

**ÇUKUROVA UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES**

MSc THESIS

Yakup Emre TANRIKULU

**INVESTIGATION OF MECHANICAL AND THERMAL
PROPERTIES OF BORON MINERAL DOPED PLASTIC
MATERIALS**

DEPARTMENT OF AUTOMOTIVE ENGINEERING

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We certify that the thesis titled above was reviewed and approved for the award of degree of the Master of Science by the board of jury on 17/01/2017.

.....
Assoc. Prof. Dr. Abdulkadir YAŞAR
SUPERVISOR

.....
Prof. Dr. Kadir AYDIN
MEMBER

.....
Asst. Prof. Dr. Kerimcan ÇELEBİ
MEMBER

This MSc Thesis is written at the Department of Institute of Natural And Applied Sciences of Çukurova University.

Registration Number:

**Prof. Dr. Mustafa GÖK
Director
Institute of Natural and Applied Sciences**

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In the memory of my dear cousin İbrahim Talib USLU

ABSTRACT

MSc. THESIS

INVESTIGATION OF MECHANICAL AND THERMAL PROPERTIES OF BORON MINERALS DOPED PLASTIC MATERIALS

Yakup Emre TANRIKULU

**ÇUKUROVA UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES
DEPARTMENT OF MECHANICAL ENGINEERING**

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: Prof. Dr. Kadir AYDIN
: Asst. Prof. Dr. Kerimcan ÇELEBİ

In this study; mechanical and thermal properties of boron containing polyethylene and polyurethane was investigated. This thesis consists of two main parts that are polymer manufacturing and characterization. Polymer blends are manufactured by extrusion method within the limits of 15% boron mineral content followed by using the injection molding method to obtain tensile and impact tests samples. To understand the mechanical properties of the samples, tensile test, impact test and hardness test is utilized. Additionally, thermal characteristics and properties are investigated using Thermogravimetric analysis and Differential Scanning Calorimetry. Experimental data showed that there is no significant decrease in tensile strength of the materials and a notable increase in stiffness of materials. In addition, polyethylene based samples indicate a decline in elongation at break whereas there is a variety of results obtained from polyurethane samples. While there was a notable decrease in the impact resistance of polyethylene-based materials, contrary to expectation there has been an increase in some polyurethane based samples. Hardness values are found to be improved for both sample types. Similar results were obtained in the two methods used for analysis the thermal properties. Although it is not as much as expected, there is a noticeable improvement in the thermal properties of both materials. Additionally, while Scanning Electron Microcopy (SEM) was utilized to monitor the dispersion of mineral filler, Melt Flow Index (MFI) measurements were used to determine the flow dynamics that are important for production. SEM images reveal that mineral filler is not as well-dispersed as expected. When the flow properties were examined an increase in viscosity was observed as expected, except for some samples.

Keywords: Colemanite, Ulexite, Polyethylene, Polyurethane

ÖZ

YÜKSEK LİSANS TEZİ

BOR MİNERALİ KATKILI PLASTİK MALZEMELERİN MEKANİK VE TERMAL ÖZELLİKLERİNİN İNCELENMESİ

Yakup Emre TANRIKULU

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: Prof. Dr. Kadir AYDIN
: Yrd. Doç. Dr. Kerimcan ÇELEBİ

Bu çalışmada; bor mineralleri içeren polietilen ve poliüretan malzemelerin mekanik ve termal özellikleri incelenmiştir. Bu tez çalışması malzemelerin üretimi ve karakterizasyonu olmak üzere iki ana bölümden oluşmaktadır. Numuneler en fazla %15 bor minerali içerecek şekilde ekstrüderde üretilmiş ve enjeksiyon kalıplama yöntemi ile çekme ve darbe test çubukları üretilmiştir. Çekme testi, darbe testi ve sertlik ölçümleri mekanik özellikleri belirlemek için kullanılırken, termogravimetrik analiz ve diferansiyel taramalı kalorimetre yöntemleri ile termal özellikler belirlenmiştir. Deneysel veriler, malzemelerin çekme direncinde önemli bir azalış gözlenmediğini, rijitliklerinde ise önemli bir artış sağlandığını ortaya koymuştur. Ayrıca, polietilen tabanlı malzemelerin kopma uzamalarında düşüş gözlenirken poliüretan malzemeler için alınan veriler çeşitlilik göstermiştir. Polietilen tabanlı malzemelerin darbe dirençlerinde dikkate değer bir düşüş söz konusuysa, poliüretan malzemeler için beklenenin aksine bazı örnekler için artış gözlenmiştir. Sertlik değerleri her iki tip malzeme içinde artış göstermiştir. Termal özelliklerde kullanılan iki analiz yönteminde benzer sonuçlar elde edilmiştir. Termal özellikler beklendiği kadar olmasa da her iki malzeme için artış göstermiştir. Ayrıca, taramalı elektron mikroskopu mineral dolgunun dağılımını analiz etmek için kullanılırken, üretimde önemli olan akış dinamiklerini belirlemek için erime akışı indeksi ölçümleri de yapılmıştır. Taramalı elektron mikroskopundan elde edilen görüntülerde, mineral dolgunun istenilen gibi homojen olarak dağılmadığı gözlemlenmiştir. Akış özellikleri incelendiğinde birkaç örnek dışında, beklendiği gibi viskozitede artış gözlenmiştir.

Anahtar kelimeler: Kolemanit, Üleksit, Polietilen, Poliüretan

GENİŞLETİLMİŞ ÖZET

Bu çalışmada, bor minerali içeren polietilen ve poliüretan malzemelerinin mekanik ve termal özellikleri incelenmiştir. Polietilen matris sisteminin mineral dolgu maddesi içeriği, karışımın termal ayrışma özelliklerini arttırmak için kolemanit ve üleksit ile birlikte $Mg(OH)_2$ ile desteklenmiştir. Poliüretan matris sistemi için sadece bor içeren mineraller kullanılmıştır.

Karışımların hazırlanması için Gülnar Makina'nın 12mm'lik aynı yönde dönen çift vidalı bir ekstrüderi kullanılmıştır. Ekstrüzyon süreç sıcaklıkları polietilen tabanlı ve poliüretan tabanlı malzemeler için farklı olup polietilenler için besleme gözünden kalıba kadar sırasıyla kullanılan sıcaklıklar 190, 200, 205, 210, 215 °C olmakla beraber poliüretanlar için 165, 170, 170, 150, 130 °C'dir. Ekstrüzyon ile çubuk şeklinde üretilen harmanlar oda sıcaklığında soğutulduktan sonra granülatör ile granül haline getirilmiştir. Daha sonra bu granüllerin bir kısmı mekanik özelliklerin incelenebilmesi için enjeksiyon kalıplama tekniği sayesinde çekme ve darbe testi numunelerine dönüştürülmüştür. Enjeksiyon kalıplama sırasında kullanılan cihaz Xplore IM 12'dir ve tıpkı ekstrüzyon işleminde olduğu gibi enjeksiyon işleminde de polietilen ve poliüretan için farklı sıcaklıklar kullanılmıştır. Polietilen bazlı karışımların enjeksiyonları için 215°C kullanılırken poliüretan bazlı karışımlar için bu sıcaklık 190°C'dir. Her iki tip malzeme için de kalıp sıcaklığı 30°C'dir ve malzeme bu kalıplara 8 bar basınç ile enjekte edilmiştir.

Karışımların mekanik özelliklerinde meydana gelen değişimleri gözlemlemek için numuneler üzerinde çekme testleri yapılmıştır. Bu testler için kullanılan numune boyu 75mm, eni 4mm ve kalınlığı 4mm'dir. Ayrıca bu testler için Shimadzu AGS-X çekme test cihazı kullanılmış olup uzama hızı 50mm/dk olacak şekilde testler tamamlanmıştır. Her bir kompozisyon için çekme testi 3 kez tekrarlanmış ve ortalamaları hesaplanmıştır. Sonuçlar; numunelerin gerilme mukavemetinde büyük bir değişiklik olmadığını, ancak polietilen numunelerinin rijitliklerinde belirgin bir iyileşmenin olduğunu ortaya koymaktadır. Polietilen

tabanlı numuneler için kopma uzamasının artan mineral miktarıyla düştüğü, buna karşın poliüretan bazlı karışımlar için verilerin tutarlı olmadığı ve verilerde belirgin bir dalgalanma gözlemlendiği görülmektedir.

