REPUBLIC OF TURKEY
ADANA ALPARSLAN TÜRKEŞ SCIENCE AND TECHNOLOGY UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
DEPARTMENT OF NANOTECHNOLOGY AND ENGINEERING SCIENCES

PREPARATION AND CHARACTERIZATION OF POLY (LACTIC ACID) / BARITE COMPOSITES

AYGÜN HATİPOĞLU
MASTER OF SCIENCE

ADANA 2020

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ADANA 2020

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.

Aygün HATİPOĞLU

ABSTRACT

PREPARATION AND CHARACTERIZATION OF POLY (LACTIC ACID) / BARITE COMPOSITES

Aygün HATİPOĞLU

Department of Nanotechnology and Engineering Sciences

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Interfacial adhesion between additive and polymer matrix plays a significant role in properties of polymeric composite materials. Surface of barite (BR) mineral was modified by silane coupling agent in order to increase compatibility between mineral additive and poly (lactic acid) (PLA) matrix. Surface properties of BR samples were characterized by Infrared spectrometry (IR). Untreated and surface silanized BR were compounded with PLA at the loading ratios of 5, 10, 15, and 20 wt% using melt-mixing process. Mechanical, thermo-mechanical, water resistance, melt flow, and morphological characterizations of composites were performed by tensile and impact tests, dynamic mechanical analysis (DMA), water absorption test, melt flow rate (MFR) test, and scanning electron microscopy (SEM) analysis, respectively.

According to results, BR additions led to increase in tensile strength and tensile modulus of PLA. The maximum improvement was obtained for 15 wt% of silanized BR filled composite. Impact strength of composites increased with addition amount of BR. DMA analysis revealed that glass transition temperature of PLA extended to higher values by the addition of BR. Inclusions of BR caused slight decrease in MFR value of PLA. Silanized BR containing composites displayed lower water absorption values compared to untreated BR, thanks to hydrophobic nature of silicon coated surface. According to SEM micro-images of composites, more homogeneous dispersion in PLA matrix was observed for treated BR particles than untreated ones due to enhancement for interfacial adhesion of BR to PLA after silanization. Silanized BR was found to be suitable for the applications of PLA-based composites.

Keywords: poly (lactic acid), surface silanization, barite, polymer composites

ÖZET

POLİ (LAKTİK ASİT) / BARİT KOMPOZİTLERİNİN HAZIRLANMASI VE KARAKTERİZASYONU

Aygün HATİPOĞLU
Nanoteknoloji ve Mühendislik Bilimleri Anabilim Dalı
Danışman: Dr. Öğr. Üyesi Ali Sinan DİKE
Nisan 2020, 42 sayfa

Polimer matris ile eklenti arasındaki arayüzey yapışması polimerik kompozit malzemelerin özelliklerinde önemli bir bir rol oynar. Barit (BR) mineralinin yüzeyi, poli (laktik asit) (PLA) ile mineral eklenti arasındaki uyumu arttırmak amacıyla silan uyumlaştırıcı ajan ile modifiye edilmiştir. BR örneklerinin yüzey özellikleri İnfrared spektrometre (IR) ile karakterize edilmiştir. Saf ve yüzeyi silanlanmış BR, ağırlıkça % 5, 10, 15, and 20 yükleme oranlarında eriyik karıştırma işlemi kullanılarak PLA ile karıştırılmıştır. Kompozitlerin mekanik, ısısal-mekanik, su dayanım, eriyik akış ve morfolojik karakterizasyonları, sırasıyla çekme ve darbe testleri, dinamik mekanik analiz (DMA), su emme testi, eriyik akış hızı (MFR) testi ve taramalı elektron mikroskopisi (SEM) analizi ile gerçekleştirilmiştir.

Test sonuçlarına göre, BR eklenmesi PLA'nın çekme dayanım ve çekme modülünü arttırmıştır. Maksimum artış %15 silanlanmış BR eklenmiş kompozit için belirlenmiştir. Kompozitlerin darbe dayanımı BR konsantrasyonu ile yükselmiştir. DMA analizi göstermiştir ki; PLA'nın camsı geçiş sıcaklığı BR eklenmesi ile daha yüksek değerlere çıkmıştır. BR eklentileri PLA'nın MFR değerinde ufak azalmaya neden olmuştur. Silanlanmış BR içeren kompozitler işlem görmemiş BR ile kıyaslandığında, silikon kaplı yüzeyin hidrofobik doğasından ötürü daha düşük su emme değerleri sergilemiştir. Kompozitlerin SEM mikro-resimlerine göre, silanlamadan sonra BR'nin PLA'ya yüzeysel yapışması arttığı için işlem görmüş BR parçacıklarında görmemiş olanlara kıyasla PLA matrisi içinde daha homojen dağılıma ulaşılmıştır. Silanlanmış BR'nin, PLA bazlı kompozitlerin uygulamaları açısından uygun olduğu bulunmuştur.

Anahtar Kelimeler: poli (laktik asit), yüzey silanlama, barit, polimer kompozitler

Dedicated to my family

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I would like to dedicate this thesis to my family.

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Table 4.1. Mechanical test results of PLA and composites. 21
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NOMENCLATURE

APTES	: Aminopropyltriethoxysilane
ATR	: Attenuated Total Reflectance
BR	: Barite
BR(S)	: Silaned Barite
DMA	: Dynamic Mechanical Analysis
IR	: Infrared
J	: Joule
MFR	: Melt Flow Rate
PE	: Polyethylene
PET	: Poly (ethylene terephthalate)
PLA	: Poly (lactic acid)
PMMA	: Poly (methyl methacrylate)
PP	: Polypropylene
PS	: Polystyrene
PTFE	: Poly (tetrafluoroethylene)
SBR	: Styrene-Butadiene Rubber
SEM	: Scanning Electron Microscopy
T_g	: Glass Transition Temperature

1. INTRODUCTION

1.1. Polymeric composite materials

Polymeric composite materials are composing of two different phases which are a base matrix and additives. Additives or fillers have ability to donate the polymer phase with additional properties. Polymer based composites include fibers and particles in polymer matrix. These additives are introduced to increase the desired properties of the composites. For example, the fillers in micron particle size generally enhance the mechanical properties such as hardness, toughness and thermal properties. Polymer composites are commonly used in industries due to the many advantages such as moderate cost, processability, enhanced thermal and mechanical properties. The matrix of these composites can be thermoplastics or thermosets (Akovali, 2001; Guzel et al., 2016; Horpan et al., 2016; Schwartz, 1983).

Environmentally friendly materials have received considerable attention by researchers working in research centers or in different industries due to ecological and economic issues in recent years. Composite materials consist of renewable products and natural resources which are named as green composites have been gradually developed for the aim of replacement for conventional petroleum-based materials. Green composites have several advantages, such as having biodegradability, low weight, and low production costs. In addition, some wastes or by-products produced during processing of some industries such as mining can be used as filler materials in composite materials. Therefore, such produced composite materials are favorable in several application areas, including construction, packaging, and transportation, thanks to these advantages (Andreopoulos & Theophanides, 1994; Guzel et al., 2016; Mann et al., 2018; Sabu et al., 2012).

The reinforcement of renewable polymers has gained importance because of their ecofriendly and recyclable properties compared to commercial petroleum-based polymers. Moreover, the hydrophilic nature of bio-based polymers makes strong adhesion with most of the fillers (Ren, 2011). Additionally, several surface treatment methods are widely applied to additives in order to obtain high performance composite materials (DeArmitt, 2011; Harris, 2003).

Mineral fillers were widely preferred for reinforcing plastics due to their low cost and naturally obtained characteristics. The influence of mineral fillers on the main properties of plastics depends on some factors, such as shape, size, loading ratio of fillers, and, most importantly, polymer–filler adhesion (Murphy, 2001; Theberge, 1982).

1.2. Barite mineral

Barite (BR), barium sulfate, mineral is a dirty white colored mineral consisting of mainly barium sulfate ($BaSO_4$) and a few amounts of anglesite ($PbSO_4$), celestite ($SrSO_4$) and anhydrite ($CaSO_4$). BR is obtained mostly in depositional environments and it is deposited through various numbers of processes, including biogenic, hydrothermal, and evaporations (Huang et al., 2013; Miller, 2011).

