MECHANICAL AND PHYSICAL CHARACTERIZATION OF BENTONITE AND BARITE FILLED LOW DENSITY POLYETHYLENE COMPOSITES

A MASTER'S THESIS
in
Chemical Engineering and Applied Chemistry
Atılım University

by
HESHAM MOHAMMED S. ELKAWASH
JANUARY 2018

MECHANICAL AND PHYSICAL CHARACTERIZATION OF BENTONITE AND BARITE FILLED LOW DENSITY POLYETHYLENE COMPOSITES

HESHAM MOHAMMED S. ELKAWASH

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
ATILIM UNIVERSITY

BY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
CHEMICAL ENGINEERING AND APPLIED CHEMISTRY
AT
THE DEPARTMENT OF CHEMICAL ENGINEERING AND APPLIED CHEMISTRY

JANUARY 2018

Approval of the Graduate School of Natural and Applied Sciences, Atılım University.

_____

Prof. Dr. Ali KARA

Director

I certify that thesis satisfies all the requirements as a thesis for the degree of Master of Science.

_____

Prof. Dr. Atilla CİHANER

Head of Department

This is to certify that we have read the thesis "Mechanical and Physical Characterization of Bentonite and Barite Filled Low Density Polyethylene Composites" submitted by "Hesham Mohammed S. Elkawash" and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

Assoc. Prof. Dr. Seha TİRKEŞ _____

Dr. Fırat Hacıoğlu
Co-Supervisor _____

Examining Committee Members
Assoc. Prof. Dr. S. Belgin İŞGÖR _____

Assist. Prof. Dr. Yasin KANBUR _____

Assoc. Prof. Dr. Seha TİRKEŞ _____

Date: 26.01.2018

I declare guarantee that all data, knowledge and information in this document has been obtained, processed and presented in accordance with academic rules and ethical conduct. Based on these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name: Hesham Mohammed S. Elkawash

Signature:

ABSTRACT

MECHANICAL AND PHYSICAL CHARACTERIZATION OF BENTONITE AND BARITE FILLED LOW DENSITY POLYETHYLENE COMPOSITES

Hesham Mohammed S., Elkawash

M.Sc., Chemical Engineering and Applied Chemistry

Supervisor: Assoc. Prof. Dr. Seha TİRKEŞ

Co-Supervisor: Dr. Fırat HACIOĞLU

January 2018, 32 pages

In this thesis study, two kind of mineral fillers, bentonite (BNT) and barite (BRT), were incorporated into low density polyethylene (LDPE) by extrusion process. Silane treatment was applied to BRT and BNT surfaces in order to increase their compatibility with polymer matrix. Surface characteristics of fillers were examined by fourier transformed infrared spectroscopy (FTIR) analysis. LDPE based composites were prepared at one constant concentration of 10% for each fillers. Test samples were prepared using injection molding. Mechanical, thermo-mechanical, melt-flow and morphological characterizations of unfilled LDPE and their composites were done by tensile and impact tests, dynamic mechanical analysis (DMA), melt flow index (MFI) test and scanning electron microscopy (SEM) technique, respectively.

Test results showed that surface treatments increased the final properties of composites because of better adhesion of BNT and BRT to LDPE matrix as compared with untreated ones. Tensile and impact strengths, storage modulus and glass transition temperature of LDPE were improved by silane treated fillers. It was concluded from MFI test that both BRT and BNT additions resulted no remarkable changes on melt flow rate of LDPE. According to SEM analysis of composites, silane treated BNT and BRT containing samples displayed homogeneous dispersions whereas debondings were observed for untreated BNT and BRT filled composites due to their weak adhesion to polymer matrix.

Keywords: Polyethylene, Bentonite, Barite, Surface Treatment, Polymer Composites, Extrusion.

ÖZ

BARİT VE BENTONİT EKLENMİŞ DÜŞÜK YOĞUNLUKLU POLİETİLEN KOMPOZİTLERİNİN MEKANİK VE FİZİKSEL KARAKTERİZASYONU

Hesham Mohammed S., Elkawash
Yüksek Lisans, Kimya Mühendisliği ve Uygulamalı Kimya
Danışman: Doç. Dr. Seha TİRKEŞ
Yardımcı Danışman: Dr. Fırat HACIOĞLU
Ocak 2018, 32 sayfa

Bu tez çalışmasında, bentonit (BNT) ve barit (BRT) olarak iki farklı dolgu maddesi düşük yoğunluklu polietilen (LDPE) içerisine ekstrüzyon işlemi ile eklenmiştir. BRT and BNT yüzeylerine, polimer matrisi ile uyumlarını artırmak amacıyla silanlama işlemi uygulanmıştır. Dolguların yüzey karakteristikleri infrared spektroskopisi (FTIR) ile incelenmiştir. LDPE bazlı kompozitler, her bir dolgu maddesi için %10 sabit konsantrasyonunda hazırlanmıştır. Test numuneleri enjeksiyonlu kalıplama kullanılarak hazırlanmıştır. Eklentisiz LDPE ve kompozitlerinin mekanik, ısısal-mekanik, eriyik-akış ve morfolojik karakterizasyonları sırasıyla, çekme ve darbe testleri, dinamik mekanik analiz (DMA), eriyik akış indisi (MFI) testi ve taramalı elektron mikroskopisi (SEM) tekniği ile gerçekleştirilmiştir.

Test sonuçları göstermiştir ki, yüzey işlemleri, BNT ve BRT'nin LDPE matrisine işlem uygulanmamış olanlara kıyasla daha iyi yapışmasından dolayı kompozitlerin son özelliklerini arttırmıştır. LDPE'nin çekme ve darbe dayanımları, depolama modülü ve camsı geçiş sıcaklığı, silanlanmış dolgular ile yükselmiştir. MFI testinden çıkarım yapılmıştır ki, BRT ve BNT eklemeleri, LDPE'nin eriyik akış hızında belirgin bir değişim ile sonuçlanmamıştır. Kompozitlerin SEM analizine göre, silanlama uygulanmış BNT ve BRT içeren örnekler homojen dağılım sergilerken işlenmemiş BNT ve BRT takviyeli kompozitlerde bu dolguların polimer matrisine zayıf yapışmalarından ötürü bağ açılmaları gözlenmiştir.

nahtar Kelimeler: Polietilen, Bentonit, Barit, Yüzey İşlemi, Polimer Kompozitler, Ekstrüzyon.

Dedicated to my family

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my thesis supervisor Assoc. Prof. Dr. Seha Tirkeş for his kind support, understanding, encouraging advices and valuable discussions throughout my thesis. His approach to the students and solving the problems will sure help me in my future academic life.

I am deeply grateful to my co-supervisor Dr. Fırat Hacıoğlu and Dr. Ümit Tayfun for their guidance and advices during my thesis.

In addition, I am also grateful to Dr. Suha Tirkeş for his help and advice concerning scanning electron microscopy techniques.

Also, I wish to represent my sincere thanks to all oh the academic members of the chemical engineering and applied chemistry department at Atılım University for their endless helps and attentions.

I also want to extend my deepest gratitude friends who have been waiting for my work achievement.

As a last but not least, I would like to dedicate my deepest gratitude to my family members for their endless supports during my study.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVATIONS

APTES	-	3-Aminopropyltriethoxy Silane
BNT	-	Bentonite
BRT	-	Barite
DMA	-	Dynamic Mechanical Analysis
FTIR	-	Fourier Transformed Infrared Spectroscopy
LDPE	-	Low Density Polyethylene
MFI	-	Melt Flow Index
PE	-	Polyethylene
SEM	-	Scanning Electron Microscopy
Si-BNT	-	Silane Treated Bentonite
Si-BRT	-	Silane Treated Barite
T_g	-	Glass Transition Temperature

CHAPTER 1

INTRODUCTION

1.1. Polymer Composites

Polymer composites are the materials which compose of mainly two different phases. Polymeric phase is defined as matrix and other phase is generally named as filler. Filler particles are embedded in continuous polymeric phase. Filler phase generally is responsible of reinforcement for a specific performance of the material. In addition to that purpose, tuning of processing parameters and lowering overall production costs are the other reasons for incorporation of fillers into plastics at large scale applications [1-3].

