanocomposites, respectively. This reduction is unimportant and it may be attributed to some negligible nonuniform distribution of carbon-based nanofiller in the HDPE matrix (Batakliiev et al., 2019). Based on SEM images, G1 and M12 cannot form a 3D network structure in the polymer matrix at the 3/2 weight ratio of GnPs/MWCNTs and some M12 agglomerates can locate between G1 particles. They may be the cause of the slight decrease in the Young's modulus.

At 5 wt.% total carbon-based nanofiller loading, for all GnPs/MWCNTs weight ratios, the higher Young's modulus of HDPE/G2/M12 nanocomposites occur and this can be attributed to the synergic effect of GnPs and MWCNTs inside HDPE matrix. In other words, a distinct synergic effect is observed for Young's modulus. Although SEM images display HDPE-rich and carbon-based rich regions, the HDPE/G2/M58 nanocomposites exhibit a similar trend as Young's modulus due the formation of 3-D MWCNTs-GnPs-MWCNTs network structure.

In case of the HDPE/G3/M12 nanocomposites, as seen in Table 7.3, the highest Young's modulus is achieved by 4/1 weight ratio of G3/M12 with an increase of up to 984.37 MPa, corresponding to a 34.20 % increment with respect to the pure HDPE. The HDPE/G3/M12 nanocomposites display a distinct synergic effect of carbon-based nanofillers for the enhancement of Young's modulus. Only the Young's modulus of HDPE/G3/M12 nanocomposite with 2/3 weight ratio obeys a mixture law. It is recorded as 877.61 MPa, which corresponds to enhancement of 19.65 % and 3.11 % compared with the pure HDPE and the HDPE/M12 nanocomposites, but reduction of 2.78 % with respect to the HDPE/G3 nanocomposites. This may be attributed to the absence of proper dispersion of carbon-based nanocomposites in the HDPE matrix.

For the HDPE/G1/M58 nanocomposites, the mixture of G1 and M58 cannot provide a synergic effect on the Young's modulus of HDPE-based nanocomposites. Furthermore, the Young's modulus for the HDPE/G1/M58 nanocomposite with weight ratio of 2/3 is observed to be lower than that of the HDPE-based nanocomposites with alone G1 and M58. In SEM images, some small gaps are observed in the nanocomposites and these lead to poorer compatibility and adhesion between G1 and M58 or HDPE matrix. In addition, isolated M58 are embedded into the G1 layers and the some G1 seems to be wrinkled in the nanocomposites. These may lead to limit the load transfer from the matrix to carbon-based nanofillers.

With the same nanofiller content of 5 wt.%, the Young's modulus of the HDPE/G3/M58 nanocomposite with 1/4 weight ratio of GnPs/MWCNTs is 871.05 MPa, which is lower than that of HDPE/G3 and HDPE/M58 nanocomposites. The reason may be some aggregates in the nanocomposites. At other weight ratios, the combination of G3 and M58 displays a clear synergic effect in enhancing Young's modulus of the HDPE/G3/M58 nanocomposites.

The synergic effect of GnPs and MWCNTs on the Young's modulus of hybrid nanocomposites may be explained that the addition of GnPs and MWCNTs limits the mobility of polymer chains under the applied load. The influence of the GnPs and MWCNTs loading may hinder the molecular motions of HDPE matrix and increase

the cross-link ratio. Moreover, the high modulus, strength and aspect ratio of GnPs and MWCNTs also contribute to the improvement of young's modulus (Zakaria et al., 2017).

Consequently, the enhancement in the Young's modulus of hybrid nanocomposites is influenced by the weight ratio of GnPs/MWCNTs and the size of GnPs and MWCNTs. There is not a liner relation between the Young's modulus and weight ratio of hybrid nanofillers. Generally, the combination of GnPs with larger surface area and MWCNTs with lower aspect ratio is beneficial for better interfacial stress transfer from the HDPE matrix to carbon-based nanocomposites. This may be attributed to a more extensive contact area, enhancing the Young's modulus, as mentioned by Navidfar & Trabzon, (2019).

In case of hybrid nanocomposites, at 5 wt/% total nanofillers content, it is evident that the size and weight ratio of GnPs and MWCNTs has an influence on the tensile strength and elongation (Table 7.4 and 7.5). However, the change in the tensile strength by changing weight ratio of GnPs/MWCNTs is not considerable. The strength of pure HDPE is 34.61 MPa and as mentioned above, at this concentration, the tensile strength of HDPE-based nanocomposites is lower than that of the pure HDPE. This can be attributed to the agglomeration of carbon-based nanofillers in the HDPE matrix. This agglomeration becomes the stress concentration site in the polymer nanocomposites, resulting in the low mechanical properties (Lin et al., 2016). In other words, the agglomerates of GnPs lead to the absence of interfacial adhesion and limit the load transfer from the HDPE matrix to nanofillers, as mentioned by Guo et al. (2019). In addition, as stated previously, the decrease in the tensile strength can be attributed to the disentanglement of HDPE molecular chains with carbon-based nanofillers, resulting the poor load transfer (Uyor, Popoola, Popoola, & Aigbodion, 2019).

As a content of 5 wt.%, the greatest tensile strength is achieved by the HDPE/G3/M58 nanocomposite with weight ratio of 3/2, while the lowest value of tensile strength is record as 25.69 MPa for the HDPE/G1 nanocomposites. The better

tensile strength is attributed to the enhanced load transfer from HDPE matrix to nanofillers. As is known, the strong bonding between HDPE and carbon-based nanofillers and good dispersion are contributed to the improved tensile strength. In addition, the improved tensile strength is also due to the creation of network structures in the HDPE matrix, decreasing the mobility of HDPE molecular chains when applied the load (Uyor et al., 2019).

Table 7.4 Tensile strength (MPa) of hybrid nanocomposites

GnPs/ MWCNTS	G1/M12	G2/M12	G3/M12	G1/M58	G2/M58	G3/M58
5\0	25.69±0.45	26.22±0.43	26.08±0.51	25.69±0.45	26.22±0.43	26.08±0.51
4\1	26.80±0.24	27.26±0.26	27.39±0.39	25.82±1.06	27.33±0.74	28.37±0.59
3\2	27.08±0.17	26.86±0.33	27.46±0.30	27.11±0.42	27.49±0.52	28.63±0.43
2\3	27.37±0.40	26.72±0.32	27.40±0.58	27.41±0.26	27.33±0.49	28.10±0.50
1\4	27.27±0.15	26.95±0.36	27.22±0.43	26.52±0.42	27.87±0.46	28.25±0.24
0\5	26.95±0.74	26.95±0.74	26.95±0.74	28.35±0.44	28.35±0.44	28.35±0.44

Table 7.5 Elongation (%) of hybrid nanocomposites

GnPs/ MWCNTs	G1/M12	G2/M12	G3/M12	G1/M58	G2/M58	G3/M58
5\0	11.27±0.70	11.14±0.25	10.63±0.58	11.27±0.70	11.14±0.25	10.63±0.58
4\1	10.96±0.22	10.26±0.41	10.08±0.4	11.26±0.36	9.33±0.29	9.98±0.54
3\2	10.74±0.34	10.43±0.21	9.77±0.20	10.81±0.27	9.3±0.61	9.84±0.54
2\3	10.1±0.38	9.98±0.39	10.27±0.53	11.16±0.58	10.11±0.59	10.00±0.40
1\4	9.79±0.43	9.93±0.41	9.97±0.16	9.59±0.47	10.07±0.45	10.57±0.64
0\5	10.17±0.58	10.17±0.58	10.17±0.58	9.97±0.13	9.97±0.13	9.97±0.13

In case of the HDPE/G1/M12 nanocomposites, the highest enhancement is obtained for the HDPE/G1/M12 nanocomposite with 2/3 weight ratio and it is over 6.54% and 1.56 % higher than for the HDPE/G1 and HDPE/M12 nanocomposites, respectively. The synergic effect of G1 and M12 is not observed at only 4/1 weight ratio, however this value is 0.56% lower than that of HDPE/M12 nanocomposites. In terms of weight ratio, there is a slight difference in tensile strength value. The similar trend is observed for other hybrid nanocomposite types.

For the HDPE/G2/M12 nanocomposites, the tensile strength of the HDPE/G2/M12 nanocomposite with 4/1 weight ratio presents the highest tensile strength with reduction of up to 21.24 % compared to the pure HDPE. Only, a slight synergic effect is observed at this weight ratio. The HDPE/G2/M12 nanocomposites with other weight ratio exhibit a slightly lower tensile strength than the HDPE/M12 nanocomposites, but higher than the HDPE/G2 nanocomposites.

For all weight ratio of GnPs/MWCNTs, the tensile strength improvement of the HDPE/G3/M12 nanocomposites is slightly higher than that with only G3 and M12. This can be attributed to the increasing contact area between the HDPE matrix and G3/M12 results in the enhanced interfacial adhesion between the HDPE matrix and nanofillers (Guo et al., 2019). In other words, the combination of G3 and M12 shows a synergic effect in the enhancing the tensile strength of the HDPE/G3/M12 nanocomposites.

In case of the HDPE/G1/M58 nanocomposites, a synergic effect is not observed for the tensile strength. The similar observation is made for the HDPE/G2/M58 nanocomposites. In addition, a synergic effect is observed for only the HDPE/G3/M58 nanocomposite with 3/2 weight ratio of GnPs/MWCNTs.

As a result, The tensile strengths of the hybrid nanocomposites with mixing weight ratio of (4/1) G2/M12, (4/1, 3/2, 2/3, 1/4) G3/M12 and (3/2) G3/M58 are higher than that of the HDPE based-nanocomposites with single type of carbon-based material (5/0 and 0/5). This reason may be that MWCNTs efficiently decrease the agglomeration and stacking between GnPs layers and together they form better reinforcement. The important synergetic effect of GnPs and MWCNTs may be due to the following two possible reasons (Ghaleb et al., 2017; Moosa et al., 2017; Navidfar & Trabzon, 2019; Yang et al., 2011).:

- 1- MWCNTs bridge between GnPs layers to obtain 3-D hybrid structure inhibiting face to face GnPs aggregation. This structure causes large surface area and increase in the contact area between HDPE and hybrid filler material.

- 2- The MWCNTs can behave as the extended tentacles for 3-D hybrid structures, becoming entangled with the chain of HDPE resulting a better interaction between the HDPE matrix and hybrid filler materials. Thus, the larger surface area and increased contact area between them can facilitate the load transfer in the tensile test.

As a result, based on the results of this study, the synergic effect of GnPs and MWCNTs on the tensile strength is evident. However, this effect is not more intensive. In addition, the weight ratio of GnPs/MWCNTs have a negligible influence on the tensile strength. And the size of GnPs and MWCNTs with higher aspect ratio contributes more effectively to the synergic effect because of the better dispersibility of carbon-based nanofillers facilitating the load transfer from the matrix to nanofillers (Guo et al., 2019).

Based on the results in Table 7.5, a synergic effect in improving elongation is not observed for HDPE-based hybrid nanocomposites. The weight ratio and size of GnPs and MWCNTs have slightly influence on the elongation of hybrid nanocomposites. The elongation value of hybrid nanocomposites is around 10 %.

The presence of agglomerates will largely reduce the load transfer efficiency (Francis et al., 2019). The agglomerates of carbon-based nanofillers acts as sites for the crack generation and stress concentration. Any discontinuity in the network structure may behave as the weakest link for the load transfer and the HDPE matrix may fail as exposed to the external loading (Bisht et al., 2018). The MWCNTs agglomerates can act as the stress concentration locations, which results in the generation of crack under the applied tensile force (Kumar et al., 2017)

Al-Saleh (2015a) reported that at 5 vol% total nanofiller loading, the tensile strength of the PP/GnPs/MWCNTs nanocomposites increases with increasing MWCNTs content in the total nanofiller loading because of the strong adhesion at PP/MWCNTs interfaces and better dispersion of MWCNTs. A synergic effect of GnPs and MWCNTs in enhancing tensile strength of hybrid nanocomposites is not discernible.

Paszkievicz et al. (2018) reported that the values of Young's modulus of nanocomposites significantly increase with adding the mixture of MWCNTs and GnPs. They indicated that as 5 wt.% total nanofiller content, the highest enhancement in the Young's modulus is achieved by the PP/MWCNTs/GnPs nanocomposite with 1/1 weight ratio. It is over 10 MPa greater than for the PP/MWCNTs/GnPs nanocomposite with 3/1 weight ratio.

The mechanical properties measurements of hybrid nanocomposites show that the coexistence of GnPs and MWCNTs indicate a distinct synergic effect of GnPs and MWCNTs in enhancing Young's modulus, but no synergic effect on the elongation. In case of tensile strength, generally, a synergic effect is observed for the combination of GnPs and MWCNTs with higher aspect ratio. While the weight ratio of GnPs and MWCNTs has a non-linear influence on the Young's modulus, it does not cause any significant difference in the tensile strength and elongation. The size of GnPs and MWCNTs has a significant effect on Young's modulus, however a slight effect on the tensile strength and elongation.

Although, the highest Young's modulus is achieved by the HDPE/G3/M12 nanocomposites, generally, the combination types including GnPs and MWCNTs with lower aspect ratio performs better than that with the GnPs and MWCNTs with higher aspect ratio. In terms of tensile strength, notwithstanding, the synergic effect is observed for the nanocomposites containing GnPs and MWCNTs with higher aspect ratio, the nanocomposites including GnPs and MWCNTs with lower aspect ratio exhibit higher tensile strength values. Considering the results of this study, the combination of a larger surface area of GnPs and higher aspect ratio of MWCNTs contributes to synergetic effect of GnPs and MWCNTs on the mechanical properties.

Generally, the co-presence of GnPs and MWCNTs indicates a distinct synergic effect on the enhancement of the mechanical properties. Firstly, MWCNTs can prevent the restacking of GnPs and help to 3-D hybrid structure. This can lead to more interface between the matrix and nanofillers, which promotes the load transport from the

polymer matrix to nanofillers. Secondly, 1-D long MWCNTs can act as the connector and form bridges between GnPs to ensure a global network inside the polymer matrix and remarkable reinforcement efficiency (Araby et al., 2015; Wang et al., 2018). Finally, the ability of GnPs and MWCNTs to synergically reinforce the HDPE matrix is attributed to the strong interfacial interaction between the matrix and nanofiller and the GnPs/MWCNTs interactions. They can absorb a considerable amount of energy and support the stress transfer when subjected to the strong tensile stress. The excellent molecular coupling and large contact areas between the matrix and nanofillers can help a lot for transporting the load throughout the tensile process. The well-dispersed hybrid network structures can distribute a world of mechanical energy (Lin et al., 2016; Navidfar & Trabzon, 2019; Zhang et al., 2018)

7.4.5 Thermal Properties

7.4.5.1 DSC Results

It is known that the mechanical and thermal properties of polymers/polymer nanocomposites are influenced by the crystallinity of samples (Arora, Pathak, & Zafar, 2019; El Achaby et al., 2012; Guo et al., 2019). In addition, Kim et al. (2019) claimed that the crystallization behavior of the polymer nanocomposites gives information about their thermodynamic behavior. Therefore, the isothermal crystallization and melting behavior of pure HDPE and its nanocomposites have been investigated by using DSC.

As it is mentioned early that the T_m , T_c , ΔH_f and X_c of pure HDPE are 130.06 °C, 116.30 °C, 205.08 J/g and 70.24 %, respectively. Irrespective of the size and type of carbon-based nanofillers, the general findings from the DSC results of the HDPE-based nanocomposites can be summarized as:

- The presence of the carbon-based nanofillers induces a little or no change for the T_m of HDPE-based nanocomposites.
- The T_m of HDPE-based nanocomposites is in the range of 129-132 °C.

- The T_c of samples increases with increasing the carbon-based nanofiller content, which indicates that the carbon-based nanofillers play the heterogeneous nucleation's roles through the HDPE crystallization (Guo et al., 2019).
- The ΔH_f of HDPE-based nanocomposites decreases with the inclusion of the carbon-based nanofiller.
- The incorporation of nanofillers makes a few effects on the crystallinity of HDPE.

7.4.5.1.1 Comparison of DSC results of HDPE/MWCNTs and HDPE/GnPs nanocomposites. In order to better interpret the synergic effect of carbon-based nanofillers, before investigating the DSC properties of hybrid nanocomposites, the DSC results of nanocomposites with MWCNTs and GnPs are compared. The results of T_m , T_c , ΔH_f and X_c as a function of the carbon-based nanofiller loading for HDPE nanocomposites with MWCNTs and GnPs are given in Tables A7.1-4 in the Appendix

The results show that T_m of all HDPE-based nanocomposites with MWCNTs or GnPs ranged from 129.74 °C to 132.17 °C. It is clearly seen from Tables A7.1-2 that while the type of carbon-based nanofillers has little or no significant influence on the T_m , the T_c values of HDPE/MWCNTs nanocomposites is little higher than that of HDPE/GnPs nanocomposites. For example, the HDPE/MWCNTs nanocomposite with 18.74 wt.% MWCNTs indicates an average increment of 5.25 °C in T_c compared to the pure HDPE, while the HDPE/GnPs nanocomposite displays a smaller increment of 3.71 °C at the same content. The comparison of different types and sizes of the carbon-based nanofillers displays that the MWCNTs seems to be a little more effective to achieve a higher T_c of the polymer matrix. In other words, MWCNTs play more effective roles of the heterogeneous nucleation during the crystallization of HDPE.

Table A7.3 shows a linear decrease of ΔH_f with gradually increasing nanofiller loading regardless of the carbon-based nanofillers type. As seen in the finding, no appreciable change in the X_c is observed when adding GnPs or MWCNTs. Based on the results (Table A7.3-4), the values of ΔH_f and X_c of the HDPE/MWCNTs

nanocomposites is lower than those of HDPE/GnPs nanocomposites. This can be explained that due to their large surface area, GnPs provides more area for the HDPE crystals nucleation.

7.4.5.1.2 The DSC results of HDPE/G2 (11.70 wt.%) /M12 nanocomposites. Although the HDPE/G2 (11.70 wt.%) nanocomposites with different contents of M12 from 0.20 to 3.82 wt.%, three samples with 0.00 wt.% M12, 0.20 wt.% M12 and 3.82 wt.% M12 were analyzed in this thesis to see the effect of hybrid nanofillers on the melting and crystallization properties. The DSC results of the HDPE/G2 (11.70 wt.%) /M12 nanocomposites are gathered in Table 7.6.

The T_m , T_c and ΔH_f and X_c of the HDPE/G2 (11.70 wt.%) nanocomposites with 0.20 wt.% of M12 are 131.72 °C, 119.34 °C, 185.80 J/g and 73.18 %, respectively, while the HDPE/G2 (11.70 wt.%) nanocomposites with 3.82 wt.% of M12 shows respective values of 129.37 °C, 121.40 °C, 181.10 J/g and 73.16 %.

The results from Table 7.6 suggest that the presence of M12 induces a little or no variation in the melting and crystallization behavior of HDPE/G2 (11.70 wt.%) /M12 nanocomposites compared to the HDPE-based nanocomposites with alone M12 and G2 at the same nanofiller loadings. A slightly lower impact on T_m , T_c , ΔH_f and X_c is observed with increasing the content of M12.

For the HDPE/G2 (11.70 wt.%) /M12 nanocomposites, the values of corresponding parameters obtained by DSC are slightly higher than the HDPE-based nanocomposites with alone M12 and G2. However, there is no significant difference. In other words, the mixture of G2 and M12 provides a synergic effect, but it is not remarkable. The reasons of the synergic effect may be that the heterogeneous nucleation agent will be more effective for hybrid nanocomposites, whose structural fluctuation causes the further decrease in the values of basal interfacial free energies and therefore the nucleation free energy (Xu et al., 2019).

Table 7.6 DSC results of HDPE/G2 (11.70 wt.%) /M12 nanocomposites

MWCNTs Fraction [wt.%]	T_m [°C]	T_c [°C]	ΔH_f [J/g]	X_c (%)
0.00	131.63	119.97	186.40	72.05
0.20	131.72	119.34	185.80	73.18
3.82	129.37	121.40	181.10	73.16

7.4.5.1.3 The DSC results of HDPE-based hybrid nanocomposites. To investigate the effect of GnPs/MWCNTs weight ratio on the melting and crystallization behavior of the hybrid nanocomposites, by keeping the total nanofiller concentration as 5 wt.%, the all weight ratios of the HDPE/G2/M12 and HDPE/M58/G2 nanocomposites have analyzed by DSC. The corresponding characterization data are given in Table 5.7.

In case of the HDPE/G2/M12 and HDPE/G2/M58 nanocomposites, one can see from Table 7.7 that the weight ratio of GnPs/MWCNTs has slightly lower effect on the T_m , T_c , ΔH_f and X_c . The average values of T_m , T_c , ΔH_f and X_c for these nanocomposites are at about 131 °C, 119 °C, 201.7 J/g and 72.5 %, respectively, independent of the GnPs/MWCNTs weight ratios. As considering these findings, to investigate the size effect of GnPs and MWCNTs in the mixed, the 3/2 weight ratio at which the highest thermal conductivity is achieved has been selected.

As seen in Table 7.8, 7.9, 7.10 and 7.11, the size and size of hybrid nanofillers (GnPs +MWCNTs) induce a little or no change in the values of T_m , T_c , ΔH_f and X_c of all hybrid nanocomposites. Based on data from this study, the presence of GnPs and MWCNTs does not provide any synergic effect. This can be explained that all parameters are almost the same for all carbon-based materials. It is stated previously that the crystallinity can influence the enhancement of thermal and mechanical properties of polymer nanocomposites. As seen from the aforementioned results, the addition of carbon-based nanofillers (MWCNTs, GnPs or GnPs +MWCNTs) cause a slightly or no change in the crystallinity of the HDPE and therefore, it is to be noted that the thermal and mechanical enhancements are not caused by variations of crystallinity.

Table 7.7 DSC results of HDPE/G2 /M12 and HDPE/G2/M58 nanocomposites

GnPs/MWCNTs	G2/M12				G2/M58			
	T_m [°C]	T_c [°C]	ΔH_f [J/g]	X_c (%)	T_m [°C]	T_c [°C]	ΔH_f [J/g]	X_c (%)
5/0	131.91	118.35	202.00	72.57	131.91	118.35	202.00	72.57
4/1	130.52	118.87	201.90	72.53	130.89	118.87	203.00	72.93
3/2	130.80	118.22	201.70	72.46	131.37	120.02	199.80	71.98
2/3	130.54	119.90	202.00	72.57	130.54	119.90	202.90	72.98
1/4	131.86	119.34	201.70	72.46	131.86	119.34	201.70	72.46
0/5	130.25	120.06	201.70	72.46	132.08	118.95	200.70	72.10

Table 7.8 T_m [°C] results of hybrid nanocomposites

GnPs/MWCNTs	G1/M12	G2/M12	G3/M12	G1/M58	G2/M58	G3/M58
5/0	130.33	131.91	130.92	130.33	131.91	130.92
3/2	130.89	130.80	131.90	131.95	131.37	131.76
0/5	130.25	130.25	130.25	132.08	132.08	132.08

Table 7.9 T_c [°C] results of hybrid nanocomposites

GnPs/MWCNTs	G1/M12	G2/M12	G3/M12	G1/M58	G2/M58	G3/M58
5/0	118.68	118.35	119.11	118.68	118.35	119.11
3/2	120.36	118.22	118.43	119.87	120.02	119.5
0/5	120.06	120.06	120.06	118.95	118.95	118.95

Table 7.10 ΔH_f [J/g] results of hybrid nanocomposites

GnPs/MWCNTs	G1/M12	G2/M12	G3/M12	G1/M58	G2/M58	G3/M58
5/0	202.40	202.00	202.80	202.40	202.00	202.80
3/2	202.10	201.70	199.90	200.70	199.80	201.70
0/5	201.70	201.70	201.70	201.70	201.70	201.70

Table 7.11 X_c [%] results of hybrid nanocomposites

GnPs/MWCNTs	G1/M12	G2/M12	G3/M12	G1/M58	G2/M58	G3/M58
5/0	72.14	72.57	72.86	72.14	72.57	72.86
3/2	72.61	72.46	70.92	72.10	71.78	72.46
0/5	72.46	72.46	72.46	72.46	72.46	72.46

7.4.5.2 TGA Results

As mentioned in other chapters, the pure HDPE exhibits one-step decomposition behavior. The values of $T_{5\%}$, $T_{50\%}$, T_{deg} and residual mass of the pure HDPE are 440.80°C, 474.46 °C, 478.79 °C and 0.84 %, respectively. However, the results of carbon-based nanofillers from Figure A7.36 show that there is negligible mass change during the entire temperature range. In other words, the carbon-based nanofillers are thermally stable up to 700 °C.

Based on the TGA results in this thesis, all nanocomposites exhibit similar thermal decomposition behavior to that of the pure HDPE, independent of carbon-based nanofillers loading values. This indicates that the type of carbon-based nanofillers cannot influence the thermal decomposition behavior of the sample. However, the degradation begins at higher temperatures and the type of carbon based nanofillers has influence on the values of corresponding characteristic thermal data.

7.4.5.2.1 Comparison of TGA results of HDPE/MWCNTs and HDPE/GnPs nanocomposites. The characteristic thermal data for the HDPE/MWCNTs and HDPE/GnPs is summarized Tables A7.4-8 in the Appendix. As stated in previously, the addition of carbon-based nanofillers (MWCNTs or GnPs) enhances the thermal stability of the HDPE-based nanocomposites.

