

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**IMPROVEMENT OF MECHANICAL AND FIRE RETARDANT PROPERTIES
OF GLASS FIBER REINFORCED POLY(BUTYLENE TEREPHTHALATE)
COMPOSITE**

M.Sc. THESIS

**Ceren YARGICI
(515131030)**

Department of Polymer Science and Technology

Polymer Science and Technology Programme

**Thesis Advisor: Prof. Dr. Nurseli UYANIK
Co-advisor: Dr. Mustafa SEZER**

MAY, 2015

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**CAM ELYAF KATKILI POLİBÜTİLEN TEREFTALAT KOMPOZİTİN ALEV
DAYANIMI VE MEKANİK ÖZELLİKLERİNİN GELİŞTİRİLMESİ**

YÜKSEK LİSANS TEZİ

**Ceren YARGICI
(515131030)**

Polimer Bilim ve Teknolojileri

Polimer Bilim ve Teknolojileri Programı

**Tez Danışmanı: Prof. Dr. Nurseli UYANIK
Eş-Danışman: Dr. Mustafa SEZER**

MAYIS, 2015

Ceren YARGICI, a M.Sc. student of ITU Institute of Science and Technology/Graduate School of Istanbul Technical University student ID 515131030, successfully defended the thesis entitled “**Improvement of Mechanical and Fire Retardant Properties of Glass Fiber Reinforced Poly(butylene Terephthalate) Composite**”, which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor : **Prof. Dr. Nurseli UYANIK**
Istanbul Technical University

Co-advisor : **Dr. Mustafa SEZER**
Arçelik A.Ş. R&D Dept.

Jury Members : **Prof. Dr. Metin Hayri ACAR**
Istanbul Technical University

Prof.Dr. Ayşe Zehra AROĞUZ
Istanbul University

Doç.Dr. Nesrin KÖKEN
Istanbul Technical University

Date of Submission : 04 May 2015

Date of Defense : 27 May 2015

To my family,

FOREWORD

I would like to express my gratitude to my thesis supervisor, Prof. Dr. Nurseli UYANIK for her continuous encouragement, guidance, helpful critics and discussions in my studies.

I would like to thank my co-supervisor also manager of Arçelik A.Ş. Material Technologies Department Dr. Mustafa SEZER for his valuable guidance, encouraging advice and discussions throughout this research.

I would like to express my thanks to Arçelik A.Ş. for invaluable support in the name of Cem KURAL.

I sincerely thank to Mehmet Ali ORAL, Hakan ÖZKAN, Burak YURT, Sinan KARASU, Kadir ERDOĞAN, Umut KILIÇ, Emin TOPRAK, Sevinç MERT, Orkun KAYMAKÇI and Nisa SIYIN for their contribution in this thesis in almost every possible way. Their high standards for scientific investigation, guidance and encouragement have helped to complete this dissertation and I extend my thanks to all members of the Material Technologies Department.

I would like to thank Deniz TAŞKIN for his valuable help and support.

I would have sincerest thanks to Ozan KOVANCI for his invaluable guidance, encouragement and priceless support and motivation. For all those times, he stood by me and heartedly supported.

Finally, I want to thank my family, especially my mother Nurgül YARGICI, my father Adnan YARGICI and my sister Ebru YARGICI for their support for the completion of my education and every part of my life. I was able to accomplish everything in my life thanks to their eternal love and support.

June 2015

Ceren YARGICI
Chemical Engineer

TABLE OF CONTENTS

	<u>Page</u>
TABLE OF CONTENTS.....	xi
ABBREVIATIONS	xv
LIST OF TABLES	xvii
LIST OF FIGURES	xix
SUMMARY	xxiii
ÖZET.....	xxvii
1. INTRODUCTION.....	1
2. BACKGROUND INFORMATION OF POLYMER COMBUSTION AND FLAME RETARDATION	3
2.1 Poly(butylene terephthalate) (PBT)	3
2.2 Glass Fiber.....	4
2.3 Composite Materials	6
2.4 Burning and Flame Retardant Mechanisms of Polymers	7
2.4.1 Polymer combustion	7
2.4.2 Flame ignition	11
2.4.3 Flame spread	12
2.5 Flame Retardancy.....	13
2.5.1 Physical action	15
2.5.2 Chemical action.....	15
2.5.3 Flame retardant classification	16
2.6 Flame Retardant Additives.....	18
2.6.1 Halogen-based flame retardants.....	18
2.6.2 Metal hydroxides.....	21
2.6.2.1 Aluminium trihydrate.....	22
2.6.2.2 Magnesium hydroxide.....	22
2.6.3 Huntite/Hydromagnesite (Ultracarb)	22
2.6.4 Silicon-based flame retardants	24
2.6.5 Nitrogen-based flame retardants	24
2.6.6 Phosphorous-based flame retardants.....	25
2.6.6.1 Red phosphorus.....	27
2.6.6.2 Organic phosphorus-based flame retardants	27
2.6.7 Boron-based flame retardants	28
2.6.7.1 Zinc borates	28
2.6.7.2 Metal borates	29
2.6.7.3 Boron phosphate	30
2.6.8 Intumescent flame retardants	30
2.6.9 Synergistic flame retardant systems.....	31
2.7 Methods of Studying Flaming Combustion	32
2.7.1 UL-94 flammability test.....	32
2.7.1.1 UL-94 vertical flammability test.....	32

2.7.1.2 UL 94 horizontal flammability test	33
2.7.2 Limited oxygen index (LOI) testing.....	34
2.7.3 Glow wire test	35
2.7.4 Thermal gravimetric analysis (TGA)	36
2.7.5 The cone calorimeter test	36
2.8 Previous Flammability Studies for PBT Composites.....	37
3. EXPERIMENTAL	43
3.1 Materials	43
3.1.1 Poly(butylene terephthalate) (PBT)	43
3.1.2 Glass fiber (GF).....	43
3.1.3 Flame retardant additives	43
3.2 Equipment.....	44
3.2.1 Twin-screw extruder	44
3.2.2 Injection molding machine.....	46
3.2.3 Ash test.....	47
3.2.4 Pyknometer.....	47
3.2.5 Scanning electron microscopy (SEM).....	48
3.2.6 Tensile test machine	48
3.2.7 Three point bending test machine	48
3.2.8 Izod impact test machine	48
3.2.9 Hardness test	49
3.2.10 Thermal gravimetric analysis (TGA)	49
3.2.11 Limiting oxygen index (LOI) flammability tester.....	49
3.2.12 Glow wire tester	50
3.3 Experimental Procedure	51
3.3.1 Composite formulations	51
3.3.2 Compounding procedure and compounding process parameters.....	52
3.3.3 Injection molding machine and process parameters	52
3.4 Characterization Experiments	53
3.4.1 Structural and morphological properties	53
3.4.1.1 Ash Content analysis	53
3.4.1.2 Measurement of density	53
3.4.1.3 Scanning electron microscopy (SEM) analysis.....	53
3.4.2 Mechanical properties	54
3.4.2.1 Determination of tensile properties	54
3.4.2.2 Determination of flexural properties	55
3.4.2.3 Determination of Izod impact strength.....	56
3.4.2.4 Determination of Hardness values	57
3.4.3 Thermal and flame retardant properties	57
3.4.3.1 Determination of thermal stability	57
3.4.3.2 Determination of oxygen index.....	57
3.4.3.3 Determination of glow wire temperature	57
4. RESULTS AND DISCUSSION.....	59
4.1 Structural and Morphological Properties Results.....	60
4.1.1 Ash content analysis.....	60
4.1.2 Measurement of density	61
4.1.3 Scanning electron microscopy (SEM) analysis.....	63
4.2 Mechanical Properties Results	67
4.2.1 Tensile properties	67
4.2.2 Flexural properties.....	72

4.2.3 Izod impact properties.....	76
4.2.4 Hardness properties.....	78
4.3 Flame Retardant and Thermal Properties Analysis.....	79
4.3.1 Thermal gravimetric analysis (TGA).....	79
4.3.2 Limiting oxygen index (LOI).....	85
4.3.3 Glow wire temperature (GWT).....	88
5. CONCLUSIONS	91
REFERENCES.....	95
CURRICULUM VITAE.....	103

ABBREVIATIONS

FR	: Flame Retardant
ATH	: Aluminium Tri Hydrate
MDH	: Magnesium Hydroxide
ABS	: Acrylonitrile Butadiene Styrene
PET	: Polyethylene Terephthalate
PVC	: Polyvinyl Chloride
APP	: Ammonium Polyphosphate
PER	: Pentaerythritol
ASTM	: American Society for Testing and Materials
IEC	: International Electrotechnical Commission
ISO	: International Organization for Standardization
BS	: British Standards
LDPE	: Low Density (non-linear) Polyethylene
LOI	: Limiting Oxygen Index
UL	: Underwriters Laboratory
GWT	: Glow Wire Temperature
GWIT	: Glow Wire Ignition Temperature
GWFI	: Glow Wire Flammability Index
L/D	: Length/Diameter
MPa	: Mega Pascal
SEM	: Scanning Electron Microscopy
FTIR	: Fourier Transform Infrared Spectroscopy
TGA	: Thermal Gravimetric Analysis
MFI	: Melt Flow Index
MFR	: Melt Flow Rate
HB	: Horizontal Burning
PMMA	: Poly(methyl methacrylate).

LIST OF TABLES

	<u>Page</u>
Table 2.1 : Decomposition and ignition temperatures* together with heats of combustion of some common thermoplastic polymers and cellulose [27].	12
Table 2.2 : Potential flame retardant fillers [40].	23
Table 2.3 : Mechanisms of action of zinc borate on different polymer matrices [45].	29
Table 2.4 : UL-94 vertical flammability test requirements for classifying material.	33
Table 3.1 : PRISM TSE24 Twin screw extruder specifications.	45
Table 3.2 : Technical properties of Arburg injection machine.	47
Table 3.3 : Formulations of PBT composites.	51
Table 3.4 : Formulations of glass fiber reinforced PBT composites.	51
Table 3.5 : Extruder process temperature parameters.	52
Table 3.6 : Tensile test specimen dimensions.	54
Table 4.1 : Ash test results of PBT composites.	60
Table 4.2 : Ash test results of glass fiber reinforced PBT composites.	61
Table 4.3 : Density test results of PBT composites.	61
Table 4.4 : Density test results of glass fiber reinforced PBT composites.	62
Table 4.5 : Average tensile test results of PBT composites.	68
Table 4.6 : Average tensile test results of glass fiber reinforced PBT composites.	68
Table 4.7 : Flexural test results of PBT composites.	72
Table 4.8 : Flexural test results of glass fiber reinforced PBT.	73
Table 4.9 : Izod impact test results of PBT composites.	76
Table 4.10 : Izod impact test results of glass fiber reinforced PBT composites.	76
Table 4.11 : Hardness value (Shore D) of PBT composites.	78
Table 4.12 : Hardness value (Shore D) of GF-PBT composites.	78
Table 4.13 : LOI (%) test values of PBT composites.	86
Table 4.14 : LOI (%) test values of glass fiber reinforced PBT composites.	87
Table 4.15 : Glow wire test results of PBT composites.	89
Table 4.16 : Glow wire test results glass fiber reinforced PBT composites.	90

LIST OF FIGURES

	<u>Page</u>
Figure 2.1 : Poly(butylene terephthalate) [11].	3
Figure 2.2 : Glass fiber manufacturing process [13].	5
Figure 2.3 : Idealized coupling of matrix and glass by organofunctional silane [14].	7
Figure 2.4 : Fire triangle of combustion [18].	8
Figure 2.5 : The combustion process [19].	9
Figure 2.6 : Material burning proces [24].	10
Figure 2.7 : (a) Free radical reaction mechanism during the combustion (b) propagation of $\bullet\text{OH}$ in the case of burning ethane [27].	12
Figure 2.8 : Schematic representation of flame spread [27].	13
Figure 2.9 : Combustion process [19].	14
Figure 2.10 : Inherently flame retardant polymers [2].	18
Figure 2.11 : Chemical structure of a) Decabromodiphenyl ethe (DECA), b) Hexabromocyclododecane (HBCD), c) Tetrabromobishenol A (TBBA), d) Tetramophthalic anhydride (TBPA) [32].	19
Figure 2.12 : Nitrogen-based flame retardants [43].	25
Figure 2.13 : Chemical structures of some phosphorus flame retardant additives[17].	28
Figure 2.14 : Boron phosphate [35].	30
Figure 2.15 : UL-94 vertical flammability test [54].	33
Figure 2.16 : UL-94 horizontal flammability test [64].	34
Figure 2.17 : Shematic test set-up of Limiting oxygen index (LOI) test [65].	35
Figure 2.18 : Glow wire test equipment configuration [57].	36
Figure 2.19 : Cone Calorimeter apparatus [56].	37
Figure 3.1 : Chemical structure of Triphenyl phosphate (TPP).	43
Figure 3.2 : Chemical structure of calcium sulphate dihydrate (CSD).	44
Figure 3.3 : Chemical structure of boron phosphate (BP).	44
Figure 3.4 : Twin screw extruder.	45
Figure 3.5 : Prism granulating unit.	46
Figure 3.6 : Arburg Allrounder 320 °C injection machine.	46
Figure 3.7 : Pyknometer illustration.	47
Figure 3.8 : Scanning electron microscopy (SEM).	48
Figure 3.9 : Izod impact testing machine.	48
Figure 3.10 : Shore D Hardness test device.	49
Figure 3.11 : Thermal gravimetric analyzer.	49
Figure 3.12 : Limiting oxygen index tester.	50
Figure 3.13 : Glow wire tester.	50
Figure 3.14 : General process parameters and illustration of injection molding machine.	54
Figure 3.15 : Tensile test specimen.	54
Figure 3.16 : Three point bending testing illustration.	56

Figure 4.1 : Density measurement results of PBT composites.	62
Figure 4.2 : Density measurement results of glass fiber reinforced PBT composites.	62
Figure 4.3 : SEM micrographs of a) GF0, b) GF1	63
Figure 4.4 : SEM micrographs of a) GF2, b) GF3	63
Figure 4.5 : SEM micrographs of a) GF4, b) GF5 Flexural test results of PBT composites.	63
Figure 4.6 : SEM micrographs of a) GF6, b) GF7	64
Figure 4.7 : SEM micrographs of a) GF8, b) GF9	64
Figure 4.8 : SEM micrographs of a) GF10, b) GF11	64
Figure 4.9 : SEM micrographs of a) GF1, B) GF2	65
Figure 4.10 : SEM micrographs of a) GF3, b) GF4	66
Figure 4.11 : SEM micrographs of a) GF5, b) GF6	66
Figure 4.12 : SEM micrographs of a) GF7, b) GF8	66
Figure 4.13 : SEM micrographs of a) GF9, b) GF10	67
Figure 4.14 : SEM micrographs of GF11 Technical properties of Arburg injection machine.	67
Figure 4.15 : Tensile Stress (MPa) results of PBT composites.	69
Figure 4.16 : Tensile stress (MPa) results of glass fiber reinforced PBT composites.	69
Figure 4.17 : Tensile modulus (MPa) results of PBT composites.	70
Figure 4.18 : Tensile modulus (MPa) results of glass fiber reinforced PBT composites.	71
Figure 4.19 : Elongation at break (%) results of PBT composites.	71
Figure 4.20 : Elongation at break (%) results of glass fiber reinforced PBT composites.	72
Figure 4.21 : Flexural strength (MPa) results of PBT composites.	73
Figure 4.22 : Flexural strength (MPa) results of glass fiber reinforced PBT composites.	74
Figure 4.23 : Flexural modulus (MPa) results of PBT composites.	75
Figure 4.24 : Flexural modulus (MPa) results of glass fiber reinforced PBT composites.	75
Figure 4.25 : Izod impact (kJ/m^2) strength results of PBT.	77
Figure 4.26 : Izod impact strength (kJ/m^2) results of glass fiber reinforced PBT. Izod impact test results of glass fiber reinforced PBT composites.	77
Figure 4.27 : Shore D hardness test results of PBT composites. Hardness value (Shore D) of PBT composites.	79
Figure 4.28 : Shore D hardness test results of GF-PBT composites.	79
Figure 4.29 : TGA diagram of boron phosphate.	80
Figure 4.30 : TGA diagram of triphenyl phosphate.	81
Figure 4.31 : TGA diagram of calcium sulphate dihydrate.	81
Figure 4.32 : TGA diagram of zinc borate.	82
Figure 4.33 : TGA diagram of PBT composites.	82
Figure 4.34 : TGA diagram of PBT composites.	83
Figure 4.35 : TGA diagram of PBT composites.	83
Figure 4.36 : TGA diagram of glass fiber reinforced PBT composites.	84
Figure 4.37 : TGA diagram of glass fiber reinforced PBT composites.	84
Figure 4.38 : TGA diagram of glass fiber reinforced PBT composites.	85
Figure 4.39 : LOI (%) test values of PBT composites. Flexural test results of PBT composites.	87

Figure 4.40 : LOI (%) test values of glass fiber reinforced PBT composites. 88

IMPROVEMENT ON MECHANICAL AND FIRE RETARDANT PROPERTIES OF GLASS FIBER REINFORCED POLY(BUTYLENE TEREPHTHALATE) COMPOSITE

SUMMARY

Poly(butylene terephthalate) (PBT) is a crystalline thermoplastic polyester resin, which is made up of terephthalic acid (or terephthalate) with 1,4-butanediol by condensation reactions. It is high molecular weight engineering plastic used as neat or as glass fiber reinforced material for applications in electrical and electronic devices, communication, and automotive parts, due to its outstanding mechanical properties and processing characteristics. It is used mainly for the production of connectors, micro switches, jacks, core of transformers, relay blocks, fans, trimmers and components for business equipment. In all these applications, the burning behavior of the material plays a crucial role, and it has been necessary to improve its fire retardancy in order to prevent users from fire hazard. This has been achieved mostly by use of flame retardant additives, and the common additives contain halogenated compound and antimony trioxide as a synergist. Even though these halogenated flame retardant systems show significant efficiency, they cause environmental problems, since the toxic and corrosive gases will be released in the increasing temperature condition or combustion process of halogenated polymer composite. This situation restricts halogenated compounds usage and promotes the use of halogen-free flame retardant additives. However, because of the lower flame resistance performance of halogen-free systems in comparison to halogenated ones, significantly higher additive contents have to be used, and this cause largely negative impact on mechanical performance of composite material. Hence, the development of efficient halogen-free flame retardant additives is one of the common problems for industrial laborites and academic institutions today. The objectives of this study, achieve high flame retardancy while increase or keep mechanical properties of PBT composites.

In experimental part of the study, PBT was used as a main polymer matrix, and obtained from SASA Company, Adana, Turkey. In order to investigate flame resistance efficiency of PBT composites, boron phosphate (BP), triphenyl phosphate (TPP), zinc borate (ZB) and calcium sulphate dihydrate (CSD) additives were chosen as a halogen-free flame retardant additives. Flame retardant fillers were used in both unreinforced PBT and glass fiber reinforced PBT (GF-PBT) composites and compounds were prepared by using a co-rotating twin screw extruder and 5 % and 10 % flame retardant additive containing samples were shaped by injection molding machine. The composites were characterized in terms of flammability and mechanical properties. Flammability of composites was determined by using a limiting oxygen index (LOI) and glow wire test (GWT). Mechanical properties such as tensile strength, elastic modulus, elongation at break, flexural strength, Izod impact (notched) strength and hardness (Shore D) properties were also studied.

So as to examine the effectiveness of four flame retardant additives with low-loading level, ZB, BP, TPP, CSD formulations were prepared. PBT0 and GF0 were

formulated as flame retardant free reference for PBT and GF-PBT flame retardant composites. After determining the effect of each flame retardant additive on PBT, flame retardant additives were used with different combinations in order to obtain any further improvement when they used together. Furthermore, 10 % loading of BP, TPP, and CSD were performed separately, in order to see higher loading effects of these flame retardants. Addition of 5% ZB to PBT did not show any improvement in comparison to PBT0 (reference composite), therefore higher loading level of ZB did not study. After PBT flame retardant composites were analyzed, all formulations were carried out with 30 % glass fiber reinforced (GF-PBT) composites. In GF-PBT formulations, it was analyzed both mechanical effects of glass fiber reinforcement and flame retardant filler behavior in glass fiber reinforced PBT composites.

SEM observations showed that glass fibers were well dispersed in PBT matrix during extrusion and polymer matrix wrapped the fibers. According to X-ray elemental mapping analyses, flame retardant additives of composite formulations were well dispersed in PBT matrix. CSD formulations (GF4, GF5) were showed some agglomerations. That result may have occurred due to the process difficulties of CSD additive in extrusion.

According to the mechanical test results, neat PBT has tensile strength value around 51 MPa. Addition of 5 % CSD increased tensile strength of PBT composite to 57 MPa and 10 % CSD caused the highest increase in the tensile strength, which was about 60 MPa. Formulations of ZB and BP additives did not show significant change when compare to neat PBT. The significant decrease was shown in formulation of TPP, which decreased the tensile strength value of PBT composite to 41 MPa with 5 % loading and to 35 MPa with 10 % loading. Addition of ZB (PBT 1) and BP (PBT 2) to PBT showed slight increase in tensile modulus value compare to neat PBT (PBT0). Noticeable decrease in tensile strength value was observed with the addition of TPP. However, when TPP was combined with BP, higher tensile modulus result was obtained compare to TPP formulations (PBT3 and PBT10). Moreover, it was observed that addition of TPP increased the elongation at break values of the composites significantly. Using 5 % TPP in PBT matrix increased elongation of break value from 82 % to 260 %. This increase in the elongation would be the influence of plasticizing and chain extension effects of TPP on the PBT matrix. ZB, BP and CSD flame retardant additives decreased elongation at break value of GF-PBT composite.

According to three point bending test results the flexural modulus value of neat PBT composite (PBT0) was around 2320 MPa. It was observed that addition of TPP additive to PBT matrix decreased flexural strength of PBT noticeably. Other flame retardant formulations (ZB, BP, CSD) flexural strength values were close to each other and between the range of 76 MPa to 82 MPa. Flexural modulus value of neat PBT composite (PBT0) was around 2320 MPa. It was observed that addition of TPP additive to PBT matrix decreased flexural modulus value. 10 % TPP addition caused the lowest result which was about 780 MPa. When TPP additive was combined with BP, flexural modulus of composites increased noticeably compare to the case composites contains only TPP additive. ZB, BP and CSD additives caused some increase in flexural modulus.

Neat PBT composite (PBT0) has an Izod (notched) impact strength value of 5.2 kJ/m². Addition of inorganic flame retardants (ZB, BP, CSD) decreased the impact strength value of PBT since they are highly stiff and hard materials. TPP addition to PBT matrix increased the impact strength value significantly. Addition of 10 % TPP to PBT caused the highest impact strength value which was about 7 kJ/m².

Addition of 30 % glass fiber to PBT matrix increased mechanical properties of composite considerably. When compare PBT with GF-PBT composite; tensile strength value increased to 105 MPa from 51 MPa, tensile modulus increased to 7905 MPa from 2210 MPa, elongation at break value decreased to 2.8 % from 82 %, flexural strength value increased to 157 MPa from 76 MPa, flexural modulus increased to 7420 MPa from 2320 MPa, Izod (notched) impact strength increased to 10.6 kJ/m² from 5.2 kJ/m², hardness value increased to 85 Shore D from 80 Shore D, respectively. When flame retardant additives used in GF-PBT composites, they showed similar behavior that was seen in PBT composites. TPP additives decreased tensile strength, tensile modulus, flexural strength and flexural modulus value and increased Izod impact strength properties significantly.

In LOI test, neat PBT (PBT0) test result was around 22.5. 5 % ZB addition to the PBT matrix did not change the LOI value of PBT composite. 5 % BP addition to PBT matrix slightly increased the LOI value of PBT0. When TPP added to PBT matrix, LOI value noticeably increased up to 26.6. Highest LOI values were obtained when 10 % TPP (PBT10) was added to PBT matrix and LOI increased to 27.2. CSD additive showed the second highest LOI value after TPP formulation. In first set of formulation it was observed that TPP is the most successful flame retardant for PBT in terms of flammability properties. However, as mentioned mechanical properties results, TPP additive decreased some mechanical properties like tensile strength and flexural strength values. In order to obtained high flame retardancy properties with high mechanical properties, TPP was combined with BP additive (PBT8 and PBT9). Even though some decreases in LOI value occurred compare to TPP base formulation, combination of TPP with BP showed high LOI results with higher mechanical properties. Other important result obtained when ZB combined with BP additive. It was observed that ZB did not have flame retardancy effectiveness on PBT and BP showed slight increase in LOI. When BP is combined with ZB, important increase was observed in flame retardancy effectiveness and higher LOI results were obtained. When 2.5 % BP was combined with 2.5 % ZB, LOI value of 23.0 was obtained and when 5% BP was combined with 5 % ZB LOI value increased up to 23.4. These test results indicated that when they were used together they showed a significant synergistic effect. When GF-PBT composites LOI results compared to PBT composites LOI results, GF-PBT composites showed lower LOI values than PBT composites. This behavior would be result of “candlewick effect” of glass fiber which is explained in literature that glass fibers could transfer the flammable pyrolysis products of polymers to the flame zone through capillary action, speed the heat flowing back to the polymers and increase the mass lose rate of polymer matrix. While neat PBT (PBT0) LOI was 22, GF-PBT (GF0) was around 21.3. In all GF-PBT formulations, flame retardants showed similar behavior that was seen in PBT composites. According test results TPP was the most successive flame retardant additive for GF-PBT composites. The synergistic effect of BP, ZB mixture was also seen in GF-PBT composites, too.

According to the glow wire test results TPP was the most efficient flame retardant additive which passed the 750 °C also, did not ignite at 850 °C. The synergistic effect of BP-ZB mixture which mentioned in LOI results section, also has seen in GWT test.

CAM ELYAF KATKILI POLİBÜTİLEN TEREFTALAT KOMPOZİTİN ALEV DAYANIMI VE MEKANİK ÖZELLİKLERİNİN GELİŞTİRİLMESİ

ÖZET

Polibütillen tereftalat (PBT) mühendislik uygulamalarında kullanılan yarı kristal termoplastik polyesterdir. PBT, tereftalik asit veya dimetil tereftalat'ın 1,4 bütandiol ile polikondenzasyonu ile üretilmektedir. Cam elyaf (GF) katkı ve katkısız PBT kompozitler özellikle elektrik ve elektronik endüstrisinde izolasyon malzemesi olarak ve otomotiv parçalarında yaygın kullanılmaktadır. Çok iyi mekanik özellikleri ve kolay proses edilebilmesi sayesinde birçok endüstride kullanım alanına sahip olup elektrik şalteri, krik, fan, priz ve benzeri bağlantı parçaları en sık görülen kullanım alanlarıdır. Tüm bu uygulamalarda malzemenin yanma dayanımı önemli bir kriter olup, oluşabilecek yangın kazalarını önlemek amacıyla yanmazlık dayanımı geliştirilmelidir. Plastik malzemelerin yanma dayanımını geliştirmek amacıyla alev geciktirici katkı malzemeleri kullanılmakta olup oluşabilecek yangın riskleri engellenmeye çalışılmaktadır. Halojen içerikli alev geciktiriciler ve antimon trioksit sinerjistler yaygın olarak kullanılmakta olan etkili alev geciktiricilerdir. Halojen içerikli alev geciktiriciler plastik malzemelerin yanmazlık performansını geliştirmekte etkili olmalarına rağmen yanma sırasında açığa çıkardıkları toksik ve korozyon gazları çevreye ve insan sağlığına zararlı etkiler yaratmaktadır. Bu sebeple halojen içerikli malzemelerin kullanım alanları kısıtlanmaya başlanmış olup halojen içermeyen alev geciktirici katkı malzemelerin kullanımı yaygınlaşmaya başlamıştır. Ancak halojen içermeyen malzemelerin alev geciktirme performansı daha düşük olup yüksek oranlarda yüklemeler gerektirmekte ve bu durum mekanik özelliklerin düşmesine neden olmaktadır. Bu sebeple yüksek mekanik özelliklere sahip halojen içermeyen alev geciktirici katkı malzemeler hem endüstriyel laboratuvarlarda hem de akademik çalışmalarda geliştirilmeye çalışılmaktadır.

Bu çalışmada cam elyaf katkı ve katkısız PBT malzemenin yanma dayanımını güçlendirmek amacıyla farklı alev geciktirici sistemler oluşturulmuştur. Bor fosfat (BP), trifenil fosfat (TPP), çinko borat (ZB), ve kalsiyum sülfat dihidrat (CSD) alev geciktirici katkı malzemeler olarak seçilmiş olup farklı oranlarda PBT ve cam elyaf katkı PBT (GF-PBT) malzemede kullanılmıştır. Ayrıca bu alev geciktiricilerin birlikte kullanılmasıyla sinerjist etkinlikleri incelenmiştir. Kompozit malzemeler çift vidalı ekstruder kullanılarak karışım haline getirilmiştir ve enjeksiyon prosesi ile test numuneleri basılmıştır. Yanmazlık özellikler limit oksijen indisi (LOI) testi ve kızgın tel (GWT) testleri ile mekanik özellikler çekme, üç nokta eğme, Izod çentikli darbe, Shore D sertlik testleri ile incelenmiştir ve karakterizasyonları gerçekleştirmiştir. Deneysel çalışmalarda öncelikle ZB, BP, TPP ve CSD alev geciktirici katkıları % 5 oranlarında PBT matris ile üretilmiş, mekanik ve yanmazlık analizleri gerçekleştirilmiştir. Hem mekanik hem de alev dayanımı özelliklerini birlikte iyileştirebilmek amacıyla ilk kısımdan elde edilen sonuçlar doğrultusunda ikili alev geciktirici karışımlar oluşturularak farklı formülasyonlar oluşturulmuştur. Daha sonra tüm formülasyonlar cam elyaf katkı PBT (GF-PBT) kompozit

malzemelerinde denenerek, bu alev geciktiricilerin GF-PBT malzemedeki etkinliği ve cam elyaf katkısının etkileri incelenmiştir.

Oluşturulan cam elyaf katkılı kompozitlerde cam elyafların yönelimini ve polimer ile arasındaki birleşimi incelemek ve alev geciktirici katkıların dağılımını incelemek amacıyla, scanning electron microscopy (SEM) analizleri gerçekleştirilmiştir. SEM analizlerine göre cam elyaflar polimer içerisinde iyi bir dağılım göstermekte olup polimer ile sarmalanmış haldedir. Yapılan X-ışını ile elementel haritalama analizine göre alev geciktirici katkılar polimer matris içerisinde iyi bir dağılım göstermektedir. Sadece CSD alev geciktiricisinin kullanıldığı formülasyonlarda bir miktar topaklaşma olduğu görülmüştür. Bu topaklaşmaların sebebinin CSD katkısının ekstruder prosesi sırasında karşılaşılan besleme problemleri sebebiyle oluştuğu düşünülmüştür.

Kompozit formülasyonlara yapılan çekme testi sonucunda katkısız PBT malzemenin çekme dayanımının 51 MPa olduğu tespit edilmiş olup en yüksek çekme dayanımı değerine CSD katkısının kullanıldığı formülasyonlarda ulaşılmıştır. % 5 CSD kullanıldığı formülde 57 MPa, % 10 CSD kullanıldığı formülde yaklaşık 60 MPa çekme dayanımı değerine ulaşılmıştır. ZB ve BP malzemelerinin kullanıldığı formüllerde, katkısız PBT ile benzer çekme dayanımı sonuçları elde edilmiştir. Öte yandan TPP katkısının kullanıldığı durumlarda çekme dayanımında düşüş gözlemlenmiştir. Benzer etki elastik modülü değerinde de gözlemlenmiş olup % 5 TPP kullanılmasıyla PBT malzemenin elastik modülü değeri 2210 MPa'dan 1470 MPa değerine düşmüştür. ZB ve BP katkıları elastik modülü değerinde çok az bir yükselmeye sebep olmuştur. Yapılan çekme testi sonuçlarına göre, TPP malzemenin kopmadaki uzama değerini çok yüksek oranda arttırdığı gözlemlenmiş olup katkısız PBT % 80 civarında iken TPP kullanımıyla yaklaşık % 260 oranında kopmada uzama değeri görülmektedir. Bu etkinin sebebinin TPP malzemenin PBT matriste göstermiş olduğu plastikleştirici ve zincir büyümesi etkilerinden kaynaklandığı düşünülmüştür. Diğer alev geciktirici katkıların eklenmesi yüzde uzama değerlerini düşürdüğü görülmüştür.

3 nokta eğme testi sonucunda elde edilen eğme dayanımı ve eğme modülü değerleri TPP kullanımıyla azalma gösterirken diğer katkılar katkısız PBT ile benzer sonuçlar göstermiştir.

Izod çentikli darbe testi sonuçlarına göre saf PBT malzemenin darbe dayanımı değeri 5.2 kJ/m²'dir. BP, CSD, ZB gibi inorganik katkıların eklenmesi PBT malzemenin darbe dayanımını düşürürken, TPP malzeme önemli derecede arttırdığı gözlemlenmiştir. % 10 TPP katkısının PBT matriste kullanılması ile 7.1 kJ/m² Izod darbe dayanımı değerine ulaşılmıştır. Bu önemli artışın TPP katkısının malzemeyi sünekleştirmesinden kaynaklandığı düşünülmüştür.

PBT matrise % 30 cam elyaf katılmasıyla PBT malzemenin çekme dayanımını değerini iki katına (105 MPa), elastik modülü değeri yaklaşık üç buçuk katına (7905 MPa), eğme dayanımı değeri iki katına (157 MPa), eğme modülü değeri yaklaşık üç katına (7420 MPa) ve darbe dayanımı değerini yaklaşık iki katına (10.6 kJ/m²) arttırdığı görülmüştür. Ayrıca kopmada uzama değeri % 83 ' den % 2.8 değerine düşmüştür. Cam elyaf kullanımıyla PBT kompozitin sertlik değeri 80 Shore D değerinden 85 Shore D değerine ulaşmıştır. Alev geciktirici katkılar cam elyaf katkılı kompozitlerde cam elyaf katkısız PBT' de göstermiş oldukları etkilere benzer davranış göstermişlerdir.

Alev geciktirici katkıların etkinliğini anlamak amacıyla öncelikle 4 katkı ile analizler gerçekleştirilmiştir. LOI yanmazlık test sonuçlarına göre katkısız PBT (PBT0) LOI değeri, 22'dir. ZB katkısının kullanılmasıyla LOI değerinde belirli bir değişim

gözlemlenmemiştir. % 5 BP kullanılması durumunda LOI değerinde çok az bir iyileşme gözlemlenmiştir. TPP katkısının kullanılması LOI değerinde önemli derecede iyileşme sağlayarak % 5 kullanımında 26,6, % 10 kullanıldığı durumda 27,2 LOI değerine ulaşılmıştır. CSD katkısı TPP’ den sonra ikinci en iyi sonuçları veren katkı olup % 10 kullanıldığı durumda 25,1 LOI değerine ulaşılmıştır.

Bu çalışmada yanmazlık özelliğini sağlarken mekanik özellikleri de iyileştirmek amaçlanmasından dolayı ilk aşamada denenen katkıların test sonuçları doğrultusunda ikili karışımlar oluşturulmuş ve analizleri gerçekleştirilmiştir.

Yapılan LOI testi ve mekanik testler sonucunda TPP malzemenin yüksek alev gecikici etkinliğinin olduğu ancak çekme dayanımı, elastik modülü gibi bazı mekanik özelliklerde düşüşe sebep olduğu gözlemlenmiştir. TPP kompozitin bu mekanik özelliklerini iyileştirmek adına BP katkısı ile birlikte kullanıldığı formülasyonlar oluşturulmuştur. % 2,5 TPP katkısının % 2,5 BP katkısıyla karıştırılarak oluşturulan PBT kompozitin LOI değeri TPP katkısına göre bir miktar düşüş göstererek 25,6 değerine ulaşırken elastik modülü, çekme dayanımı, eğme modülü, eğme dayanımı gibi mekanik özelliklerinde iyileşme göstermiştir. % 5 TPP ile % 5 BP katkılarının birlikte kullanıldığı formasyonda ise bu değer 24,4 LOI değerine düşmüş mekanik özellikler ise iyileşmiştir. Ayrıca TPP katkısının kullanıldığı formasyonlarda darbe dayanımının önemli derecede iyileştiği gözlemlenmiştir.