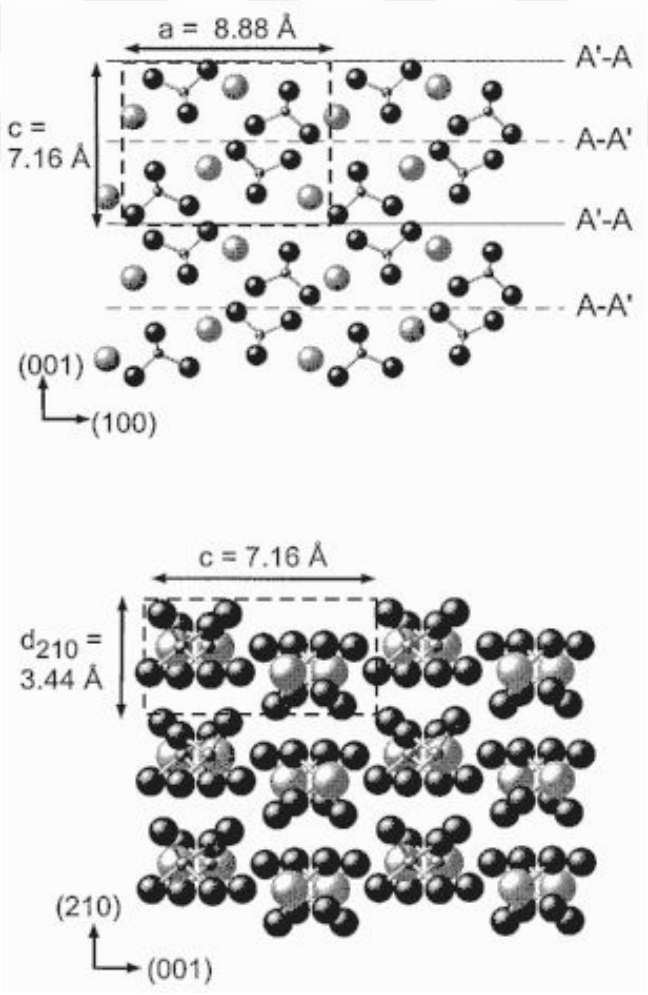

Figure 2.1. Schematic demonstration of the crystal structure of barite.

Figure 2.1 demonstrates the crystal structures of barium sulfate. Barium atoms are indicated with large light spheres. Oxygen atoms are displayed by large dark spheres and Sulphur atoms are represented with small light spheres in Figure 2.1 (Fenter et al., 2001).

BR mineral has found effective usage as in extender rubber, paints and coatings industry, as an oxidizer in glass production, and as an indicator for medical X-ray photographs in health sector (Ciullo, 1996).

BR containing polymer composites have been used in medical, industrial, and construction applications, thanks to BR that provides improvements on radioactivity shielding (El-Sarraf and El-Sayed, 2013; Binici et al., 2014) mechanical (Chmielewska et al., 2014; Hang et al., 2006), abrasion resistance (Murakami, 2009; Kim et al., 2004; Rogers et al., 2009; Qi et al., 2014; Xu et al., 2017), and sound isolation (Binici et al., 2012; Hedayati & Arefazar, 2008; Tayfun, 2006) properties. Additionally, natural barite with various particle size are used as an additive in production of polyurethane foams to gain high levels of density and load bearing capacity (Wypych, 2010).

1.3. Poly (lactic acid)

Poly (lactic acid) (PLA) is the most popular candidate among natural polymers, which are derived from renewable sources. The synthesis of PLA is carried out by condensation polymerization reactions of lactic acid monomers. Another way of synthesis of PLA is performed by catalytic ring-opening polymerization of the lactide monomers (Rydz et al., 2015; Saldivar-Guerra & Vivaldo-Lima, 2013). The reaction scheme which indicates the common reactions on production of PLA is displayed in Figure 2.2 (Rasal et al., 2010).

PLA is a versatile biopolymer that its use is considered as reduction of the municipal solid waste disposal problem for recently packaging and consumer products (Bajpai et al., 2012; Ebnesajjad, 2012; Niaounakis, 2014; Weber et al., 2002). Reinforcing efforts of bio-polymers such as PLA with suitable fillers have been a popular research topic because these polymers have some limitations, including poor toughness and melt strength, low thermal stability, and narrow processing window (Rasal et al., 2010; Murariu & Dubois, 2016).

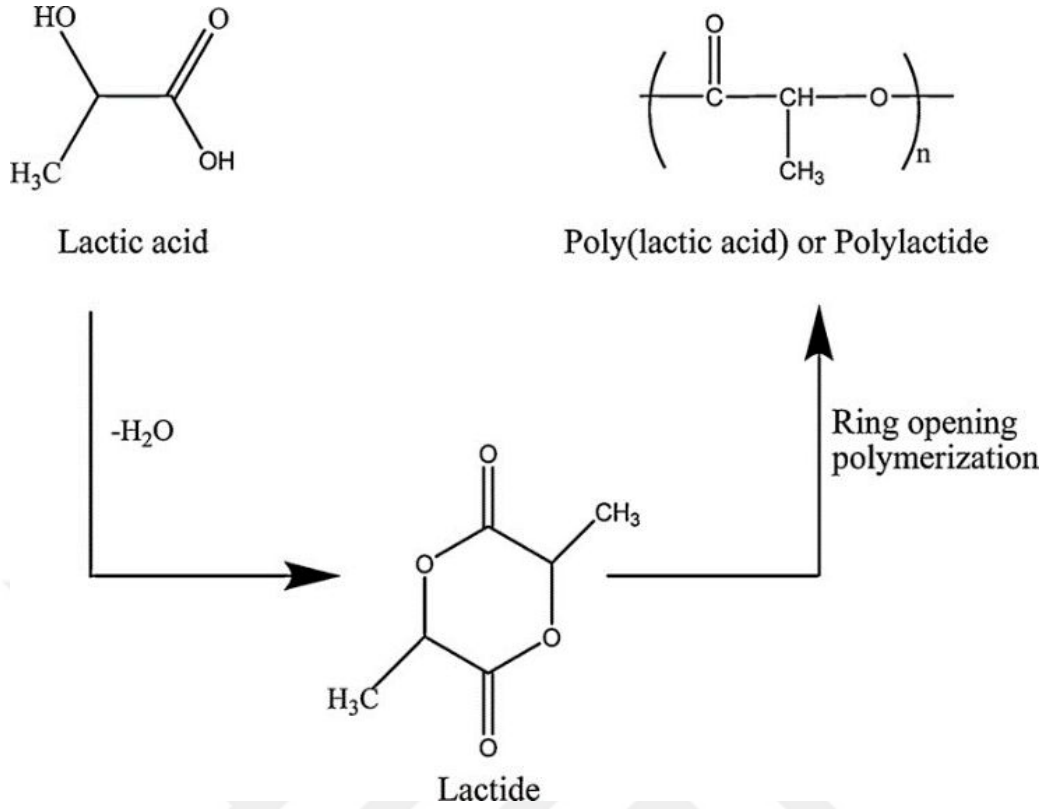

Figure 2.2. Schematic demonstration of the production of PLA.

1.4. Extrusion process

Extrusion process is the most common and cost-effective technique preferred conventionally in plastic industry. Melt compounding of polymeric materials is conventionally performed by extrusion process. This method is used efficiently for the purpose of obtaining required plastic material in various forms by melting polymer and adding fillers into extruder device. This process is proper production technique for thermoplastic composite parts. Compounding polymers using extruder is taken place in high shear medium with elevated temperature in order to provide homogeneous mixing (Anderson, 2008; Cheremisinoff, 1987; Lafleur & Vergnes, 2014; Rauwendaal, 2014)

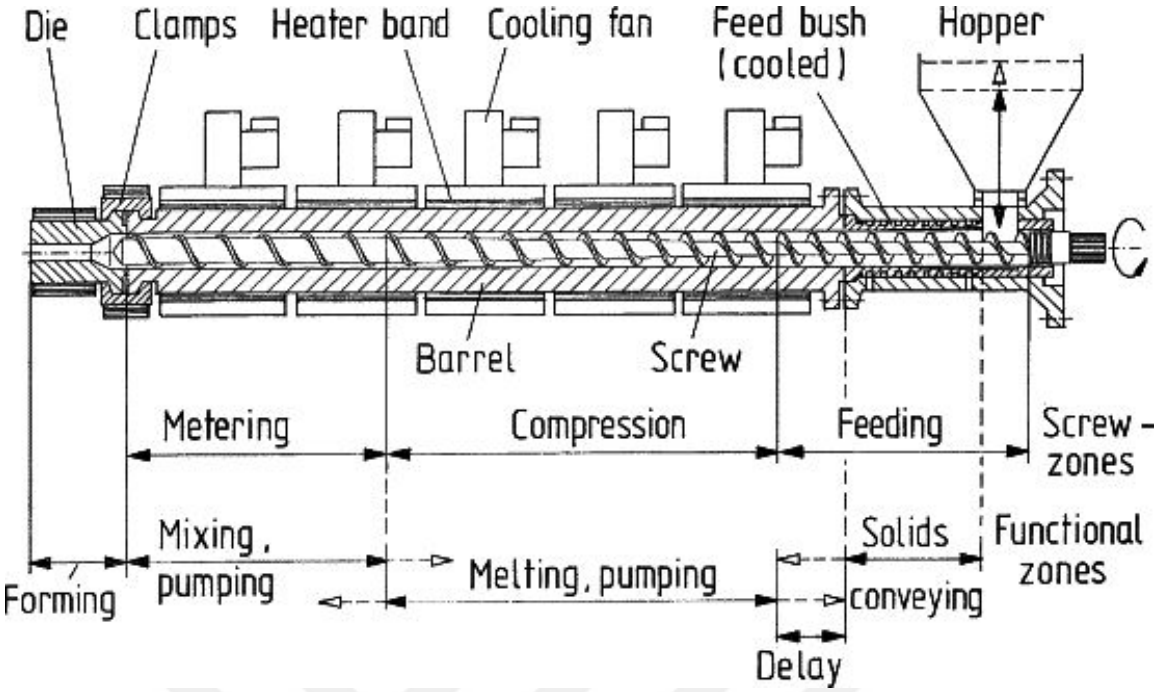

Figure 2.3. Schematic drawing of extrusion process.