Irrespective of size, the HDPE/MWCNTs nanocomposites are thermally more stable than the HDPE/GnPs nanocomposites. This can be ascribed to the following possible reasons:

- 1- more homogenous dispersion of MWCNTs in the HDPE matrix at the same processing conditions,
- 2- the better bonding between the HDPE matrix and MWCNTs, and
- 3- better matrix-MWCNTs interaction.

As mentioned by Wegrzyn, Galindo, et al. (2015), the influence is stronger as the MWCNTs are used as the nanofillers likely because of the better dispersion obtained

at the same processing conditions. In theory, 2-D GnPs nanomaterials should exhibit better thermal stability because of better barrier properties which distract the combustion gasses emission from the sample bulk. However, the well-dispersed MWCNTs create a uniform network in the polymer matrix displaying the mentioned barrier properties at the enough level.

In contrast to our results, results of a similar study, by El Achaby & Qaiss (2013) using HDPE matrix, showed that the HDPE/GnPs nanocomposites displayed a greater thermal stability than the HDPE/MWCNTs nanocomposites. The level of the interfacial interaction in the HDPE/GnPs nanocomposites was higher than that ever possible in the HDPE/MWCNTs nanocomposites. They interpreted this to the greater surface area and the platelet-like surface of GnPs compared to MWCNTs, being translated onto a greater interfacial zone in the HDPE nanocomposites with GnPs compared to the HDPE/MWCNTs nanocomposites (El Achaby & Qaiss, 2013).

7.4.5.1.2 The TGA results of HDPE/G2 (11.70 wt.)/M12 nanocomposites. Although the HDPE/G2 (11.70 wt.)/M12 nanocomposites with a variety of M12 loading were produced, two samples including 0 wt.% M12 and 3.82 wt.% M12 were mainly analyzed in this thesis to see the influence of M12 addition into the HDPE/G2 (11.70 wt.%) nanocomposites on the thermal stability. TGA thermographs of the HDPE/G2 (11.70 wt.)/M12 nanocomposites (The inset shows the derivative thermogravimetric (DTG) curves) were given in Figures A7.37 and Table 5.11 summarizes the characteristic values of the decomposition process of the HDPE/G2 (11.70 wt.)/M12 nanocomposites obtained by TGA.

Table 7.12 TGA results of HDPE/G2 (11.70 wt.)/M12 nanocomposites

MWCNTs Fraction [wt.%]	$T_{5\%}$ [°C]	$T_{50\%}$ [°C]	T_{deg} [°C]	Residual Mass [%]
0.00	456.34	485.53	487.62	11.68
3.82	464.65	491.45	492.35	17.68

TGA curves display (Figure A7.37) that the HDPE/G2 (11.70 wt.)/M12 nanocomposites decompose with a clear one-step process, independent of carbon-

based nanofillers loading values. The thermal stability of the HDPE/G2 (11.70wt.%) nanocomposites shows a gradually improving tendency with the addition of M12.

As seen in Table 7.12, the addition of 3.82 wt.% of M12 into the HDPE/G2 (11.70wt.%) nanocomposites leads to a shift of $T_{5\%}$ of 8 °C toward higher temperature. The $T_{50\%}$ of the HDPE/G2 (11.70 wt.%) nanocomposites is found at about 485.53 °C, it increase to 491.45 °C in the HDPE/G2 (11.70 wt.%) nanocomposites with 3.82 wt.% M12. As the content of M12 increases, the degradation of the nanocomposites is delayed further. The inclusion of 3.82 wt.% M12 leads to a shift of about 14 °C. At 15.81 wt.% of filler content, the T_{deg} for the HDPE/(G2 (11.0 wt.%)/M12 nanocomposites are 492.35 °C, it is 4.73 °C higher than that of the HDPE/G2 nanocomposites and is 2 °C lower than that of the HDPE/M12 nanocomposites. In addition, the residual mass of the HDPE/(G2 (11.0 wt.%)/M12 nanocomposites is almost 1% lower compared to those of the HDPE/M12 and the HDPE/G2 (11.0 wt.%)/M12 nanocomposites.

According to our results, the enhanced thermal stability of HDPE/G2 nanocomposites is less notable than that of the HDPE/M12 and the HDPE/G2 (11.0 wt.%)/M12 nanocomposites. The results clearly show that the addition of M12 enhances thermal stability of nanocomposites. However, the HDPE/G2 (11.0 wt.%)/M12 nanocomposites do not represent a synergic effect of GnPs and MWCNTs for the thermal stability, but their thermal stability obeys mixture law. This enhancement may be attributed to:

- 1- a strong interfacial interaction between the HDPE chains and hybrid nanofillers
- 2- the combined stabilizing influence caused by GnPs and MWCNTs together
- 3- occurring an interlocked nanostructure between GnPs and MWCNTs (J.-H. Lin et al., 2016; Roy, Srivastava, Pionteck, & Mittal, 2015).

The results show that there does not exist a synergic effect between G2 and M12 on the thermal stability as well as electrical conductivity. However, the HDPE/G2 (11.0 wt.%)/M12 nanocomposites exhibit better thermal conductivity and mechanical properties than HDPE/G2 nanocomposites and HDPE/ M12 nanocomposites at the

same filler loadings. This can be explained by non-sufficient uniform dispersion of the carbon-based nanofillers.

7.4.5.2.3 The TGA results of hybrid nanocomposites. Even though the hybrid nanocomposites with a variety of GnPs/MWCNTs weight ratio were prepared, four samples including 5/0, 4/1, 1/4 and 0/5 of GnPs/MWCNTs weight ratios were mainly used in this thesis to investigate the effect of weight ratio and size on the thermal stability.

The results of TGA on the hybrid nanocomposites with 5 wt.% nanofillers are shown in Figure A7.38-43 and the corresponding characteristic thermal data are given in Table 7.13-16. Figures present that, as stated within the thermal properties part of other nanocomposites, all hybrid nanocomposites decompose with one-step process, in dependent of the size of GnPs and MWCNTs. However, the presence of carbon-based nanofillers has an obvious stabilization influence on the thermal degradation of specimens.

These results illustrate that none of the thermal stability properties indicate any signs of a synergic effect. i.e., no synergic effect exists in the hybrid nanocomposites, but only a mixture law is obeyed. The values of HDPE-based hybrid nanocomposites lie between the values of the HDPE-based nanocomposites with single nanofillers.

The study brings out that by keeping the total nanofillers loading as 5 wt.%, the thermal stability of hybrid nanocomposites displays considerable variation on altering the weight ratio of GnPs and MWCNTs in the HDPE-based nanocomposite. The addition of GnPs and MWCNTs helps improve the thermal stability of the HDPE-based nanocomposites and the thermal stability increase gradually with increment in the content of MWCNTs in total nanofiller loading. In other words, $T_{5\%}$, $T_{50\%}$ and T_{deg} monotonously increase in the six types nanocomposites as the amount of MWCNTs increases in the total filler content. This is expected because, as mention above, the upgrade of the thermal stability brought by MWCNTs is higher than GnPs under the same filler loadings.

As seen in Table 7.13, the weight loss of 5% is at around 462 °C for the hybrid nanocomposites with 0/5 weight ratio of GnPs/MWCNTs in irrespective of the size of carbon-based nanofillers. As stated in the previous chapter, the value of $T_{5\%}$ for the HDPE/GnPs nanocomposites changes with varying the size of GnPs. The $T_{5\%}$ values of the HDPE/G1/MWCNTs, the HDPE/G2/MWCNTs and the HDPE/G3/MWCNTs nanocomposites are 444.15 °C, 449.43 °C and 446.79 °C, respectively. However, the value of $T_{5\%}$ exhibit a slight dependence on the size of GnPs and MWCNTs. Only, the HDPE/G1/M12 nanocomposites at the GnPs/MWCNTs weight ratio of 4/1 is considerably lower than others. This can be explained by non-uniform dispersion of hybrid nanofillers in the HDPE matrix.

The $T_{5\%}$ of hybrid nanocomposites exhibits gradually improving tendency with increasing the MWCNTs content in the total filler loading. When the weight ratio of GnPs/MWCNTs decreased 4/1 to 1/4, expecting the HDPE/G1/M12 nanocomposites, the values of $T_{5\%}$ for the hybrid nanocomposites are shifted by about 2-3 °C to higher temperature up to around 460 °C.

The similar tendency is observed however the thermal interval is lower that the observed at $T_{5\%}$ as mentioned before. So that, for $T_{50\%}$, an average temperature increases of 8-9 °C. The 50% weight loss in the hybrid nanocomposites with 5/0 and 0/5 weight ratios of GnPs/MWCNTs occurs as exposed to heat at 480.17 °C and 488.88 °C, respectively, irrespective of their size. One can say from the results given in Table 7.14 that the $T_{50\%}$ of hybrid nanocomposites increases with increasing the weight ratio of GnPs/MWCNTs, but the size of GnPs and MWCNTs in the mixing fillers has a slightly influence. At the same weight ratio of GnPs/MWCNTs, the maximum difference in $T_{50\%}$ between two samples is about 2 °C.

Table 7.15 gives information about T_{deg} where the rate of heat release is maximized. The variation tendency of T_{deg} in the hybrid nanocomposites is similar to that of $T_{50\%}$ above. The T_{deg} is around 483 and 491 for the hybrid nanocomposites with GnPs/MWCNTs weight ratios of 5/0 and 0/5, respectively. For all types of the hybrid nanocomposites, peak shifts to higher temperatures with decreasing GnPs in the total

nanofillers content. TGA analysis of the hybrid nanocomposites suggests a mild improvement of thermal stability in range 7-8 °C. In addition, as mentioned above, the maximum temperature difference of about 2 °C at the same weight ratios.

Table 7.13 $T_{5\%}$ [°C] results of hybrid nanocomposites

GnPs/MWCNTs	G1/M12	G2/M12	G3/M12	G1/M58	G2/M58	G3/M58
5/0	444.15	449.43	446.79	444.15	449.43	446.79
4/1	452.60	457.47	456.01	456.79	457.17	458.32
1/4	461.77	459.07	458.88	459.02	460.93	460.96
0/5	462.29	462.29	462.29	462.52	462.52	462.52

Table 7.14 $T_{50\%}$ [°C] results of hybrid nanocomposites

GnPs/MWCNTs	G1/M12	G2/M12	G3/M12	G1/M58	G2/M58	G3/M58
5/0	479.08	480.64	480.79	479.08	480.64	480.79
4/1	482.58	483.70	483.79	482.71	482.70	483.36
1/4	487.88	487.46	485.76	485.62	487.36	485.72
0/5	488.73	488.73	488.73	489.03	489.03	489.03

Table 7.15 T_{deg} [°C] results of hybrid nanocomposites

GnPs/MWCNTs	G1/M12	G2/M12	G3/M12	G1/M58	G2/M58	G3/M58
5/0	482.09	483.38	483.40	482.09	483.38	483.40
4/1	485.58	486.55	486.38	485.07	485.07	486.13
1/4	490.19	489.70	488.04	488.06	490.13	489.30
0/5	490.37	490.37	490.37	491.94	491.94	491.94

Table 7.16 Residual Mass [%] results of hybrid nanocomposites

GnPs/MWCNTs	G1/M12	G2/M12	G3/M12	G1/M58	G2/M58	G3/M58
5/0	5.33	6.08	4.67	5.33	6.08	4.67
4/1	6.58	5.12	4.55	6.46	6.46	5.44
1/4	5.38	6.06	6.15	6.10	5.39	6.32
0/5	4.88	4.88	4.88	5.39	5.39	5.39

The residual amount of the hybrid nanocomposites exhibits a fluctuation change with the weight ratio of GnP/MWCNTs and the combinations of GnPs and MWCNTs with different sizes, indicating that the hybrid nanocomposites exhibits non-sufficient

uniform dispersion or aggregated carbon-based nanofillers. The residual mass of the hybrid nanocomposites is in range of 4.67-6.58 %.

From the obtained results, it can be clear concluded that the incorporation of GnPs and MWCNTs induces a significant enhancement of the thermal stability of HDPE due to barrier effect of them, resulting in the enhancement of the resistance to thermal decomposition and thus inhibiting the diffusion of the volatile degradation products from the polymer onto the gas phase and the oxygen permeation from the surface. As mentioned by El Achaby & Qaiss (2013) and Yuan et al. (2014), this stabilization effect can be due to:

- 1- the enhanced interfacial interactions between the HDPE matrix and carbon-based nanofillers
- 2- better dispersion of the carbon-based nanofillers within the HDPE matrix.

These cause an increment in the activation energy for the thermal decomposition.

However, there is not observed a clear synergic effect of GnPs and MWCNTs. In all cases, the greatest enhancement is observed as adding only MWCNTs. This is most likely because of non-enough homogeneity of carbon-based nanofillers in the hybrid nanofillers. In other words, the dispersion of nanofillers in the HDPE/MWCNTs is better than in the HDPE/GnPs and hybrid nanocomposites. The SEM results described in the previous part of this chapter display that some agglomerates and voids in the hybrid nanocomposites are observed. It is mentioned that these voids and agglomerates may be reasons of the lower thermal enhancement.

7.5 Conclusion

In this chapter, due to much better performance of HDPE/M12 and HDPE/G2 nanocomposites, firstly the amount of G2 was kept constant at 11.70 wt.% and loading MWCNTs is in the range of 0.2-3.82 wt.% to investigate the synergic effect of hybrid carbon-fillers. To investigate the size effect of hybrid nanofillers on the final properties, the concentration of the total nanofiller was decided based on the electrical percolation threshold. So, we selected 5 wt.% HDPE/GnPs/MWCNTs systems, being

higher than the electrically conductive percolation for MWCNTs, for the subsequent experiments. The total amount of two used carbon nanofillers were kept constant at 5 wt% and six filler weight ratios between two carbon nanofillers (GnPs/MWCNTs), such as 5/0, 4/1, 3/2, 2/3, 1/4 and 5/0, were considered to study the effects of used filler weight ratios and size on the properties of the HDPE-based nanocomposites. From the findings, we may conclude that;

- Based on XRD results, the size and weight ratio of GnPs and MWCNTs does not have an important effect on the crystalline structure. Actually, the addition of GnPs and/or MWCNTs does not have a significant influence on the original crystal structure of the HDPE matrix. However, the type, size, and weight ratio of nanofillers influence the intensity of diffraction.
- According to FTIR results, the type, size, content, and weight ratio of carbon-based nanofillers cause unimportant variation in the characteristic peaks of the HDPE matrix. But, a slight variation in the intensity and spectral pattern of these peaks may be due to the π - π interaction of the HDPE and carbon-based nanofillers.
- The dispersion of the hybrid nanocomposites is strongly related to the weight ratio of GnPs/MWCNTs. In general, while MWCNTs can contact each other and form a conductive network, GnPs lose their excellent disk-shape because of the melt mixing methods. In addition, 1D MWCNTs and 2D GnPs can contact each other by creating a bridge network in the hybrid nanocomposites.
- Although all parameters are the same during the production of HDPE/M12, HDPE/M58, HDPE/G1, HDPE/G2 and HDPE/G3 nanocomposites, the electrical conductivity is different, i.e. the order of enhancement in the electrical conductivity is HDPE/G1 < HDPE/G3 < HDPE/G2 < HDPE/M58 < HDPE/M12.
- The addition of M12 has strong effect on the AC conductivity response of the HDPE/G2 (11.70 wt.%) nanocomposites. With increasing MWCNTs into the HDPE/G2 (11.70 wt.%) nanocomposites, the electrical conductivity transit from AC conductivity (frequency-dependent) to DC conductivity

(frequency-independent). In addition, the critical frequency is broadened to higher frequency with increasing M12 loading.

- The incorporation of M12 into the HDPE/G2 (11.70 wt.%) nanocomposites lead to increase in the electrical conductivity and decrease in the percolation threshold, but no synergic effect on enhancing electrical properties is observed.
- The size of carbon-based nanofillers in the mixed and GnPs/MWCNTs weight ratio strongly influence the electrical properties.
- The combination of GnPs and MWCNTs with higher AR (M12) is more effective to form continuous conducting pathways.
- In case of the hybrid nanocomposites with lower AR (M58), the size of GnPs have a slight influence on the electrical properties.
- For the HDPE/GnPs/M12 nanocomposites, the electrical conductivity of samples increases with increasing M12 in the total nanofiller loading.
- There is no synergic effect between G1 (smaller diameter and thicker thickness) and M12 influencing the electrical conductivity.
- Although G2 (large diameter) among GnPs and M12 among carbon-based nanofillers display the best performance in the electrical conductivity improvement for the nanocomposites with single nanofiller, the HDPE/G3/M12 nanocomposite with 2/3 weight ratio of GnPs/MWCNTs exhibit the highest electrical conductivity value.
- The combination of G2 with larger surface area and M12 with higher aspect ratio make more contribution to the synergic effect of hybrid nanocomposites.
- In terms of GnPs/MWCNTs weight ratio, although the highest electrical conductivity is achieved by 3/2 weight ratio of G3/M12, the best results are generally achieved by GnPs/MWCNTs weight ratio of 1/4.
- The magnitude of the thermal conductivity at any content of nanofillers is in the order as HDPE/M12 > HDPE/G2 > HDPE/M58 > HDPE/G3 > HDPE/G1. It is observed that the size of carbon-based nanofillers influence the thermal conductivity.

- The thermal conductivity of HDPE/G1(11.70 wt.)/M12 nanocomposites increases with increasing the M12 content. One can see that there is a clear synergic effect influencing thermal conductivity.
- The all HDPE/G1(11.70 wt.)/M12 nanocomposites display synergic efficiency higher than 1. This clearly demonstrates synergic effect of G2 and M12 in improving thermal conductivity of samples. The synergic efficiency increases with increasing M12 content and reaches the maximum value at 1.93 wt.% M12 and then the further inclusion leads to decrease.
- The thermal conductivity of hybrid nanocomposites with 5 wt.% is affected by the weight ratio of GnPs and MWCNTs and their sizes.
- For all weight ratio, all hybrid nanocomposites exhibit a marginal thermal conductivity enhancement.
- All hybrid nanocomposites, by keeping total nanofillers content as 5wt.%, show significant change with weight ratio of GnPs/MWCNTs.
- In case of hybrid nanocomposites, for all weight ratios, M12 is found be more beneficial than M58 to create thermally conducting networks and obtain higher thermal conductivity values.
- In terms of thermal conductivity, three synergic effects, such as negative, positif and no synergic effect are observed.
- The positif synergic effect is observed at 2/3 and 1/4 weight ratios of GnPs/MWCNTs for the HDPE/G1/M12 nanocomposites and 3/2 and 2/3 weight ratios of GnPs/MWCNTs for the HDPE/G2/M12 nanocomposites.
- The HDPE/G1/M58 nanocomposite with 4/1 weight ratio of GnPs/MWCNTs and HDPE/G2/M58 nanocomposite with 4/1, 3/2 and 2/3 weight ratios of GnPs/MWCNTs exhibit negative synergic effect on thermal conductivity.
- For all other hybrid nanocomposites, the thermal conductivity values lie between the HDPE/GnPs and HDPE/MWCNTs nanocomposites.
- The highest thermal conductivity (0.504 W/mK). is achieved by the HDPE/G2/M12 nanocomposites including 3/2 weight ratio at 5wt.% total filler content.

- The synergic efficiency strongly depends on the sizes of GnPs and MWCNTs and their weight ratio.
- Generally, synergic efficiency is less than 1, indicating that there is not distinct synergic effect of GnPs and MWCNTs.
- The combination of GnPs with large diameter (G2) and MWCNTs with high aspect ratio (M12) is more effective to achieve greater thermal conductivity. It is followed by the combination of GnPs with small diameter, but same thickness (G1) and the same MWCNTs (M12).
- As comparing GnPs with same diameter, thicker one shows better performance than thinner one.
- The combination of GnPs with large diameter (G2) and MWCNTs with lower aspect ratio (M58) have negative synergic effect on thermal conductivity.
- There is a distinct synergic effect between GnPs and MWCNTs in improving Young's modulus.
- While the synergic effect of GnPs and MWCNTs on the tensile strength is observed for the hybrid nanocomposites with GnPs and M12, there is no synergic effect in enhancing elongation.
- The weight ratio of GnPs and MWCNTs have non-linear effect on the Young's modulus, it does not lead to any considerable variation in the tensile strength and elongation.
- The size of GnPs and MWCNTs influences strongly on the Young's modulus, however slightly on tensile strength and elongation.
- The addition into the HDPE/G2 (11.70 wt.%) nanocomposites leads to a slight or no variation in the crystallization behavior. A little impact on T_m , T_c , ΔH_f and X_c is observed with the inclusion of M12.
- The coexistence of G2 and M12 provides a synergic effect on the values of corresponding parameters obtained by DSC, however it is not considerable.
- The size and weight ratio of GnPs and MWCNTs has a slight effect on the melting and crystallization behavior of samples.
- In case of hybrid nanocomposites with 5 wt.% total nanofillers loading, the coexistence of GnPs and MWCNTs does not have any synergic effect.

- The incorporation of carbon-based nanofillers (MWCNTs, GnPs, MWCNTs and GnPs) leads to a little or no change in the crystallinity of HDPE and thus, the thermal and mechanical enhancements are not caused by the crystallinity variation.
- Independent of size and type of carbon-based nanofillers, all nanocomposites exhibit similar thermal degradation behavior to that of the pure HDPE.
- The nanocomposites with MWCNTs show lower thermal stability than with GnPs.
- For the HDPE/G2 (11.70 wt.%)/M12 nanocomposites, the coexistence of G2 and M12 does not cause any synergic effect, but their thermal stability obeys the mixture law.
- In case of hybrid nanocomposites with 5 wt.% total nanofillers loading, the none of the thermal stability properties show any sing of synergic effect.
- The thermal stability of hybrid nanocomposites increases with the weight ratio of GnPs/MWCNTs. Their thermal stability increases with increasing MWCNTs content in the mixed.

CHAPTER EIGHT

CONCLUSIONS & RECOMMENDATIONS

The main aim of the current dissertation is to investigate the effects of synergic, weight ratio and size of carbon-based nanofillers on the thermal, electrical, and mechanical properties. To determine the size effect of carbon nanofillers on the synergic effect between carbon-based filler materials and on the properties of final nanocomposites, two MWCNTs and three GnPs with different dimensions have been used to determine the size influence on the properties of the HDPE-based nanocomposites.

As mention in Chapter 1, there are numerous studies on the polymer nanocomposites with GnPs or MWCNTS, making a comparison between GnPs and MWCNTs with regards to their performance is hard. Since the filler content, filler size, the preparation method and/or conditions and the measurement techniques change widely from the case to case, and these factors have significant influence on determining the final properties of the polymer nanocomposites. In addition, there is lack of correlation between size effect of nanofiller and properties of polymer nanocomposites. Therefore, to better understand and obviously interpret the size and synergic effect of GnPs and MWCNTs on the hybrid nanocomposites, first, the size effect of MWCNTs or GnPs on the properties of HDPE-based nanocomposites with single carbon nanofiller has investigated.

Later, to understand the synergic effect of GnPs and MWCNTs, the properties of nanocomposites with GnPs and MWCNTs exhibiting better performance were investigated. Finally, the influences of size, weight ratio and synergic effect of GnPs and MWCNTs for the HDPE-based hybrid nanocomposites with 5 wt.% total nanofillers loading at six different weight ratios of GnPs/MWCNTs (5/0, 4/1, 3/2, 2/3, 1/4 and 0/5) were determined.

All nanocomposites were prepared by melt mixing and compression molding. The preparation and measurement processes for all sample were carried out at the same conditions.

To make it easier and more understandable to interpret, while the size effect of MWCNTs on the properties are interpreted in terms of aspect ratio, but GnPs are interpreted in terms of thickness and diameter.

The major finding of this thesis can be summarized as follows:

For MWCNTs and GnPs;

- Based on the findings of two types of MWCNTs from XPS, the surface properties of both MWCNTs do not demonstrate significant change in terms of aspect ratio. The surface chemical composition for three types of GnPs exhibits a small difference and this small difference will not influence the properties of HDPE/GnPs nanocomposites.
- It is clear from the XRD results, the size of MWCNTs and GnPs does not cause a remarkable difference in its crystalline structure.
- Both types of MWCNTs and GnPs are not degraded until 700 °C.

For all nanocomposites;

- The XRD results show that the size and addition of carbon nanofillers do not have a considerable effect on the original structure of HDPE. Because there is no reaction or interaction between the HDPE and carbon-based nanofillers.
- The size and content of GnPs and MWCNTs do not lead to any variation in the characteristic peaks in the HDPE matrix identifiable in the FTIR spectra.
- Addition of carbon-based nanofillers leads to a linear increase in the thermal conductivity.
- All nanocomposites show a moderate thermal conductivity enhancement due to high interfacial thermal boundary resistances between the matrix and carbon nanofillers, restricting the phonon transport between them.

- There is no thermal percolation for all nanocomposites.
- The Young's modulus of the nanocomposites increases with increasing the carbon-based nanofillers content.
- The tensile strength of the samples rapidly decreases due to poor dispersion and weak interfacial interaction between the HDPE and nanofillers at preliminary stage and then increases with increase of filler loadings. However, these values are below the pure HDPE's value.
- There is a slight influence of carbon-based nanofiller loadings on the melting temperatures. However, the crystallization temperature of the nanocomposites increases with the addition of carbon nanofillers and the heat of fusion decreases.
- All nanocomposites exhibit the similar thermal decomposition behavior with that of the pure HDPE.
- The addition of carbon-based nanofillers into the matrix causes enhancing in the thermal stability.