Mekanik özelliklerin incelenmesi için kullanılan bir diğer yöntem ise darbe testidir. Bu test için kullanılan numunenin boyu 60mm, eni 3mm ve yüksekliği 6mm'dir. Kırılmanın sağlanması ve malzemelerin birbirine göre darbe dayanımının hesaplanması için bütün numuneler 5 saniye sıvı azotun içinde bekletildikten sonra teste tabi tutulmuştur. Her bir karışım için test 3 kere tekrarlanmıştır ve bunların ortalaması hesaplanmıştır. Polimerik malzemelere mineral dolgu maddesinin eklenmesi genellikle polimerin darbe dayanıklılığı özelliklerinde keskin bir düşüşe neden olur. Polietilen tabanlı karışımlarda kullanılan $Mg(OH)_2$ 'nin karışımın darbe özelliklerinde dikkate değer bir etkisinin olmadığı gözlenmiştir. Öte yandan, kolemanitin ve üleksitin artan miktarlarda eklenmesi, polimer harmanlarının darbe özelliklerini olumsuz olarak etkilendiği söylenebilir. Bununla birlikte, özellikle poliüretan numuneleri ile elde edilen sonuçlarda belirgin bir fark bulunmamaktadır.

Mekanik özelliklerin incelenmesi sertlik ölçümleriyle sürdürüldü. Bu ölçümler için Sauter marka Shore A ve Shore D manuel sertlik ölçüm cihazları kullanılmıştır. Polietilen tabanlı numuneler için Shore A kullanılırken, poliüretan tabanlı numuneler için Shore D kullanılmıştır. Her bir numune için 6 farklı ölçüm alınmış ve bu ölçümlerin ortalaması hesaplanmıştır. Mineral katkısının miktarının ve çeşidinin değişmesiyle oluşturulan karışımlar göz önüne alındığında, sertlik değerlerinin mineral katkısıyla arttığı gözlenmiş, fakat değişimin en fazla yüzde 10 mertebelerinde olduğu tespit edilmiştir. Dolayısıyla, polimer harmanında mineral takviyesinin büyük bir etkisinin olmadığı sonucuna varılmıştır.

Karışımların termal özellikleri Termogravimetrik analiz (TGA) ve Diferansiyel Taramalı Kalorimetre (DSC) kullanılarak araştırılmıştır. Bu analizler için Hitachi STA7000 ve DSC7000X kullanılmıştır. Termogravimetrik analizlerde her iki çeşit polimer tabanlı karışımlar içinde sıcaklık oda sıcaklığı ile 1000°C

aralığındadır. Ayrıca bütün analizlerde 20°C/dakika ısıtma hızı kullanılmış ve bu analizler 50ml/dakika azot akışı altında gerçekleştirilmiştir. Diferansiyel taramalı kalorimetrede ise polietilen tabanlı karışımlar için 0 ile 400°C sıcaklık aralığında analizler yapılırken poliüretan tabanlı karışımlar için -80 ile 400°C sıcaklık aralığında analizler yapılmıştır. Her iki tip karışımlar için ısıtma hızı 20°C ve azot akış hızı 50ml/dakika'dır. Polimerin bozulmasındaki toplam değişimin beklenenden az olduğu bulunmuştur. Sistemin bozunma dinamikleri ile birlikte Diferansiyel taramalı kalorimetre verileri, Termogravimetrik analizin numune ağırlığında bir kayıp olduğuna işaret ettiği sıcaklıklar çevresinde çok sayıda çoklu endotermik tepe bulunduğu gözlenmiştir. Ayrıca, poliüretan numuneleri için camsı geçiş sıcaklığı incelenmiş ve yaklaşık -50°C olduğu bulunmuştur. Bu çalışmada kullanılan soğutucu yalnızca -70 ° C ile sınırlı olduğu için, polietilen bazlı numuneler için camsı geçiş sıcaklıkları elde edilememiştir.

Termoplastik sistemlerin imalat özelliklerini incelemek için önemli bir parametre olan erime akış indeksi de bu çalışmada incelenmiştir. Erime akış indeksi polimerin molekül ağırlığı, dallanma derecesi, katkı maddelerinin varlığı ve işleme yöntemleri gibi birçok farklı parametre ile değişkenlik gösterebilir. Mineral dolgu maddelerinin eklenmesinin viskoziteyi arttırdığı ve bu nedenle üretimin daha zor olacağı düşünülmektedir. Erime akış indeksi ölçümleri Zwick Roell Mflow cihazı ile gerçekleştirilmiştir. Polietilen bazlı karışımlar için yapılan analizlerde sıcaklık 190°C olmakla beraber 5 kilogramlık ağırlık kullanılmıştır. Poliüretan bazlı numuneler için ise bu değerler sırasıyla 180°C ve 2.16 kilogramdır. Analizler sonucunda dalgalanmalar olsa bile genel olarak mineral katkısı ile MFI değerlerinin düştüğü gözlenmiştir.

Ayrıca, polimer yapısındaki mineral dolguların dağılımını analiz etmek için taramalı elektron mikroskobu ile görüntüler elde edilmiştir. Bu görüntüleme sırasında kullanılan cihaz, FEI Quanta SEM FEG 650'dir. 600'den 1000'e kadar çeşitli büyütme oranlarında görüntüler elde edilmiştir. Görüntüleme için kullanılan akselerasyon voltajı 20 kilovoltur. Yalıtkan olan numunelerin yüzeyleri altın ile

kaplanarak iletken bir yüzey elde edilebilir. Ancak, arka planı kaybetmemek için kaplama yapılmamıştır. Buna ek olarak, numunelerin elemental dağılımını inceleyip mineral varlığını ispat etmek için EDS (Enerji dağılımlı X-ışını Spektroskopisi) kullanılmıştır. Sonuçlar, mineral katkı maddelerinin çok iyi dağılmadığını ve numunelerin içerisinde aglomerasyon (topaklanma) olabileceğini göstermiştir.

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ABBREVIATIONS

LDPE	: Low Density Polyethylene
HDPE	: High Density Polyethylene
LLDPE	: Linear Low Density Polyethylene
TPU	: Thermoplastic Polyurethane
MFI	: Melt Flow Index
TGA	: Thermogravimetric Analysis
DSC	: Differential Scanning Calorimetry
XRF	: X-Ray Fluorescence
SEM	: Scanning Electron Microscope

1. INTRODUCTION

1.1 Polymer

Polymer is a word that was derived from combination of the “poly” which means very and “meros” which means parts in Greek. Polymers are chain molecules composed of repeating units that contain radical groups, usually covalently bonded, on the carbon skeleton (Turan, 2012). Polymers that consist of chemical units called monomers are synthetic materials with a high molecular weight and a chain-like structure. A polymer combining with other monomer molecules through a polymeric polymerization take place a long chain of macromolecules consisting of repetitive structures. Thus, various types of polymers are obtained using various monomers or combinations of monomers (Turan, 2012).

The unique properties and low densities of polymers make them an alternative to ceramics and metals in many applications. Moreover, easily shaping, corrosion and abrasion resistance, toughness and low friction coefficients are considered as their main advantages. When polymer is chosen as the material to be presented to the end user, not only mechanical properties but also electrical, optical and thermal features should be considered properly (Saçak, 2002).

There is a rapid development in polymer industry which is largely based on petroleum industry, thus new polymer types are offered to use. New products which are obtained by mixing graphite, glass and carbon fibers with polymers, is an important step in the development of polymers. The mechanical properties of these materials are close to metals. The polymeric materials which has developed properties will contribute to human life due to their advantages(Çetinel, 2000).

When a mass of polymer chains is heated, the mobility of the polymer chains increases. The increase in the mobility initially formed in the small parts of the polymer chain, then covers larger parts and spreads over throughout as the temperature increases. Then the polymer chains begin to slip over one another and

the solid polymer will melt and flow. The ability of becoming liquid at certain temperature is used when polymers are formed. Thus, polymer parts can be used after cooling and removing from mold.

In thermoset polymer, molecules which chemically linked together by crosslinks, creates three dimensional rigid networks. Thermoset polymers cannot be melted again and reshaped by heat and pressure when these crosslinks occur during polymerization reaction (Schwartz, 1997). Due to simplicity of their processing, thermoset polymers are generally used as matrix materials in polymer based composites (Akovali, 2001). Wet-out between matrices and fibers can be obtained when thermosets are considered because polymerization starts with chemicals which have really low viscosity (Schwartz, 1997). Even though thermosets have more rigidity and better high temperature performance then they compared with thermoplastics, they generally need more time for processing (Strong, 1989).

Unlike thermosets, thermoplastic polymers do not contain chemical bonds between long chain molecules. Molecules are held together by interatomic bonds such as hydrogen and van Der Waals bonds (Muccio, 1994). Thermoplastics can be softened and molten by heat and reprocessable (Akovali, 2001). Superiorities of thermoplastics over thermosets are their high impact strength and fracture resistance which increase the damage tolerance of composites (Schwartz, 1997). Therefore, the application area should be considered while making the choice between thermoplastic and thermoset.

1.1.1 Polyethylene

Even though polyethylene is the one of the major olefin polymers, it becomes more important each year due to its good electrical insulation properties, chemical resistance, light weight, flexibility and fair price (Rubin, 1990; Salamone, 1996). Polyethylene is classified according to two different parameters which could be easily determined in 1950's with minimum equipment. These are resin density

and melt index (Kirk-Othmer, 1993). With respect to density, there are there main groups which are low density polyethylene (LDPE), high density polyethylene (HDPE) and linear low density polyethylene (LLDPE).