The final properties of polymer composites depend on the mixing homogeneity and adhesion between phases. The surface properties of filler particles highly effect the wetting characteristics and compatibility for polymer matrix. Hydrophobicity, polarity and surface functionality play key role to bond their surface to polymer phase. Surface treatment of fillers is the common method that provides practical modification in order to improve their compatibility with polymeric matrix [4,5].

Fillers are mainly classified according to their geometry. They can be forms of particulate, plate-like, fiber or needle-shaped. Among these, particulate or spherical geometry is the most common one and most of the traditional fillers are in that form. The properties of particulate filled polymeric composite materials are mainly depended on the dispersion of fillers into polymer matrix [6-9].

Extrusion is the conventional process applied for production of polymer composites in industrial scale. Fillers or additives can be mixed effectively with molten polymer at desired amount by applying that method. The temperature, speed and time of mixing are the main parameters that influence the resulting composite material.

Injection molding is another most favoured processing method in large scale applications. Required shapes of plastics can be tuned by the design of the mold in that process [10-12].

1.2. Low Density Polyethylene

Low density polyethylene (LDPE) is a type of polyethylene which has highly branched long-chain structure. The structure of LDPE and difference of its structure from other polyethylene types is represented in Figure 1.

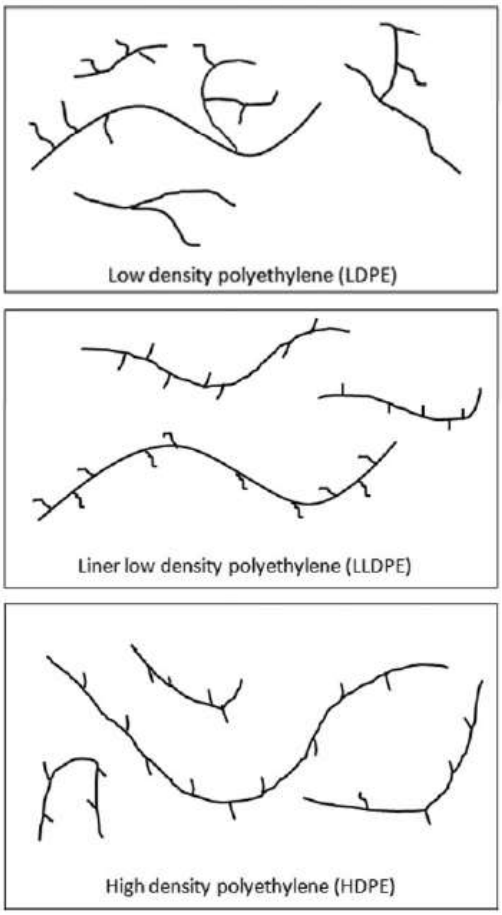

Figure 1. The Structure of LDPE and the Other Types of PE [15]

The production of LDPE is made conventionally by polymerization of ethylene at high pressure conditions. It has a density, glass transition temperature (T_g) and melting temperature of 0.915-0.925 g/cm^3, -120 ºC and 106-112 °C, respectively [13].

The uses of LDPE include a broad range of applications such as films, packaging, storage cups, containers, house wires, pipes, bags, toys, glasses, carpet backings, wires and several plastic parts [13].

LDPE may used as a matrix material for production of composites by using varied types of fillers. By this way, mechanical and physical performance of LDPE can be improved. The basic usage areas of LDPE based composites are composed of packaging films, automotive parts, electrical components, biomedical applications and energy storage materials [14,15].

1.3. Barite

Barite is a naturally occuring mineral which composed of barium sulfate. Turkey has one of the biggest barite reserves around the world [16].

The main uses of barite mineral consist of production of glass, paints, filter compounds, automobile coatings, drilling fluids, sound deadening materials, medical indicators and radiation shielding materials. Additionally, it has found usage as a filler material for rubber and plastics [17,18].

1.4. Bentonite

Bentonite is natural clay obtained from volcanic deposit areas. It mainly consists of silicate and alumina as contamination. Bentonite mineral is also considered as an inorganic polymer due to it has high plasticity [19].

The main application areas of bentonite are across a wide range of cosmetics, ceramics, porcelains, detergents, paints, cat litters, papers, drilling fluids, plasticizing agents, rheological thickeners and disposal of several wastes [20].

1.5. Literature Review

Research studies based on BNT and BRT filled polymer composites were conducted by several research groups. Different types of characterizations were investigated for these composites.

Chmielewska et al. investigated the effect of barite concentration on mechanical, thermo-mechanical and thermal properties of epoxy based composites and they found that highly filled barite composites showed increase in thermal stability of epoxy composites [21].

Kim et al. postulated that tribological performance of novolac resin was improved after barite addition [22].

According to findings of Roger et al., barite addition caused improvement on the abrasion resistance of thermoplastic Olefins which used as automotive components [23].

Ge et al. found that barite increased the nucleation activity for polyethylene terephthalate based composites [24,25].

Several researchers investigated the influence of barite to radioactivity shielding of polymer composites [26-30].

Kraus et al. performed the thermal, mechanical and morphological characterizations of bentonite filled LDPE composites in order to predict the surface properties of composites [31].

Seyidoglu and Yilmazer reported that compatibilizer addition increased the mechanical properties of bentonite loaded linear LDPE composites [32].

Ge et al. studied the influence of silane coupling agents on the tribological performance of bentonite filled nitrile butadiene rubber based composites [33].

Liborio et al. applied a treatment method for bentonite and they fabricated BNT filled polypropylene based composites by using extrusion [34].

Flame resistance properties of BNT containing polymer composites were also studied by varied researchers in the literature [35-38].

1.6. Aim of the Study

Polyethylene based composites that containing low cost fillers may have great potential for several applications from packaging to ordinary plastic parts. These

composite materials can only have desired properties if mineral powders were dispersed in polymer matrix uniformly.

For this reason, the primary purpose of this thesis study was to investigate the effect of silane treatment of both barite and bentonite powder in order to improve their compatibility with LDPE phase. The mechanical and physical characterizations are the basic properties which affect their possible usage. For instance, tensile and impact strengths, percent elongations, tensile and storage modulus, melt flow rates and morphological observations of unfilled LDPE and its composites were examined.

Test results were demonstrated based on the effects of BRT and BNT addition to LDPE matrix and comparisons of silane treated and untreated fillers in the case of interfacial interactions.

CHAPTER 2

EXPERIMENTAL

2.1. Materials

2.1.1. Low Density Polyethylene

LDPE was purchased under the trade name of LDPE G03-5 from PETKİM A.S., Izmir, Turkey. It has a density of 0.919-0.923 g/cm^3 according to standard of ASTM D-1505 cited by the supplier.

2.1.2. Barite

Barite was supplied as powder form by Karakaya Bentonite Incorporation, Ankara, Turkey. Chemical composition and the basic physical characteristics of BRT sample were listed in Table 1 and Table 2, respectively.

Table 1. Chemical Composition of Barite

Characteristics	Composition (wt %)	Test Standard
$BaSO_4$	92≤	EN 12912
Acid Soluble Material	≤3	EN 12902

Table 2. Physical Properties of Barite

Characteristics	Value	Unit	Test Standard
Specific Gravity	4.2-4.5	g/cm^3	-
Bulk Density Packed	2500-2600	kg/m^3	EN 12902
Bulk Density Loose	2200-2400	kg/m^3	EN 12902
Volume Mean Diameter	9.4	μm	ISO 13320
Volume Median Diameter	4.95	μm	ISO 13320

2.1.3. Bentonite

Bentonite powder was obtained from Karakaya Bentonite Incorporation, Ankara, Turkey. Chemical composition and the physical properties of BNT sample were listed in Table 3 and Table 4, respectively.