The main components of the extruder device are namely feeder zone, screw, barrel and die as demonstrated in Figure 2.3 (Grünschloss, 2001). The screws are the basic part having several functions such as transportation of polymer pellets, melting of polymer and mixing fillers homogeneously in molten polymer phase. In addition to dispersing additives through barrel, screws provide conveying the molten plastic. The last component where the molten and mixed polymer reaches inside the extruder is die. The final shape of plastic is form at this part. Resulted polymeric material at the end of the process can be shaped in several forms such as chip, pellet, sheet, pipe, film, tube, and rod which are controlled by die design (Cogswell, 1972; Giles et al., 2004; Kohlgrüber, 2012; Middleman, 1977; Rubin, 1990).

1.5. Injection molding process

Injection molding is most favorable processing methods for shaping of plastic-based materials. This process is used to produce finished polymeric parts that ranging from household devices to automobile appliances (Belofsky, 1995; Kutz, 2016; 1994; Rubin & Rubin, 1972; Strong, 2006).

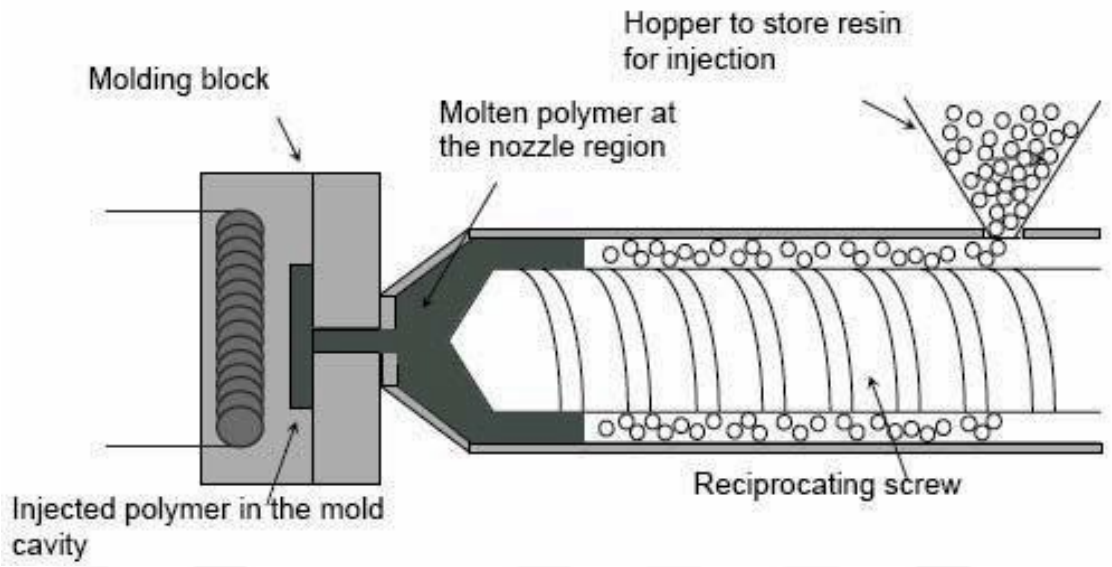

Figure 2.4. Schematic drawing of injection molding process.

The basic stages and equipments of injection molding process are represented in Figure 2.4 (Ahn et al., 2005).

This common process is composing of cycling operation with three major steps including filling, packing and cooling operations. Initially, solid polymer is melted by pushing toward to the nozzle. The temperature of melting plastic is controlled by the help of temperature control system. Then, polymer melt undergoes injection through the close mold using accelerated pressure. The pressure applied on molten polymer using rolling screw during this stage. The cooled mold gives the desired shape for molten plastic thanks to its well-designed cavities. At the final step, the mold is opened and the injected article is removed manually or automatically (Crawford, 1998; Harper & Petrie, 2003; Malloy, 1994; Rosato & Rosato, 2012; Rubin & Rubin, 1972).

2. LITERATURE REVIEW

2.1. Barite reinforced polymer composites

Barite has been used as an additive for various polymer matrices, including polyethylene, polypropylene, polycarbonate, poly (methyl methacrylate), polystyrene-polypropylene blends, poly (ethylene terephthalate), poly (tetrafluoroethylene), poly (dimethyl siloxane) elastomer, epoxy resin, thermoplastic polyurethane, natural rubber, and styrene-butadiene rubber. Additionally, a few number of studies were obtained in the literature regarding the BR filled PLA (Hatipoglu & Dike, 2020).

Several research groups published studies related with BR reinforced polyolefin-based composites. Elkawash et al. reported that polyethylene composites involving silane modified-BR showed enhanced mechanical and physical performance compared to untreated BR (Elkawash et al., 2020). Kohandel et al. investigated the effect of BR inclusion to mechanical and rheological behavior polypropylene (PP) composites (Kohandel et al., 2016). Wang et al. reported that PP matrix can be toughened with the addition of BR particles (Wang et al., 2003). Ren et al. prepared PP-based composites filled with high content of BR using extrusion process. They found that silicone coupling agent acted as more effective modifier compared to titanate coupling agent in the case of enhancement on mechanical performance of composites (Ren et al., 2002). Hammer and Maurer postulated that BR incorporation to polystyrene–polypropylene blends led to reduction for domain size of polystyrene phase (Hammer & Maurer, 2012; Hammer & Maurer, 2014)

Hacioglu performed a PhD thesis study to investigate the degradation behavior of BR filled polycarbonate (PC) based composites which were subjected to gamma irradiation. He postulated that PC containing BR particles can be used in radioactive waste management field (Hacioglu, 2017).

Ge et al. produced BR filled poly (ethylene terephthalate) (PET) composites using melt mixing method and they showed that BR can act as a nucleating agent for PET matrix and its nucleation activity can be improved by surface-treated BR particles (Ge et al., 2009). According to findings published by Yan and his colleagues, granulation process of BR

powder caused increase in dispersion homogeneity of BR particles into poly (tetrafluoroethylene) (PTFE) matrix and mechanical strength of PTFE/BR composites was improved (Yan et al., 2016).

Cisneros-Pineda et al. fabricated poly (methyl methacrylate) (PMMA) based bone cement containing BR powder with varying concentrations. They observed that mechanical performance and injectability of prepared bone cement highly depend on the amount of BR (Cisneros-Pineda et al., 2011).

Kumar at al. performed surface modification of BR and production of BR filled poly (dimethyl siloxane) elastomer composites. According to their experimental results, surface modified BR displayed increase in thermal and X-ray shielding properties of composites (Kumar at al., 2018). El-Sarraf and El-Sayed suggested that BR addition yield improvement for gamma-ray shielding behavior of epoxy and polyester based composites (El-Sarraf & El-Sayed, 2013).

Lu and his co-workers investigated that reduction in the molecular weight of the polyurethane elastomer occur due to the moisture remaining in the BR led to hydrolyzing for polymer (Lu et al., 2004).

Wang et al. studied the effect of silane treatment of BR to wear resistance, tensile properties and hardness of natural rubber composites. They observed that related properties increased with modified BR additions (Wang et al., 2001). Several additives including BR were used for styrene-butadiene rubber (SBR) by Hundiwale et al. (Hundiwale et al., 2003).

There has been two published works found in the literature which is related with PLA/BR composite system for biomedical applications. In one of those studies, a novel bioabsorbable radiopaque stent material containing PLA and BR was developed by Lamsa and his colleagues. They postulated that PLA-BR based stent showed lower level of toxicity compared to reference steel material during their specific experiments (Lamsa et al., 2006). In the case of similar research study regarding BR filled PLA composite, Nuutinen et al. evaluated the use of BR as a radiopaque additive for bioresorbable PLA fibers using melt

blending followed by drawing process. They demonstrated that BR loaded PLA fibers can be optimized by tuning intrinsic viscosity during processing (Nuutinen et al., 2003).