For HDPE/MWCNTs nanocomposites;

- The micrographs of TEM show that the MWCNTs with higher aspect ratio indicate a slightly better dispersion in the HDPE matrix.
- The HDPE-based nanocomposites including both types of MWCNTs indicate polynomial increase in the electrical conductivity.
- The nanocomposites with higher aspect ratio of MWCNTs show higher electrical conductivity and lower percolation threshold due to more uniform dispersion with less entanglement and agglomeration, which results in increasing MWCNTs-MWCNTs contact and creating a more efficient electrically conductive networks. This outcome is agreed with TEM micrographs. The slight difference in the electrical properties can be because of the difference in the aspect ratio of two types of MWCNTs.
- MWCNTs with higher aspect ratio exhibit higher thermal conductivity improvement, especially, it provides three to four-fold greater thermal conductivity enhancement than the smaller ones at lower filler loadings. This can be explained that the higher ones favor the formation of a

percolated network enabling the phonons passage over longer distance without transport from the particle to particle and in a network formed by higher ones, the need number of contacts per unit distance raises exponentially and therefore does the number of interfacial thermal resistance scattering the phonon-mediated heat transfer.

- The increase in the Young's modulus is the more pronounced for the nanocomposites with higher aspect ratio MWCNTs relative to ones with lower aspect ratio.
- While Young's modulus increases with increasing aspect ratio of MWCNTs, the tensile strength and elongation are not remarkable influenced by aspect ratio.
- The aspect ratio of MWCNTs does not lead to change in the melting temperature, crystallization temperature, heat of fusion and crystallinity of samples. Because they are nearly the same for all carbon-based nanocomposites.
- MWCNTs with higher aspect ratio gives a much better enhancement in the thermal stability. It is known that the increase in the thermal stability is attributed to barrier effect, good dispersion of MWCNTs and the interactions of HDPE-MWCNTs. In this thesis, a greater enhancement may be because of better dispersion of higher aspect ratio ones. However, the aspect ratio of MWCNTs has an insignificant effect on the residual mass.

In summary, MWCNTs with high aspect ratio seem to a more favorable type of MWCNTs to achieve the best improvements for all properties.

For HDPE/GnPs nanocomposites;

- According to SEM images, it is found that GnPs with largest lateral size are in more contact with each other and it indicates a higher number of GnP pathways, resulting higher thermal and electrical conductivity. For the same lateral size, the GnPs with thinner thickness exhibit better dispersion in the HDPE matrix.

- The size of GnPs have significant effect on the electrical and thermal conductivity of the nanocomposites.
- The lateral size of GnPs is a more significant key factor for thermal conductivity and electrical properties.
- For a fixed lateral size, an optimal thickness exists that gives the highest electrical conductivity and lowest percolation threshold. In this thesis, the optimum thickness seems to be closer to 5-8 nm than 50-100 nm as comparing GnPs with the same lateral size.
- Compared to GnPs with different lateral sized but the same thickness, higher lateral size ones give lower percolation threshold and higher electrical conductivity.
- GnPs with higher lateral size lead to a greater improvement in the thermal conductivity. This can be explained that this GnPs can more easily connect with each other to form an effective conductive network in the matrix and decrease the phonon scattering between the GnPs-matrix interfaces.
- For a given lateral size, thinner ones demonstrate a slightly higher increase in the thermal conductivity compared to thicker ones. For 5 μm of lateral size, the optimum thickness for thermal conductivity enhancement is nearly 5-8 nm over 50-100 nm.
- The improvement in the thermal conductivity of samples can be enhanced by optimizing the lateral size and thickness of GnPs.
- GnPs with smaller lateral size and thickness (larger surface area and aspect ratio) display the most efficient enhancement in the Young's modulus of samples. Because a larger surface area provides a more effective stress transfer between the HDPE and GnPs.
- Due to better dispersion, the GnPs with larger lateral size and thickness achieves a higher enhancement in the tensile strength.
- As considering the obtained results, the size of GnPs induced slight change in the melting temperature, crystallization temperatures, heat of fusions and crystallinity of HDPE.
- At low contents of GnPs, the thermal stability of HDPE/GnPs nanocomposites decreases due to the agglomeration of GnPs. This

agglomeration may increase the molecular mobility and reduce thermal stability of samples.

- The size of GnPs does not cause a considerable change in the $T_{50\%}$, T_{deg} and residual mass, it only influences $T_{5\%}$.

As a result, GnPs with larger lateral size and thickness exhibit better performance to achieve the best improvement in the nanocomposites.

For comparison of MWCNTs and GnPs;

- MWCNTs give much better enhancement in the electrical properties relative to GnPs. The nanocomposites including MWCNTs with higher aspect ratio show the lowest percolation threshold and the highest electrical conductivity among all types of carbon nanofillers.
- MWCNTs with higher aspect ratio perform better in the thermal conductivity compared to GnPs; while the HDPE nanocomposites containing GnPs with higher lateral size exhibit slightly higher increment than MWCNTs with lower aspect ratio. One seems that if the lateral size of GnPs is enough large, GnPs from more effective conductive filler than MWCNTs with lower aspect ratio. Therefore, the size of nanofiller should be taken in consideration when making a comparison of carbon-based nanocomposites in terms of the thermal conductivity.
- The nanocomposites with GnPs show better performance in enhancing mechanical properties than with MWCNTs.

For HDPE nanocomposites including GnPs with the largest lateral size (%11.70 wt.%) and MWCNTs with higher aspect ratio;

- The synergic effect of GnPs and MWCNTs has not remarkable effect on the crystalline structure of the nanocomposites, but it only influences the peak intensity.
- The addition of MWCNTs with higher aspect ratio into the HDPE-based nanocomposites with larger lateral size leads to increase in the electrical conductivity and decrease the percolation threshold, however there is no

synergic effect on improving the electrical properties. The conductive network facilitating the movements of electron formed by MWCNTs and GnPs is less efficient than by only MWCNTs.

- In terms of thermal conductivity, there is a distinct synergic effect between the carbon-based nanofillers and the thermal conductivity of samples increases with increasing MWCNTs loadings.
- There is a distinct synergic effect between GnPs and MWCNTs in improving Young's modulus.
- The addition of MWCNTs into the HDPE/GnPs nanocomposites leads to a slight or no variation in the crystallization behavior. A little impact on T_m , T_c , ΔH_f and X_c is observed with the inclusion of MWCNTs.
- The coexistence of GnPs with largest lateral size and higher aspect ratio MWCNTs does not lead to any synergic effect, but their thermal stability obeys the mixture law.

For hybrid nanocomposites with 5 wt.% of total loading;

- The crystalline structures of samples are not affected by the size, weight ratio and synergic effect of GnPs and MWCNTs. They only influence the intensity of peak.
- The weight ratio of GnPs and MWCNTs strongly influences the dispersion of carbon nanofillers in the hybrid nanocomposites.
- In hybrid nanocomposites, the MWCNTs generally can contact to each other, GnPs are not the excellent disc-shape because of the melt-mixing.
- In general, 2D GnPs and 1D MWCNTs can connect with each other by creating a bridge network in the hybrid nanocomposites. That is to say, 3D conducting network structure can be formed.
- The electrical properties of samples are strongly affected by size and weight ratio of GnPs and MWCNTs.
- Compared to MWCNTs, the hybrid nanocomposites with higher aspect ratio MWCNTs show higher electrical conductivity enhancement than with lower ones. Because MWCNTs with higher aspect ratio is more efficiency

to create electrically conducting networks with GNPs and there is more number physical contact between this MWCNTs and GNPs.

- For all weight ratio of GNPs/MWCNTs, there is no synergic effect between the GNPs with smaller lateral size and higher thickness and MWCNTs with higher aspect ratio. This can be explained by less effective conducting network between them.
- In case of hybrid nanocomposites including GNPs and MWCNTs with higher aspect ratio, the electrical conductivity increases with increasing MWCNTs loadings.
- For the samples with lower aspect ratio of MWCNTs, the size of GNPs leads to a slight change in the electrical conductivity.
- Even though GNPs with larger lateral size and thickness among GNPs and MWCNTs with high aspect ratio among all carbon-nanofillers exhibit the best performance, the highest electrical conductivity is achieved by the nanocomposites containing GNPs with smaller lateral size and thickness and MWCNTs with higher aspect ratio at 2/3 weight ratio of GNPs/MWCNTs. Because, the combination of them make more contribution to the synergic effect. In the light GNPs/MWCNTs weight ratio, the best results are generally achieved at the GNPs/MWCNTs of 1/4 for the electrical conductivity.
- The weight ratio and size of GNPs and MWCNTs influence on the thermal conductivity of hybrid nanocomposites.
- In hybrid nanocomposites, MWCNTs with high aspect ratio are more beneficial than with smaller ones to form effective thermally conducting network and achieve higher thermal conductivity.
- In terms of thermal conductivity, there are observed three synergic effects, such as negative, positive and no synergic effect.
- The positive synergic effect is observed at 2/3 and 1/4 weight ratios of GNPs/MWCNTs for the HDPE/GNPs with smaller lateral size and higher thickness/MWCNTs with high aspect ratio nanocomposites and 3/2 and 2/3 weight ratios of GNPs/MWCNTs for the HDPE/GNPs with largest lateral size /MWCNTs with high aspect ratio nanocomposites.

- The HDPE/GnPs with smaller lateral size and higher thickness/MWCNTs with high aspect ratio nanocomposite with 4/1 weight ratio of GnPs/MWCNTs and the HDPE/GnPs with largest lateral size /MWCNTs with high aspect ratio nanocomposite with 4/1, 3/2 and 2/3 weight ratios of GnPs/MWCNTs exhibit negative synergic effect on thermal conductivity.
- For all other hybrid nanocomposites, the thermal conductivity values lie between the HDPE/GnPs and HDPE/MWCNTs nanocomposites.
- The highest thermal conductivity is achieved by the the HDPE/GnPs with largest lateral size /MWCNTs with high aspect ratio nanocomposites including 3/2 weight ratio at 5wt.% total filler content.
- The combination of GnPs with large lateral size and MWCNTs with high aspect ratio is more effective to achieve greater thermal conductivity. It is followed by the combination of GnPs with small diameter, but same thickness and the same MWCNTs.
- As comparing GnPs with same diameter, thicker one shows better performance than thinner one.
- The combination of GnPs with large diameter and MWCNTs with lower aspect ratio have negative synergic effect on thermal conductivity.
- There is a distinct synergic effect between GnPs and MWCNTs in improving Young's modulus.
- While the synergic effect of GnPs and MWCNTs on the tensile strength is observed for the hybrid nanocomposites with GnPs and high aspect ratio MWCNTs, there is no synergic effect in enhancing elongation.
- The weight ratio of GnPs and MWCNTs have non-linear effect on the Young's modulus, it does not lead to any considerable variation in the tensile strength and elongation.
- The size and weight ratio of GnPs and MWCNTs has a slight effect on the melting and crystallization behavior of samples and the coexistence of GnPs and MWCNTs does not have any synergic effect.
- The incorporation of carbon-based nanofillers (MWCNTs, GnPs, MWCNTs and GnPs) leads to a little or no change in the crystallinity of

HDPE and thus, the thermal and mechanical enhancements are not caused by the crystallinity variation.

- In case of hybrid nanocomposites with 5 wt.% total nanofillers loading, the none of the thermal stability properties show any sing of synergic effect.
- The thermal stability of hybrid nanocomposites increases with the weight ratio of GnPs/MWCNTs. The nanocomposites with MWCNTs show higher thermal stability than with GnPs, therefore their thermal stability increases with increasing MWCNTs content in the mixed.

Future Research and Recommendations

Some recommendations for future works are summarized as following:

- Due to the limitation of instrument, the mechanical properties, thermal and electrical conductivity of pure GnPs and MWCNTs have not been measurement. Properties of nanofillers will be measured to understand if their size actually has any effect on the properties.
- To increase the alignment and dispersion of carbon-based nanofiller within polymer for enhanced properties, non- destructive methods (e.g. a magnetic field) will be applied during preparation process.
- The size of carbon-based nanofillers in the polymer nanocomposites will be determined by non- destructive methods (e.g. X-ray Computed Tomography).
- To establish a general correlation between the nanofiller sizes and properties of nanocomposites, the studies will be carried out by using different polymers and/or different preparation methods.
- The synergic effect of GnPs and MWCNTs is found to be dependent on hybrid nanofiller loading. The properties of hybrid nanocomposites will be further at various concentration of nanofillers.
- The polymer nanocomposites reinforced by self-hybrid nanofillers (including two types of MWCNTs or two/three types of GnPs) will be

studied to determine the possible synergic property improvements by self-hybrid.

- The effects of synergic, size and weight ratio of hybrid nanofiller on the properties of the hybrid nanocomposites including two types of MWCNTs and one type of GnPs or one type of MWCNTs and two types of GnPs will be investigated.
- Further insight into the synergetic effect mechanisms between GnPs and MWCNTs will be studied by investigating in the different wide range of size and aspect ratio of nanofillers and GnPs/MWCNTs weight ratio. And All effects may be correlated with each other.
- Results from a more detailed and comprehensive parametric study, a correlation between theoretical and experimental data will be obtained.
- It is known that GnPs and MWCNTs are anisotropic materials and there are important differences in their thermal conductivity in in-plane and through-plane directions. This shows that the thermal conductivity of carbon-based nanocomposites could be anisotropic. So, the thermal conductivity measurements will be carried out in in-plane and through-plane direction.
- In the literature, there is a deficiency for theoretical thermal conductivity model which can define such influence or forecast the optimal ratio, dispersion, and synergy of hybrid nanofillers.
- In terms of thermal conductivity, many hybrid nanocomposites with different loading and ratio of hybrid nanofiller fabricated by different preparation method will be analyzed by various measurement technique in terms of thermal conductivity. Based on obtained results, a general theoretical thermal conductivity model including effects of fabrication method, measurement method, ratio and synergy of hybrid nanocomposites will be developed.

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APPENDICES

List of Publications

Three journal papers were published within the thesis. The list of publications that is ordered according to the publishing dates is presented below:

Evgin, T., Koca, H. D., Horny, N., Turgut, A., Tavman, I. H., Chirtoc, M., ... Novak, I. (2016). Effect of aspect ratio on thermal conductivity of high density polyethylene/multi-walled carbon nanotubes nanocomposites. *Composites Part A: Applied Science and Manufacturing*, 82, 208–213.

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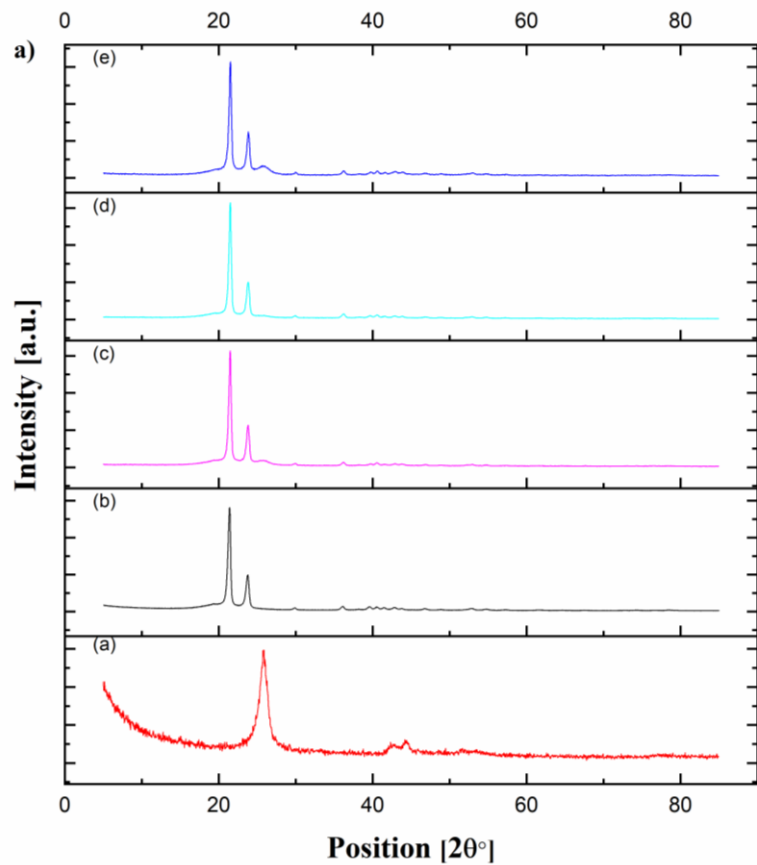


Figure A5.1 XRD pattern of a) M12, b) HDPE, c) HDPE/4.06 wt.% M12, d) HDPE/11.70 wt.% M12 e) HDPE/18.74 wt.% M12 nanocomposites

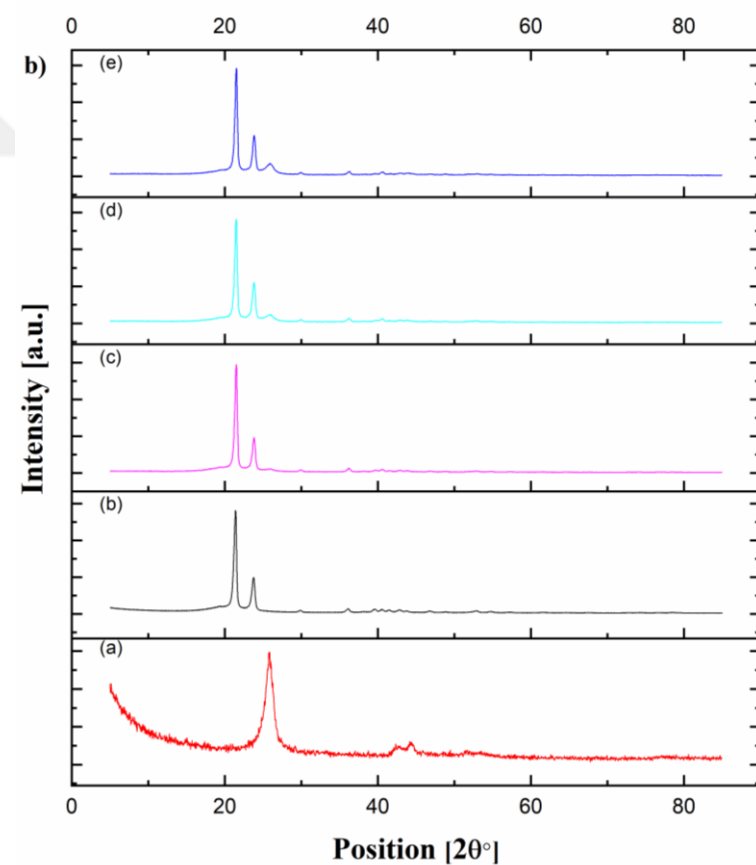


Figure A5.2 XRD pattern of a) M58, b) HDPE, c) HDPE/4.06 wt.% M58, d) HDPE/11.70 wt.% M58 e) HDPE/18.74 wt.% M58 nanocomposites

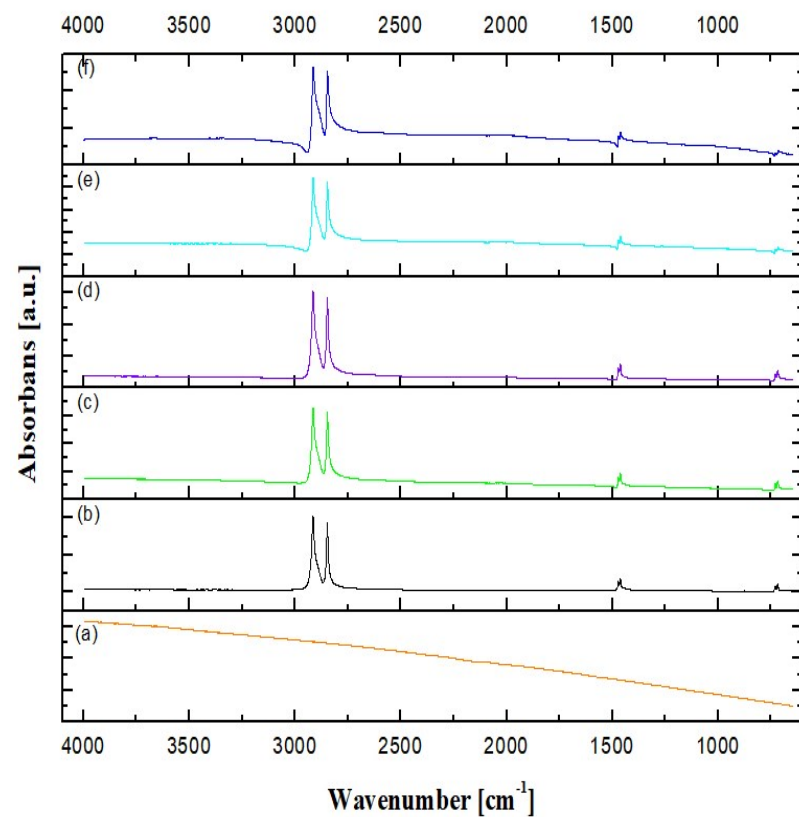


Figure A5.3 FTIR results of a) M12, b) HDPE, c) HDPE/2.05 wt.% M12, d) HDPE/4.06 wt.% M12, e) HDPE/11.70 wt.% M12, f) HDPE/18.74 wt.% M12 nanocomposites

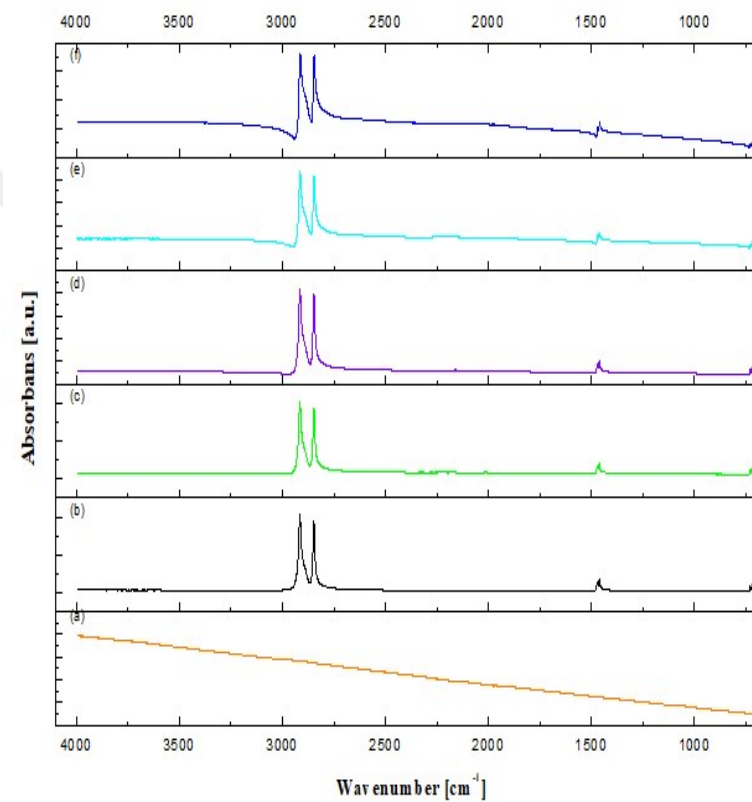


Figure A5.4 FTIR results of a) M58, b) HDPE, c) HDPE/2.05 wt.% M58, d) HDPE/4.06 wt.% M58, e) HDPE/11.70 wt.% M58 f) HDPE/18.74 wt.% M58 nanocomposites