Table 1.1 Classification of polyethylene according to density (Kroschwitz & Seidel, 2005)

Name	Acronym	Density(g/cm ³)
High density polyethylene	HDPE	>0.940
Medium density polyethylene	MDPE	0.926-0.940
Linear low density polyethylene	LLDPE	0.915-0.925
Low density polyethylene	LDPE	0.910-0.940

Crystallinity of polymer which can be determined by density, is a significant feature because it affects stiffness, rigidity and barrier properties of products. When crystallinity decreases due to density, hardness decreases and flexibility increases (Mark, 2004).

While LDPE is generally used in bags, textile products, moisture barriers, greenhouses, cable insulation; HDPE is used where injection molding of complex shapes is required but low load is applied such as film, sheet, wire and cable insulation, pipes and drums (Bafna, 2004).

1.1.2 Low Density Polyethylene (LDPE)

The first commercially used polyolefin is low density polyethylene. It was produced in 1933 by high pressure polymerization of ethylene (Mark, 2004). Therefore, LDPE is also called as high pressure low density polyethylene due to production method. LDPE is manufactured through free-radical catalyzed reaction by using free radical starter at high temperature among 150-300°C and high pressure 103-345 MPa (Young, 1991). Duration of this process is generally about among 10-50 seconds (Salamone, 1996).

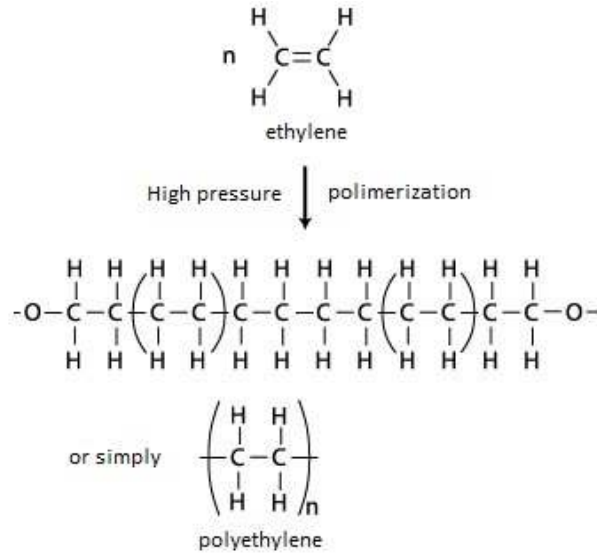


Figure 1.1 Schematic of polymerization of ethylene (Işık, 2005)

Initiation, propagation and termination are three main steps of polymerization (Rubin, 1990). An initiator which reacts with ethylene is required to decompose into free radicals. When radical groups combination is come true or hydrogen radical is transferred one chain to another, termination takes place.

1.1.3 Properties of LDPE

The most important distinguish properties of polyethylene are toughness, high impact strength, low brittleness temperature, flexibility, processability, film transparency, chemical resistance to polar compounds, low permeability to water, and superior electrical properties (Kroschwitz, 1990).

LDPE has mechanical properties which are between rigid polymers such as polystyrene and soft polymers such as polyvinyl. The table given below shows most important properties of LDPE.

Table 1.2 Properties of LDPE (Fried, 2003)

Property	ASTM	LDPE
Specific Gravity	D792	0.91- 0.93
Crystallinity	-	50-70
Melt temperature, °C	-	98-120
Tensile strength, MPa	D638	4.1-16
Tensile modulus, MPa	D638	100-260
Elongation to break, %	D638	90-800
Impact strength	D256	No break

LDPE is an important material for packaging application because of its high resistant to penetration against neutral or reactive property. It is also used as vessel to transport chemicals safely due to its high impermeability property. Although LDPE has high resistant to penetration property against most polar liquids, water and aqueous solution, non-polar liquids can penetrate into LDPE.

Thanks to remarkable electrical properties of LDPE, it is highly appropriate for cable insulation for even if high frequency electrical power supplies in electronics.

Length of the LDPE molecules can vary from thousands carbons to billion carbons. Average molecular weight of polymers determines melt viscosity. The more molecular weight, the higher melt viscosity, tensile strength, flexural stiffness. However, increase in molecular weight result in decrease in transparency, haze and gloss (Kirk-Othmer, 1993).

Because of the fact that LDPE has relatively low melting point about 106-112°C and wide melting range, it can be easily processed. Owing to having glass transition temperature lower than room temperature (~ -120°C), LDPE has soft and flexible nature. Moreover, it does not rupture when Izod impact test is applied (Seymour & Carraher, 1984).

Even though LPDE is suffer from thermal and ultraviolet degradation, degradation can be delayed several years under favor of some adjuvants.

1.1.4 Thermoplastic Polyurethane (TPU)

Thermoplastic polyurethane which is block copolymer involves not only hard but also soft segments in its nature. There are excessively polarized groups such as glycols or diamine reacted with diisocyanate in hard segment. This increase the strength via crosslinking (Bhowmick & Stephens, 2000). Polyester or polyether units compose the soft segment of TPU. In consequence of this phase separation, hard segments are distributed as micro domains. These hard segments are maintained intact by the forces of hydrogen bonding between different chains in the structure (Chen, Tien, & Wei, 2000).

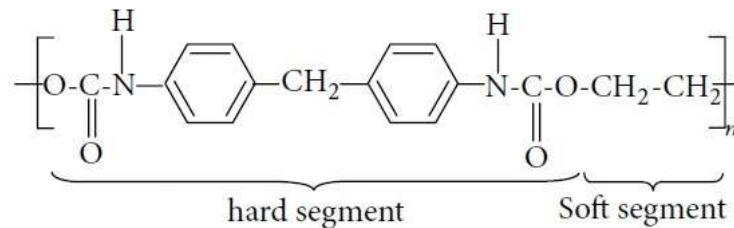


Figure 1.2 Structure of thermoplastic polyurethane (Manrique-Juárez et al., 2013)

Thermoplastic polyurethane has admirable features such as excellent mechanical properties, chemical resistance and easy processability. In addition to these superior properties, TPU has proper cost because of being fully recyclable polymer. TPU has wide range applications such as automotive industry, footwear, sporting goods, medical devices, tubes, hoses, wires and cables (Tayfun, 2015). Moreover, TPU is known as one of the most biocompatible materials because of its biocompatibility and bio stability properties. Therefore, it is used in biomedical area for several applications. It was used for the first time in 1958 to obtain breast prostheses coated with polyurethane (Pangman, 1958).

There is some type of reactants obtained from petroleum or renewable resources which are used in production of TPU. TPUs are declared as bio-based, supposing that renewable resources are consumed for production (Mohanty, Misra, & Drzal, 2005). This makes it possible to create recyclable eco composites by using natural resources (Markarian, 2008). Furthermore, actuators can be made from polyurethane when it doped with carbon based nanomaterials because of electrostriction effect (Wongtimnoi, Guiffard, Bogner-Van de Moortèle, Seveyrat, & Cavaillé, 2013). TPU can gain shape memory actuation when they are loaded with carbonaceous fillers (Gunes, Jimenez, & Jana, 2009; Koerner, Price, Pearce, Alexander, & Vaia, 2004).

1.2 Boron

Boron in elemental form is at III A group of periodic table. While atomic number of boron is 5, atomic mass of it is about 11. However, elemental boron cannot be found in nature. It has complicated chemistry which is similar with silicon (Cotton & Wilkinson, 1988).

Elemental boron is solid at room temperature. Boron solids occur as either black monoclinic crystals or yellow, brown amorphous powder. These forms have different specific gravities. Boron can be found as two different isotopes which are ^{10}B (19.78%) and ^{11}B (80.22%) (Budavari, 1989). Boron can be thought as inert apart from strong oxidizing agent. There is an explosion risk of boron dust which is flammable (Lewis & Sax, 1992).

1.2.1 Boron Minerals and Their Reserves

There are 803 million tons boron deposits in Turkey. Turkey has the 72% of boron deposits of the world. Turkey which has 31% of total production based on B_2O_3 is the one of the most important producer. The quality and tenor of these reserves are high. It is thought that these reserves will meet world's boron consumption for 250-500 years (Sirin, 2003).

Turkey, the USA, Russia has the most important boron bearing in the world respectively. The table given below shows the boron reserves of the world.