2.2. Aim of the study

The main target of this thesis study is the investigation of mechanical, thermo-mechanical, water resistance; melt-flow and morphological behaviors of BR reinforced PLA-based bio-composites to enlighten their larger volume fabrication in industrial applications including mainly packaging and other products for outdoor usage. For this purpose, melt blending process was applied to produce the composite samples. The main different aspect of this thesis study than the previously published ones is the investigation of the use of BR mineral as an additive for PLA composites. The evaluation of performance of BR containing PLA composites is important because of their large-scale production in mainly packaging and outdoor applications.

BR powders were subjected to silane modification in order to increase of interfacial interactions between filler and matrix. The surfaces of neat and silane treated BR samples were examined using infrared spectroscopy (IR) in attenuated total reflectance (ATR) mode.

Composites were prepared by lab-scale micro-compounder and test specimens were shaped using injection molding process.

In addition to mechanical (tensile and impact tests) and thermo-mechanical (dynamic mechanical analysis-DMA) studies, water absorption test was performed to evaluate the outdoor applications of composites, melt flow rates (MFR) were reported to investigate the ease of processability of materials and scanning electron microscopy (SEM) technique was conducted to postulate the dispersion homogeneity of BR particles into PLA phase.

3. MATERIALS AND METHODS

3.1. Materials

3.1.1. PLA

The commercial PLA polymer was supplied from Natureworks LLC, USA under the trade name of Ingeo biopolymer 6100D. It has a density of 1.24 g/cm^3 and a relative viscosity of 3.1 according to CD Internal viscotek method cited by producer.

Table 3.1. Properties of PLA used in this study

Specification	Test standard	Value	Unit
Specific gravity	ASTM D792	1.24	g/cm^3
Relative viscosity	ASTM D5225	3.1	-
Melt index	ASTM D1238	24	g/10 mins
Glass transition temperature	ASTM D3417	55-60	°C
Crystalline melt temperature	ASTM D3418	165-180	°C

3.1.2. Barite

Barite powder was purchased from Karakaya Bentonite Inc., Ankara, Turkey. It has a density of 4.2 g/cm^3 and a volume mean diameter of 9.4 microns according to experimental data provided by supplier. The basic properties of barite mineral used in this work are listed in Table 3.1 (Hacioglu, 2017).

Table 3.2. Properties of barite used in this study.

Specification	Test standard	Value	Unit
Composition	EN 12912	$BaSO_4$: 92	wt%
Specific gravity	-	4.2	g/cm^3
Bulk density (loose)	EN 12902	2200	kg/m^3
Bulk density (packed)	EN 12902	2500	kg/m^3
Particle size	ISO 13320	9.4	μm

3.1.3. Silane coupling agent

Silane coupling agent containing amino functional groups with a specific name of aminopropyltriethoxysilane (APTES) was used in this study for the purpose of creating silane layer on BR surface. Ethanol used as solvent for APTES during modification process. APTES and ethanol were obtained from Merck AG Company, Germany. The chemical formula of APTES is illustrated in Figure 3.1.

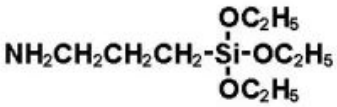

Figure 3.1. The chemical formula of silane coupling agent used in this study.

3.2. Surface treatment of barite

Silanization process was applied to BR samples according to similar treatment routes in literature (Kanbur & Tayfun, 2017; Natalia & Hatsuo, 1997; Shokoohi et al., 2008). BR powders were mixed in 2 wt. % of APTES/ethanol solution for 2 hours at room temperature. After mixing, samples were dried at 70 ^{o}C overnight at a laboratory oven. Untreated and silane treated BR samples were coded as BR and BR(S), respectively.

3.3. Production of composites

PLA and its composites were compounded by twin-screw 15 cc DSM Xplore micro-extruder as displayed in Figure 3.1. Processing temperature of 210 ˚C, mixing time of 5 minutes and mixing speed of 100 rpm were applied during compounding process. Neat PLA was mixed with these processing parameters and named as PLA. Addition amounts of BR and BR(S) in PLA were 5, 10, 15 and 20 by weight % as listed in Table 3.2.

Table 3.3. Compositions of prepared composites.

Samples	PLA content (wt%)	BR content (wt%)	BR(S) content (wt%)
PLA (neat)	100	0	0
PLA-BR 5	95	5	0
PLA-BR 10	90	10	0
PLA-BR 15	85	15	0
PLA-BR 20	80	20	0
PLA-BR(S) 5	95	0	5
PLA-BR(S) 10	90	0	10
PLA-BR(S) 15	85	0	15
PLA-BR(S) 20	80	0	20

Figure 3.2. The lab-scale micro-compounder used in this study.

After extrusion process, composites were obtained with 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 215˚C and 40 ˚C, respectively.

The representative photographs of micro-injector device used in this study and obtained test specimens after injection molding process are provided in Figure 3.3 and Figure 3.4, respectively.

Figure 3.3. Photograph of micro-injector used in this study.

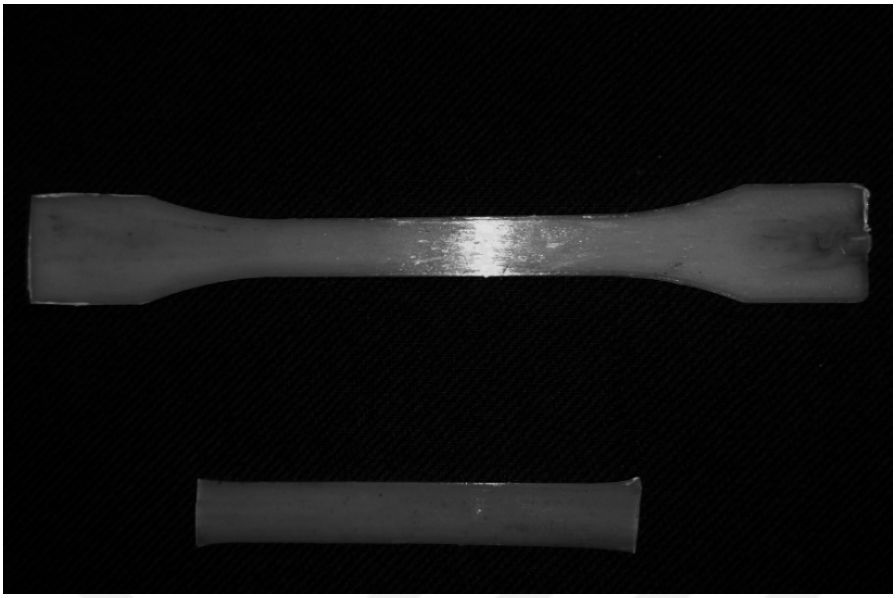

Figure 3.4. Photograph of prepared test specimens by injection molding.

3.4. Characterization techniques

3.4.1. Infrared spectroscopy

Far infrared spectroscopy technique in attenuated total reflectance (ATR) mode was conducted to investigate the surface characteristics of untreated and silane treated BR powders using Bruker Optics, 66/S series IR spectrometer at the resolution of 4 cm^{-1} with 32 scans. The photograph of IR spectrometer used in this study is given Figure 3.5.

Figure 3.5. Photograph of IR spectrometer used in this study.

3.4.2. Tensile tests

Tensile tests were performed using Lloyd LR 30 K universal tensile testing device represented in Figure 3.6. 5 kN load cell and 5 cm/min was applied as crosshead speed according to the standard of ASTM D638. Tensile strength, percentage strain and tensile modulus values were recorded of minimum of three samples with standard deviations.

Figure 3.6. Photograph of tensile testing device used in this study.

3.4.3. Impact tests

Impact energy values of PLA and its composite samples were recorded by Coesfeld material impact tester with the 4 J pendulum according to standard of ASTM D256 procedure. The measured impact energy values in J were converted to impact strength values in kJ/m^2 using the dimensions of test samples. The photograph of impact tester used in this work is presented in Figure 3.7.

Figure 3.7. Photograph of impact tester device used in this study.

3.4.4. Dynamic mechanical analysis

Thermo-mechanical behavior of PLA and PLA/BR composites was examined by dynamic mechanical analysis. DMA tests of PLA and composite samples with the dimensions of 50×7.5×2.5 mm^3 were studied using Perkin Elmer DMA 8000 in dual cantilever bending mode. Temperature range of analysis applied between -150 °C and 200 °C at the heating rate of 10 °C/min under the inert nitrogen atmosphere.