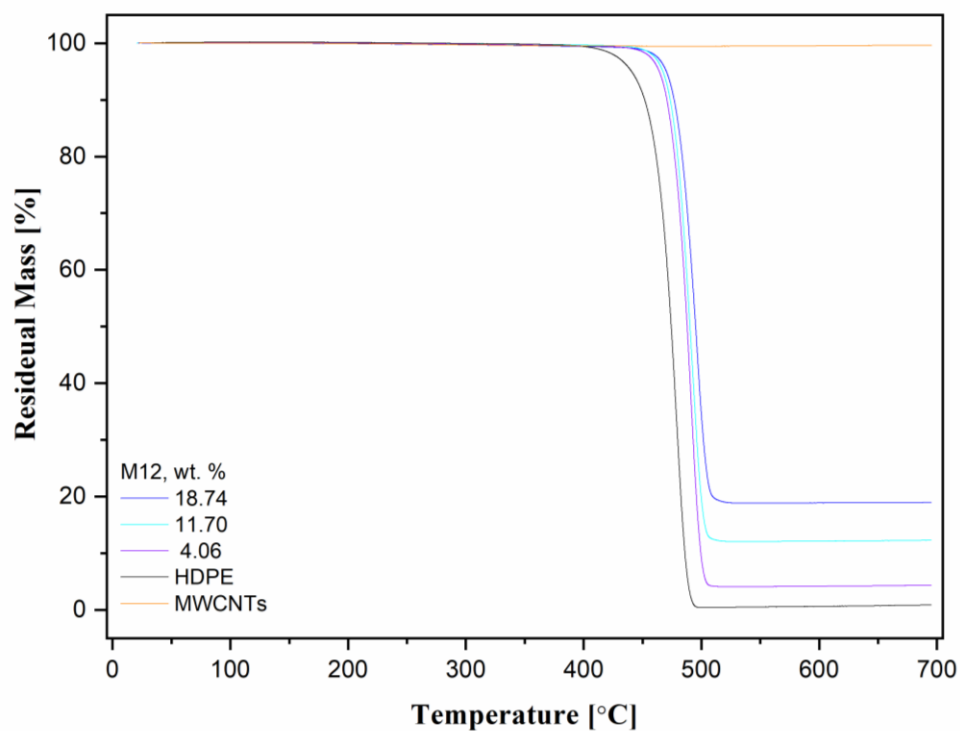


Figure A5.5 TGA curves of the HDPE/MWCNTs nanocomposites with M12

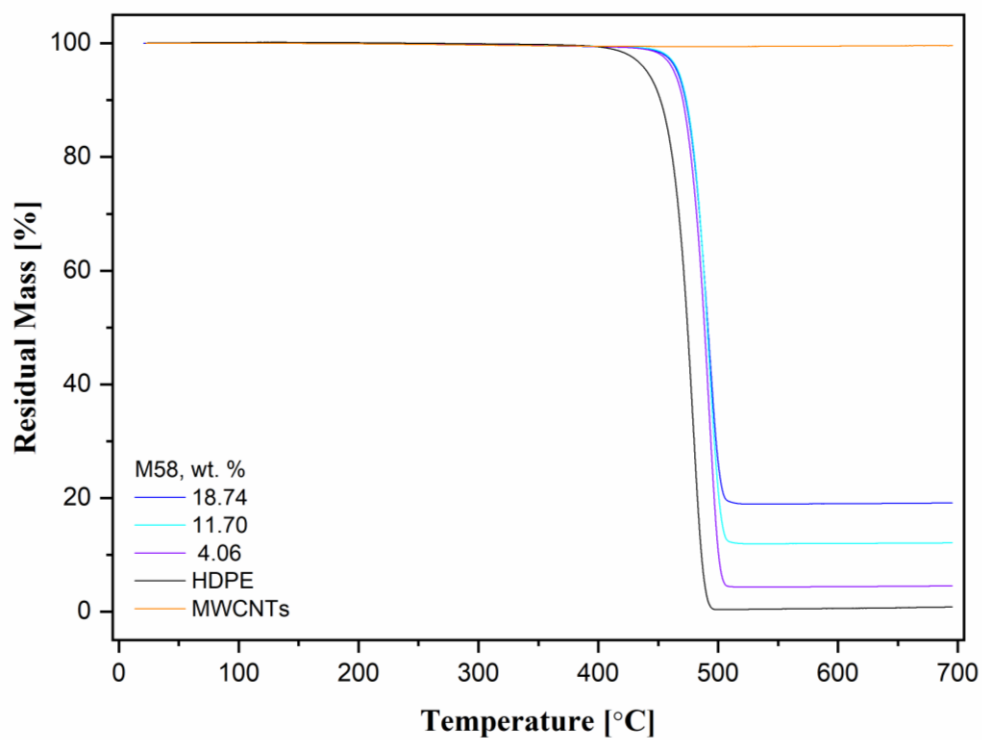


Figure A5.6 TGA curves of the HDPE/MWCNTs nanocomposites with M58

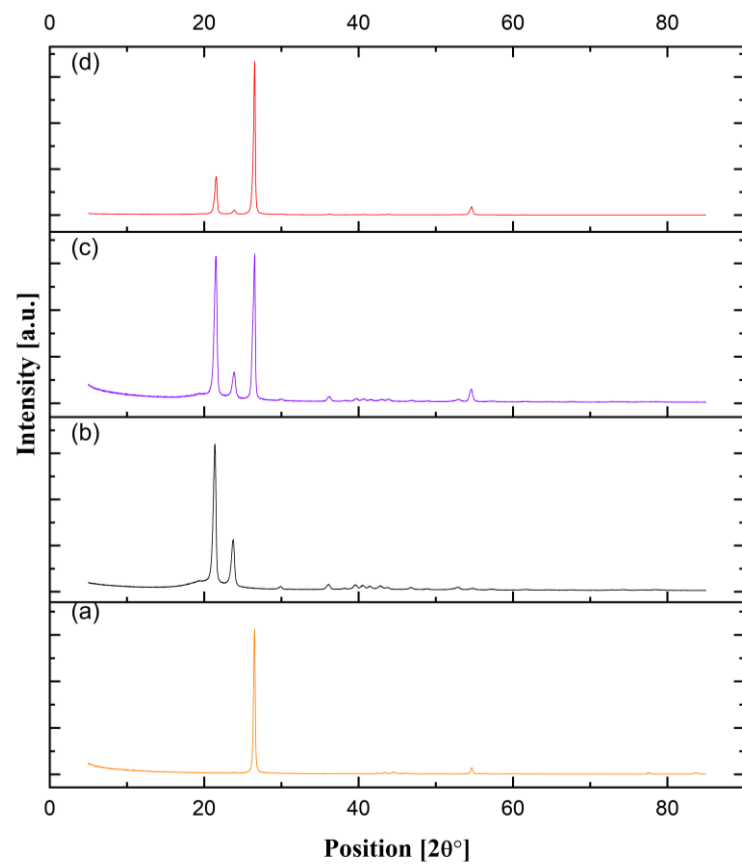


Figure A6.1. XRD pattern of a) G1, b) HDPE, c) HDPE/2.05 wt.% G1, d) HDPE/26.81 wt.% G1 nanocomposite

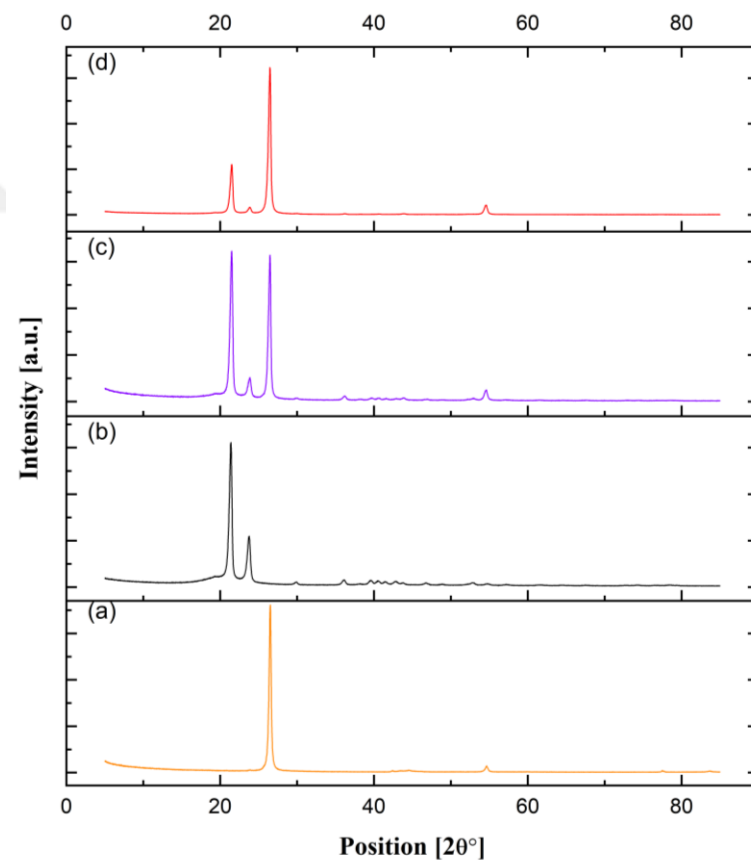


Figure A6.2. XRD pattern of a) G2, b) HDPE, c) HDPE/2.05 wt.% G2, d) HDPE/26.81 wt.% G2 nanocomposite

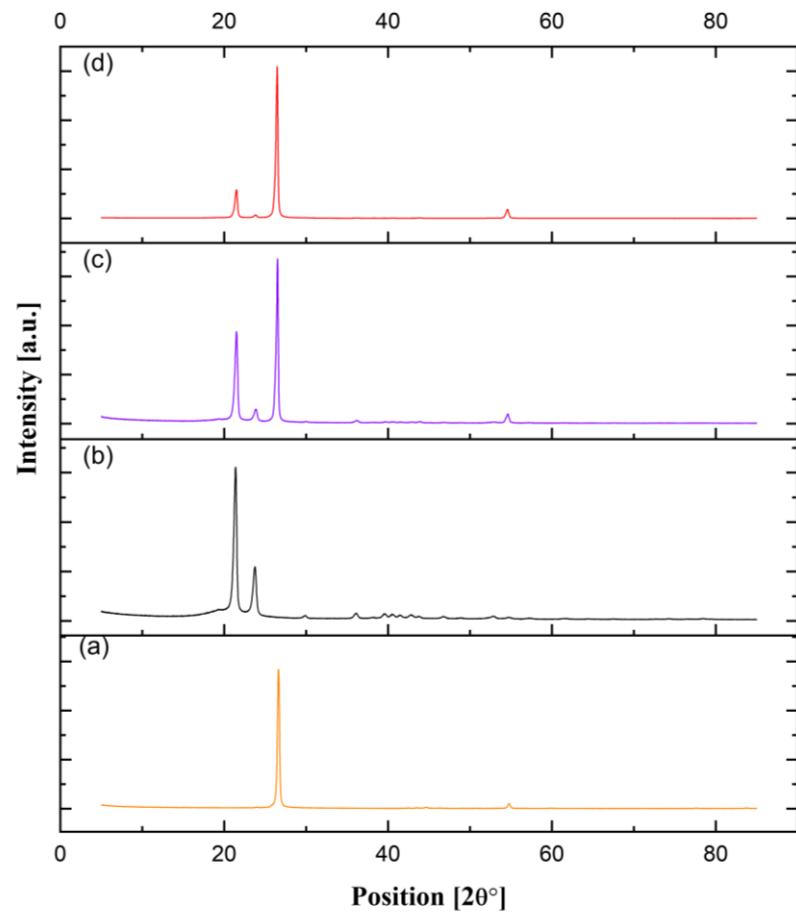


Figure A6.3. XRD pattern of a) G3, b) HDPE, c) HDPE/2.05 wt.% G3, d) HDPE/26.81 wt.% G3 nanocomposite.

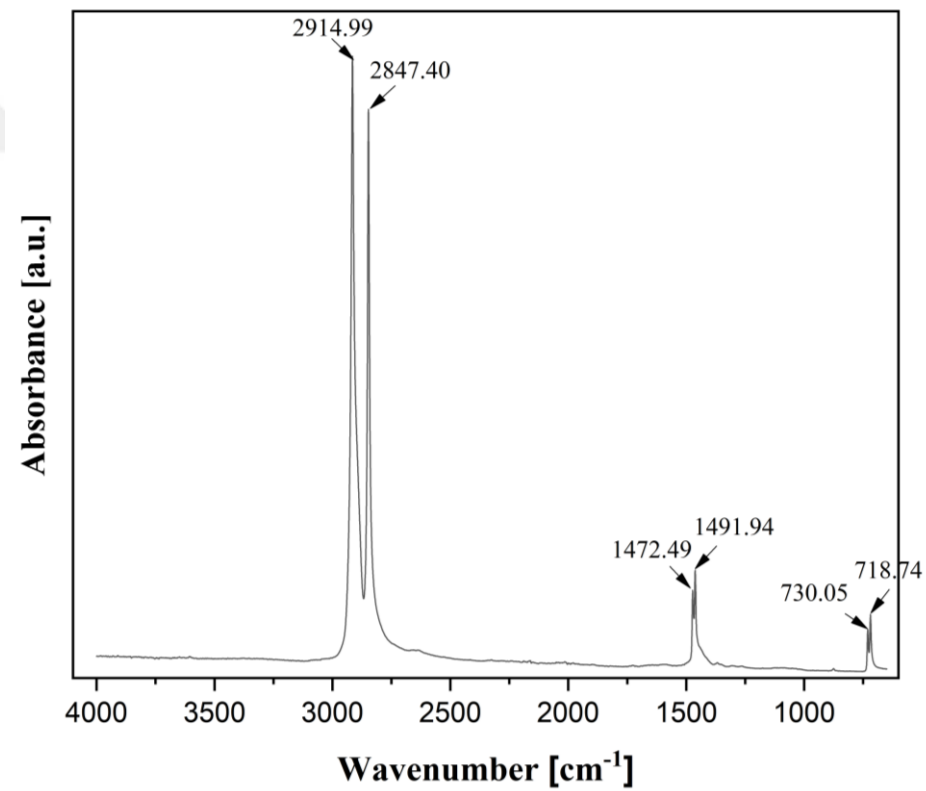


Figure A6.4. FTIR spectroscopy of HDPE

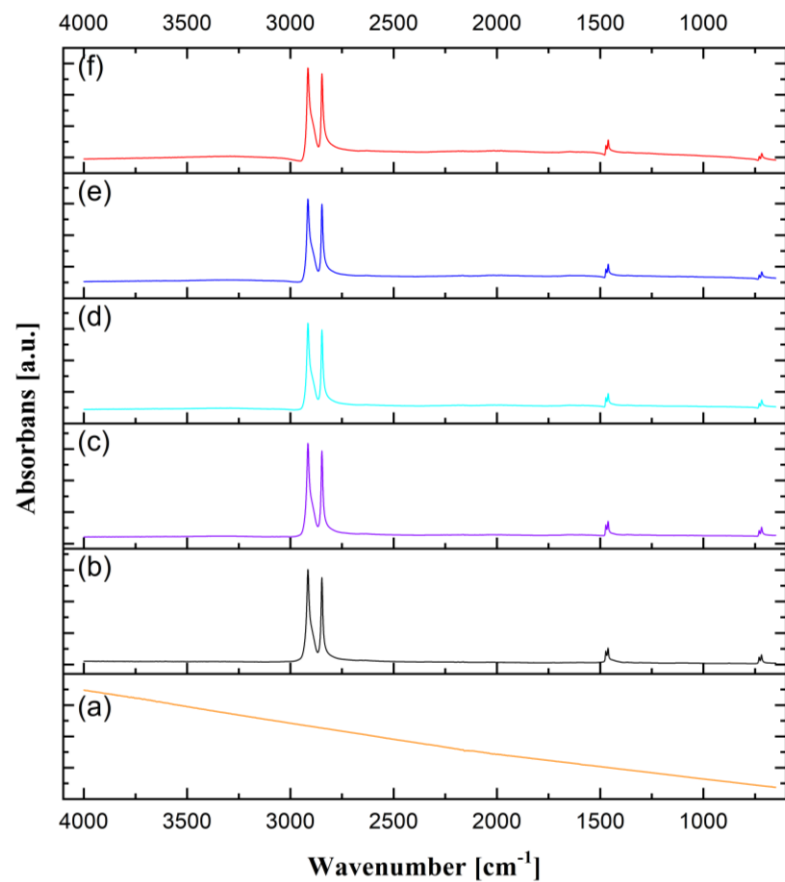


Figure A6.5. FTIR spectroscopy of a) G1, b) HDPE, c) HDPE/2.05 wt.% G1, d) HDPE/11.80 wt.% G1, e) HDPE/18.74 wt.% G1, and f) HDPE/26.81 wt.% G1 nanocomposite.

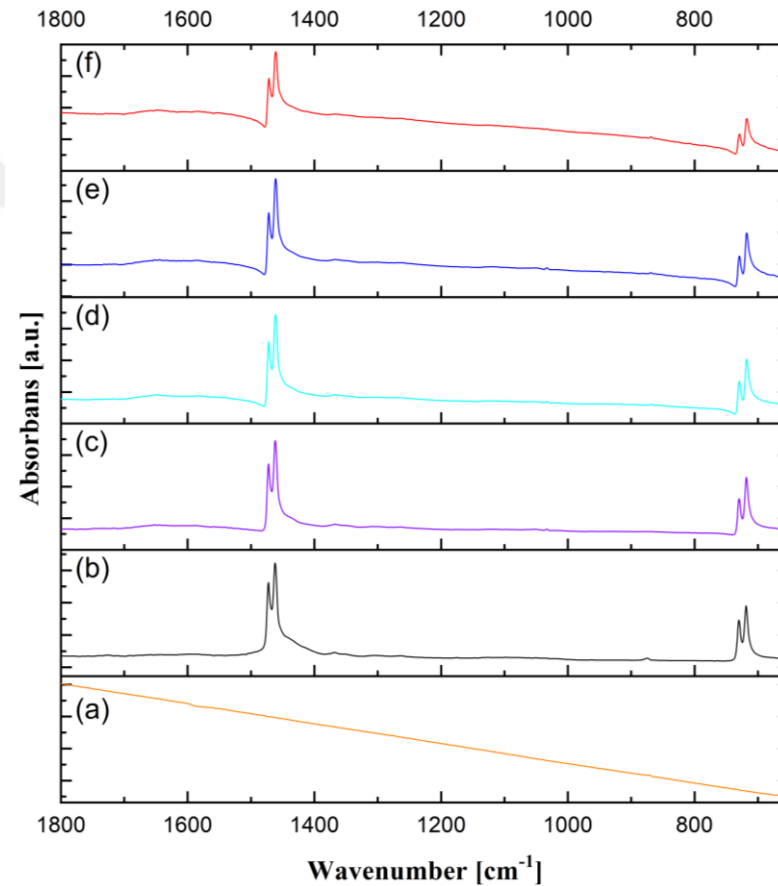


Figure A6.7. FTIR spectroscopy of a) G1, b) HDPE, c) HDPE/2.05 wt.% G1, d) HDPE/11.80 wt.% G1, e) HDPE/18.74 wt.% G1, and f) HDPE/26.81 wt.% G1 nanocomposite in the range of 650-1800 cm^{-1} .

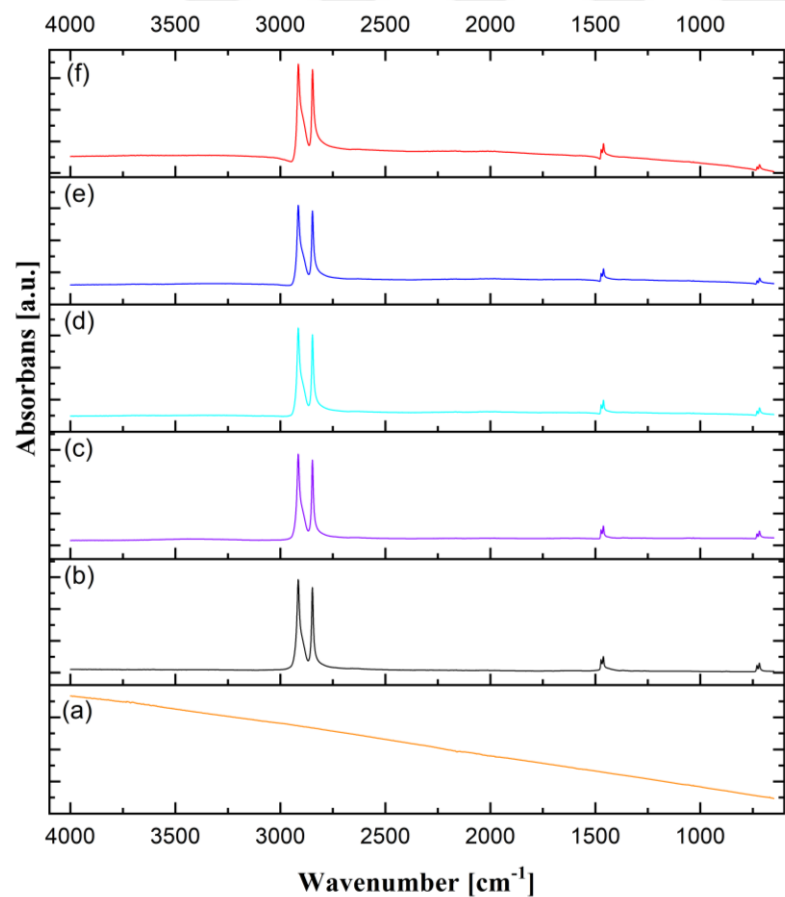


Figure A6.8 FTIR spectroscopy of a) G2, b) HDPE, c) HDPE/2.05 wt.% G2, d) HDPE/11.80 wt.% G2, e) HDPE/18.74 wt.% G2, and f) HDPE/26.81 wt.% G2 nanocomposite

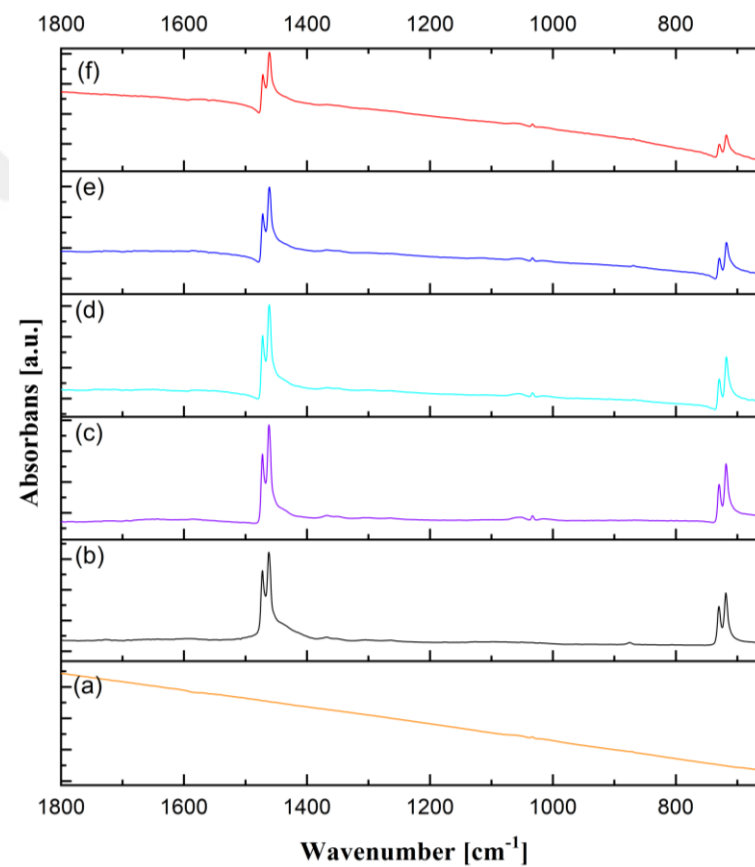


Figure A6.9 FTIR spectroscopy of a) G2, b) HDPE, c) HDPE/2.05 wt.% G2, d) HDPE/11.80 wt.% G2, e) HDPE/18.74 wt.% G2, and f) HDPE/26.81 wt.% G2 nanocomposite in the range of 650-1800 cm^{-1}

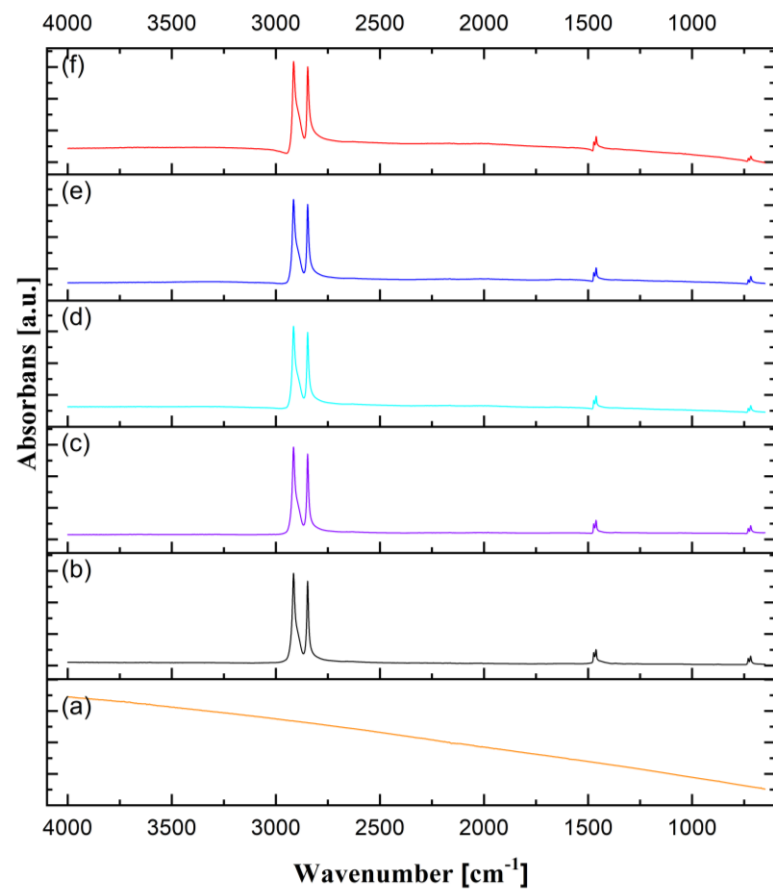


Figure A6.10 FTIR spectroscopy of a) G3, b) HDPE, c) HDPE/2.05 wt.% G3, d) HDPE/11.80 wt.% G3, e) HDPE/18.74 wt.% G3, and f) HDPE/26.81 wt.% G3 nanocomposite

