REPUBLIC OF TURKEY
ADANA ALPARSLAN TÜRKEŞ SCIENCE AND TECHNOLOGY UNIVERSITY

INSTITUTE OF GRADUATE SCHOOL
DEPARTMENT OF NANOTECHNOLOGY AND ENGINEERING SCIENCES

MECHANICAL, THERMAL, STRUCTURAL AND MORPHOLOGICAL CHARACTERIZATION OF POLYBUTYLENE TEREPHTHALATE NANOCOMPOSITES CONTAINING ORGANOCLAYS

YILDIZ BAŞ
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ADANA 2022

I hereby declare that all information in this thesis has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all information that is not original to this work.

[Signature]

Yıldız BAŞ

ABSTRACT

MECHANICAL, THERMAL, STRUCTURAL AND MORPHOLOGICAL CHARACTERIZATION OF POLYBUTYLENE TEREPHTHALATE NANOCOMPOSITES CONTAINING ORGANOCLAYS

Yıldız BAŞ
Department of Nanotechnology and Engineering Sciences
Supervisor: Assoc. Prof. Dr. Ali Sinan DİKE
February 2022, 50 pages

In order to investigate the effects of organoclay addition on the properties of Polybutylene terephthalate (PBT) nanocomposites loaded with two different types of organoclays are fabricated using melt-mixing technique in a twin-screw extruder. Quaternary ammonium salts with dimethyl, benzyl, hydrogenated tallow and dimethyl, dehydrogenated tailed modified Turkish organoclays (trade names of esanNANO 2-130 and esanNANO 1-140, Eczacıbaşı Esan, İstanbul, Turkey) are blended with PBT (Advanite SB88, Sasa Polyester A.Ş., Adana, Turkey) at the compositions of 1%, 3%, 5% and 10% weight ratios. Test samples are shaped using lab-scale injection molding device. Mechanical, thermo-mechanical, thermal stability, melt-flow, structural and morphological behaviors of the nanocomposite samples are investigated by performing tensile, impact and shore hardness tests, dynamic mechanical analysis (DMA), thermo-gravimetric analysis (TGA), melt flow rate measurements and X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) methods, respectively. Based on these test and analyses, NC 130 clay gave better results than NC 140 in terms of tensile, hardness and melt-flow behaviors, whereas, NC 140 clay showed higher performances as impact resistance, thermo-mechanical, and density.

Keywords: poly (butylene terephthalate), nanocomposites, organoclay, polymer composites

ÖZET

ORGANOKİLLER İÇEREN POLİBÜTİLEN TEREFTALAT NANOKOMPOZİTLERİNİN MEKANİK, ISISAL, YAPISAL VE MORFOLOLİK KARAKTERİZASYONU

Yıldız BAŞ
Nanoteknoloji ve Mühendislik Bilimleri Anabilim Dalı
Danışman: Doç. Dr. Ali Sinan DİKE
Şubat 2022, 50 sayfa

Organokil ilavesinin polibütilen tereftalat (PBT) özellikleri üzerindeki etkilerini araştırmak için iki farklı tipte organokil içeren nanokompozitler, çift vidalı ekstrüder ile eriyik karıştırma tekniği kullanılarak üretilmiştir. Dimetil,benzil,hidrojenleştirilmiş ve dimetil, hidrojenleştirilmiş kuyruğa sahip kuaterner amonyum tuzları ile modifiye edilmiş Türk organokilleri (ticari isimleri esanNANO 2-130 ve esanNANO 1-140, Eczacıbaşı Esan, İstanbul, Türkiye) ile PBT (Advanite SB88, Sasa Polyester A. Ş., Adana, Türkiye) %1, %3, %5 ve %10 ağırlıkça oranlarda harmanlanmıştır. Test numuneleri, laboratuvar ölçekli enjeksiyon kalıplama cihazı kullanılarak şekillendirilmiştir. Nanokompozit numunelerin mekanik, ısısal-mekanik, ısısal kararlılık, eriyik akışı, yapısal ve morfolojik davranışları sırasıyla, çekme, darbe ve Shore sertlik, dinamik mekanik analiz (DMA), termo-gravimetrik analiz (TGA), eriyik akışı ölçümleri testleri ve X-ışını kırınım analizi (XRD), taramalı elektron mikroskobu (SEM) yöntemleri yapılarak araştırılmıştır. Bu test ve analizlere göre NC 130 kili çekme, sertlik ve eriyik akış davranışları açısından NC 140'a göre daha iyi sonuçlar verirken, NC 140 kili darbe dayanımı, termo-mekanik ve yoğunluk olarak daha yüksek performans göstermiştir.

Anahtar Kelimeler: poli (bütilen terefitalat), nanokompozitler, organokil, polimer kompozitler

Dedicated to my family

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my advisor Assoc. Prof. Dr. Ali Sinan Dike for his kind support, guidance, encouraging, effective criticism and valuable discussions during my thesis study.

I would like to thank Prof. Dr. Teoman Tinçer for providing his polymer rheology laboratory at METU in processing and characterization steps of composite samples.

I am also grateful to Dr. Ümit Tayfun for his valuable help and support on using material processing devices and test equipment.

I am thankful to Mr. Sercan Öztaş who works for SASA Polyester A.Ş. for providing me PBT chips.

I wish to express my thanks to thanking Dr. Öykü Akar for her affords and help regarding several characterization steps.

I also thank Assoc. Prof. Dr. Mehmet Kodal for his help based on DMA analysis.

I believe that librarians are hidden heroes of the academy. I am also thankful to Mrs. Betül Yüksekbaş and all staff of the library of Adana Science and Technology University who provide me so many documents related with this study.

Also, I would like to all academic and administrative staff in the Graduate School of the Adana Alparslan Türkeş Science and Technology University for their great contributions.

Last, but not least, I would like to dedicate this thesis to my beloved family.

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NOMENCLATURE

Å	: Angstrom
ABS	: Acrylonitrile butadiene styrene
PA-6	: Polyamide-6
LDPE	: Low density polyethylene
PLA	: Poly (lactic acid)
MMT	: Montmorillonite
MFR	: Melt Flow Rate
PE	: Polyethylene
PBT	: Poly (butylene terephthalate)
DMA	: Dynamic Mechanical Analysis
IR	: Infrared
MFI	: Melt Flow Index
SEM	: Scanning Electron Microscope
TGA	: Thermal Gravimetric Analysis
T_g	: Glass Transition Temperature
XRD	: X-ray Diffraction

1. INTRODUCTION

1.1. Polymeric composite materials

Composite materials are simply described as a mixture containing reinforcement additives embedded in a matrix. Matrix is the continuous phase and reinforcing material is the discontinuous phase in the composite system. The combination of these two phases results in improved properties with respect to property of each constituent. The main purpose of processing composite materials is reaching enhancement in several material performances including mechanical behavior, physical characteristics, thermal, dimensional and tribological stability. In addition, to optimize properties, material costs can be reduced by incorporating low-cost additives (Hollaway, 1994; Schwartz, 1983).

Polymers are the most favored matrix materials of composites for varied application fields. Polymeric composites can be thermoset or thermoplastic which are chosen according to the final application of composite material. In most cases, reinforcing fillers have higher mechanical strength and lower density compared to polymeric matrix material. The variety of reinforcing additives ranging from fibers to plate-like inorganic materials (Chang and Lees, 1988; Iyer and Drzal, 1990)

Thermoplastics have a two-dimensional structure (linear or branched) and are soluble in certain solvents. However, thermosets feature three-dimensional network topologies and are insoluble due to crosslinks between major chains (Biron, M., 2018; Jancar et al., 1992; Mathijsen, 2016).

1.2. Nanocomposites

A nanocomposite is a multiphase solid substance in which one of the phases has a diameter of fewer than 100 nanometers (nm), or structures with nanoscale repeat intervals between the various phases that make up the material. In the case of dispersing small amounts of nanofillers into polymer matrices, mechanical behavior, gas and solvent barrier properties, thermal degradation, and chemical resistance can be improved while avoiding traditional

micro-filler drawbacks such as embrittlement, loss of transparency, and lightness (Balazs et al., 2006; Dubey et al., 2017; Grimsdale and Müllen, 2005; Rao et al., 2006).

There are three main types of nanocomposite materials:

1) Iso-dimensional nanoparticles, such as spherical silica nanoparticles and semiconductor nanoclusters, have three dimensions on the order of nanometers.
2) Nanotubes or whiskers are elongated structures with two nanometer-scale dimensions and a larger third dimension, such as carbon nanotubes or cellulose whiskers.
3) Nanocomposites with just one dimension in the nanoscale range, such as polymer-layered crystal nanocomposites, in which the filler is present as one to a few nanometer thick sheets with hundreds to thousands of nanometers in length (Friedrich et al., 2005; Malhotra et al., 2012; Thomas et al., 2012).

Polymer-layered silicate nanocomposites which belong to this third class are used in this thesis study.

1.3. Nanoclay

Clay minerals are hydrous aluminum phyllosilicates, also known as layered silicates that include diverse cations such as iron, magnesium, and alkali metals. These clay minerals are quite abundant and may be found in a variety of environments, including sedimentary rocks (Albdiry et al., 2013; Floody et., 2009; Okamoto, 2006; Ray and Easteal, 2007).

Clays are made up of tetrahedral and octahedral sheets. The ratio of these two sheets in the structure is used to categorize the structure. In the stacking morphology of clay particles, for example, a 2:1 clay structure shows that one octahedral sheet is sandwiched between two tetrahedral sheets. While clay minerals can have both 1:1 and 2:1 structures, the 2:1 structure, often known as a smectite structure, is more frequent in clay products. Bonding between the tetrahedral and octahedral sheets in the development of a 2:1 structure requires that the tetrahedral sheet be corrugated or twisted, resulting in a ditrigonal distortion of the hexagonal array, followed by flattening of the octahedral sheet. This reduces the total distortion forces of the crystallite, resulting in a layered flat form. Small molecules can easily intercalate between these layers since they are weakly packed together with a regular van der Waals gap (Jlassi et al., 2017; Ray et al., 2013; Utracki, 2004; Zanetti et al., 2000). As a result, the phyllosilicates

are the most typically utilized in the creation of nanocomposite materials, such as montmorillonite, hectorite, and saponite, belong to the structural family of 2:1 layered silicates.

The representative image of 2:1 layered silicates with (A) type 1:1 and (B) type 2:1 is provided in Figure 1.1. In this image, d stands for the basal distance between clay layers (Akbari et al., 2010; Gao, 2004; Kuilla et al., 2010).

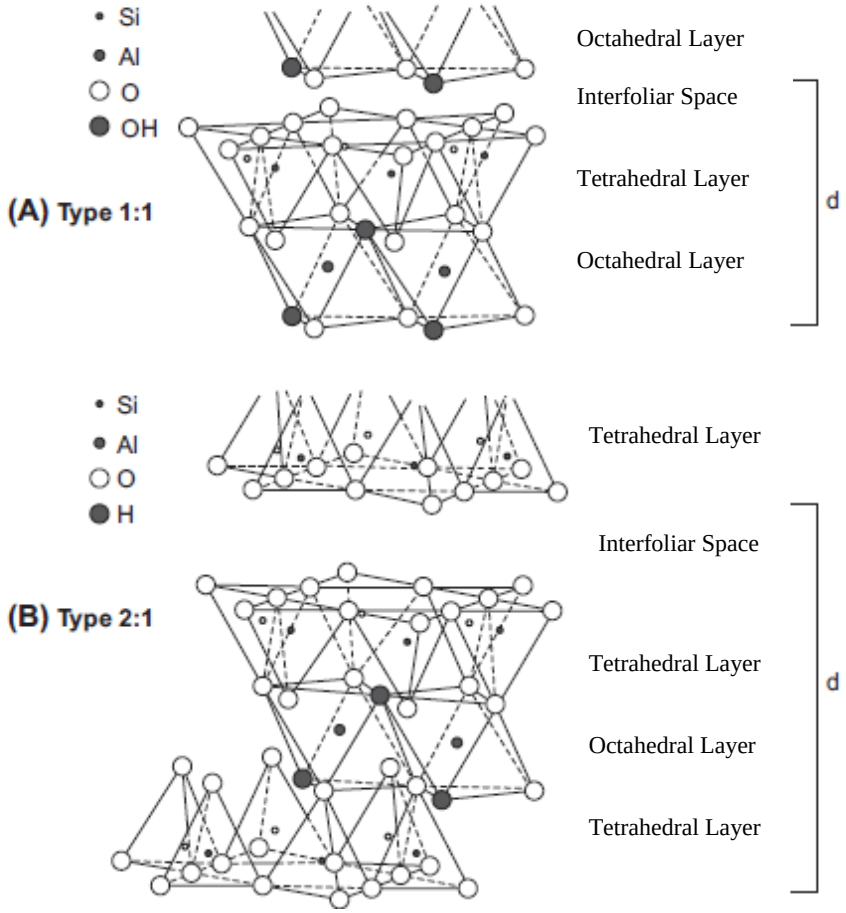

Figure 1.1. A schematic of the crystal structures of clay minerals

The basic raw material for nanoclay products is montmorillonite (smectite clay). The surface features of smectite clay mineral may be modified due to its plate-like structure. Following treatment with organic modifiers, the beginning basal spacing between these plates is about 15; after treatment with organic modifiers, the basal spacings are approximately 32-36

Angstrom(Å). Increased basal spacing is resulted in more homogenous dispersion inside polymer structures (Giannelis, 1996; Ray and Okamoto, 2003).