Table 1.3 Reserves of Boron in World (Sirin, 2003)

Country	Definite reserves(ton)	Probable + Possible reserves	Total reserve	Percent in total (%)	Life span (years)
Turkey	224	375	563	64	389
USA	40	40	80	9	55
Russia	40	60	100	11	69
China	27	9	36	4	25
Kazakhstan	14	1	15	2	10
Chile	8	33	41	5	28
Bolivia	4	15	19	2	13
Peru	4	18	22	2	15
Argentina	2	7	9	1	6

Even though Turkey that has the highest and largest quality reserves, has the first rank when boron production is considered, the production capacity of US higher than Turkey. Colemanite, ulexite and tincal are momentous minerals of Turkey. There minerals involve varied amounts of B_2O_3 which is important for industrial application and deposits in Turkey are rich in terms of B_2O_3 . Eti Holding is single executer of processing of boron minerals in Turkey. This holding has four plant in Eskişehir-Kırka, Balıkesir-Bigadiç, Bursa-Kestelek and Kütahya-Emet because the known boron reserves are in these regions (Kar, Şen, & Demirbaş, 2006).

Colemanite ($Ca_2B_6O_{11}.5H_2O$), ulexite ($NaCaB_5O_9.8H_2O$) and tincal ($Na_2B_4O_7.4H_2O$) ores are the three major production areas of boron production in Turkey (Kar et al., 2006). Distribution of boron reserves in Turkey is given Figure

3. Which ores are in which production area and the reserves of these ores are given in Table 4.

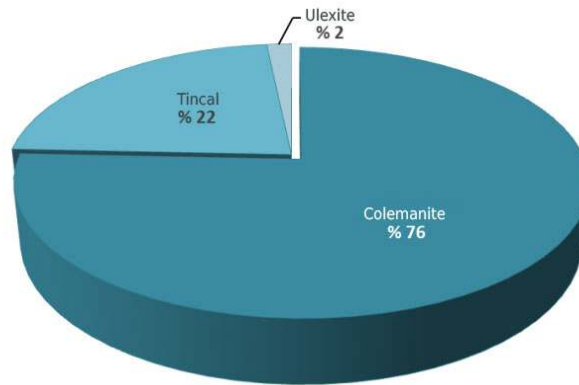


Figure 1.3 Distribution of Boron Reserves in Turkey (Boren, 2012b)

Table 1.4 Boron Mineral Reserves of Turkey (Eti, 2001)

Production area	Ore	Reserve (million tons)	B ₂ O ₃ -based reserves	Tenor (BO %)
Kırka	Tincal	604	156	26-27.5
Bigadiç	Ulexite	49	14	28-30
	Colemanite	576	167	28-30
Emet	Colemanite	835	225	26-28
Kestelek	Colemanite	7.5	2	29-31

1.2.2 Application Areas of Boron

Although boron minerals can be used as concentrates in some application, refined boron products and special boron chemicals have wider application area. There are lots of application area for boron minerals and compounds and borates.

Glass industry is the industry that uses the most boron. Boron is used to increase the viscosity of glass, develop surface hardness and increase strength of product. On the other hand, in ceramic industry, it also used in glazing and frits.

Boron oxide is consumed to ensure thermal balance between glass and material and also arrange the thermal expansion coefficient of glaze. Adding boron to glaze is also increase the mechanical strength of glaze and gives scratch resistance.

Borates can be used for flame retardancy. Boron delays the combustion by closing the surface of material and inhibit its contact with oxygen. While zinc borate is preferred for polymeric materials, boric acid, borax decahydrate and pentahydrate are used for cellulosic materials.

Boron compounds are frequently used in metallurgy. They are utilized as slag forming agents in non-ferrous metal industry due to their sticky, smooth, protective and burr-free liquid forming features at high temperature. Furthermore, hardness and strength of steel can be enhanced by adding boron.

Sodium borohydride is better choice for storing hydrogen because of non-flammable/non-explosive and environmental friendly nature. By increasing the use of hydrogen as fuel, sodium will increase its importance in the energy sector day by day. On the other hand, it can also be used directly as fuel in fuel cells.

Colemanite can be exploited in cement industry for decreasing the temperature of clinker production and increase the cement properties. Moreover, using colemanite in cement production also decrease the quantity of carbon dioxide which is released to air (Boren, 2012a).

1.3 Aim of the Study

The aim of the study is to examine the effects of boron containing mineral fillers, in the case of colomanite and ulexite in the mechanical and thermal properties of polyethylene and polyurethane matrices. Turkey has the largest boron reserves thus finding new emerging areas and increasing quantity of boron consumption is important from the view of economic prosperity. Samples obtained at the end of study has a potential to be utilized in different industries. Addition of boron containing mineral fillers is achieved by different means such as extrusion and injection molding. Different characterization methods are p in order to analyze

and interpret the data in terms of mechanical and thermal properties. Further analyses techniques such as scanning electron microscopy and melt flow index are utilized to investigate morphological and manufacturing characteristics of the process.

2. LITERATURE REVIEW

Thermal decomposition, utilized as a flame retardancy mechanism has quite a history behind it. The reaction kinetics and thermal decomposition dynamics of colemanite was investigated in 1988. This provides an insight towards the decomposition mechanism of monocrystalline colemanite structure using different characterization methods such as thermal analysis, X-ray diffraction, IR spectroscopy and optical analysis. The results reveal that decomposition of colemanite occurs in a two-step manner starting with the disintegration of water molecules followed by the breakdown of borate structure (Waclawska, Stoch, Paulik, & Paulik, 1988).

The first use of boron-containing mineral fillers in polyolefin matrix systems was reported in 1997. Polypropylene and polyethylene copolymer matrices are reinforced by two different boron-containing compounds along with a mix of antimony trioxide compounds. The study further includes $\text{Mg}(\text{OH})_2$ and talc-reinforced composites in copolymer systems. Outcomes of the study indicate that boron-containing composites increase the flammability behavior of the composite sufficient up to a limit of 40%. The same limit for $\text{Mg}(\text{OH})_2$ containing composites is roughly 64%. The rationale behind using talc in the research is to provide a reference point the flammability properties of given composites. It should also be noted that high compositions of mineral filler have a detrimental effect on the impact toughness properties of the composite (Montezin, Cuesta, Crespy, & Georlette, 1997).

The limits of mineral filler composition thus become a vantage point for these systems. Rheology is a sufficient tool to understand the viscosity of a specific materials, which can be correlated to mechanical properties. Another study a new material system that combines zinc borate with another composite system of EVA- $\text{Mg}(\text{OH})_2$. In addition to viscosity tests, the study incorporates an understanding as to the mechanical properties of these composites via blowing tests. It's concluded

that the addition of zinc borate improves flammability properties of the material significantly (Carpentier, Bourbigot, Le Bras, & Delobel, 2000).

Investigation and development of PE-Mg(OH)₂ composites was done in 2003. The compatibility of these two phases within structure is accomplished using different compatibilizers such as hydroxyl, carboxylic and stearic acid with a mix ratio of 60% matrix to 40% mineral filler. The effects of different compatibilizers are examined using tensile and impact tests, differential scanning calorimetry, morphological tests and flammability tests. Stiffness and toughness tests particularly conclude that PE/Al(OH)₂ and PE/Mg(OH)₂ show better properties in terms of mechanical properties (Hippi, Mattila, Korhonen, & Seppälä, 2003).

A new perspective is contributed, in the production method of these composites. A high energy grinding system is incorporated in order to create a sintering-like effect between PVC granules and Al(OH)₂/Zinc borate mixes with varied compositions. Flammability and mechanical properties of these sintered structures are found to be sufficient for the process conditions (Pi, Guo, & Ning, 2003).

The effectiveness of colemanite mineral fillers in a PP matrix using limiting oxygen index and amount of residue tests was showed in 2006. The compatibility is accomplished using acidic and carbonific elements in the structure. A statistical approach is deployed in the study that leads to an optimal composition for the maximum LOI value, which is found to be 40.3 (Atikler et al., 2006).

Although mineral fillers are usually in natural form, a new approach to the use of synthetic mineral fillers in composite structures is adopted. An addition of synthetic hydromagnesite to an already Al(OH)₂ reinforced LDPE/EVA matrix composite system. Results are interpreted via thermogravimetric analysis and differential scanning calorimetry and is concluded that synthetic fillers indeed improve the flammability behavior of the composite systems consequently (Haurie et al., 2006).

The focus on PE matrix systems was maintained with the study of Wu et al. with an undisclosed commercial flame retardant/zinc borate mineral filler mix. Thermal and morphological properties of the varying mixes was examined using LOI/UL-94 tests, thermogravimetric analysis, Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD). The results indicate that a highly non-flammable complex system is obtained at higher temperatures (600°C). It is also concluded by SEM images that zinc borate addition causes significant changes in ash properties, which then yield better flammability results (Wu, Shu, & Hu, 2007).

The effect of zinc borate addition on thermal and mechanical properties of polyurethane was investigated in 2009. They observed that zinc borate has a significant effect on the oxidative stability of plain polyurethane by oxygen induction time test. Zinc borate doped polyurethane was compared with commercial stabilizer in this study. According to oxygen induction time and weathering chamber test, zinc borate containing polyurethane has much better performance. It also provides better flame retardancy. They also complete the mechanical test and thermogravimetric analysis to characterize this product (Yıldız, Seydibeyoğlu, & Güner, 2009).