Table 3. Chemical Composition of Bentonite

Characteristics	Composition (wt %)	Test Standard
SiO_2	50-70	EN 12902
Al_2O_3	10-20	EN 12485
MgO	1.0-4.5	EN 12485
CaO	0.5 -4.0	EN 12485
Na_2O	0.5-3.0	EN 12485

Table 4. Physical Properties of Bentonite

Characteristics	Value	Unit	Test Standard
Mass Loss at 105 °C	0-15	%	EN 12902
Specific Gravity	2.4	g/cm^3	-
Bulk Density Packed	800	Kg/m^3	EN 12902
Particle Size	≤500	µm	EN 12902
Volume Mean Diameter	20.6	µm	ISO 13320
Volume Median Diameter	7.45	µm	ISO 13320

2.2. Production of Polymer Composites

2.2.1. Extrusion

BNT and BRT powders were subjected to silane treatment by mixing them in 2 wt% 3-Aminopropyltriethoxysilane (APTES)/ethanol solution for 2 hours at room temperature. After drying process, silane treated BNT and BRT samples were named as Si-BNT and Si-BRT, respectively. Untreated BNT and BRT powders were coded as BNT and BRT, respectively.

LDPE and filler powders were dried at 100˚C for 10 hours in order to remove their moisture contents before processing. Filling ratios of both BNT and BRT were kept constant as 10 wt% because of optimum concentrations for these fillers were found as that loading level in previous thesis studies performed by our research group [39,40]. LDPE based composites were produced by laboratory scale twin screw extruder (15 ml micro-compounder, DSM Xplore, Netherlands) that is represented in Figure 2. Processing parameters used during fabrication of composites are listed in Table 5.

Table 5. Extrusion Parameters of PE Based Composites

Parameters	**Specification**	**Unit**
Process Temperature	190	^{o}C
Mixing Time	5	min
Screw Speed	100	rpm

Figure 2. Lab-scale Extruder

2.2.2. Injection Molding

Composite samples obtained from extrusion process were shaped using lab-scale injection molding instrument (Microinjector, Daca Instruments, UK) as shown in Figure 3. Molding parameters which were applied during injection molding are listed in Table 6.

Table 6. Injection Molding Parameters of PE Based Composites

Parameters	Values	Unit
Barrel Temperature	200	^{o}C
Mold Temperature	50	^{o}C
Injection Pressure	8	Bar
Holding Time	2	min

Figure 3. Injection Molding Instrument

Test specimens were shaped as standard dog-bone sample during injection molding process. These test samples have dimensions of 7.6×2.0×80 mm^3 as demonstrated in Figure 4. Gauge length of dog-bone shaped test samples is 50 mm.

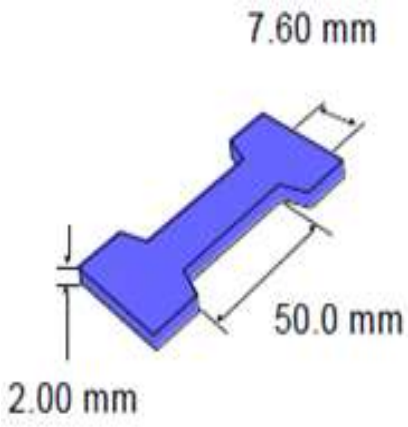

Figure 4. Dimensions of Tensile Test Sample

2.3. Characterization Techniques

Characterizations of test samples were done according to related standards for each methods. All of the experimantal data were recorded as an avarage of minimum required number of specimens.

2.3.1. FTIR Analysis

Fourier transformed infrared spectroscopy (FTIR) analysis were performed in attenuated total reflectance (ATR) mode with IR-spectrometer of Bruker VERTEX 70. The measurements were carried out at a resolution of 2 cm^{-1} with 32 scans between 600 cm^{-1} and 3800 cm^{-1} wavenumbers.

2.3.2. Tensile Test

Tensile test measurements of composites were done by Instron 5565A tensile testing machine with the accordance of ASTM D-638 standard. Crosshead speed of 5 cm/min and 5 kN load cell were applied. Tensile strength, percent elongation at break and tensile modulus values were recorded as an average of minimum five samples. Representative photograph of tensile testing machine is shown in Figure 5.

Figure 5. Tensile Testing Machine

2.3.3. Impact Test

Unnotched izot impact tests were performed using Coesfeld-Material impact tester. Impact energy measurements were done according to ASTM D256 standard with 4 J pendulum. Recorded values represent an average value of at least five samples with standard deviations. Figure 6 represents the impact tester used in this study.

Figure 6. Impact Testing Apparatus

2.3.4. Dynamic Mechanical Analysis (DMA)

DMA measurements were performed with DMA 8000, Perkin Elmer dynamic mechanical thermal analyzer as seen in Figure 7. Test specimens obtained from injection molding with dimensions of 7.6x2.0x50 mm^3 were used for DMA test in dual cantilever bending mode at the temperature range of -65°C to 95°C with 1 Hz constant frequency and heating rate of 5 °C/min.

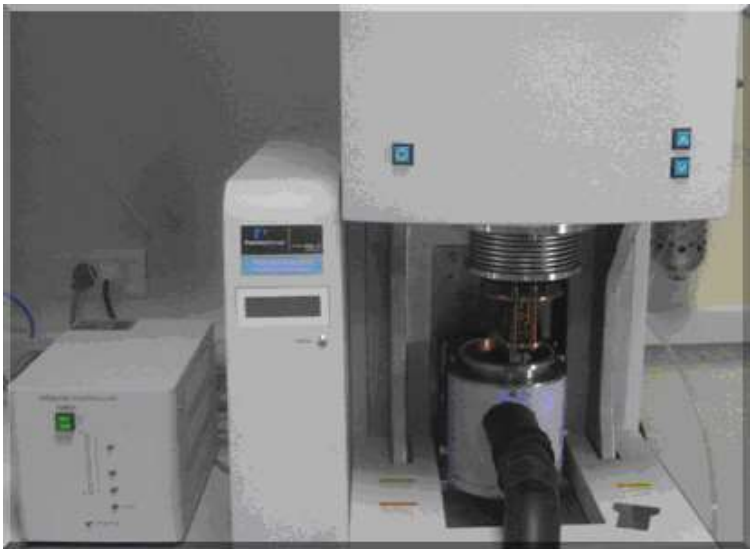

Figure 7. DMA Test Equipment

2.3.5. Melt Flow Index Test (MFI)

Melt flow rate measurements of LDPE and its composites were performed by melt flow indexer (Coesfield Meltfixer LT) equipment which was represented in Figure 8. Tests were carried out under a standard load of 2.16 kg at the processing temperature of LDPE at 200 ^{o}C. MFI values of each sample were calculated as an average value of at least ten samples with standard deviations.

Figure 8. Melt Flow Indexer

2.3.6. Scanning Electron Microscopy (SEM)

Morphological characterizations of LDPE and composites were conducted by using JSM-6400 electron microscope. Surfaces of fractured samples were coated with a thin layer of gold for obtaining of conductive surfaces. SEM micrographs were taken at x2000 and x4000 magnifications in order to examine dispersion of BNT and BRT particles into LDPE matrix.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. FTIR Analysis

Surface characteristics of pristine and silane treated BNT and BRT filler were examined by FTIR analysis. Representative FTIR spectra of BNT and BRT were given in Figure 9 and Figure 10, respectively.