1.4. Poly (butylene terephthalate)

Poly (1, 4-butylene terephthalate) (PBT) is a synthetic semi-crystalline thermoplastic that belongs to the polyester group of resins and has properties comparable to other thermoplastic polyesters. Chemical structure of PBT is shown in Figure 1.2. It is a high-performance material with an excellent balance of mechanical and electrical characteristics, as well as strong dimensional stability, heat resistance, and processing benefits. PBT is readily moldable and thermoformable (Abobo et al., 2021; Gallo, 2009; Yokouchi et al., 1976).

However, it is well known that thermal, oxidative, and hydrolytic degradation can occur at the processing temperature (250–280°C). PBT is gradually damaged by thermo- and photo-oxidative processes that occur over its lifespan, depending on the temperature and outdoor usage. Furthermore, its flammability and severe dripping during combustion restrict its applicability; this is why the thermal breakdown of polyesters such as poly (ethylene terephthalate) (PET) and PBT has remained a focus of research. (Illers, 1980; Chisholm et al., 2002; Samperi et al., 2004).

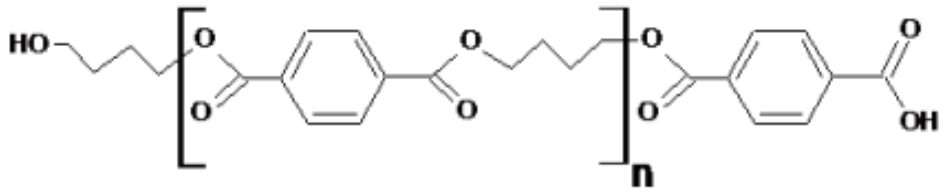

Figure 1.2. Chemical structure of linear poly (butylene terephthalate)

1.5. Extrusion process

Extruders are used for research in material science laboratories as well as large-scale manufacturing lines in the commercial plastics sector. The extruder can be used to combine components and extrude a complex polymer that is then cooled, cut, and sold as a pellet. The extruder might be part of the blow molding or injection molding processes. Die temperature

and barrel temperatures in various extruder zones are process factors. Die pressure is a process variable that may be controlled when a die valve is present (Bourban et al., 1998; Ciullo, 1996). Schematic representation of an extruder is given in Figure 1.3.

The key advantages of using a twin-screw extruder to produce thermoplastic-based nanocomposites are that they can combine components more effectively than single-screw extruders and that there is no solvent involved, making them more environmentally sustainable. This technology has a significant impact on productivity, efficiency, and the flexibility of systems. (Akpan et al.,2019; Fard and Anderson, 2013; Martelli, 1983; Middleman, 1977).

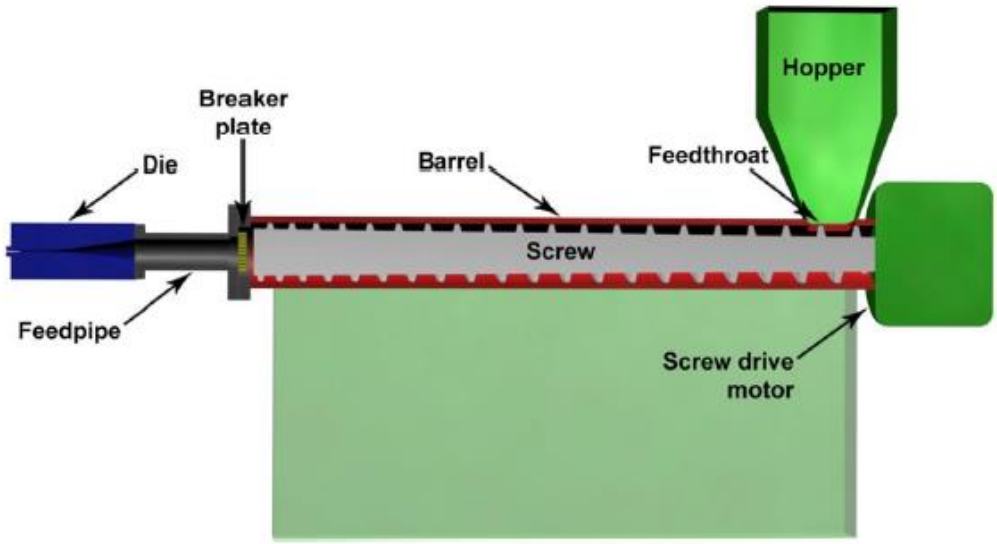

Figure 1.3. Schematic representation of an extruder.

With twin-screw extrusion, the screw speed and addition rate may be modified independently, and it can be operated at a certain extrusion rate at different screw speeds below the torque limit. Because the extrusion rate and screw speed are decoupled, it can be adjusted the time and intensity of the melting and mixing operations without exceeding material temperature limits or causing damage (Djuric, 2009; Martelli, 1983, Middleman, 1977).

1.6. Injection molding process

Injection molding is one of the most cost-effective methods of producing polymer-based products. This process is used to generate finished polymeric components for everything from

household items to automotive equipment. (Dekel and Kenig; 2021, Fu et al., 2020; Rubin and Rubin, 1972).

The basic stages and types of equipment of injection molding process are represented in Figure 1.4.

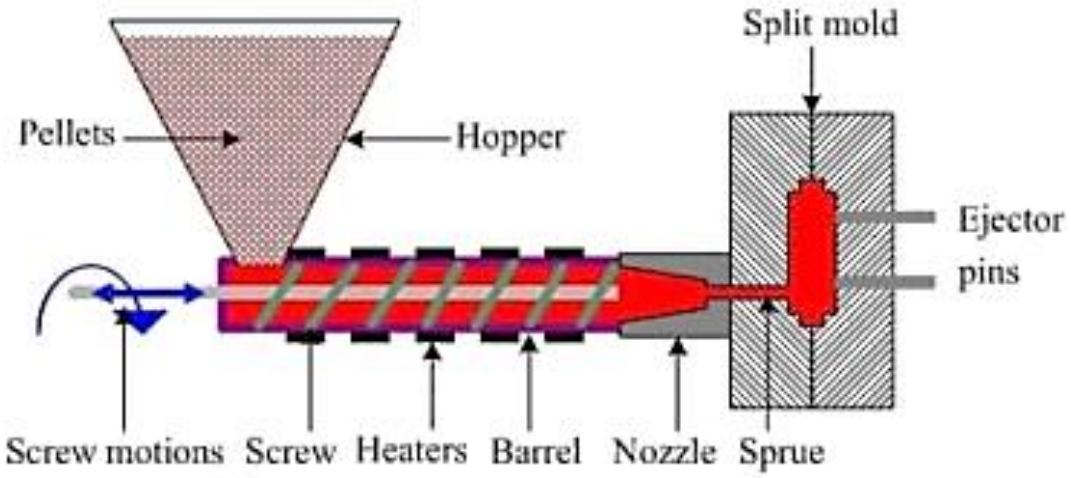

Figure 1.4. Schematic drawing of injection molding process.

This common process comprises a three-step cycle operation: filling, packaging, and chilling. To begin, a melted solid polymer is pushed toward the nozzle. To control the temperature of melting plastic, a temperature control system is employed. The polymer melt is then pumped under high pressure into the tight mold. During this stage, molten polymer is subjected to rolling screw pressure. The cooled mold gives the optimum shape for molten plastic due to its well-designed cavities. Finally, the mold is opened and the injected product is removed either manually or automatically. (Altan et al., 1993; Harper and Petrie, 2003; Rosato and Rosato, 2012).

2. LITERATURE REVIEW

2.1. Organoclay-filled polymer nanocomposites

In recent years, Polymer-clay nanocomposites have been studied by many researchers. In one of these studies, Santiago et al. performed the production of organoclay-filled poly (sodium acrylate) composites. They investigated the enhancement in thermal stability and swelling behavior after the addition of organoclay (Santiago et al., 2007).

Singh and Ghosh examined the torsional, structural and tensile behavior of organoclay reinforced acrylonitrile butadiene styrene (ABS) terpolymer composites using melt mixing. They found that the rigidity and modulus of elasticity of ABS were improved by the addition of organoclay (Singh and Ghosh, 2014).

Dike and Yilmazer performed several research studies related to polystyrene nanocomposites loaded with different types of nanoclays. They implied that aliphatic and aromatic elastomers can be integrated into polymer/clay system as compatibilizers to promote intercalation and exfoliation structures for clay layers into polystyrene matrix. They proved that elastomeric and aliphatic compatibilizers act as dispersion enhancers for nanoclay layers into polymeric phase (Dike, 2011; Dike and Yilmazer, 2020a; Dike and Yilmazer, 2020b).

Guven et al. used calcium organoclay as an additive in a polymer emulsion of styrene-co-butyl acrylate copolymer (Guven et al., 2014). Additionally, superabsorbent applications of organoclay containing various polymer composites were also studied in the literature (Alexandre and Dubois, 2000; Li and Wang, 2005; Tao et al., 2006).

Akar et al. prepared polyamide-6 (PA-6) composites filled with two types of organoclays in a recently published study. Their findings suggested that organo-modified clays inclusions caused an increase in thermal, structural and mechanical performance of PA-6 (Akar et al., 2021).

Ge et al. studied the influence of silane coupling agents on the tribological performance of organoclay-filled nitrile butadiene rubber-based composites (Ge et al., 2017).

Kraus et al. performed the thermal, mechanical and morphological characterizations of organoclay filled low density polyethylene (LDPE)-based composites in order to predict the surface properties of composites (Kraus et al., 2016). Similarly, Seyidoglu and Yilmazer reported that compatibilizer addition increased the mechanical properties of organoclay-loaded linear LDPE composites (Seyidoglu and Yilmazer, 2012).

Investigations dealing with LDPE-based composites filled with organoclay were also performed by Majeed et al. They evaluated the barrier performance of LDPE/clay nanocomposite films after the inclusion of compatibilizer containing anhydride-grafted polyethylene and they obtained extension in interlayer spacing between clay layers through PBT phase (Majeed et al., 2014).

Tayfun and Dogan examined the use of organoclay in the melt spinning process of poly (lactic acid) (PLA) fiber in terms of dyeability. They postulated that organoclay inclusions let to increase in tensile strength and dyeability, whereas, reduction in percent crystallinity of PLA fiber (Tayfun and Dogan, 2016).

Keyfoglu and Yilmazer proposed the influence of chain extension-branching agent modification of nanoclay in addition to tunning process parameters to PET-based nanocomposites. They revealed that composites filled with maleic anhydride-modified organoclay at the loading level of 3% exhibited the best performance based on the structural and mechanical behaviors (Keyfoglu and Yilmazer, 2004). Liborio et al. applied a treatment method for organoclay and they fabricated organoclay-filled polypropylene-based composites by using extrusion (Liborio et al., 2015).

Additionally, numerous research works were reported to investigate the flame retardancy of nano-clay containing polymers thanks to the establishment of synergistic interactions between flame retardant reagents and organoclay. According to these studies, it can be deduced that organoclays can be effectively used for the development of thermally stable and fire-resistant polymeric composites in the presence of phosphorus and boron-based flame retardants (Doğan and Bayramlı, 2011; Doğan and Bayramlı, 2014; Doğan et al., 2013; Doğan and Bayramlı, 2021; Durmuş et al., 2007; Hu et al., 2006; Kausar et al., 2017; Lu et al., 2018;

Nazare et al., 2006; Oliveira et al., 2017; Tai et al., 2012; Qin et al., 2005; Yurddaskal et al., 2018).

2.2. Organoclay-filled PBT-based nanocomposites

PBT polymer was also studied in research works dealing with the polymer/organoclay composite system. For instance, there have been several published works found in the literature which are related with organoclay-filled polymer nanocomposite systems for a variety of industrial applications.

Xiao et al. prepared clay/PBT nanocomposite through direct melt intercalation method using thermally stable organically modified montmorillonite as filler. They also found a remarkable improvement in melting temperature and rate of crystallization of the resulted clay/PBT nanocomposites. Twin screw extrusion was also used for melt intercalation of clay/PBT nanocomposites (Xiao et al., 2005).

Another example is the study of Chang et al. in which they prepared clay/PBT nanocomposites through in situ interlayer polymerization and found that thermal and mechanical properties of PBT can be enhanced by the dispersion of a very small amount of organoclay exceedingly (Chang et al., 2003).

Quispe et al. in 2015 conducted a study with composites based on post-industrial waste or primarily recycled poly (butylene terephthalate) and 5 wt.% of organically modified montmorillonite clays using a twin-screw extruder and melt blending technique. It is a good example of how improvements can be achieved on the physical properties of recycled PBT with a small content of organically modified montmorillonite to add value to primarily recycled engineering thermoplastics (Quispe et al., 2015).