Boron-containing mineral fillers attracted much attention especially after 2010 upon sufficient flammability results. Four different boron containing mineral fillers that includes zinc borate (ZnB), boron phosphate (BPO₄), boron silicon containing preceramic oligomer (BSi) and lanthanum borate (LaB) was utilized. The composite properties are determined using LOI/UL-94 tests and thermogravimetric analysis. Results of the study conclude that boron phosphate shows the highest LOI and heat release rate values whereas total heat release is minimal for this particular material (Doğan, Yılmaz, & Bayramlı, 2010).

Increase in flammability properties can be achieved by different type of mechanisms. Up to now, obtaining flame retardancy by intumescent was preferred. However; endothermic decomposition was thought as fire retardant mechanism especially after 2010. At this point; the study which related with carbonate and

hydroxide containing minerals was done is important. In this study, endothermic decomposition dynamics of not only $\text{Al}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$, but also mixture of magnesium/calcium carbonate was inspected. Thermal properties of these compounds was deeply investigated by LOI, UL 94 and conic calorimeter (Hull, Witkowski, & Hollingbery, 2011).

By using combination of $\text{Al}(\text{OH})_2$ and colemanite mineral as a filler in polyethylene matrix was investigated in 2013. Change in flammability properties by altering the amount of boron mineral in polymer matrix was examined and the positive effect of colemanite on this property was proved. Apart from that, the relation between mineral filler and the elastic modulus and high ductility was also showed in this study (Isitman & Kaynak, 2013).

The effect of colemanite and ulexite on mechanical properties of epoxy was investigated in 2016. Improvement in mechanical properties was seen up to 5% boron mineral in material structures. Moreover; the dispersion of mineral filler was investigated by using X-ray Diffraction and Scanning Electron Microscopy (Guzel, Sivrikaya, & Deveci, 2016).

3. MATERIAL AND METHODS

3.1 Materials

3.1.1 Polymers

Polyethylene with a trade name Petilen F2-12 was used in this study. It was supplied from Petkim Petrochemical Holding Inc. in a 5kg polyethylene bag. Properties of Petilen F2-12 given by supplier is shown at Table 3.1.

Table 3.1 Properties of polyethylene (Petilen F2-12) (Petkim, 2016)

Property	Value	Unit	Method
Melt Flow Rate (190°C/2.16kg)	2.5	g/10 min	ASTM D1238
Density	0.92	g/cm ³	ASTM D1505
Melting Point	110	°C	ASTM D3418
Tensile Strength at Yield	10-11	MPa	ASTM D882
Tensile Strength at Break	17-23	MPa	ASTM D882
Elongation at Break	>200	%	ASTM D882
Tear Strength	240-330	cN	ASTM D1922
Haze	6.3	%	ASTM D1003
Gloss, 45°	77	GU	ASTM D2457
Vicat Softening Point	92	°C	ASTM D1525

The commercial thermoplastic polyurethane (Ravathane ® R130A65) was procured from Ravago Petrochemistry Inc. in a 5kg polyethylene bag. Properties of Ravathane R130A65 given by supplier is shown at Table 3.2.

Table 3.2 Properties of polyurethane (Ravathane R130A65) (Ravago, 2016)

Property	Value	Unit	Method
Tear Strength	80	kN/m	ISO 34-1
Abrasion Resistance	40	mm ³	ISO 4649
Tensile Strength	23	MPa	ISO 37
Strain	925	%	ISO 37
Hardness	67	Shore	ISO 868
Specific Gravity	1150	kg/m ³	ISO 1183
Drying Temperature	90-100	°C	
Drying Time	12	h	
Moisture Content	<0.1	% wt	

3.1.2 Boron

Colemanite and ulexite are supplied from Bigadiç Boron Works of Eti Maden in a 10 kg bags. Chemical specification of the products given from Eti Maden is given in Table 3.3. Table 3.4 shows the results of XRF which is carried out in Adana Science and Technology University.

Table 3.3 Chemical Specification of colemanite and ulexite (EtiMaden, 2016)

Component	Content	
	Colemanite	Ulexite
B ₂ O ₃	40.00 ± 0.5%	37.00 ± 1.00%
CaO	27.00 ± 1.00%	19.00% max
SiO ₂	4.00-6.50%	4.00% max.
SO ₄	0.6% max.	0.25% max.
As	35 ppm max.	40 ppm max.
Fe ₂ O ₃	0.08% max	0.04% max.
Al ₂ O ₃	0.40% max	0.25% max.
MgO	3.00% max	2.50% max.
SrO	1.50% max	1.00% max.
Na ₂ O	0.50% max	3.50% min.

Table 3.4 XRF Results of colemanite and ulexite

Component	Content	
	Colemanite	Ulexite
B ₂ O ₃	48.3791%	55.7486%
CaO	28.3434%	20.1105%
SiO ₂	2.1593%	3.1208%
Fe ₂ O ₃	0.0129%	0.0158%
Al ₂ O ₃	0.0370%	0.0426%
MgO	1.3511%	2.2324%
SrO	0.6175%	0.8993%
Na ₂ O	0.0319%	7.0315%
CO ₂	18.1825%	10.6311%

3.1.3 Composition of samples

Compositions of all samples which are prepared for this study and their notations are given in Table 3.5 and 3.6 according to polymer type, respectively.

Table 3.5 Compositions of polyethylene based samples

	PE	Mg(OH) ₂	Colemanite	Ulexite
PE	100	0	0	0
PE0	70	30	0	0
PE1	70	25	5	0
PE2	70	20	10	0
PE3	70	15	15	0
PE4	70	25	0	5
PE5	70	20	0	10
PE6	70	15	0	15
PE7	70	20	3	7
PE8	70	20	5	5
PE9	70	20	7	3

Table 3.6 Compositions of polyurethane based samples

	PUR	Colemanite	Ulexite
PUR	100	0	0
PUR1	95	5	0
PUR2	90	10	0
PUR3	85	15	0
PUR4	95	0	5
PUR5	90	0	10
PUR6	85	0	15
PUR7	90	3	7
PUR8	90	5	5
PUR9	90	7	3

3.2 Methods

3.2.1 Polymer Processing

Although there are various methods such as fiber spinning, blow molding and calendering for producing different types of products, the most commonly used methods in the polymer industry are extrusion and injection molding.

3.2.1.1 Extrusion

The raw material can be transformed into a continuous and specially shaped product by help of extrusion (Simon, 2003). Extruders which are basically a pump can perform different type of operation thanks to their pumping function. Schematic view of a typical extruder is given Figure 3.1. The raw materials are generally loaded to extruder in solid forms such as pellets, granules, flakes or powder. These raw materials can be fed together in a mixture or separately from one or more feeders. If solid materials are fed to extruder, melting operation is come true. It is generally called as plasticizing, and such an extruder is plasticizing extruder. Moreover, it is called as melt extruder when feed is liquid. The mixture

function of extruder can be used when dissimilar polymers, or polymers with liquids or pigments or filler are fed (Middleman, 1977).

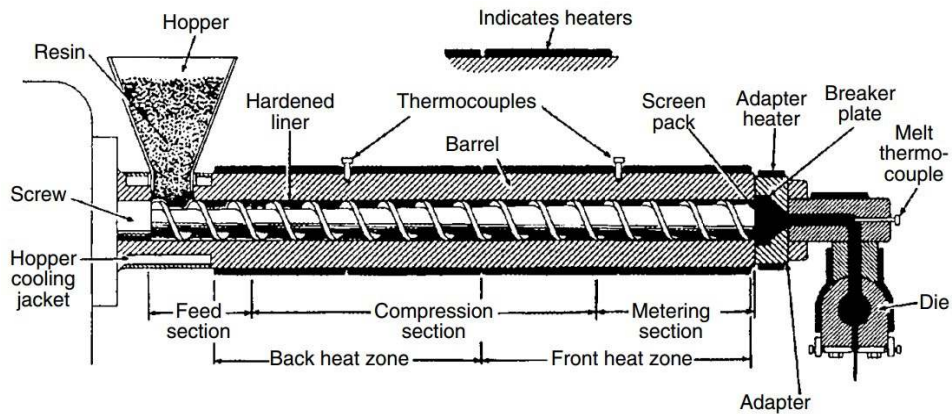


Figure 3.1 Schematic view of an extruder (Harper, 2000)

There are many type of extruder due to their designs. However, the most important difference between them is mode of operation which are continuous and discontinuous. Discontinuous extruders which give an intermittent polymer are suitable for batch type operations such as blow molding and injection molding. While batch extrusion machines have mutual elements, continuous extrusion machines have a rotating element. Classification of polymer extruders is given Table 3.7 (Middleman, 1977).