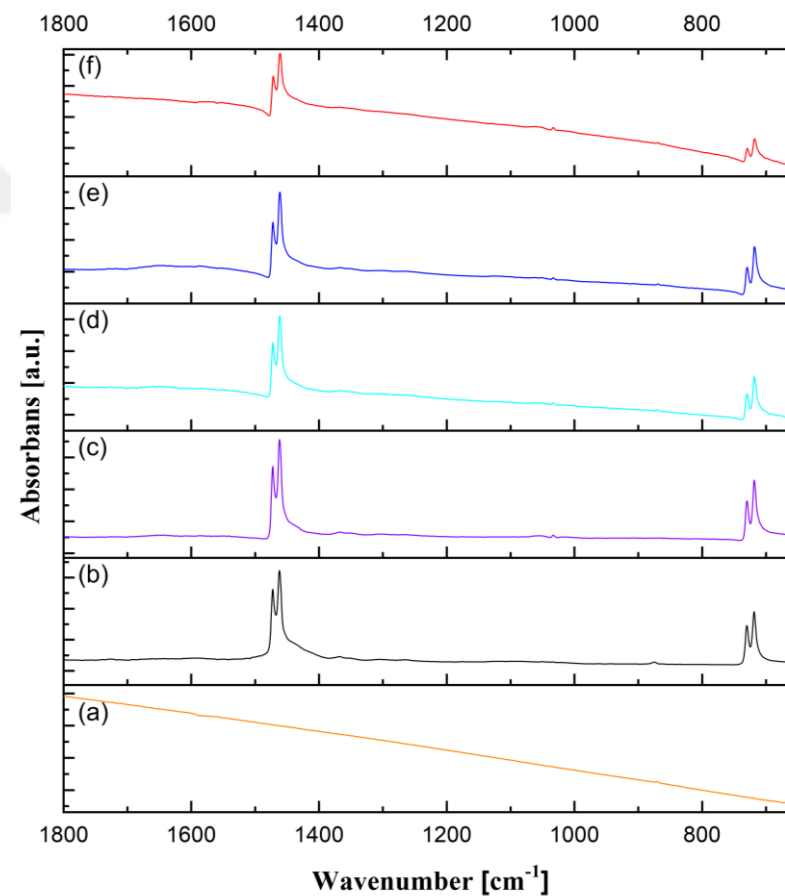


Figure A6.11 FTIR spectroscopy of a) G3, b) HDPE, c) HDPE/2.05 wt.% G3, d) HDPE/11.80 wt.% G3, e) HDPE/18.74 wt.% G3, and f) HDPE/26.81 wt.% G3 nanocomposite in the range of 650-1800 cm^{-1}

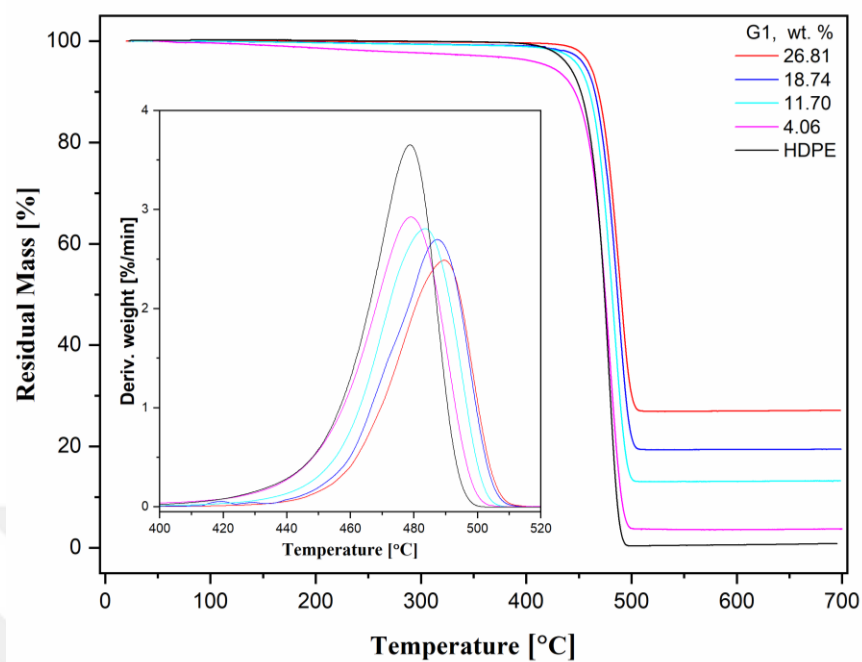


Figure A6.12 TGA thermographs of the HDPE/GnPs nanocomposites with G1 (The inset shows the derivative thermogravimetric (DTG) curves)

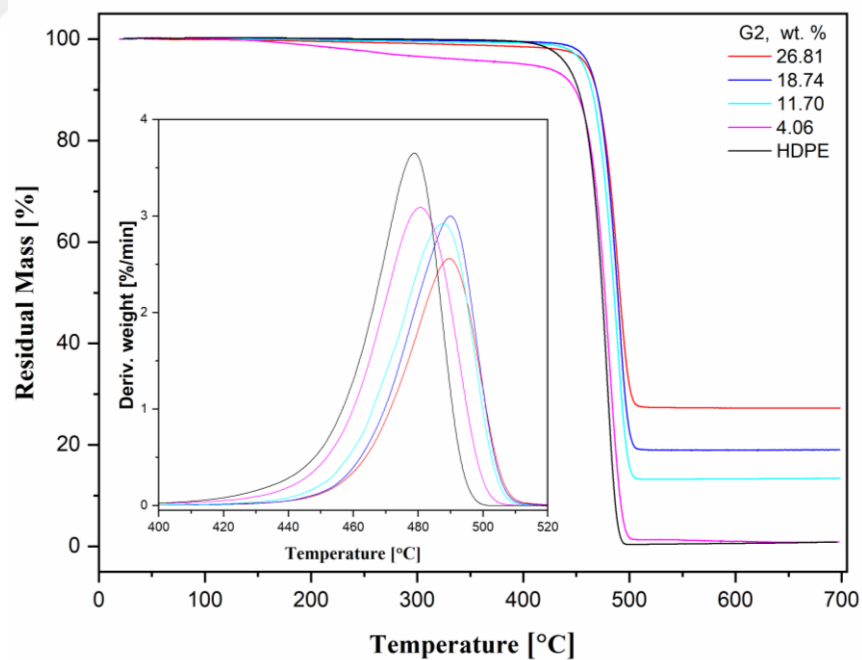


Figure A6.13 TGA thermographs of the HDPE/GnPs nanocomposites with G2 (The inset shows the derivative thermogravimetric (DTG) curves)

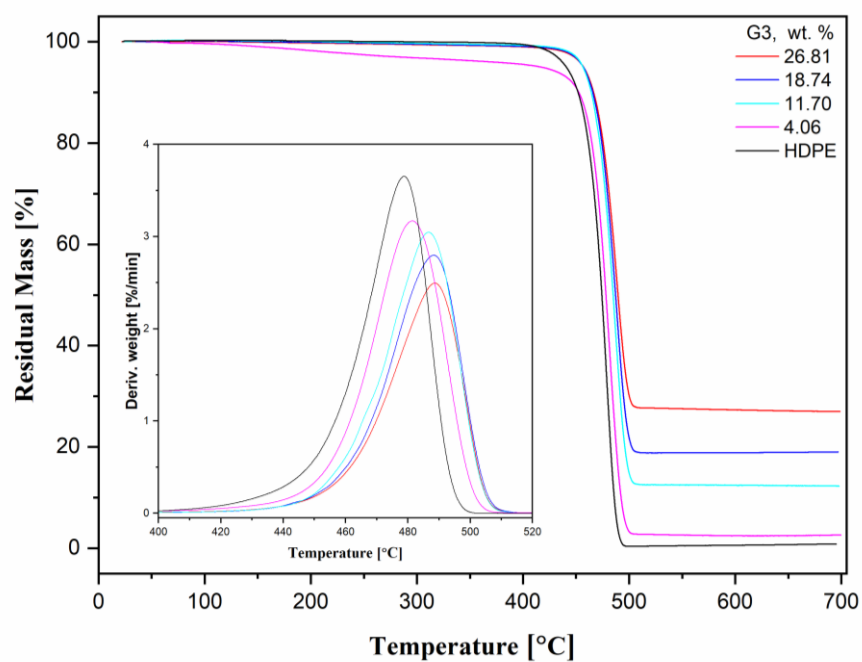


Figure A6.14 TGA thermographs of the HDPE/GnPs nanocomposites with G3 (The inset shows the derivative thermogravimetric (DTG) curves)

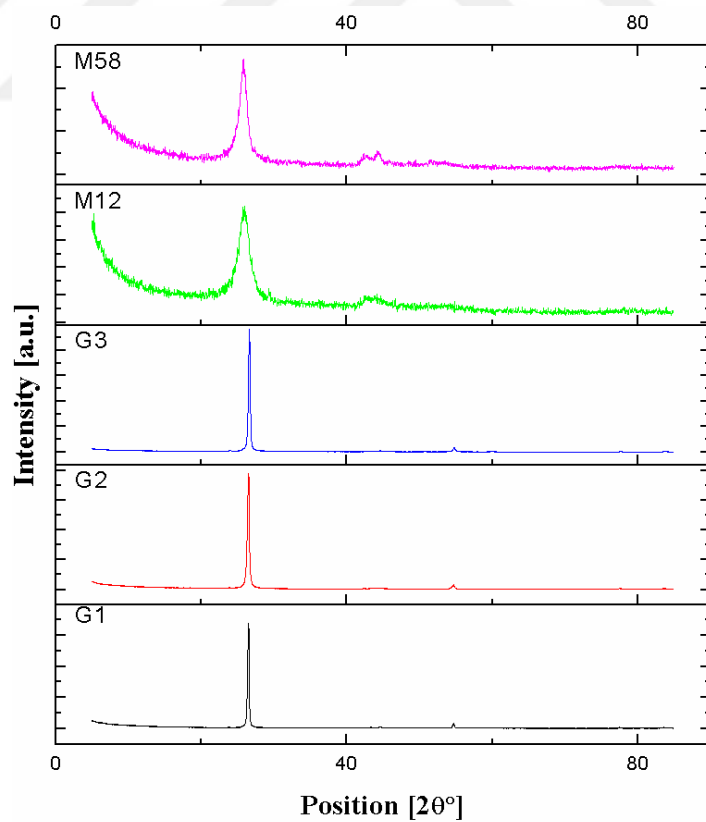


Figure A7.1 XRD patterns of carbon-based materials

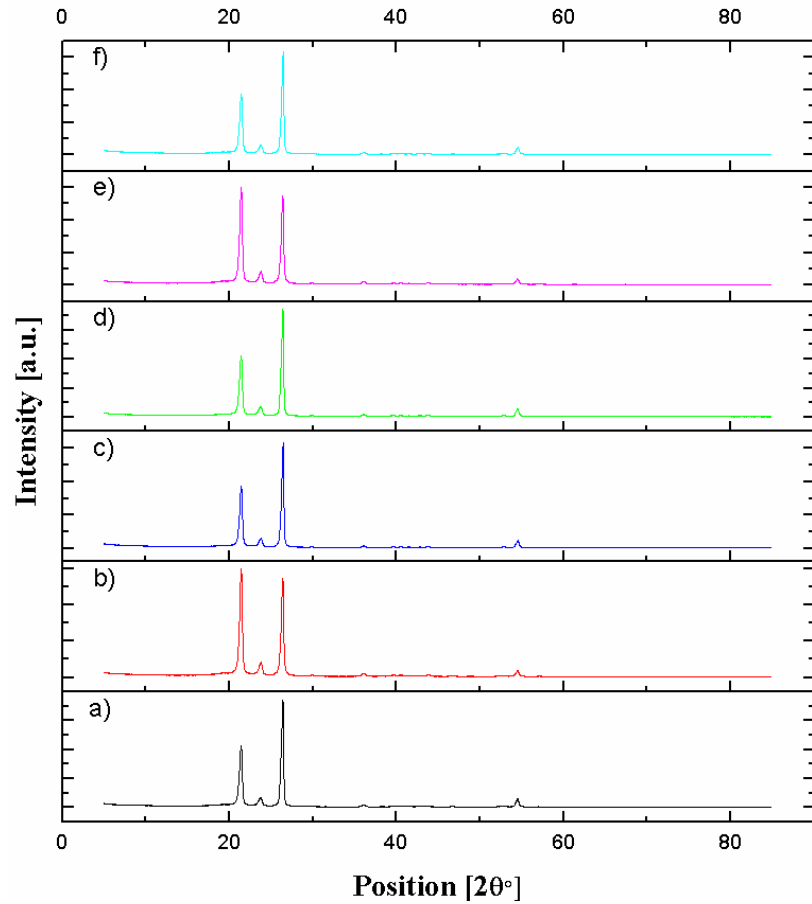


Figure A7.2 XRD patterns of the a)HDPE/G1/M12, b)HDPE/G2/M12, c)HDPE/G3/M58, d)HDPE/G1/M58 e)HDPE/G3/M12, f)HDPE/G2/M58 HDPE/G3/M58 nanocomposites (5wt.%) containing GnPs/MWCNTs of 5/0 weight ratio

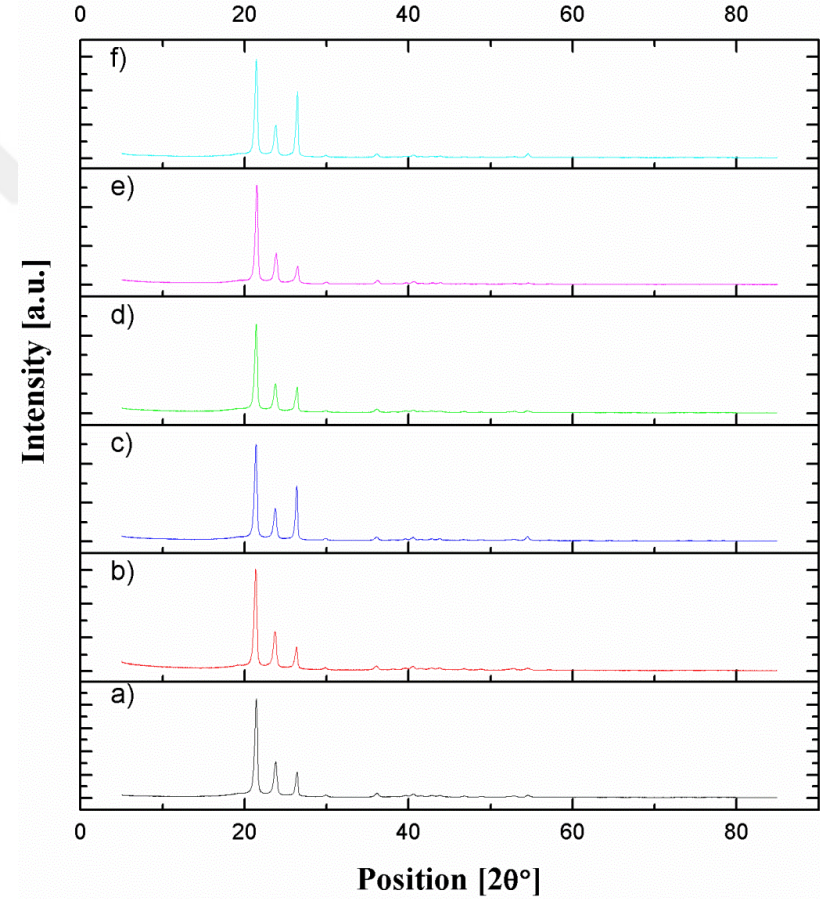


Figure A7.3 XRD patterns of the a)HDPE/G1/M12, b)HDPE/G2/M12, c)HDPE/G3/M58, d)HDPE/G1/M58 e)HDPE/G3/M12, f)HDPE/G2/M58 HDPE/G3/M58 nanocomposites (5wt.%) containing GnPs/MWCNTs of 1/4 weight ratio

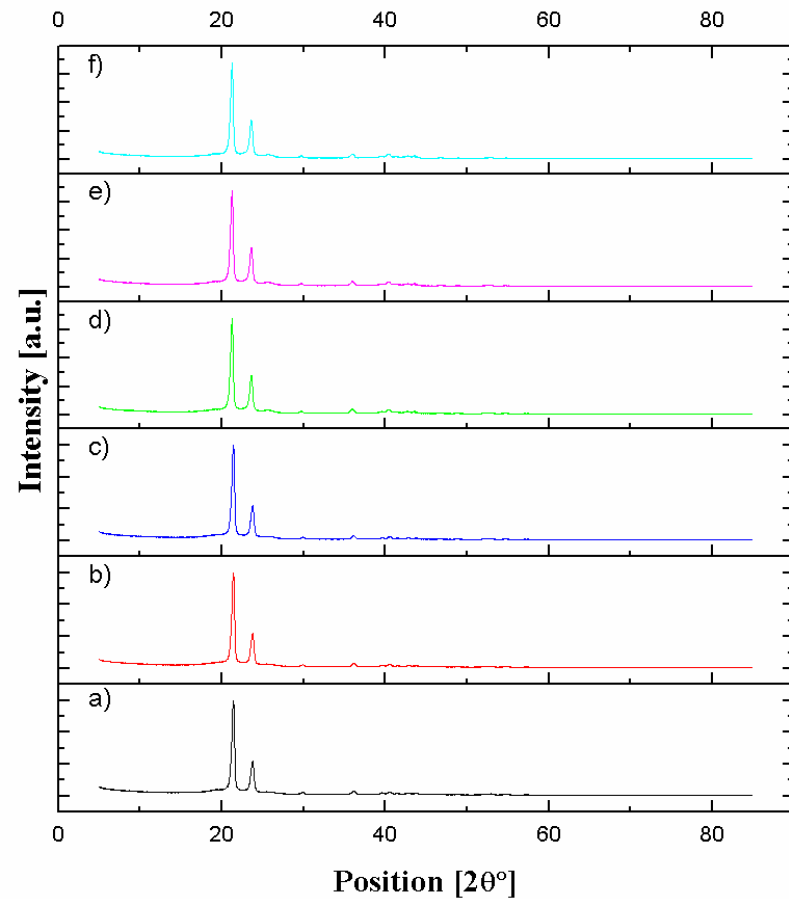


Figure A7.4 XRD patterns of 5:0 the a)HDPE/G1/M12, b)HDPE/G2/M12, c)HDPE/G3/M58, d)HDPE/G1/M58 e)HDPE/G3/M12, f)HDPE/G2/M58 HDPE/G3/M58 nanocomposites (5wt.%) containing GnPs/MWCNTs of 0/5 weight ratio

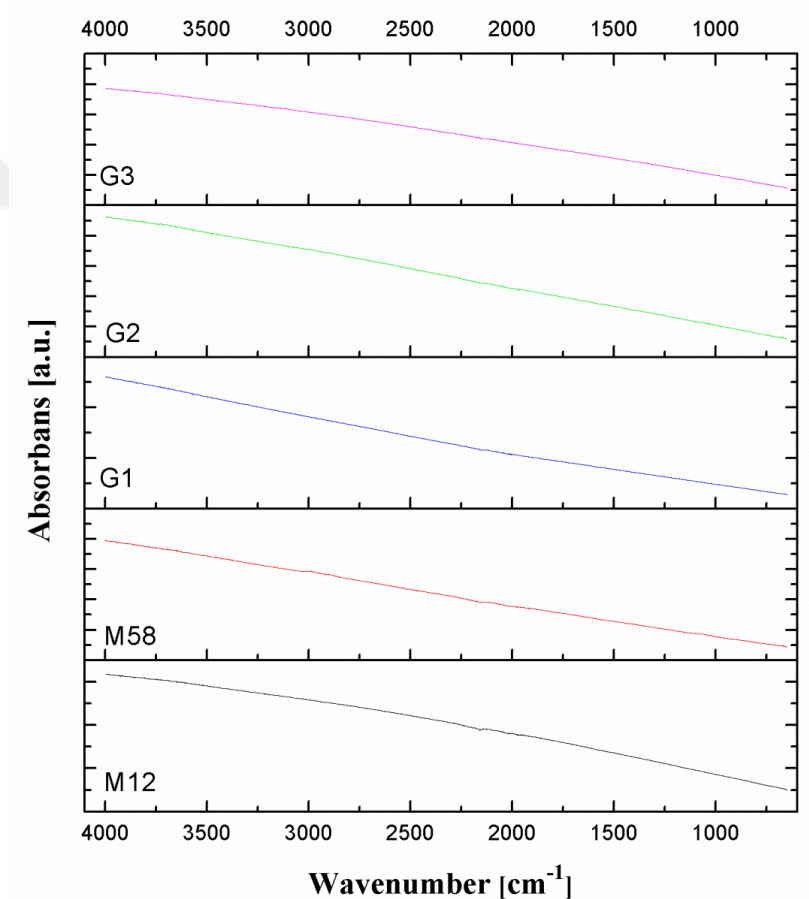


Figure A7.5 FTIR results of carbon-based materials

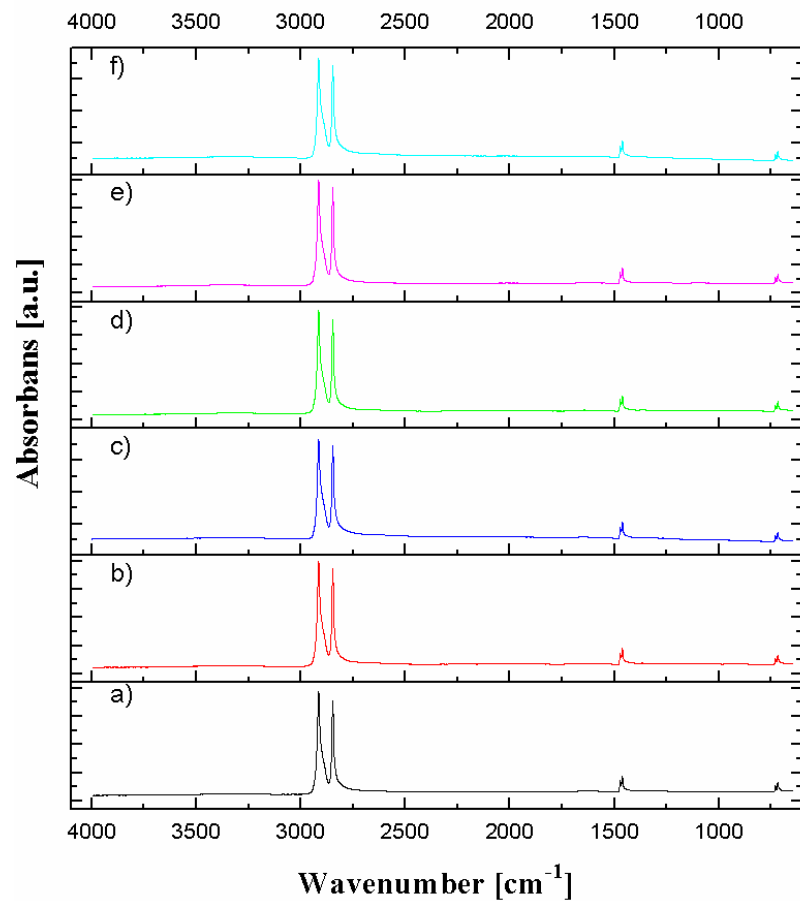


Figure A7.6 FTIR results of the a)HDPE/G1/M12, b)HDPE/G2/M12, c)HDPE/G3/M58, d)HDPE/G1/M58 e)HDPE/G3/M12, f)HDPE/G2/M58 HDPE/G3/M58 nanocomposites (5wt.%) containing GnPs/MWCNTs of 5/0 weight ratio

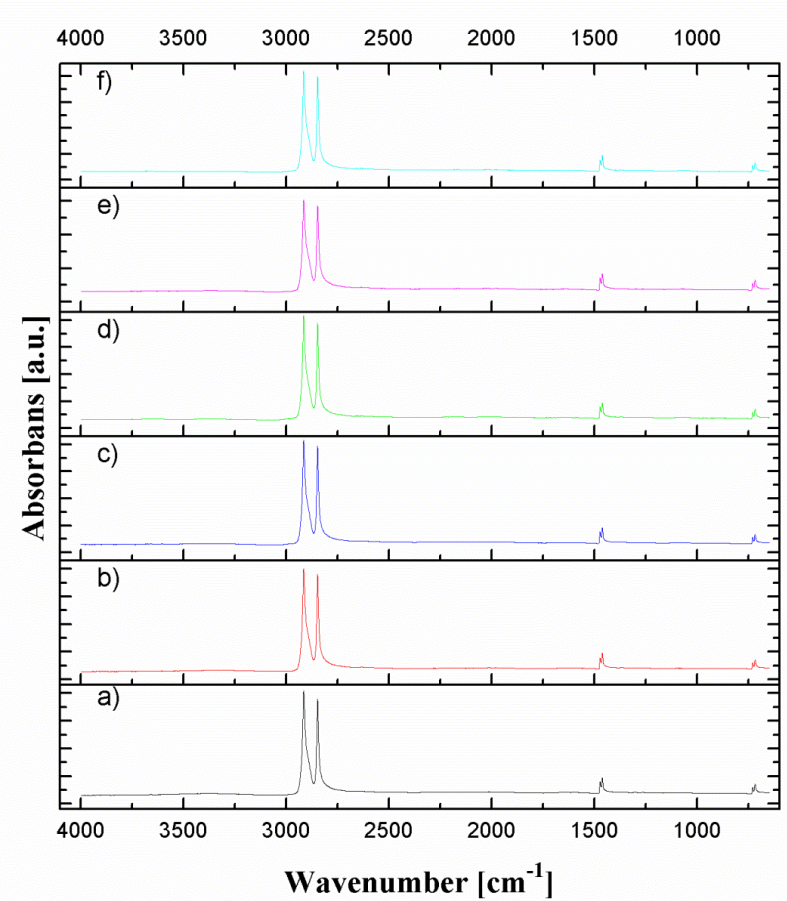


Figure A7.7 FTIR results of the a)HDPE/G1/M12, b)HDPE/G2/M12, c)HDPE/G3/M58, d)HDPE/G1/M58 e)HDPE/G3/M12, f)HDPE/G2/M58 HDPE/G3/M58 nanocomposites (5wt.%) containing GnPs/MWCNTs of 4/1 weight ratio