In a study of Acierno et al. performed in 2004, the effect of organoclay inclusion on the structure and properties of PBT-based nanocomposite system was investigated. In terms of mechanical properties, the silicate nanoscale dispersion significantly increased the stiffness and reduced the ductility compared to PBT. They also experienced weight loss by organoclay inclusions during hybrid compounding. They concluded that the absorbed volatile fraction by the PBT matrix causes compositional changes and caused a decrease in the thermal stability of composites (Acierno et al., 2004).

Saeed et al. in 2015, prepared Kaolin clay/poly (butylene terephthalate) (clay/PBT) composites films by solution casting technique. They confirmed the dispersion of kaolin into PBT matrix by SEM analysis. They concluded that the size of spherulites of PBT was decreased by the incorporation of clay into PBT due to the nucleation effect of kaolin clay. The mechanical properties of clay/PBT composites were significantly enhanced with respect to neat PBT and the thermal stability of PBT was improved up to 10 °C by the addition of kaolin into the polymer matrix. It was also found that the solvent uptake of clay/PBT nanocomposite was lower than unfilled PBT (Saeed and Khan, 2015).

Li et al. in 2001 conducted a comprehensive assessment of polymer clay nanocomposite (PCN) systems. They tried to show how the organic modifiers affect the polymer crystallinity and elastic modulus of PCN systems. Nanoclay exhibited intercalated and partially exfoliated structure, whereas, organoclay formed intercalation in PBT phase due to the strong interactions between ammonium cation and silicate layers of organoclay (Li et al., 2001).

Katti et al. conducted a comprehensive study of PBT/clay and PA6/clay nanocomposite systems based on molecular dynamics and experimental techniques. Although the same amount of modified clay was used in the preparation steps of composites, they observed dramatic changes in crystallinity and improvement in mechanical properties. According to their findings, polymers with higher crystallinity required significantly higher attractive and repulsive interaction energies between polymers and their modifiers to reach a similar change in crystallinity compared to other polymers having lower crystallinity (Katti et al., 2012).

In another research reported by Nirukhe et al., three different intercalating agents were used to prepare different organically modified montmorillonite (MMT). They fabricated PBT/clay nanocomposites by melt-mixing with clay compositions ranging from 1 to 5 wt%. They observed that composites involving intercalating agents yield high thermal stability stem from the pyridinium cations compared to neat clay. They concluded that mechanical and thermal properties strongly depended on the nanocomposite structure and clay content. It was found that the addition of a small amount of organoclay (up to 3 wt %) was enough to level up the mechanical properties of PBT. They also showed that the inclusion of organoclay affects the crystallinity of the polymer since the clay acts as a nucleating agent according to DSC analysis (Nirukhe et al., 2009).

Soudmand et al. investigated the toughness of PBT-based nanocomposites filled with nanoclay based on mechanical characterizations and subsequent microstructural observations. In their study, clay and nano-precipitated calcium carbonate were selected as nano-reinforcing phases. They showed that the fracture morphology of compact tension samples showed a low extent of plastic deformation for neat PBT. According to their results, relative to PBT, the stress intensity factor increased up to 57% and 45% with the addition of clay. They implied that nanocomposites displayed a crack initiation zone of fibrillated morphology. (Soudmand et al., 2020).

2.3. Aim of the study

The main purpose of this thesis research is to investigate the effect of two different types of organoclay additions on structural, mechanical, thermal, thermo-mechanical, physical and morphological characteristics of PBT-based nanocomposites. A comprehensive performance study of two kinds of nanoclay modified with quaternary ammonium salts with dimethyl, benzyl, hydrogenated tallow and dimethyl, dehydrogenated tallow was conducted after the fabrication step of nanocomposites using melt-extrusion process followed by injection molding technique.

Similar research studies dealing with organoclay-filled polymeric composites, PBT and its nanocomposites in the literature were checked over and reviewed as a survey. The basic difference of this thesis study from described previously published works is the experimental evaluation of property enhancement of PBT nanocomposites after compounded with organoclays based on the dispersion promoter effect of ammonium salts through nanoclay interlayers into PBT matrix.

Organoclay samples and prepared composites were subjected to X-ray spectroscopy and SEM analysis to visualize the structural and morphological properties. In addition to mechanical performances such as tensile, hardness, and impact tests, thermal (TGA), thermo-mechanical (DMA), physical as density and melt-flow measurements were reported for basic understanding and comparison of the influences of two grades of organoclays.

3. MATERIALS AND METHODS

3.1. Materials

3.1.1. PBT Polymer

The commercial PBT thermoplastic polymer was purchased from Sasa Polyester A.Ş. (Adana, Türkiye) with the trade name of Advanite SB88. PBT chips used in this thesis study are shown in Figure 3.1.

Figure 3.1. The photograph of PBT used in this thesis.

3.1.2. Organoclays

Organoclay powders (Figure 3.2) used in thesis study were supplied from Eczacıbaşı Esan, İstanbul, Turkey. Two kinds of nanoclay grade were used with the commercial names of esanNANO 2-130 (NC 130) and esanNANO 1-140 (NC 140) which were coated by different quaternary ammonium salts containing dimethyl, benzyl, hydrogenated tallow and dimethyl, dehydrogenated tallow, respectively. The structures of neat clays and organo-modified clays with the chemical structures of related ammonium salts integrated into their structures are demonstrated in Figure 3.2 for NC 130 and Figure 3.3 for NC 140 samples.

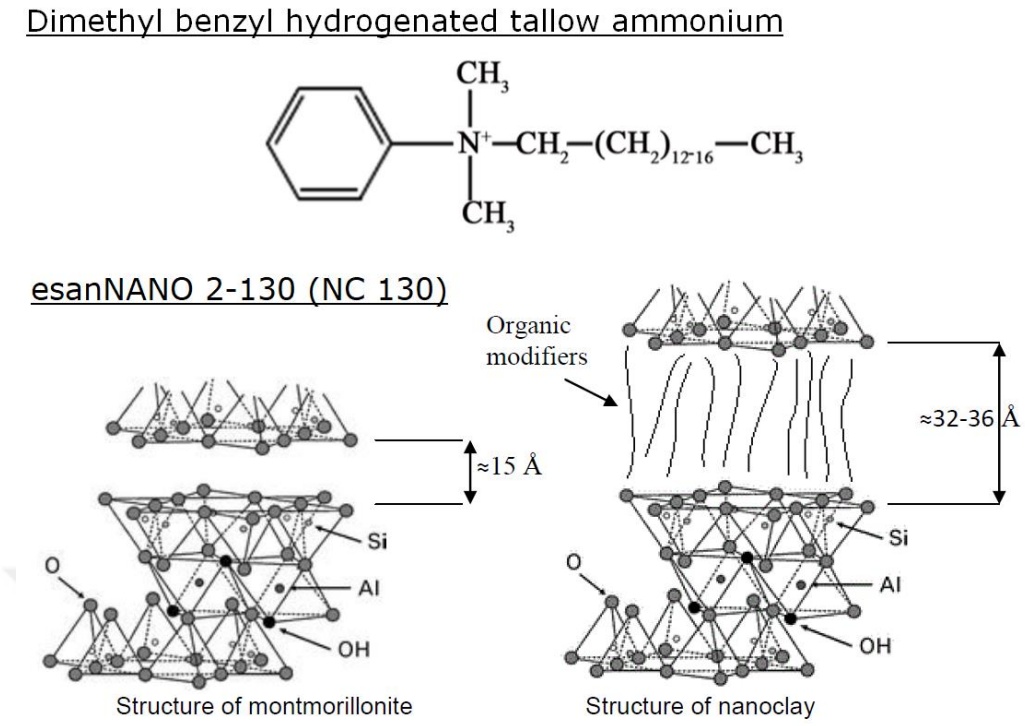

Figure 3.2. Demonstration of NC 130 and the chemical structures of related ammonium salt

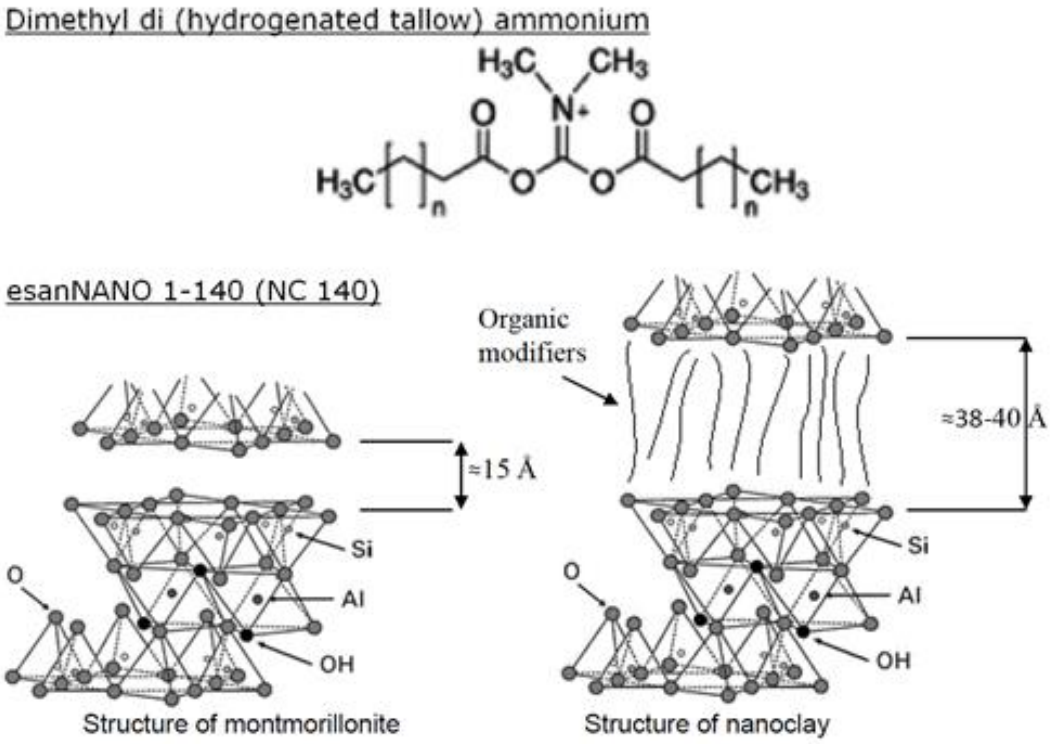

Figure 3.3. Demonstration of NC 140 and the chemical structures of related ammonium salt

The chemical composition obtained from X-ray fluorescence analysis and basalt spacing parameter (d-value) estimated by X-ray diffractometry analysis of organoclay grades provided by the producer is listed in Table 3.1.

Table 3.1. The chemical compositions of organoclays used in this study.

Composition (%)	**NC 130**	**NC 140**
Al_2O_3	11.37	6.67
SiO_2	49.80	44.3
Na_2O	0.16	0.70
Fe_2O_3	0.59	0.41
K_2O	0.31	0.30
CaO	0.33	0.47
MgO	2.43	1.41
TiO_2	0.04	0.04
d value (Å)	34.66	38.62

The photograph of NC 130 and NC 140 used in this thesis study is exhibited in Figure 3.4. As can be seen from Figure 3.4, NC 130 clay has a yellowish color and NC 140 is pure white-colored.

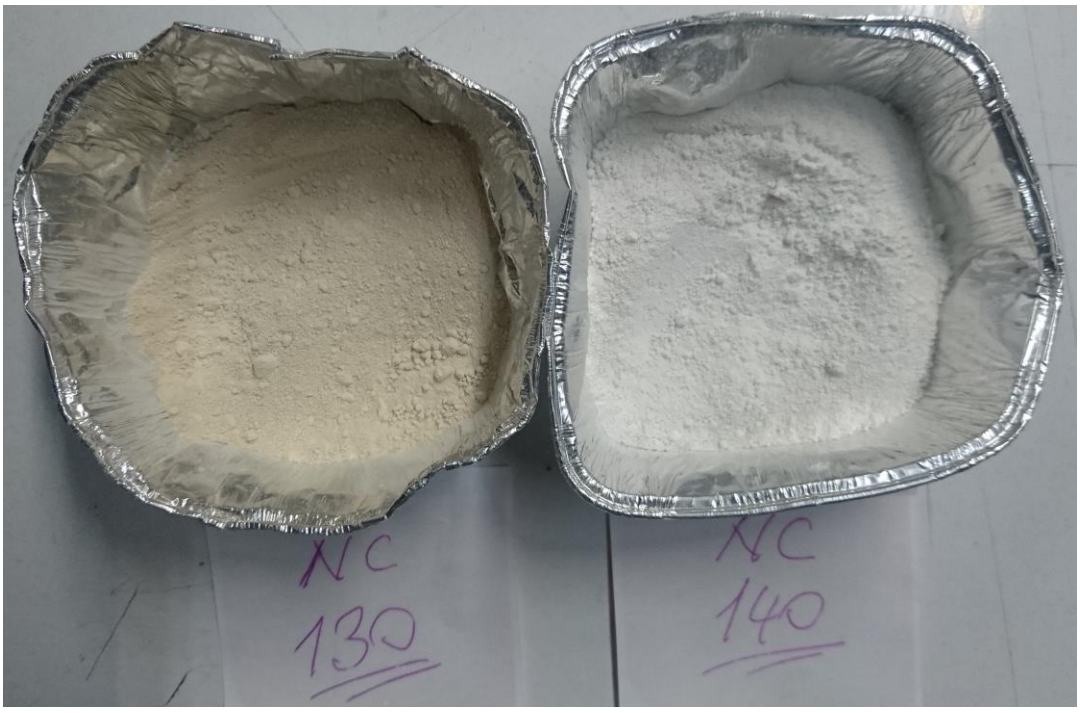

Figure 3.4. The photograph of organoclay powders used in this study.