3.4.5. Melt flow rate measurement

Melt flow rates (MFR) parameters of samples were measured by Meltfixer LT, Coesfeld. The tests were conducted using the standard load of 5 kg at the processing temperature of 210 °C. The MFR values were calculated and expressed as g/10 min. Meltfixer device used in this study is demonstrated in Figure 3.8.

Figure 3.8. Photograph of melt flow rate device used in this study.

3.4.6. Water absorption analysis

In order to determine the water absorption values of neat PLA, PLA-BR and PLA-BR(S) composites, samples were conditioned according to standard of ASTM D570. Test samples were subjected to conditioning in water bath at room temperature; they were taken out from water and weighted periodically in 10 days' period. Figure 3.9 represents the photograph of the test samples immersed in water bath during water absorption measurements.

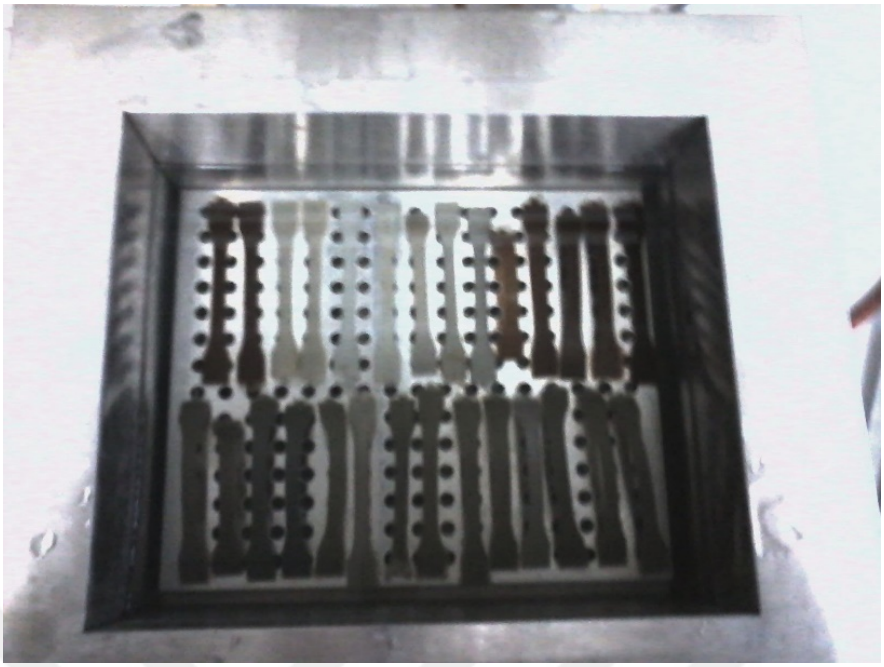

Figure 3.9. Photograph of water absorption test applied in this study.

3.4.7. Scanning electron microscopy

The fractured surfaces of composites after impact test were examined by FEI Quanta 400F FESEM scanning electron microscope (SEM) in order to investigate the morphological properties of composite samples. SEM micro-photographs were captured at magnifications of 1,000 and 3,500.

4. RESULTS AND DISCUSSIONS

4.1. Results of infrared spectroscopy

IR spectrum of BR and BR(S) samples are represented in Figure 4.1.

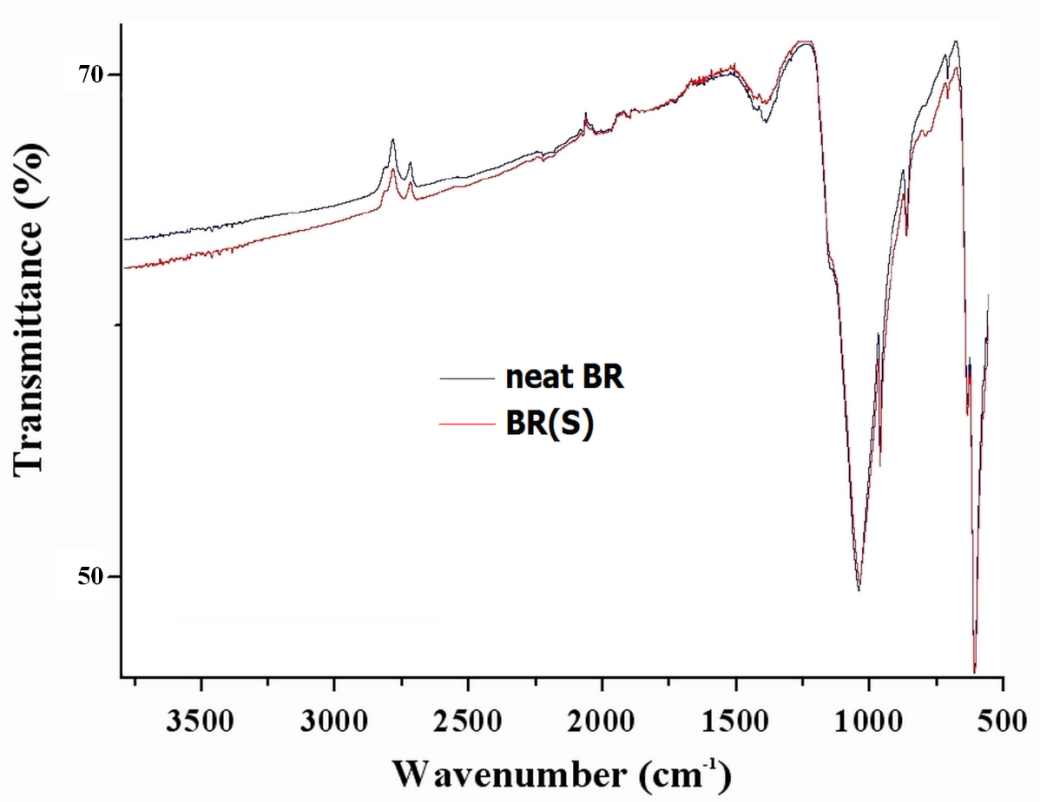

Figure 4.1. IR spectra of BR samples.

The two peaks around 610 cm^{-1} and 630 cm^{-1} assign bending vibration of the SO_4^{2-} ion of barite as mentioned in the literature (Adler & Kerr, 1965; Shen et al., 2007). The shoulder peak at 980 cm^{-1} and intense peak at 1070 cm^{-1} are due to symmetrical vibrations of SO_4^{2-} group (Ramaswamy et al., 2010; Wylde et al., 2011). These characteristic sulfate based S-O stretching bands are observed both of BR and BR(S) samples with equal intensities.

The peaks located in the region from 1200 cm^{-1} to 1400 cm^{-1} wavenumbers assign to oxygen related bonds as determined in the literature (Dogan et al., 2016; Silverstein & Webster, 2006; Tayfun et al., 2017) and it can be clearly seen that untreated BR sample gives higher intensities compared to BR(S). This finding indicates that silane coupling agent causes

reduction of oxygen functionality on barite surface by forming bonds with these groups. It can be obtained from the spectra of BR(S) that there are shoulder peaks around 800 cm^{-1}. These peaks can be seen only for BR(S) sample which are due to Si-O vibrations (Kanbur & Tayfun, 2018; Kilinc et al., 2019; Manna et al., 1999). This result is another identification of silane covered the neat barite surface during treatment process.

4.2. Results of tensile test

Mechanical test data of PLA and composites are listed in Table 4.1 and the stress versus strain curves are given in Figure 4.2.

Table 4.1. Mechanical test results of PLA and composites.

Samples	Tensile Strength (N/m^2)	Young's Modulus (GPa)	Elongation at Break (%)	Impact Strength (kJ/m^2)
PLA (neat)	58.4±1.6	1.0±0.1	11.6±0.7	11.6±0.4
PLA-BR 5	55.6±1.8	1.1±0.2	7.8±0.3	6.0±0.2
PLA-BR 10	60.7±2.3	1.2±0.1	8.0±0.6	7.8±0.3
PLA-BR 15	63.2±2.0	1.2±0.2	7.8±0.5	9.1±0.3
PLA-BR 20	58.8±2.2	1.2±0.1	8.3±0.4	9.2±0.3
PLA-BR(S) 5	62.9±1.8	1.2±0.2	7.6±0.3	9.9±0.4
PLA-BR(S) 10	65.5±2.0	1.3±0.2	8.5±0.5	11.4±0.3
PLA-BR(S) 15	67.5±1.9	1.3±0.2	7.7±0.5	12.8±0.4
PLA-BR(S) 20	63.8±2.5	1.3±0.2	8.3±0.6	13.2±0.4

It can be seen from Table 4.1 that tensile strength increases with the addition amount of BR. This increasing trend reaches to maximum at optimum concentration of 15 wt. %. Further additions of BR causes sharp decrease in tensile strength. This behavior may due to agglomeration formations of barite particles into PLA matrix at 20% filling ratio.