LOI testi sonuçlarına göre ZB katkısının tek başına kullanılması durumunda yanmazlık etkinliği göstermediği, BP malzemenin is az miktarda iyileşme gösterdiği gözlemlenmiştir. % 2,5 BP ve % 2,5 ZB malzemelerinin birlikte kullanıldığı durumda LOI değeri önemli derecede artarak 23 LOI değerine ulaşmıştır. % 5 BP ile % 5 ZB katkısının kullanıldığı durumda ise 23,4 LOI değerine ulaşılmıştır. Bu test sonuçlarına göre BP katkısının ile ZB katkısını birlikte kullanılması ile sinerjistik etki elde edildiği görülmüştür. Bu malzemelerin ikisi de inorganik yapıda olup çekme dayanımı, eğme dayanımı gibi mekanik özellikleri katkısız PBT ile benzer sonuçlar vermekte, darbe dayanımında ise bir miktar düşüş gözlemlenmektedir.

Cam elyaf katkılı PBT kompozitlere yapılan LOI testi sonuçlarının cam elyafsız PBT malzemeye göre daha düşük sonuçlar verdiği gözlemlenmiştir. Bu etkinin sebebinin literatürde belirtilen cam elyafın “fitil etkisi” yaratmasından kaynaklandığı düşünülmüştür. Alev geciktiricilerin cam elyaf katkılı PBT kompozitlerde ve cam elyaf katkısız kompozitlerde benzer etkiler verdiği görülmüştür. PBT kompozitlerde olduğu gibi GF-PBT kompozitlerde de TPP katkısı en etkili yanmazlık katkısı olup % 10 katılması durumunda 24,4 LOI değerine ulaşılmaktadır. PBT kompozitlerde gözlemlenen BP-ZB sinerjistik etkinliği GF-PBT kompozitlerinde de gözlemlenmiştir.

Yapılan kızgın tel testi sonuçlarına göre %10 TPP katkısının hem 750 °C hem de 850 °C testlerinden geçtiği gözlemlenmiştir. BP ve ZB katkılarının birlikte kullanıldığı kompozitler her iki testi de geçerken ayrı ayrı kullanıldıklarında iki testi de geçememektedirler. Böylece BP ve ZB katkılarının sinerjistik etkinlik gösterdiği kızgın tel testinde de gözlemlenmiştir.

Yapılan çalışmalar sonucunda TPP katkısının PBT malzemede etkili bir alev geciktirici katkısı olduğu ve mekanik özelliklerini iyileştirmek amacıyla BP ile birlikte kullanımının en başarılı sonuçları verdiği belirlenmiştir. Ayrıca BP ve ZB malzemelerinin birlikte kullanılmasının iyi bir sinerjistik etkinlik oluşturduğu gözlemlenmiştir.

1. INTRODUCTION

In the 21st century, better, cheaper and safer material requirements has accelerated applications area of polymer derived products in different industries such as automotive, aerospace, building construction industries [1]. Due to remarkable properties of polymers like low weight and ease of processing, enhance quality of modern life [2]. Even though polymeric materials have several prodigious features, they are organic materials and thus, the flammability is one of the significant challenges for applications. Fire hazards arise from polymeric materials are of particular concern among government regulatory bodies, consumers, and manufacturers because of economic and environmental result, so improving the flame resistance of polymeric material is became a significant topic [3].

Poly(butylene terephthalate) (PBT) is a very important engineering thermoplastic polymer that is used especially in automotive, electrical and electronic industries. It contains several attractive features such as high strength and rigidity, low moisture absorption, excellent electrical properties, chemical resistance, rapid molding cycles and reproducible mold shrinkage [4]. Owing to its good performance characteristics, PBT market is growing expeditiously and common applications are wiring devices, enclosures and connectors to insulation systems, loose buffer tubes, circuit breakers. In order to increase strength, stiffness and heat distortion temperatures glass fiber reinforcement used with PBT. In most of these fields, both for PBT and glass fiber reinforced PBT flammability and electrical properties are became crucial and need to be improved [5].

In recent years, safety requirements are becoming more significant. To improve polymeric materials fire resistance and support protection from fire, flame retardants (FR) are used while polymeric material compounding. They can be affective in polymer by making materials less easily ignitable and/or by reducing flame spread [6]. Their working mechanism consists of different steps like increasing the ignition temperature, reduction of the rate of burning, reduction of the flame spread, reduction of the smoke generation.

Flame retardant materials that incorporated into polymeric compound can divided into several categories such as inorganic, organic, mineral, halogen containing or phosphorus-containing etc. In recent years, halogenated flame retardants are not preferable because of reaction mechanism of polymer under fire cause lots of harmful impact on environment like formation of smoke, toxic gasses and corrosive decomposition products [7]. In addition, environmental organizations such as the USA's EPA and Europe's EEA indicate importantly harmful effects of these materials [8]. As a result, halogen-free flame retardants usage in plastic materials take attention instead of conventional halogenated ones.

According to the BCC Research market report, the worldwide flame retardant consumption amounts to around 1.8 million tons a year in 2013 and it is expected to increased 2.4 million tons in 2018. It is predicted that the market growth of inorganic FR aluminum trihydrate (ATH) at 28 % growth from 2012 to 2018 and phosphorus based FRs at 56 % growth over the period. Furthermore, chemical safety and the limitations of regulations about flame retardant environment and human health effects are the major concerns for application [9].

The aim of this study is to produce PBT composite with the help of non-halogenated flame retardant additives with enhancement of the mechanical properties. Two different set of flame retardant composite were formulated. In the first stage, boron phosphate (BP), triphenyl phosphate (TPP), calcium sulphate dihydride (CSD) and zinc borate (ZB) additives were added to 30 % glass fiber (GF) reinforced PBT at different weight percentages and compounding. In the second stage, same flame retardant additives was added unreinforced PBT and characterized.

2. BACKGROUND INFORMATION OF POLYMER COMBUSTION AND FLAME RETARDATION

2.1 Poly(butylene terephthalate) (PBT)

Polymer is defined as a large molecule constructed from repetition of small, simple chemical units. This repeating unit known as the monomer and composed of many repeated units polymer is formed. In order to obtain polymers with different physical and chemical features, different chemical side groups can be added to main chain or main chain can be modified [10].

Poly(butylene terephthalate) (PBT) is a semi crystalline thermoplastic engineering polymer that prepared by polycondensation of 1,4-butanediol with either terephthalic acid or dimethyl terephthalate. The first synthesis of terephthalates made by Whinfield and Dickson in 1940s. Celanese corporation produced fiber-reinforced PBT compounds in 1970. The easy processing and rapid crystallization properties of PBT has made it rather widely used thermoplastic material in industry. Nowadays, different grades of PBT exist in market like mineral filled, glass fiber reinforced, impact modified, and flame-retardant grades. It is characterized by the following features: high stiffness and strength, high toughness at low temperatures, high heat-deflection temperature, high stress-cracking resistance, high resistance to fuels, oils, fats, and many solvents, low coefficient of linear expansion, low water absorption, good friction and wear characteristics, and good processability. PBT is used as an insulator in the electrical and electronics industries and suitable for automotive, telecommunication, machine components, and food and medical applications [11]. The PBT chemical structure is shown in Figure 2.1.

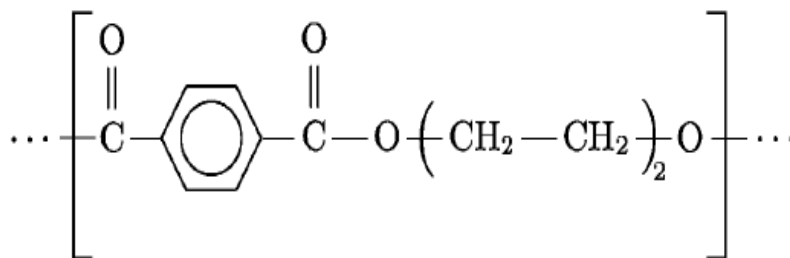


Figure 2.1 : Poly(butylene terephthalate) [11].

PBT melting point is 225~235 °C, the thermal deformation temperature 160~180 °C, the vitrification transition temperature between 22~43 °C. For non-reinforced PBT, the tension strength is only 50 MPa, but when it is reinforced, the tensile strength can increase to 170 MPa. For glass fiber reinforced materials, the shrinkage rate in flow direction can be decreased; however, the shrinkage rate in vertical direction has no difference from common materials. Since it has high crystallization rate, the stickiness of PBT is very low, and the processing cycle is short in general. The optimum processing method for PBT is injection molding and other methods include extrusion, blow molding, coating and other secondary processing molding. Moreover, PBT is required to dry before molding, the moisture content should be below 0.02 % [12].

2.2 Glass Fiber

Glass fiber (GF) is a material consisting of extremely fine filaments of glass. The main raw materials for glass fiber are silica sand, boric acid, feldspars, sodium sulfate, anhydrous borax, boric acid in different quantities and some other minor ingredients (e.g., clay, coal, and fluoro spar) [13]. Its manufacturing is the high-temperature conversion of these raw materials into a homogeneous melt in a refractory furnace, then fabrication of this melt into glass fiber. Generally, the melt temperature is about 1260°C. The glass fiber manufacturing process can be divided into 3 main phases; raw materials handling, glass melting and refining, and wool glass fiber forming and finishing [14].

In the first step silica sand and other ingredients are put in a batch silo. They are mixed and then fed into the high temperature furnace (1540 °C -1425 °C). The molten glass flows to the fore hearth stage where the temperature is reduced to 1260 °C. Then, molten glass flow through a plate, which contains many tiny holes and forms filaments. These filaments are then pulled mechanically to make smaller filaments. One of the most important step for glass fiber processing is chemical sizing which applied in order to protect fiber from loss of strength. Sizing protects fibers from these defects and holds fibers together. This chemical treatment applied on the surface of the fiber in order to reduce the friction between the fibers to prevent breakage. At finishing stage, this chemical application to surface of fiber in order to ensure bonding with matrix material for composite applications. Typical finishes

would be polyvinyl acetate modified with chromic chloride complex and/or organosilane coupling agents. Many filaments are bundled together to form tows or strands, and they can be cut into short fibers [13, 14]. The manufacturing process of glass fiber is illustrated schematically in Figure 2.2.

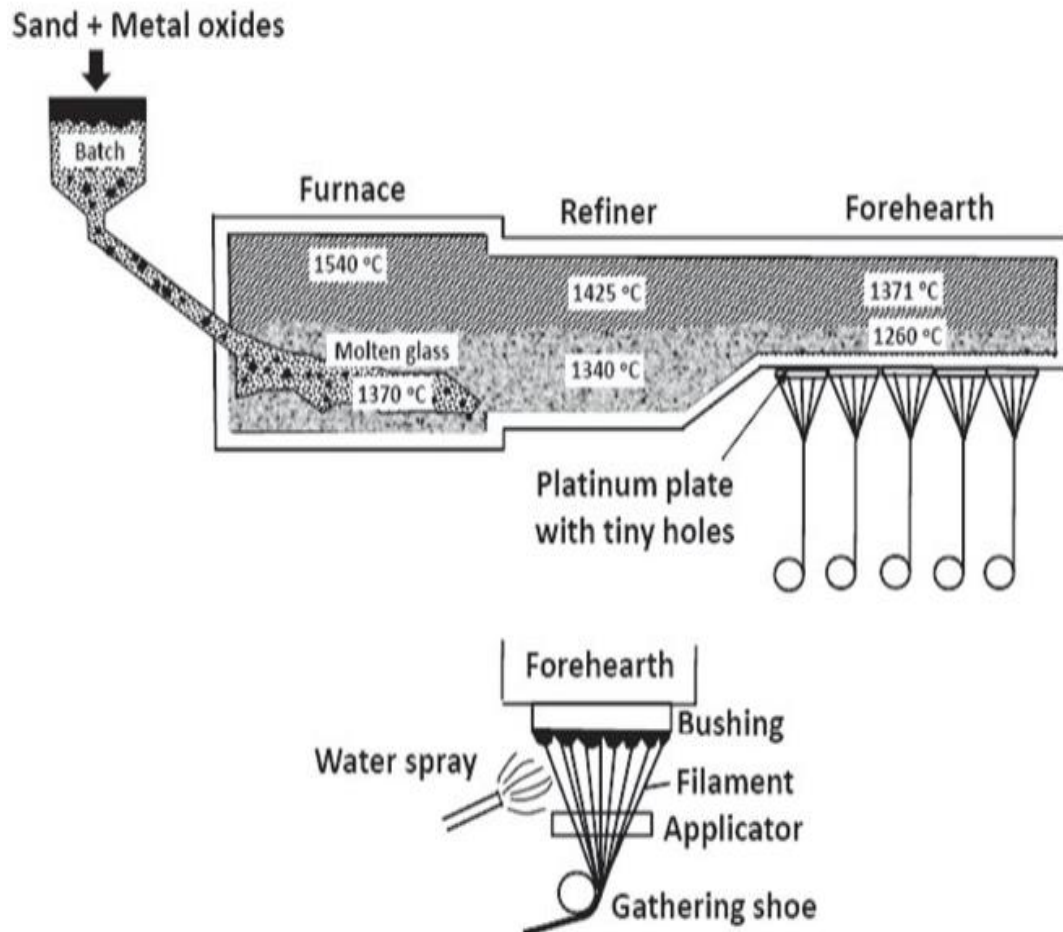


Figure 2.2 : Glass fiber manufacturing process [13].

Different types of glass fiber compositions are manufactured but in composite applications three types of them which are E glass, S glass (and its variation S2), and C glass are commonly used. When high strength and electrical resistivity important for application, E glass fibers have a composition of calcium aluminoborosilicate and calcium oxide is used. This glass fiber generally used for short fiber reinforcement of engineering thermoplastic composite reinforcement applications such as; boats, seats, or trays. S glass has higher strength and used in advanced composite applications. For chemical resistance required applications C class is used which is durable for corrosive environments [14].

2.3 Composite Materials

Composite materials are materials made from two or more constituent materials with significantly different physical or chemical properties, that when combined, produce a material with characteristics different from the individual components. The individual components remain separate and distinct within the finished structure. Composites are combinations of two materials in which one of the material is called the reinforcing phase, is in the form of fibers, sheets or particles, and is embedded in the other materials called the matrix phase.

Composite materials produce for many reasons like; make stronger, lighter or less expensive materials when compared to traditional materials. Fiber reinforcement of plastics is one of the most common composite applications. These composite materials consist of a polymeric matrix with fiber reinforcement. Fibers are the most common reinforcement material for composites in order to improve properties of plastic material. These fibers present at different scales, and vary between the micrometer level up to the centimeter level [15, 16].

The principal role of the reinforcement is to provide strength, stiffness, and other mechanical features to the composite. There are several manufacturing method, processing conditions, and combinations for composite productions [14]. Generally, orientation of the fibers is important for make higher mechanical properties product.

The common fibers used for making composites are glass, carbon, Kevlar and thermoplastic fibers. These fibers are individual filaments produced by drawing from a melt of the material, or by drawing from thermoplastic molecules. Glass fiber is one of the most common reinforcement material used in industry. In order to improve conjunction between the glass fiber and matrix materials, coupling agents can be used which are compatible at the one end with the silane structure of the glass and the other end with matrix. Coupling agents are used for enhance mechanical properties like tensile, flexural or compressive strength of composite by in increase bonding fiber with matrix [14, 15]. The bridging nature of the organofunctional coupling agent is illustrated in Figure 2.3. Organosilanes have ability to incorporate an organic-compatible functionality and an inorganic-compatible functionality within the same molecule.

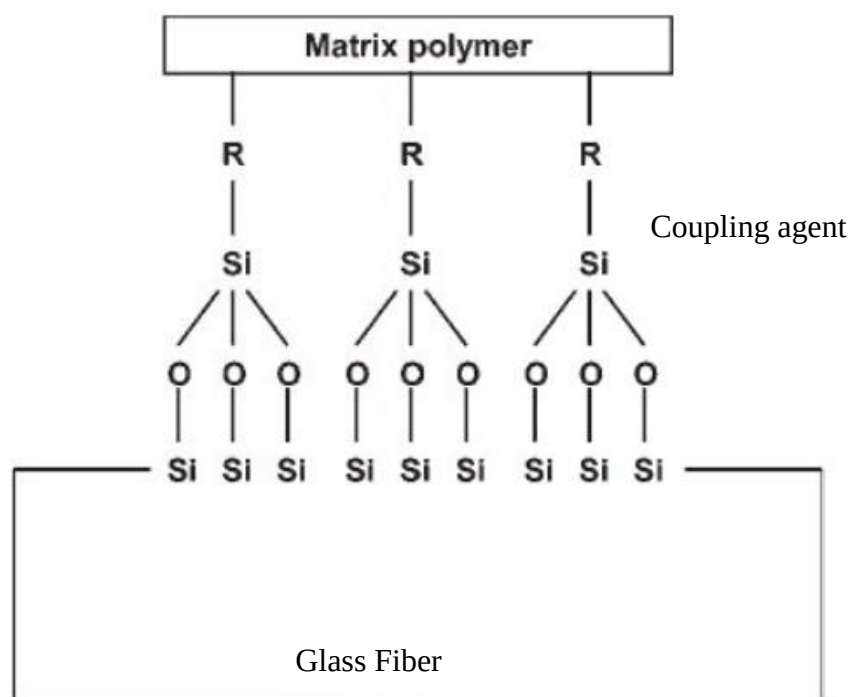


Figure 2.3 : Idealized coupling of matrix and glass by organofunctional silane [14].

2.4 Burning and Flame Retardant Mechanisms of Polymers

Burning mechanism of polymers was identified with several primary principles as early as 1947 [2]. Combustion reactions release the energy stored in the chemical bonds of the molecules of the fuel. This fuel can be any substance like wood, hydrocarbons, coal, animal fats and polymers. Basically, the heat, oxygen and the fuel are the three main factors of burning process, but when it examined more detailed, it contains number of reactions and transport phenomena in the solid, gaseous and interfacial phases and it is complex process. An overview of the current knowledge on the burning process and flame retardant mechanism of polymers was given in the introduction [17].

2.4.1 Polymer combustion

Polymers are chemical compounds consist of mainly carbon and hydrogen atoms, so they are highly combustible materials. When the amount of heat required to initiate combustion is applied to these materials, they decompose or pyrolysis and generating combustible gases. These combustible gasses mix with the oxygen of the ambient air and compose an ignitable blend that ignite spontaneously or due to the existence of an external source such as a spark or a flame. At the time of combustion, heat is

released, a part of which is transferred to the substrate promoting further decomposition with required concentration of the combustible gases and then a self-sustaining combustion cycle will be established [2,3]. Combustion cycle depends on amount of heat released during the combustion of the fuel. After heat quantity reaches a certain level, in the solid phase new decomposition reactions occurs and more products that are combustible are formed. The combustion cycle proceed and these three main factors are stated as fire triangle and illustrated in Figure 2.4. [18].



Figure 2.4 : Fire triangle of combustion [18].

The amount of energy needed to initiate combustion process is depending on the physical characteristics of the polymeric material. For example, after a certain amount of heat applied to semi-crystalline thermoplastics, it starts to soften, melt and drip. The amount of heat relates to polymer heat-storage capacity and its enthalpy of fusion and degree of crystallinity. For amorphous thermoplastics and most thermosets, heating step cause directly to polymer decomposition instead of softening and melting because of the absence of a melting point [19].

Polymer combustion is a complex process consist of four main stages which are heating, thermal decomposition or pyrolysis, ignition and combustion. First, polymer is heated to a certain level that it decomposes and liberates flammable gaseous products, which are diffuse into the flame zone. Under an ignition source, combustion in the gas phase is occurred and more heat is released. Under steady-state conditions, some of heat moved back to the polymer surface and so, more products that are volatile are liberated and combustion cycle is accelerated. The schematic diagram of polymer combustion process is represented in Figure 2.5.

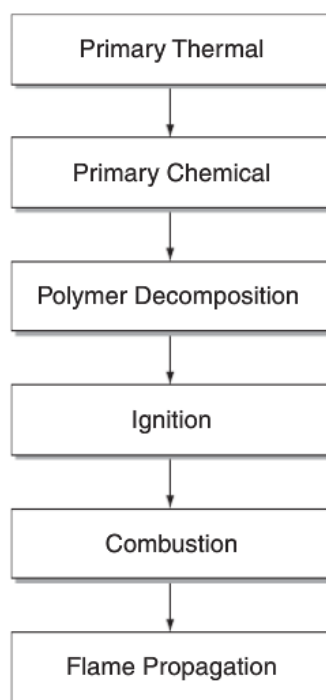


Figure 2.5 : The combustion process [19].

Fire is self-supporting combustion consists of release of heat, smoke and fire gases, and accompanied by flames and/ or glowing combustion [20]. Henceforward, combustion reactions are occurred in the gas phase and the main mechanism is free radical reactions. Radicals such as $\bullet\text{H}$, $\bullet\text{O}$, $\bullet\text{OH}$, and a small amount of $\bullet\text{HO}_2$, $\bullet(\text{H})\text{CO}$, and $\bullet\text{CH}_3$ are exist in hydrocarbon flame and free radical reactions occurs which propagates the fuel combustion. Chain branching reactions in the combustion process like below [21]:



These reactions increase radical formation and so burning reactions of polymeric material [8]. The main exothermic reaction that provides most of the energy to maintain the flame is:



Figure 2.6. schematically shows the material burning process. The combustion process of polymeric material can be sum up as following stages [22, 23]:

-Primary thermal: the ignition source heats the polymeric material and increase the temperature of material.

- Primary chemical: After heating, degradation of material starts.
- Polymer decomposition: Polymeric material degradation is accelerated and decomposition products are produced.
- Ignition: The combustible gases ignite to start combustion due to sufficient oxygen and the ignition source are found.
- Combustion: The burning gasses generate combustion at or near the surface of the polymeric material and, when sufficient energy formed at that stage process can become self-sustaining.
- Flame propagation: Depend on the polymer, charred surface layers and flames are formed on material and emission of smoke and toxic gases exist at this stage.

Essentially decomposition and combustion are the two main successive chemical process of burning of material which associated by ignition and thermal feedback. At first, the material decomposes (pyrolysis) and then decomposition products are combusted, which contain production of heat and this heat promotes the decomposition [24].

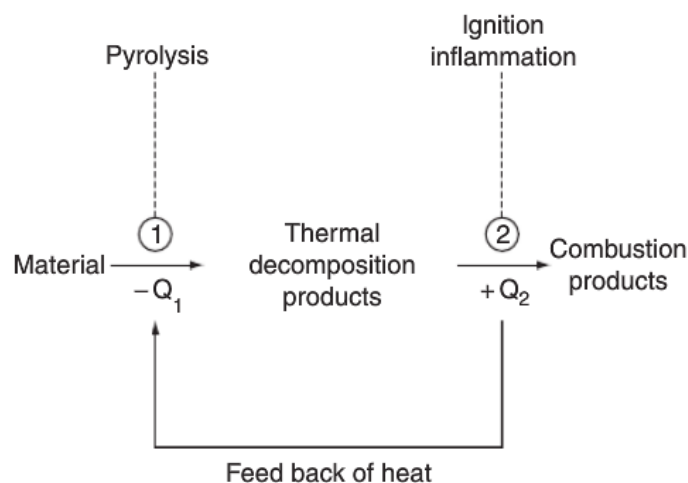


Figure 2.6 : Material burning proces [24].

From the point of fire, thermal decomposition is basically occurred by chemical decomposition of solid material and produces gaseous combustible vapors [25]. Owing to heat, polymer chains will starts to break down and volatile fuel molecules are formed. The most significant mechanism of polymer thermal decomposition is as following: (1) random chain scission, in which the polymer chains split at random locations into smaller fragments; (2) chain-end scission, where individual monomer

units are respectively removed from the chain ends; (3) chain stripping, during which elimination of atoms not part of the polymer chain or pendant groups are cleaved without breaking of the backbone; and (4) cross-linking, in which bonds are created between polymer chains. In most cases, the thermal decomposition of a polymer involves more than one of these reaction mechanisms. While some polymers fall exclusively into one category, others exhibit mixed behavior. This decomposition process can be accelerated by chemical attack on the polymer chains. For instance, higher atmospheric oxygen condition can increase the decomposition. Once ignition has occurred, a proportion of the heat from the flame will be transferred back to an adjacent non-flaming part of the polymer surface, pyrolysis of the polymer causes a repeat of the ignition process. This results in flame spread across the surface [26]. After polymer reaches the decomposition temperature, it liberates one or more decomposition products which are listed below:

- Combustible gases, such as methane, ethane, ethylene, formaldehyde, acetone and carbon monoxide,
- Non-combustible gases, such as carbon dioxide, hydrogen chloride, hydrogen bromide and water vapor,
- Non-combustible fluids, generally partially degraded polymer and organic compounds with high molecular masses,
- Solid particles or polymer component transported in agitated gases appearing in the form of smoke
- Solid bodies, such as char and ash [27].

2.4.2 Flame ignition

Flammable polymeric material ignites when surrounding with oxygen in air and exposure to a heat source. Presence of an external flame or spark material can be 'flash' ignite if the lower flammability limits is reached, or if the temperature is above the auto-ignition temperature auto-ignition can be occurred. As a result of ignition, a flame appears and this flame producing heat due to exothermic process. Some of this heat transferred back to surface of the material in order to the production of flammable volatiles and endothermic polymer pyrolysis. By this way, flame spread starts. Different parameters can affect the ignition such as temperature,

and physical and chemical features of the polymer material, oxygen availability. The flash and auto-ignition temperatures of some common polymers are given in Table 2.1 [2, 27].

Table 2.1 : Decomposition and ignition temperatures* together with heats of combustion of some common thermoplastic polymers and cellulose [27].

Polymer	Decomposition Range/ ⁰ C	Flash ignition temperature/ ⁰ C	Auto-ignition temperature/ ⁰ C	ΔH _c /kJ kg ⁻¹
LDPE	340-440	340	350	46.5
Polypropylene	330-410	350-370	390-410	46
Polystyrene	300-400	345-360	490	42
PVC (rigid)	200-300	390	455	20
PMMA	170-300	300	450	26
Cellulose	280-380	210	400	17

*determined by ASTM D 1929

2.4.3 Flame spread

After the ignition, pyrolysis of polymeric material will be accelerated and cause spreads over material surface. The hydrocarbon diffusion is the basic principle of flame chemistry. Liberation of reactive $\bullet\text{H}$ and $\bullet\text{OH}$ radicals raises the chain branching step and these lead to rapid flame spread. An illustration combustion of ethane is given in Figure 2.7. and in Figure 2.8. schematic description of flame spread along a surface is given [27].

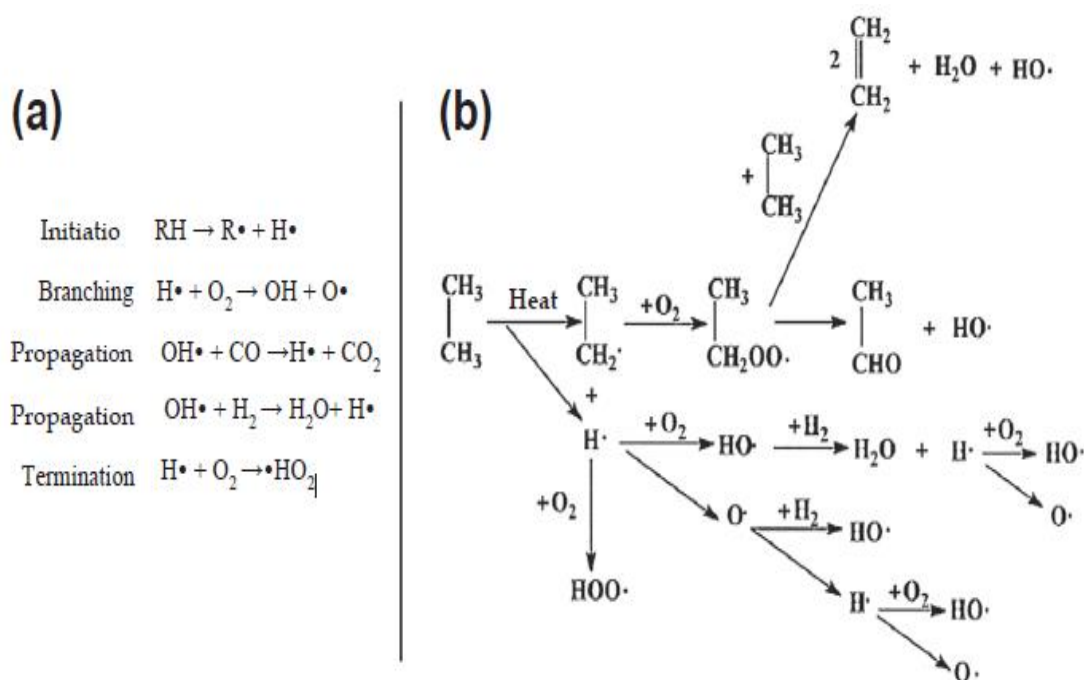


Figure 2.7 : (a) Free radical reaction mechanism during the combustion (b) propagation of $\bullet\text{OH}$ in the case of burning ethane [27].

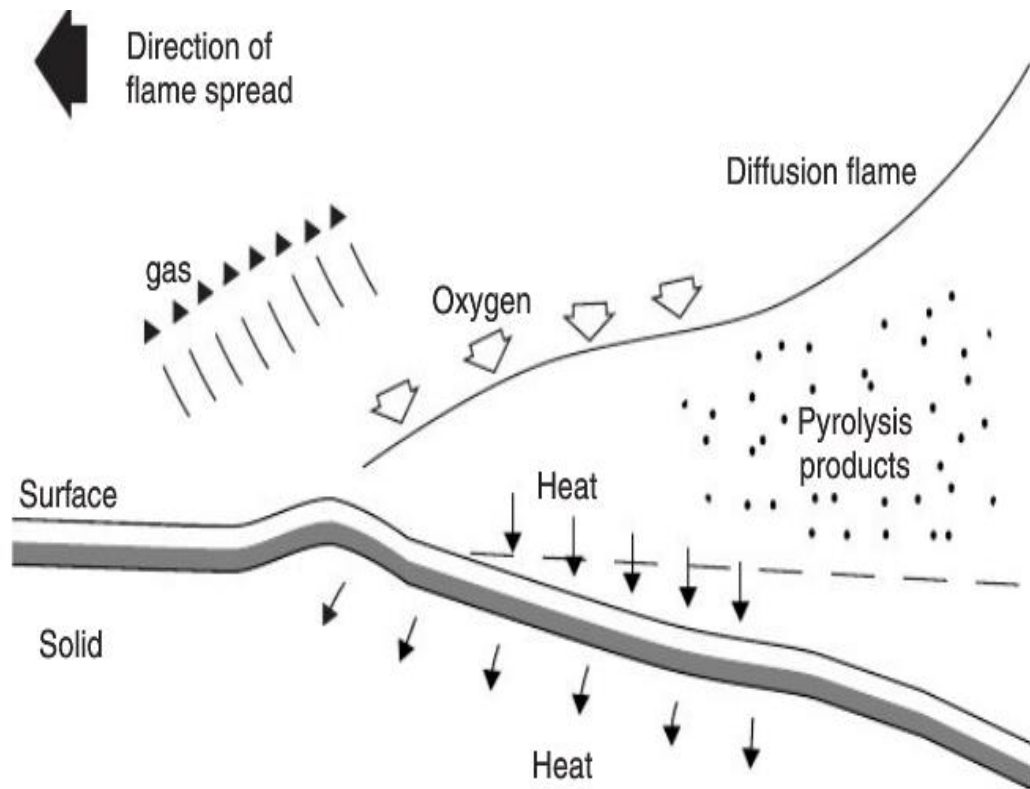


Figure 2.8 : Schematic representation of flame spread [27].

2.5 Flame Retardancy

Polymeric materials are usually flammable and hence improve of flame resistance of polymer and lowering the fire hazards of these materials are one of the crucial subject. There are several type of methods exist to developed flame retardancy of a polymer and mixing flame retardant additive with polymer is one of these methods [10].

Flame retardants main purpose is inhibit or to stop the polymer combustion process and the different type of flame retardants can be functioned in a polymer in different way. They can be function physically by cooling, formation of a protective layer or fuel dilution or chemically reacting in the condensed or gas phase [19]. In Figure 2.9 combustion process is shown.

In the gas phase mechanism flame retardant materials act mainly through scavenging free radicals that are responsible for the branching of radical chain reactions in the flame. Furthermore, high amount of incombustible gases released and these dilute flammable gases and sometimes dissociate endothermically.

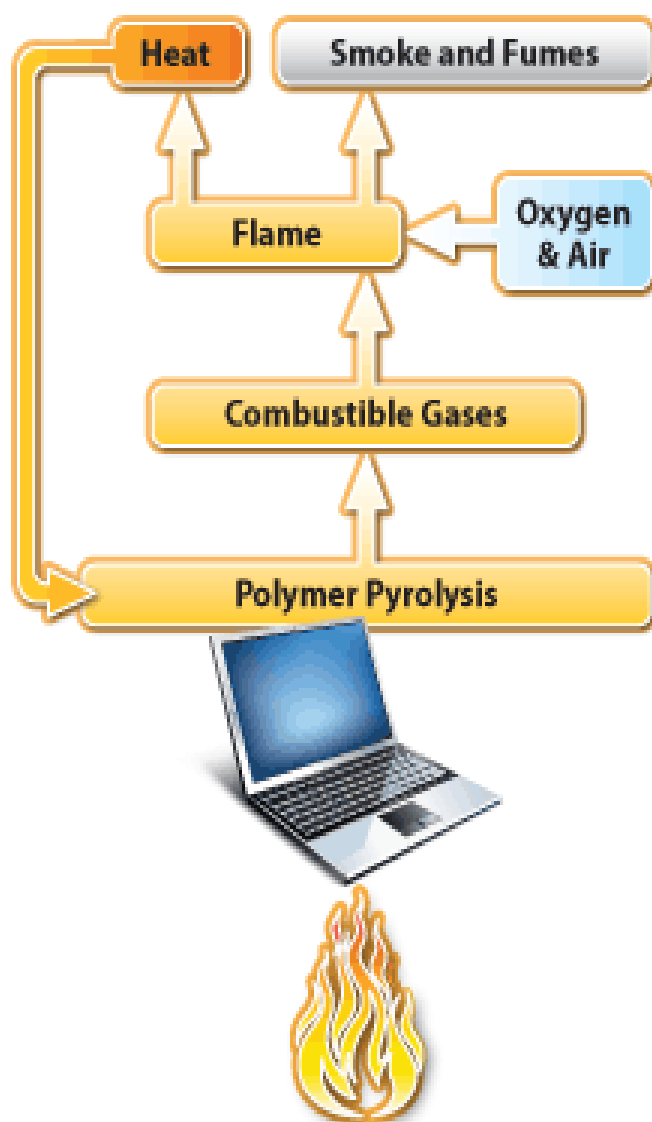


Figure 2.9 : Combustion process [19].

Heat is absorbed by endothermic reaction and temperature can be decreased. Consequently, combustion process is delayed and flame can be extinguished by this physical mechanism in gas phase.

In the condensed-phase mechanisms flame retardant materials can reduce the flammable volatiles and increase the formation of less flammable carbonaceous char, which operates as a barrier between the polymer and the flame. In addition, it decreases the amount of heat transferred to the polymer, hampers the diffusion of oxygen to the area of decomposition, and impedes the escape of volatile flammable gases generated during polymer decomposition. Char formation is the most irruptive factor of condensed phase mechanism. Char formation could be increased by catalysis or oxidative dehydrogenation.

Generally, the above mentioned mechanisms occurred in combinations. Selecting of appropriate flame retardant is depend on variety factors, which are represents as follows:

- Flame retardant should be effective in distinct polymer matrix.
- Flame retardant should be stable in the processing conditions of the polymer, thus, the degradation temperatures of flame retardant and polymer should be close values.
- Additive should compatible with polymer and should not destroy the polymer properties (mechanical properties, electrical performance, color, etc.).
- It should be cost efficient.
- The toxicity and the environmental impacts of the flame retardant should be considered [3].

2.5.1 Physical action

Flame retardant acts in polymeric material combustion process various ways. The endothermic decomposition of some flame retardant additive prompts a temperature decrease by heat consumption. This comprises some cooling of the reaction medium to below the polymer combustion temperature. Aluminum trihydrate (ATH) acts under this principle, and its efficiency depends on the amount incorporated in the polymer. When the flame retardant decomposes, inert gases (H_2O , CO_2 , NH_3 , etc.) are produced and they dilute the fuel in the solid and gaseous phases so that the lower ignition limit of the gas mixture is not exceeded. The other physical action of flame retardants is the formation of a protective solid or gaseous layer where thermal degradation takes place. This protective layer can reduce the heat transfer from the heat source to the material and so the degradation rate of the polymer. Also, the fuel gases can be physically removed from the oxygen, which inhibits the combustion process [28].