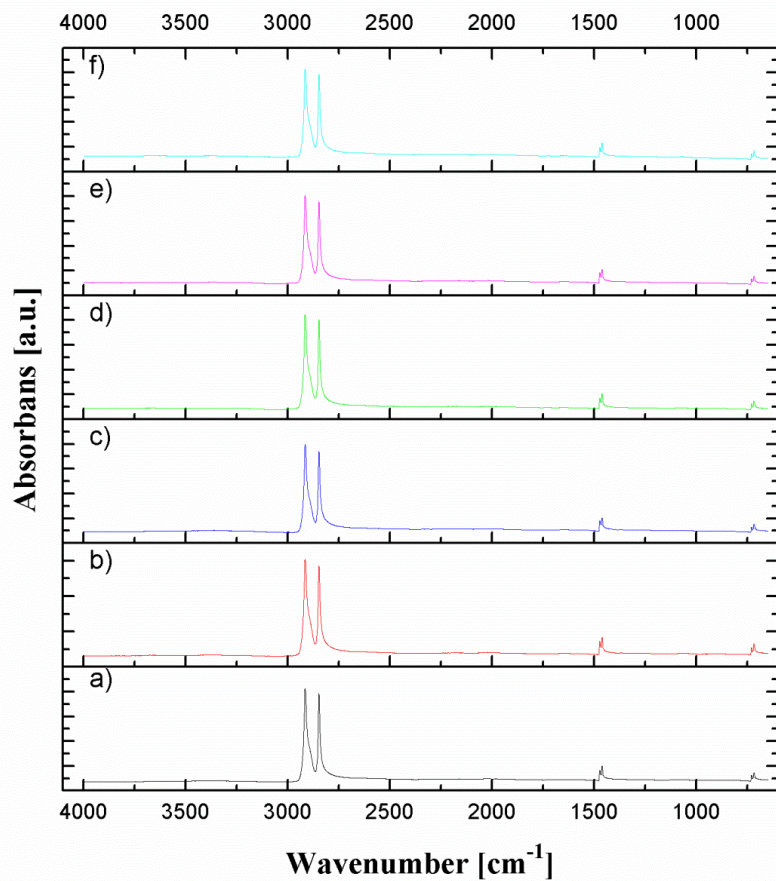


Figure A7.8 FTIR results of the a)HDPE/G1/M12, b)HDPE/G2/M12, c)HDPE/G3/M58, d)HDPE/G1/M58 e)HDPE/G3/M12, f)HDPE/G2/M58 HDPE/G3/M58 nanocomposites (5wt.%) containing GnPs/MWCNTs of 3/2 weight ratio

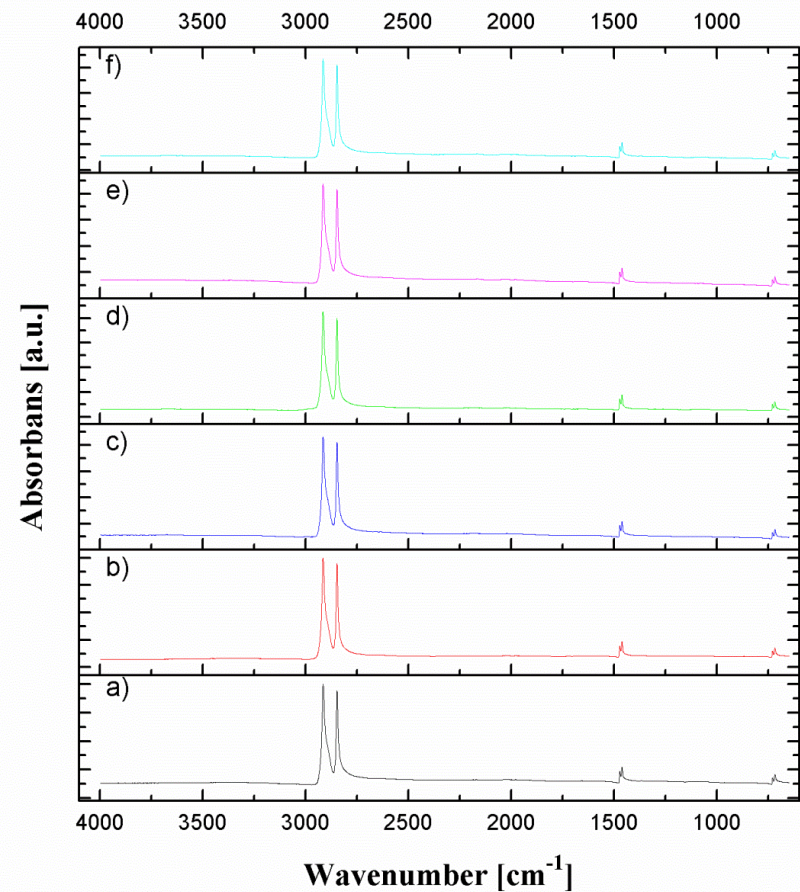


Figure A7.9 FTIR results of the a)HDPE/G1/M12, b)HDPE/G2/M12, c)HDPE/G3/M58, d)HDPE/G1/M58 e)HDPE/G3/M12, f)HDPE/G2/M58 HDPE/G3/M58 nanocomposites (5wt.%) containing GnPs/MWCNTs of 1/4 weight ratio

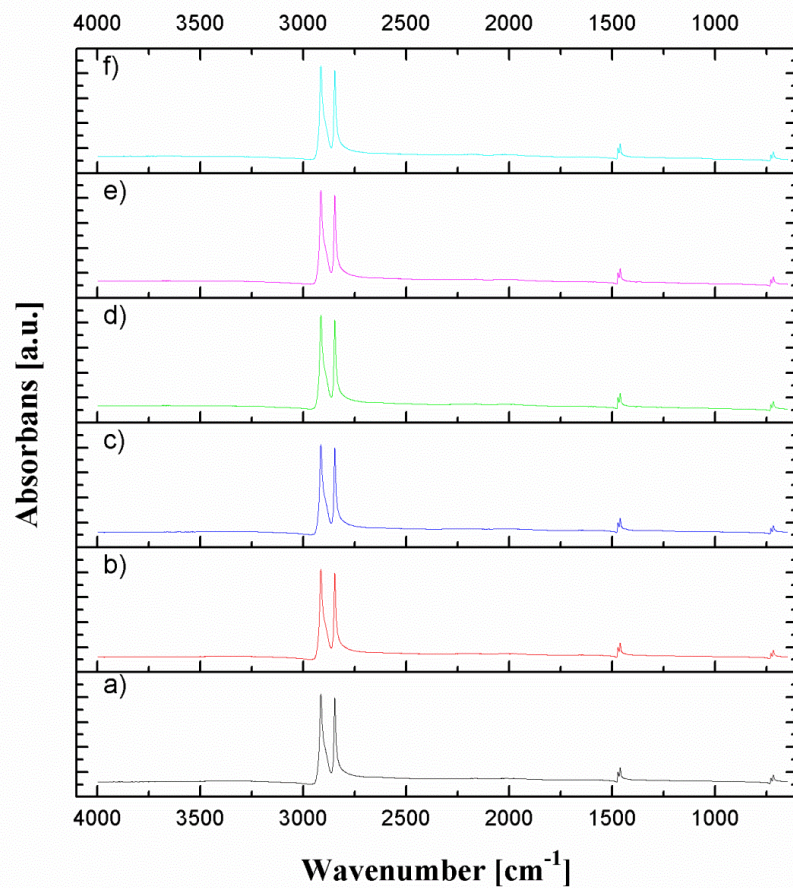


Figure A7.10 FTIR results of the a)HDPE/G1/M12, b)HDPE/G2/M12, c)HDPE/G3/M58, d)HDPE/G1/M58 e)HDPE/G3/M12, f)HDPE/G2/M58 HDPE/G3/M58 nanocomposites (5wt.%) containing GnPs/MWCNTs of 0/5 weight ratio

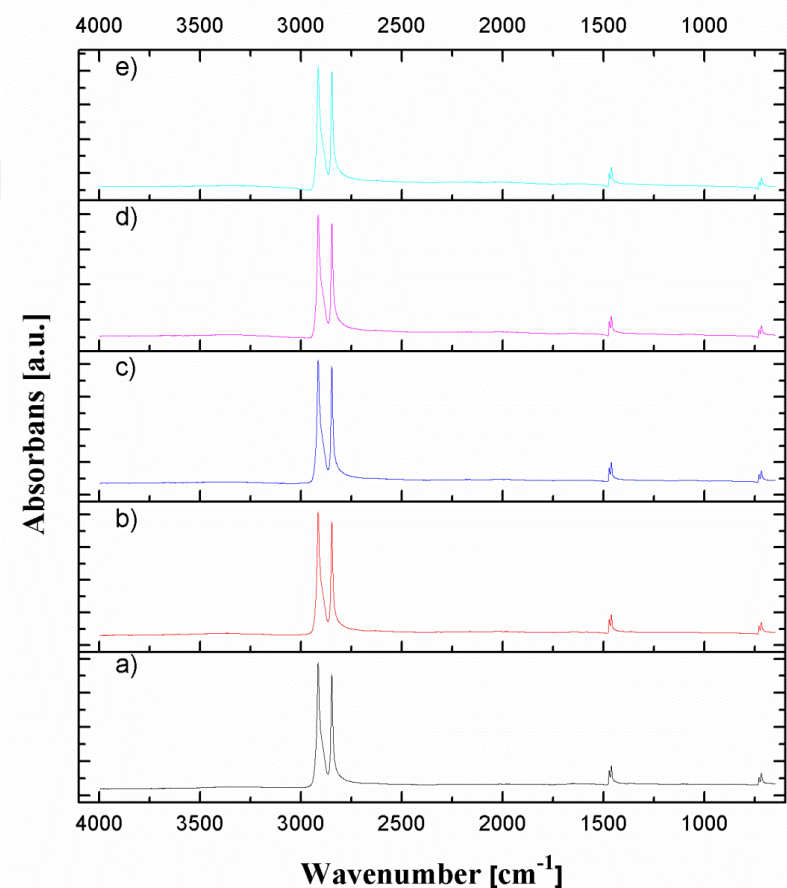


Figure A7.11 FTIR results of the HDPE/G1/M12 nanocomposites (5wt.%) containing GnPs/MWCNTs of a) 5/0, b)4/1, c)3/2, d)1/4 and 0/5 weight ratio

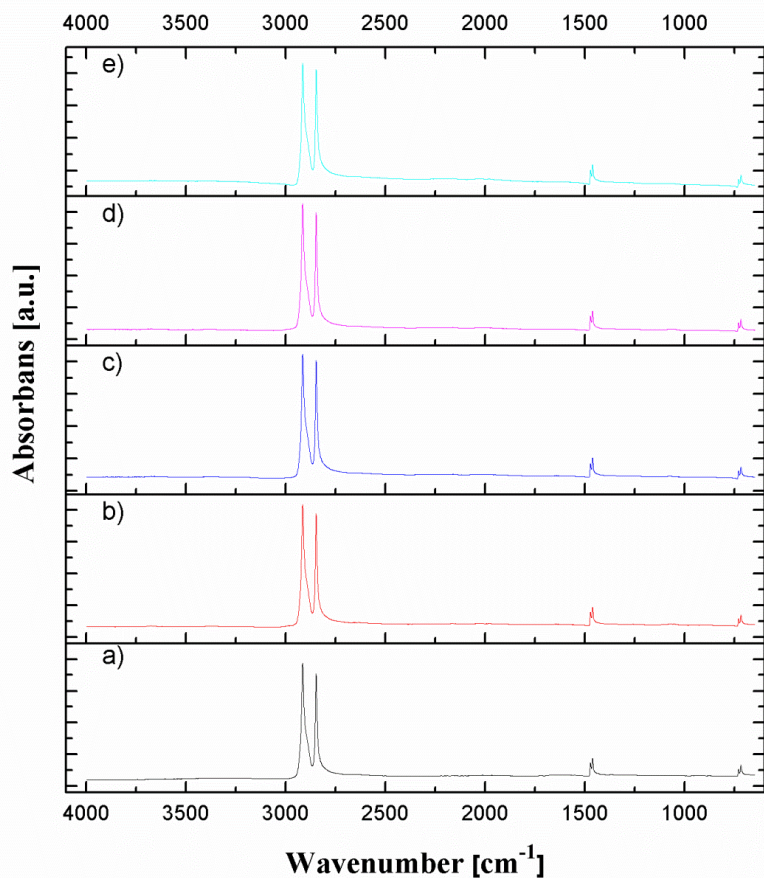


Figure A7.12 FTIR results of the HDPE/G1/M58 nanocomposites (5wt.%) containing GnPs/MWCNTs of a) 5/0, b)4/1, c)3/2, d)1/4 and 0/5 weight ratio

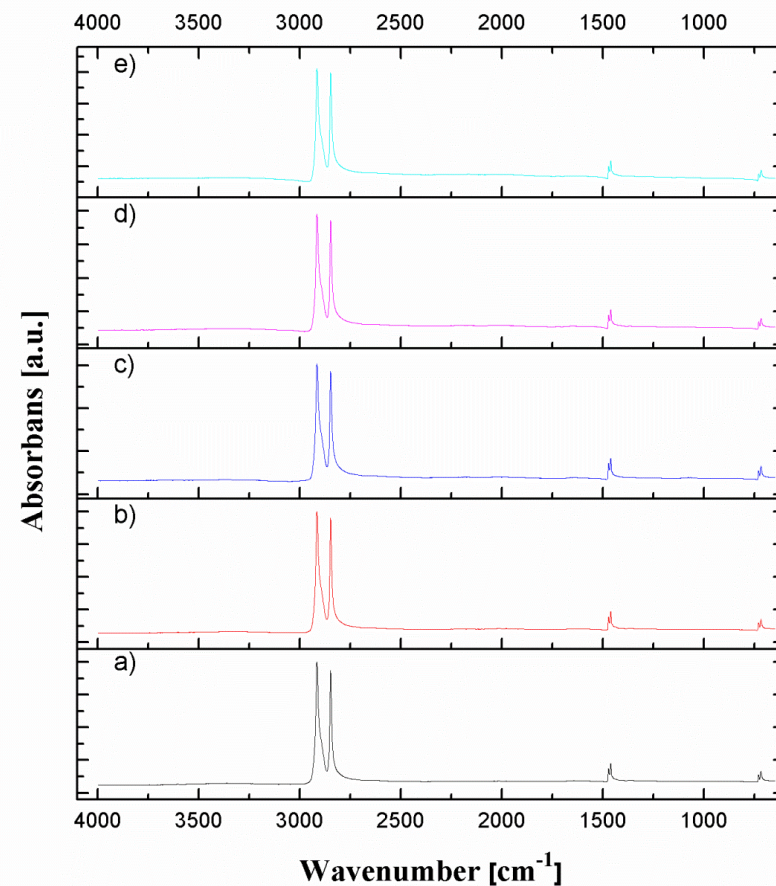


Figure A7.13 FTIR results of the HDPE/G2/M12 nanocomposites (5wt.%) containing GnPs/MWCNTs of a) 5/0, b)4/1, c)3/2, d)1/4 and 0/5 weight ratio

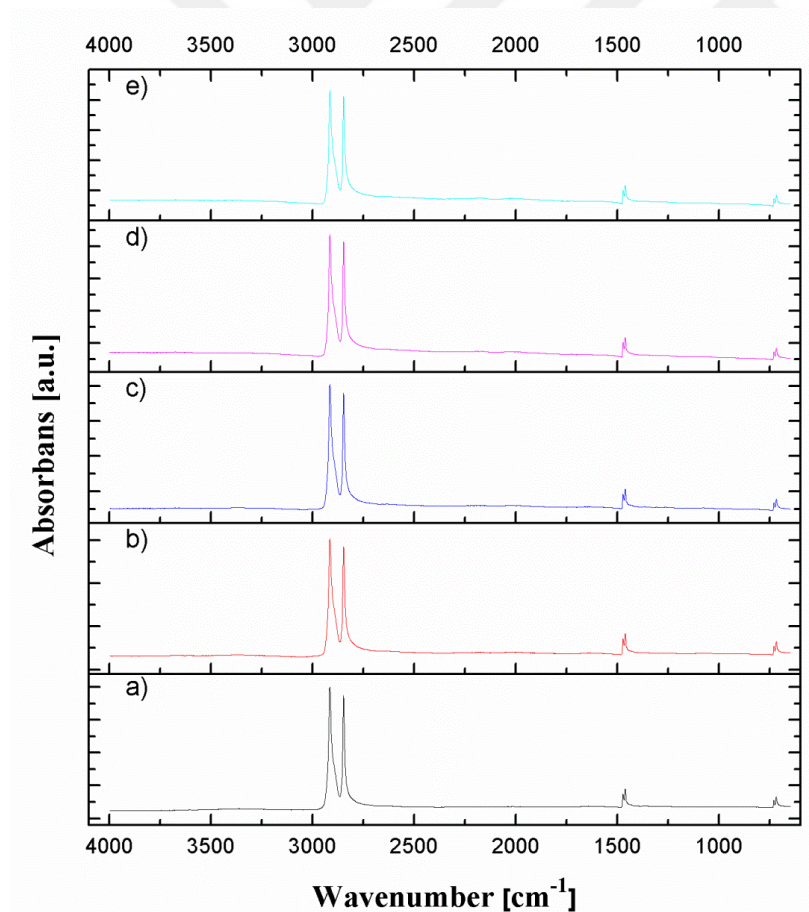


Figure A7.14 FTIR results of the HDPE/G2/M58 nanocomposites (5wt.%) containing GnPs/MWCNTs of a) 5/0, b)4/1, c)3/2, d)1/4 and 0/5 weight ratio

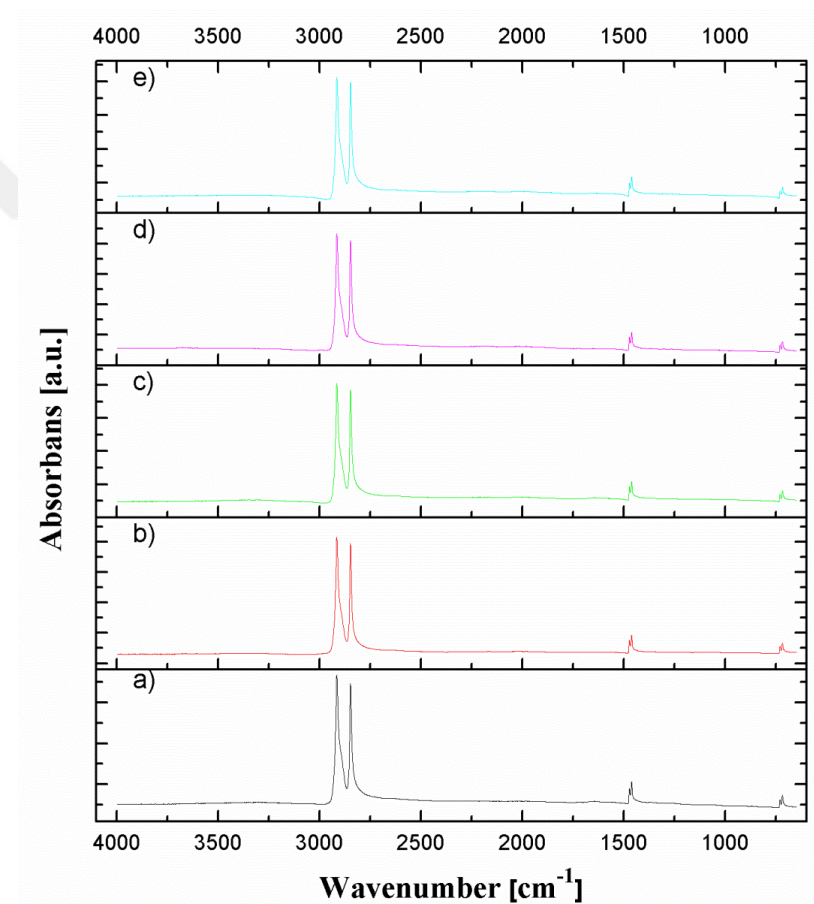


Figure A7.15 FTIR results of the HDPE/G3/M12 nanocomposites (5wt.%) containing GnPs/MWCNTs of a) 5/0, b)4/1, c)3/2, d)1/4 and 0/5 weight ratio

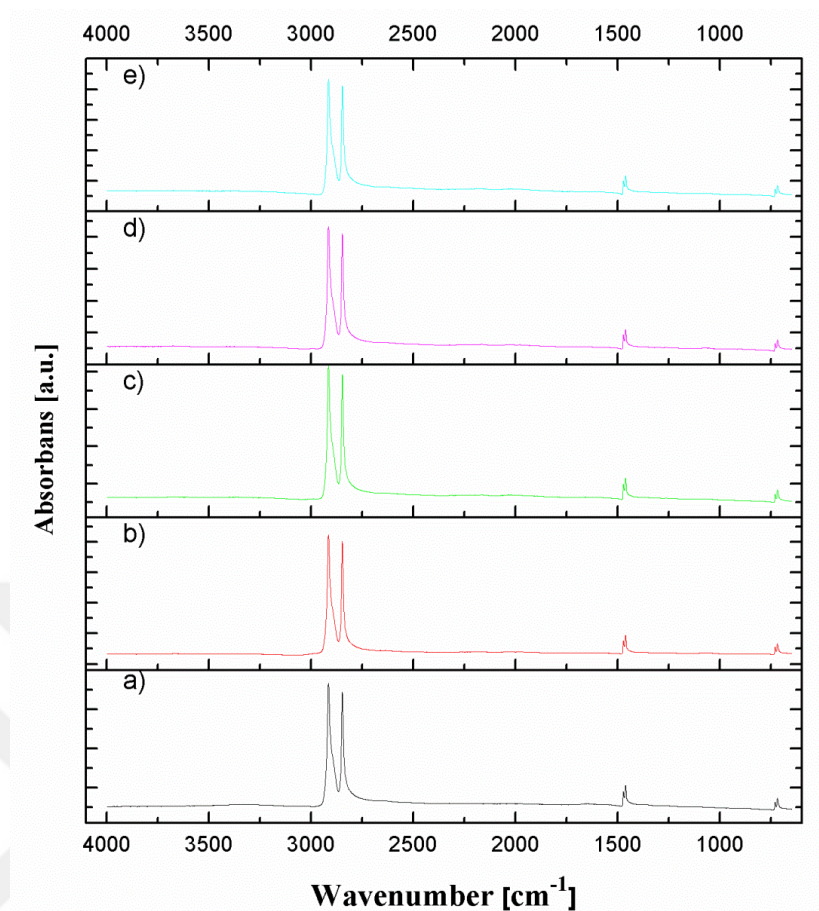


Figure A7.16 FTIR results of the HDPE/G3/M58 nanocomposites (5wt.%) containing GnPs/MWCNTs of a) 5/0, b)4/1, c)3/2, d)1/4 and 0/5 weight ratio

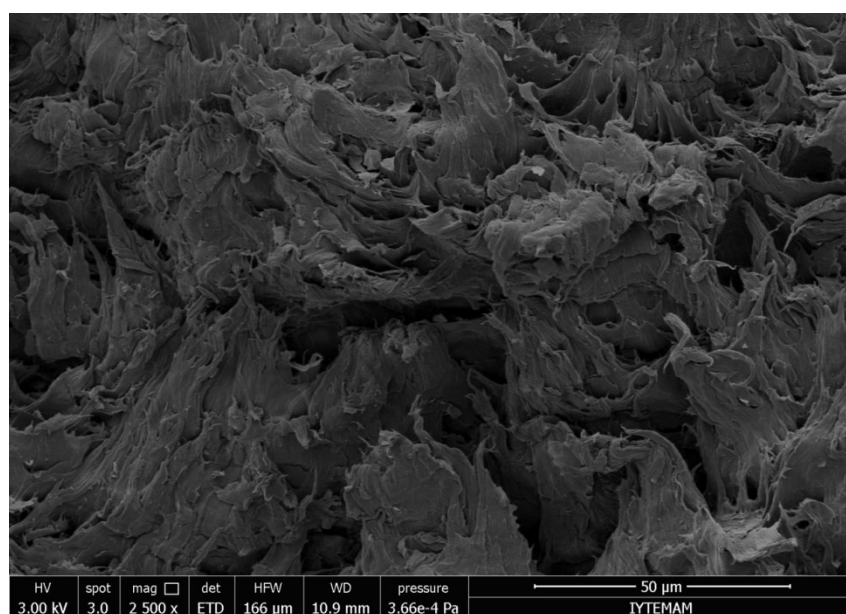


Figure A7.17 SEM image of the HDPE/G2 (11.70 wt.)/M12 (4wt.%) nanocomposites (2 500 ×)

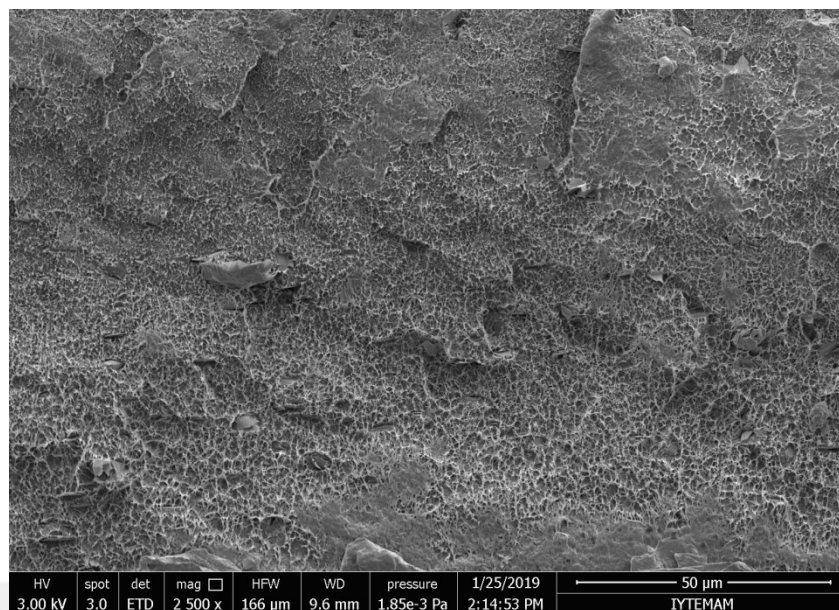


Figure A7.18 SEM image of the HDPE/G1/M12 nanocomposites with 1/4 weight ratio of GnPs/MWCNTs (5wt.%) (2 500 ×)