3.2. Production of composites

PBT chips and organoclay powders were compounded by twin-screw 15cc Xplore micro-extruder located in polymer rheology laboratory at METU as shown in Figure 3.5.

Figure 3.5. The lab-scale micro-compounder used in this study.

PBT chips and organoclay powders were pre-dried at 100˚C in 2 hours using an oven. Processing temperature of 240˚C, mixing time of 5 minutes and mixing speed of 100 rpm was applied during the compounding process. Neat PBT was also mixed using the same processing parameters and named as PBT. Loading amounts of NC 130 and NC 140 into PBT matrix were 1, 3, 5 and 10 by weight % and contents of composites are listed in Table 3.2.

Table 3.2. Compositions of prepared composites.

Sample Codes	PBT content (wt%)	NC 130 content (wt%)	NC 140 content (wt%)
PBT	100	0	0
PBT/1% NC 130	99	1	0
PBT/3% NC 130	97	3	0
PBT/5% NC 130	95	5	0
PBT/10% NC 130	90	10	0
PBT/1% NC 140	99	0	1
PBT/3% NC 140	97	0	3
PBT/5% NC 140	95	0	5
PBT/10% NC 140	90	0	10

After the extrusion process, composites were obtained as chip form and dog-bone shaped test samples with the dimensions of 80×7.5×2.5 mm^3 were prepared using Daca Instruments micro-injection molding machine at a barrel temperature and mold temperature of 245˚C and 80 ˚C, respectively. The photograph of micro-injector equipment located in polymer rheology laboratory at METU is displayed in Figure 3.6.

Figure 3.6. Photograph of micro-injector used in this study.

3.3. Characterization techniques

3.3.1. XRD Analysis

The structural investigations of organoclays, PBT and organoclay-filled PBT nanocomposites were carried out by XRD analysis using X'Pert PRO, PAN analytical with Ni-filtered CuKα radiation (λ = 0.154 nm) at 40 mA and 45 kV. XRD device utilized in Esan Eczacıbaşı R&D laboratory and PBT test sample were represented in Figure 3.7.

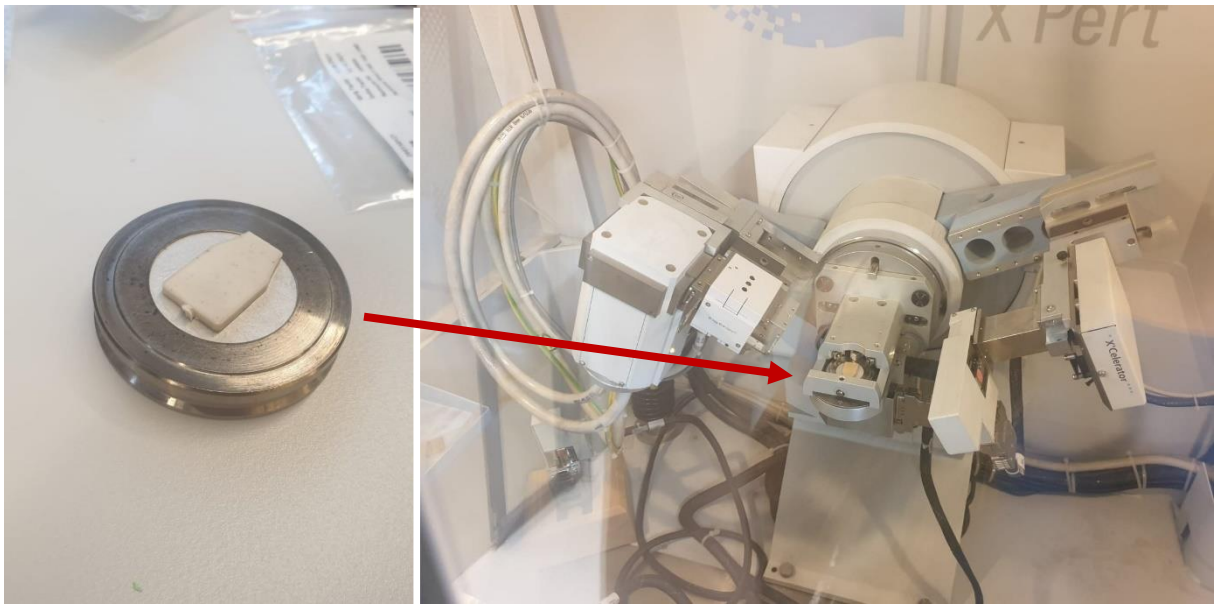

Figure 3.7. Photographs of XRD test sample and XRD device.

3.3.2. Tensile tests

Tensile tests were performed using a universal tensile testing device (Lloyd LR 30 K) in polymer rheology laboratory at METU as shown in Figure 3.8. Tests were done with dog-bone test samples using parameters of 5 kN load cell and 10 mm/min as crosshead speed according to ASTM D-638 standard.

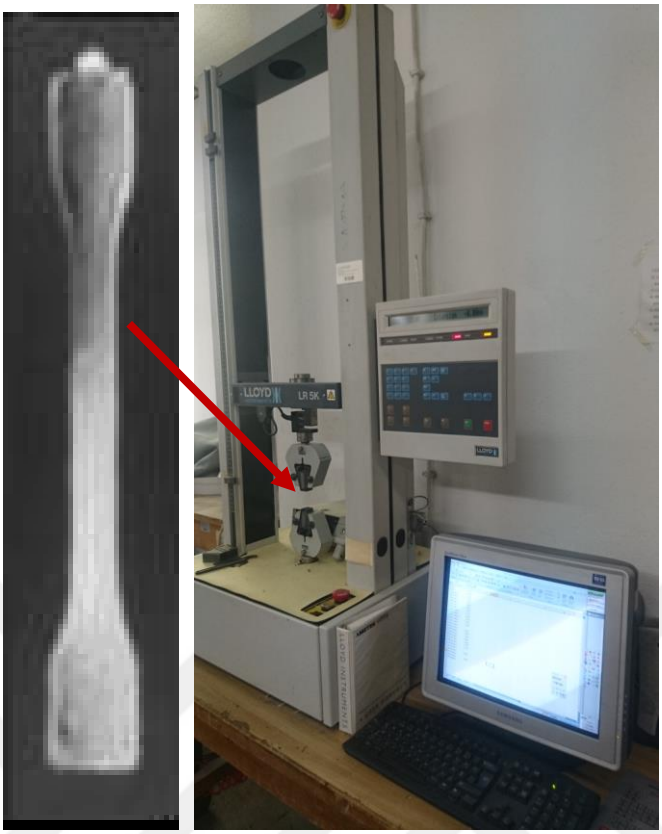

Figure 3.8. Photographs of test sample and tensile testing device used in this thesis.

3.3.3. Hardness analysis

Shore hardness tests were performed by Zwick Roell R5LB041 hardness analyzer. Shore D hardness values of test samples were recorded according to ISO 7619-1 standard procedure.

3.3.4. Impact tests

Coesfeld impact tester device was utilized in polymer rheology laboratory at METU to investigate impact energy values of PBT and its composite samples using a 4 J pendulum. Figure 3.9 displays the impact tester used in this thesis study.

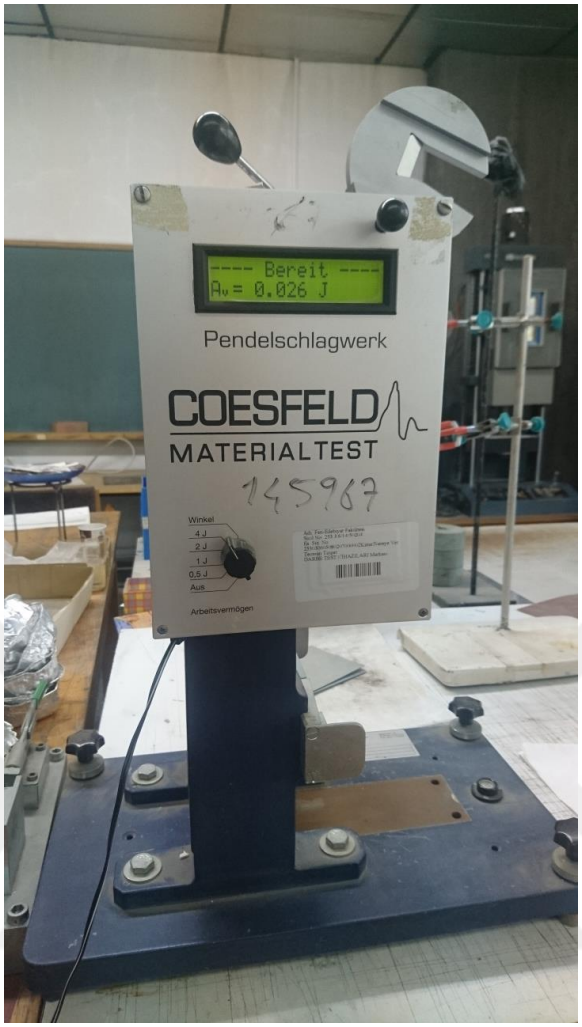

Figure 3.9. Photograph of impact tester device used in this study

3.3.5. Thermal gravimetric analysis

TGA analyzes were done by applying a heating rate of 10 ºC/min using Perkin Elmer Diamond TG/DTA thermal test equipment. Analysis was carried out under the nitrogen atmosphere with a flow rate of 50 ml/min in the heating range of 25-650 ºC.

3.3.6. Dynamic mechanical analysis

DMA investigations were done using dual cantilever bending mode in 25-200 ºC temperature range and 10 ºC/min constant heating rate by utilizing Hitachi HT, DMA7100 analyzer located in polymer characterization laboratory at Kocaeli University under the nitrogen atmosphere.

3.3.7. Melt flow rate measurement

Melt flow measurements of unfilled PBT and composite samples were estimated using Coesfeld Meltfixer LT in polymer rheology laboratory at METU which is represented in Figure 3.10. The standard load of 2.16 kg was used at 240 °C during MFR measurements.

Figure 3.10. Photograph of melt flow rate device used in this study.

3.3.8. Density Measurements

Density measurements were applied to PBT and composite samples using a Mettler Toledo Easy D30 digital density meter at R&D laboratory of Esan Eczacıbaşı in which average results of recorded values of at least three samples were reported.

3.3.9. Scanning electron microscopy

SEM images of composites were taken with the magnifications varied from 1.000 to 10,000 by FEI Quanta 400F FESEM scanning electron microscope device.

4. RESULTS AND DISCUSSIONS

4.1. XRD Analysis

XRD curves NC 130 clay, PBT polymer and PBT/NC 130 coded composite samples are given in Figure 4.1.

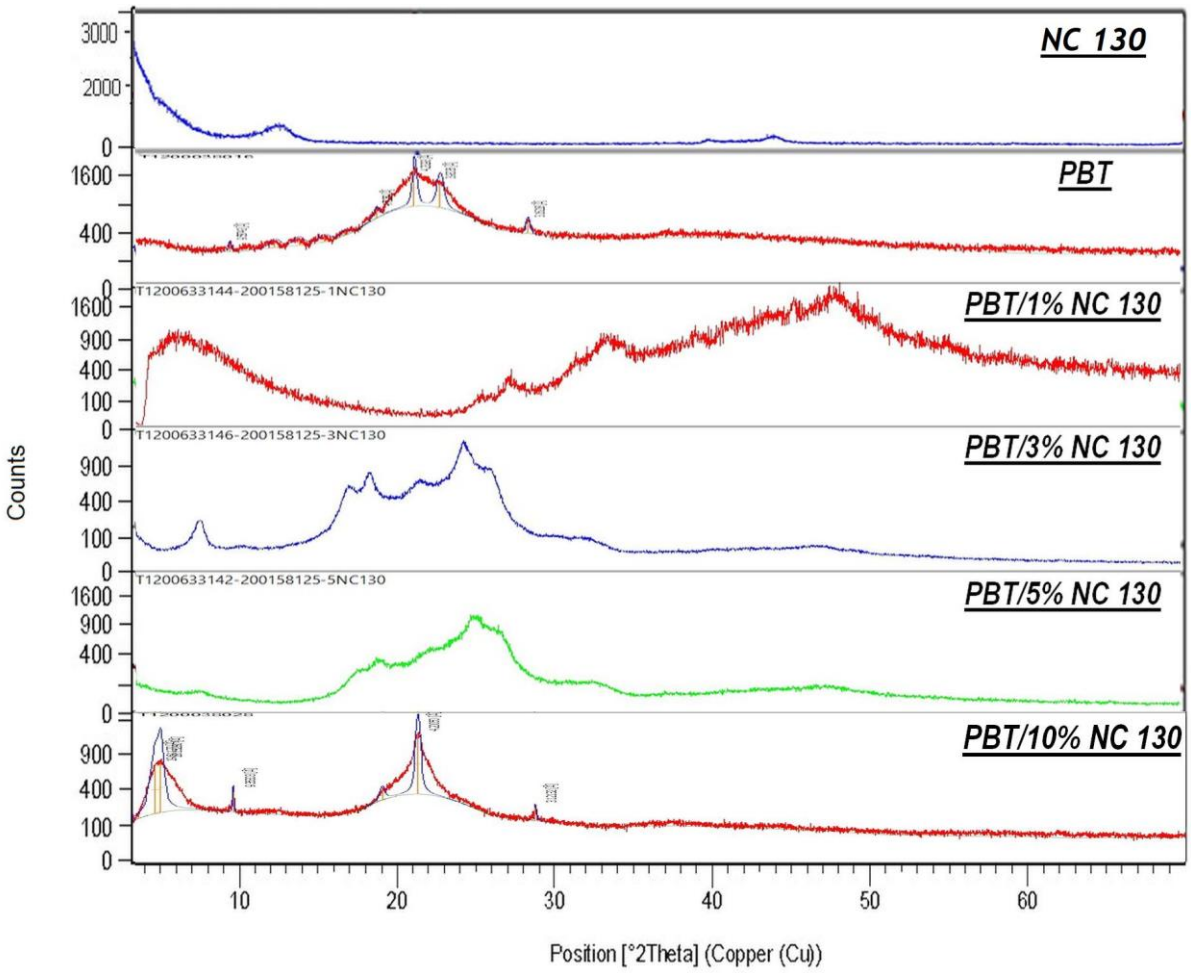

Figure 4.1. XRD curves of NC 130, PBT and PBT/NC 130 composites.