2.5.2 Chemical action

The significant chemical reactions of polymer combustion occur in gas phase and condensed phase. The flame retardant additives liberate free radicals such as $\bullet Cl$ and $\bullet Br$ in the gas phase and these radicals interrupt the combustion process by react with

highly reactive species such as $\bullet\text{OH}$ and $\bullet\text{H}$ and give the inert products instead of reactive radicals. Hence, the exothermic process that occurs in the flame is reduced and the system cools down, and the supply of flammable gases is decreased and eventually completely suppressed. In particular, metallic oxides can act as flame inhibitors. The active radicals $\bullet\text{OH}$ are adsorbed on the surface of oxide particles. A part of the collision energy is transferred to the oxides and $\bullet\text{OOH}$ radicals, which are less reactive than the initial $\bullet\text{OH}$ radicals are formed. As another example, the “hot” radicals $\bullet\text{OH}$ and $\bullet\text{H}$ can react in the gas phase with other radicals, such as halogenated radicals $\bullet\text{X}$ issued from the degradation of the flame retardant, to create less energetic radicals.

Two types of chemical reactions can take place in the condensed phase. The first is flame retardant accelerate the split of the polymer chains. By this way, polymer drips and thus moves away from the flame action zone. The second chemical reaction type is by chemical transformation of the degrading polymer chains, flame retardant can lead a carbon (charring) layer on polymer surface. This carbon layer behave like insulating layer between the gas phase and the condensed phase [28].

2.5.3 Flame retardant classification

Different classifications can be made to categories flame retardants. According to chemical composition flame retardants can be classified six main categories which are boron, aluminum, phosphorus, antimony, chlorine, and bromine based additives. They also can be classified by how they are integrated into a polymer.

Flame retardants classification by how they are integrated into a polymer:

Additive flame retardants are integrated into polymers by physical mixing, and are not chemically bound to the polymer matrix. Polymer and flame retardant additive are mixed and any chemical reaction is occurred. Processing of additive flame retardants is easier than reactive flame retardants, since they are incorporated into the product at the final stages of manufacturing.

Reactive flame retardants are integrated into polymers by chemical reactions and must be incorporated at an early stage of manufacturing. They make chemical bonds with polymer matrix and became permanent part of the polymer structure. Hence, in comparison to additive flame retardants, they have a greater impact on the chemical and physical features of the product [29].

Both reactive and additive flame retardants can significantly change the properties of the polymers such as: viscosity, flexibility, density, electrical properties, tensile strength, and flexural strength; and may also increase the susceptibility of the polymers to photochemical and thermal degradation. Flame retardants can also be coated on the external surface of the polymer to form a protective barrier or to improve their compatibility with the polymeric matrix [29].

Besides flame retardants additives, some polymers shows naturally flame resistance properties. These polymers are identified as inherently flame retardant polymers, and they show relatively higher thermal stability than common polymers. The main principle of these polymers can be headline as follow;

- Their molecular rearrangements generally consists of complex pathway
- To maximize the bonding energy, resonance stabilization of aromatic polymer rings should be used.
- Compounds with strong covalent bonds should be used.
- In the polymer structure all of the rings should have normal bond angles (no bond strain or weak points).
- Multiple bonding to several centers should be applied.

The aromatic polyesters, polyethers and polyamides, the polyarylates and polycarbonates, and phenolic resins are example of these polymers, which have highly aromatic content. The poly(aryl ketone)s and ether ketones, poly(aryl sulphide)s and sulphones, polyimides, and thepolybenzimidazoles, benzoxazoles and benzthiazoles are some other inherently flame retardant polymer that show above average thermal and thermo-oxidative stability. Polymers such as Kevlar and Teflon are common place in today's market and these materials are non-combustible, but they are not flame extinguishing. These polymers can form char during the burning process. To form additional rings either by Claisen-Cope or Diels Alder rearrangement can be applied. The following polyamide, similar to Dupont's Nomex, forms a more stable benzoxazole structure on heating [2]. In Figure 2.10 examples of inherently flame retardant polymers are shown. It can be seen on the Figure 2.10 that Polyetheretherketone (PEEK), Polyetherimid, Poly(1,45-phenylene terephthalamide) Kevlar and Polytetrafluoroethylene (Teflon) in chemical and commercial trade name and chemical structures of polymers were also illustrated.

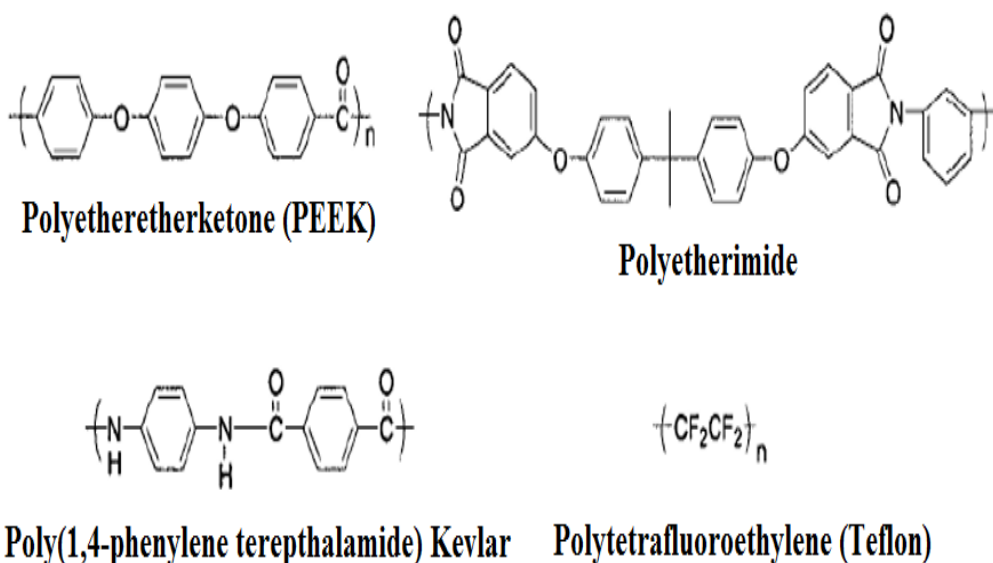


Figure 2.10 : Inherently flame retardant polymers [2].

2.6 Flame Retardant Additives

The additive flame retardant can be physically mixed with polymeric materials and compounds do not react chemically with the polymers. They increased the flame resistance of polymeric material by increase the time to ignition, develop the self-extinguishability of the polymer, reduce the heat release rate during combustion and prevent the formation of flammable drops and volatiles.

Even though additive flame retardants are widely used in polymers, there are some drawbacks such as poor miscibility, high volatility impact on the properties of polymers and high liberation of carbon monoxide (CO) and smoke [30]. The expected features of flame retardants are high efficiency in used polymer, thermal stability at processing temperature of polymer, environment-friendly, low cost, compatible with polymer matrix and other additives and no toxicity [31]. Several type of flame retardant additive present commercially and they can be divided into six main categories which are boron, aluminum, phosphorus, antimony, chlorine, and bromine based additives. Nitrogen and silicon based additives can also have some degree of flame retardant properties on polymer.

2.6.1 Halogen-based flame retardants

Halogen containing flame retardants act mainly by chemical interference with the radical chain mechanism. During combustion of polymeric material, in the gas phase

the amount of combustible substances remains constant but the heat discharged in the combustion decreases. Halogen radicals liberated from flame retardant remove (scavenged) high energy $\bullet\text{OH}$ and $\bullet\text{H}$ radicals which composed during combustion process, and by this way they interfere the combustion [2].

Bromine is the more sufficient halogenated compound since its weaker bonding to carbon allow it to interfere at a more proper point in the combustion process. It is assumed that the effective agent, hydrogen bromide is liberated over a narrow temperature range so that it is available at a high concentration in the flame zone. Hydrogen chloride is produced from chlorine-containing products and is liberated over a broad temperature range. As a result, it is present at a lower concentration and so less effective [32]. Example of specific halogenated flame retardants that used in polymeric systems are shown in Figure 2.11 [32, 33].

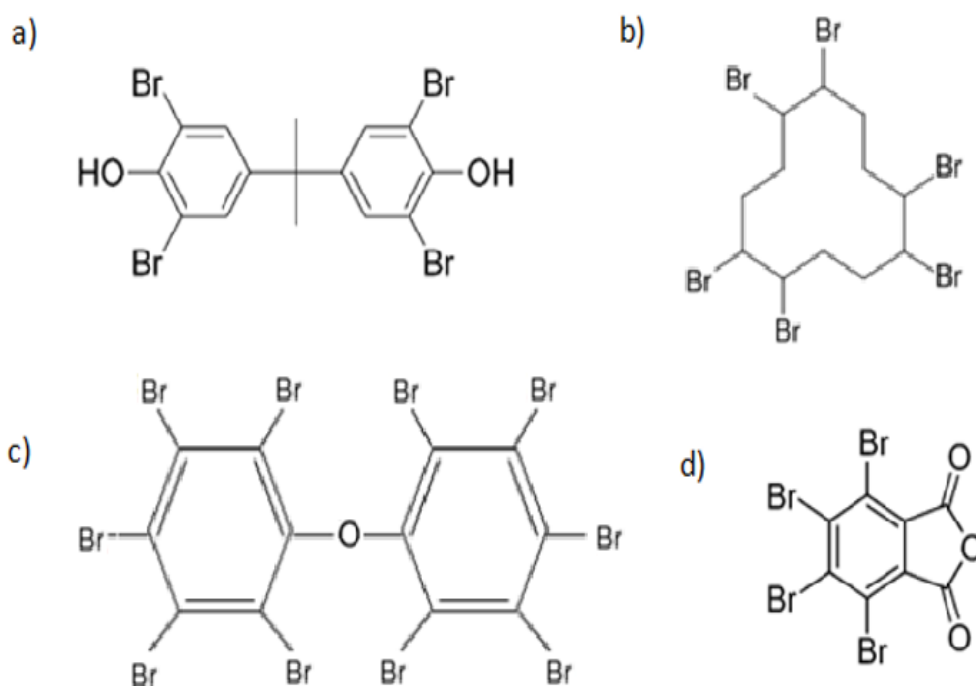


Figure 2.11 : Chemical structure of a) Decabromodiphenyl ether (DECA), b) Hexabromocyclododecane (HBCD), c) Tetrabromobisphenol A (TBBA), d) Tetramethylphthalic anhydride (TMPPA) [32].

Halogenated flame retardants perform in the gas phase and they interfering with the radical mechanism. Chain branching reactions produced the high-energy $\bullet\text{OH}$ and $\bullet\text{H}$ radicals and halogen-containing flame retardant detached these radicals and interfere the combustion.

At first the halogenated flame retardant breaks down to radicals ($\bullet X$ represents $\bullet Cl$ or $\bullet Br$).



The halogen radical reacts to form the hydrogen halide by hydrogen abstraction;



which in turn interferes with the radical mechanism:

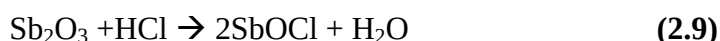


The high energy $\bullet OH$ and $\bullet H$ radicals are removed by reaction with HX and replaced with low-energy $\bullet X$ radicals. HX produces the actual flame retardant effect. The hydrogen halide consumed is regenerated by reaction with hydrocarbon. HX performs as a catalyst [32].



Antimony trioxide (Sb_2O_3) does not have flame retardant properties by itself, but it is an effective synergist for halogenated flame retardants. Sb_2O_3 acts as a synergistic catalyst facilitating the breakdown of halogenated flame retardants to active molecules [17]. It performs as a catalyst and facilitates the breakdown of halogenated flame retardants to active molecules. It also reacts with the halogens to produce volatile antimony halogen compounds, which are themselves directly effective in removing the high energy $\bullet H$ and $\bullet OH$ radicals which feed the flame phase of the fire, thus reinforcing the flame suppressing effect of the halogenated flame retardants [34].

Flame retardant synergistic effect is significantly seen the formulation of halogenated mixed with antimony trioxide flame retardant system. Synergism of two or more additives shows the higher flame retardancy performance than that expected from individual contribution [35, 36].



-Antimony trihalide breaks down to form hydrogen halide and this interferes with the radical chain mechanism.



SbO and SbOH are formed produced inhabitation together with hydrogen halides [32].



2.6.2 Metal hydroxides

Metal hydrate flame retardants are one of the largest volume flame retardant additive group in the flame retardant market. Aluminiumhydroxide (ATH) and magnesium hydroxide are the most used metal hydrate products, and other products like brucite, mixture of hydromagnesite and huntite, magnesium aluminium ahydrocarbonates, and certain other mixed metal hydroxides are less frequently used products. These metal hydroxide flame retardant are represented as environmentally friendly and does not harmful for human health [37].

Alumina trihydrate (aluminium trihydroxide) and magnesium hydroxide structures normally do not contain water of hydration. In order to generate free water, the hydroxyl groups bonded to metal undergo endothermic decomposition and, this starts at about 220 °C for ATH and 330 °C for magnesium hydroxide. The endothermicity is main principle of mode of action of ATH and magnesium hydroxide [2].

Some inorganic compounds are useful for use as flame retardants in polymeric materials because such compounds can be effective in the range of decomposition temperatures of the plastic, mainly between 150 °C and 400 °C. While organic compounds can be affected from influence of heat, inorganic compounds do not evaporate and they decompose, giving off non-flammable gases like water, carbon dioxide, sulphur dioxide, hydrogen chloride, mostly in endothermic reactions. They

perform by diluting the mixture of flammable gases and by shielding the surface of the polymer against oxygen attack in the gas phase [31].

2.6.2.1 Aluminium trihydrate

ATH is the most widely used flame retardants because of its cost and easy processibility with polymeric materials. It can use in wire and cable insulation and other elastomeric products, synthetic marble and synthetic onyx, latex for carpet back-coatings, phenolics, epoxies, and saturated polyesters. It is decomposition temperature range from 180 to 220 °C. ATH transform to aluminium oxide by endothermic reaction and water formation is occurred.

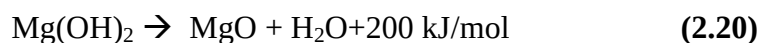


In the combustion process, because of endothermic reaction, the polymer is cooled, fewer pyrolysis products are formed. The residue of aluminium builds up to create a protective layer. The water vapor liberated has a diluting effect in the gas phase and forms an oxygen displacing protective layer over the condensed phase [31].

2.6.2.2 Magnesium hydroxide

Like ATH, magnesium hydroxide also release water which cools the burning substrate and blankets the substrate to limit the oxygen available for combustion. It is decomposition temperature is between 330-340 °C. Like ATH, it requires high loading levels (50-60 %) for effective flame retardancy [31].

Since it has higher decomposition temperature, it is more convenient for high temperature thermoplastic applications like engineering plastics. It is more expensive than ATH. Magnesium hydroxide performs as a flame retardant and smoke suppressant. Wire and cable are the most widely used applications of magnesium hydroxide, which commonly used like 60-65 % loading to polypropylene [35].

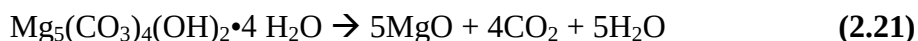


2.6.3 Huntite/Hydromagnesite (Ultracarb)

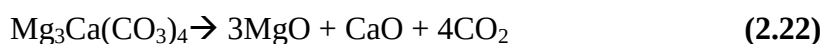
Ultracarb is a natural mineral, which consists of mixture of huntite and hydromagnesite. This mineral have several industrial usage area and especially used in wire and cable applications as a flame retardant. Furthermore, It is sold in Greece

and Turkey by Minelco Company. Huntite/hydromagnesite mixtures are used as flame retardant and smoke-suppressant fillers in a variety of polymer types [10].

Hydromagnesite is known as basic magnesium carbonate, which shows a platy structure. It is endothermically decomposition temperature change between 220 °C to 550 °C. It releases water and carbon dioxide while decomposing and this endothermic decomposition property gives it flame retardant feature.



Huntite mineral is mixed of calcium magnesium carbonate. It decomposes endothermically releasing inert gases and releasing water over a temperature range of approximately 450 °C to 800 °C.



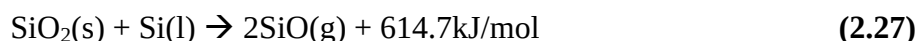
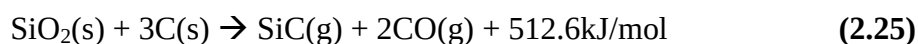
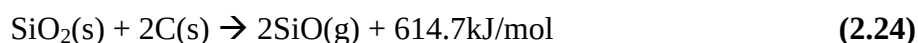
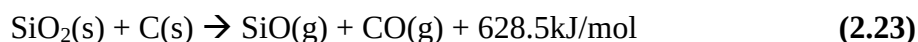
Ultracarb mixture release water and carbon dioxide and total decomposition weight loss about 53 % when it is heated. It gives off first little mass loss about 230 °C and then gives main mass loss at about 420 °C and 550 °C. Huntite and hydromagnesite minerals are used in polymeric systems to improve flame retardancy properties of plastic [38, 39]. Minerals with potential fire retardant benefits and their decomposition temperatures are shown in Table 2.2 [40].

Table 2.2 : Potential flame retardant fillers [40].

Potential Material (Common Name and Formula)	Onset of decomposition(°C)	Volatile Content (% w/w)		
		Total	H ₂ O	CO ₂
Nesquehonite (MgCO ₃ .3H ₂ O)	70-100	71	39	32
Alumina trihydrate (Al(OH) ₃)	180-200	34.5	34.5	0
Basic magnesium carbonate, hydromagnesite (4MgCO ₃ .Mg(OH) ₂ .4H ₂ O)	220-240	57	19	38
Sodium dawsonite (NaAl(OH) ₂ CO ₃)	240-260	43	12.5	30.5
Magnesium hydroxide (Mg(OH) ₂)	300-320	31	31	0
Calcium hydroxide Ca(OH) ₂	430-450	24	24	0
Boehmite AlO(OH)	340-350	15	15	0
Magnesium phosphate octahydrate Mg ₃ (PO ₄) ₂ .8H ₂ O	140-150	35.5	35.5	0
Calcium Sulphatedehydrate, gypsum (CaSO ₄ .2H ₂ O)	30-130	21	21	0

2.6.4 Silicon-based flame retardants

Silicon based flame retardant environmentally friendly alternative to existing materials. It also improves the dielectric features and brittleness of the polymeric material. The most common silicon based flame retardant is silica (SiO_2). It performs endothermic decomposition and reaction between silica and carbon formed a chemical shielding effect. However, it can affect the flame retardant properties of the compound, since the reaction may yet break charring structure. Furthermore, synergistic effect of silicon based flame retardant with other flame retardants is indicated by some researchers. Silica affects flammability properties of materials [41]. The reaction of SiO_2 and carbon at high temperature is as follow:



2.6.5 Nitrogen-based flame retardants

Nitrogen based flame retardants are believed to act by both condensed phase and gas phase mechanism. In the condensed phase, melamine is converted into cross-linked structures, which promote char formation and ammonia is liberated in these reactions. In the gas phase mechanism, the release of molecular nitrogen dilutes the volatile polymer decomposition products.

The nitrogen containing flame retardants divided into three chemical groups: pure melamine, melamine derivatives, i.e. salts with organic or inorganic acids such as boric acid, cyanuric acid, phosphoric acid or pyro/poly-phosphoric acid, and melamine homologues such as melam, melem and melon [42].

Melamine contains 67 weight percent nitrogen atoms and it is thermally stable crystalline product with high melting temperature (345°C). Melamine can form thermally stable salts with strong acids like melamine cyanurate, melamine phosphate, and melamine pyrophosphate. Melamine and melamine salts are displayed by various flame retardant mechanisms. Melamine based salts decompose

and reformed melamine volatilizes by heating and, it performs more condensation than pure melamine and give higher amount condensation products [43].

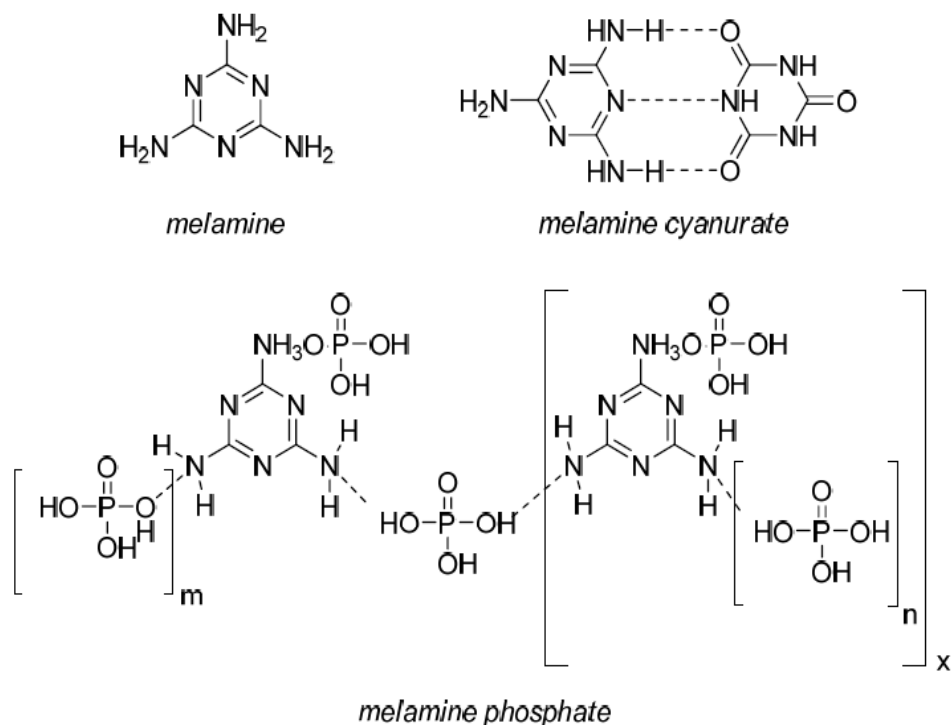


Figure 2.12 : Nitrogen-based flame retardants [43].

2.6.6 Phosphorous-based flame retardants

The phosphorus-based flame retardants can be divided into several categories such as phosphonates, phosphates, phosphinates, phosphine oxides, and red phosphorus. These phosphonated flame retardant agents can be used as additives or they can be used at synthesis stage and take place in the polymer chain [33].

Phosphorus-containing flame retardants perform in the condensed phase and also vapor phase. They are particularly effective in materials with high oxygen or nitrogen containing plastics as well as cellulose and its derivatives [32]. The chemical nature, initial concentration of phosphorous flame retardant and the reaction between polymers and the phosphorus compound has important role on flame retardant mechanism. The function of phosphorus compounds is related to following factors:

- During the combustion of polymeric material, the phosphorus compound shows specific effect on condensed phase action. At this stage, chemical transformations

of polymer occurred and the non-volatile char residues are increased, the pyrolysis fuel products are decreased.

- At the surface of polymeric material viscous melted layer or glassy layer of polymethaphosphoric acid is formed. This layer acts as a protective plate which inhibit the heat transfer from the flame to the polymer and diffusion of reagents.
- Prevent the gaseous phase flame reactions.
- Carbonized polymer pyrolysis product on heterogeneous oxidation are effected the function of phosphorus compounds [36].

In the condensed phase, thermal decomposition causes the production of phosphoric acid, which condenses readily to produce pyrophosphate structures and release of water. Consequence of water liberation, the oxidizing gas phase is diluted. Furthermore, the dehydration reactions of the terminal alcohols can be catalyzed by phosphoric acid and pyro-phosphoric acid, and this leading to the production of carbocation and carbon-carbon double bonds. At high temperature cross linked or carbonized structures are formed. Ortho- and pyro-phosphoric acids are converted metaphosphoric acid and derivatives. The phosphate anions (pyro- and polyphosphates) then take place with the carbonized residues, in char formation. This produced char layer (carbonized layer) function as a protective barrier and isolates the polymer from flames by;

- (1) Limiting the volatilization of fuel and keeps from the liberation of new free radicals;
- (2) Limiting oxygen diffusion and so, decrease combustion;
- (3) Insulating the polymer underneath from the heat.

Char forming proceed by two mechanism which are redirection of the chemical reactions include in decomposition in support of reactions yielding carbon rather than CO or CO₂ and, production of a surface layer of protective char.

In the gas phase, scavengers of $\bullet\text{H}$ and $\bullet\text{OH}$ radicals is occurred by $\bullet\text{PO}_2$, $\bullet\text{PO}$ and $\bullet\text{HPO}$ active radicals which volatilize from phosphorus flame retardant. When compare the other halogenated flame retardant radicals volatiles of phosphorated compounds are the most efficient ones which is five times more effective than

bromine and 10 times more effective than chlorine radicals. The mechanism of radical scavenging by P can be illustrated as follow;



2.6.6.1 Red phosphorus

Red phosphorus (P_n) is the most concentrated source of phosphorus for flame retardancy. It is thermally stable up to 450 °C and, it is one of the efficient flame retardant additive, especially in oxygen containing polymers such as polyesters, polyamides and polyurethane. In commercial usages, it is effectively perform in small quantities (less than 10 %) and it is encapsulated with a high concentration of polymer [35].

Even though its flame retardancy mechanism has not yet been clearly identified but it is thought to be through the free radical scavenging mechanism proceed. It is also found that red phosphorus depolymerizes into white phosphorus (P_4) and this P_4 can volatilize at high temperature or produce phosphoric acid by diffused from polymer to the burning surface and oxidized. This phosphoric acid performing like char forming agent and provide protective layer. The notable drawback of red phosphorus is it can liberate highly toxic phosphine (PH_3) through reaction with moisture in the melting process. Nevertheless, phosphine formation can be prevented by prior polymeric encapsulation of the red phosphorus. Furthermore, color of the final product can be a disadvantage for some applications. [19, 35]

2.6.6.2 Organic phosphorus-based flame retardants

Organophosphorus compounds consist of phosphate esters, phosphonates and phosphinates. They can proceed as additives or as reactive (co)monomers/ oligomers. Because of low efficiency and being highly volatile substance, (alkyl-substituted) triaryl phosphates such as cresyl diphenyl phosphate, isopropylphenyl diphenyl phosphate, tertbutylphenyl diphenyl phosphate or tricresyl phosphate have narrow usage area in plastic industry [17]. Examples of some phosphorus flame retardant additives are shown in Figure 2.13.

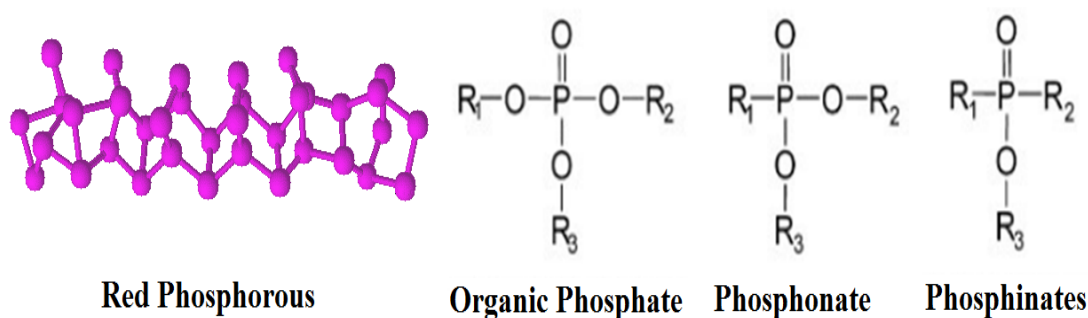
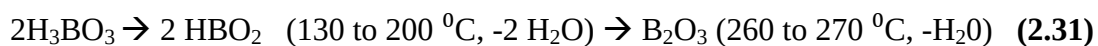


Figure 2.13 : Chemical structures of some phosphorus flame retardant additives[17].

2.6.7 Boron-based flame retardants

Boron is an element having symbol B and with an atomic number of 5. It has number of different forms and amorphous boron, a dark powder, unreactive to oxygen, water, acids and alkalis are the most common ones. When it reacts with metals, it gives borides [44]. Boron containing compounds flame retardant mechanisms proceed by the endothermic process with release of water and the formation of a glassy protective layer. They can be effective in the condensed phase, and in some cases, in the gas phase as well.



The boron oxide formed softens at 325 °C and starts to flow above 500 °C. When it use in oxygen-containing substrate, charring can occur as a result of acid-catalyzed elimination of water. The formation of the glassy coating on polymer isolate the material against oxygen and heat release of flammable gasses is decreased. Other boron compounds such as barium metaborate or calcium borate show only negligible flame retardant efficiency for plastics [32].

2.6.7.1 Zinc borates

Zinc borates most frequently used boron compound with chemical composition of $x\text{ZnO} \cdot y\text{B}_2\text{O}_3 \cdot z\text{H}_2\text{O}$. There are several type of zinc borates which release different amounts of hydration water. Their endothermic decomposition take place (503 kJ/kg) between 290 °C and 450°C and liberates water, boric acid and boron oxide (B_2O_3) compounds.

Zinc borate is used in plastic industry for several utility and flame retardant and smoke suppressant properties are the main benefits of it. They can function in

polymeric material alone or use as synergist with other additives. The main usage area of zinc borate as a flame retardant is PVC and some engineering plastics. It is more efficient in halogen containing systems [45, 46]. Mechanisms of action of zinc borate on different polymer matrices are represented in Table 2.3.

Table 2.3 : Mechanisms of action of zinc borate on different polymer matrices [45].

Polymer	Benefits
PVC	Smoke suppressant Flame retardant Synergist of antimony oxide Lowers total fire retardant cost Char promoter Smoke suppressant/char promoter
Polyolefins	Afterglow suppressant Improves elongation properties Anti-arcing agent Anti-tracking agent
Polyamides	Synergist of halogen sources Afterglow suppressant Used in both halogen containing and halogen-free nylons
Elastomers	Smoke suppressant Afterglow suppressant Char promoter Anti-arcing and anti-tracking agent
Epoxy resin	Smoke suppressant Char promoter Partial or complete replacement of antimony oxide

2.6.7.2 Metal borates

Metal borates can occur in nature as mineral or synthetic form and find extensive industrial application in both forms. There are a number of different types of boron mineral can be found in the nature and borax (sodium borate decahydrate) and colemanite (calcium borate pentahydrate) are the most common ones of them. Boron, oxygen, metal and hydrogen elements collocate in different configurations in crystalline metal borates structure. For crystal forms of metal borates, water molecules can be included. Furthermore, metal borates can be divided into two groups, which are hydrated borates and anhydrous borates. In industry generally

hydrated borates are used which containing B-OH groups in structure and contain molecular water [47].

2.6.7.3 Boron phosphate

Boron phosphate is an inorganic compound with chemical formula BPO_4 . It can be produced by phosphoric acid and boric acid evaporation and heating. It is also produced from triethyl phosphate and boron trichloride reactions [48]. It vaporizes at $1450\text{ }^{\circ}\text{C}$ - $1462\text{ }^{\circ}\text{C}$ without decomposition. It usually has tetra-coordinated structure. In Figure 2.14 boron phosphate structure with BO_4 group is shown. It was reported that 5 % boron phosphate and 2 % silicone oil flame retardant system used in polyamide (PA)/PPE blend and get V-0 rating at 1.6 mm in the UL-94 test [35].

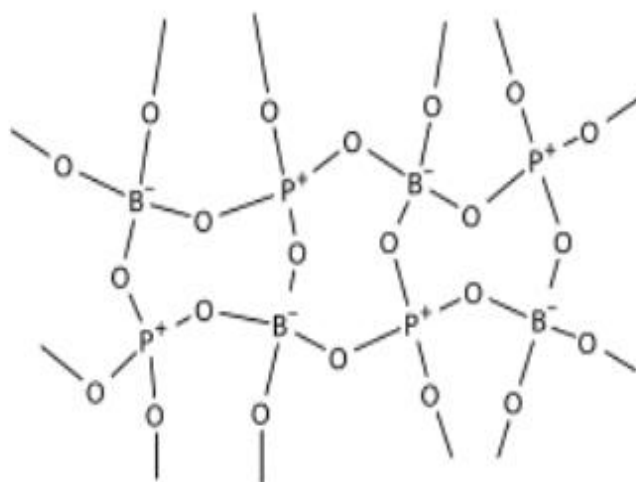
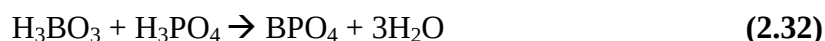


Figure 2.14 : Boron phosphate [35].

2.6.8 Intumescent flame retardants

Intumescent systems work by producing a char like foam that protects the substrate under the heat of the flame. Its flame retardancy mechanism consists of the formation of a voluminous, insulating protective layer and simultaneous foaming steps. A typical intumescent flame retardant content consists of three main component, which are charring agent (carbon donor), catalyst (acid donor) and blowing agent (acid donors).

- Charring agent: polyalcohols such as starch, pentaerythritol
- Catalyst: ammonium polyphosphate, usually a P compound
- Blowing agent: melamine or other compound decomposing to yield CO₂ or NH₃ [49].

Most common intumescent formulation is ammonium polyphosphate (APP), pentaerythritol (PER) and melamine system which is used in thermoplastic applications especially in polyolefins and used in fire retardant intumescent coatings. It is mainly combined of inorganic acid sources (e.g. ammonium polyphosphate, etc.), carbonifics (e.g. pentaerythritol, sorbitol, etc.) and spumifics, which generate the non-flammable gases (e.g. melamine, etc.) [50].

2.6.9 Synergistic flame retardant systems

A way of achieving improved flame retardant activity is to create a flame retardant system, which comprise mixtures of two or more additives. This flame retardant system shows better performance when they used together instead of separately [51]. The development of synergistic flame retardant system can both lower the cost needed to achieve an acceptable level of flammability and decrease the potential environmental effect.

As an illustration, it is indicated that blends of melamin polyphosphate (MPP) with other flame retardants such as metal phosphanates increased flame retardant performance of glass fiber reinforced polyamide 6 (PA6) compound. According to some studies addition of solid acids in MPP formulations increase the char production of PA6 at combustion process [52].

Another example that zinc borate synergist effect in in different polymers, especially in intumescent flame retardant systems which shows increased char formation and better char quality. Zinc borates also shows synergistic performance in aluminium and magnesium hydroxides, phosphorus-based intumescent systems and organophosphorus compounds. These are also showed smoke suppressant characteristics in some flame retardants [52]. Even though other boron containing compound like boron-silicon containing preceramic oligomers, boron phosphate, ammonium pentaborate and calcium borates have yet rarely been investigated, these studies indicated high synergistic effects of boron compounds [53].

2.7 Methods of Studying Flaming Combustion

2.7.1 UL-94 flammability test

The UL-94 test is an Underwriters Laboratory test method measures the linear burning rate of a vertically or horizontally mounted sample. In the test, the standardized burner flame is applied to the bottom edge of a vertically mounted sample for 10 seconds, or the end of a horizontally mounted sample. The test specimen is a bar of 13 mm width 125 mm length with varying thickness. According to the burning time of specimen, sample is classified one of three rating V-0, V-1, V-2. The UL rating should always be reported with the thickness; just reporting the UL rating without mentioning thickness is insufficient [54]. The criteria for UL-94 rating is represented as follow:

- HB slow burning on a horizontal specimen burning rate lower than 76 mm/min for 3 mm thickness
- V-0 burning stops within 10 seconds on a vertical specimen; no drips allowed
- V-1 burning stops within 30 seconds on a vertical specimen; no drips allowed
- V-2 burning stops within 30 seconds on a vertical specimen; drips of flaming particles are allowed
- 5V burning stops within 60 seconds after five applications of a flame larger than used in V-testing each of five seconds, to a test bar
- 5VB plaque specimens may have a burn-through (have a hole) 5VA plaque specimens may not have a burn-through (no hole) – highest UL rating

2.7.1.1 UL-94 vertical flammability test

Vertical burn test is described by ASTM D-568 and ASTM D-3801 standard test methods. In this test, the specimens are clamped vertically. After ignition, the ignition source (usually a bunsen burner) is withdrawn and the length of burn of the sample in a set period of time (10 seconds) is measured. If the sample does not burn for the entire time, the time to extinguish is noted. Materials which burn while the ignition source is in contact but go out quickly when it is removed are termed self-extinguishing. This test is most useful in measuring the burning characteristics of similar materials. Dripping of the resin should be noted. Figure 2.15 shows the basic

vertical test apparatus [54]. In Table 2.4 UL-94 vertical flammability test requirements for classifying material is represented.