BR(S) filled composites exhibit about 5-6 points higher tensile strength values compared to BR filled ones for all addition amounts according to Table 4.1. Improvement of adhesion of inorganic BR surface to organic polymer is the reason of this finding.

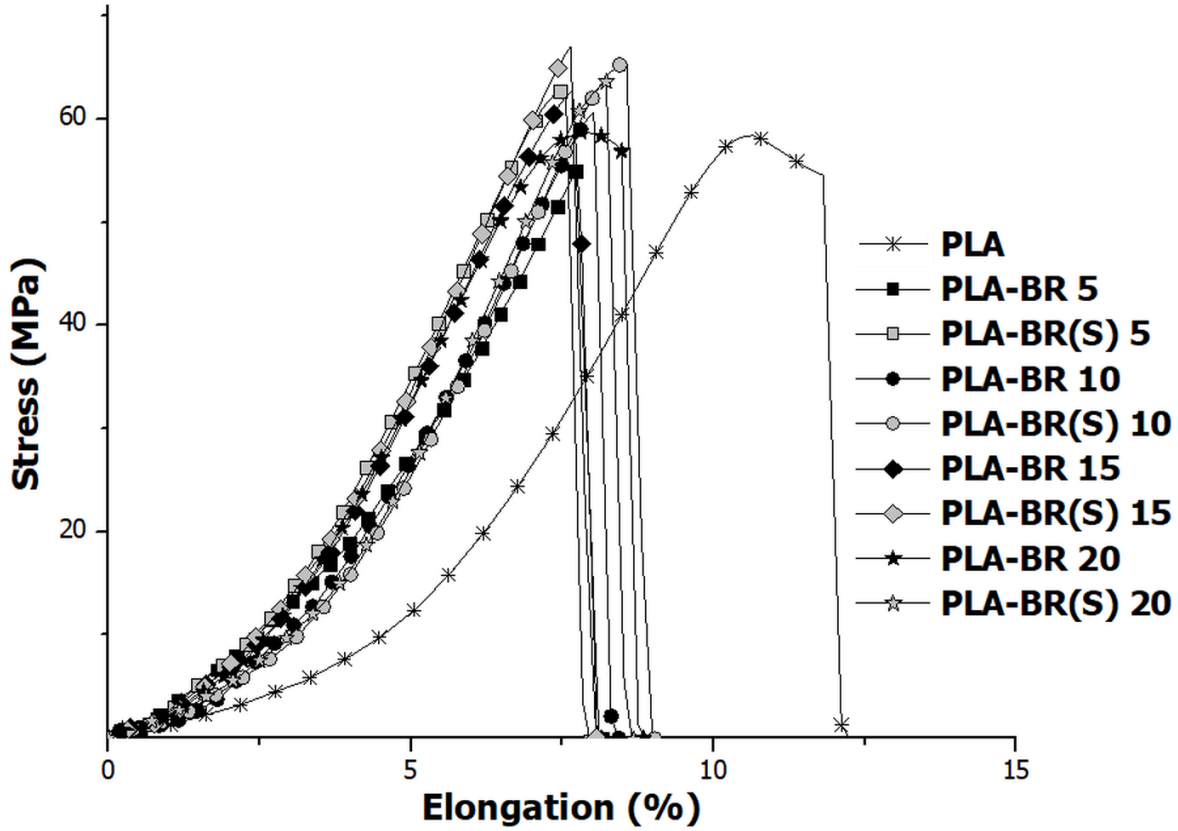

Figure 4.2. Stress versus strain curves of PLA and composites.

The highest strain value is obtained for neat PLA according to Figure 4.2. Elongation at break of PLA decreases about 3-4 points with the barite additions regardless of untreated or treated samples. Composites show slightly higher Young's modulus results with respect to PLA. It can be seen from the results that surface treatment and addition amount cause minor effect to the modulus of composites.

4.3. Results of impact test

Impact strength values of PLA and its composites are listed in the last column of Table 4.1 and represented as bar graphs in Figure 4.3.

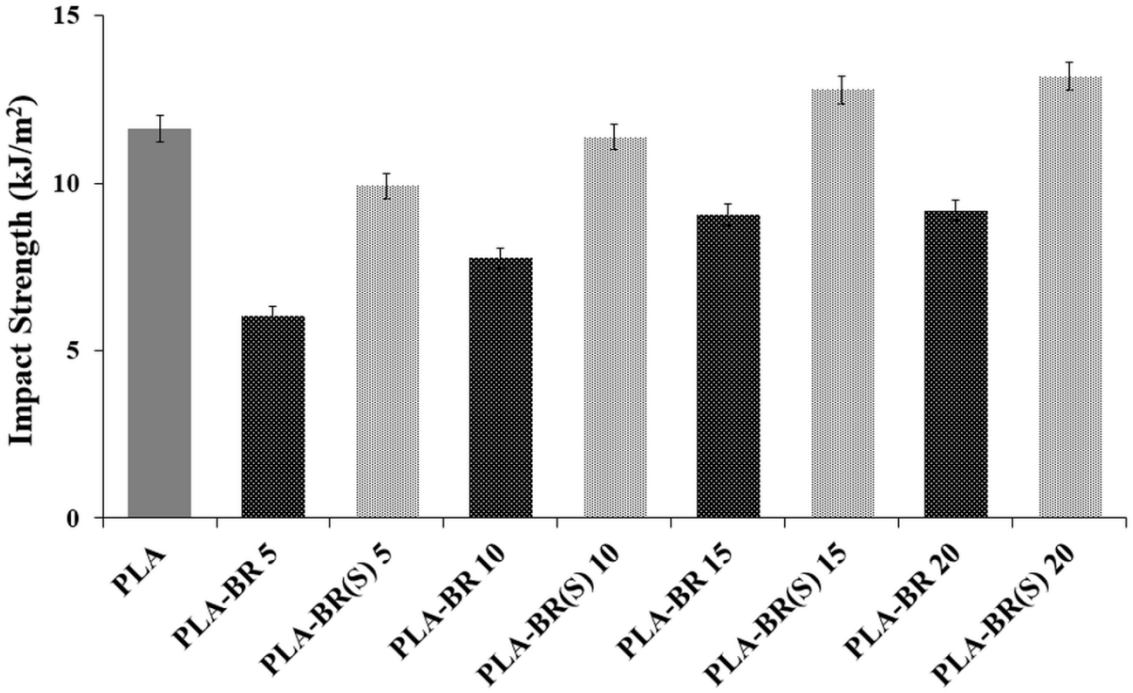

Figure 4.3. Impact test results of PLA and composites.

According to Figure 4.3, impact strength of composites shows improvement with increase in addition amount. BR additions to PLA cause significant reductions with all loading ratios. On the other hand, BR(S) additions with 15% and 20% addition amount gives higher impact strength results compared to neat PLA.

PLA-BR(S) composites also show about 4 points higher impact strength values than that of untreated ones at the same addition amount of PLA-BR composites for all of the loading ratios. These results are related with more homogeneous dispersion of treated BR particles into PLA matrix occurs with respect to untreated BR particles.

4.4. Results of dynamic mechanical analysis

Storage modulus and Tan delta curves that were derived from DMA data are illustrated in Figure 4.4 and Figure 4.5, respectively.