Table 3.7 Classification of Polymer Extruders (Rauwendaal, 2014)

Screw extruders (continuous)	Single screw extruders	Melt fed Plasticating Single stage Multi stage Compounding
	Multi screw extruders	Twin screw extruders Gear pumps Planetary gear extruders Multi (>2) screw extruders
Disk or drum extruders (continuous)	Viscous drag extruders	Spiral disk extruder Drum extruder Diskpack extruder Stepped disk extruder
	Elastic melt extruders	Screwless extruder Screw or disk type melt extruder
Reciprocating extruders (discontinuous)	Ram extruders	Melt fed extruder Plasticating extruder Capillary rheometer
	Reciprocating single screw extruders	Plasticating unit in injection molding machines Compounding extruders

The molten polymer is dragged through the barrel in all kind of extruders. Mixing in single screw extruder is low when it is compared with twin screw extruders. Some enhancers are used to increase mixing in single screw extruders.

There are two screws which are co-rotating or counter-rotating in twin-screw extruders. Co-rotating means that screws rotate in the same direction.

However, counter-rotating means that they rotate in opposite direction. Twin-screw extruders can be used for materials which are difficult to feed thanks to their positive displacement characteristics. Counter-rotating twin-screw extruders are the first choice for profile extrusion. Because the maximum positive displacement is provided by these type extruders. However, co-rotating extruders are commonly used for applications such as compounding, mixing, tipping and chemical reaction due to complex low in them. Superiorities of twin-screw extruders are good mixing and good control over residence time (Shah & Gupta, 2004). Classification of twin-screw extruders is given Table 3.8.

Table 3.8 Classification of twin screw extruders (Rauwendaal, 2014)

Intermeshing Extruders	Co-rotating extruders	Low speed extruders (profile extrusion) High speed extruders (compounding, devolatilization)
	Counter-rotating extruders	Conical Extruders (profile extrusion) Cylindrical Extruders (profile extrusion)
Nonintermeshing Extruders	Counter-rotating extruders	Equal Screw Length Unequal Screw Length
	Co-rotating extruders	Not used in practice
	Coaxial extruders	Inner melt transport forward Inner melt transport rearward Inner solid transport rearward Inner plasticaling, rearward transport

Intermeshing and non-intermeshing terms are used to specify the distance between the screws. In non-intermeshing screws type, the screws are placed apart from each other but side by side. However, for intermeshing screws, the screws that have no clearance between them turn without touching each other. In co-rotating extruders, screws rotate in opposite direction in intermeshing zone, while rotation of screws is in same direction in counter-rotating extruders in intermesh region (Mert, 2007). The polymer is transport by drag flow in non-intermeshing extruders. They are usually used for devolatilization, reactive extrusion operation, coagulation and halohenation of polyolefins since precise heat and shear control can be performed on such extruders. On the other hand, in extruders with an intermeshing design, the screws are interlocked and the polymer is transferred from one screw to the other so that the polymer is transported in positive direction and mixed. They are generally used in applications requiring mixing and compounding at the same time. These types of extruders are also used in bringing together small agglomerates such as carbon dioxide due to having high capacity of dispersing (Harper, 2000). screw configurations of twin screw extruder are shown in Figure 3.2.

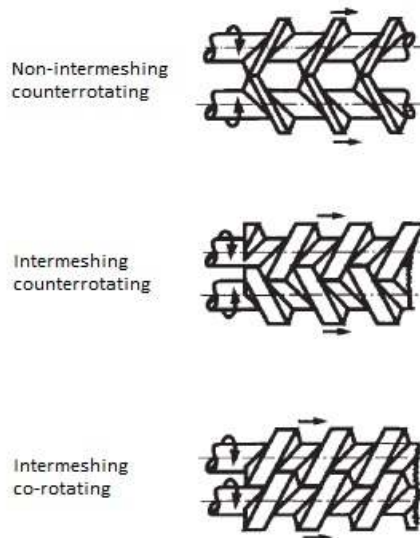


Figure 3.2 Screw configurations for twin screw extruders (Todd, 1998)

In this study, a co-rotating twin screw extruder was used. The brand of extruder is Gülnar Makina and it has 12 mm twin screw with L/D=24. Moreover, maximum achievable screw speed is 800 rpm. By using control panel, temperatures of barrel zones and die and speed of screw can be set thus it is possible to make different experiments with different processing temperature. Extruder which is used in this study is shown in Figure 3.3.



Figure 3.3 Gülnar Makine 12 mm twin screw extruder

Although screw speed was constant in all experiments, temperatures of mixing zones and die are different for polyethylene and polyurethane based mixtures during the extrusion process. While temperatures were 190, 200, 205, 210, 215 °C for hopper, mixing zones and die respectively for polyethylene, they were 165, 170, 170, 150, 130 °C for polyurethane. Screw speed was 100 rpm for both type. Molten products were cooled by air. Then they were passed through the pelletizer and collected in a resalable bag.

3.2.1.2 Injection Molding

Injection molding is one of the most common processing methods for plastics. There is a wide range of uses, from household items to car bumpers. Injection molding used in a large part of industrial production is the one of the most important polymer flow process (Middleman, 1977).

The working principle of injection molding used for the first time in 1872 especially for cellulose was depending on pressure die casting technique. There has been very little development in the coming years even though this was an important invention. In 1920 the first German machine was built. This machine consisted of very simple parts and was fully manual. Another important development in the history of injection molding was the introduction of hydraulically driven machines at the end of the 1930s when many types of thermoplastics have become available. The new generation of equipment, produced in the 1950s, was better at melting polymers and in basic design similar to today's machines although control system are more complicated today (Crawford, 1998).

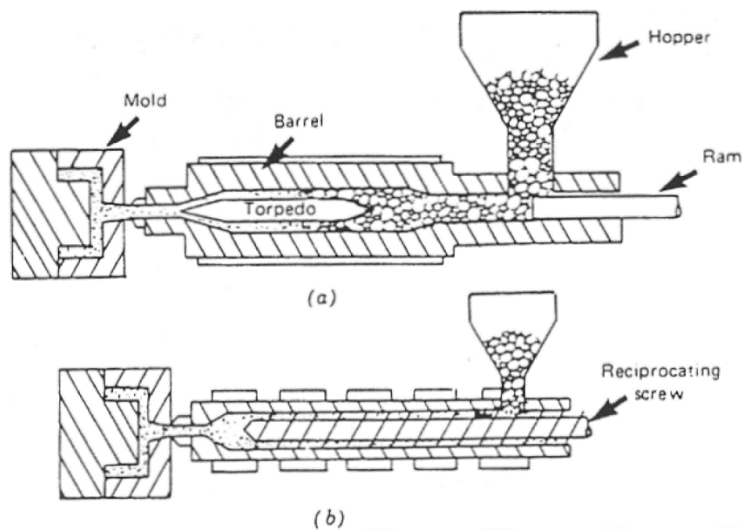


Figure 3.4 (a) ram-fed (b) screw fed injection molding machine (Billmeyer, 1984)

Injection molding, which is a simple cyclic process, consists of three main steps which are filling, packing and cooling. At the beginning polymer melt is repelled forward along a nozzle to cooled hollow of a closed mold which shapes the plastic. When the solidification of the plastic part is completed, the mold is opened and the part is removed. The pressure applied to the polymer in the screw section is kept constant throughout filling step. The packing step pressure is increased and the pressure is kept very high in order to be able to avoid shrinkage and shape changes during the cooling step (Middleman, 1977). Although the temperature of the melt which should be higher than melting point of polymer is controlled by the temperature control unit, it can be influenced from the injection speed and the back pressure (Ferdinand Rodriguez, Cohen, Ober, & Archer, 2003).

Producing pieces in large volume, having high production rates and not needing finishing process are outstanding of injection molding. Injection molding which is nearly automatic decreases the labor costs. Glass and carbon filled polymers or polymer combination can be produced thanks to injection molding. Furthermore, it allows to produce tiny parts which are not possible to produce with other methods (Rubin, 1990). Although injection molding has advantages, injection molding machines and molds are expensive (Tripathi, 2002). Other problems about injection molding are thermal degradation, jetting and short shot. If the flow inside the mold is not uniform, jetting may take place. A short shot can be seen due to the drop in flow due to insufficient process pressures. The flow rate continues to decrease unless pressure is high enough that may cause short shot which is incomplete part because of premature solidification within side of mold (F. Rodriguez, Cohen, Ober, & Archer, 2014). The increase in temperature may occur from high viscosity and slow flow toward mold. Thus thermal degradation may happen (Middleman, 1977).

In this study, just after the extrusion of the samples, they are molded by using laboratory scale injection molding machine which is Xplore IM 12 in Erciyes University. The photograph of this device is given in Figure 3.5. It composed of a

mold that is on the left side of the machine and a pressure cylinder which is at the right side. 16 bars pressure and 400°C temperature can be attained by the injection molding machine.