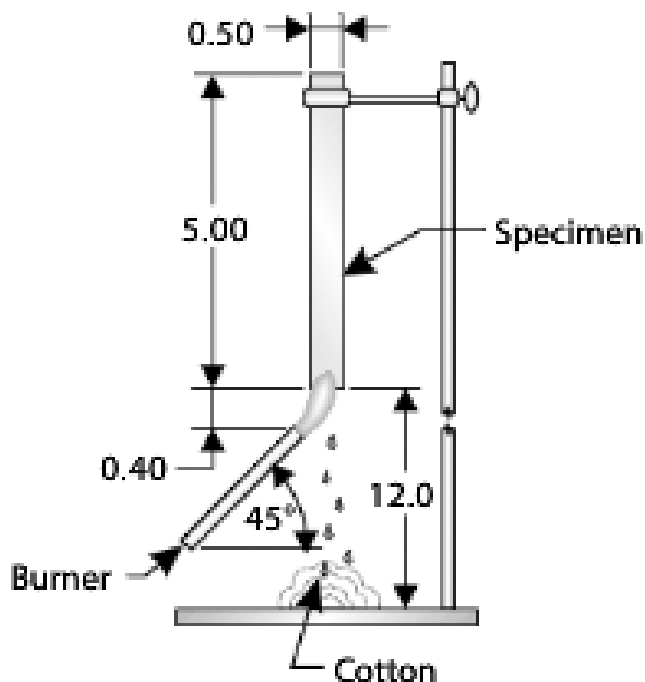


Figure 2.15 : UL-94 vertical flammability test [54].

Table 2.4 : UL-94 vertical flammability test requirements for classifying material.

	V-0	V-1	V-2
Number of flame applications	2×10 s	2×10 s	2×10 s
Max. burning time one specimen	10 s	10 s	30 s
Max. burning time 5 specimens	50 s	250 s	250 s
Dripping ignition of cotton	No	No	Yes
After glow	30 s	60 s	60 s
After glow ignition of cotton	None	None	Yes

2.7.1.2 UL 94 horizontal flammability test

Horizontal burning test is described by ASTM D-635 standard test method. In this test, sample is supported horizontally. This test method generally used when the vertical test cannot distinguish between materials. Horizontal test apparatus is given in Figure 2.16.

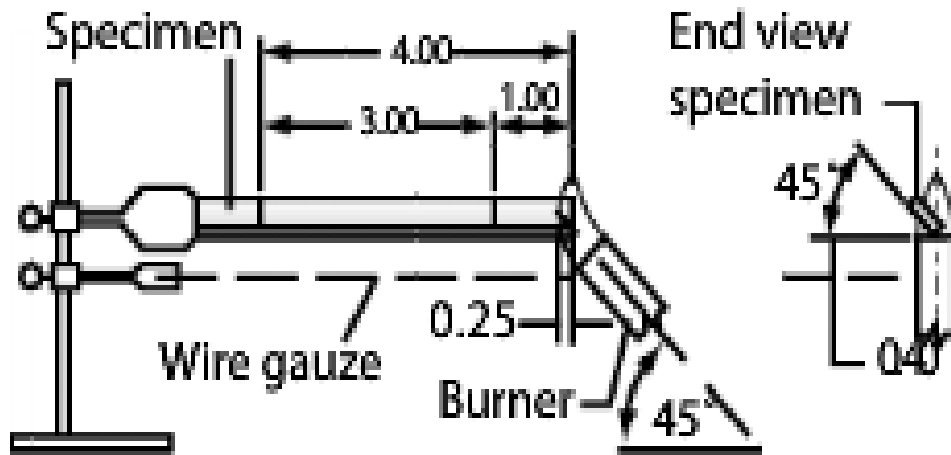


Figure 2.16 : UL-94 horizontal flammability test [64].

2.7.2 Limited oxygen index (LOI) testing

Limiting Oxygen Index (LOI) test is introduced by ASTM D-2863 or BS ISO 4589-2 standard test methods. It is widely used for the determination of the relative flammability of polymeric materials. The oxygen index indicates the minimum concentration of oxygen in a mixture of oxygen and nitrogen that will cause the ignition and flaming combustion of the test material. This test gives information about materials on a numerical basis and promotes the selection of plastic material. Thickness of specimen, fillers, flame retardants are the factors affecting the LOI test result.

The LOI is measured on specimens placed vertically at the center of a glass chimney. Percentages of nitrogen and oxygen in the mixture is determined and then feed to the chimney. Flame is applied to the specimen surface. If the specimen does not ignite in 30s, the concentration of oxygen is then increased and when the specimen shows stable candle-like combustion for more than 3min after the removal of flame source limiting oxygen index is determined [38]. Figure 2.17. shows a schematic diagram and a typical equipment layout [54,55].

LOI value is calculated according to the equation given below:

$$\text{LOI} = \frac{[\text{O}_2]}{[\text{O}_2] + [\text{N}_2]} \times 100 \quad (2.34)$$

Where;

O_2 = Volumetric flow of oxygen at concentration determined

N_2 = Volumetric flow of nitrogen

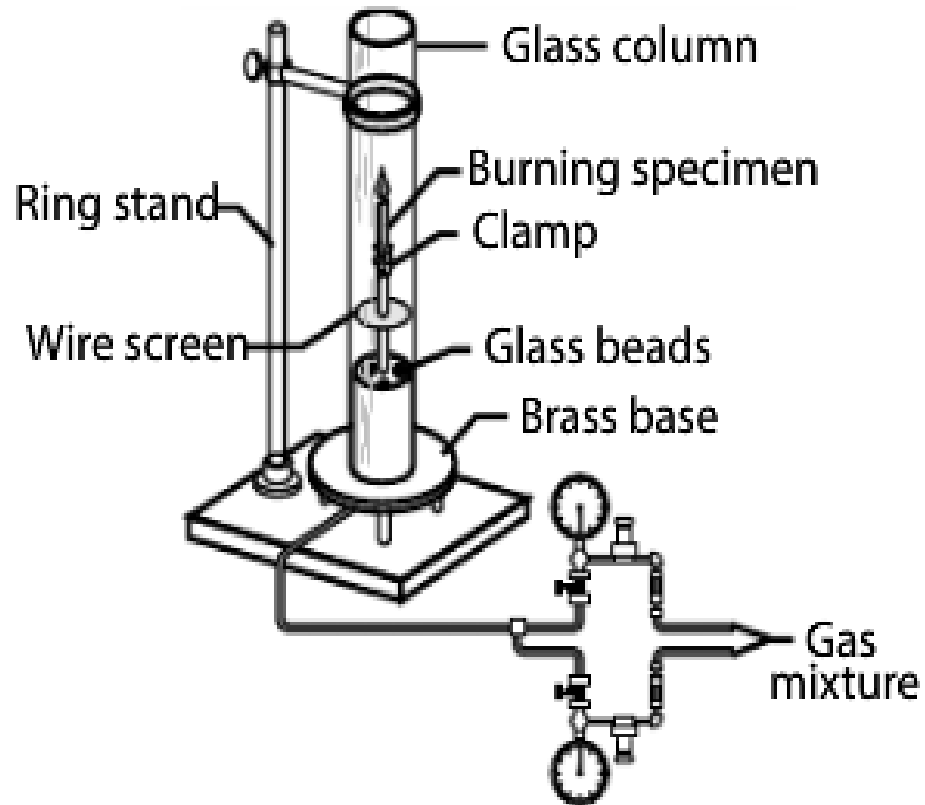


Figure 2.17 : Schematic test set-up of Limiting oxygen index (LOI) test [65].

2.7.3 Glow wire test

Glow wire test (GWT) is used for determination of minimum ignition temperature of material. AS/NZS 4695, ASTM D6194, BS EN 60695 standards are defined this test method. The specimen is pushed against a tip consisting of a U-shaped wire coil heated by an electric current and the minimum ignition temperature is determined [56].

When components use under overload or faulty conditions their performance is effected and the surrounded parts of the component may lead to an ignition of the plastic material in the contact area. Thus, in order to simulate this external thermal stresses glow wire test applies heat or ignition sources such as glowing elements or overloaded resistors to component.

The specimen have passed the glow wire test when there is no flame and no glowing or If flames or glowing of the specimen extinguish within 30 seconds after removal of the glow wire and the surrounding parts and the layer below have not burned away completely [55, 57]. In Figure 2.18, the glow wire test equipment configuration is shown.

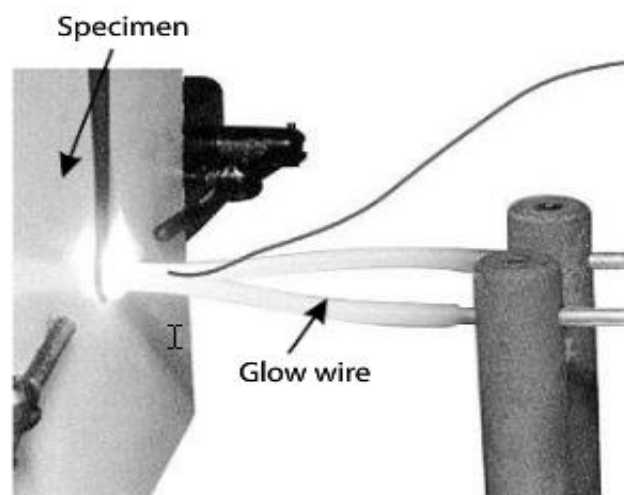


Figure 2.18 : Glow wire test equipment configuration [57].

2.7.4 Thermal gravimetric analysis (TGA)

The thermogravimetric analysis (TGA) is technique use to perform quantitative analyze of polymeric materials in a controlled atmosphere. The main principle is increase the temperature of test ambient and records the mass change of polymer caused by heat to cause physical and chemical reactions. Dehydration, decomposition, or oxidation can cause mass changes under increasing temperature. This test provides accurate quantifications of main components such as plasticizer, polymer and organic species and can also make filler analysis of compounds.

By the help of TGA test, it can be determine when and how the flame retardant mechanism is being activated by comparing the flame retardant polymeric compound with non- flame retardant polymer. In addition, TGA can help to understanding of flame retardancy of polymers by measuring the amounts of residual char. A correlation has been found to an increasing resistance to burning of the polymeric material with increasing amounts of residual char [56, 57].

2.7.5 The cone calorimeter test

Cone calorimeter is described by ISO5660, ASTM E1354 standard test methods. Combustion of material under well-ventilated conditions is examined by cone calorimeter test. Heat release, smoke generation, and mass loss rate of burning materials along with a variety of other parameters related to the combustion of the sample. Heat release rate (HRR), time to ignition (TTI), the maximum value of HRR plotted versus time [peak HRR (PHRR)] and the total amount of heat released during

the combustion process [total heat release (THR)] are the parameters researched with this test.

The sample, a 10cm x 10cm square plaque of thickness between 6 mm and 50 mm is mounted horizontally on a load cell beneath a conical shaped radiant heater. A controlled heat flux range of 0-100 kW/m² is applied to the sample. When the mixture of gases above the test specimen is higher than the lower flammability limit, it is ignited by an electric spark source. Depending of the material the duration of test can change but, it normally continues 10 minutes [56]. In Figure 2.19. the cone Calorimeter test apparatus are shown.

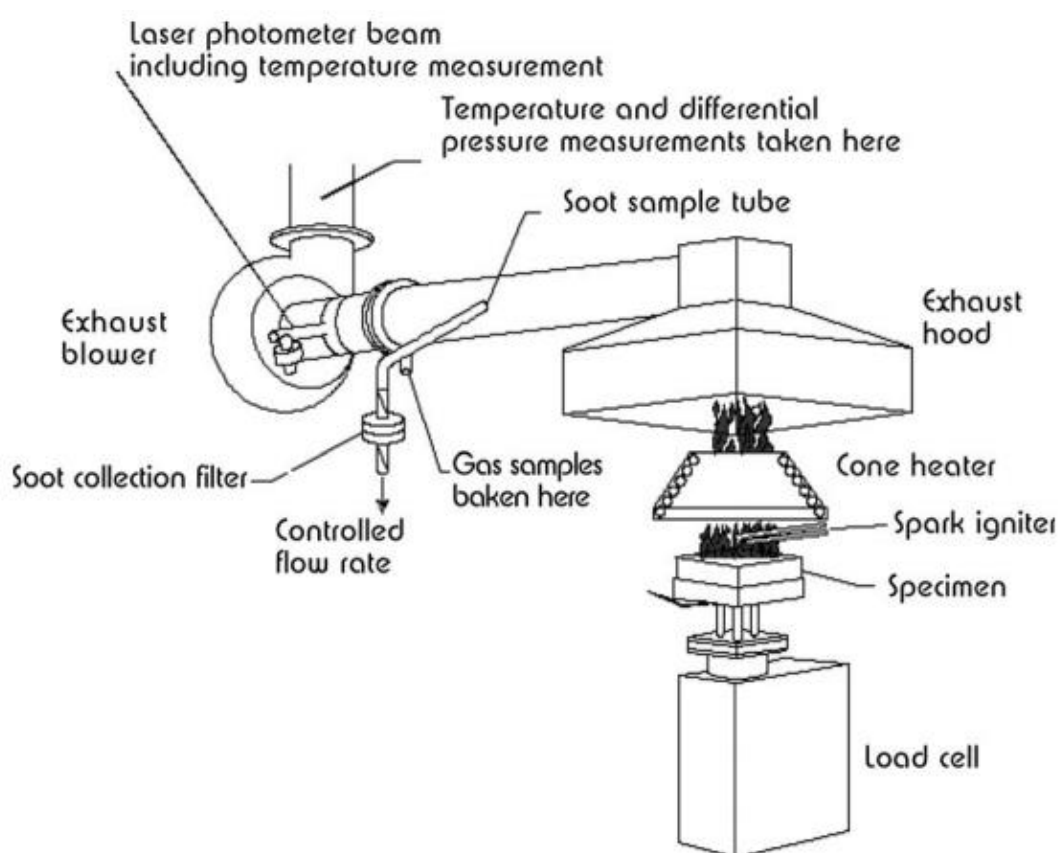


Figure 2.19 : Cone Calorimeter apparatus [56].

2.8 Previous Flammability Studies for PBT Composites

In this section, literature overview about flame retardant PBT compounds is introduced. Several studies on the flame retardancy performance of PBT compounds have been conducted in recent years. The most common flame retardant systems for PBT and PBT compounds are halogenated and antimony source as a synergist, whereas recently halogen-free systems are of interest due to environmental

considerations [58]. In general, phosphorus or phosphorus-nitrogen (melamine) based additives most frequently used as halogen-free flame retardant additives in PBT studies. Also, some recent studies intensely focus on polymers with flame retardants grafted onto the polymer backbone [59, 60].

Ramani and Dahoe investigated comparison between the halogenated flame retardant systems with that of halogen-free flame retardant systems for glass reinforced PBT compound. 10 wt-% of brominated polystyrene used as halogenated formulations, 15 wt-% of aluminium diethyl phosphinate (AlPi) used as halogen-free formulation and 15.5 wt % of AlPi and 2.5 wt-% of natural montmorillonite clay modified with methyl, octadecyl, bis-2-hydroxyethyl quaternary ammonium salt used in formulations. All formulations obtained V-0 UL-94 rating. PBT with brominated flame retardant additives shows an LOI value of 28.0. The addition of AlPi to PBT compound increased the LOI further to 31.5 and addition of a slight amount of natural montmorillonite clay to the combination to formulation increased LOI value further to 35.5. It is concluded that halogen-free formulations are promising alternatives to replace the halogenated flame retardants [61].

A study done by Scharrel et al. looked at the pyrolysis, fire behavior and mechanical properties of a blend of PBT with a PET-P-DOPO which is the flame retardant substance with chemical formula 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide grafted into PET backbone, and compared with PBT/aluminium diethylphosphinate (AlPi) composites. By using this method disadvantages of flame retardant additives such as migration to surface, deterioration of the mechanical properties of the polymer matrix is prevented. PBT 20 % AlPi formulation exhibited a high LOI (45.4) and a V-0 classification in the UL-94 test and PBT 26 % PET-P-DOPO formulation V-2 showed classification and 22.4 LOI value. According to the cone calorimeter test results of PBT/PET-P-DOPO blends were reduced due to flame inhibition (15 %) and charring (8 %) [62].

Hu et al. worked on the fire retardant efficiency of melamine (MA) and triphenyl phosphate (TPP) in PBT by using the LOI and the UL-94 test. PBT blend with 10 % MA and 20 % TPP increased LOI value from 20.9 to 26.6 and achieved UL-94 V-0 rating. Furthermore, SEM and DSC show that MA+TPP is compatible with PBT and accelerates crystallization and increases crystallinity of PBT. TGA results show that MA + TPP blend interacts with PBT and promotes charring [63].

Fang et al. examined the phosphorus nitrogen containing intumescent flame retardant (PeN IFR) PBT compound. PeN IFR was synthesized via the reaction of a caged bicyclic phosphorus (PEPA) compound and 4,4'-diamino diphenyl methane (DDM) in two steps then compounding with PBT. Addition of 20 % PeN IFR shows the ranking reaches V-2 in UL-94 test shows short combustion time and dripping at both the first and second flame application. When the addition level is up to 20 % PeN IFR in PBT, the formulation reaches V-1 ranking but some drips occur at the second application. In formulation 10 % polyurethane (PU) and 20 % PeN IFR added into the PBT, formulation achieved V-0 ranking and dripping were not detected. Results showed that the PeN IFR is an effective flame retardant for PBT, especially when it is used together with PU [64].

Hu et al. studied the performance of environmentally friendly flame retardant nano-clay and aluminum hypophosphite (AHP) additives in glass fiber reinforced PBT (GRPBT) composite. The commercial exfoliated nano-clay with particle size of less than 50 nm was the product of Na⁺-Montmorillonite ion-exchanged with methyl tallow bis(2-hydroxyethyl) ammonium, where tallow was a mixture of ~65 % C18, ~30 % C16, ~5 % C14. They were fabricated through melt blending process. Thermal combustion properties of GRPBT composites were characterized by microscale combustion calorimetry. Compared with neat GRPBT, while the HRC and THR value of 20 % AHP composites were decreased by 42 % and 33 %, 5 % nanoclay with 15 % AHP composites values were reduced by 51 % and 34 % respectively. While neat GRPBT LOI values was 22, 15 % AHP and 20 % AHP containing composites LOI values were increased to 28 and 29, respectively. While 20 % AHP composites achieved V-1 rating, 15 % AHP and 5 % nano-clay containing composites achieved V-0 rating in UL-94 test. Also, it is indicated that the incorporation of AHP and nano-clay in glass fiber reinforced PBT provided improvements in elastic modulus [65].

Schartel and Braun investigated the flame retardancy mechanisms of aluminium diethylphosphinate (AlPi) and its synergist effectiveness with melamine cyanurate (MC) in 30 % glass fiber reinforced PBT (GRPBT). The combined flame retardant material contained a total of 20 % of the flame retardant mixture. For the materials containing AlPi, increased LOI values of 43 were achieved for PBT/GF-AlPi and PBT/GF-AlPi-MC, respectively. The decomposition behavior was analyzed and it is

shown that during the decomposition of polyester composite, diethylphosphinic acid was formed and released to the gas phase. In consequence of the diethylphosphinic acid formation a slight amount of carbon char was induced. Aluminium phosphates also remained in residue. The MC decomposed mainly independently of the polymer and the phosphinate salt to fuel dilution gases (isocyanic acid, carbon dioxide). According to the cone calorimeter tests, a dominant gas-phase action was examined for the composites containing aluminium phosphinate. Also, it is indicated that MC influenced the results of combustion tests through a fuel dilution effect [66].

Gong et al. studied the reducing of fire hazards of PBT by synthesizing the manganese–cobalt oxide/graphene hybrids. The cone test results had showed that peak HRR and SPR values of manganese–cobalt oxide/graphene hybrids composites were lower than that of pure PBT and cobalt oxide (Co_3O_4) composites. Furthermore, the incorporation of manganese–cobalt oxide/graphene hybrids gave rise to apparent decrease of pyrolysis products containing aromatic compounds, carbonyl compounds, carbon monoxide and carbon dioxide, attributed to combined impact of physical barrier for graphene for organic volatiles and carbon monoxide. Organic volatiles and CO were deeply oxidized to non-flammable and non-toxic CO_2 by MnCo_2O_4 –graphen hybrids, which would reduce the toxicity of pyrolysis products, thus benefiting fire rescues [67].

Schartel et al. investigated the flame retardancy of PBT flame retardant composite which containing aluminium diethylphosphinate (AlPi) and/or nanometric metal oxides such as TiO_2 or Al_2O_3 . Decomposition behaviour was analysed by thermogravimetry; evolved gas analysis and residue analysis; fire behaviour was analysed by flammability tests, cone calorimeter measurements, and the chemical analysis of residue. According to the analyses, AlPi acts mainly in the gas phase through the release of diethylphosphic acid, which provides flame inhibition. Part of AlPi remains in the solid phase reacting with the PBT to phosphine terephthalate salts that decompose to aluminium phosphate at higher temperatures. Furthermore, the metal oxides interact with the PBT decomposition and promote the formation of additional stable carbonaceous char in the condensed phase. In UL 94 test, a combination of metal oxides and AlPi provide the better classification. When the AlPi is combined with metal oxide nanoparticles, the fire performance of PBT improves; in particular a V-0 classification is achieved using only 10-8 wt-% of AlPi

and small percentages of nanoparticles. The combination of efficient flame inhibition due to the release of phosphorus and a solid-phase action by the metal oxide is postulated. A good dispersion of small percentages of nanometric mineral fillers into PBT seems to be promising in terms of better fire retardant performance, allowing the reduction of the higher levels of flame retardant additive normally required to achieve a good fire classification in terms of UL-94, LOI and cone calorimeter [68].

Even the main matrix is not PBT, Kılıç et al. studied the performance of boron based and phosphorus based flame retardant additives on poly(ethylene terephthalate) (PET) matrix. In the study, 3.5 mole hydrated zinc borate and boron phosphate were synthesized and different combinations of triphenyl phosphate, triphenyl phosphine oxide, zinc borate and microwave produced boron phosphate were used in PET matrix and characterized. According to smoke density test results, boron phosphate is an efficient smoke suppressant for PET. It liberates $\bullet\text{O}$ radical during the decomposition, and that radical reacts with carbon monoxide and the other partially burnt decomposition products to transform them to the less combustible carbon dioxide. Furthermore, it was indicated that triphenyl phosphate and triphenyl phosphine oxide increased significantly the impact strength of PET. For triphenyl phosphate additive, it is also mentioned that up to ten weight percent loading, it acts as chain extender and beyond this percentage, it acts as plasticizer. According to the LOI test results, LOI of neat PET was determined as 21 %, and with the addition of 5 % triphenyl phosphate LOI was increased to 29.5 [69].

3. EXPERIMENTAL

3.1 Materials

3.1.1 Poly(butylene terephthalate) (PBT)

Poly(butylene terephthalate) (PBT) was used as a main polymer matrix, grade Advanite 53002 from SASA Company, Adana, Turkey with the melt flow index of 22 g/10 min (MFI; 250 °C / 2.16 kg) and melting temperature 220 °C.

3.1.2 Glass fiber (GF)

E- glass type glass fiber was used as a reinforcement material in PBT matrix. It was supplied from Nippon Electric Glass Co. Its filament diameter is 13 µm and strand length is 3 mm.

3.1.3 Flame retardant additives

Zinc borate, which is a white crystalline or amorphous powder, was supplied from MELOS A.S. Its particle size range from 5 to 45 µm.

Triphenyl phosphate was purchased from Acros Organics with 98 % purity. Its chemical formula is $C_{18}H_{15}O_4P$ and melting point is 47-53 °C. In Figure 3.1. chemical structure of TPP is shown.

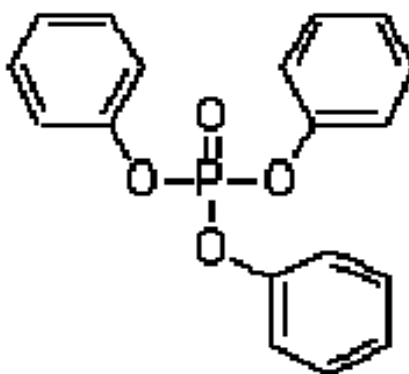


Figure 3.1 : Chemical structure of Triphenyl phosphate (TPP).

Calcium sulphate dihydrate was purchased from Fisher company with 98 % purity. Its chemical formula is $CaO_4S.2H_2O$, and chemical structure is shown in Figure 3.2.

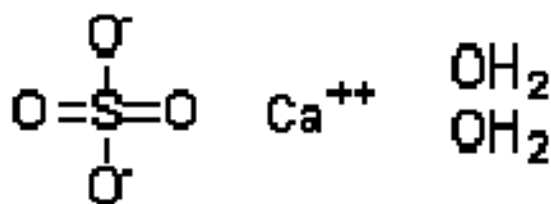


Figure 3.2 : Chemical structure of calcium sulphate dihydrate (CSD).

Boron phosphate was purchased from Changzhou Zhongyo Chemical Co. Its chemical formula is BO_4P and chemical structure is shown in Figure 3.3.

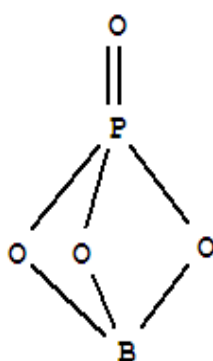


Figure 3.3 : Chemical structure of boron phosphate (BP).

3.2 Equipment

3.2.1 Twin-screw extruder

In this study, PRISM TSE24 IIC twin-screw extruder was used for the preparation and melt mixing of all the flame retardant composites. The extruder equipment are; three Brabender DSR28 gravimetric feeders, degassing port connected to the Edwards rotary vacuum pump by hoses, water bath and fixed length pelletizer or chopper. It has seven modular barrel segments with length of 96 mm or 4D. In order to control melt temperature at the 3rd, 5th, and 7th zone of barrel up to the internal surface to melt thermocouples are exist. Electrical resistances and water cooling channels are controlled by thermoregulator. Degassing unit is connected to the Edwards rotary vacuum pump by hoses at the 6th barrel zone to remove gasses which consist of during compounding. PRISM TSE24 IIC Twin-screw extruder is shown in Figure 3.4 and in Table 3.1 PRISM TSE24 twin screw extruder specifications are given.



Figure 3.4 : Twin screw extruder.

Specifications of the twin screw extruder is represented in Table 3.1.

Table 3.1 : PRISM TSE24 Twin screw extruder specifications.

	Units	PRISM TSE24
Screw diameter	mm	24
Typical output	kg/h	2 to 50
Maximum screw speed	rpm	1000
L/D (shaft length/screw diameter)	-	28:1
Channel depth	mm	5.15
Screw diameter/channel depth	-	5.15
Screw/barrel clearance	mm	0.2
Shaft center line distance	mm	18.75
Shaft center line/radius ratio	-	1.5625
Free area	cm ²	3.8
Total volume	cm ³	511
Free volume	cm ³	228
Barrel peripheral surface area	cm ²	830
Surface area/total volume	m ² /liter	0.14
Surface area/Free volume	m ² /liter	0.31
Free area	cm ²	3.8
Total volume	cm ³	511
Max. channel shear rate @ 1000 rpm	s ⁻¹	244
Max. power	kW	9
Max. torque/shaft	Nm	43
Max. channel shear rate @ 1000 rpm	s ⁻¹	244

Spaghetti form of polymer obtained from extruder die to cooling water bath. They are cut into small pieces called granules by the fixed length Prism granulating unit as shown in Figure 3.5.



Figure 3.5 : Prism granulating unit.

3.2.2 Injection molding machine

Arburg Allrounder 320 °C injection machine is shown in Figure 3.6. It was used to mold flame retardant composites in order to produce sample for the characterization tests. Injection unit equipment are; hopper, heat controlled barrels-cylinder, screw and motor. Injection molding is defined as a process where melt polymer forced into a mold cavity and cooled down in it by taking its shape. A plastic injection machine is mainly divided into three parts which are known as mold, clamping unit and injection unit. Polymeric materials are in the form of pellets and they are loaded into a hopper on top of the injection unit during the injection process. The pellets are fed into injection machine from feeding hopper and heated until they melt. In Table 3.2 technical properties of Arburg injection machine are given.



Figure 3.6 : Arburg Allrounder 320 °C injection machine.

Table 3.2 : Technical properties of Arburg injection machine.

	Unit	
Screw diameter	mm	30
Max. injection pressure	bar	1068
Max. volumetric displacement	cm ³	71.4
Wax. Shot weight	g	70
Hydraulic motor power	W	1800
Max. clamping force	tonnes	30
Max. screw speed	rpm	115
Screw back pressure	bar	25

A water cooling chiller; Piovan ST092 was used to kept mold temperature constant at 60 °C during the injection process.

3.2.3 Ash test

Ash test is used to determine the total filler content. Test comprise taking a known amount of sample, placing the weighed sample into a dried / pre-weighed porcelain crucible, burning away the polymer in an air atmosphere at temperatures above 500 °C, and weighing the crucible after it is has been cooled to room temperature in a desiccator. Ash residue remaining in the crucible is considered filler.

3.2.4 Pyknometer

The densities of specimens were measured with AccuPyc 1330 Pyknometer. The machine is shown in Figure 3.7.



Figure 3.7 : Pyknometer illustration.

3.2.5 Scanning electron microscopy (SEM)

Investigation of the morphology of PBT compounds was done by a scanning electron microscope (Zeis Supra 55VP) as shown in Figure 3.8



Figure 3.8 : Scanning electron microscopy (SEM).

3.2.6 Tensile test machine

Tensile tests were performed by using Zwick universal tensile testing machine Z020 equipped with 20 kN load cell as load indicator and long stroke extensometer as extension indicator.

3.2.7 Three point bending test machine

Flexural properties of PBT composites were measured by using Instron 4505 universal testing machine equipped with 10 kN load cell as load indicator and three point bending fixture.

3.2.8 Izod impact test machine

Izod impact strength of PBT composites was measured by using Zwick/Roell Izod impact machine. The test machine is shown in Figure 3.9.



Figure 3.9 : Izod impact testing machine.

3.2.9 Hardness test

Hardness values of the composites were determined with a Shore D hardness tester, TH210. A representative picture of hardness test is given in Figure 3.10.



Figure 3.10 : Shore D Hardness test device.

3.2.10 Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) were performed by using Q500 thermal gravimetric analyzer. The test machine is shown in Figure 3.11



Figure 3.11 : Thermal gravimetric analyzer.

3.2.11 Limiting oxygen index (LOI) flammability tester

This test was carried out by using limiting oxygen index test apparatus which consists of test chimney, specimen holders, gas measurement and control devices, flame igniter, timing device, fume extraction system, and gas supplies. The oxygen

index test measures the minimum concentration of oxygen, expressed as volume percent, in a mixture of oxygen and nitrogen that will just support combustion of a material under the conditions specified in the test method. In Figure 3.12 limiting oxygen index tester is shown.



Figure 3.12 : Limiting oxygen index tester.

3.2.12 Glow wire tester

PTL Glow – wire test apparatus is using to determine the fire resistance of polymeric material by for glow wire test. PTL Glow wire test equipment are; glow wire, thermocouple, temperature indicator, supply circuit, test fixture, indicator board and test chamber. In Figure 3.13 the glow wire tester is shown.

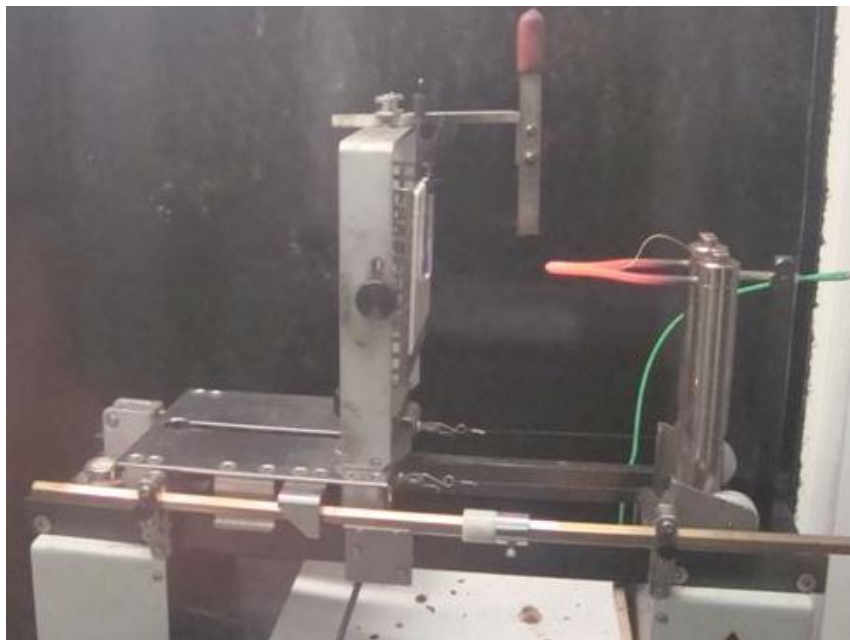


Figure 3.13 : Glow wire tester.

3.3 Experimental Procedure

3.3.1 Composite formulations

Flame retardant systems are blended with glass fiber reinforced and unreinforced PBT compounds by using co-rotating twin-screw extruder. In all sets of experiments, PBT was dried prior to mixing in extrusion in order to prevent the hydrolytic degradation during extrusion. After drying they were mixed in a twin screw extruder and pelletized. The flame retardant formulations of PBT and 30 % glass fiber reinforced PBT (GF-PBT) composites are given Table 3.3. and Table 3.4. respectively. The percentage of GF in PBT was chosen due to the preferences of electrical and electronic appliances industry. They prefer 30 % GF to add PBT.

Table 3.3 : Formulations of PBT composites.

Sample	ZB	BP	TPP	CSD	PBT	Glass Fiber
PBT0	-	-	-	-	100	-
PBT1	5	-	-	-	95	-
PBT2	-	5	-	-	95	-
PBT3	-	-	5	-	95	-
PBT4	-	-	-	5	95	-
PBT5	-	-	-	10	90	-
PBT6	5	5	-	-	90	-
PBT7	2.5	2.5	-	-	95	-
PBT8	-	5	5	-	90	-
PBT9	-	2.5	2.5	-	95	-
PBT10	-	-	10	-	90	-
PBT11	-	10	-	-	90	-

Table 3.4 : Formulations of glass fiber reinforced PBT composites.

Sample	ZB	BP	TPP	CSD	PBT	Glass Fiber
GF0	-	-	-	-	70	30
GF1	5	-	-	-	65	30
GF2	-	5	-	-	65	30
GF3	-	-	5	-	65	30
GF4	-	-	-	5	65	30
GF5	-	-	-	10	60	30
GF6	5	5	-	-	60	30
GF7	2.5	2.5	-	-	65	30
GF8	-	5	5	-	60	30
GF9	-	2.5	2.5	-	65	30
GF10	-	-	10	-	60	30
GF11	-	10	-	-	60	30

3.3.2 Compounding procedure and compounding process parameters

The PBT was fed into extruder from inlet zone with using first feeder. Glass fiber were fed into extruder from second (side feeder) feeder. The mixtures flame retardants were fed into extruder from third feeders. The feeders were calibrated to obtain weight percent metering. In all formulations, processing aid, which is ester of montanic acids with multifunctional alcohols, was used in order to decrease the torque of extruder during compounding. The compounded materials were taken from the extruder via the holes of the die and cooled down in water bath and the pelletized by pelletizer. The properties of final product are affected process parameters that are known as temperature, screw speed etc. Extruder screw speed kept constant at 100 rpm and feeding rate kept constant at 4 kg/h for all formulations. Compounding process temperature parameters are given in the Table 3.5. Process parameters were chosen according to the literature survey. It is know that while low extrusion rate cause polymer degradation, high extrusion rate cause sharkskin surface on output which know as surface defect result of flow rate increases in extrusion proses. Moreover, temperature parameters were selected so as not to cause degradation. Thus, optimal process parameters were used and they did not cause any polymer degradation or sharkskin effects. All the process parameters were kept constant in order to prevent the negative effects.

Table 3.5 : Extruder process temperature parameters.

Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7	Zone 8
40	235	250	250	250	250	240	230

3.3.3 Injection molding machine and process parameters

After extrusion process in order to the give the shape of test samples, pellet form of PBT compounds are loaded into a hopper of injection unit. Test specimens in terms of tensile test, three point bending test, impact test, hardness test and also the flammability tests were produced with Arburg Allrounder 320 °C injection machine according to ISO standards. General process parameters and illustration of injection molding machine are given Figure 3.14. The process parameters of injection molding machine were chosen according to literature survey and kept constant so as to prevent the negative effects. These process parameters were optimized in order not to experiencing the flush and shrinkage problems.