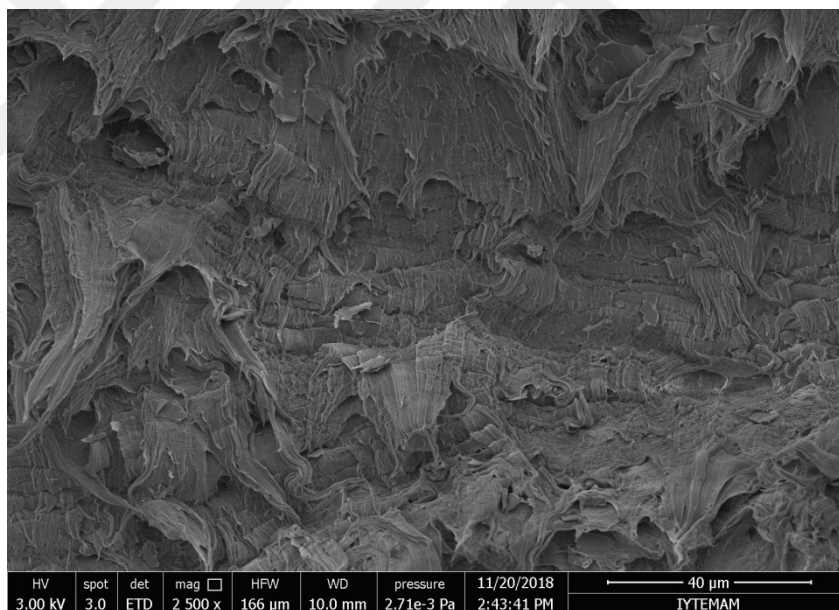


Figure A7.19 SEM image of the HDPE/G1 /M12 nanocomposites with 3/2 weight ratio of GnPs/MWCNTs (5wt.%) (2 500 ×)

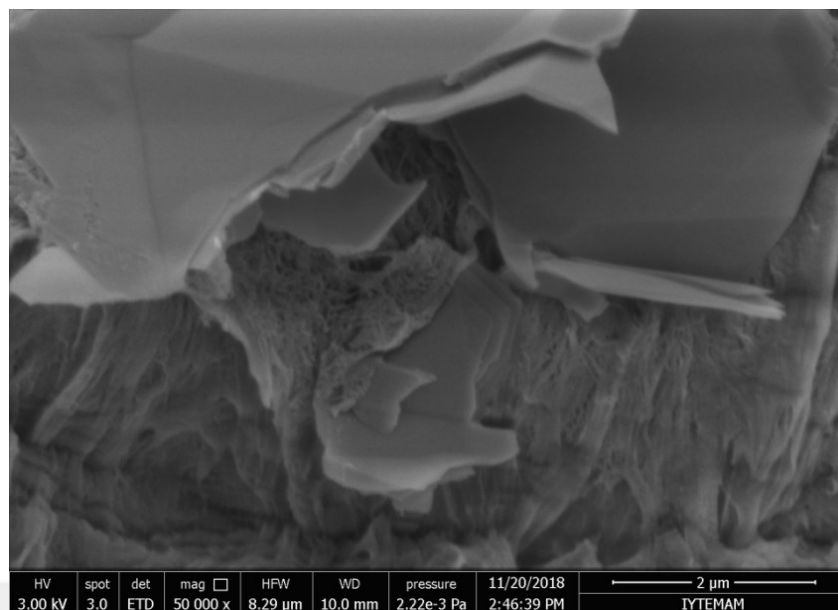


Figure A7.20 SEM image of the HDPE/G1/M12 nanocomposites with 3/2 weight ratio of GnPs/MWCNTs (5wt.%) (50 000 ×)

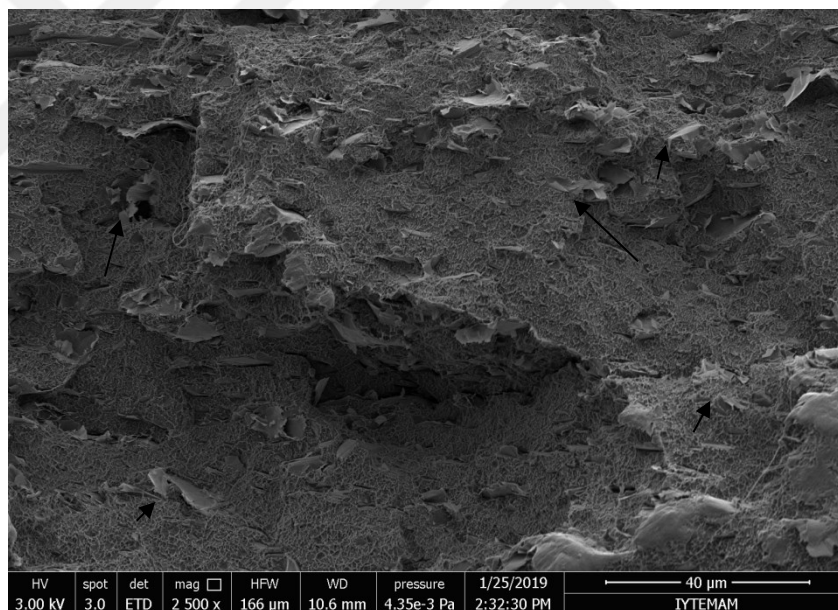


Figure A7.21 SEM image of the HDPE/G2/M12 nanocomposites with 1/4 weight ratio of GnPs/MWCNTs (5wt.%) (2 500 ×)

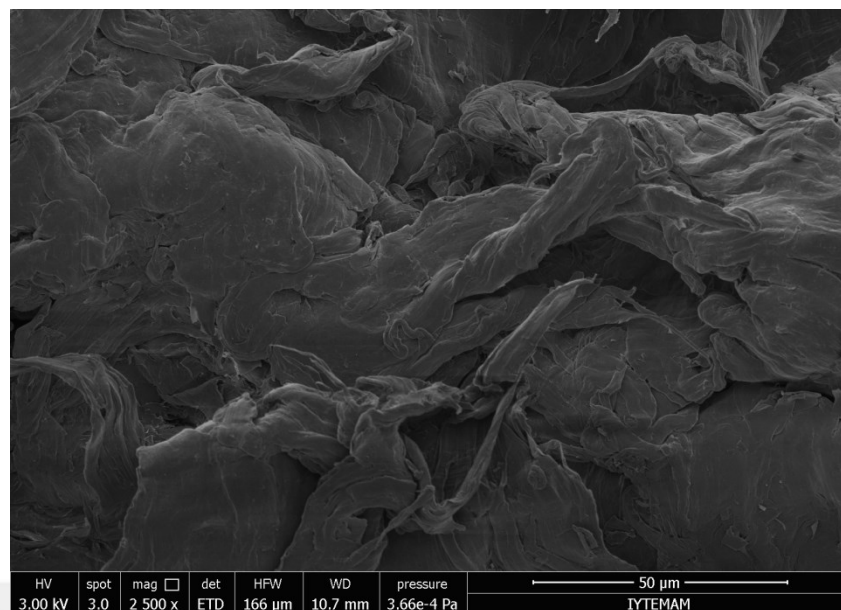


Figure A7.22 SEM image of the HDPE/G2/M12 nanocomposites with 3/2 weight ratio of GnPs/MWCNTs (5wt.%) (2 500 ×)

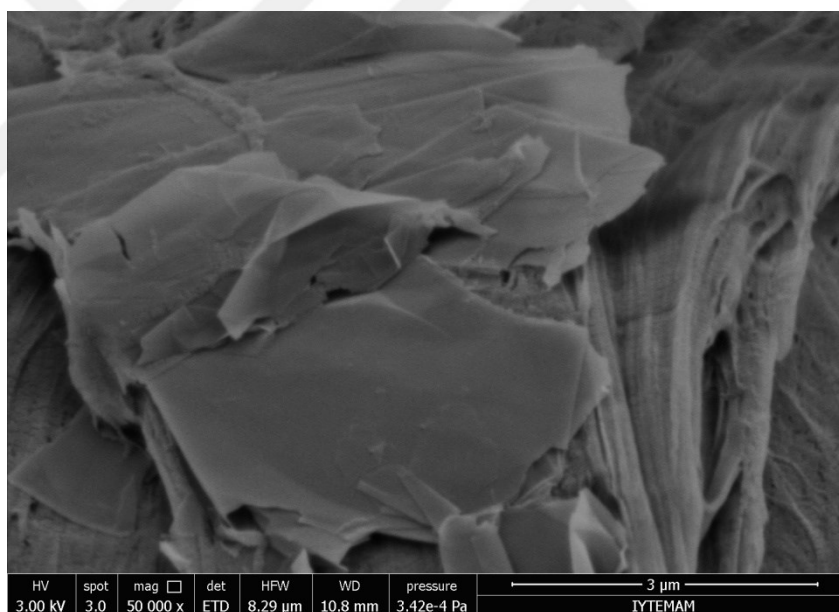


Figure A7.23 SEM image of the HDPE/G2/M12 nanocomposites with 3/2 weight ratio of GnPs/MWCNTs (5wt.%) (50 000 ×)

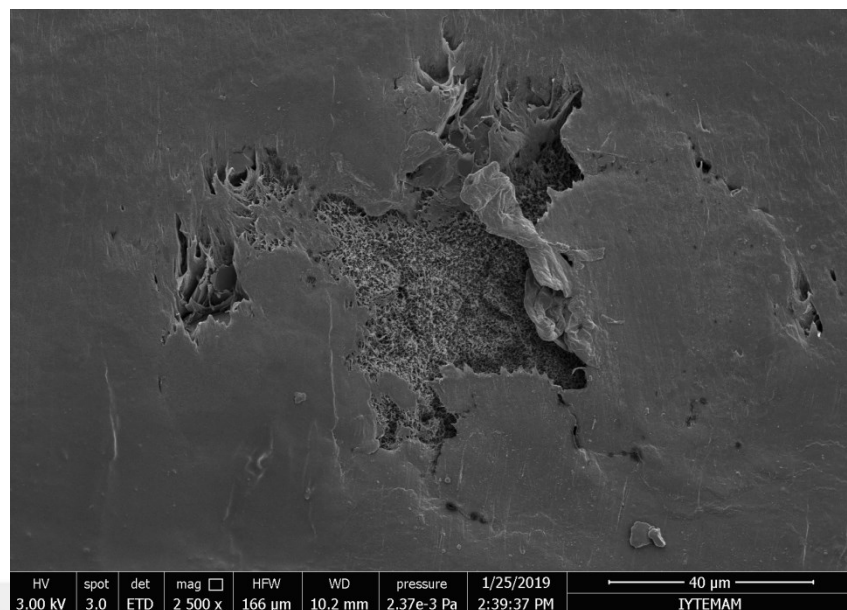


Figure A7.24 SEM image of the HDPE/G3/M12 nanocomposites with 1/4 weight ratio of GnPs/MWCNTs (5wt.%) (10 000 ×)

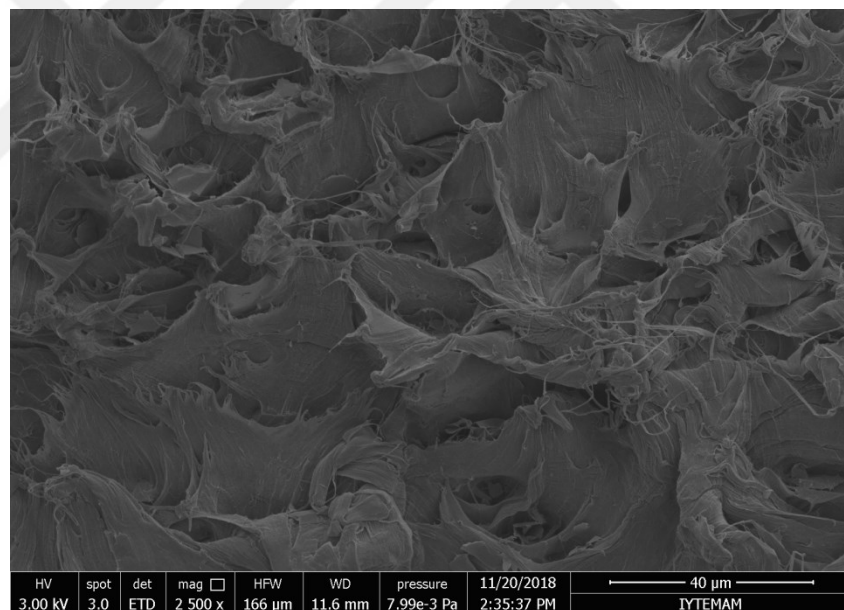


Figure A7.25 SEM image of the HDPE/G3/M12 nanocomposites with 3/2 weight ratio of GnPs/MWCNTs (5wt.%) (2 500 ×)

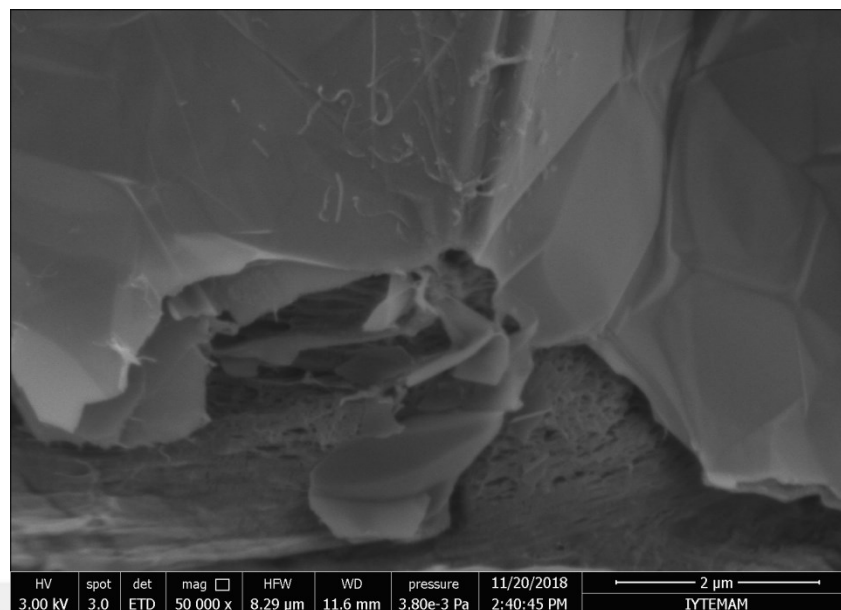


Figure A7.26 SEM image of the HDPE/G3/M12 nanocomposites with 3/2 weight ratio of GnPs/MWCNTs (5wt.%) (50 000 ×)

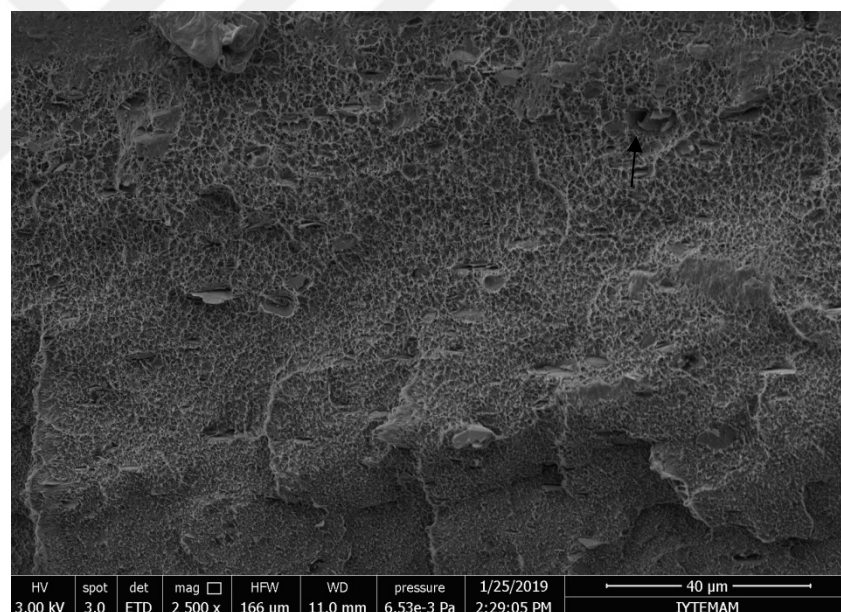


Figure A7.27 SEM image of the HDPE/G1/M58 nanocomposites with 1/4 weight ratio of GnPs/MWCNTs (5wt.%) (2 500 ×)

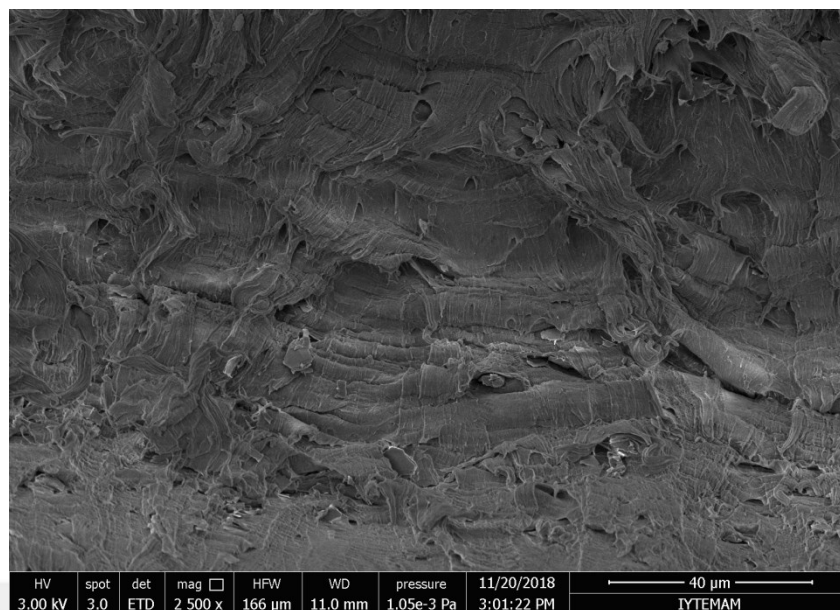


Figure A7.28 SEM image of the HDPE/G1/M58 nanocomposites with 3/2 weight ratio of GnPs/MWCNTs (5wt.%) (2 500 ×)

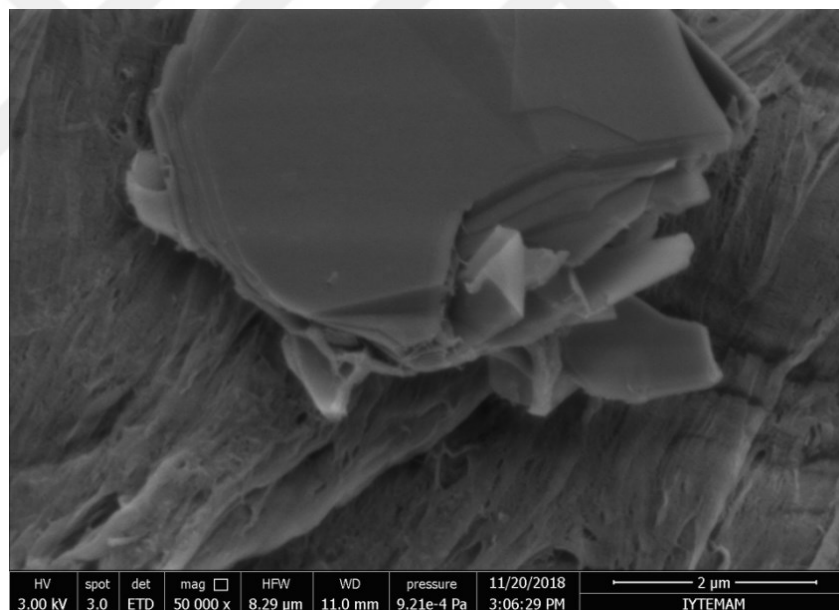


Figure A7.29 SEM image of the HDPE/G1/M58 nanocomposites with 3/2 weight ratio of GnPs/MWCNTs (5wt.%) (50 000 ×)

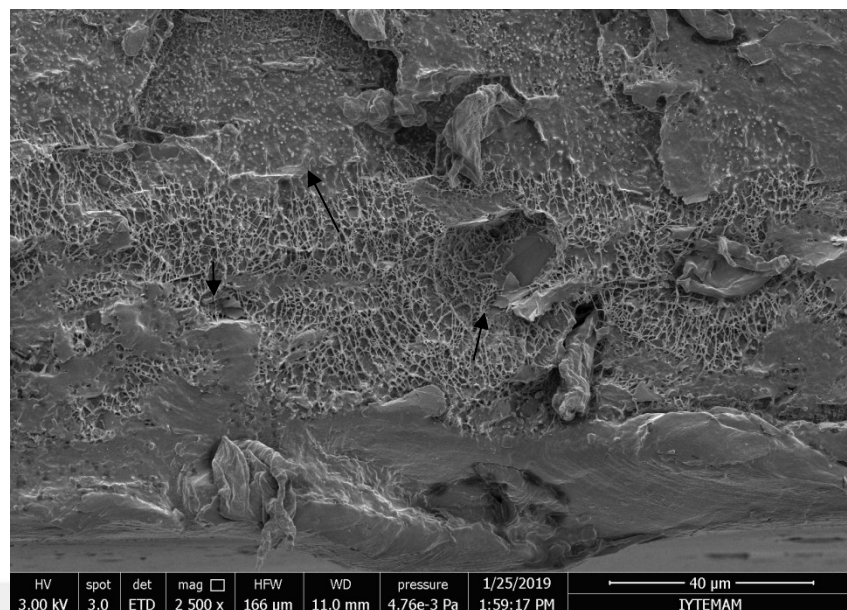


Figure A7.30 SEM image of the HDPE/G2/M58 nanocomposites with 1/4 weight ratio of GnPs/MWCNTs (5wt.%) (10 000 ×)

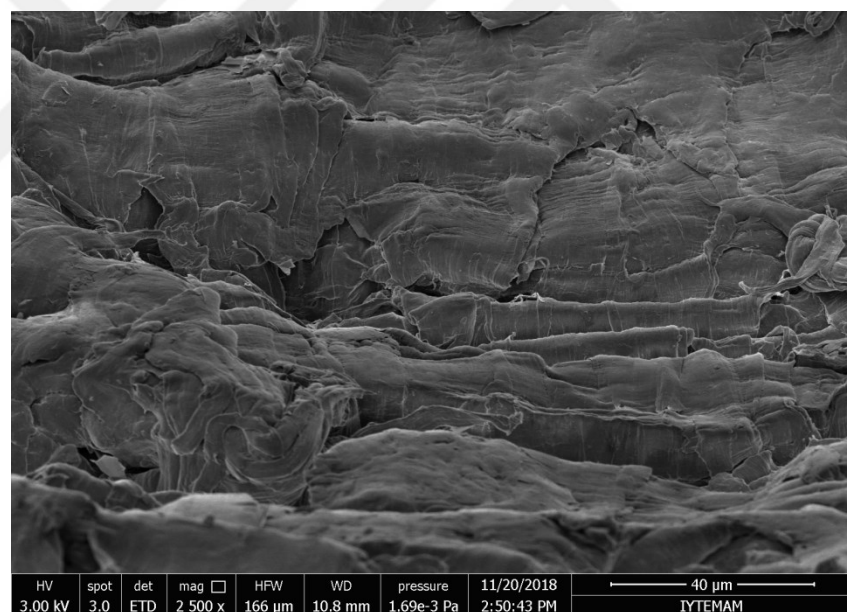


Figure A7.31 SEM image of the HDPE/G2/M58 nanocomposites with 3/2 weight ratio of GnPs/MWCNTs (5wt.%) (2 500 ×)

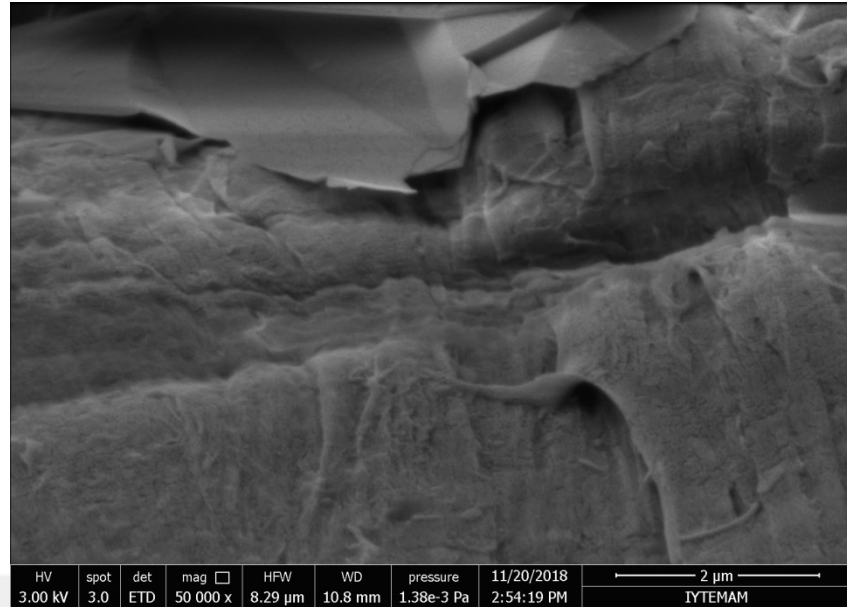


Figure A7.32 SEM image of the HDPE/G2/M58 nanocomposites with 3/2 weight ratio of GnPs/MWCNTs (5wt.%) (50 000 ×)