Figure 3.5 Xplore IM 12

Granules was placed into cylinder by using spoon before the molding process. Two minutes was waited to make polymers melt. Then the melt was injected to the mold with pressure of 8 bars. Two sample was acquired for each molding operation. Two different type molds which had dog-bone and rectangular shape were used. Melt temperature was set to 215°C and 190°C for polyethylene and polyurethane based samples, respectively. Mold temperature was set to 30°C for both polymer type.

3.2.2 Mechanical Properties

The use of polymers is considerably widespread compared to other materials since they can provide the desired mechanical properties at low cost. They are exposed to extrinsic loads during their application. Therefore, designation of mechanical properties and understanding them is important for not only theory but also practice. There are different kind of tests and testing instruments such as tensile test, impact test and hardness.

3.2.2.1 Tensile Test

In order to determine the force required to break the specimen and measure the elongation to breaking point, tensile tests are performed. These may be the most basic type of mechanical test which is used to determine the ductility of material. The test is applied according to standardized testing method. The shape of the specimens is rectangular or dog-bone which can be seen in Figure 3.6 according to this standard.

The edges of the specimen are held by the jaws of the testing machine. Then jaws are spaced by performing of a known force. Specimen elongates until the load which specimen can resist, because it is pulled. It breaks when the applied load is higher than this load. Stress-strain diagram that is used to calculate specify the tensile modulus, can be obtained by tensile test. Thanks to tensile test either modulus or toughness that can be described as energy that can be absorbed by material until break point are determined (Rubin, 1990). While area under the stress-strain curve gives the information about toughness, resilience which is the energy that can be absorbed by material elastically can calculated by the area under the linear part of this curve.

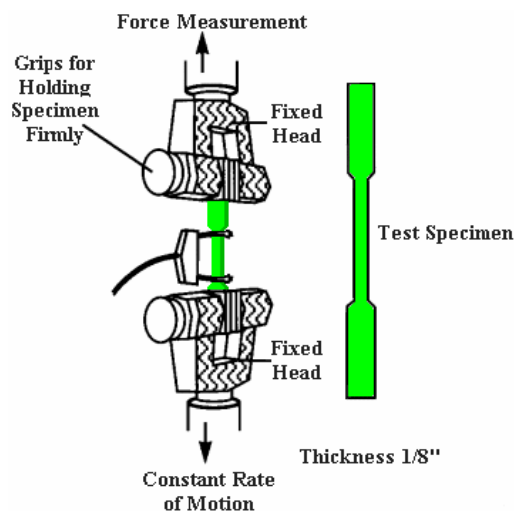


Figure 3.6 Tensile specimen and tensile test procedure (Anonymous)

There are several types of stress-strain curves which represent the different material properties. Some of them are shown in Figure 3.7.

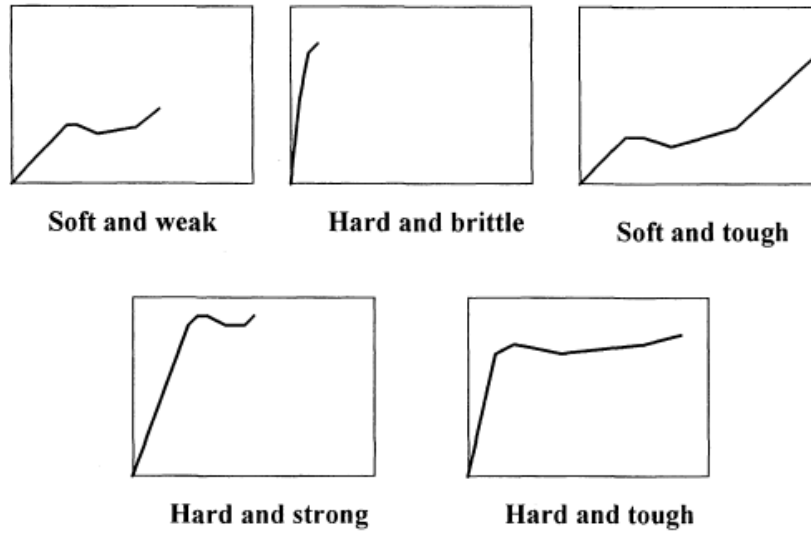


Figure 3.7 Different types of stress-strain curves (Billmeyer, 1984)

Tensile tests of all sample were conducted under favor of Shimadzu AGS-X tensile tester. Shape and dimensions of samples are given in Figure 3.8 and Table 3.9 respectively. The test was continued until the samples failed. The tests were repeated three times and average of them was calculated. Tensile strength, modulus and yield strain were designated by using stress-strain data which was obtained from tests.

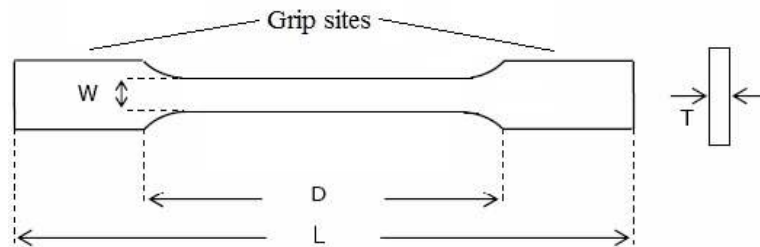


Figure 3.8 Tensile test specimen

Table 3.9 Dimension of tensile test specimen

Symbol	Dimensions (mm)
L: Specimen length	75
D: Distance between grips	43
W : Width of narrow section	4
T: Thickness	4

3.2.2.2 Impact Test

Impact resistance can be defined as the resistance of a material or sample against a sudden load without failure. It depends on material properties such as mechanical properties as well as shape of sample, environment and mode of loading (Mark, 2004).

Pendulum type and falling weight impact instruments are the types of impact test instruments. Specimens can be prepared as notched or without notched and different sizes. In this machines, there is an arm which rotates about a pivot point. A mass is added at the end of this arm. The arm is lifted to its original position, then when it is released it strikes the sample which is mounted. There are two kind of pendulum type machines which are Charpy and Izod types. Schematic representation of these are given in (Mark, 2004).

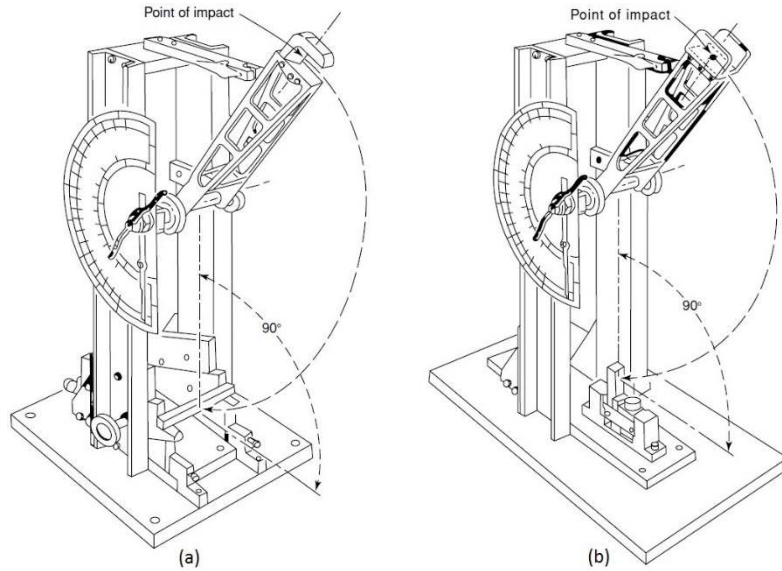


Figure 3.9 (a) Charpy (b) Izod type impact machines

A specimen which is notched, pretends stress concentrator and accelerates the brittle fracture is supported as cantilever in Izod test. By overturning the specimen, Izod impact strength of sample without notch can be determined. Without notch or oppositely notched samples which are supported at their edges can be used in Charpy impact test. Impact resistance and toughness are proportional to each other. While reaction to high and sudden load is measured by impact resistance, low strain rate designates the fracture toughness. Area under the result of tensile test gives toughness which can be enhanced by introducing new phase into polymer. This enhancement also increases impact strength (Mark, 2004).

TE Common Non-Metallic Pendulum Impact Testing machine which is shown in Figure 3.10 was used to perform un-notched charpy impact test, in this study. The length, width and height of the samples were 60, 3, 6 mm, respectively. All the samples were held in liquid nitrogen for five seconds to compare samples impact energies relatively. The tests were repeated three times and average of them was calculated.



Figure 3.10 TE Common Non-Metallic Pendulum Impact Testing machine

3.2.2.3 Hardness

Hardness of a material is specified from the penetration distance of a steel ball into the material. Scratch and abrasion resistance are the other types of hardness measurement methods especially for coatings and molded objects (Ferdinand Rodriguez et al., 2003).

The hardness measurements are related with compressive modulus thus while stiff materials are thought as hard, flexible materials are thought as soft (F. Rodriguez et al., 2014). There is various scales such as Brinell, Vickers, Knoop and Rockwell due to different indentors and loads (Callister & William D., 2007).