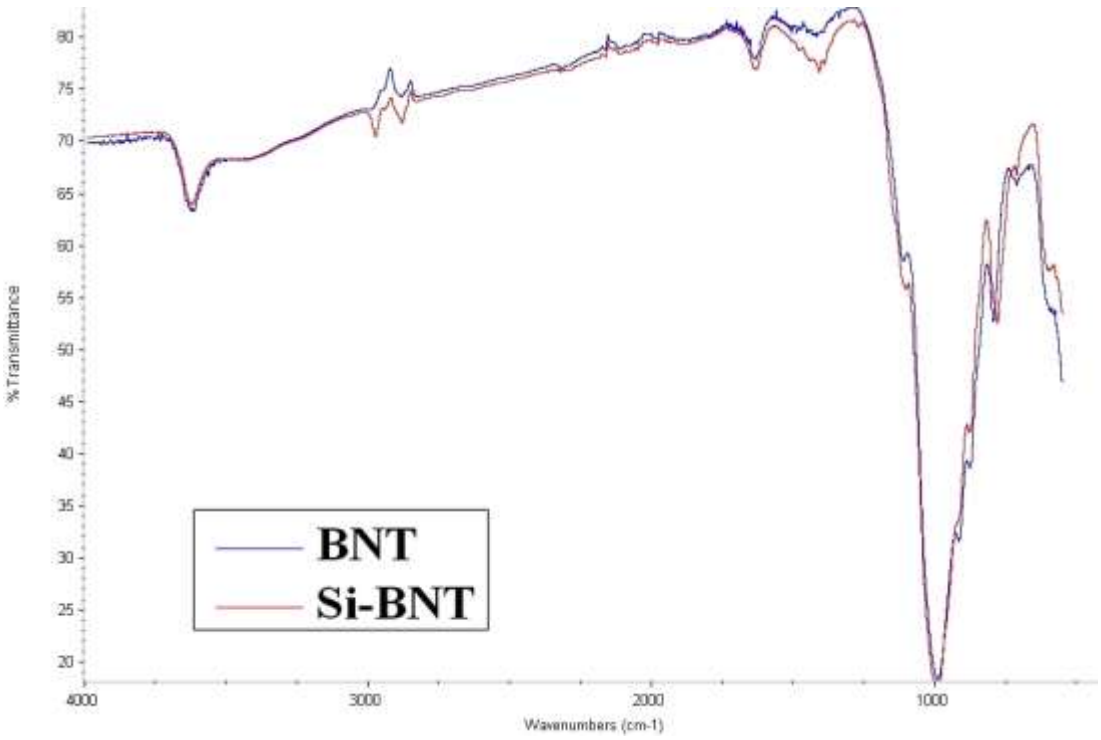

Figure 9. FTIR Spectrum of BNT and Si-BNT Samples

According to Figure 9, intensities of absorption bands indicate the oxygen functionalities were increased after surface treatment of BNT. These bands can be described as indicative peaks of C–O stretching at 900 cm^{-1} and 1200 cm^{-1}, COO- asymmetric stretching at around 1600 cm^{-1} and O-H stretching at about 3300 cm^{-1} wavenumbers. Another peaks were seen in the range of 2800 cm^{-1} and 2900 cm^{-1} may correspond to stretching vibrations of $–CH_2$ and $–CH_3$ groups. These bands were found as higher because of silane coupling agent having propyl groups.

Because of BRT includes SiO_2 content more than half of its composition (see Table 3), Si-O related shoulder peaks between 500 cm^{-1} and 800 cm^{-1} were seen as already exist for untreated BNT sample.

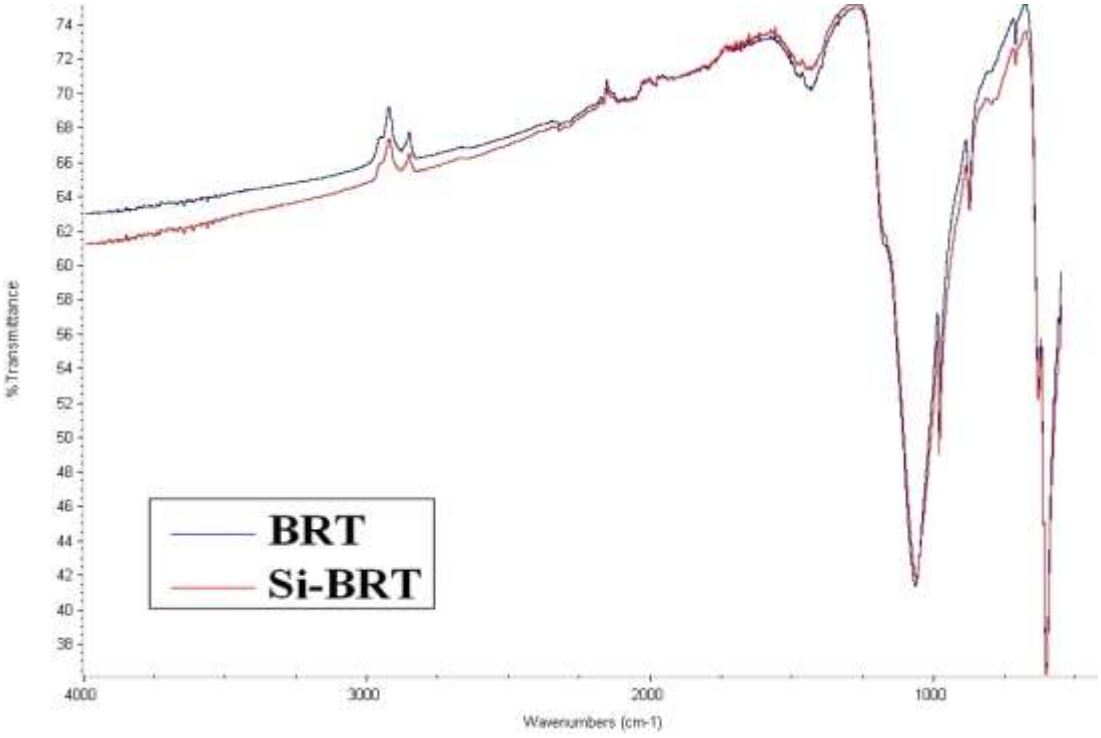

Figure 10. FTIR Spectrum of BRT and Si-BRT Samples

It was clearly seen from the Figure 10 that, increments in intensities of oxygen related peaks were also observed for silane treated BRT samples with the exception of hydroxyl stretching peaks at 3300 cm^{-1}. As a difference from the spectrum of BRT, there was no Si-O related peaks existence for BRT at the range of 500 cm^{-1} and 800 cm^{-1} and shoulder peaks stem from silane groups were observed for Si-BRT sample.

These observations showed that silane modification caused some chemical changes on the surfaces of both BNT and BRT fillers.

3.2. Tensile Test

Tensile test data of LDPE and its composites which is composed of tensile strength, elongation at break and tensile modulus were listed in Table 7. Tensile strength versus percent elongation curves were given in Figure 11, additionally.

Table 7. Tensile Test Data of LDPE and Composites

Samples	**Tensile Strength** (MPa)	**Elongation at Break** (%)	**Tensile Modulus** (MPa)
PE	10.3±0.3	67.6±2.3	100.5±4.5
PE/BNT	10.8±0.5	81.9±5.0	86.9±2.8
PE/Si-BNT	12.7±0.7	66.4±3.8	81.8±4.2
PE/BRT	12.6±0.5	88.0±4.5	78.0±3.3
PE/Si-BRT	13.0±0.4	74.1±4.1	84.9±3.5

As the Table 7 examined it can be seen that tensile strength of unfilled LDPE was improved by the addition of both fillers. It can be also concluded that silane treated samples gave higher strength values as compared with the untreated ones. The increment of tensile strength for BNT containing composites were found as sharper than that of BRT filled composites after silane treatment.

Untreated BNT and BRT additions to LDPE were resulted as increase in elongation at break parameters as can be seen from the curves in Figure 11. On the other hand, silane treated samples showed remarkable decrease on elongation values of untreated BNT and BRT containing composites. Similar results were found for PE based composites in the literature that high tensile strength and low percent elongation values were obtained as the strong interfacial adhesion was achieved where poor adhesion caused low tensile strength and high elongation at break [41].

All of the composites displayed reductions on tensile modulus of LDPE. Tensile modulus values of composites were found as similar each other and about 20 points lower than that of unfilled LDPE sample.