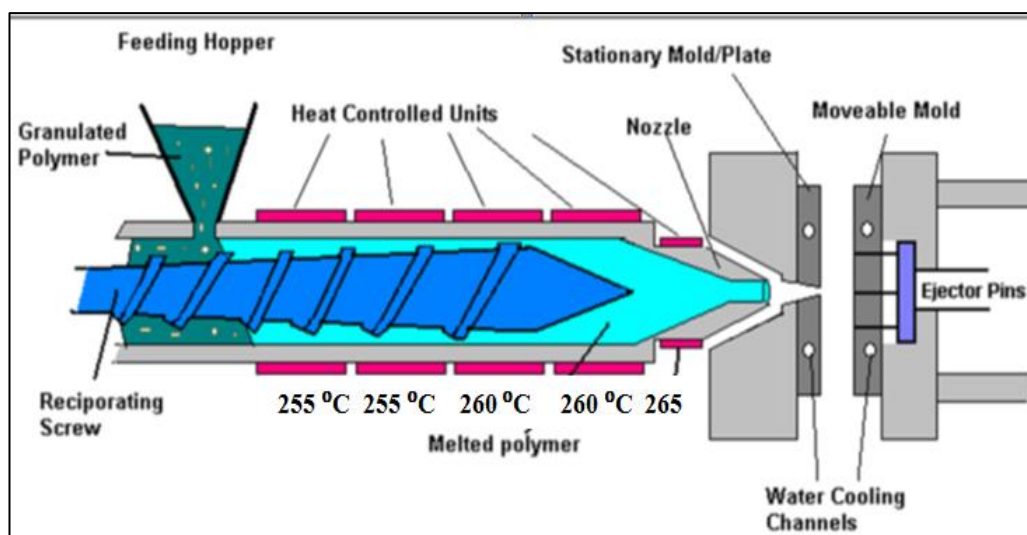


Figure 3.14 : General process parameters and illustration of injection molding machine.

3.4 Characterization Experiments

3.4.1 Structural and morphological properties

3.4.1.1 Ash Content analysis

An ash test is used to determine the total filler content. Ash content of specimens were measured according to ASTM D2584 standard. First, a known amount of sample was taken in porcelain crucible, then burning away the polymer in an air atmosphere at temperatures at 600 °C, then it was cooled to room temperature in a desiccator and weighted. The ash test result is expressed as percent ash.

3.4.1.2 Measurement of density

The density of specimens was measured according to the ISO 1183 test standard [70]. The specimen was weighed in the air first and then placed in the AccuPyc 1330 pyknometer. The volume of specimens was calculated using this machine by first vacuuming the air in the measuring vessel and then filling up the vessel with nitrogen (N₂).

3.4.1.3 Scanning electron microscopy (SEM) analysis

The aim is to examine the interface between PBT and glass fiber particles and dispersion of flame retardants in the matrix. Injection molded test bars having dimensions of 4 ± 0.2 mm, 10 ± 0.2 mm, 80 ± 0.2 mm were left in a desiccator for at

least 48 hours to get rid of post crystallization or physical aging and any hydrolysis effect. 2 mm notched test specimens were submerged in liquid nitrogen for 2 hours and broken with a sudden impact. The fractured surfaces were coated with carbon before the SEM investigation to provide electro conductivity.

3.4.2 Mechanical properties

3.4.2.1 Determination of tensile properties

Tensile tests were performed according to ASTM D638M-91a test standard. Testing speed was set to 5mm/min and gauge length (L_0) was set to 70 mm. Averages of 5 specimens were reported. Tensile test sample is indicated in Figure 3.15 and test specimen dimensions are indicated in Table 3.6. Test specimens were conditioning before testing. They were waited in a heat and humidity controlled room for 48 hours to prevent the specimens from the post crystallization or physical ageing effects (at 23 ± 2 °C and 50 % humidity). Tensile stress, tensile strain, elastic modulus values are obtained by tensile test.

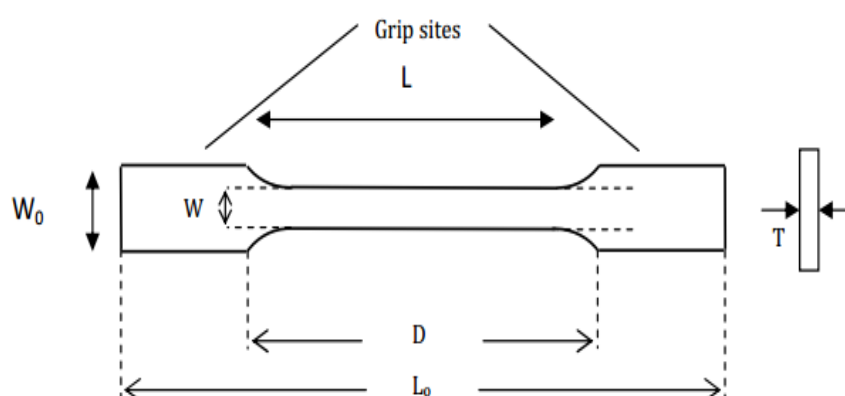


Figure 3.15 : Tensile test specimen

Table 3.6 : Tensile test specimen dimensions.

Dimensions	Specimen Dimensions (mm)
L_0 – overall length	75
W – width of narrow section	5
L – length of narrow section	30
W_0 – width of overall	10
D – distance between grips	50
T – thickness	2.1

The thickness and width within the parallel portion of specimens were measured by a screw micrometer reading at least 0.02 mm. After the measurement, the specimen was fixed to self-aligning grips of the tensile test machine with a distance of 123 mm between grips. The extensometer was attached to the specimen over the parallel portion of the grip and the machine was started. The loads and corresponding deformations were recorded at the time interval of 0.2 seconds.

Tensile properties were measured as follow:

- Tensile stress or yield stress is indicated as σ_y (tensile load per unit area of original cross section within the narrow parallel portion). Tensile stress expressed in Newton per square millimeter (N/mm^2) is the first point on the load / extension curve at which an increase occurs without an increase in load.
- Tensile strain or percentage elongation at yield is indicated as ϵ_y . Tensile strain is the percentage elongation corresponding to tensile point.
- Elastic modulus or Young modulus is calculated from the slope of the line in this region where stress is proportional to strain [71].

3.4.2.2 Determination of flexural properties

In order to measure the flexural properties of samples Instron 4505 universal testing machine, which equipped with 10 kN load cell as load indicator and three point bending fixture is used. Three point bending test is shown in Figure 3.16. Test was performed according to ISO 178 standard. Test specimens were conditioning before testing for 48 hours (at 23 ± 2 °C and 50 % humidity). Test dimensions are of 4 ± 0.2 mm, 10 ± 0.5 mm, 80 ± 0.5 mm. Span of two lower arms of bending fixture was set to 60 mm. Testing speed was set to 1 mm/min and the extension was measured from travel of traverse of testing machine. According to the test following properties are calculated [72].

-Flexural stress (σ_f) calculated as following equation:

$$\sigma_f = (3 \times F \times L) / (2 \times b \times h^2) \quad (3.1)$$

F: applied load (MN)

L: span length

b: width

h: thickness of specimen

Flexural stress is express in megapascal (MPa) or newton per square millimeter (N/mm²).

-Flexural modulus or apparent modulus of elasticity (E_b) is calculated as following equation. It is calculated from linear portion of the load extension curve by using at least five values of the deflection and load.

$$E_b = (L^3 \times F) / (4 \times b \times h^3 \times Y) \quad (3.2)$$

E_b : Flexural modulus (N/mm²)

L: span length (m)

b: width of specimen (m)

h: thickness of specimen (m)

F: load at chosen point (N)

Y: deflection corresponding to load F (m)

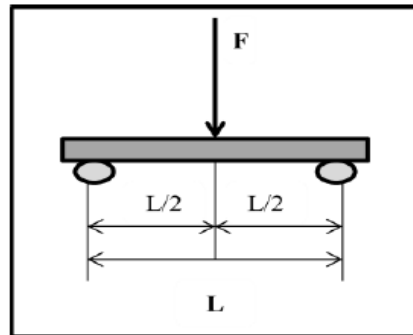


Figure 3.16 : Three point bending testing illustration.

3.4.2.3 Determination of Izod impact strength

Zwick/Roell Izod impact machine were used to measure Izod (notched) impact strength of specimens. Test was performed according to the ISO 180 standard [73]. Test specimens dimensions are 4 ± 0.2 mm, 10 ± 0.2 mm, 80 ± 0.2 mm and they were conditioning before testing for 48 hours (at 23 ± 2 °C and 50 % humidity). 2 mm notch with notch base radius 0.25 ± 0.05 mm was machined at mid-span of specimen. Before testing the specimens, blank test was performed to ensure the total friction losses.

The notched surfaced of the specimen should face to the pendulum in the test machine. The pendulum was released and impact energy was recorded and calculated as follow:

$$\text{Izod Impact Strength} = A_k / (X \times Y_k) \times 10^3 \quad (3.3)$$

A_k : impact energy (J)

X : thickness (m)

Y_k : difference of width and notch depth (m)

3.4.2.4 Determination of Hardness values

Hardness values of the composites polymers were determined with a Shore D hardness tester, TH210 according to ASTM D2240 test standard.

3.4.3 Thermal and flame retardant properties

3.4.3.1 Determination of thermal stability

Thermal gravimetric analysis (TGA) of PBT composites were carried out by using Q500 thermal gravimetric analyzer from 20 °C to 800 °C at a heating rate 20 °C/min. Nitrogen was used as a carrier gas with a constant flow rate during analysis.

3.4.3.2 Determination of oxygen index

The oxygen index test measures the minimum concentration of oxygen, expressed as volume percent, in a mixture of oxygen and nitrogen that will just support combustion of a material under the conditions specified in the test method. A concentration of O₂ greater than that required to sustain combustion is first measured; from that point on, the oxygen is decreased at a slow rate until the flame is extinguished [74].

3.4.3.3 Determination of glow wire temperature

Test specimens were kept at temperature of 23 ± 2 °C and 50 ± 5 % relative humidity for at least 40 hours prior to testing. Thickness of specimens must be 0.25 mm or greater than 6.4 mm. The specimen was mounted in the test so that the surface that comes in contact with the tip of the glow-wire was vertical and any losses to supporting means were insignificant. The pre-selected glow-wire temperature was maintained for at least 60 seconds prior to conducting the test. The specimen was brought in contact with the tip of the glow-wire at an applied force of 1.0 ± 0.2 N for 30 ± 1 s. For the purpose of this test, ignition will be deemed to have occurred if either sustained flaming occurs or the tissue paper on the indicator board placed underneath the apparatus exhibits flames caused by particles falling from the test specimen [75].

4. RESULTS AND DISCUSSION

Since the aim of the project obtained high flame retardancy with high mechanical properties, different flame retardant additives were used with different combinations to see any further improvement when they used together. In experimental part flame retardant fillers were used with unreinforced PBT and then 30 % glass fiber reinforced PBT.

In the first part PBT composites were produced according to the Table 3.3 formulations. In order to see effectiveness of four flame retardant additive with low loading level (5 %) PBT1, PBT2, PBT3, PBT4 (ZB, BP, TPP, and CSD) formulations produced. PBT0 were used as a reference for PBT flame retardant composites and it did not contain flame retardant additive. PBT5, PBT9, PBT10 formulation was prepared in order to analyses higher loading effect of CSD, TPP and BP respectively. Since 5 % ZB did not show any improvement compare to reference, higher loading of ZB did not perform.

In the second part PBT composites, all PBT formulations were performed with glass fiber reinforced PBT composites (GF series). These formulations were represented in Table 3.4. In these set of formulations, it was analyzed both mechanical effects of glass fiber reinforcement and flame retardant filler behavior in the glass fiber reinforced PBT composites. GF0 were used as a reference for GF-PBT and PBT composites and it did not contain flame retardant additive.

In order to optimize the mechanical and flame retardancy properties together, TPP-BP and ZB-BP binary combinations prepared in PBT and GF-PBT composites.

The prepared 24 samples of PBT and glass fiber reinforced PBT (GF series) composites from the point of view of flammability, thermal, mechanical, and morphological characterizations are given and discussed together in the following sections. Flammability of composites was determined by using a limiting oxygen index (LOI) and glow wire test (GWT). Mechanical properties such as tensile strength, elastic modulus, flexural strength, Izod impact and were also studied.

4.1 Structural and Morphological Properties Results

4.1.1 Ash content analysis

Ash contents analysis of PBT composites were done according to the procedure explained in section 3.4.1.1. Experimental ash content test results of PBT samples and GF-PBT samples are shown in Table 4.1 and Table 4.2 respectively. In order to control formulations percentages of contents after extrusion and injection process, TGA test of flame retardant additives were performed and expected inorganic contents were calculated. In TGA analysis, which will explain in section 4.3.1, inorganic content of ZB, BP, TPP, CSD were obtained weight percentages of 86 %, 88 %, 0 %, 80 % at 600 °C respectively. According to TGA results, formulations expected inorganic contents were calculated. When test results are analyzed, it can be say that ash test results complied with expected inorganic contents of formulations.

Table 4.1 : Ash test results of PBT composites.

Samples	Ash (%)	Expected (%)
PBT0	0.0	0.0
PBT1	4.3	4.3
PBT2	4.5	4.4
PBT3	0.1	0.0
PBT4	4.0	4.0
PBT5	6.3	8.0
PBT6	8.7	8.7
PBT7	4.1	4.4
PBT8	4.0	4.4
PBT9	2.5	2.2
PBT10	0.1	0.0
PBT11	9.7	8.8

In order to calculate glass fiber reinforced composites expected inorganic content, TGA results of flame retardants summed with glass fiber percentage for each formulation. Measurements technique has ± 0.05 % in the standart.

Table 4.2 : Ash test results of glass fiber reinforced PBT composites.

Samples	Ash (%)	Expected (%)
GF0	29.5	30.0
GF1	35.6	34.3
GF2	33.9	34.4
GF3	30.0	30.0
GF4	32.3	34.0
GF5	38.4	38.0
GF6	40.1	38.7
GF7	34.2	34.4
GF8	33.7	34.4
GF9	33.8	32.2
GF10	28.9	30.0
GF11	36.8	38.8

4.1.2 Measurement of density

Measurement of density was done as defined in section 3.4.7. The PBT composites test results are given in Table 4.3 and Figure 4.1. According to test results, neat PBT has a density of 1.32 g/cm³, and flame retardant PBT composites have similar density results which changing between the range of 1.23 - 1.40 g/cm³. In Table 4.4 and Figure 4.2 GF- PBT composites density results are given. When 30 % glass fiber added to PBT matrix, density value increased to 1.54 from 1.32 (PBT0, GF0). In addition, GF series composites density values were changing between the ranges of 1.54-1.65 g/cm³.

Table 4.3 : Density test results of PBT composites.

Samples	Density (g/cm ³)
PBT0	1.32
PBT1	1.36
PBT2	1.23
PBT3	1.32
PBT4	1.36
PBT5	1.38
PBT6	1.40
PBT7	1.35
PBT8	1.33
PBT9	1.34
PBT10	1.33
PBT11	1.40

Table 4.4 : Density test results of glass fiber reinforced PBT composites.

Samples	Density (g/cm ³)
GF0	1.54
GF1	1.61
GF2	1.59
GF3	1.58
GF4	1.58
GF5	1.65
GF6	1.65
GF7	1.61
GF8	1.59
GF9	1.61
GF10	1.54
GF11	1.63

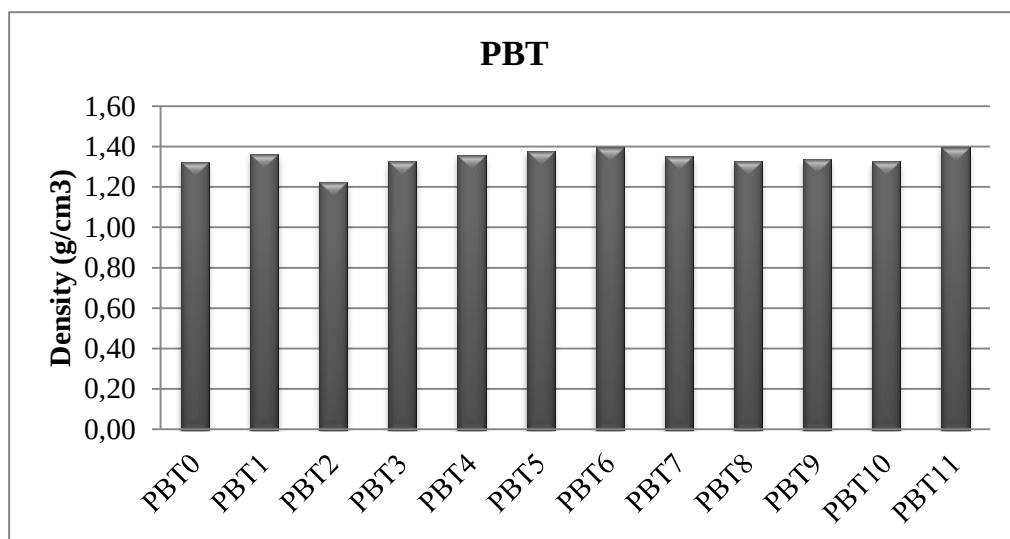


Figure 4.1 : Density measurement results of PBT composites.

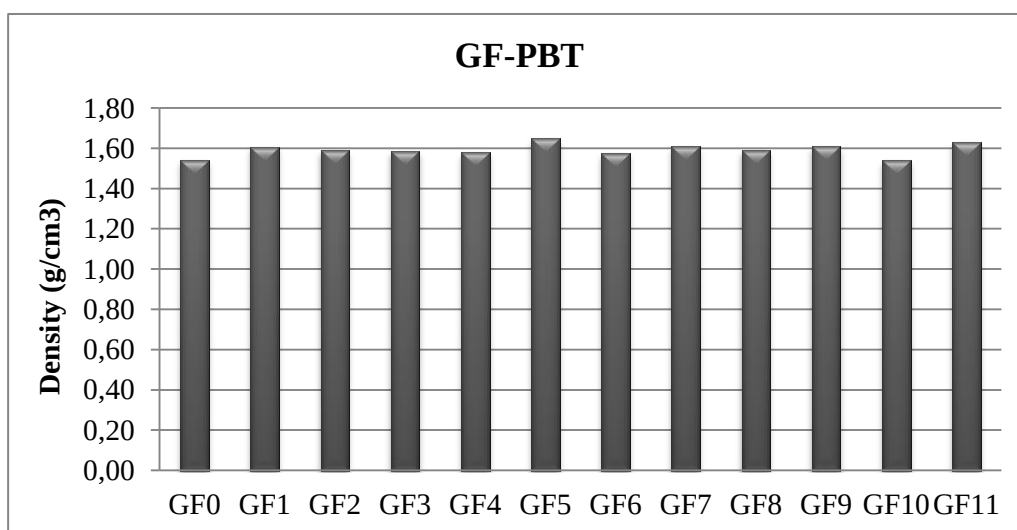


Figure 4.2 : Density measurement results of glass fiber reinforced PBT composites.

4.1.3 Scanning electron microscopy (SEM) analysis

Scanning electron microscopy analysis was carried out for glass fiber reinforced PBT composites samples by the procedure given in Section 3.4.1.3. Figure 4.3 to Figure 4.8 show the SEM micrographs of GF-PBT (GF series) composites. SEM observations showed that glass fibers were well dispersed in PBT matrix during extrusion and polymer matrix wrapped the fibers.

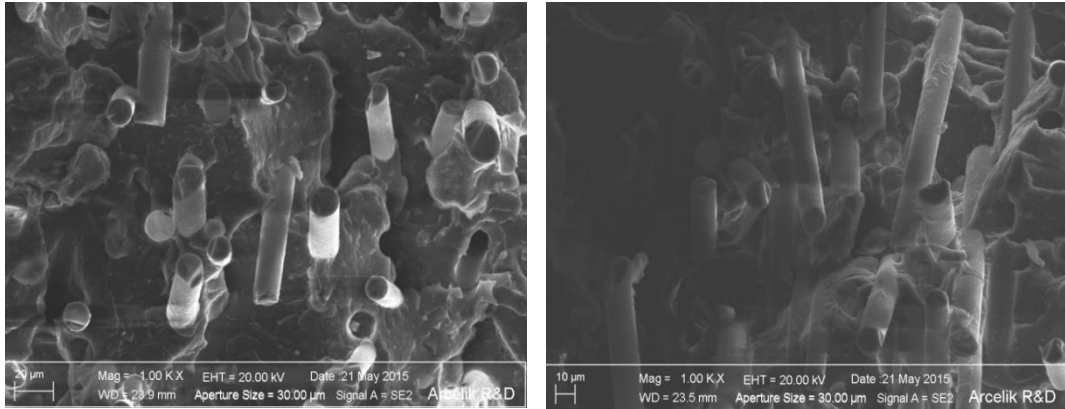


Figure 4.3 : SEM micrographs of a) GF0, b) GF1

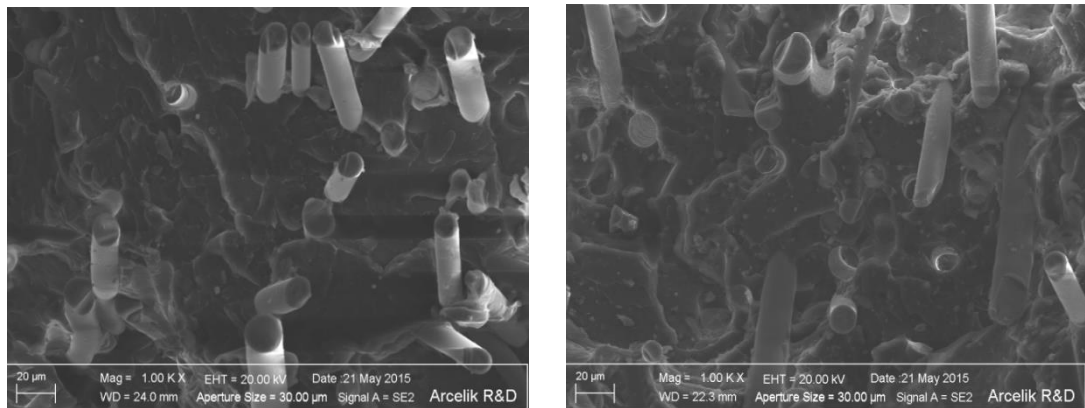


Figure 4.4 : SEM micrographs of a) GF2, b) GF3

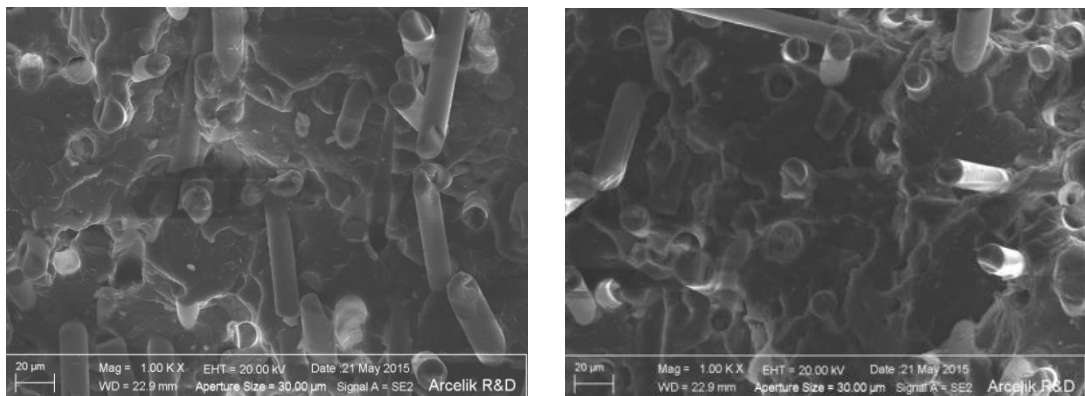


Figure 4.5 : SEM micrographs of a) GF4, b) GF5

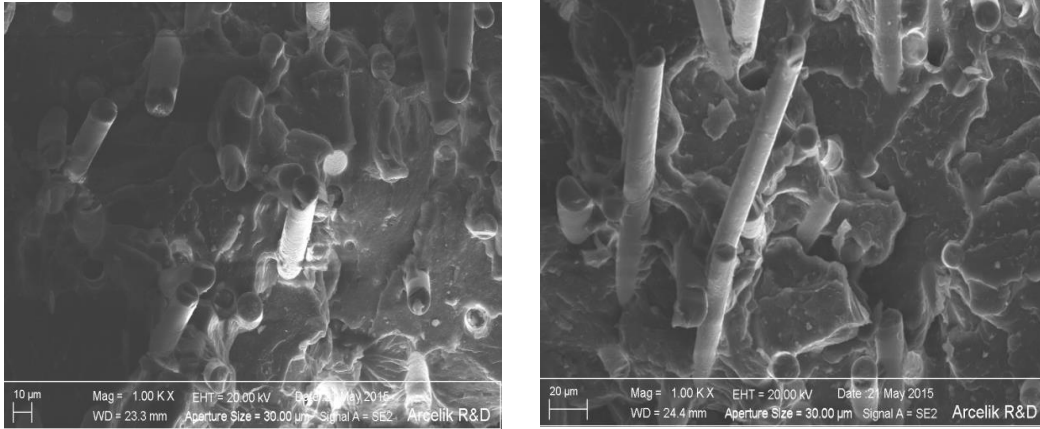


Figure 4.6 : SEM micrographs of a) GF6, b) GF7

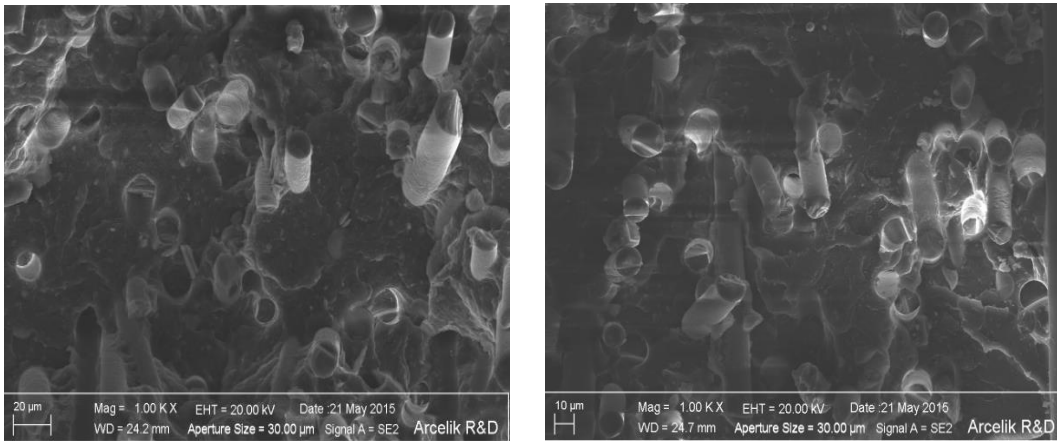


Figure 4.7 : SEM micrographs of a) GF8, b) GF9

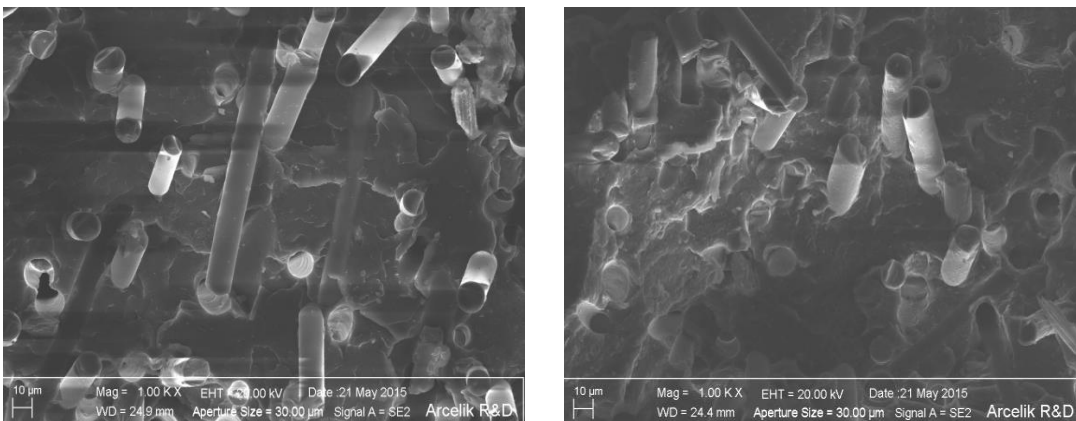


Figure 4.8 : SEM micrographs of a) GF10, b) GF11

For better understanding, the flame retardant additives distribution in PBT matrix, element mapping analysis was performed with energy dispersive X-ray spectroscopy on GF-PBT composites. In Figure 4.9 (a) red points denote Zn atoms and ZB

distribution in GF1 composite, which contain 5 % ZB is seen. In Figure 4.9 (b) red points denote P atoms and BP distribution in GF2 composite, which contain 5 % BP is seen. In Figure 4.10 (a) blue points denote P atoms and TPP distribution in GF3 composite, which contain 5 % TPP is seen. In Figure 4.10 (b) red points denote Ca atoms and CSD distribution in GF4 composite Which contain 5 % CSD is seen. In Figure 4.11 (a) blue points denote Ca atoms and CSD distribution in GF5 composite, which contain 10 % CSD is seen. In Figure 4.11 (b) green points denote P atoms and red points denote Zn atoms, BP and ZB distributions in GF6 composite which contain 5 % BP and 5 % ZB are seen. In Figure 4.12 (a) red points denote P atoms and green points denote Zn atoms, BP and ZB distributions in GF7 composite, which contain 2.5 % BP and 2.5 % ZB are seen. In Figure 4.12 (b) red points denote P atoms and blue points denote B atoms, TPP and BP distributions in GF8 composite, which contain 5 % TPP and 5 % BP are seen. In Figure 4.13 (a) yellow points denote P atoms and red points denote B atoms, TPP and BP distributions in GF9 composite, which contain 2.5 % TPP and 2.5 % BP are seen. In Figure 4.13 (b) blue points denote P atoms and TPP distribution in GF10 composite, which contain 10 % TPP is seen. In Figure 4.14 (a) red points denote P atoms and BP distribution in GF11 composite, which contain 10 % BP is seen. According to elemental X-ray mapping analyses, flame retardant additives of composite formulations were well dispersed in PBT matrix. Some agglomerations was seen in composites of CSD additive (GF4, GF5). That result may have occurred due to the process difficulties of CSD additive in extrusion.

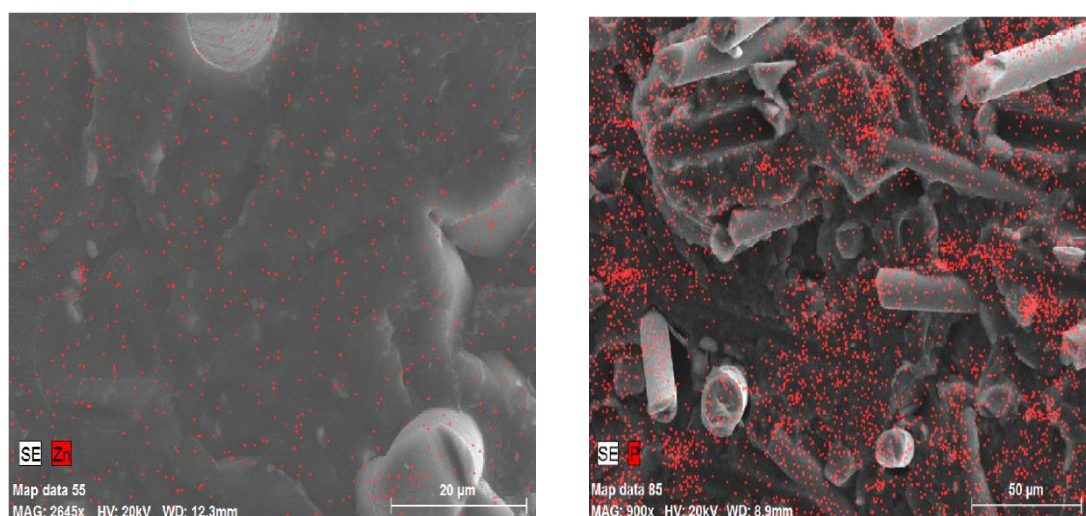


Figure 4.9 : SEM micrographs of a) GF1, B) GF2

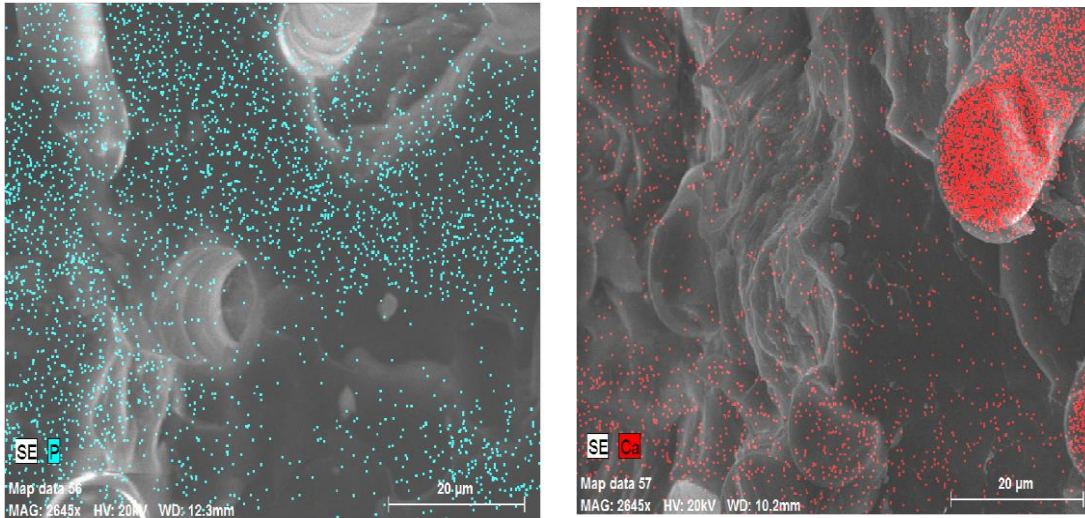


Figure 4.10 : SEM micrographs of a) GF3, b) GF4

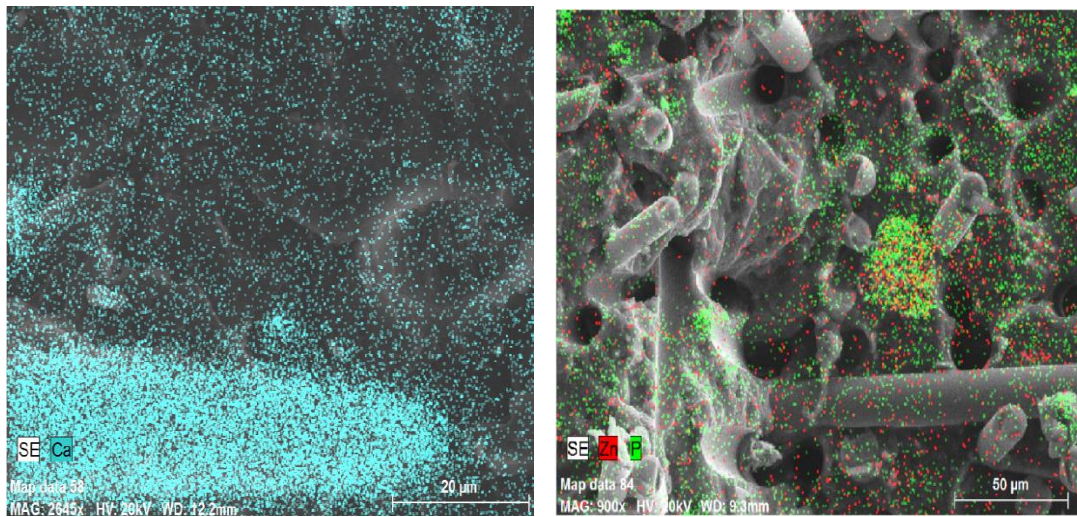


Figure 4.11 : SEM micrographs of a) GF5, b) GF6

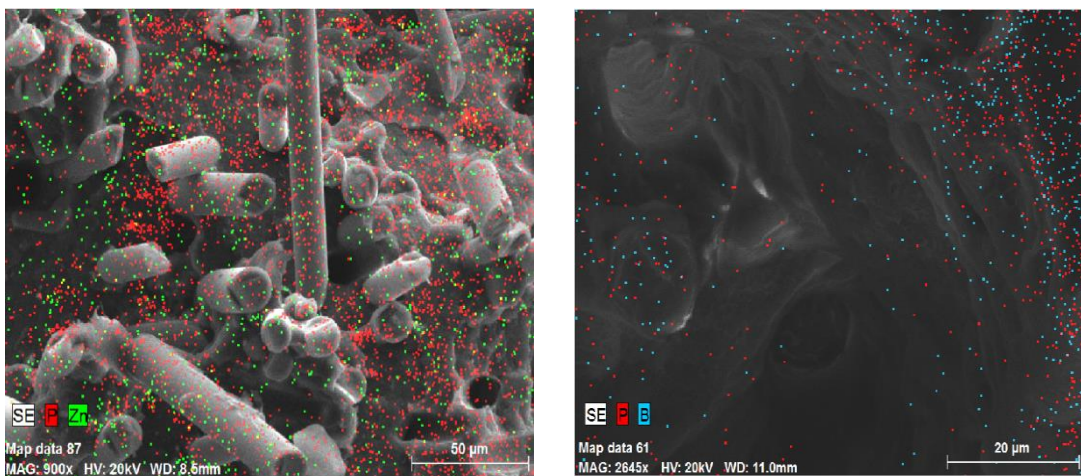


Figure 4.12 : SEM micrographs of a) GF7, b) GF8

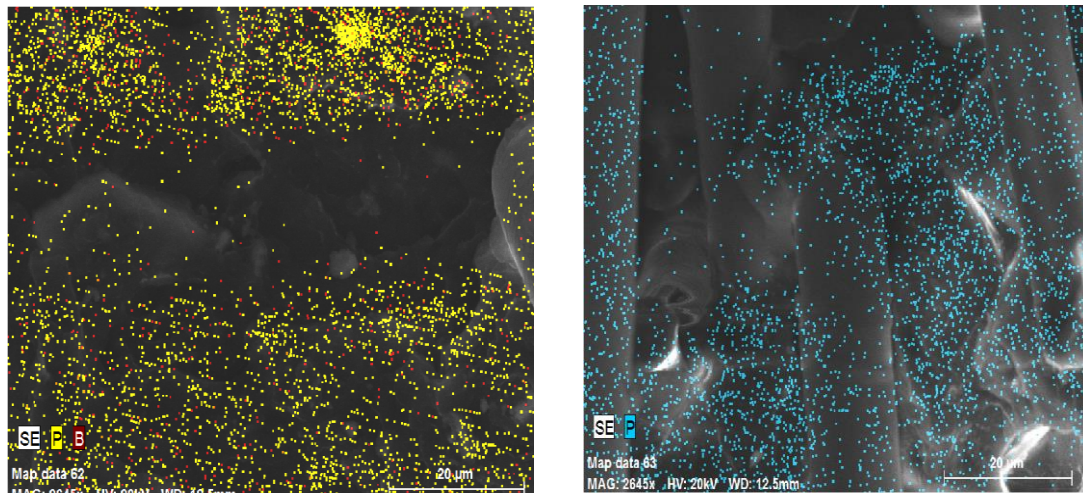


Figure 4.13 : SEM micrographs of a) GF9, b) GF10

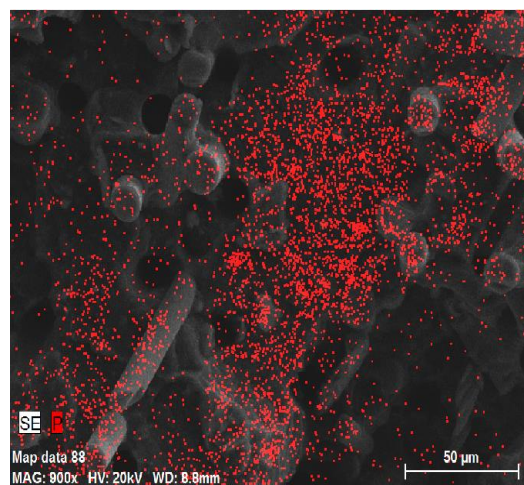


Figure 4.14 : SEM micrographs of GF11

4.2 Mechanical Properties Results

Mechanical properties of PBT composites were determined by using mechanical testing method.