PBT gave a distinct band centered about $2\theta = 20^{o}$ and this band shifted to higher values for PBT/1% NC 130 sample. The characteristic peaks of both organoclays can be seen at nearly $2\theta = 8^{o}$ from their curves in Figure 4.1 and Figure 4.2. This peak started to disappear for NC 130 and NC 140 as the adding amount increased. It can be observed from XRD curves of composites with 5% content of both organoclays, this characteristic peak was completely lost.

The absence of this peak in XRD curve of a composite indicates that clay layers intercalated into polymer matrix (Rajakumar and Nanthini, 2011; Schampera et al., 2015).

XRD curves NC 140 clay, PBT polymer and PBT/NC 140 named composite samples are shown in Figure 4.2.

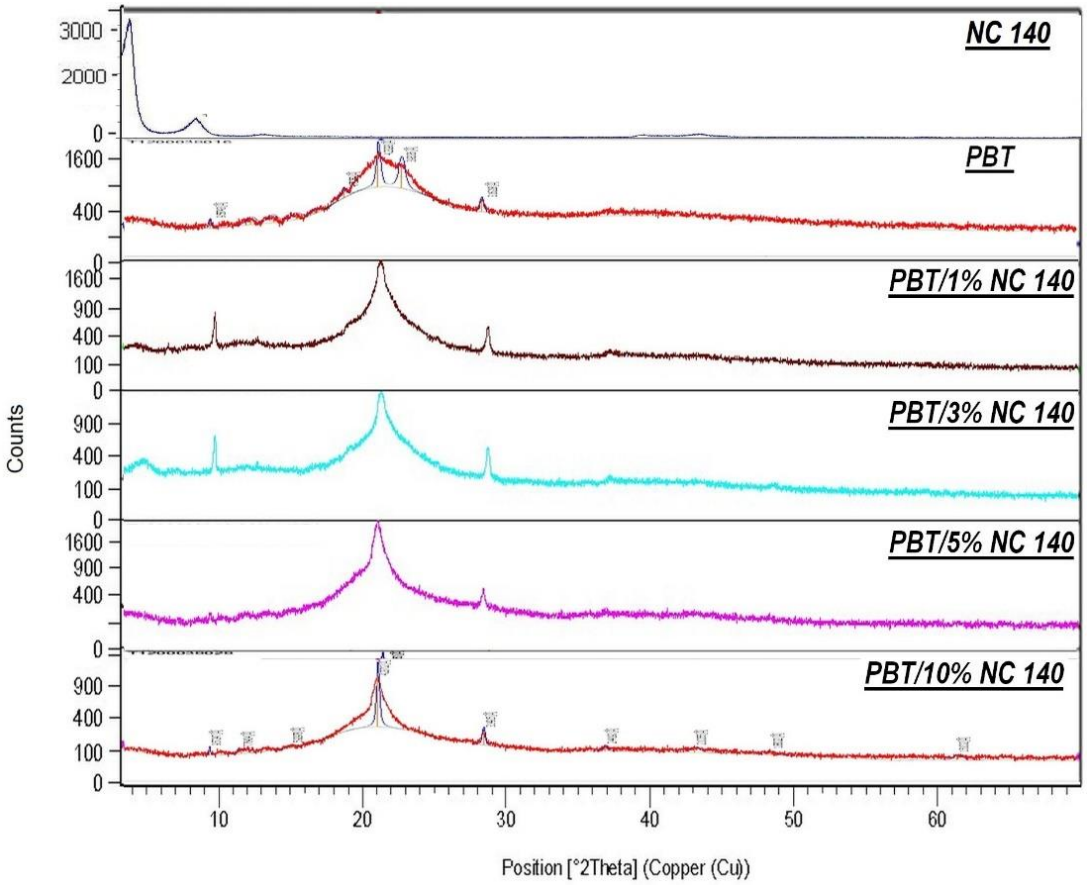

Figure 4.2. XRD curves of NC 140, PBT and PBT/NC 140 composites.

The Bragg peaks of composite samples seen at around 2θ=30-40∘ range are related to distance between clay layer and named as d-spacing (Brilihart et al., 1994; Moore and Reynolds, 1997; Iulianelli et al., 2015) The magnitude of this peak was found to be increased for PBT/1% NC 140 and PBT/3% NC 140 composites. According to these findings, NC 140 clay exhibited more significant improvement in terms of intercalation and dispersion of organoclay plates into PBT phase.

4.2. Mechanical Characterizations

Mechanical test data of PBT and its composites including tensile parameters, impact strength values and hardness parameters are listed in Table 4.1.

Table 4.1. Mechanical test results of PBT and composites.

Samples	Tensile Strength (MPa)	Youngs Modulus (GPa)	Elongation at Break (%)	Impact Strength (kJ/m^2)	Hardness (Shore D)
PBT	34.0±0.8	0.64±0.3	9.1±0.4	9.5±0.6	75.0±0.1
PBT/1% NC 130	42.8±0.4	0.72±0.1	11.6±0.8	16.4±0.7	72.6±0.2
PBT/3% NC 130	43.5±0.3	0.73±0.1	12.7±0.7	14.9±0.4	74.3±0.2
PBT/5% NC 130	42.7±0.3	0.75±0.2	10.8±0.8	11.5±0.4	75.5±0.1
PBT/10% NC 130	41.4±0.2	0.73±0.1	10.3±0.5	9.6±0.3	77.1±0.2
PBT/1% NC 140	40.7±0.4	0.63±0.2	11.2±0.6	18.8±0.6	69.8±0.2
PBT/3% NC 140	42.1±0.2	0.65±0.1	12.4±0.4	15.2±0.5	71.4±0.1
PBT/5% NC 140	41.6±0.3	0.66±0.2	12.2±0.3	13.5±0.3	73.0±0.2
PBT/10% NC 140	40.8±0.2	0.59±0.2	12.0±0.3	10.5±0.4	75.2±0.1

4.2.1. Results of Tensile Test

Tensile strength of PBT was found to be 34 MPa. NC 130 clay additions gave distinct improvements on the strength value of PBT. The greatest result was obtained for 3% NC 130 filled composite among all of the prepared samples. The amount of increase in tensile strength for this sample was estimated approximately as 28% improvement with respect to that of PBT. Composites reinforced with NC 130 clays yielded higher strength values compared to NC 140 containing composites. This finding indicates that NC 130 showed a better reinforcing ability to PBT matrix than NC 140 clays which may be due to the establishment of an enhanced interaction between clay layers and PBT phase in the presence of pendant benzyl group on the ammonium salt tallow of NC 130.

Tensile strength increased by the concentration of both organoclays up to the adding amount of 3%. After that point, tensile strength reduced dramatically and the lowest strength values were obtained for PBT/10% NC 140 sample among composites.

The strength versus strain curves of PBT and relevant composites are given in Figure 4.3.

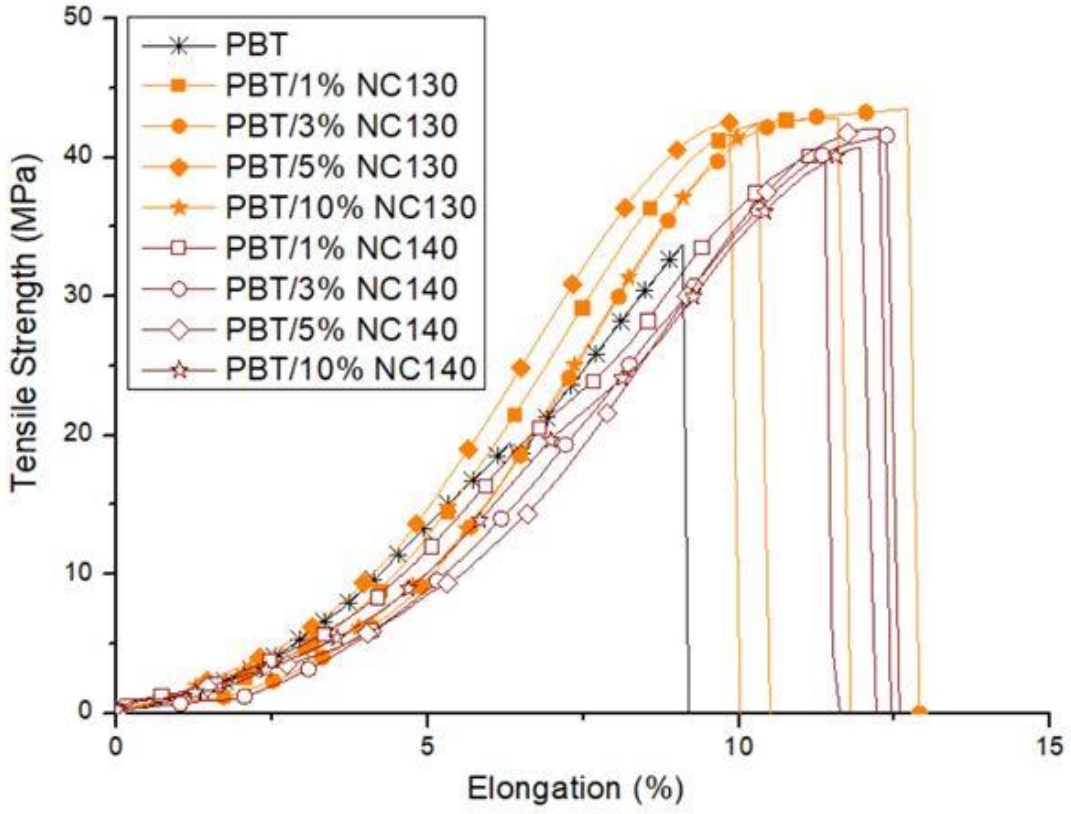

Figure 4.3. Stress versus strain curves of PBT and composites.

The transcendence of NC 130 containing composites over NC 140 containing ones according to tensile behaviors can be observed visually from their characteristic strength versus strain curves in Figure 4.3.

As the elongation at break parameters evaluated, it can be said that all of the composites showed higher elongation results than that of neat PBT. In contrast to tensile strength findings, NC 140 additions resulted in increase for elongation values.

NC 130 and NC 140 inclusions displayed different trends in Youngs modulus results according to Table 4.1. NC 130 clay led to a distinct increase in modulus values. On the other hand, only slight improvements were obtained for composites involving NC 140. Moreover, PBT/10% NC 140 yielded lowering for Youngs modulus of PBT.

4.2.2. Results of Hardness Test

According to Shore D hardness results listed in Table 4.1, organoclay additions caused decrease at lower filling ratios, initially. Hardness of composites improved as the contents of clays increased and the maximum hardness values were reached for composites involving 10% amount of NC 130 and NC 140. Enhancement of hardness with the addition of plate-like fillers was an expected behavior thanks to the layered structure of nanoclay (Liu et al., 2011; Mohamed et al., 2020; Taheri and Sadeghi, 2015; Shah et al., 2016). However, intercalation of NC 130 and NC 140 resulted in the reduction of hardness of composites at low amounts of additives due to a high level of dispersion degree can be achieved. Similar to tensile test results, NC 130 displayed higher Shore hardness values compared to NC 140.

4.2.3. Results of Impact Test

Figure 4.4 and Figure 4.5 demonstrated the changes in impact strength values according to organoclay inclusions.