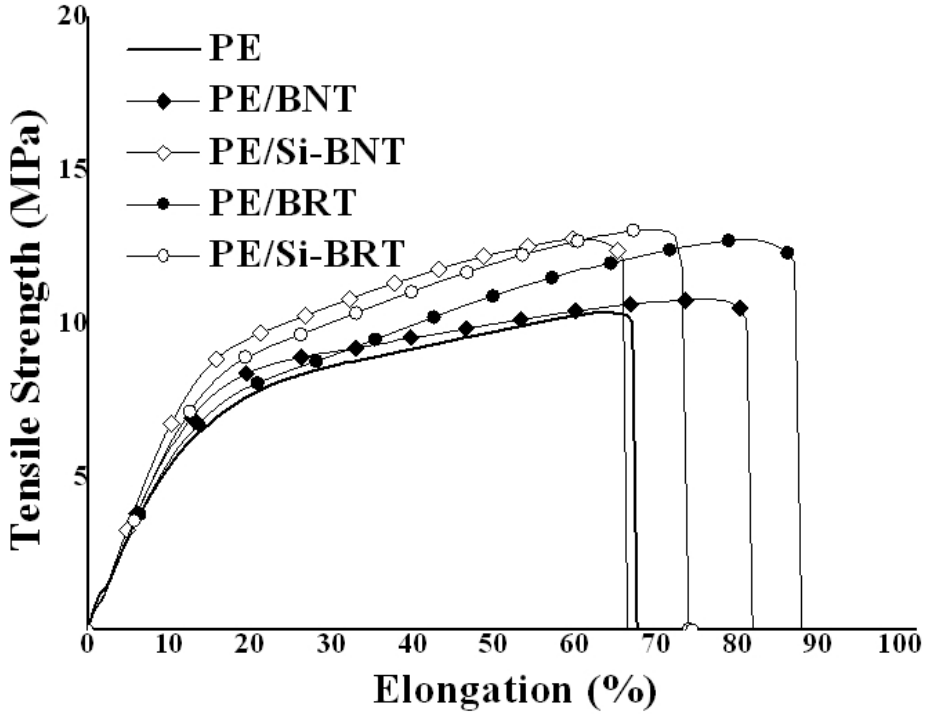

Figure 11. Tensile Strength vs Elongation Curves

3.3. Impact Test

Impact test results of unfilled PE and its composites were represented as impact strength values and bar graphs in Figure 12.

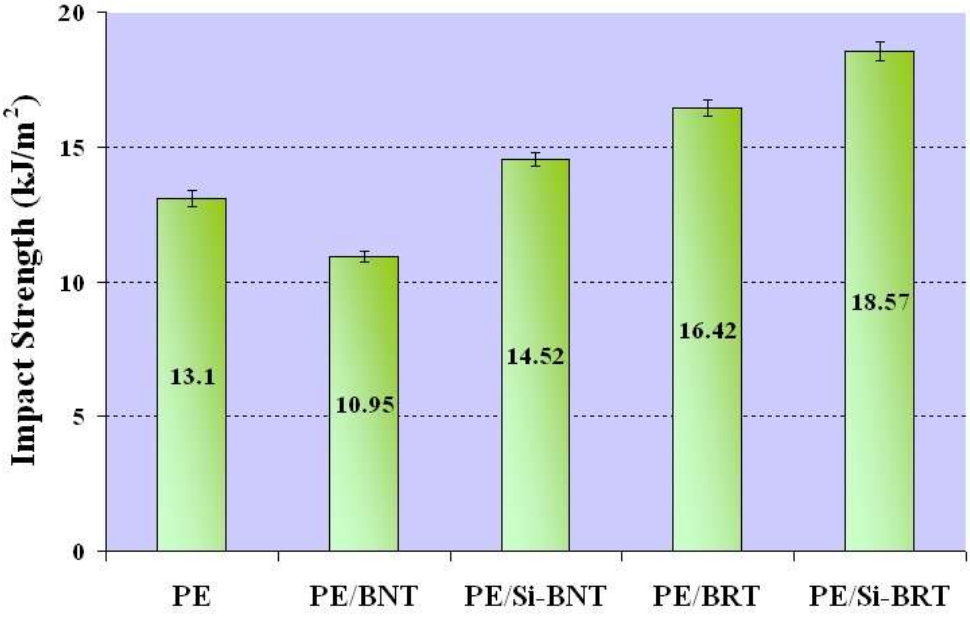

Figure 12. Impact Strength Values of LDPE and Composites

BNT addition into LDPE caused a reduction according to Figure 12. On the contrary, silane treated BNT showed a slight improvement as compared with the unfilled LDPE.

On the other hand, both BRT and Si-BRT containing samples displayed remarkable increase in impact strength of PE. It can be clearly seen that, silane treated BRT filled composite gave relatively higher impact strength value than untreated BRT. The highest impact test result was observed for that composite among the other samples.

The same trend was observed in a similar study that, toughness and strength of composites were increased by the uniform dispersion of barite particles after surface modifier was used [42].

3.4. DMA Study

Thermo-mechanical properties of unfilled PE and composite samples were examined by the help of DMA analysis. Storage modulus and tan delta curves as the function of temperature were exhibited in Figure 13 and Figure 14, respectively.

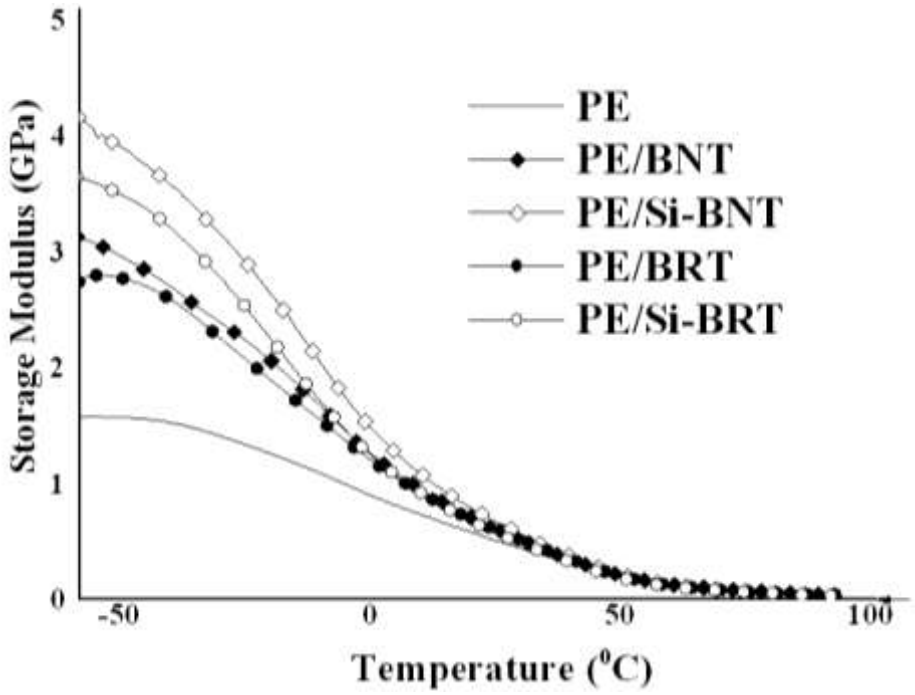

Figure 13. Storage Modulus vs. Temperature Curves

According to Figure 13, all of the composites displayed extensively higher storage modulus than unfilled LDPE sample. These increments were observed as two-fold for untreated BNT and BRT where about three-fold for silane treated BNT and BRT containing composites relative to PE. It can be seen that, silane treatments resulted in remarkable improvements for storage modulus of both fillers. The maximum storage modulus was found on Si-BNT loaded composite among all of the samples. The improvement of storage modulus may be caused from the stiffness effect of barite according to similar study in the literature [43].

Tan δ versus temperature curves of LDPE and composites were shown in Figure 14. It can be seen from the Figure 14 that all the filler additions exhibited shifts of glass transition temperature (T_g) of unfilled LDPE to about 5 ^oC higher temperatures. This result may be due to the restriction of chain motions after additions of BNT and BRT to LDPE matrix [44,45].