4.2.1 Tensile properties

Tensile test was done according to the procedure explained in section 3.4.2.1. The effects of ZB, BP, TPP, CSD additives on mechanical properties of PBT and glass fiber reinforced PBT (GF-PBT) composites were investigated. Tensile strength, tensile modulus and elongation at break results are represented in order to analysis tensile properties of composites. For each PBT and GF-PBT (GF series) composites, average tensile test results from five specimens with standard deviations were given in Table 4.5 and Table 4.6 respectively.

Table 4.5 : Average tensile test results of PBT composites.

Samples	Tensile Strength (MPa)	Tensile Modulus (MPa)	Elongation at Break (%)
PBT0	51 ± 0.5	2210 ± 95	82 ± 42
PBT1	50 ± 0.30	2265 ± 150	112 ± 45
PBT2	49 ± 4.5	2260 ± 125	8.0 ± 5
PBT3	41 ± 0.35	1470 ± 40	287 ± 8
PBT4	57 ± 2.80	2595 ± 220	21 ± 3
PBT5	60 ± 1.80	2775 ± 200	12 ± 2
PBT6	55 ± 0.45	2505 ± 70	14 ± 2
PBT7	54 ± 0.30	2345 ± 50	26 ± 11
PBT8	42 ± 0.95	1685 ± 120	25 ± 7
PBT9	47 ± 1.45	1770 ± 405	132 ± 70
PBT10	35 ± 0.70	1040 ± 40	261 ± 30
PBT11	56 ± 1.5	2890 ± 70	4 ± 1

Table 4.6 : Average tensile test results of glass fiber reinforced PBT composites.

Samples	Tensile Strength (MPa)	Tensile Modulus (MPa)	Elongation at Break (%)
GF0	105 ± 0.90	7905 ± 715	2.8 ± 0.07
GF1	93 ± 1.02	8970 ± 160	2.4 ± 0.05
GF2	95 ± 1	8720 ± 420	2.2 ± 0.12
GF3	70 ± 0.85	5100 ± 530	2.7 ± 0.07
GF4	87 ± 1.60	7455 ± 345	2.4 ± 0.28
GF5	99 ± 4.02	9185 ± 700	2.2 ± 0.31
GF6	85 ± 0.84	9380 ± 250	1.7 ± 0.31
GF7	90 ± 1.18	8715 ± 355	2.1 ± 0.04
GF8	111 ± 0.89	8955 ± 255	3.1 ± 0.06
GF9	79 ± 1.74	6990 ± 450	2.4 ± 0.13
GF10	67 ± 1.4	5120 ± 140	2.8 ± 0.04
GF11	81 ± 5.28	8895 ± 230	4.4 ± 0.18

Tensile properties of unreinforced PBT based flame retardant composites are given in Figure 4.15. Neat PBT has tensile strength value around 51 MPa. Addition of 5 % CSD increased tensile strength of PBT composite to 57 MPa and 10 % CSD loading caused the highest increase in the tensile strength, which was about 60 MPa. CSD is a crystalline additive and have high hardness structure; this would explain the increase in tensile strength. Formulations of ZB and BP additives did not show significant change when compare to neat PBT. When ZB was combined with BP; it was found that tensile strength value increased up to 54 MPa (PBT6, PBT7). The significant decrease was shown in formulation of TPP, which decreased the tensile strength value of PBT composite to 41 MPa with 5 % loading and to 35 MPa with 10 % loading.

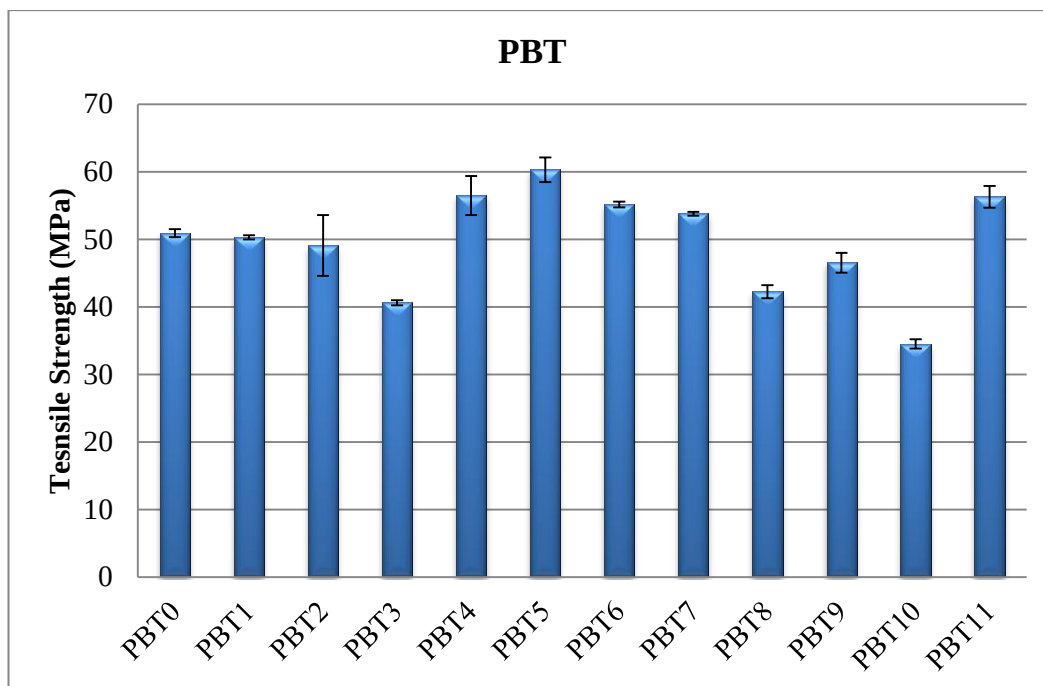


Figure 4.15 : Tensile Stress (MPa) results of PBT composites.

Tensile properties of GF- PBT based flame retardant composites are given in Figure 4.16. Tensile strength value of PBT increased to twice with 30 % glass fiber reinforcement and raised to 105 MPa from 51 MPa. Furthermore, this high increase was seen all glass fiber reinforced flame retardant composites (GF-PBT). All flame retardant PBT composite approximately increased to twice with 30% glass fiber addition.

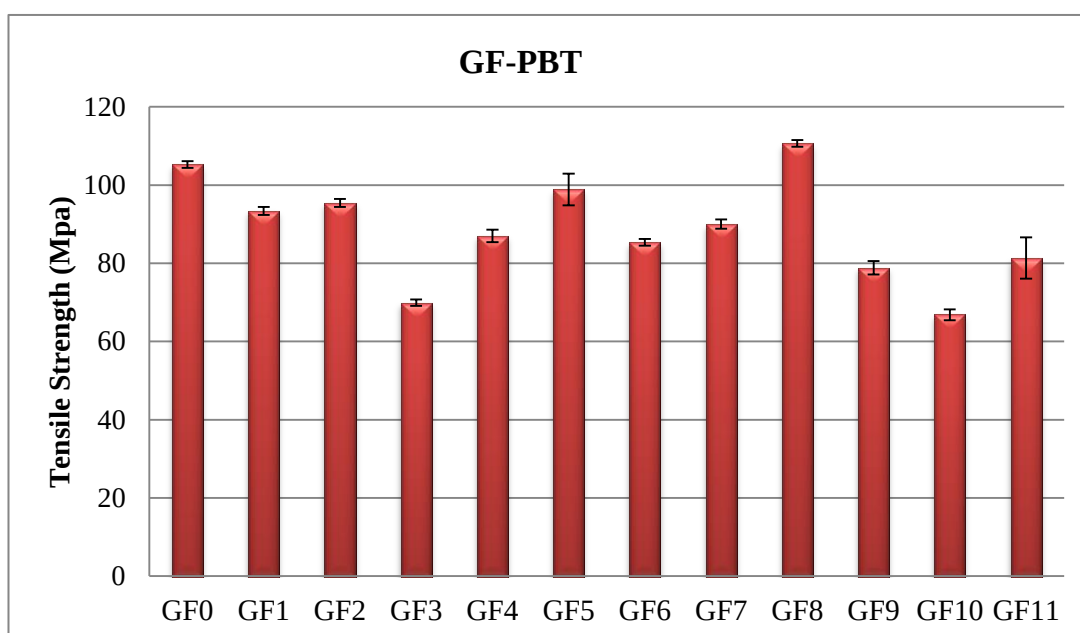


Figure 4.16 : Tensile stress (MPa) results of glass fiber reinforced PBT composites.

In Figure 4.17 tensile modulus data of the PBT flame retardant composites are given. Neat PBT composite has a tensile modulus value around 2210 MPa. Addition of 5 % ZB (PBT1) and 5 % BP (PBT2) to PBT showed slight increase in tensile modulus value compare to neat PBT (PBT0). When BP additive loading level increased to 10 %, highest tensile modulus value was obtained (2890 MPa). Noticeable decrease was observed with the addition of TPP. Addition of 5 % TPP to PBT decreased the elastic modulus to 1470 MPa and addition of 10 % TPP decreased the elastic modulus to 1040 MPa that was the lowest tensile modulus result. When 2.5 % TPP was combined with 2.5 % BP, higher tensile modulus result was obtained compare to neat TPP formulations (PBT3 and PBT10) but still lower than neat PBT composite tensile modulus value. The same trend was seen when 5 % TPP combined with 5 % BP in PBT composite. Mixture of BP with ZB formulations (PBT6, PBT7) showed slight increase in tensile modulus of PBT composites.

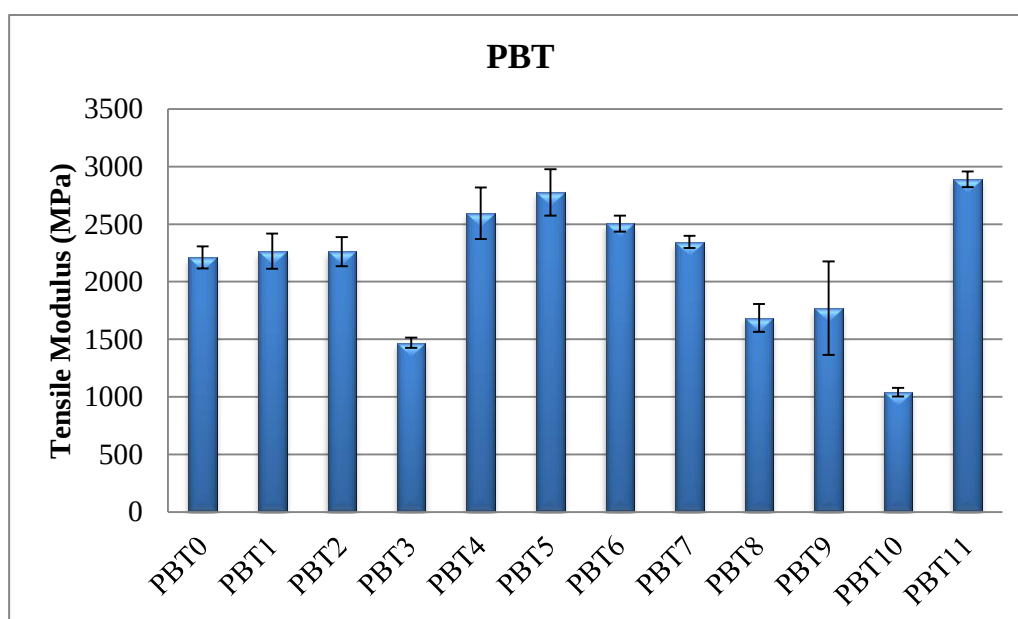


Figure 4.17 : Tensile modulus (MPa) results of PBT composites.

In Figure 4.18 tensile modulus data of the GF-PBT flame retardant composites are given. Tensile modulus value of neat PBT was increased to three and a half times with 30 % glass fiber reinforcement and was raised to 7905 MPa from 2210 MPa. TPP additive decreased tensile modulus value noticeably in both formulation (GF3, GF10) and the lowest tensile modulus is 5100 MPa was obtained when 5 % TPP added to GF-PBT composites. Formulations of ZB, BP, and CSD flame retardant showed similar results with neat GF-PBT (GF0) composite.

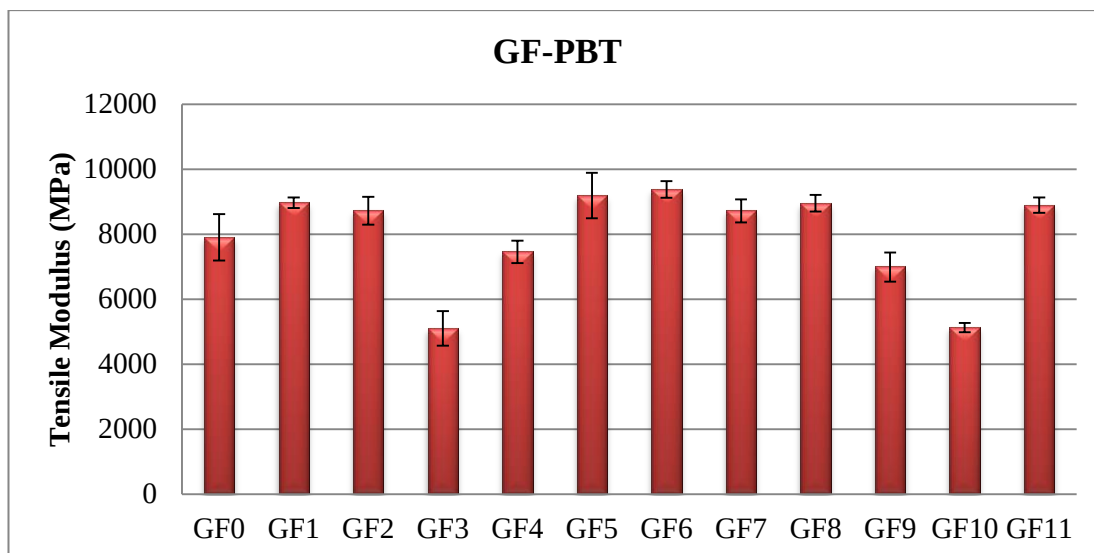


Figure 4.18 : Tensile modulus (MPa) results of glass fiber reinforced PBT composites.

In Figure 4.19 elongation at break values data of the PBT flame retardant composites are given. It was observed that addition of TPP increased the elongation at break values of the composites significantly. Using TPP in PBT matrix increased elongation of break value of PBT composites to 260 % from 82 %. This huge increase in the elongation could be the influence of plasticizing and chain extension effects of TPP on the PBT matrix. Another reason of high elongation could be because of that TPP may decrease the crystallinity of PBT matrix. Furthermore, ZB, BP and CSD flame retardant additives decreased elongation at break value of PBT composite since they are stiffer and harder additives.

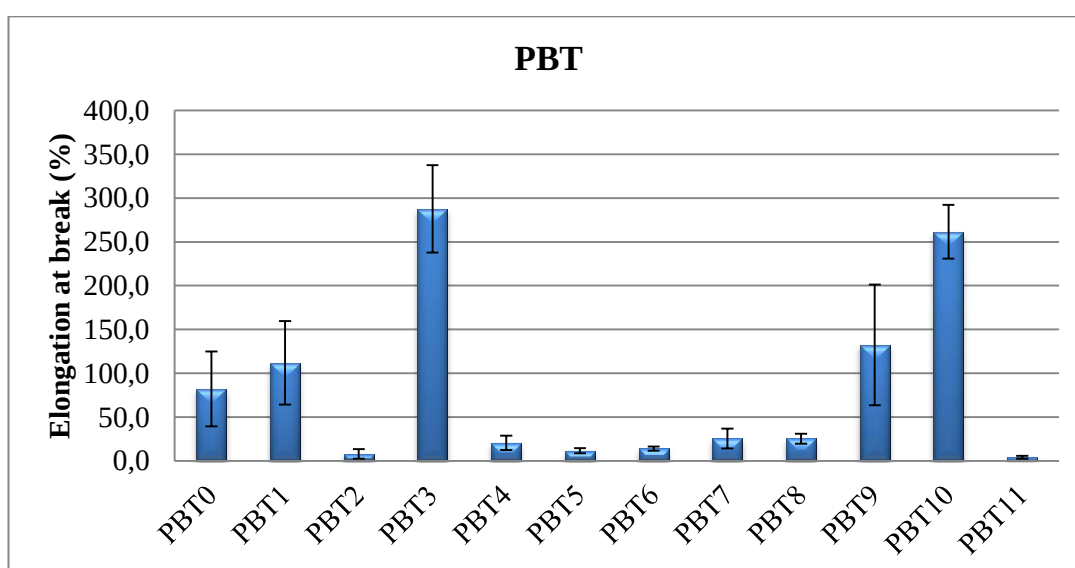


Figure 4.19 : Elongation at break (%) results of PBT composites.

In Figure 4.20 elongation at break values data of the GF-PBT flame retardant composites are given. 30 % glass fiber reinforcement decreased elongation of break value of PBT to 2.8 % from 82.2 %. When TPP additive used in GF-PBT composite elongation value of composites increased. GF-PBT composites tensile stress results were close to each other between the ranges of 1.4 % to 3.1 %.

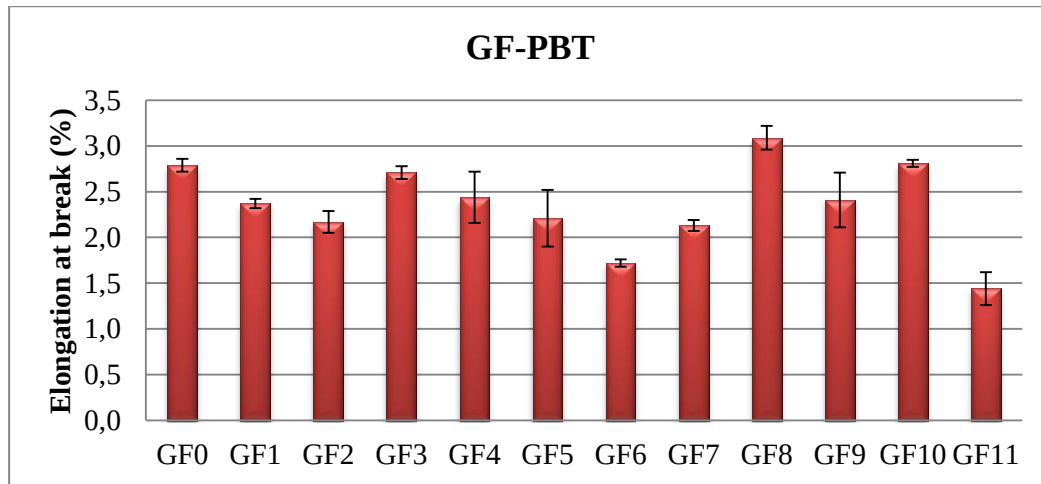


Figure 4.20 : Elongation at break (%) results of glass fiber reinforced PBT composites.

4.2.2 Flexural properties

Flexural test was done as three point bending method according to the procedure explained in section 3.4.2.2. For each PBT and GF-PBT composites, average test results from five specimens with standard deviations were given in Table 4.7 and Table 4.8 respectively.

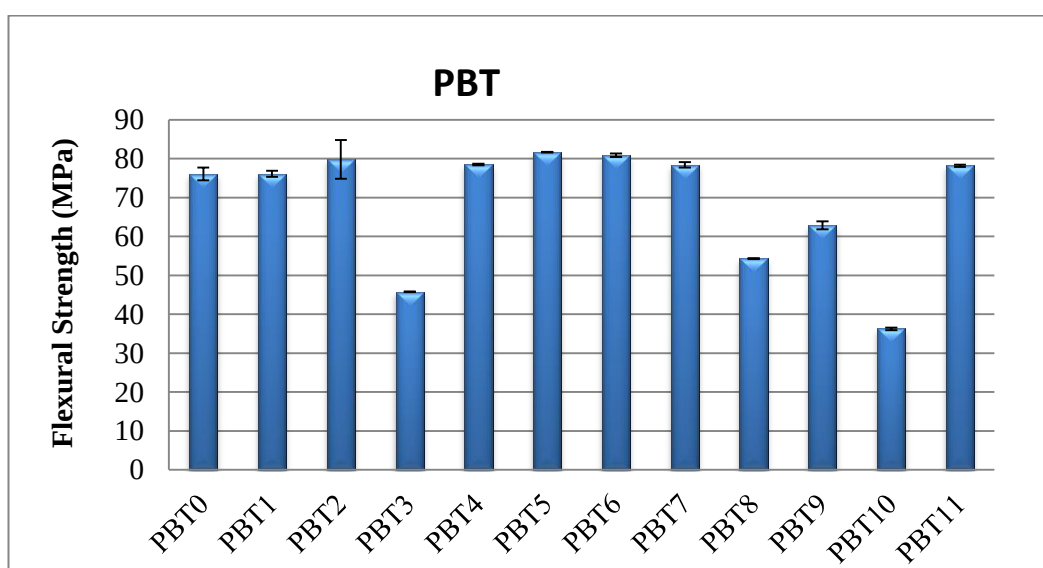
Table 4.7 : Flexural test results of PBT composites.

Samples	Flexural Strength (MPa)	Flexural Modulus (MPa)
PBT0	76 ± 1.65	2320 ± 30
PBT1	76 ± 0.77	2395 ± 20
PBT2	80 ± 5.00	2445 ± 30
PBT3	46 ± 0.09	1125 ± 10
PBT4	78 ± 0.20	2415 ± 75
PBT5	82 ± 0.10	2615 ± 7
PBT6	81 ± 0.40	2655 ± 4
PBT7	78 ± 0.70	2455 ± 12
PBT8	54 ± 0.08	1470 ± 50
PBT9	63 ± 1.02	1840 ± 40
PBT10	36 ± 0.32	780 ± 20
PBT11	78 ± 0.30	2535 ± 25

Table 4.8 : Flexural test results of glass fiber reinforced PBT.

Samples	Flexural Strength (MPa)	Flexural Modulus (MPa)
GF0	157 ± 0.3	7420 ± 30
GF1	130 ± 12	7235 ± 515
GF2	133 ± 2.5	7330 ± 180
GF3	98 ± 0.7	4850 ± 110
GF4	128 ± 4	6430 ± 100
GF5	166 ± 0.8	8595 ± 50
GF6	120 ± 1.4	8025 ± 115
GF7	133 ± 0.5	7545 ± 220
GF8	168 ± 1.7	8010 ± 15
GF9	110 ± 0.4	5700 ± 100
GF10	93 ± 1.1	4410 ± 20
GF11	142 ± 0.8	9085 ± 50

Three point bending test was carried out for understanding the effects of different flame retardant additives (BP, CSD, ZB, TPP) on the mechanical properties of polymeric composites. In Figure 4.21 flexural strength values data of the PBT flame retardant composites are given. The Flexural strength value of neat PBT composites was around 76 MPa. It was observed that addition of TPP additive to PBT matrix decreased flexural strength value noticeably. 10 % TPP addition caused the lowest result which was about 36 MPa. When TPP was combined with BP, flexural modulus of these composites was increased compare to neat TPP formulation. Other flame retardant formulations (ZB, BP, CSD) flexural strength values were close to each other and between the range of 76 MPa to 82 MPa.

**Figure 4.21 :** Flexural strength (MPa) results of PBT composites.

In Figure 4.22 flexural strength values data of GF-PBT flame retardant composites are given. According to the three point bending test results, flexural strength value of PBT increased to twice with 30 % glass fiber reinforcement and raised to 157 MPa from 76 MPa. Flame retardant base composite showed similar behaviour and increased approximately to twice with glass fiber reinforcement. Addition of 10 % TPP to GF-PBT composite decreased the flexural strength values of to 93 MPa which was the lowest flexural strength results in GF-PBT composites.

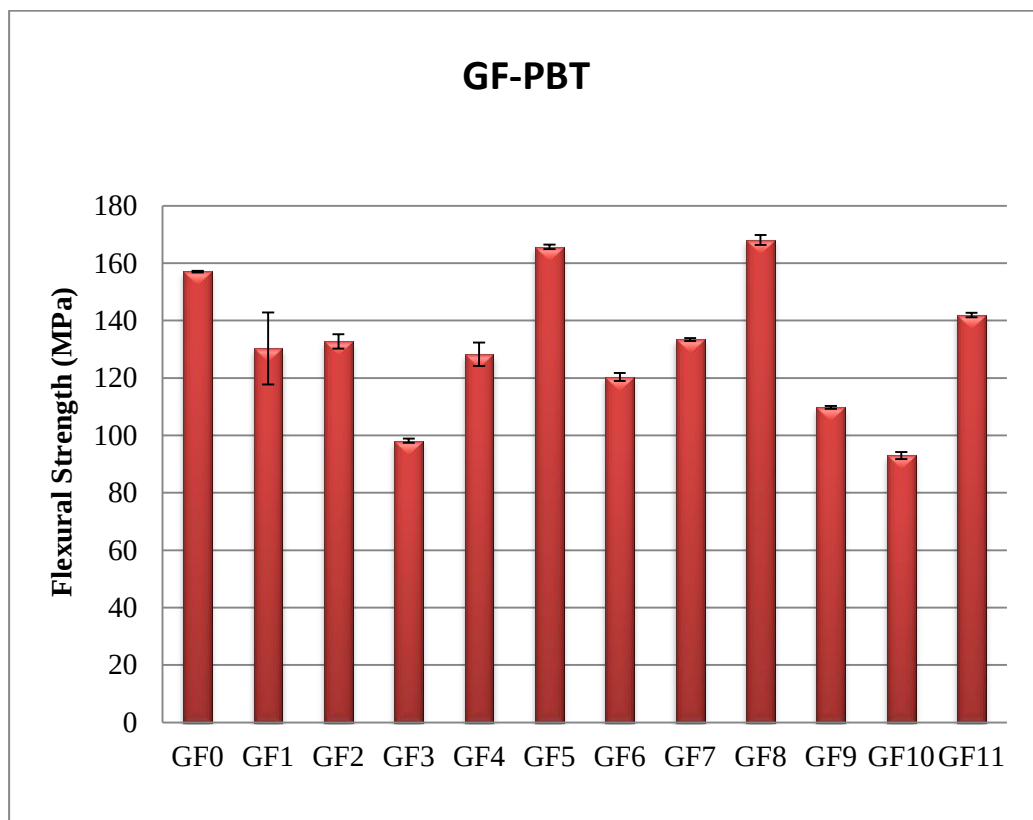


Figure 4.22 : Flexural strength (MPa) results of glass fiber reinforced PBT composites.

In Figure 4.23 flexural modulus values data of the PBT flame retardant composites are given. The flexural modulus value of neat PBT composite (PBT0) was around 2320 MPa. It was observed that addition of TPP additive to PBT matrix decreased flexural modulus value. Adding 10 % TPP to PBT caused the lowest result which was about 780 MPa. When TPP additive was combined with BP flexural modulus of composites increased compare to the composite contains only TPP additive but still lower than flame retardant-free PBT formulation. ZB, BP and CSD introduce stiffness to the polymer matrix that causes some increase in flexural modulus.

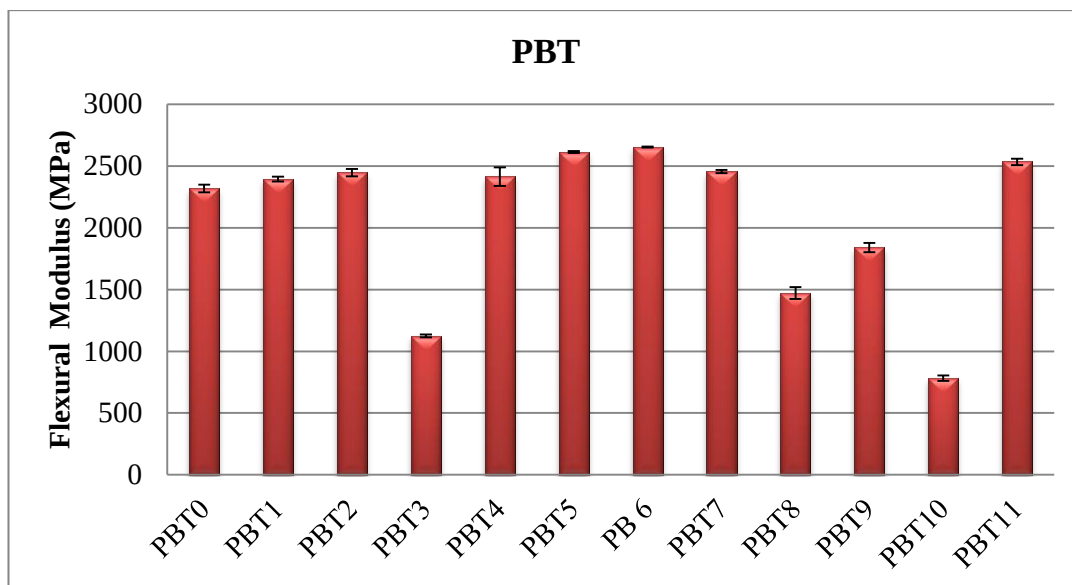


Figure 4.23 : Flexural modulus (MPa) results of PBT composites.

In Figure 4.24 flexural modulus values data of the GF-PBT flame retardant composites are given. Flexural modulus value of PBT increased nearly tripled with 30% glass fiber reinforcement and raised to 7420 MPa from 2320 MPa. Flame retardant based GF-PBT formulations behaviour show similar trend of PBT formulations. While the organic additive TPP decreased the flexural modulus, other additives gave close results with GF0 composite. 10 % BP addition to PBT matrix caused the highest flexural modulus result which was the 9085 MPa.

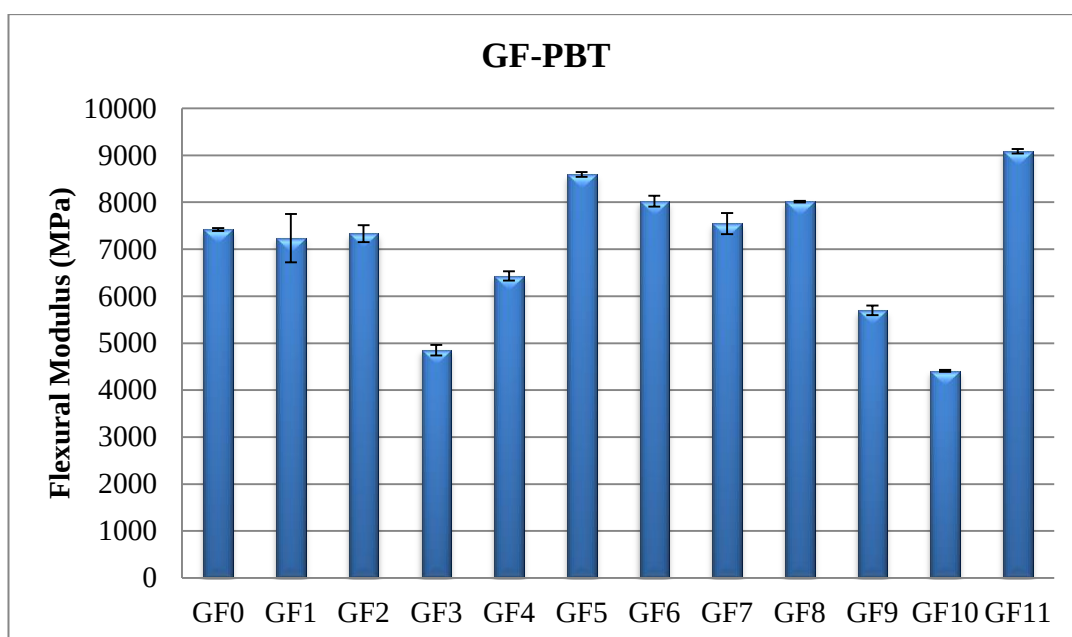


Figure 4.24 : Flexural modulus (MPa) results of glass fiber reinforced PBT composites.

4.2.3 Izod impact properties

Izod (notched) impact test was done according to the procedure explained in section 3.4.2.3. It is used to characterize the responses of the materials to a sudden impact and energy. For each PBT and GF-PBT composites, average Izod (notched) impact results from ten specimens with standard deviations were given in Table 4.9 and Table 4.5 respectively.

Table 4.9 : Izod impact test results of PBT composites.

Samples	Izod Impact Strength (kJ/m ²)
PBT0	5.2 ± 0.30
PBT1	5.0 ± 0.21
PBT2	4.4 ± 0.16
PBT3	5.2 ± 0.16
PBT4	4.5 ± 0.11
PBT5	4.3 ± 0.21
PBT6	4.5 ± 0.22
PBT7	4.6 ± 0.12
PBT8	4.8 ± 0.13
PBT9	4.6 ± 0.11
PBT10	7.1 ± 0.28
PBT11	4.4 ± 0.47

Table 4.10 : Izod impact test results of glass fiber reinforced PBT composites.

Samples	Izod Impact Strength (kJ/m ²)
GF0	10.7 ± 0.24
GF1	8.9 ± 0.25
GF2	6.5 ± 0.43
GF3	8.0 ± 0.34
GF4	7.4 ± 0.27
GF5	7.3 ± 0.41
GF6	5.3 ± 0.58
GF7	6.5 ± 0.42
GF8	9.5 ± 0.50
GF9	6.7 ± 0.26
GF10	10.0 ± 1.00
GF11	5.7 ± 0.40

The impact strength values of the flame retardant PBT composites are given in Figure 4.25. Neat PBT composite (PBT0) has an impact strength value of 5.2 kJ/m².

Addition of inorganic flame retardants (ZB, BP, CSD) decreased the impact strength value of PBT since they are highly stiff and hard materials. TPP addition to PBT matrix noticeably increased the impact strength values because of the plasticizing effect of the TPP. Addition of 10 % TPP to PBT caused the highest impact strength value which was about 7 kJ/m².