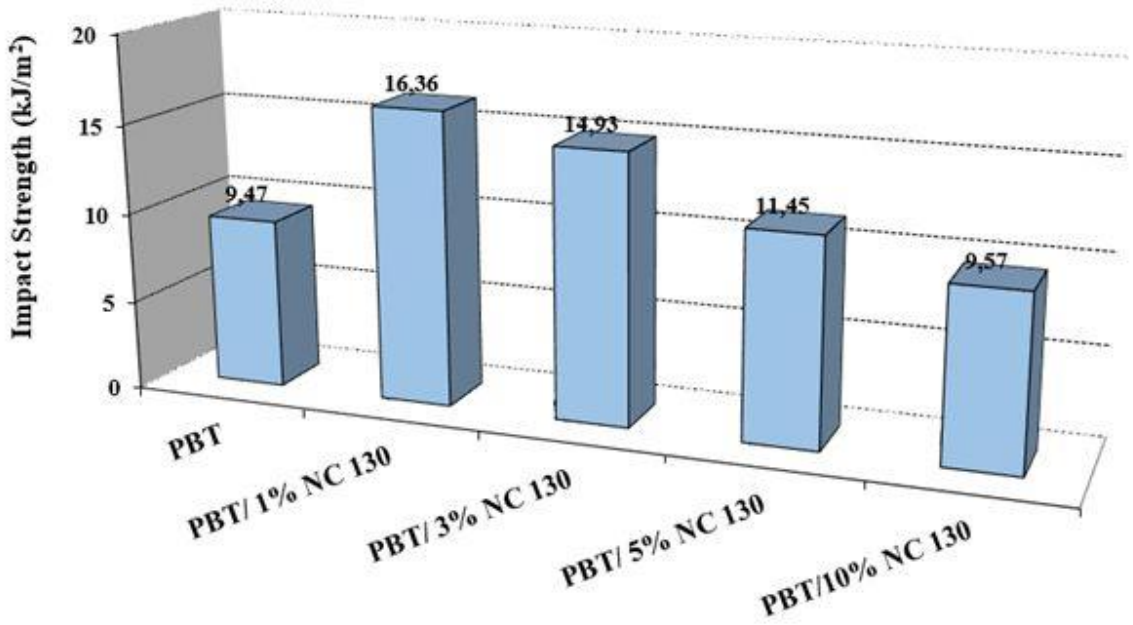

Figure 4.4. Impact test results of PBT/NC130 composites.

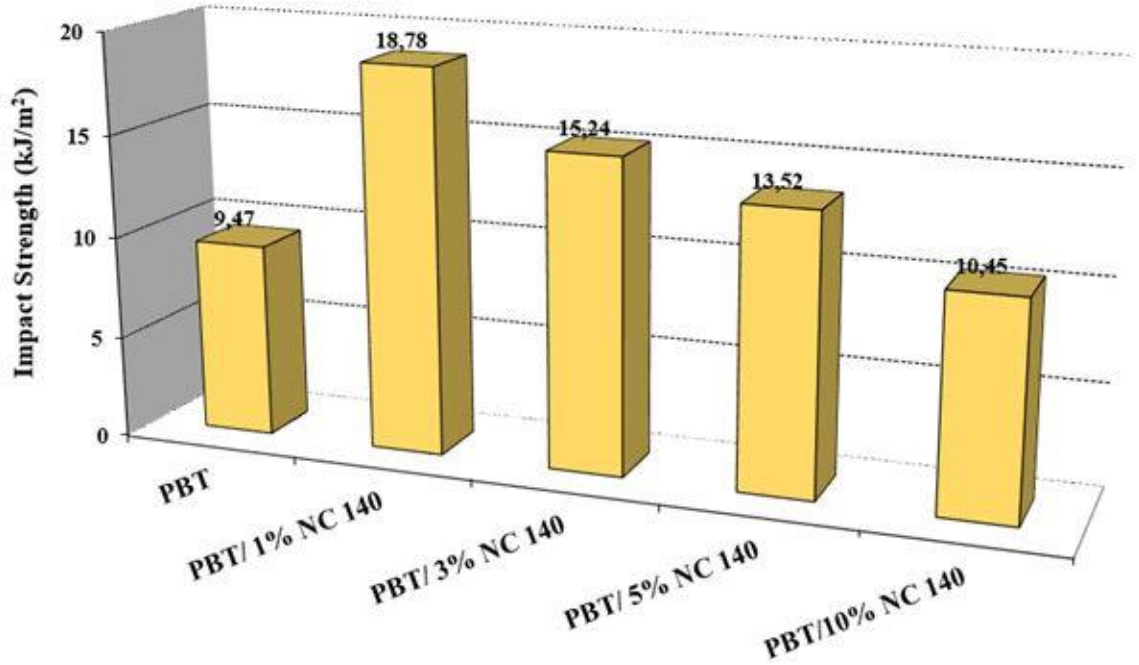

Figure 4.5. Impact test results of PBT/NC140 composites.

It was clearly observed from impact test results that organoclay-containing composites gave remarkably higher impact strength than neat PBT. The greatest impact performance was reached for composites filled with NC 140 clay at its lowest adding amount. Impact strength of PBT showed an almost two-fold increase by the addition of 1% NC 140.

Similarly, PBT/1% NC 130 sample exhibited the greatest impact strength among NC 130 loaded composites. A sudden reduction in impact performance was found with further inclusions of organoclays.

As a diverse trend from tensile and hardness findings, NC 140 clay yielded higher performance in terms of impact strength. This result can be explained as dimethyl, dehydrogenated ammonium modification of clay resulted in better impact resistance to crack propagation during deformation (Alyamac and Yilmazer, 2004; Soudmand et al., 2020; Soudmand and Shelesh-Nezhad, 2020; Wahit et al., 2006) compared to dimethyl, benzyl, hydrogenated tallow integrated NC 130 clay.

4.3. Results of Thermal Analysis

TGA and DTGA curves of NC 130 and NC 140 containing nanocomposites versus temperature are represented by Figure 4.6, Figure 4.7 respectively. Thermal analysis data are shared in Table 4.2.

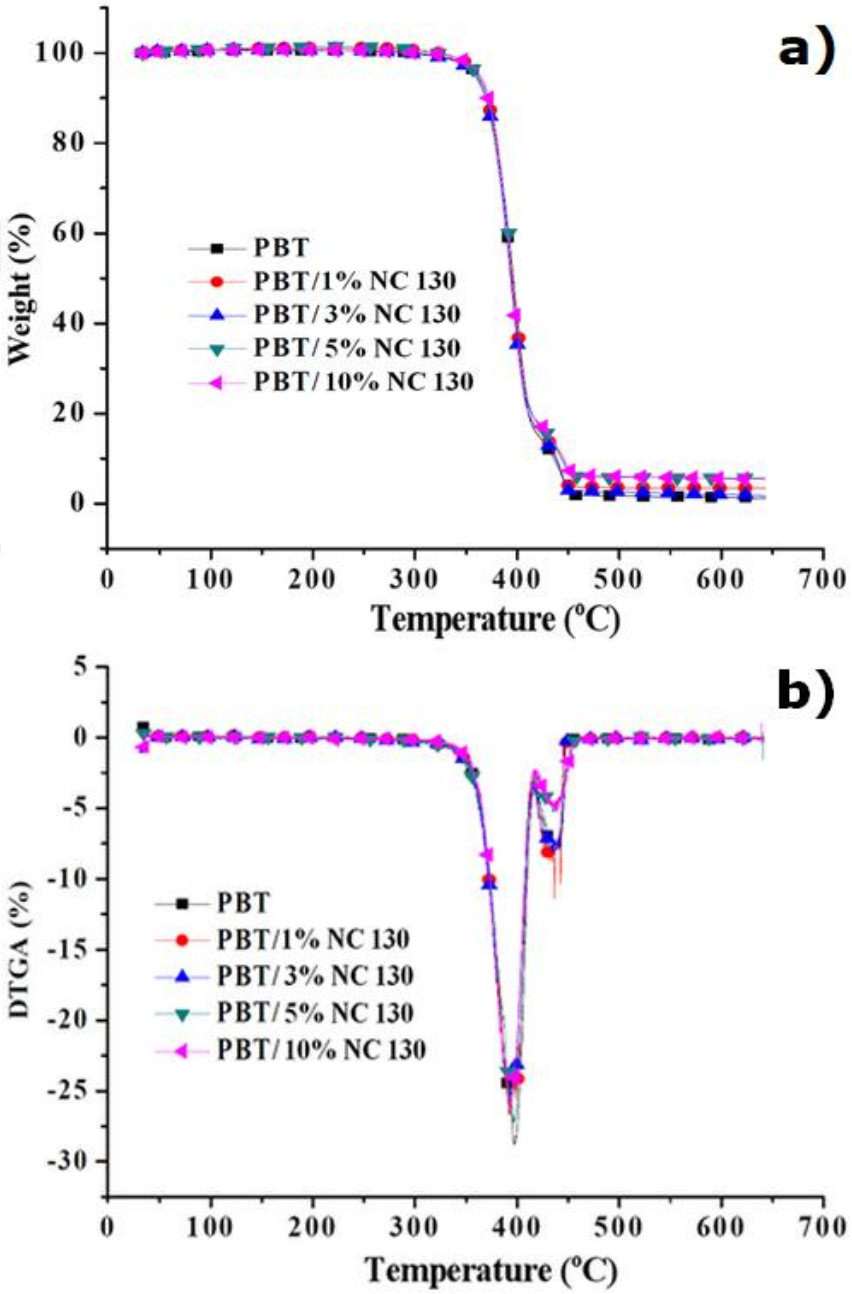

Figure 4.6. TGA (a) and DTGA (b) curves of PBT/ NC130 nanocomposites.

Table 4.2. Thermal analysis results of PBT and composites.

Samples	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	T_{max} (°C)	char (%)
PBT	359	370	441	1.2
PBT/ 1% NC 130	360	372	447	3.3
PBT/ 3% NC 130	358	369	442	4.0
PBT/ 5% NC 130	357	370	439	5.7
PBT/ 10% NC 130	361	371	444	8.9
PBT/ 1% NC 140	368	375	504	3.1
PBT/ 3% NC 140	367	374	488	3.7
PBT/ 5% NC 140	366	375	459	5.6
PBT/ 10% NC 140	368	377	447	9.5

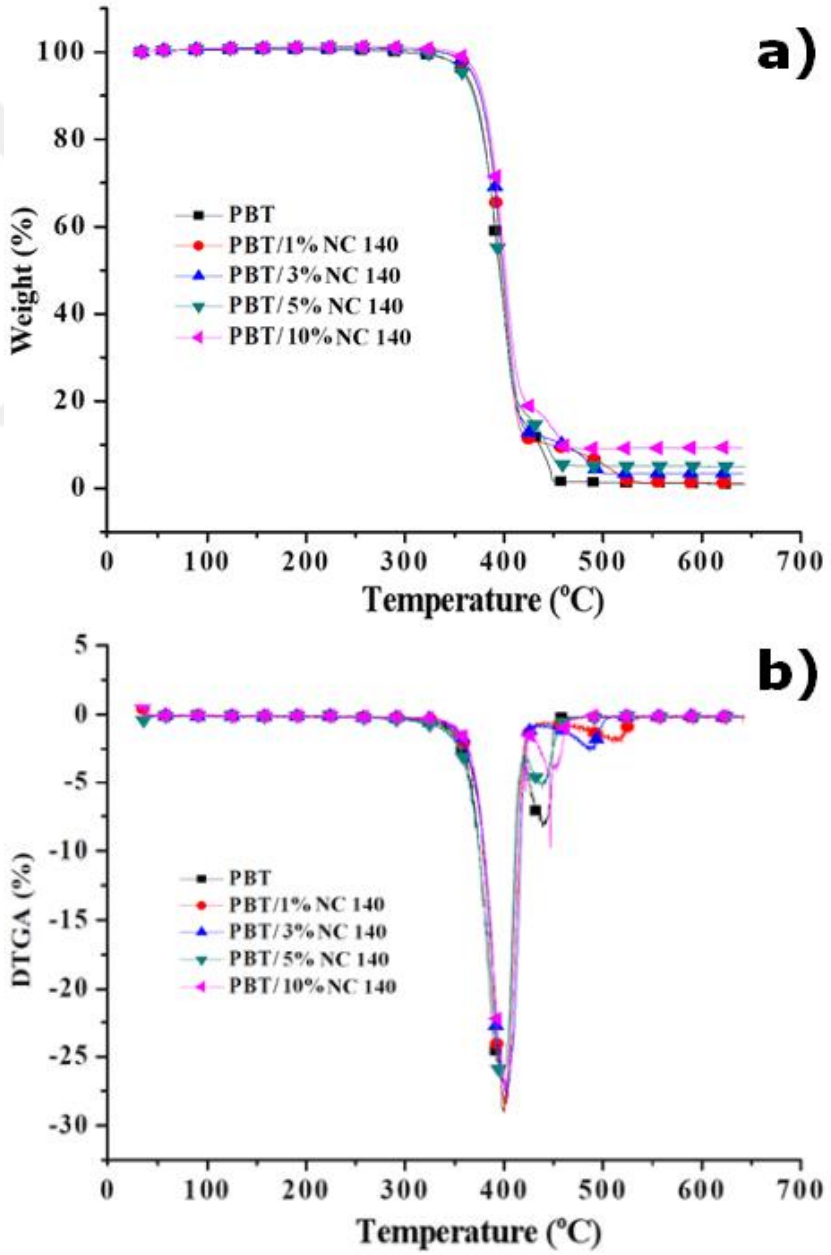

Figure 4.7. TGA (a) and DTGA (b) curves of PBT/ NC140 nanocomposites.