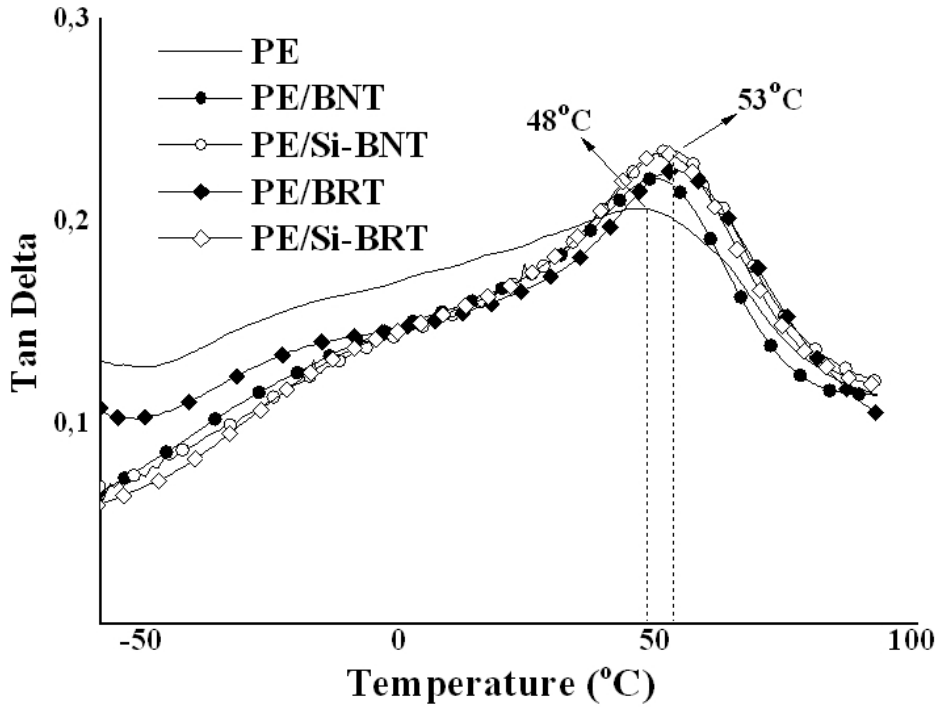

Figure 14. Tan δ vs. Temperature Curves

3.5. MFI Test

MFI values of LDPE and its composites were shown as bar graphs in Figure 15. All of the filler additions caused slight increase in MFI value of PE. Silane treated BNT and BRT samples gave relatively lower MFI values according to their untreated

samples. As an overall conclusion from these results it can be said that, BNT and BRT additions resulted no indicative problems on the processing of PE based composites because of similar MFI values were observed.

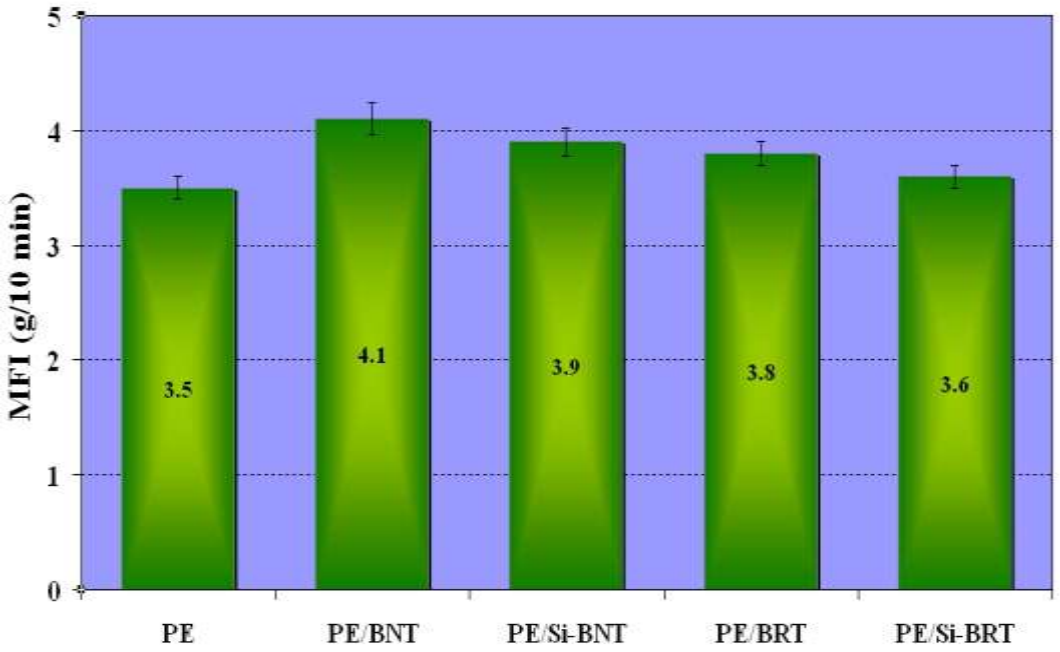

Figure 15. MFI Values of PE and Composites

3.6. SEM Analysis

Morphological studies of composites were carried out by the help of SEM analysis. For that purpose, fractured surfaces of LDPE composites were used and their micrographs were taken at x2000 and x4000 magnifications as shown in Figure 16.

SEM micrographs of composites showed that large gaps were formed between untreated filler particles and PE matrix. BNT and BRT particles can be seen as agglomerates due to their tendency to stick each other rather than adhesion to polymer phase. The micrographs of Si-BNT and Si-BRT filled composites displayed that silane treated filler particles were dispersed more homogeneously and they showed more compatibility to PE phase as compared with untreated samples. It can be clearly observed that surfaces of Si-BRT and Si-BNT particles were covered by polymer matrix, for instance no gaps and debondings were formed between phases. These results support the previous test findings which indicated the silane treatment of both BNT and BRT caused improvement of their compatibility to LDPE matrix.

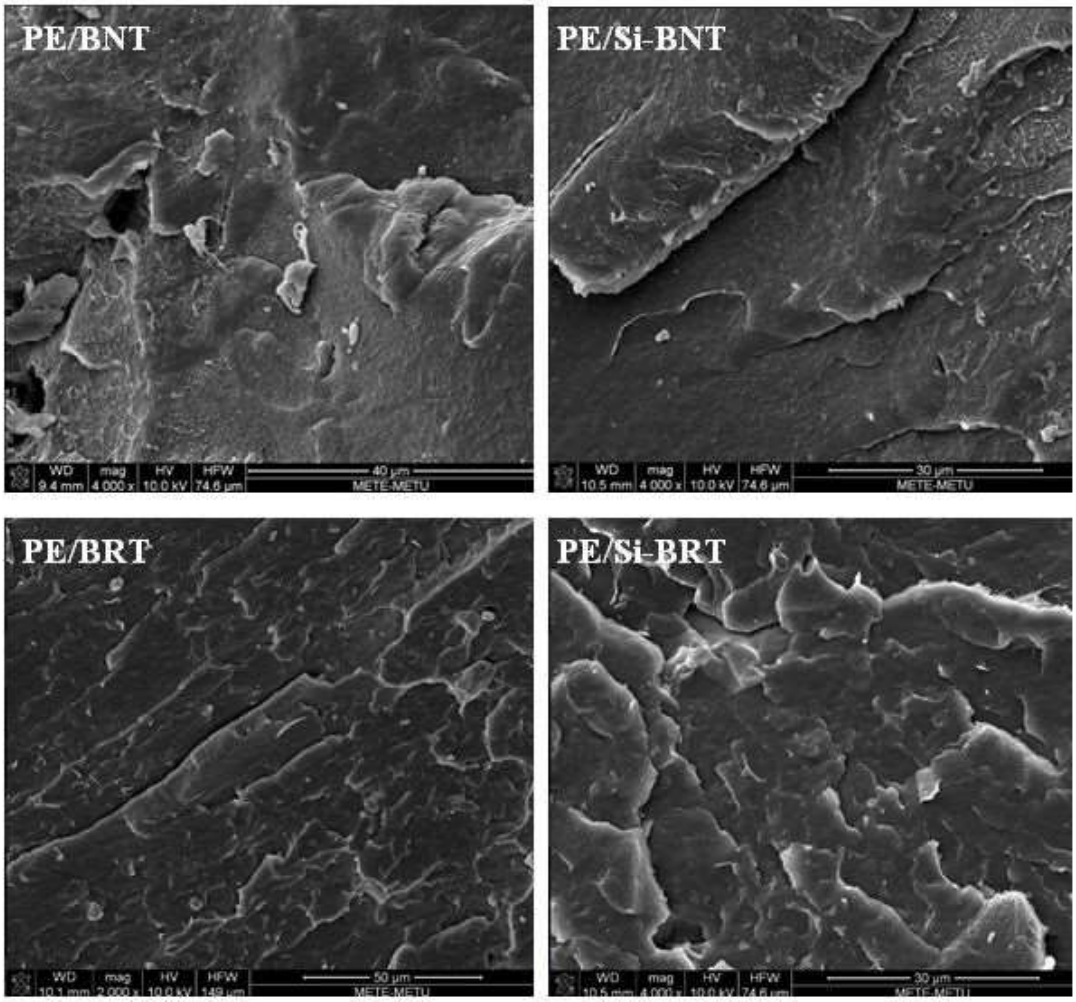

Figure 16. SEM Micrographs of Composites

CHAPTER 4

CONCLUSION

This thesis study dealt with effect of silane treatment of BRT and BNT fillers to the mechanical and physical performances of their LDPE based composites. Surface properties of both fillers after applied silane treatment were examined by FTIR spectroscopy. Mechanical, thermo-mechanical, melt-flow and morphological characterizations of PE and its composites were observed with tensile and impact tests, DMA study, melt flow index test and scanning electron microscopy (SEM) technique, respectively.