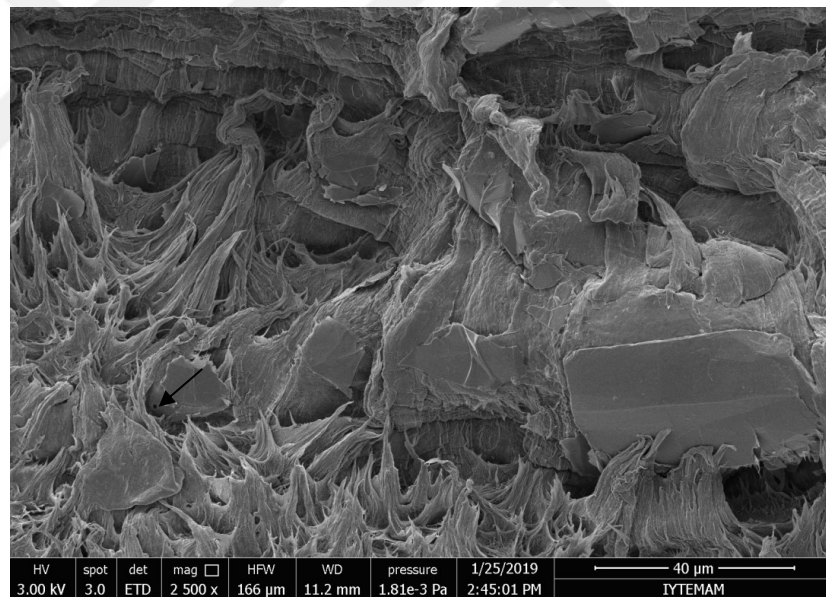


Figure A7.33 SEM image of the HDPE/G3/M58 nanocomposites with 1/4 weight ratio of GnPs/MWCNTs (5wt.%) (10 000 ×)

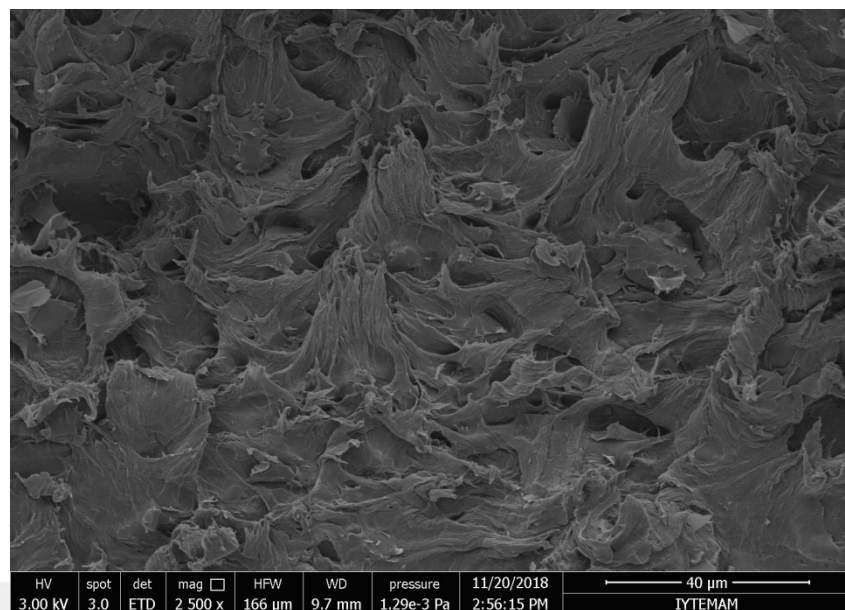


Figure A7.34 SEM image of the HDPE/G3/M58 nanocomposites with 3/2 weight ratio of GnPs/MWCNTs (5wt.%) (2 500 ×)

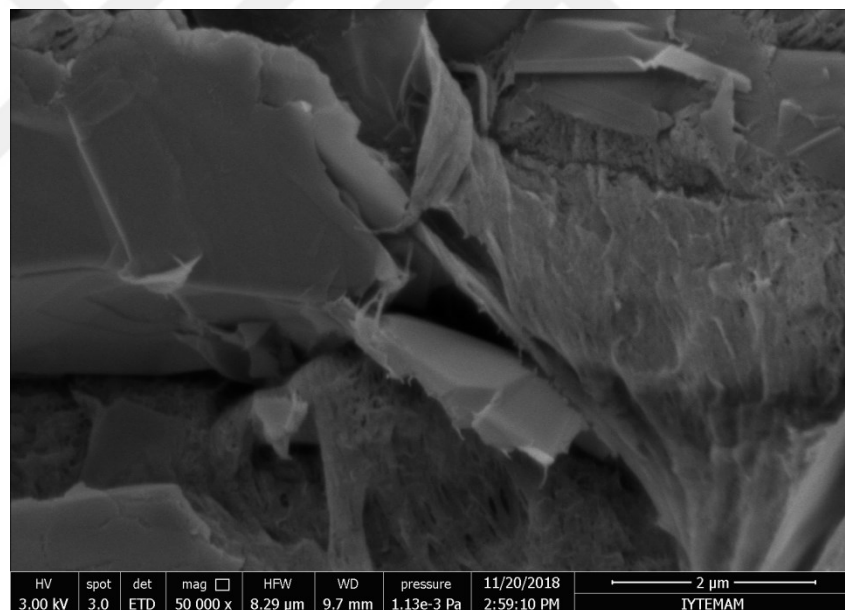


Figure A7.35 SEM image of the HDPE/G3/M58 nanocomposites with 3/2 weight ratio of GnPs/MWCNTs (5wt.%) (50 000 ×)

Table A7.1 T_m [°C] results of HDPE/MWCNTs and HDPE/GnPs

Filler Content [wt.%]	HDPE/M12	HDPE/M58	HDPE/G1	HDPE/G2	HDPE/G3
0.00	130.06	130.06	130.09	130.09	130.09
4.06	132.03	131.56	131.82	132.17	132.01
11.70	132.80	130.91	130.89	131.63	132.05
18.74	129.74	130.54	130.43	131.69	131.38
26.81			131.80	131.18	131.39

Table A7.2 T_c [°C] results of HDPE/MWCNTs and HDPE/GnPs

Filler Content [wt.%]	HDPE/M12	HDPE/M58	HDPE/G1	HDPE/G2	HDPE/G3
0.00	116.30	116.30	116.30	116.30	116.30
4.06	119.25	119.10	117.66	117.31	117.33
11.70	118.02	120.33	118.67	119.97	118.47
18.74	121.31	121.75	119.56	120.63	119.83
26.81			121.02	121.57	120.06

Table A7.3 ΔH_f [J/g] results of HDPE/MWCNTs and HDPE/GnPs

Filler Content [wt.%]	HDPE/M12	HDPE/M58	HDPE/G1	HDPE/G2	HDPE/G3
0.00	205.80	205.80	205.80	205.80	205.80
4.06	196.90	196.80	200.60	205.20	204.20
11.70	180.90	180.90	189.10	186.40	189.50
18.74	165.30	165.20	173.70	172.20	174.50
26.81			153.10	153.10	153.90

Table A7.4 X_c [J/g] results of HDPE/MWCNTs and HDPE/GnPs

Filler Content [wt.%]	HDPE/M12	HDPE/M58	HDPE/G1	HDPE/G2	HDPE/G3
0.00	70.24	70.24	70.24	70.24	70.24
4.06	70.07	70.04	71.36	73.00	72.64
11.70	69.92	69.92	73.10	72.05	73.25
18.74	69.39	69.35	72.96	72.33	73.24
26.81			71.39	71.39	71.77

Table A7.5 $T_{5\%}$ [°C] results of HDPE/MWCNTs and HDPE/GnPs

Filler Content [wt.%]	HDPE/M12	HDPE/M58	HDPE/G1	HDPE/G2	HDPE/G3
0.00	440.77	440.77	440.77	440.77	440.77
4.06	464.32	463.49	421.66	425.42	415.48
11.70	467.46	466.98	449.97	456.34	456.46
18.74	470.34	466.11	456.05	461.50	456.16
26.81			461.05	459.45	457.16

Table A7.6 $T_{50\%}$ [°C] results of HDPE/MWCNTs and HDPE/GnPs

Filler Content [wt.%]	HDPE/M12	HDPE/M58	HDPE/G1	HDPE/G2	HDPE/G3
0.00	474.44	474.44	474.44	474.44	474.44
4.06	487.98	488.56	475.11	476.86	478.31
11.70	490.45	490.97	481.68	485.53	485.06
18.74	495.24	491.51	486.82	488.91	487.37
26.81			490.19	490.99	489.64

Table A7.7 T_{deg} [°C] results of HDPE/MWCNTs and HDPE/GnPs

Filler Content [wt.%]	HDPE/M12	HDPE/M58	HDPE/G1	HDPE/G2	HDPE/G3
0.00	478.79	478.79	478.79	478.79	478.79
4.06	490.90	492.31	479.07	480.62	481.45
11.70	492.03	491.88	483.55	487.62	486.63
18.74	495.03	492.09	487.31	489.92	488.27
26.81			489.52	489.54	488.64

Table A7.8 Residual Mass [%] results of HDPE/MWCNTs and HDPE/GnPs

Filler Content [wt.%]	HDPE/M12	HDPE/M58	HDPE/G1	HDPE/G2	HDPE/G3
0.00	0.84	0.84	0.84	0.84	0.84
4.06	4.32	4.56	3.88	1.53	3.09
11.70	12.26	12.13	13.19	13.52	11.68
18.74	18.92	19.15	19.58	19.02	19.24
26.81			27.44	27.31	26.75

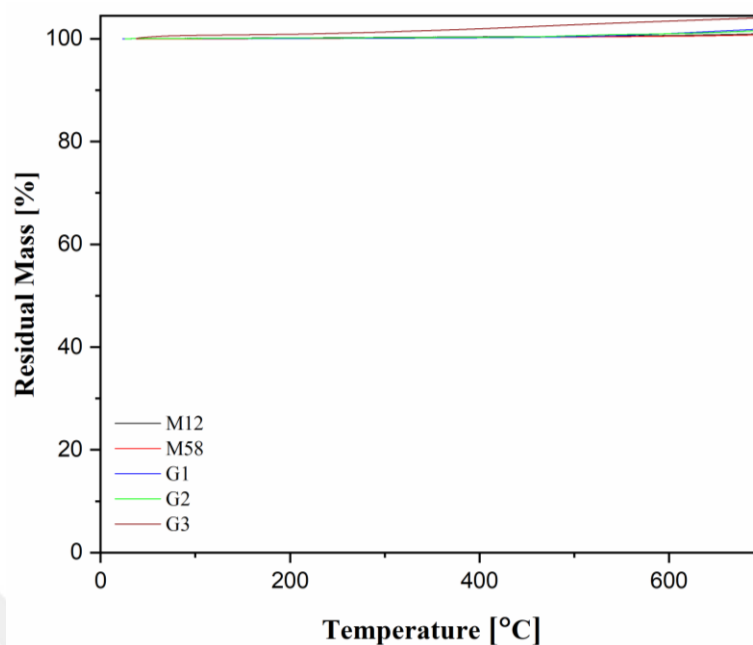


Figure A7.36 TGA thermographs of the carbon-based nanofillers (The inset shows the derivative thermogravimetric (DTG) curves)

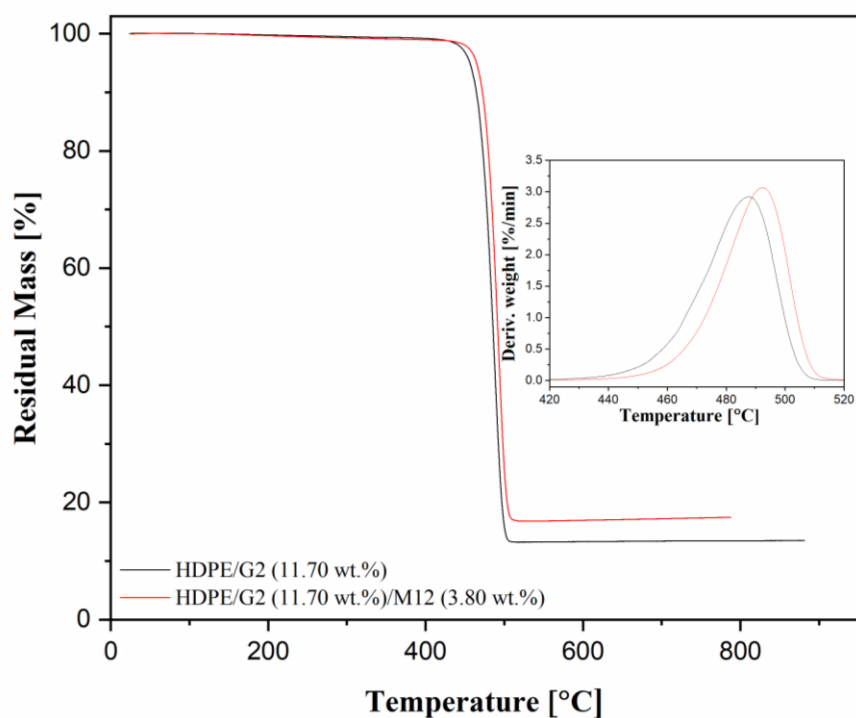


Figure A7.37 TGA thermographs of the HDPE/G2 (11.70 wt.%) / M12 nanocomposites (The inset shows the derivative thermogravimetric (DTG) curves)

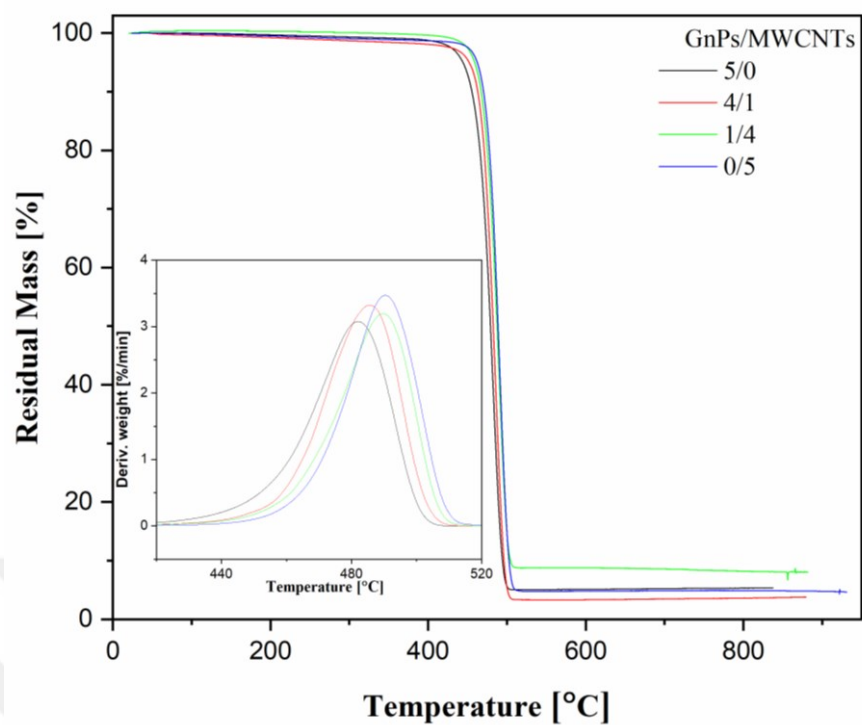


Figure A7.38 TGA thermographs of the HDPE/G1/M12 nanocomposites (The inset shows the derivative thermogravimetric (DTG) curves)

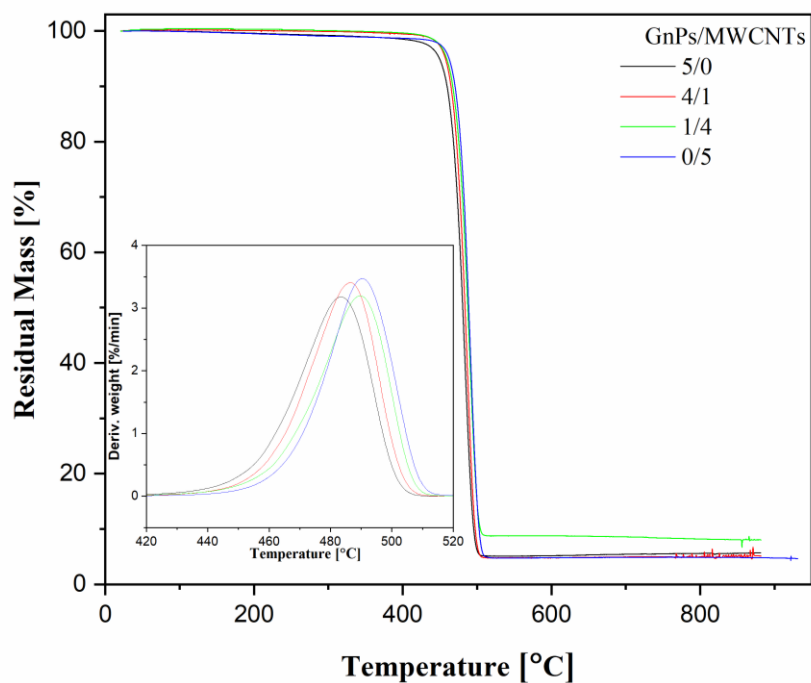


Figure A7.39 TGA thermographs of the HDPE/G2/M12 nanocomposites (The inset shows the derivative thermogravimetric (DTG) curves)

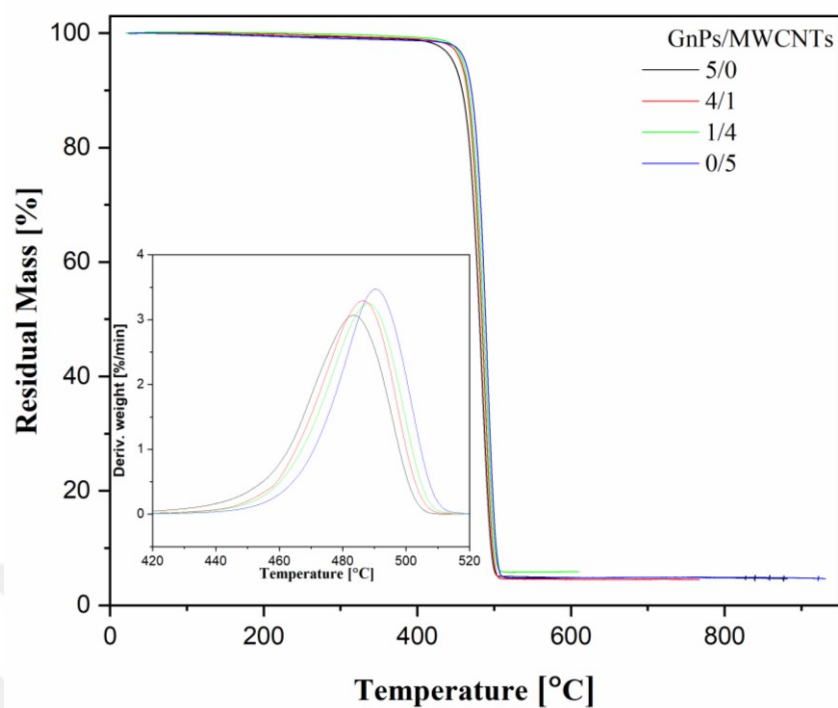


Figure A7.40 TGA thermographs of the HDPE/G3/M12 nanocomposites (The inset shows the derivative thermogravimetric (DTG) curves)

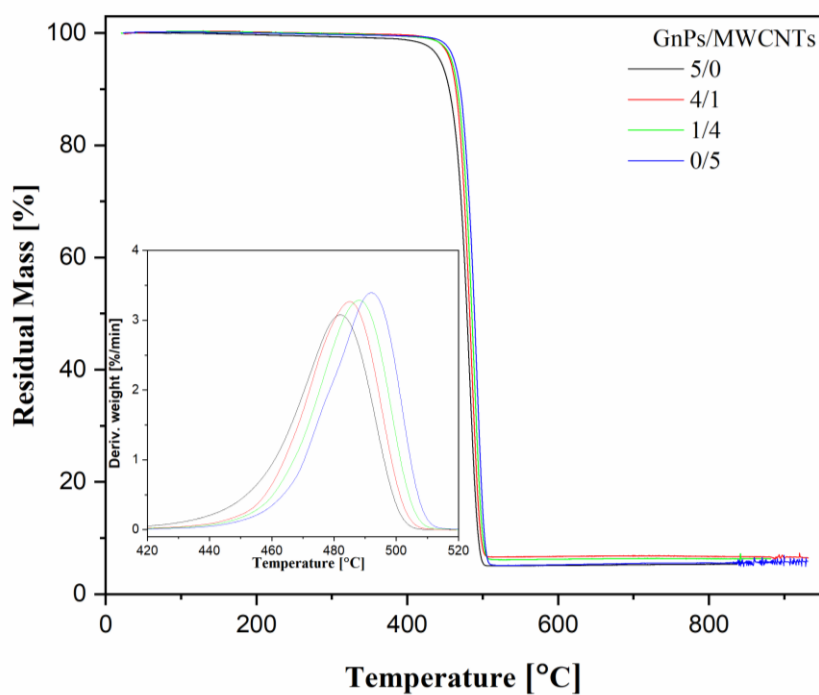


Figure A7.41 TGA thermographs of the HDPE/G1/M58 nanocomposites (The inset shows the derivative thermogravimetric (DTG) curves)

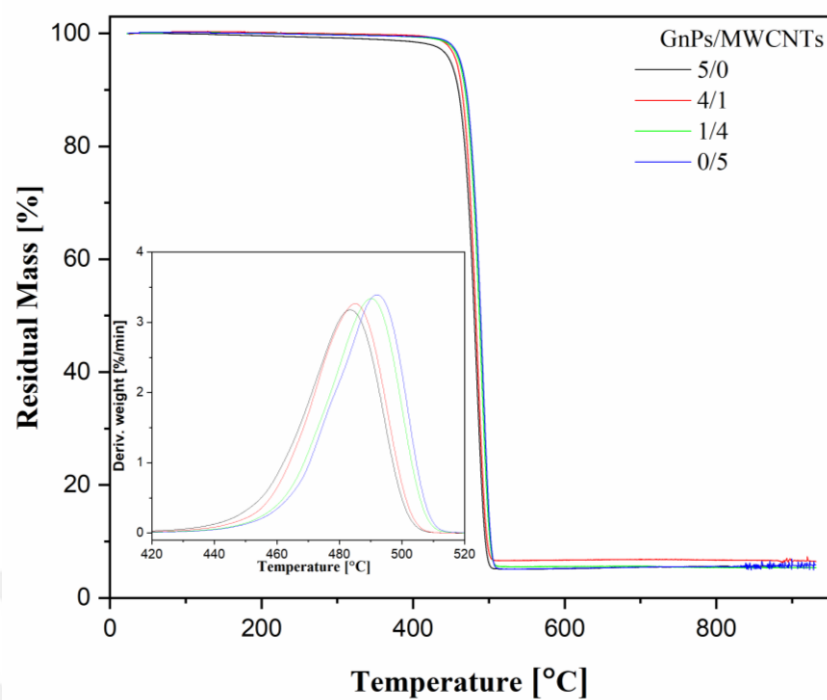


Figure A7.42 TGA thermographs of the HDPE/G2/M58 nanocomposites (The inset shows the derivative thermogravimetric (DTG) curves)

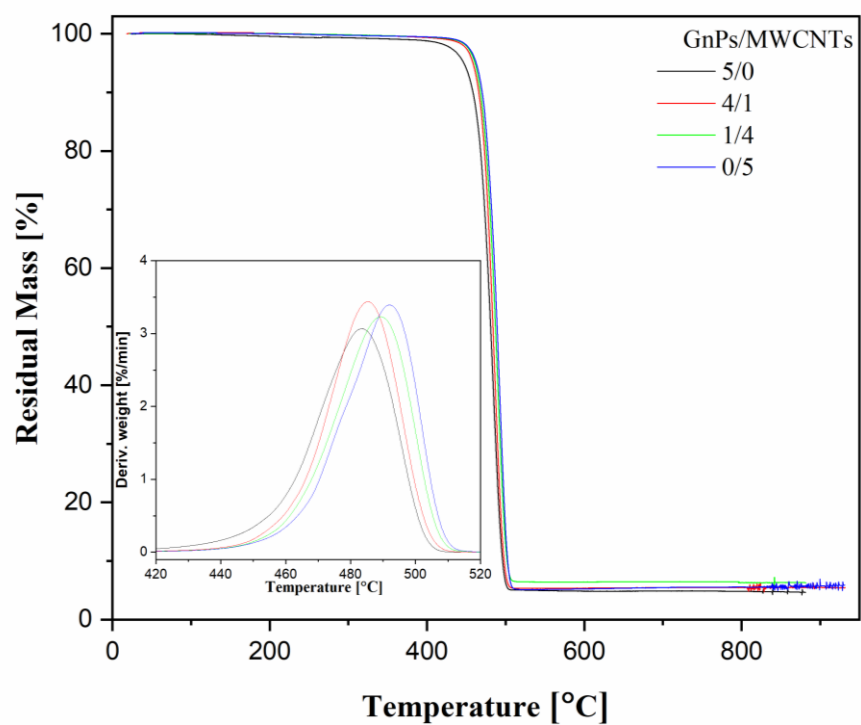


Figure A7.43 TGA thermographs of the HDPE/G3/M58 nanocomposites (The inset shows the derivative thermogravimetric (DTG) curves)