According to thermal analysis data displayed in Table 4.2, NC 130 additions caused no obvious changes to $T_{5\%}$ and $T_{10\%}$ parameters of PBT since nearly identical values were obtained. TGA and DTGA curves in Figure 4.6 displayed this observation.

On the other hand, composites containing NC 140 led to a remarkable increase in thermal analysis values. Improvement in thermal stability of PBT after the incorporation with NC 140 clay was visually observed TGA and DTGA curves of composites in Figure 4.7.

The presence of higher d-spacing between layers of NC 140 clay compared to NC 130 might be the reason for these findings due to the positive effect of intercalation of clay layers on the formation of a thermal barrier. For this reason, PBT/NC 140 composite samples gave higher performance than that of NC 130 in terms of thermal resistance.

Based on the char ratios of samples, composites yielded higher residue content compared to neat PBT, as expected. NC 130 and NC 140 clays gave nearly identical char amounts at the end of the analysis.

4.4. Results of Dynamic Mechanical Analysis

Storage modulus, loss modulus and tan delta curves of PBT and its composite samples that were derived from DMA data are illustrated in Figure 4.8, Figure 4.9 and Figure 4.10, respectively.

Storage modulus of neat PBT extended up to higher levels with the inclusions of organoclays regardless of clay grades. Although both clay types gave nearly identical storage modulus curves, NC 140 filled composites exhibited slightly higher modulus values compared PBT/NC 130 composites.

Composite samples with 10% loading displayed the highest storage modulus levels at elevated temperatures.

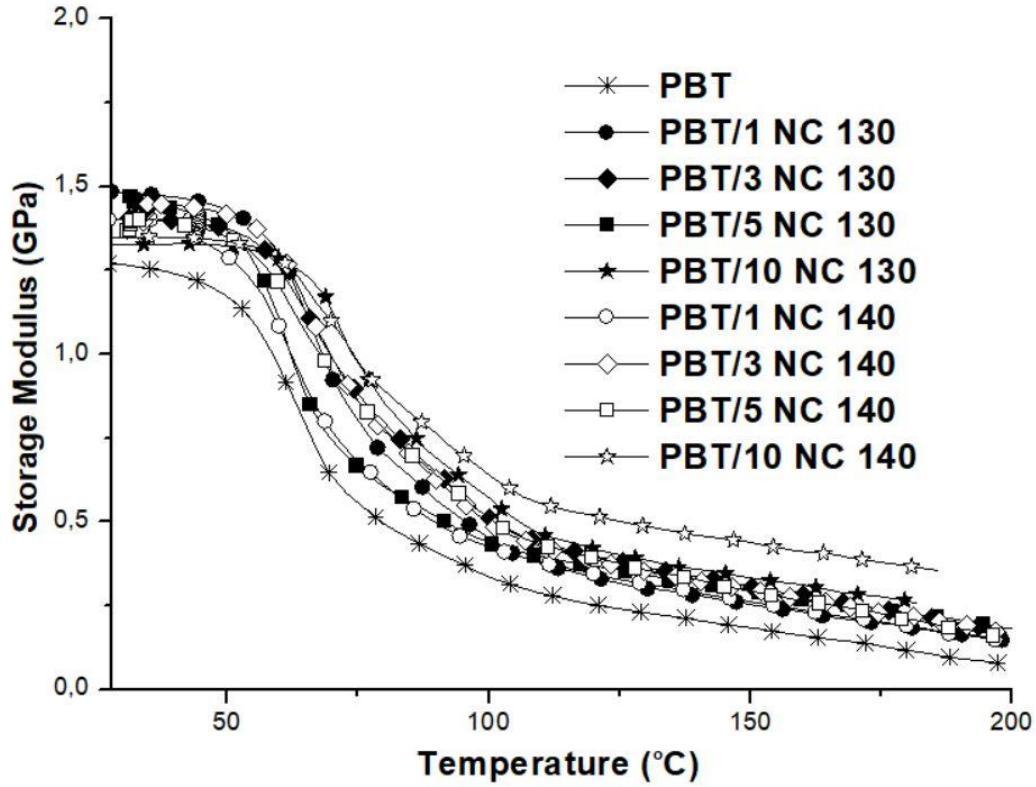

Figure 4.8. Storage modulus curves of PBT and composites.

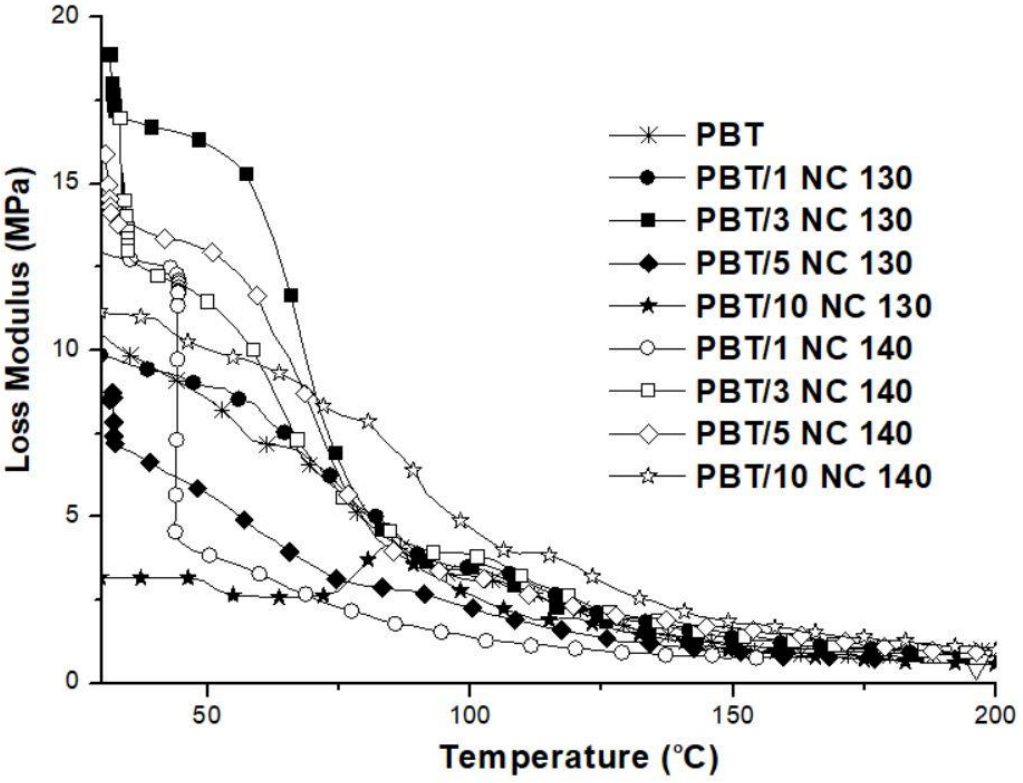

Figure 4.9. Loss modulus curves of PBT and composites.

According to loss modulus curves shared in Figure 4.9, organoclay inclusions led to an increase in loss modulus of neat PBT. Adding amounts of NC 130 and NC 140 showed a negative effect on the loss modulus of composites. It can be said that loss modulus values reduced as the contents of organoclays increased.

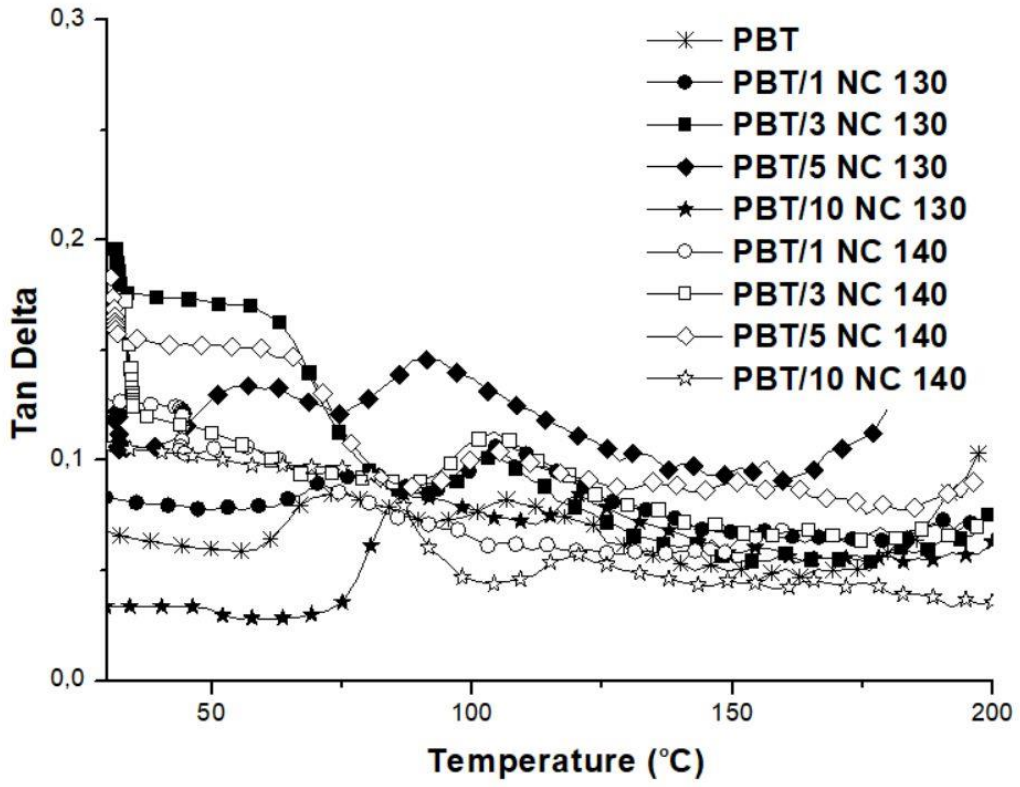

Figure 4.10. Tan delta curves of PBT and composites.

Tan delta curves of samples revealed that the peak value of PBT shifted to higher temperatures by the additions of clays. The peak temperature of tan delta curve corresponds to the specific glass-transition temperature of the polymer (T_g). Inclusions of NC 130 and NC 140 caused to increase in T_g value of PBT.

4.5. Results of Melt Flow Test

MFR parameter is related to viscosity and rheology of polymeric material. MFR values of PBT and composites are indicated in bar chart format in Figure 4.6 and listed as numerical data in Table 4.3.

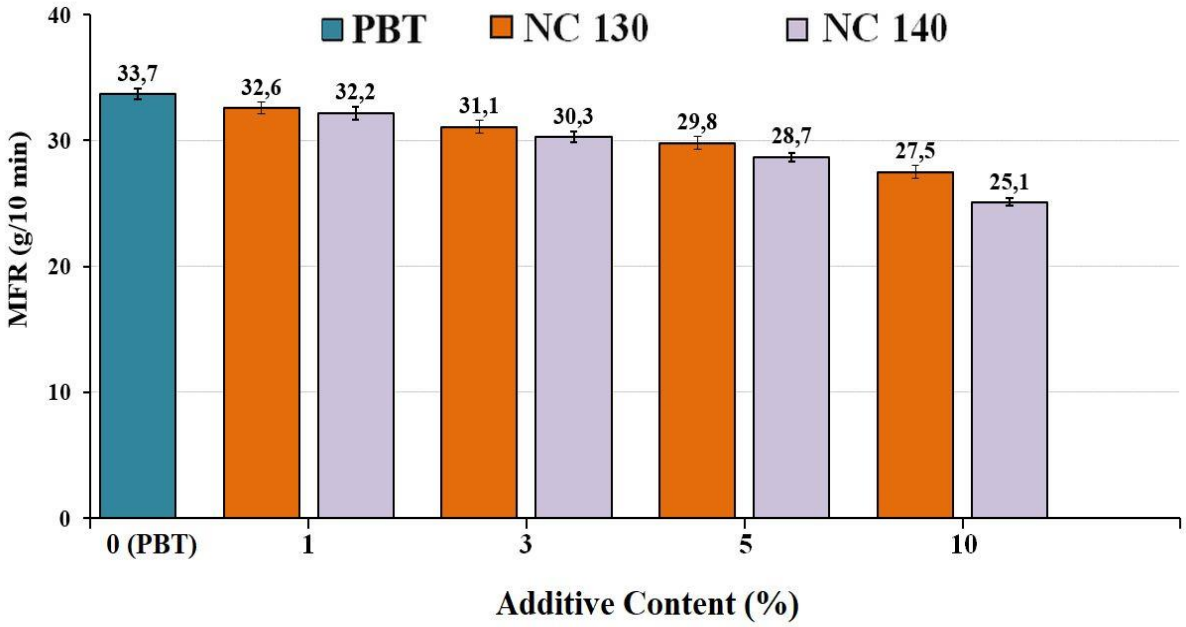

Figure 4.11. MFR test results of PBT and composites.