FTIR study proved that oxygen functionalities of BNT and BRT surfaces were increased by applying silane treatment. There were also formed some Si- related groups on the BRT surface after silane modification. As a result, silane treatment made some chemical changes on the surfaces of both BNT and BRT.

Tensile test results indicated that, tensile strength of LDPE increased with the addition of fillers. Silane treated samples exhibited higher tensile strength values relative to untreated BNT and BRT. In contrast to that result, lower elongation at break values were found for Si-BRT and Si-BNT containing composites than untreated ones. Tensile modulus of unfilled PE showed reductions after all the filler incorporations.

According to impact test findings, BRT filled composites gave higher impact strength as compared with BNT loaded ones. It was also observed that silane treatment resulted in remarkable increase for both of BNT and BRT samples.

It was observed that, storage modulus of PE increased with the additions of all fillers as DMA results implied. As a similar result with previous ones, relatively higher storage modulus values were found for silane treated BNT and BRT filled

composites than untreated samples. BNT and BRT additions also caused improvements on T_g of LDPE according to Tan delta curves.

MFI test results represented that, there were no significant differences on melt flow rates between unfilled PE and composites. This means addition of BRT and BNT into LDPE will be resulted almost no problems during processing of composites.

According to SEM micrographs of composites, gap and debonding formations were observed between untreated filler particles and LDPE matrix. Silane treated BRT and BNT samples were covered by polymer phase and they showed more homogeneous dispersion relative to untreated filler containing composites.

As a result, it can be said that silane treatment improves the compatibility of mineral fillers such as BNT and BRT to LDPE phase. This result affects the mechanical and physical properties of BNT and BRT filled PE based composites positively.

REFERENCES

[1] R. Petrucci, L. Torre, Modification of Polymer Properties, Elseiver Publishing, 2017.

[2] G. Wypych, Handbook of Fillers (4th Edition), Chemtec Publishing, 2016.

[3] L. Mascia, The Role of Additives in Plastics, Edward Arnold, U.K., 1974.

[4] J. Drelich, J.D. Miller, A Critical Review of Wetting and Adhesion Phenomena in the Preparation of Polymer-Minaral Composites, Minerals and Metallurgical Processing, 12(4), 197-204, 1995.

[5] M. Xanthos, Functional Fillers for Plastics, Wiley-VCH, 2005.

[6] G.V. Kozlov, Y.G. Yanovskii, G.E. Zaikov, Structure and Properties of Particulate-Filled Polymer Composites: The Fractal Analysis, Nova Science Pub. Inc., UK ed., 2010.

[7] J.-Z. Liang, Reinforcement and Quantitative Description of Inorganic Particulate-filled Polymer Composites, Composites Part B: Engineering, 51, 224-232, 2013.

[8] R.N. Rothon, Particulate-Filled Polymer Composites, 2nd Edition, Rapra Technology Limited, UK, 2003.

[9] D. M. Bigg, Mechanical Properties of Particulate Filled Polymers, Polymer Composites, 8(2), 115–122, 1987.

[10] A.B. Strong, Plastics Materials and Processing, Prentice Hall, New Jersey, 2006.

[11] C. Rauwendaal, Polymer Extrusion, Hanser Publisher, Munic, 2001.

[12] C.L. Weir, Introduction to Molding, Society of Plastics Engineers, CT, 1975.

[13] I.I. Rubin,Handbook of Plastic Materials and Technology, John Wiley & Sons Inc., New York, 1990.

[14] P.M. Visakh, M.J.M. Morlanes, Polyethylene-Based Blends, Composites and Nanocomposites, Scrivener Publishing LLC, Canada, 2015.

[15] P.N. Khanam, M.A.A. AlMaadeed, Processing and Characterization of Polyethylene-based Composites, Advanced Manufacturing: Polymer & Composites Science, 1, 63-79, 2015.

[16] M.M.Miller, Barite, 2009 Minerals Yearbook, U.S. Geological Survey, 2011.

[17] P.A. Ciullo, Industrial Minerals and Their Uses, Noyes Publications, 1996.

[18] T. Huang, S.M. Lei, E.W. Wang, G.M. Bao, Progress of Purification and Application of Barite, Applied Mechanics and Materials, 423-426, 511-514, 2013.

[19] C. Klein, C.S. HurlbuT, Manual of Mineralogy, John Wiley and Sons Inc., USA, 1993.

[20] A.G. Clem, R.W. Doehler, Industial Apllications of Bentonite. New York, Macmillan, 1963.

[21] D. Chmielewska, M. Pacyna, T. Sterzyński, Thermo-mechanical Properties of Epoxy Composites Highly Filled with White Barite, Przemysl Chemiczny, 93, 90-92, 2014.

[22] S.J. Kim, M.H. Cho, R.H. Basch, J.W. Fash, H. Jang, Tribological Properties of Polymer Composites Containing Barite or Potassium Titanate, Tribology Letters, 17, 655-661, 2004.

[23] S. Rogers, P. Walia, R.N. Van, D.J. Van, T. Traugott, Breakthrough Material for Low Gloss and Abrasion Resistance with Molded-in-color Automotive Interior Components, Annual Technical Conference-ANTEC, Conference Proceedings, 2, 1037-1041, 2009.

[24] C. Ge, L. Shi, H. Yang, S. Tang, Nonisothermal Melt Crystallization Kinetics of Poly(ethylene terephthalate)/Barite Nanocomposites, Polymer Composites, 31, 1504-1514.

[25] C. Ge, P. Ding, L. Shi, J. Fu, Isothermal Crystallization Kinetics and Melting Behavior of Poly(ethylene terephthalate)/Barite Nanocomposites, Journal of Polymer Science, Part B: Polymer Physics, 47, 655-668, 2009.

[26] M.A. El-Sarraf, A.A. El-Sayed, Insulating Epoxy/Barite and Polyester/Barite Composites for Radiation Attenuation, Applied Radiation and Isotopes, 79, 18-24, 2013.

[27] S. Abdul-Majid, F. Othman, Neutron Attenuation Characteristics of Polyethylene, Polyvinyl Chloride, and Heavy Aggregate Concrete and Mortars, Health Physics, 66(3):327-38, 1994.

[28] H. Binici, O. Aksogan, A.H. Sevinc, A. Kucukonder, Mechanical and Radioactivity Shielding Performances of Mortars Made with Colemanite, Barite, Ground Basaltic Pumice and Ground Blast Furnace Slag, Construction and Building Materials, 50, 177-183, 2014.

[29] F. Hacioglu, Degradation of Polycarbonate, Bentonite, Barite, Carbon Fiber and Glass Fiber Filled Polycarbonate via Gamma Irradiation and Possible Use of Polycarbonate in Radioactive Waste Management, PhD Thesis, Polymer Science and Technology, METU, 2017.

[30] H.-M. Yang, Y.-H. Hu, H.-H. Zhang, Application of Sb-SnO2/Barite (SSB) Conductive Powder in Conductive Paint and Shield Property of Coated Layer. Journal of Functional Materials, 37, 1433-1435, 2006.