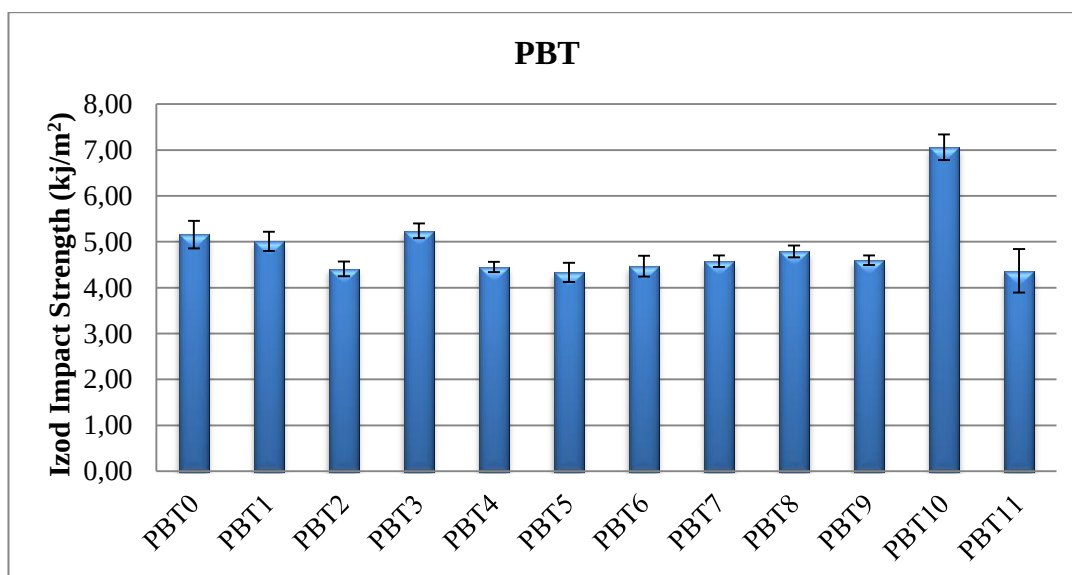


Figure 4.25 : Izod impact (kJ/m²) strength results of PBT.

The impact strength values of the GF- PBT flame retardant composites are given in Figure 4.26. Izod impact strength value of PBT increased to about twice when 30 % glass fiber added to PBT matrix and impact strength of PBT raised to 10.6 kJ/m² from 5.2 kJ/m². TPP addition to GF-PBT composite increased significantly the impact strength values.

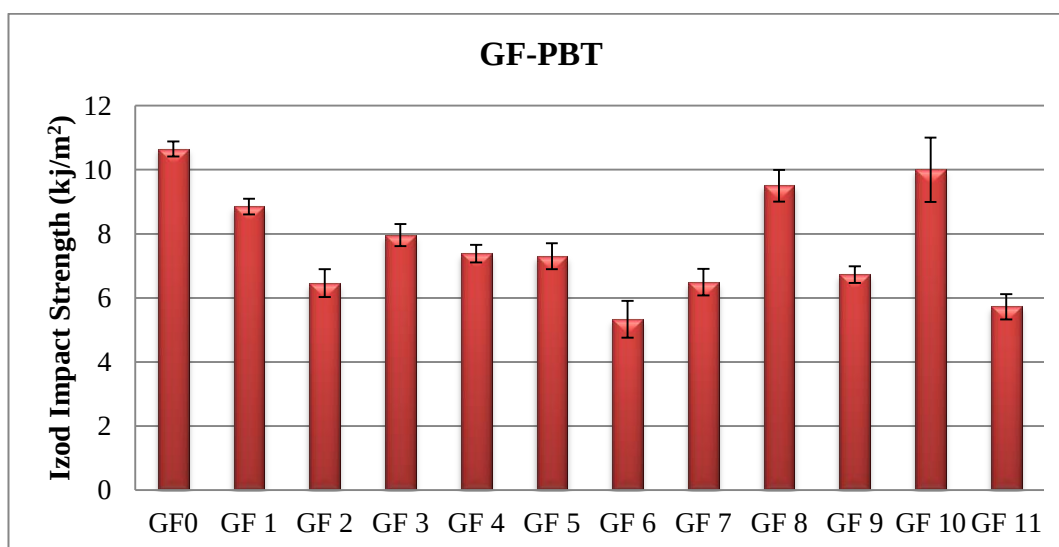


Figure 4.26 : Izod impact strength (kJ/m²) results of glass fiber reinforced PBT.

4.2.4 Hardness properties

Shore Hardness test results of PBT and GF-PBT composites were represented in Table 4.11 and Table 4.12 respectively. According to the test results glass fiber reinforcement increased hardness value slightly from 80 to 85 Shore D. Furthermore, As mentioned before TPP act as a plasticizer on PBT matrix, thus TPP formulations decreased the hardness values of both PBT and GF-PBT composites. In Figure 4.27 and Figure 4.28 composites Hardness Shore D values are represented.

Table 4.11 : Hardness value (Shore D) of PBT composites.

Samples	Hardness (Shore D)
PBT0	80
PBT1	82
PBT2	81
PBT3	79
PBT4	80
PBT5	81
PBT6	82
PBT7	81
PBT8	79
PBT9	80
PBT10	76
PBT11	82

Table 4.12 : Hardness value (Shore D) of GF-PBT composites.

Samples	Hardness (Shore D)
GF0	85
GF1	86
GF2	85
GF3	81
GF4	84
GF5	84
GF6	85
GF7	85
GF8	85
GF9	83
GF10	79
GF11	81

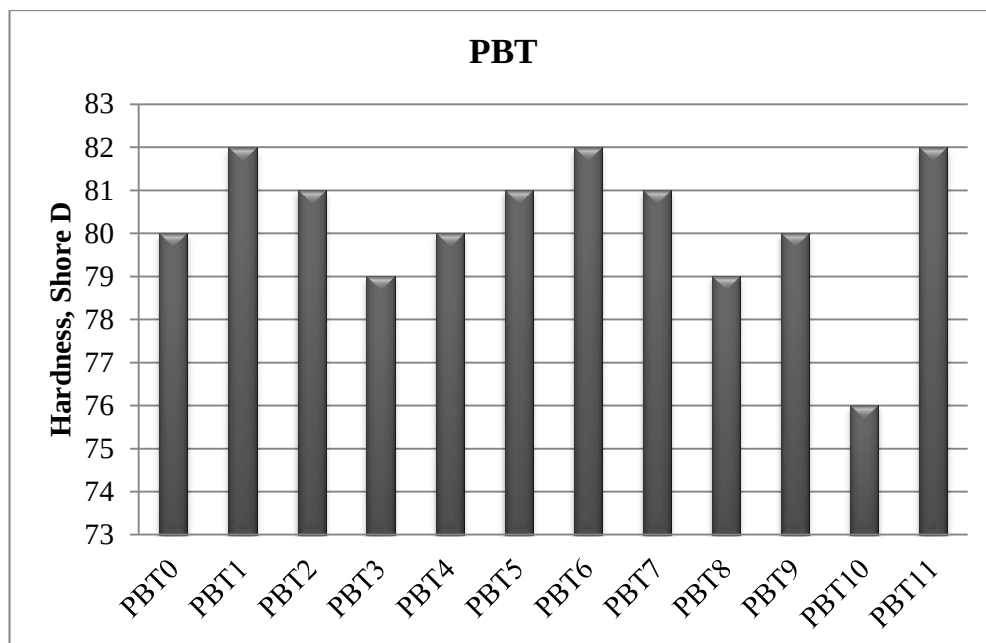


Figure 4.27 : Shore D hardness test results of PBT composites.

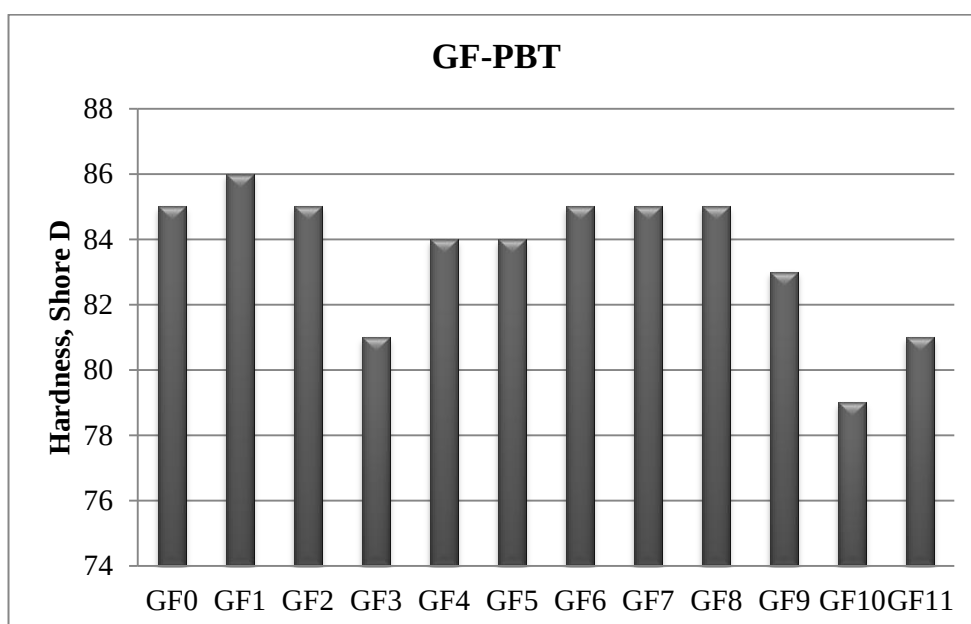


Figure 4.28 : Shore D hardness test results of GF-PBT composites.

4.3 Flame Retardant and Thermal Properties Analysis

4.3.1 Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) was done according to the procedure explained in section 3.4.5. The raw materials were analyzed individually as shown from Figure 4.29 to 4.32. TGA analysis indicates the thermal decomposition range of the composite and the remaining char after burning and the char yield. TGA is a

complementary analysis to characterize the flame retardancy of the composites especially used to determine the mechanism of action of the additives in the condensed phase.

According to TGA analyses mass losses of boron phosphate are 6 %, 3 %, 2 %, and 2 % respectively for four steps. It starts to decompose at the temperature of 100 °C, the loss of crystalline water is occurred and 87 % of boron phosphate char remained at 800 °C. A mass loss of triphenyl phosphate is 100 % and it occurred between the temperature of 200 °C and 230 °C. Mass loss of calcium sulphate dihydrate is approximately 20 % and occurred at 100 °C. Mass loss of zinc borate is approximately 20 % and occurred between temperature of 300 °C and 450 °C.

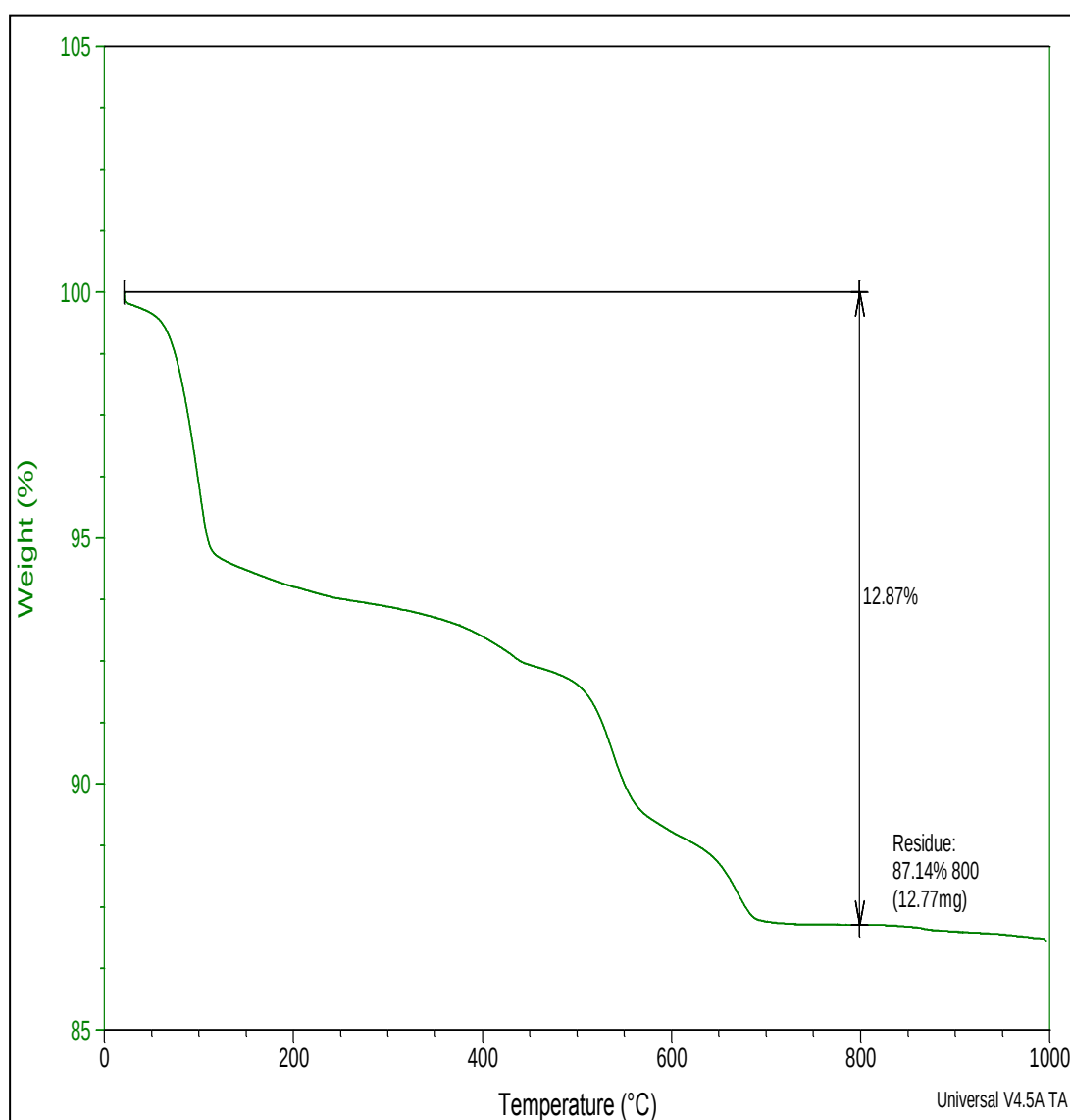


Figure 4.29 : TGA diagram of boron phosphate.

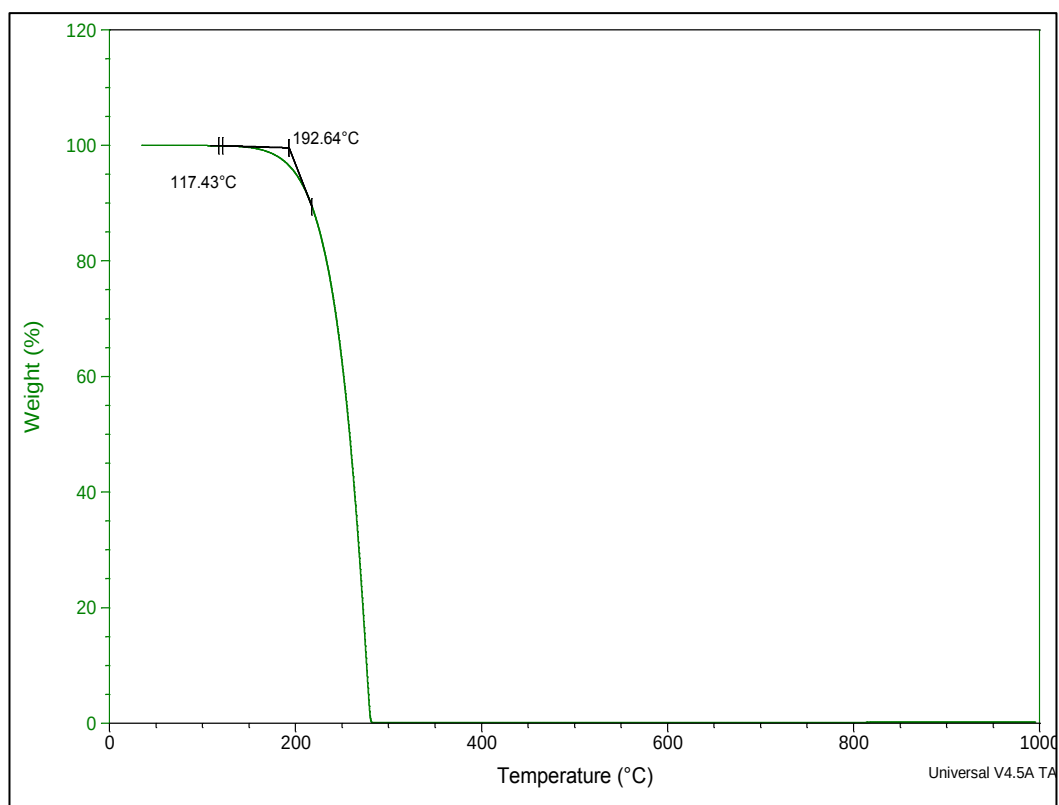


Figure 4.30 : TGA diagram of triphenyl phosphate.

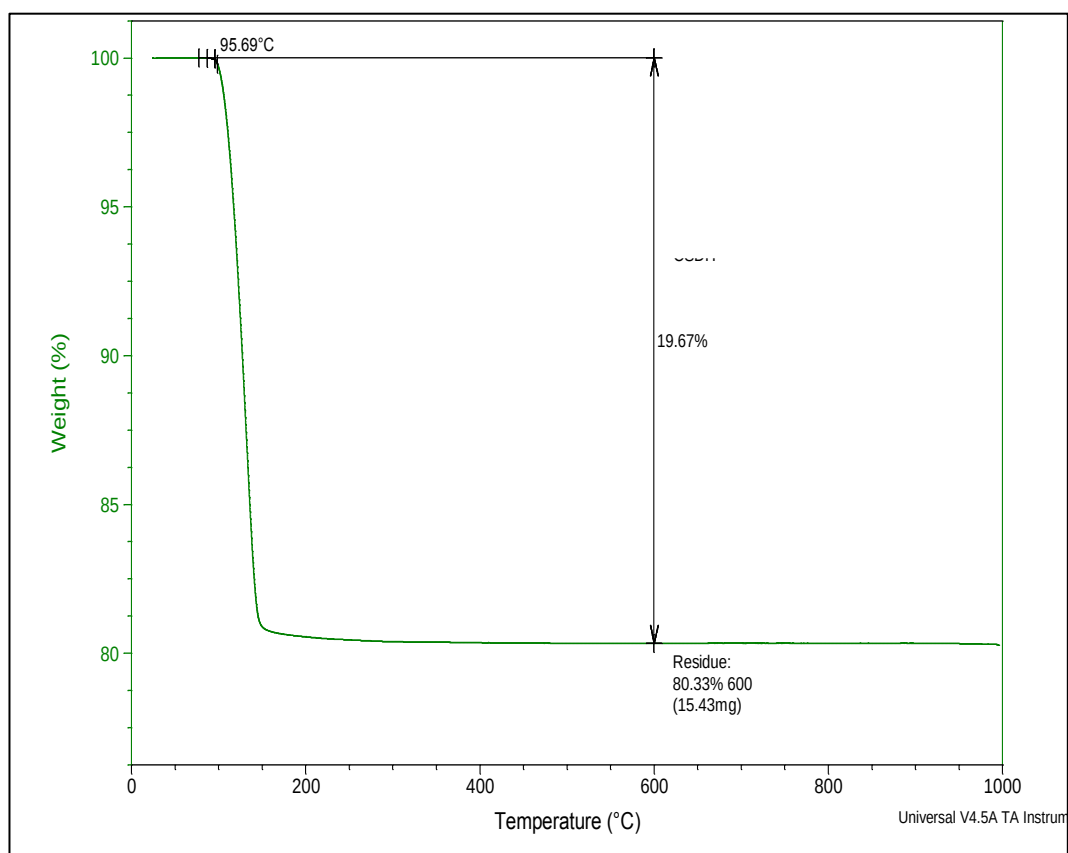


Figure 4.31 : TGA diagram of calcium sulphate dihydrate.

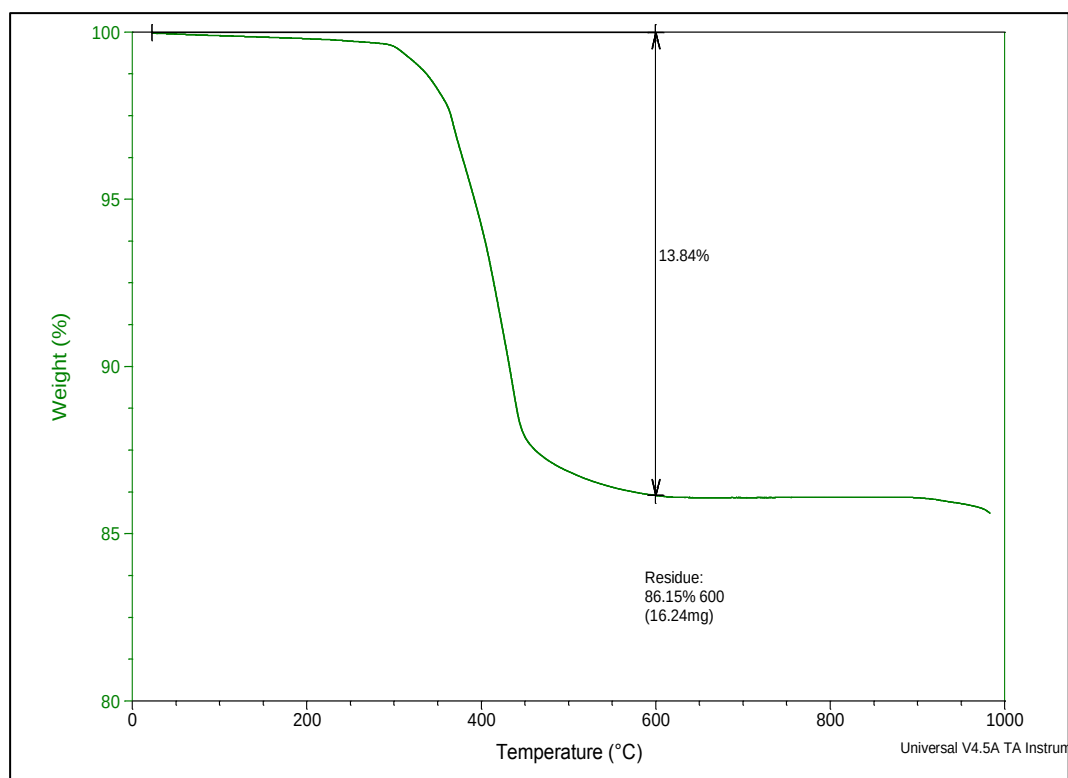


Figure 4.32 : TGA diagram of zinc borate.

The TGA curves of PBT composites were given in Figure 4.33, Figure 4.34 and Figure 4.35. According to these analyses, all formulations showed decomposition in one step and decomposition of composites started at approximately 350 °C.

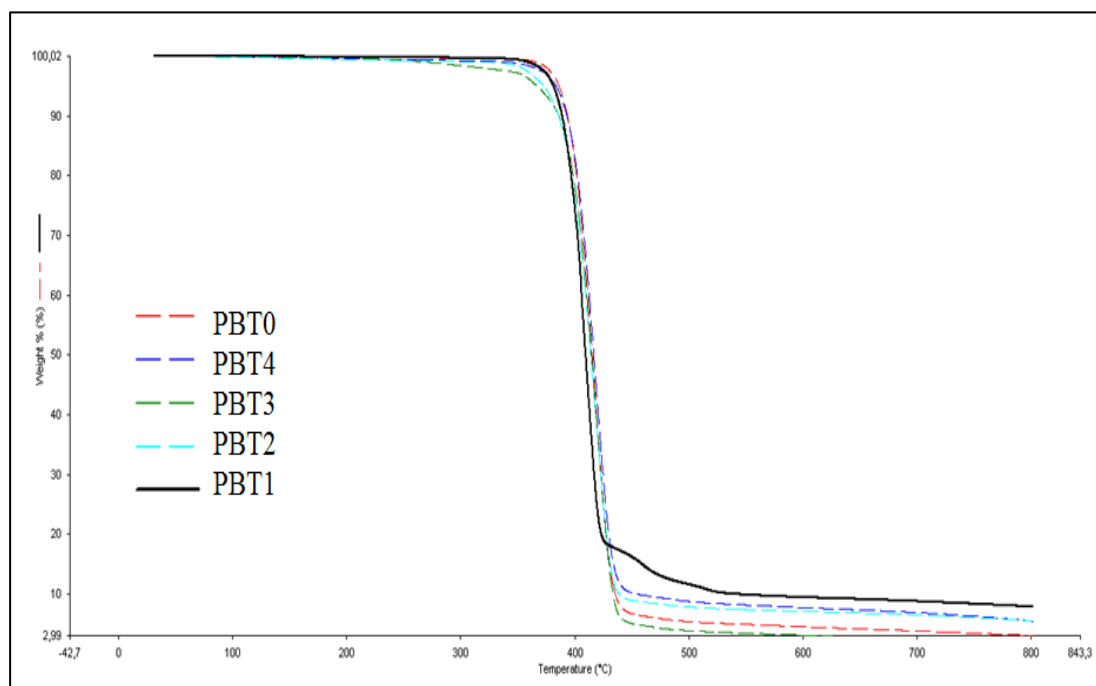


Figure 4.33 : TGA diagram of PBT composites.

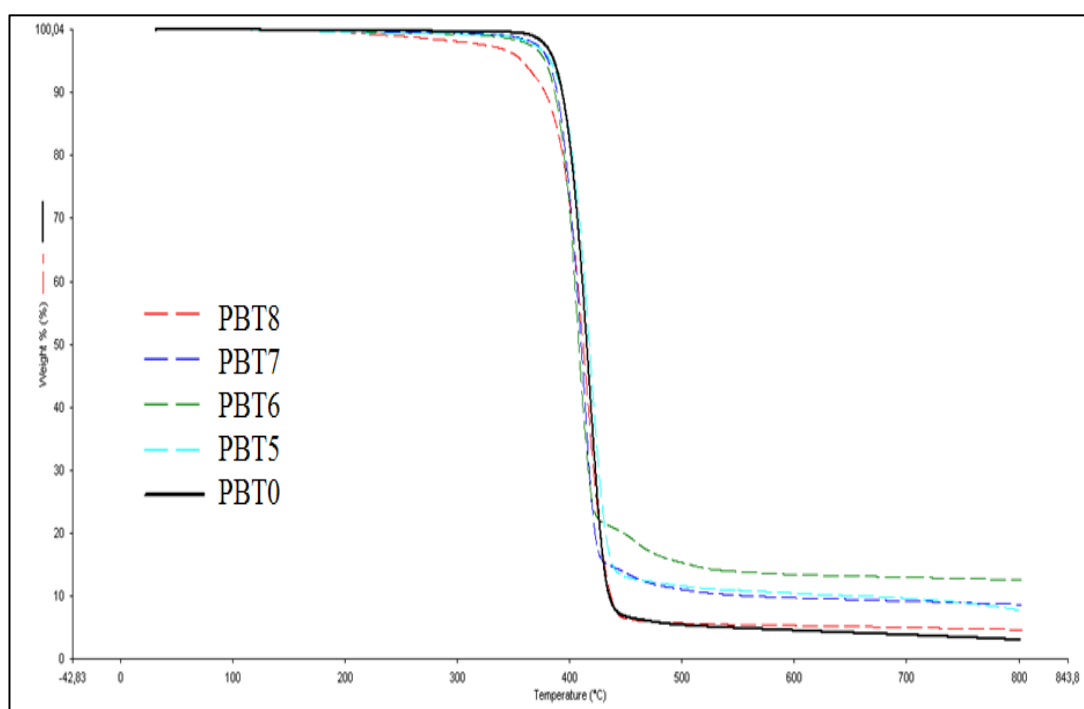


Figure 4.34 : TGA diagram of PBT composites.

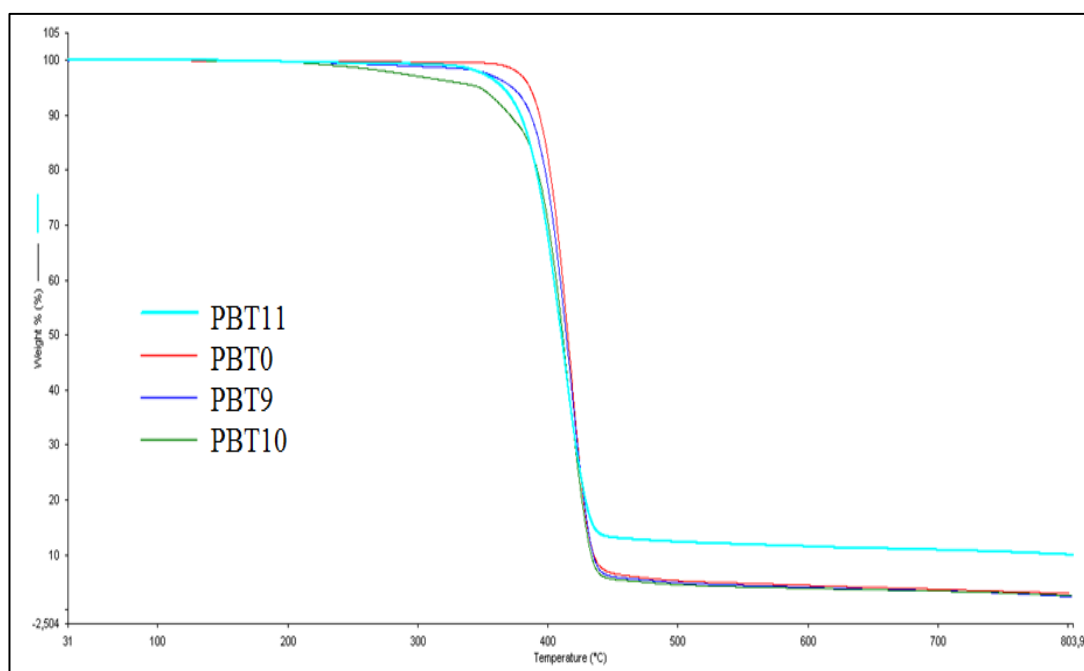


Figure 4.35 : TGA diagram of PBT composites.

The TGA curves of glass fiber reinforced PBT composites were given in Figure 4.36, Figure 4.37, and Figure 4.38. According to these analyses, all formulations showed decomposition in one step and decomposition of composites started at approximately 350 °C.

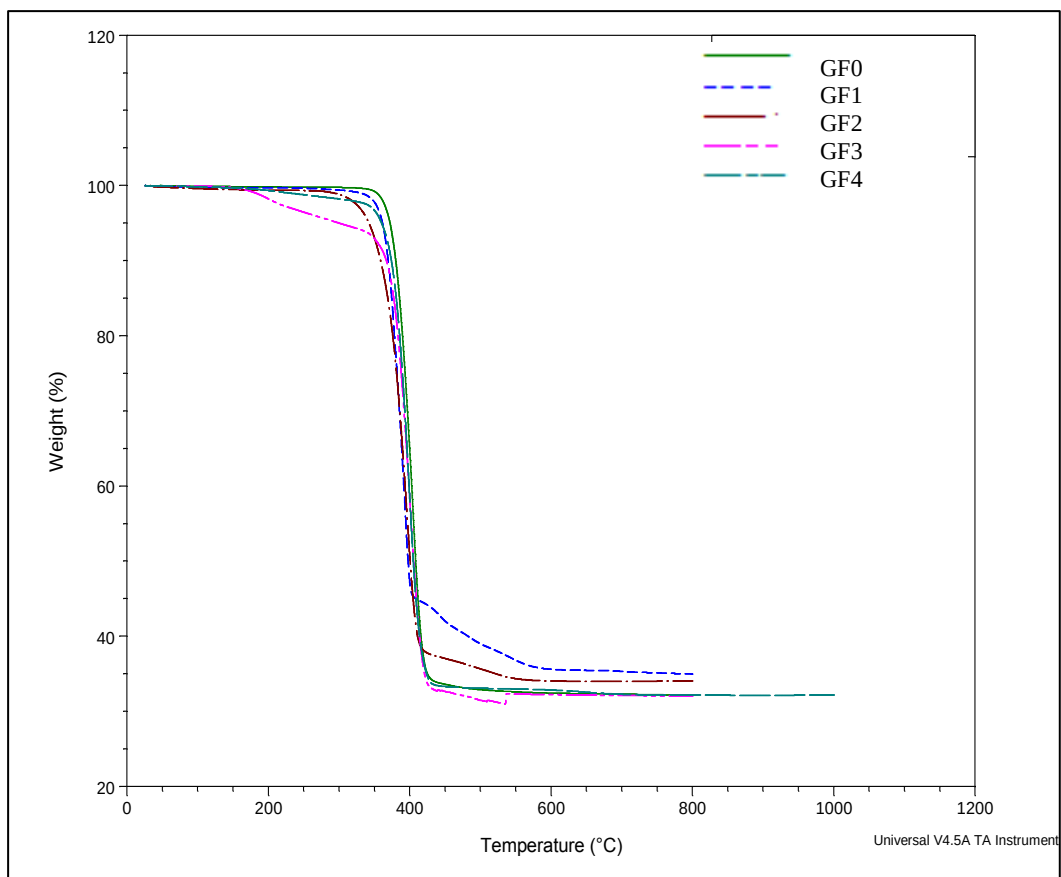


Figure 4.36 : TGA diagram of glass fiber reinforced PBT composites.

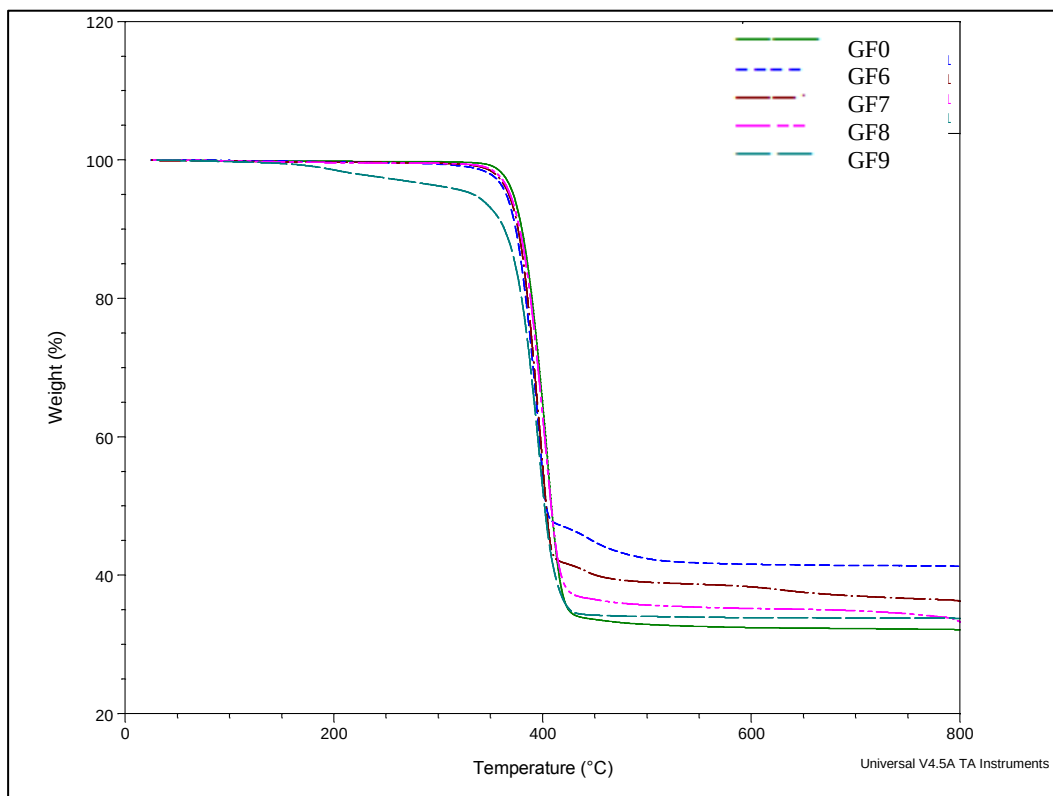


Figure 4.37 : TGA diagram of glass fiber reinforced PBT composites.