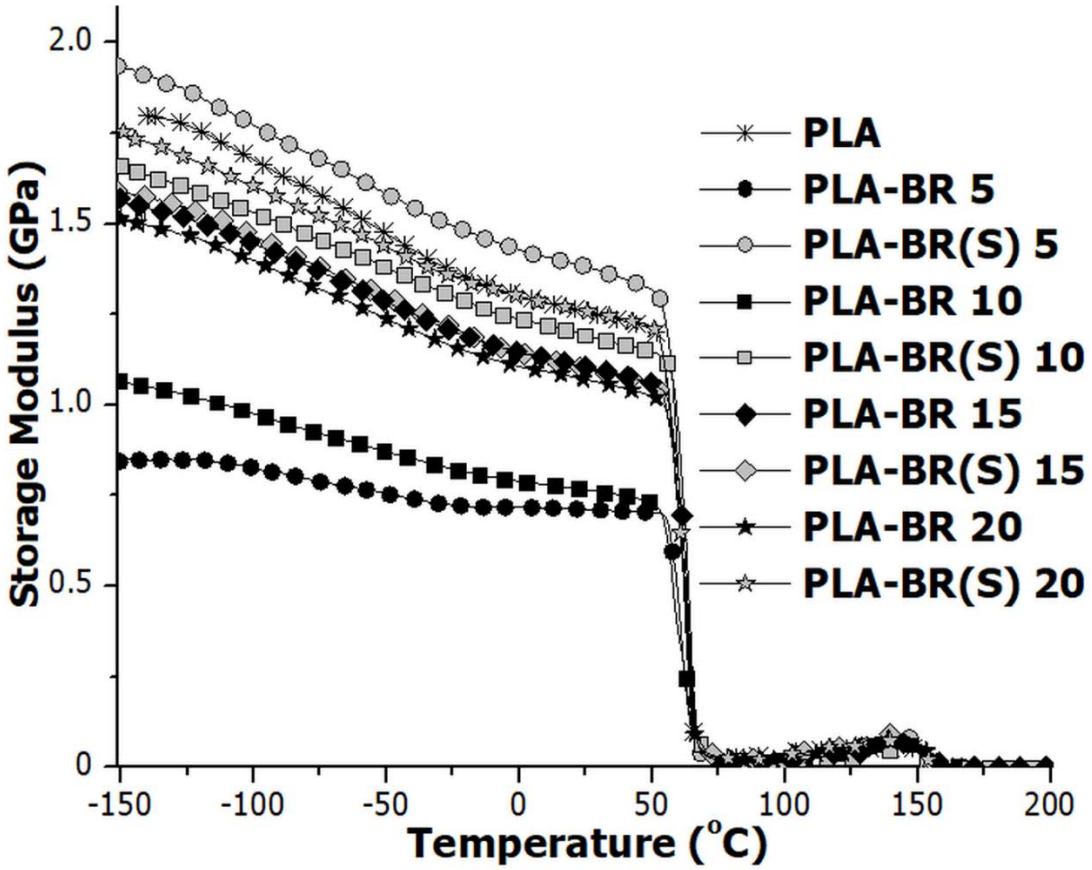

Figure 4.4. Storage modulus curves of PLA and composites.

As can be seen from Figure 4.4, storage modulus curves reduce immediately around 70 ^{o}C due to the glass transition temperature (T_g) of PLA. Untreated BR addition causes lowering on storage modulus of PLA for all of their concentrations. PLA/BR(S) composites give higher storage modulus than that of untreated BR composite.

The highest modulus value is obtained for PLA-BR(S) 5 sample among composites. This candidate exhibits the higher result compared to neat PLA in the case of storage modulus. The temperature value at the peak of tan delta curve indicates the T_g of polymer.

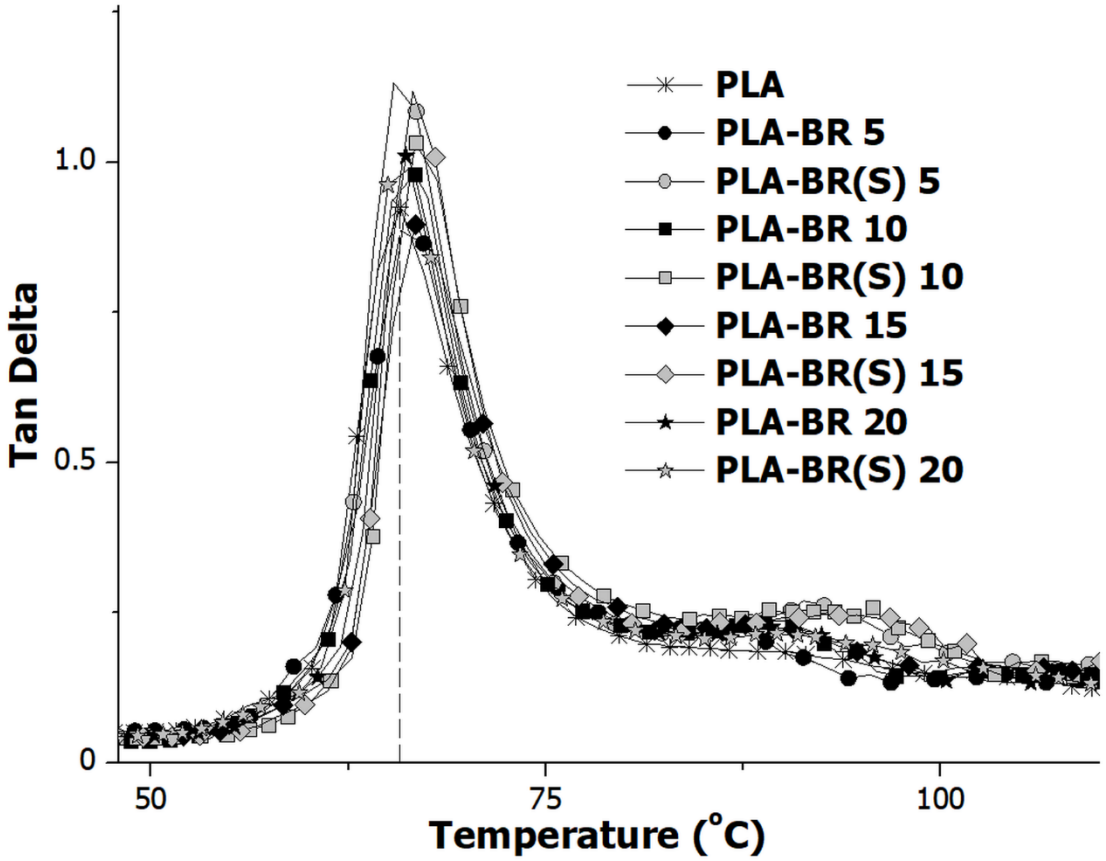

Figure 4.5. Tan delta curves of PLA and composites.

It can be observed from the tan delta curves displayed in Figure 4.5 that, T_g of PLA shifts to higher temperatures with the additions of BR and BR(S). The greatest increase for T_g is obtained in PLA-BR(S) 15 composite. Other composite samples give similar results in the case of tan delta. These results may cause from the restriction of polymer chain motions after addition of barite particles (Donnet, 2013; Kanbur & Tayfun, 2019).

4.5. Results of melt flow rate measurements

MFR values are indicated as bar chart format in Figure 4.6.

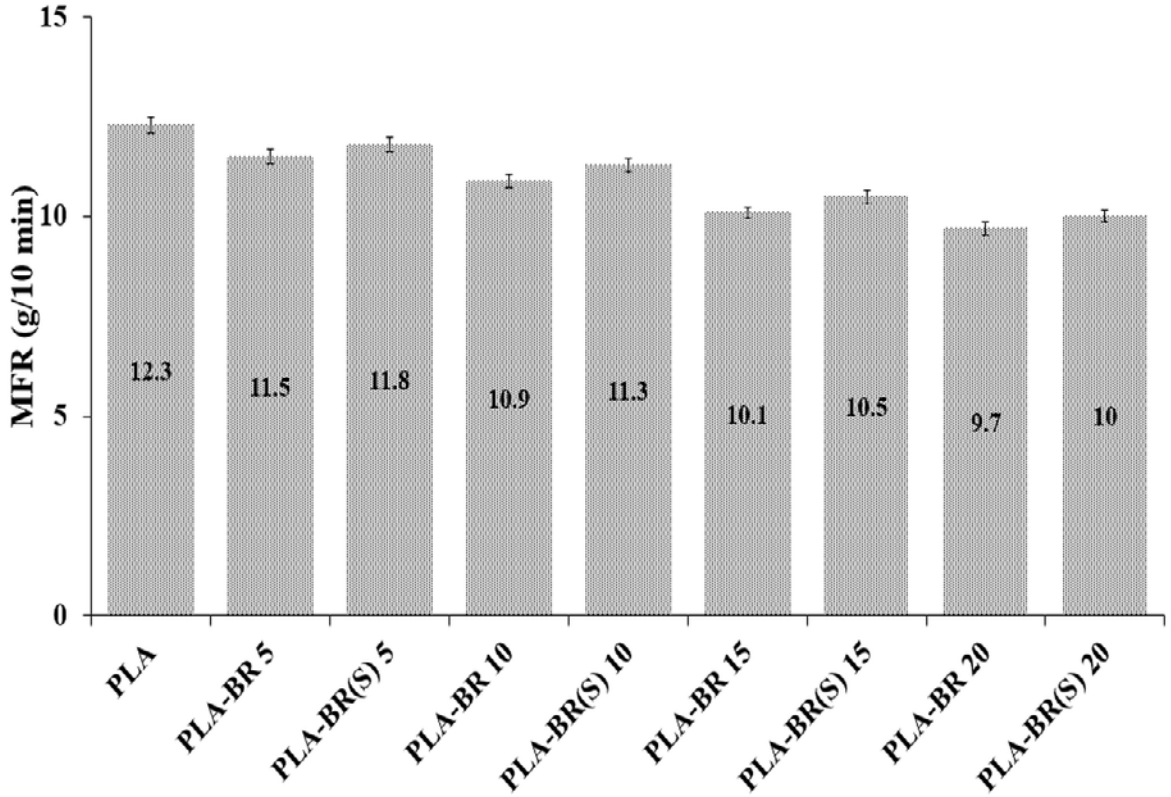

Figure 4.6. MFR test results of PLA and composites.