[31] E. Kraus, D.-A. Nguen, A. Efimova, I. Starostina, O. Stoyanov, Acid-Base Properties of Polyethylene Composites with Clays, Journal of Applied Polymer Science, 133(30), 2016.

[32] T. Seyidoglu, U. Yilmazer, Use of Purified and Modified Bentonites in Linear Low-density Polyethylene/Organoclay/Compatibilizer Nanocomposites, Journal of Applied Polymer Science, 124(3), 2430–2440, 2012.

[33] X. Ge, Y. Zhang, F. Deng, U.R. Cho, Effects of Silane Coupling Agents on Tribological Properties of Bentonite/Nitrile Butadiene Rubber Composites, Polymer Composites, 38(11), 2347-2357, 2017.

[34] P. Liborio, V.A. Oliveira, M.F.V. Marques, New Chemical Treatment of Bentonite for the Preparation of Polypropylene Nanocomposites by Melt Intercalation, Applied Clay Science, 111, 44-49, 2015.

[35] S.V. De Oliveira, E.M. Araújo, C.M.C. Pereira, A.M.D. Leite, Polyethylene/Bentonite Clay Nanocomposite with Flame Retardant Properties, Polimeros, 27, 91-98, 2017.

[36] A. Kausar, S. Haider, B. Muhammad, Nanocomposite Based on Polystyrene/Polyamide Blend and Bentonite: Morphology, Thermal, and Nonflammability Properties, Nanomaterials and Nanotechnology, 7, 2017.

[37] M. Yurddaskal, E. Celik. Effect of Halogen-free Nanoparticles on the Mechanical, Structural, Thermal and Flame Retardant Properties of Polymer Matrix Composite, Composite Structures, 183(1), 381-388, 2017.

[38] A. Durmus, M. Woo, A. Kasgoz, C.W. Macosko, M. Tsapatsis, Intercalated Linear Low Density Polyethylene (LLDPE)/Clay Nanocomposites Prepared with Oxidized Polyethylene as a New Type Compatibilizer: Structural, Mechanical and Barrier Properties, European Polymer Journal, 43(9), 3737-3749, 2007.

[39] L.M.A. Alhallak, The Mechanical and Thermal Properties of Bentonite Filled Acrylonitrile-Butadiene-Styrene Composites, MSc Thesis, Chemical Engineering and Applied Chemistry, Atılım University, 2017.

[40] S.A.A. Madkour, Mechanical and Thermal Properties of Acrylonitrilebutadiene-Styrene-Barite Composites, MSc Thesis, Chemical Engineering and Applied Chemistry, Atılım University, 2017.

[41] Z. Fang, Q. Hu, Influence of Interfacial Adhesion on Stress-Strain Properties of Highly Filled Polyethylene, Die Angewandte Makromolekulare Chemie, 265(1), 1–4, 1999.

[42] Y. Xu, X.-Z. Zhang, C.-X. Zhou, W.-S. Wu, L.-Y. Shi, B. Yang, Study on the Mechanical Properties and Structure of PVC/BaSO4 Nano-composites, Polymeric Materials Science and Engineering, 23(5), 144-147, 2007.

[43] F. Kohande, S.S. Sararoudi, L. Barangi, AIP Conference Proceedings, 31st International Conference of the Polymer Processing Society, PPS 2015, 1713, 2016.

[44] R. Sahraeian, M. Esfandeh, S.A. Hashemi, Rheological, Thermal and Dynamic Mechanical Studies of the LDPE/Perlite Nanocomposites, Polymers & Polymer Composites, 21(4), 243-249, 2013.

[45] P. Lv, C. Liu, Z. Rao, Review on Clay Mineral-based Form-stable Phase Change Materials: Preparation, Characterization and Applications, Renewable and Sustainable Energy Reviews, 68, 707-726, 2017.

APPENDIX

Result Analysis Report

Sample Name: 18778-01(BENTONIT) - Average	**SOP Name:**	**Measured:** 10 Kasım 2016 Perşembe 09:57:30	
Sample Source & type: ODTÜ	**Measured by:** PBA	**Analysed:** 10 Kasım 2016 Perşembe 09:57:31	
Sample bulk lot ref:	**Result Source:** Averaged		
Particle Name: Default	**Accessory Name:** Hydro 2000S (A)	**Analysis model:** General purpose	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 12.87 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 1.639 %	**Result Emulation:** Off
Concentration: 0.0073 %Vol	**Span :** 7.581	**Uniformity:** 2.36	**Result units:** Volume
Specific Surface Area: 1.68 m²/g	**Surface Weighted Mean D[3,2]:** 3.571 um	**Vol. Weighted Mean D[4,3]:** 20.623 um	

d(0.1): 1.368 um d(0.5): 7.445 um d(0.9): 57.806 um

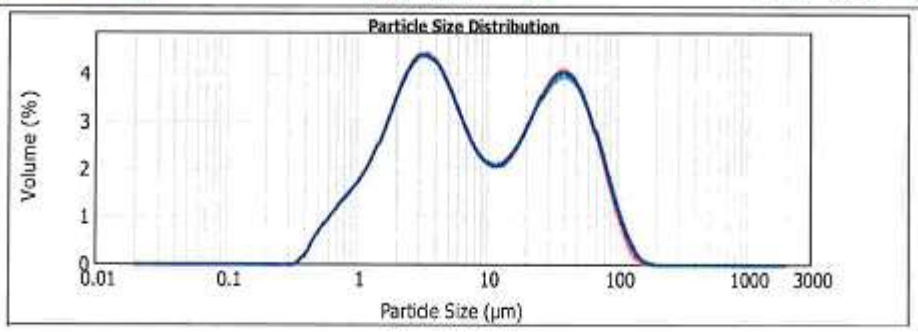

Figure A1. Particle Size Distribution Analysis Report of Bentonite [29]

Result Analysis Report

Sample Name: 18778-02(BARIT) - Average	**SOP Name:**	**Measured:** 10 Kasım 2016 Perşembe 10:02:22	
Sample Source & type: ODTÜ	**Measured by:** PBA	**Analysed:** 10 Kasım 2016 Perşembe 10:02:23	
Sample bulk lot ref:	**Result Source:** Averaged		
Particle Name: Default	**Accessory Name:** Hydro 2000S (A)	**Analysis model:** General purpose	**Sensitivity:** Normal
Particle RI: 1.520	**Absorption:** 0.1	**Size range:** 0.020 to 2000.000 um	**Obscuration:** 10.02 %
Dispersant Name: Water	**Dispersant RI:** 1.330	**Weighted Residual:** 2.713 %	**Result Emulation:** Off
Concentration: 0.0039 %Vol	**Span :** 4.902	**Uniformity:** 1.5	**Result units:** Volume
Specific Surface Area: 2.92 m²/g	**Surface Weighted Mean D[3,2]:** 2.052 um	**Vol. Weighted Mean D[4,3]:** 9.356 um	

d(0.1): 0.699 um d(0.5): 4.946 um d(0.9): 24.946 um

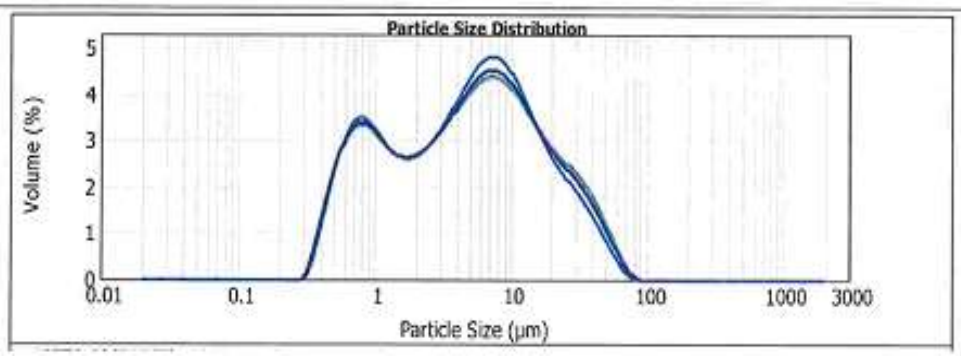

Figure A2. Particle Size Distribution Analysis Report of Barite [29]