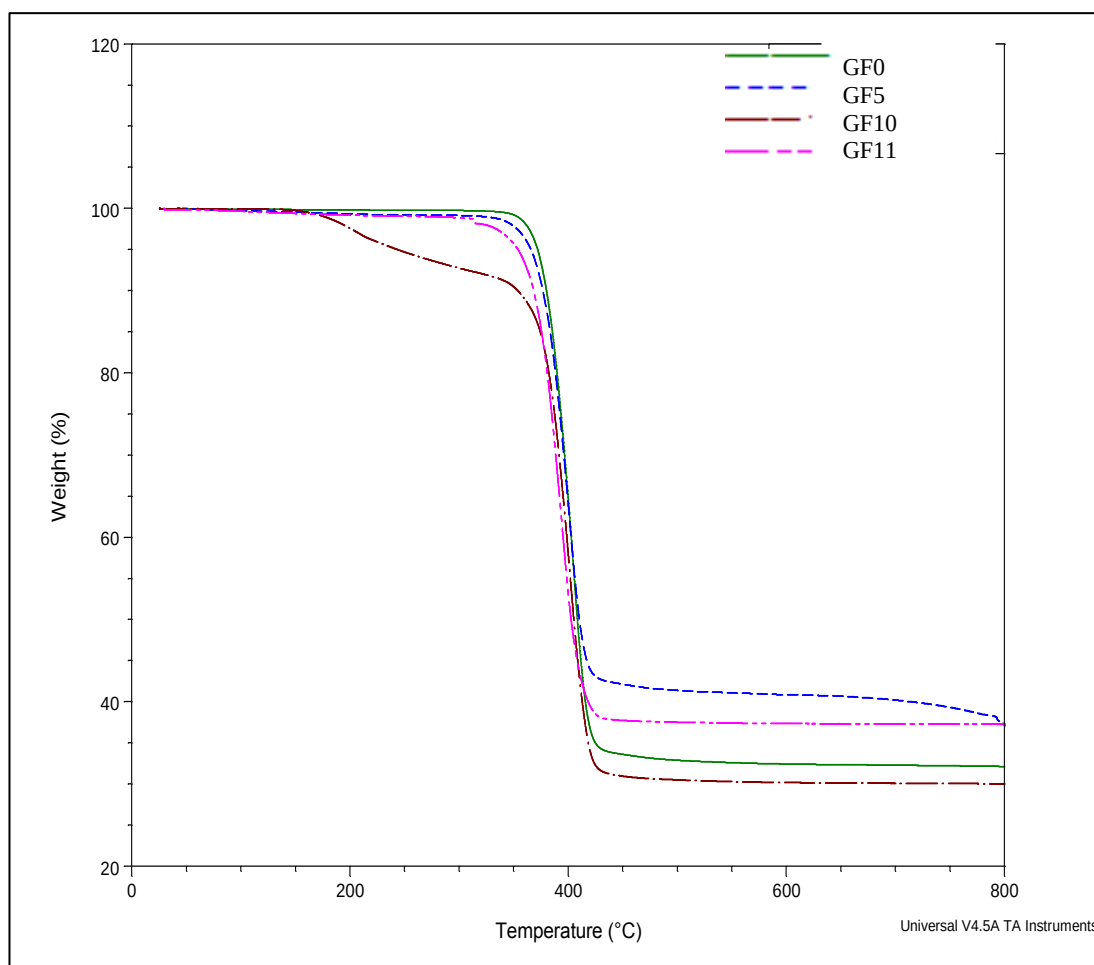


Figure 4.38 : TGA diagram of glass fiber reinforced PBT composites.

4.3.2 Limiting oxygen index (LOI)

Limiting oxygen test was done according to the procedure explained in section 3.4.2. The limiting oxygen index test method provides to determine the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that supports combustion of neat PBT and GF-PBT flame retardant composites. LOI test values of PBT composites are given Table 4.13 and Figure 4.39.

LOI value of neat PBT (PBT0) was around 22. According to the LOI results, ZB addition to the PBT matrix did not change the LOI value of PBT composite. Adding 5 % BP to PBT matrix increased slightly the LOI value of PBT0. When TPP added to PBT matrix, LOI value noticeably increased up to 26.6. Highest LOI values were obtained when 10 % TPP (PBT10) was added to PBT matrix and LOI was increased to 27.2. CSD additive showed the second highest LOI value after TPP in formulations were fed to the system 5 % proportion.

In first set of formulation it was observed that TPP is the most successful flame retardant for PBT in terms of flammability properties. However, as mentioned mechanical properties results, TPP additive decreased some mechanical properties like tensile strength and flexural strength values. In order to obtained high flame retardancy properties with high mechanical properties, TPP was combined with BP additive (PBT8 and PBT9 formulations). Even though some decreases in LOI value occurred compare to TPP base formulation, combination of TPP with BP showed high LOI results with higher mechanical properties.

It was observed that ZB did not have flame retardancy effectiveness on PBT and BP showed slight increase in LOI. When BP is combined with ZB, important increase was observed in flame retardancy effectiveness and higher LOI results were obtained. When 2.5 % BP was combined with 2.5 % ZB, LOI value of 23.0 was obtained; further increase of BP content to 5 % and ZB content to 5 %, increases LOI value to 23.4. These test results indicated that when they were used together they showed a significant synergistic effect. LOI results of PBT composites are given Figure 4.39.

Table 4.13 : LOI (%) test values of PBT composites.

Samples	LOI (%)
PBT0	22.0
PBT1	22.1
PBT2	22.4
PBT3	26.6
PBT4	24.4
PBT5	25.1
PBT6	23.4
PBT7	23.0
PBT8	24.6
PBT9	25.6
PBT10	27.2
PBT11	22.7

LOI test values of GF-PBT composites are given Table 4.14 and Figure 4.40. When GF-PBT composites LOI results compared to PBT composites LOI results, GF-PBT composites showed lower LOI values than PBT composites. This behavior would be result of “candlewick effect” of glass fiber. Candlewick effect interpreted in literature that in the combustion process of glass fiber reinforced polymer

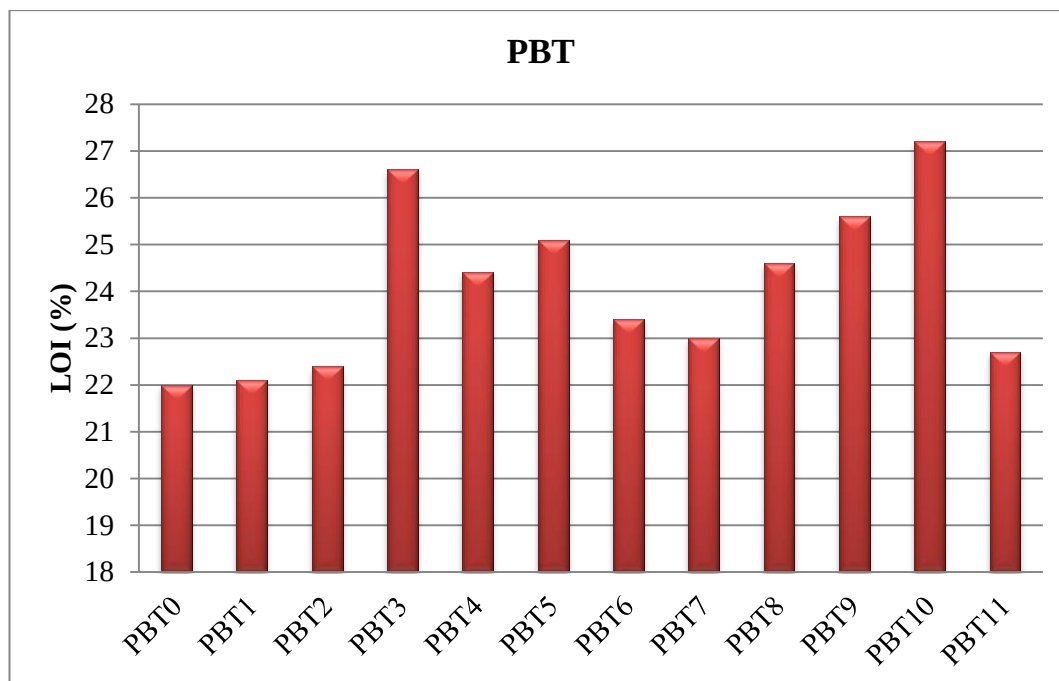


Figure 4.39 : LOI (%) test values of PBT composites.

composites, glass fibers could transfer the flammable pyrolysis products of polymers to the flame zone through capillary action, speed the heat flowing back to the polymers and increase the mass lose rate of polymer matrix [76, 77]. While neat PBT (PBT0) LOI was 22, GF-PBT (GF0) was around 21.3. In all GF-PBT formulations, flame retardants showed similar behavior as in PBT composites. According to test results of GF1, GF2, GF3 and GF4 formulations, TPP was the most successive flame retardant additive for GF-PBT composites. The synergistic effect of BP, ZB mixture was seen in GF-PBT composites, too.

Table 4.14 : LOI (%) test values of glass fiber reinforced PBT composites.

Samples	LOI (%)
GF0	21.3
GF1	21.4
GF2	22.0
GF3	24.2
GF4	22.5
GF5	23.3
GF6	23.0
GF7	22.3
GF8	23.1
GF9	23.3
GF10	24.4
GF11	22.2

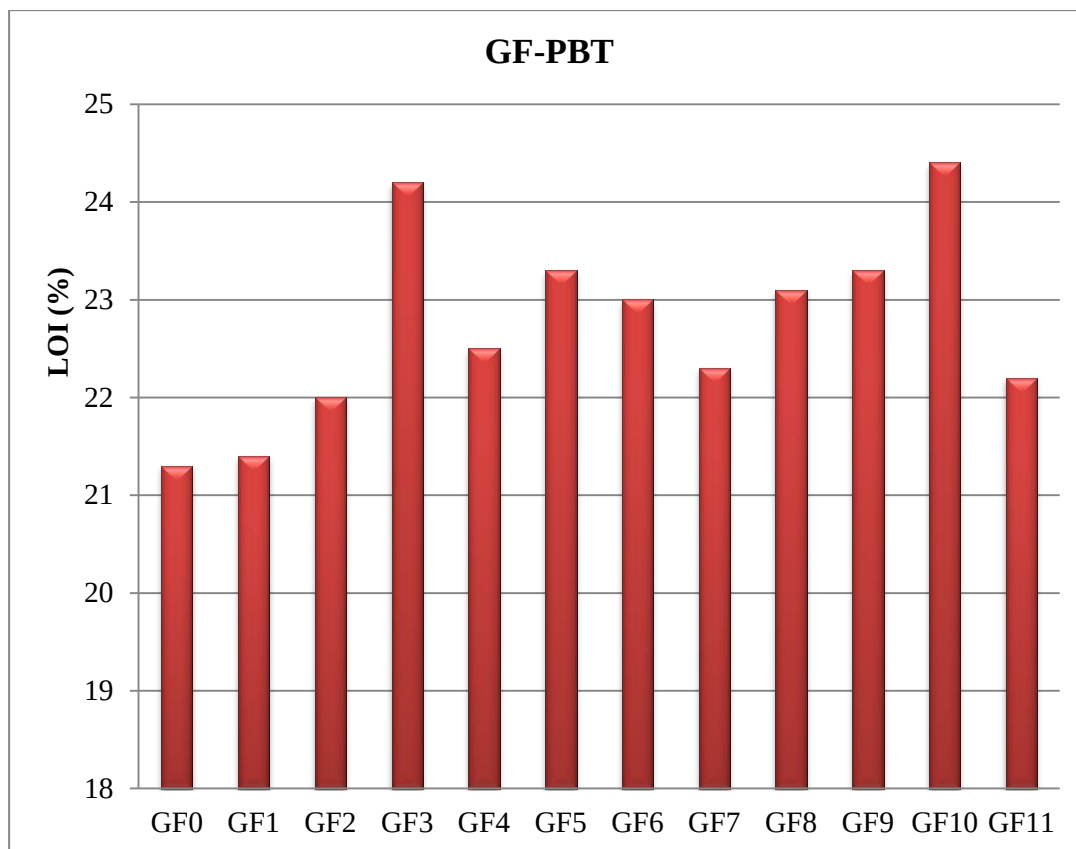


Figure 4.40 : LOI (%) test values of glass fiber reinforced PBT composites.

4.3.3 Glow wire temperature (GWT)

Glow wire test was done according to the procedure explained in section 3.4.3. GWT test results provide a way of comparing the ability of materials to extinguish flames and their ability to not produce particles capable of spreading fire. The glow wire tests were done at temperatures of 750 °C and 850 °C.

In Table 4.15 PBT composites glow wire test results are given. The glow wire test results showed that specimens PBT4, PBT7, PBT9, and PBT10 achieved the both test at temperature of 750 °C and 850 °C.

Adding 10 % TPP additive to PBT, single test result which did not ignite at 850 °C (PBT10). The synergistic effect of BP-ZB mixture which mentioned in LOI results section, also has seen in GWT test. While 5 % BP (PBT2) and 5 % ZB (PBT1) did not passed the both test, 2.5 % BP with 2.5 % ZB combination (PBT7) achieved both test at temperature of 750 °C and 850 °C. Furthermore, addition of 10 % BP to PBT passed the GWT at temperature of 750 °C.

Table 4.15 : Glow wire test results of PBT composites.

Samples	Glow wire 750 °C		Glow wire 850 °C	
	Ignition time (s)	Extinguish time (s)	Ignition time (s)	Extinguish time (s)
PBT0	3	Sample does not extinguish	1	Sample does not extinguish
PBT1	3	Sample does not extinguish	1	Sample does not extinguish
PBT2	5	32	6	Sample does not extinguish
PBT3	3	4	4	Sample does not extinguish
PBT4	2	30	1	30
PBT5	4	30	1	Sample does not extinguish
PBT6	5	30	1	Sample does not extinguish
PBT7	3	30	1	30
PBT8	4	32	1	Sample does not extinguish
PBT9	4	30	1	30
PBT10	4	2	There is no flame and no glowing.	0
PBT11	2	30	1	Sample does not extinguish

In Table 4.16 glass fiber reinforced PBT composites glow wire test results are given. According to the GWT test results of GF-PBT composites, TPP additive formulations (GF3, GF10) did not ignite at 750 °C test and extinguish in 61 s at 850 °C test, thus it was the most promising flame retardant additive for GF-PBT composites. The synergistic effect of BP and ZB mixture also was seen in GWT test of GF-PBT composites. While 5 % BP (GF2) and 5 % ZB (GF1) did not pass the both test, 2.5 % BP with 2.5 % ZB combination (GF7) achieved test at temperature of 750 °C.

Table 4.16 : Glow wire test results glass fiber reinforced PBT composites.

Samples	Glow wire 750 °C		Glow wire 850 °C	
	Ignition time (s)	Extinguish time (s)	Ignition time (s)	Extinguish time (s)
GF0	3	Sample does not extinguish	1	Sample does not extinguish
GF1	10	Sample does not extinguish	1	Sample does not extinguish
GF2	16	Sample does not extinguish	1	Sample does not extinguish
GF3	There is no flame and no glowing.	-	7	61
GF4	10	35	1	Sample does not extinguish
GF5	5	30	1	Sample does not extinguish
GF6	There is no flame and no glowing.	-	1	Sample does not extinguish
GF7	There is no flame and no glowing.	-	1	Sample does not extinguish
GF8	17	30	16	Sample does not extinguish
GF9	17	Sample does not extinguish	16	Sample does not extinguish
GF10	There is no flame and no glowing.	-	8	61
GF11	1	2	1	Sample does not extinguish

5. CONCLUSIONS

In literature, it is known that flame retardant additives generally decrease mechanical properties of polymeric material since high amount of loading required for high flame retardancy. The objectives of this study, achieve high flame retardancy while increase or keep mechanical properties of PBT composites.

In order to investigate flame resistance efficiency of PBT and glass fiber reinforced PBT (GF-PBT) composites boron phosphate (BP), triphenyl phosphate (TPP), zinc borate (ZB) and calcium sulphate dihydrate (CSD) additives were selected. PBT compounds were prepared by using a co-rotating twin screw extruder and injection molding machine. The composites were characterized in terms of flammability and mechanical properties. Flammability of composites was determined by using a limiting oxygen index (LOI) and glow wire (GWT) tests. Mechanical properties such as tensile strength, elastic modulus, elongation at break, flexural strength, flexural modulus, impact strength, and hardness properties were also studied.

In experimental part, flame retardant fillers were used in both unreinforced PBT and glass fiber reinforced PBT. So as to examine the effectiveness of four flame retardant additives with low-loading level of ZB, BP, TPP, CSD formulations prepared. PBT0 and GF0 were formulated as flame retardant free reference for PBT and GF-PBT flame retardant composites. After determining the effect of each flame retardant additive on PBT, flame retardant additives were used with different combinations in order to see any further improvement when they used together. Furthermore, 10 % loading of BP, TPP, and CSD were performed separately, in order to see higher loading effects of these flame retardants. Addition of 5 % ZB to PBT did not show any improvement according to PBT0 (reference composite), therefore higher loading of ZB did not study. After PBT flame retardant composites were analyzed, all formulations were carried out with glass fiber reinforced PBT composites. In this set of formulations, it was analyzed both mechanical effects of glass fiber reinforcement and flame retardant filler behavior in glass fiber reinforced PBT composites. As a result of this study following conclusions are obtained.

- SEM observations showed that glass fibers were well dispersed in PBT matrix during extrusion and polymer matrix wrapped the fibers. According to elemental X-ray mapping analyses, flame retardant additives of composite formulations were well dispersed in PBT matrix. CSD formulations (GF4, GF5) were showed some agglomerations in PBT matrix. That result may have occurred due to the process difficulties of CSD additive in extrusion.
- According to the mechanical test results TPP flame retardant additive decreased tensile strength, tensile modulus, flexural strength, flexural modulus, and hardness (Shore D) properties of PBT composite and increased elongation at break value and Izod (notched) impact strength properties. Inorganic flame retardants (ZB, BP and CSD) caused decreased in impact strength test results of PBT composites.
- Addition of 30 % glass fiber to PBT matrix increased mechanical properties of composite considerably. When compare PBT with GF-PBT composite; tensile strength value increased to 105 MPa from 51 MPa, tensile modulus increased to 7905 MPa from 2210 MPa, elongation at break value decreased to 2.8 % from 82 %, flexural strength value increased to 157 MPa from 76 MPa, flexural modulus increased to 7420 MPa from 2320 MPa, Izod (notched) impact strength increased to 10.6 kJ/m² from 5.2 kJ/m², hardness value increased to 85 Shore D from 80 Shore D. When flame retardant additives used in GF-PBT composites, they showed similar behavior that was seen in PBT composites. TPP additives decreased tensile strength, tensile modulus, flexural strength and flexural modulus value and increased Izod impact strength properties significantly.
- LOI value of neat PBT (PBT0) was around 22. According to the LOI results, ZB addition to the PBT matrix did not change the LOI value of PBT composite. Adding 5 % BP to PBT matrix slightly increased the LOI value of PBT0. When TPP added to PBT matrix, LOI value noticeably increased up to 26.6. Highest LOI values were obtained when 10 % TPP (PBT10) was added to PBT matrix and LOI was increased to 27.2. CSD additive showed the second highest LOI value after TPP in formulations were fed to the system 5 % proportion.

- In first set of formulation it was observed that TPP is the most successful flame retardant for PBT in terms of flammability properties. However, as mentioned mechanical properties results, TPP additive decreased some mechanical properties like tensile strength and flexural strength values. In order to obtain high flame retardancy properties with high mechanical properties, TPP was combined with BP additive. Even though some decreases in LOI value occurred compared to TPP base formulation, combination of TPP with BP showed high LOI results with higher mechanical properties.
- It was observed that ZB did not have flame retardancy effectiveness on PBT and BP showed slight increase in LOI. When BP is combined with ZB, important increase was observed in flame retardancy effectiveness and higher LOI results were obtained. When 2.5 % BP was combined with 2.5 % ZB, LOI value of 23.0 was obtained; further increase of BP content to 5 % and ZB content to 5 %, increases LOI value to 23.4. These test results indicated that when they were used together they showed a significant synergistic effect.
- When GF-PBT composites LOI results compared to PBT composites LOI results, GF-PBT composites showed lower LOI values than PBT composites. This behavior would be result of “candlewick effect” of glass fiber. While neat PBT (PBT0) LOI was 22, GF-PBT (GF0) was around 21.3. In all GF-PBT formulations, flame retardants showed similar behavior as in PBT composites. According to test results of GF1, GF2, GF3 and GF4 formulations, TPP was the most successive flame retardant additive for GF-PBT composites. The synergistic effect of BP, ZB mixture was seen in GF-PBT composites, too.
- The glow wire test results showed that specimens PBT4, PBT7, PBT9, and PBT10 achieved the both test at temperature of 750 °C and 850 °C. Addition 10 % TPP to PBT, single test result which did not ignite at 850 °C (PBT10). The synergistic effect of BP, ZB mixture which mentioned in LOI results section, also has seen in GWT test. While 5 % BP (PBT2) and 5 % ZB (PBT1) did not pass the both test, 2.5 % BP with 2.5 % ZB combination (PBT7) achieved both test at temperature of 750 °C and 850 °C. Similar results were obtained for glass fiber reinforced composites. According to the

GWT test results of GF-PBT composites, TPP additive formulations (GF3, GF10) did not ignite at 750 °C test and extinguish in 61 s at 850 °C test, Thus it was the most promising flame retardant additive for PBT. The synergistic effect of BP and ZB mixture also was seen in GWT test of GF-PBT composites.

REFERENCES

- [1] **Döring, M., Rakotomalala, M., and Wagner, S.** (2010). Recent Developments in Halogen Free Flame Retardants for Epoxy Resins for Electrical and Electronic Applications, *Materials*, **3**, issue 8, pp. 4300-4327.
- [2] **Horrocks, A.R., Price D.,** (2001). Fire Retardant Materials, *Woodhead*, p. 1-30, ISBN 9781855734197.
- [3] **Kiliaris, P., and Papaspyrides, C.D.** (2014). Polymer Green Flame Retardants, *Elsevier*, p. 1-35, ISBN: 978-0-444-53808-6.
- [4] **Fakirov S.,** (2002). Handbook of Thermoplastic Polyesters, *Polymer International*, Vol. 1, pp. 10-17, ISBN 3-527-29790-1.
- [5] **Sullalti, S., Colonna, M., Berti, C., Fiorini, M., and Karanam, S.** (2012). Effect of Phosphorus Based Flame Retardants on UL-94 And Comparative Tracking, Index Properties of Poly(Butylene Terephthalate), *Polymer Degradation and Stability*, Vol.97, pp. 566–572.
- [6] **Hirschler, M. M.** (2014). Flame Retardants and Heat Release: Review of Data on Individual Polymers, *Fire and Materials*, Vol. 39, issue 1, DOI: 10.1002/fam.2242.
- [7] **Bourbigot, S., Le Bras, M., Leeuwendal, R., Shen, K.K., Schubert, D.,** (1999). “Recent Advances in the Use of Zinc Borates in Flame Retardancy of EVA”, *Polymer Degradation and Stability*, 64, 419-425.
- [8] **Maic, Y.W., Caic, G.P., Yub, Z.Z., and Dasaria, A.** (2013). Recent Developments in the Fire Retardancy of Polymeric Materials, *Progress in Polymer Science*, **38**, pp. 1357-1387.
- [9] **Url-1** < <http://pinfa.org/media/newsletters/191-non-halogen-fire-safety-solutions-pinfa-newsletter-issue-nd-35-2.html> > accessed at 15.03.2015
- [10] **Hollingbery, L.,** (2011). Decomposition and Fire Retardancy of Naturally Occurring Mixtures of Huntite and Hydromagnesite.
- [11] **Cowie, J.M.G.,** (1991). Polymers: Chemistry & Physics of Modern Materials, 2nd edition, ISBN 0748740732

- [12] **Wang, R., Chen, X., and Xu, Q.** (2014). Progress of Research on Modification in Polybutylene Terephthalate, *Advanced Materials Research Vols.* 860-863, pp. 855-861.
- [13] **Url-1** <<http://www.epa.gov/ttnchie1/ap42/ch11/final/c11s13.pdf>> accessed at 01.05.2015
- [14] **Hoa, S.V.** (2009). Principles of the Manufacturing of Composite Materials, *DEStech Publications Inc.*, pp. 101-141, U.S.A.
- [15] Gibson, F.R. (2012). Principles of Composites Material Mechanics, *CRC Press*, (3rd ed.), U.S.
- [16] **Strong, A.B.** (2008). Fundamentals of Composites Manufacturing Materials, Methods, and Applications (2nd Ed.), *Society of Manufacturing Engineer*, U.S.A.
- [17] **Prinz, K.** (2011) Flame Retardant and Dyeing Treatment of Cellulose Fabrics Using a Combined “Grafting from” and PIGP Process, *M.Sc thesis, Dipl. Ing. TU Dresden*.
- [18] **Pal,G, and Kasy, H.M.** (1991). Plastics: Their Behaviour in Fires, *Elsevier*, Vol. 6, pp.32-86, ISBN 0444987665.
- [19] **Gallo E.,** (2009). Progress in Polyesters Flame Retardancy: New Halogen-free Formulations.
- [20] **Grellmann, W.** (2007). Polymer Testing, Testing of Composite Materials, pp.511-563, Germany.
- [21] **Speight G.,J.** (2011): Handbook of Industrial Hydrocarbon Process, *Elsevier publications*, pp. 355-391.
- [22] **Nelson, G. L.** (1995). Fire and Polymers II: Materials and Tests for Hazard Prevention, Washington, D.C., *American Chemical Society*, ISBN 9780841232310.
- [23] **Hartzell, G. E.** (1997). Fire Protection Handbook, 20th ed., National Fire Protection Association, Quincy.
- [24] **Krevelen, D.W., and Nijenhuis, K.** (2009). Properties of Polymers: Their Correlation with Chemical Structure; their Numerical Estimation and Prediction from Additive Group Contributions, *Elsevier*, 4th ed., pp. **819-864**.

- [25] **Beyler, C.L., and Hirschler, M.M.** (1995). Thermal Decomposition of Polymers", C.L. Chapter 1-7 in SFPE Handbook of Fire Protection Engineering (2nd Edn)", Editor-in-chief: P.J. DiNenno, pp. 1.99-1.119, NFPA, Quincy, MA, 1995.
- [26] **Hull, R.T.** (2009). Fire Retardancy of Polymers New Strategies and Mechanism, *Royal Society of Chemistry*, U.K.
- [27] **Horrocks, A.R. and Price, D.** (2011). Fire retardant materials, Polymer Combustion, Condensed Phase Pyrolysis and Smoke Formation, *Wood head Publishing Lt*, USA.
- [28] **Url-2** <http://www.nist.gov/el/fire_research/upload/chapter-3.pdf> accessed at 15.04.2015
- [29] U.S. EPA. (2008). "Flame Retardants in Printed Circuit Boards (Review Draft)."
- [30] **Cullis, C. F., and Hirschler, M.** (1981). The Combustion of Organic Polymers, *Clarendon Press*, Oxford.
- [31] **Troitzsch, J.,** (1998). Overview of Flame Retardants, *Chimica Oggi/Chemistry Today*, **16**, p. 325-344.
- [32] **Gachter, R., and Müller, H.** (1990). Plastics Additives, *Hanser Publisher*, 3rd ed. pp. 709-746, New York.
- [33] **Dubois, P., Laoutid, F., Bonnaud, L., Alexandre, M., and Cuesta, J.M.L.** (2009). New Prospects in Flame Retardant Polymer Materials: From Fundamentals to Nanocomposites, *Materials Science and Engineering*, **63**, 100-125.
- [34] **Url-3** <<http://www.cefic-efra.org>> accessed at 24.04.2015
- [35] **Wilkie, C. A., Morgan, A. B.,** (2010). Fire Retardancy of Polymeric Materials. *Taylor&Francis Group*, p. 1-13.
- [36] **Lomakin, S. M., Zaikov, G.E.** (2003). Modern Polymer Flame Retardancy, *Brill Academic Publishers*, p. 52-95.
- [37] **Innes, A., Innes, J.,**(2003). Plastic Flame Retardants: Technology and Current Developments, *Rapra Technology*, U.K.
- [38] **Weil, E.D., Levchik, S.V.** (2009). Flame Retardants for Plastics and Textiles: Practical Applications, *Hanser Verlag*, p.50-70.
- [39] **Roger N. R.**(2003). Particulate-Filled Polymer Composites (2nd Ed., *Rapra Technology Limited*, U.S.

- [40] **Braun, U., Bahr, H., and Scharrel, B.** (2010). Fire Retardancy Effect of Aluminium Phosphinate and Melamine Polyphosphate in Glass Fibre Reinforced Polyamide 6.
- [41] **Ren, Y., Liu, Y., and Dong, E.** (2011). Development of Environmental Friendly Flame Retardants for Wood Plastic Composites (WPC), *Advanced materials Research*, Vols. 332-334, p.1880-1884.
- [42] **Url-4** <http://www.flameretardants-online.com/images/userdata/pdf/375_EN> accessed at 20.04.2015
- [43] **Price, D., Billingham, N.C, and Doi, Y., and Grassie N.** (1995). Fire Retardant Polymers, *Polymer Degradation and Stability*, Vol. 54, issue 2-3, pp. 205-215.
- [44] **Url-5** <<http://www.lenntech.com/periodic/elements/b.htm>> accessed at 20.04.2015
- [45] **Morgan, A.B., Wilkie, C.A.** (2007). Flame Retardant Polymer Nanocomposites, Wiley-Interscience, New Jersey.
- [46] **Lomakin, S.M., Zaikov, G.E.** (2003). New concepts in polymer science: Modern polymer flame retardancy, VSP, Utrecht.
- [47] **Schubert, D.M., Alam, F., Visi, M.Z., and Knobler, C.B.** (2003). Structural Characterization And Chemistry of The Industrially Important Zinc Borate, $Zn[B_3O_4(OH)_3]$, *Chem. Mater.*, 15, 866-871.
- [48] **Corbridge, D.E.C.** (2013). Phosphorus: Chemistry, Biochemistry and Technology, 6 th ed, *Taylor&Francis Group*, p 204-210.
- [49] **Harper, C.A.** (2004). Handbook of Building Materials for Fire Protection, *Mcgraw-HILL*, pp. Flame Retardants for Plastics, Dr. Elisabeth S. Papazoglou, US.
- [50] **Li, B., Xu, M.,** (2006). Effect of A Novel Charring-Foaming Agent On Flame Retardancy and Thermal Degradation of Intumescent Flame Retardant Polypropylene, *Polymer Degradation and Stability*, **91**, issue 6, p. 1380–1386.
- [51] **Wei, Y.** (2012). Investigations on Synergistic Flame Retardancy and Mechanisms of Halogen-free Flame Retardant Polyester Composites, city university of Hong Kong, (Doctoral dissertation).

- [52] **Hu, Y., Tai, Q., Yuen, R.K.K., Yang, W., and Qiao, Z.** (2012). Iron-montmorillonite and zinc borate as synergistic agents in flame-retardant glass fiber reinforced polyamide 6 composites in combination with melamine polyphosphate, *Composites*, **43**, 415-422.
- [53] **Kaynak, C., and Isitman, N.A.** (2011). Synergistic Fire Retardancy of Colemanite, a Natural Hydrated Calcium Borate, in High-Impact Polystyrene Containing Brominated Epoxy and Antimony Oxide, Ankara, Turkey.
- [54] **Campo, E.A.** (2006). **The Complete Part Design Handbook For Injection Molding of Thermoplastic**, *Hanser publisher*, pp. 723-756.
- [55] **Hull, T.R., and Kandola, B.K.** (2009). Fire Retardancy of Polymers New Strategies and Mechanisms, *RSC Publishing*, ISBN 978-0-85404-149-7.
- [56] **Wypych, G.** (2010). Handbook of Fillers, *Chemtech Publishing*, 3rd ed. pp.520-530, ISBN 978-1-895198-41-6.
- [57] **Forrest, M.J.**, (2002). Analysis of Plastics, *iSmithers Rapra Publishing*, p. 190-200, ISBN 9781859573334.
- [58] **Hao , J., Du, J., Si, M., Feng, J., and Xu, L.** (2013). Synergistic Flame Retardant Effects and Mechanisms of Nano-Sb₂O₃ in Combination with Aluminum Phosphinate in Poly(Ethylene terephthalate), *Polymer Degradation and Stability*, **100**, 70-78.
- [59] **Marcelo M. Hirschler, M.M.** (2014). Flame Retardants and Heat Release: Review of Data on Individual Polymers, *Fire and Materials*, USA.
- [60] **Hirschler, M.M.** (2014). Flame Retardants and Heat Release: Review of Traditional Studies on Products and on Groups of Polymers, *Fire and Materials*, **39**, Doi: 10.1002/fam.2243.
- [61] **Ramani, A., and Dahoe, A.E.** (2014). On the Performance and Mechanism of Brominated and Halogen-free Flame Retardants in Formulations of Glass Fibre Reinforced Poly(Butylene Terephthalate), *Polymer Degradation and Stability*, **104**, pp.71-86.
- [62] **Schartel, B., Brehme, S., Köppl, T., and Fischer, O.** (2012). Phosphorus Polyester-an Alternative to Low-Molecular-Weight Flame Retardants in Poly(Butylene Terephthalate), *Macromolecular Chemistry and Physics*, **213**, issue 22, 2386–2397.

- [63] **Hu, Y., Xiao, J., Yang, L., Cai, Y., Song, L., and Chen, Z.** (2006). Fire Retardant Synergism Between Melamine and Triphenyl Phosphate in Poly(Butylene terephthalate), *Polymer Degradation and Stability*, **91**, 2093-2100.
- [64] **Fang, Z., Tong, L., and Gao, F.** (2006). Effect of a Novel Phosphorous Nitrogen Containing Intumescent Flame Retardant on the Fire Retardancy and the Thermal Behavior of Poly(butylene terephthalate), *Polymer Degradation and Stability*, **91**, 1295-1299.
- [65] **Yang, W., Hua, Y., Tai, O., Lu, H., Song, L., and Yuen, R.K.K.** (2011). Fire and Mechanical Performance of Nanoclay Reinforced Glass-Fiber/PBT Composites Containing Aluminum Hypophosphite Particles, 794–800.
- [66] **Schartel, B., and Braun, U.,** (2008). Flame Retardancy Mechanisms of Aluminium Phosphinate in Combination with Melamine Cyanurate in Glass-Fibre-Reinforced Poly(1,4-butylene terephthalate), *Macromol. Mater. Eng.* 293, 206–217.
- [67] **Wang, D., Qhanga, Z., Zhou, K., Yuan, W.Y., and Gong, X.** (2014). The Influence of Manganese–Cobalt Oxide/Graphene On Reducing Fire Hazards of Poly(Butylene Terephthalate) , *Journal of Hazardous Materials*, 278, 391–400.
- [68] **Schartel, B., Gallo, E., Braun, U., Russo, P., and Acierno, D.,** (2009). Halogen-free Flame Retarded Poly(butylene Terephthalate) (PBT) Using Metal Oxides/PBT Nanocomposites in Combination With Aluminium Phosphinate, *Polymer degradation and Stability*, **94**, 8 , pp. 1245-1253.
- [69] **Kılıç, M.,** (2009). Production and Characterization of Boron Based Additives and the Effect of Flame Retardant Additives on PET Based Composites, *PhD Thesis, Middle East Technical University*.
- [70] **ISO 1183** (1999). Methods for Determining Density of Non-Cellular Plastics, *International Standard Organization*.
- [71] **ISO 527** (1993). Determination of Tensile Properties, *International Standard Organization*.
- [72] **ISO 178** (2001). Plastics, Determination of Flexural Properties of Rigid Plastics. *International Standard Organization*.
- [73] **ISO 180** (2000). Plastics, Determination of Izod Impact Strength of Rigid Materials, *International Standard Organization*.

- [74]**ASTM D2863** (2010).Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index), *American Society for Testing and Materials*.
- [75]**ASTM D6194** (2010). Standard Test Method for Glow Wire Ignition of Materials, *American Society for Testing and Materials*.
- [76] **Hu, Y., Yuen, R.K.K, Yang, W., and Lu, H.,** (2011). Enhancement of the Fire Retardancy Performance of Glass-Fiber Reinforced Poly(ethylene Terephthalate) Composite with the Incorporation of Aluminum Hypophosphite and Melamine Cyanurate, *Composites*, 1057-1065.
- [77] **Liu, Y., Chen, W., Liu, P, and Wang, Q.,** (2015).Interfacial Carbonation for Efficient Flame Retardance of Glass Fiber- Reinforced Polyamide 6, *Polymer Chemistry*, ,6, 4409-4414.

CURRICULUM VITAE

Name Surname: Ceren YARGICI

Place and Date of Birth: Konya - 12.03.1990

Adress: Libadiye Cad. Kireç fırını sokak Teletaş Çamlıca Sitesi

Üsküdar /İSTANBUL

E-mail: cerenyargici@gmail.com

B.Sc. : Istanbul Technical University- Chemical Engineering

M.Sc.: Istanbul Technical University-Polymer Science and Technology