MFR of neat PBT lowered with clay inclusions. Reduction of MFR carried on as additive content increased. It can be deduced that the change in MFR values obtained in a narrow range as 10% decrease for composite samples containing low amounts of NC 130 and NC 140. However, 10% loading of clays resulted in a dramatic drop down for MFR of PBT as a 20-25% reduction. NC 140 filled composite displayed the lowest MFR value among prepared samples.

As a comparison based on clay types, NC 130 loaded PBT composites gave slightly higher MFR values than that of NC 140 clay.

Table 4.3. Density and MFR test results of PBT and composites.

Samples	Density (g/cm^3)	MFR (g/10 min)
PBT	1.315±0.2	33.7±0.2
PBT/ 1% NC 130	1.309±0.2	32.6±0.1
PBT/ 3% NC 130	1.314±0.1	31.1±0.2
PBT/ 5% NC 130	1.328±0.3	29.8±0.2
PBT/ 10% NC 130	1.341±0.2	27.5±0.3
PBT/ 1% NC 140	1.297±0.1	32.2 ±0.1
PBT/ 3% NC 140	1.308±0.2	30.3±0.2
PBT/ 5% NC 140	1.319±0.1	28.7±0.2
PBT/ 10% NC 140	1.330±0.2	25.1±0.1

4.6. Results of Density Measurements

Density data of neat PBT and its composites are shown in Table 4.3. The density of PBT was measured as 1.315 g/cm^3. Low amounts of clay inclusions gave a reduction in the density of PBT. Relatively higher density values were obtained for highly-filled PBT/NC 130 and PBT/NC 140 composite samples. Composites involving NC 140 exhibited lower density compared to NC 130 containing composites. The lowest density value was obtained for PBT/1% NC 140 sample in which a 1.8% decrease was measured concerning the density of PBT.

4.7. Results of SEM Analysis

SEM micro-images of composites involving NC 130 and NC 140 organoclays are represented in Figure 4.12 and Figure 4.13, respectively.

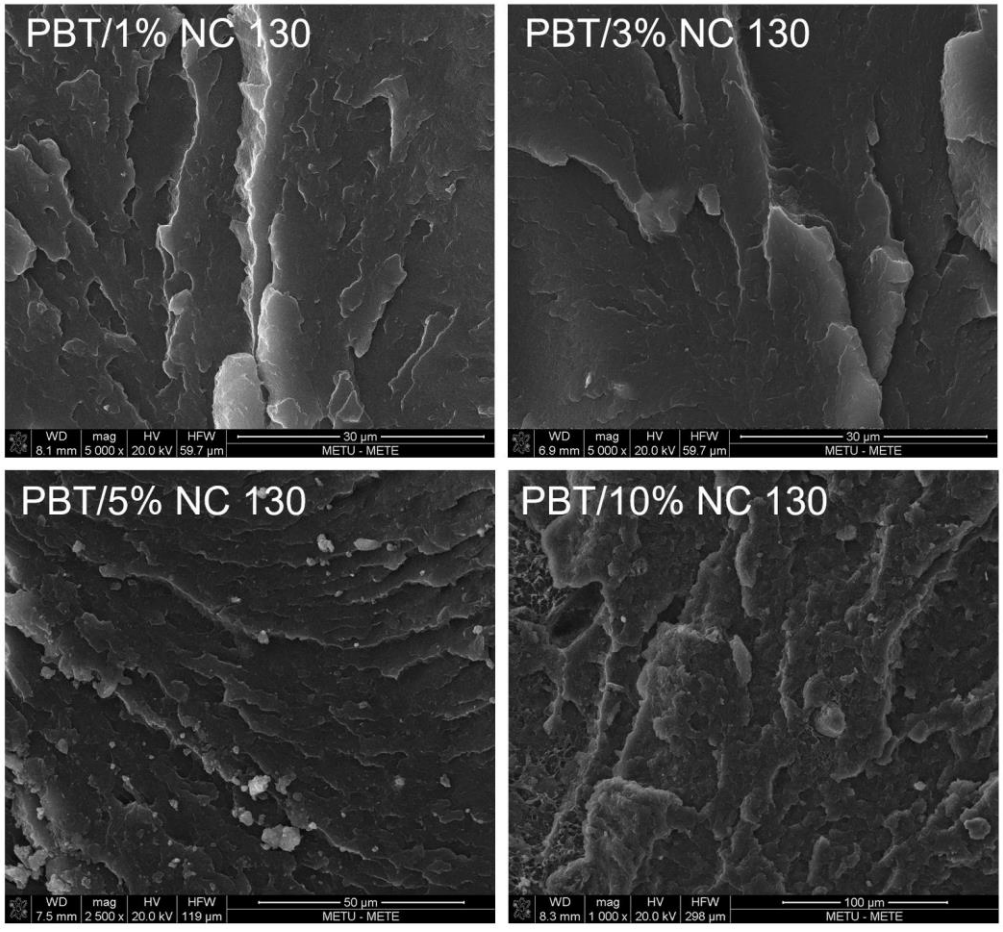

Figure 4.12. SEM micro-images of PBT/NC130 composites.

NC 130 clay displayed uniform dispersion into PBT phase for its low adding amounts according to SEM micro-images of PBT/1% NC 130 and PBT/4% NC 130. The formation of agglomerated clay regions was observed as the additive content increased. The poor dispersion was obtained from SEM micro-image of 10% NC 130 filled composite sample in Figure 4.12.

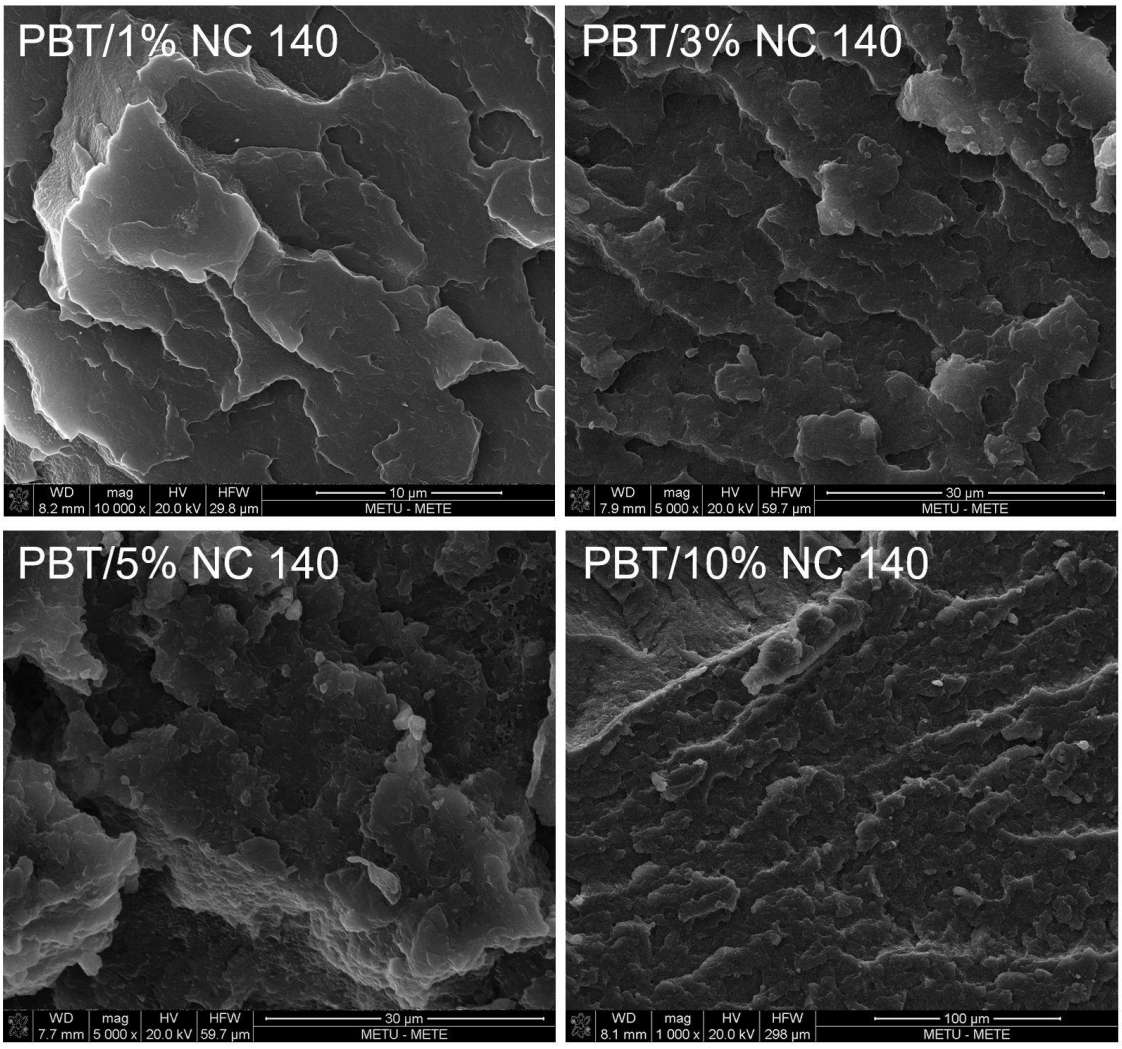

Figure 4.13. SEM micro-images of PBT/NC140 composites.

SEM micro-images of PBT/NC 140 samples in Figure 4.13 exhibited similar observations in which NC 140 clays dispersed homogeneously into PBT matrix at low filling ratios. Accordingly, clay particles started to form agglomerates as their concentrations increased.

The decrease in the degree of dispersion for highly-filled PBT/clay system as observed from SEM micro-images was the main reason for obtaining reductions for investigated performances of composites containing 10% of organoclays as described in previous results.

5. CONCLUSIONS

In this thesis study, organoclay containing PBT-based nanocomposite materials were produced using an extrusion process. The effects of two grades of organoclay inclusions to PBT matrix were examined by means of mechanical, thermal, physical, structural, thermo-mechanical and morphological behaviors.

Structural properties of PBT nanocomposites involving NC 130 and NC 140 organoclays were evaluated by XRD analysis. It was found that low amounts of both clay grades exhibited intercalated structure into PBT phase.

Mechanical test results showed that both organoclay additions were resulted in increase of tensile and impact performance of PBT. Tensile strength of composites was improved up to 3% adding content of both organoclays. Further additions of clays caused a decrease in the strength values of composites. The greatest strength performance was obtained for PBT/3% NC 130 sample. NC 130 clay displayed higher tensile strength values in comparisonto NC 140 grade. Similar to tensile strength results, Youngs modulus of PBT improved by the addition of organoclay powders. PBT/NC 130 composite samples gave higher Youngs modulus values than NC 140 incorporated composites at their identical loading amounts. Elongation at break parameter of PBT was found to be enhanced after the inclusions of both clay types.

Shore hardness of neat PBT exhibited a decreasing trend for lower contents of clays. However, hardness values of composites were improved as the filling ratio of NC 130 and NC 140 increased. As a comparison, NC 130 grade showed higher values than NC 140 in terms of Shore hardness parameter.

Impact test findings revealed that organoclay additions with 1% concentration resulted in a remarkable increase in impact strength of PBT. Further inclusions caused a reduction in impact strength of composites. The greatest impact performance was achieved for the sample of PBT/1% NC 140. Composites containing NC 140 clay displayed better impact resistance compared to NC 130-filled composites.

According to thermal analysis conducted by TGA studies, the clay incorporations resulted in improvements for thermal stability of neat PBT. PBT/NC 140 composites gave relatively higher thermal performance than that of NC 130 clay. Thermal stability and the amount of char residue of composite samples are increased in accordance with the addition ratios of organoclays.

By the help of DMA test results, it was obtained that storage modulus and loss modulus curves of PBT shifted to higher values after being compounded with organoclays. NC 140 containing composites displayed higher performance compared to NC 130 by the means of storage modulus and loss modulus results. Tan delta curves implied that additions of both organoclays yielded a significant increase in glass transition temperature of PBT.

As density measurements were examined, the density value of PBT was found to be decreased in the case of low loadings of NC 130 and NC 140. PBT/NC 140 composite samples exhibited lower density values than NC 130 containing composites as their identical filling amounts compared.

Melt-flow test showed that MFR parameter of PBT was reduced by the additions of clay powders. All of the composite samples gave lower MFR values with respect to neat PBT. Composites filled with NC 130 clay yielded slightly higher results compared to NC 140 in terms of MFR parameter.

The morphology and dispersion quality of each composite sample was claimed by SEM micro-images. Organoclay particles exhibited uniform dispersion for composites containing low contents (1% and 3%) of clays. On the contrary, poor dispersion of clays was observed with the help of SEM micro-images of PBT/10% NC 130 and PBT/10% NC 140 samples.

As an overall conclusion according to discussed findings of composites, NC 130 clay gave better results than NC 140 in terms of tensile, hardness and melt-flow behaviors, whereas, NC 140 showed higher performances as impact resistance, thermo-mechanical, density, since the reduction in density and weight lowering are highly required for mainly transportation sector, and thermal properties were considered.

6. RECOMMENDATIONS

Based on the findings in this study, instead of neat PBT, PBT based nanocomposites can be prepared and used in many applications.

7. PUBLICATIONS

A manuscript about this study will be prepared and submitted to the related peer-reviewed academic journals as soon as possible.

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