According to Figure 4.6, all of the MFR values are obtained in a narrow range. This result implies that processing of composites can be accomplished smoothly in the large scale applications.

BR inclusions cause slight decrease for MFR of neat PLA. MFR values display reduction trend with increase in concentration. Silane treated BR containing composites yield relatively higher MFR which may be cause from the better adhesion of their surface than that of untreated BR.

4.6. Results of water absorption test

Water absorption test data of PLA and composites for time period of 15 days as the constant values achieved are listed in Table 4.2.

Table 4.2. Water absorption test results of PLA and composites.

Samples	Water Absorption (%)
PLA (neat)	0.9±0.1
PLA-BR 5	1.8±0.1
PLA-BR 10	2.1±0.1
PLA-BR 15	2.7±0.2
PLA-BR 20	3.5±0.2
PLA-BR(S) 5	1.5±0.1
PLA-BR(S) 10	1.7±0.1
PLA-BR(S) 15	2.0±0.2
PLA-BR(S) 20	2.4±0.1

Table 4.2 indicates that unfilled PLA sample absorbs nearly 1% of water, where BR containing composites give higher amount of water. Water absorption values of composites increase with the increasing addition amount.

It can be clearly seen from Table 4.2 that, BR(S) filled composites exhibit lower absorption values as compared with the same concentrations of BR filled composites.

The lowest water absorption is obtained for PLA-BR(S) sample among composites. This finding can be explained by hydrophobicity of silanized surface (Arbelaiz et al., 2015; Dike, 2020; Hu et al. 2010; Tayfun et al., 2016).

4.7. Results of SEM analysis

SEM micro-images of composites with the lowest (5%) and the highest (20%) addition amount are displayed in Figure 4.7.

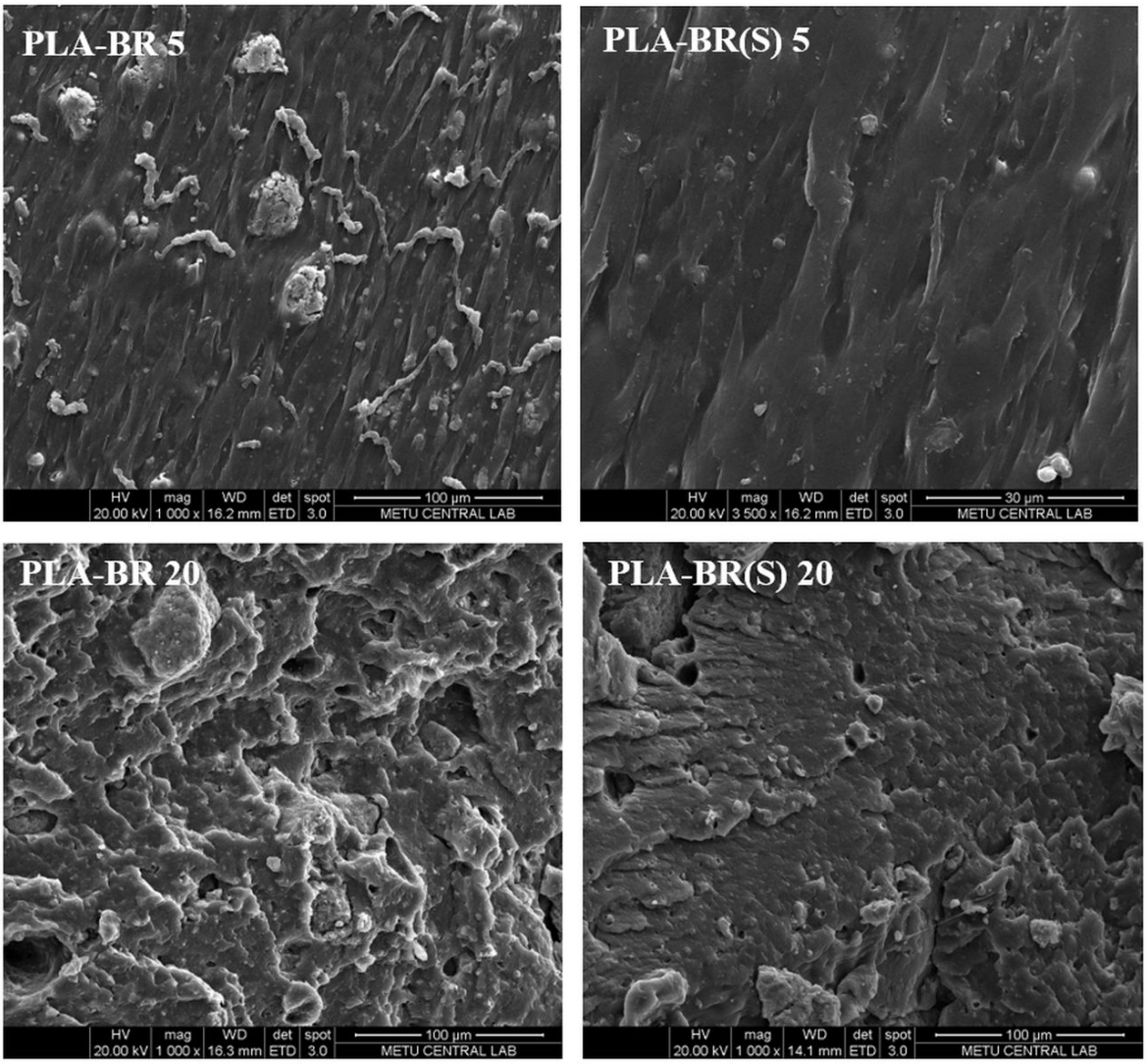

Figure 4.7. SEM micro-images of selected composites prepared in this study.

According to SEM micro-images given in Figure 4.7, untreated BR particles form agglomerates by sticking together despite of PLA. In contrast, homogeneous dispersion of barite particles is observed for BR(S) containing composites. It can be seen from the SEM micro-image of PLA-BR(S) 5 composite that surfaces of barite particles are covered by PLA matrix. Some agglomeration regions are observed for 20% concentration of BR(S) but these regions are seen more predominantly for untreated BR containing composite with the same filling ratio.

These findings are the evidence for achievement of well-dispersion and adhesion improvement of BR particles with PLA matrix thanks to surface treatment.

5. CONCLUSIONS

In this thesis, effects of surface silanization and loading ratio of barite on mechanical, thermo-mechanical, melt flow, water absorption and morphological behaviors of PLA based composites were studied. IR spectroscopy was performed to determine the surface properties of BR samples. Tensile test, impact test, DMA analysis, MFR measurements, water absorption test and SEM analysis were applied to investigate the properties of composites.

IR analysis reveals that surface of untreated BR is covered by silane coupling agent after treatment.

Mechanical test results show that BR(S) reinforced PLA composites give higher tensile strength and impact strength values compared to untreated BR filled ones. The optimum addition amount is obtained for 15% BR containing composites in the case of tensile strength. Additions of both BR samples cause reduction for elongation of PLA.

According to DMA study, storage modulus of neat PLA decreases after the addition of BR and BR(S) with the exception of 5% BR(S) containing composite. It is found from the tan delta curves that glass transition temperature of PLA increases slightly with the inclusion of BR(S) samples.

MFR measurements reveal that all of the composites exhibit lower MFR values with respect to neat PLA but the quantities of these reductions are found as negligible for causing problems in processing steps of composites.

Water absorption test implied that incorporations of BR samples display increasing trend for the water absorption behavior of PLA. Silane treated BR filled composites give lower water absorption values than untreated BR.

SEM study claims that BR(S) particles show more homogeneous dispersion compared to BR particles inside the PLA matrix. This finding indicates the improvement of mechanical and physical performance of composites after addition of BR(S) into PLA due to increasing of adhesion of BR surface to polymer matrix after treatment process.

6. RECOMMENDATIONS

Based on the findings reported in this thesis study, silane treatment is obtained as suitable and practical method for PLA-BR composite system. Application of this method to BR for different BR containing polymer composites is recommended in order to improve their performances.

7. PUBLICATIONS

This study was published as research article in an international SCI indexed journal of ‘Polymers and Polymer Composites’ entitled with ‘Effects of concentration and surface silanization of barite on the mechanical and physical properties of poly (lactic acid)/barite composites’ in the 2nd issue of the 28th volume on February, 2020 (DOI: 10.1177/0967391119883083).

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