Hardness tests are generally performed more than the other mechanical test. Because they are simple and cheap because special sample preparation is not needed and testing machines are relatively inexpensive. Moreover, test can be considered as nondestructive because the only deformation is small indentation and there is no fracture or excessively deformation. Furthermore, some other

mechanical properties such as tensile strength can be estimated from hardness test (Callister & William D., 2007).

The thickness of the specimen should be at least ten times higher than the indentation depth. The distance between specimen border and indentation or the distance between two different indentations should be at least three indentation diameters. Surface smoothness is the one of the most desired property of materials to hardness test. Inaccuracy can be occurred if the thickness of specimen is not enough or center of the different indentation points are too close to each other (Mert, 2007).

Shore hardness measurements were performed by using manual Sauter Shore A and Shore D meters which are shown in Figure 3.11 hardness tester in this study. Six hardness measurements were taken from each specimen at room temperature, and average of them was calculated.



Figure 3.11 Sauter Shore meters

3.2.3 Thermal Analysis

Thermogravimetry (TGA), differential thermal analysis and differential scanning calorimetry (DSC) are the most commonly used methods in order to

determine physical and chemical change of a specimen under temperature change. In this study, thermogravimetric analysis and differential scanning calorimetry are used.

3.2.3.1 Thermogravimetric Analysis (TGA)

Weight loss or gain of specimen as a function of temperature can be determined thanks to TGA technique. When materials are heated, they can lose weight by drying or chemical reactions which give gases to atmosphere. Some materials can gain weight by reacting with the atmosphere due to heat. The amount and the rate of weight change in a material can be measured as a function of increasing temperature in a controlled atmosphere which is generally nitrogen thanks to TGA. The analysis can be performed also in oxygen atmosphere to determine oxidative stability of polymer. Thus stability of the material against temperature increase can be determined. This is also used to characterize materials that show weight change and weight changes because of oxidation, decomposition or dehydration (Billmeyer, 1984).

TGA analysis instrumentation relies on two different methods where the whereabouts of the sample or how it is supported mean a great deal in terms of process characteristics. In the first case the sample is placed on an alumina container that is supported by a very sensitive weight measurement device whereas in the latter the container is suspended usually by a very chemically inert metal rod that is connected to again a weight sensor. The balance is adjusted as zero and sample is heated according to preset thermal cycle. The weight signal, sample temperature and elapsed are transferred to computer. The result of TGA curve is percent weight change versus material temperature (Seymour & Carraher, 1984).

In this study, TGA was carried out to determine thermal stability of the samples by using Hitachi STA7000 which is shown in Figure 3.12. Tests were performed from room temperature to 1000 °C with a heating rate 20°C/min under nitrogen flow of 50ml/min.



Figure 3.12 Hitachi STA7000

3.2.3.2 Differential Scanning Calorimetry (DSC)

Differential scanning calorimeter is the most widely used thermal analyzer in recent years. The DSC term was first used in 1963 at Perkin-Elmer for representing new thermal analyzer that is developed by them (Watson, O'Neill, Justin, & Brenner, 1964). Heat flows and temperatures related with endothermic and exothermic transitions is measured by DSC. It is generally used in plastics laboratories because important properties such as transitions, heat capacity and crystallization kinetics are easily characterized (Lobo & Bonilla, 2003).

Two identical small pans are placed to operate at the same temperature in DSC analysis. Then the temperature can be programmed to increase or decrease at same rate. Sample is placed in one pan and the other pan is empty. Required electrical power to keep two pans at same temperature is measured by DSC. Less or more power, depending on the reaction type, is required to keep the sample and the reference pan at the same temperature when the sample changes phase or state. Area under the curve is the electrical equivalent of the heat of reaction because power value is recorded. The temperature of sample pan and empty pan are brought to some temperature then heated at constant rate. For ensuring the constant rate smaller amount of electrical power is required for empty pan due to being empty (Mark, 2004).

There are two types currently used DSC instruments which are heat flux and power compensation instruments. Schematic drawing of these are shown in Figure 3.13. In power compensated calorimeters, apart heaters are used to transfer heat for sample and reference while heat is transferred to sample and reference via same disk (Billmeyer, 1984).

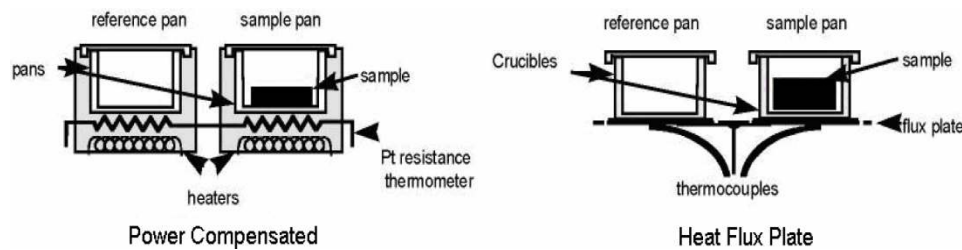


Figure 3.13 Types of Differential Scanning Calorimeters (Anonymous)

For determining glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m) and heat of fusion of polymers (ΔH_f), DSC are used. It is also used in kinetics of chemical reactions such as oxidation and decomposition studies. Moreover, % crystallinity can be calculated by converting measured heat of fusion (area under the curve) when heat of fusion is known for complete crystalline polymer (Sandler, 1998). Typical DSC curve is given in Figure 3.14.

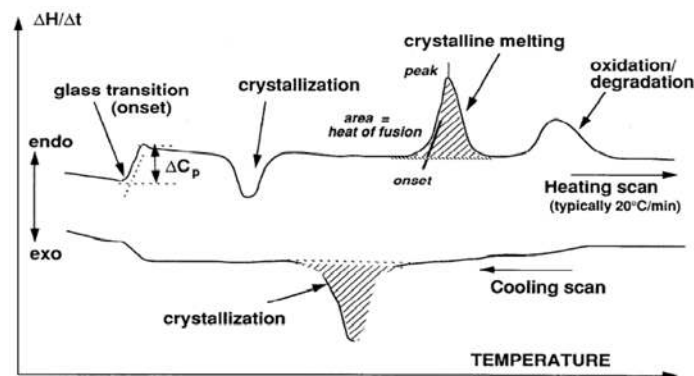


Figure 3.14 Typical DSC curves (Cengiz, 2008)

Although there is some advantage of differential scanning calorimeter such as requiring short time and small sample, being comparative rather than absolute method is the disadvantage of DSC.

In this study, glass transition, crystallization and melting temperatures of samples were measured under nitrogen atmosphere thanks to Hitachi DSC7000X which is shown in Figure 3.15. Weight of the samples were typically about 10 mg. Measurements were executed in the temperature range from 0 to 400 °C with 20 °C/min heating rate for polyethylene based samples. The temperature range was - 80 to 400 °C for polyurethane based samples with same heating rate.



Figure 3.15 Hitachi DSC7000X

3.2.4 Melt Flow Index (MFI)

Melt flow index, also known as melt flow rate, is used to characterize behavior of the molten polymers (Rubin, 1990). Although it is not an intrinsic property for polymers, it is always specified due to determining the general behavior of polymers. It is used to determine the flow behavior of a polymer at a given temperature and pressure. Lower the melt flow index, higher the melt viscosity or melt flow resistance. At the same time, MFI is unstraightforward measure of molecular weight. High MFI indicates to low molecular weight.

The melt flow index machine whose schematic drawing is given Figure 3.16 is basically ram extruder. Barrel is heated to proper temperature for flowing of polymer. Then polymer is placed to the barrel. Polymer is compelled to flow from die by the weight when the polymer is molten and bubble free. After a certain period of time, usually 10 minutes, polymer that was extruded is weighed and melt flow index is defined as grams per 10 minutes.

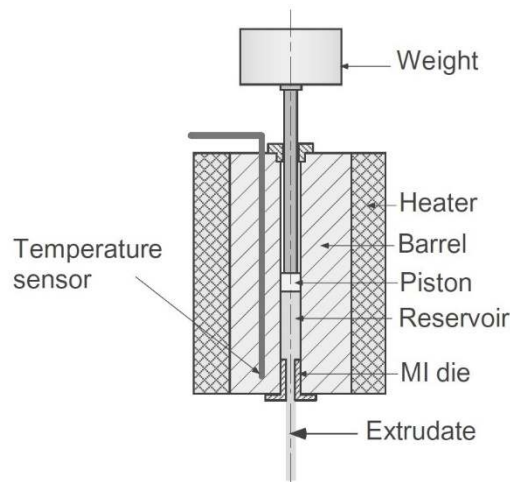


Figure 3.16 MFI test apparatus (Rauwendaal, 2014)

MFI test are carried out at 125°C to 300°C temperature range and 0.325 kg to 21.6 kg loads which provides pressure of 0.46 to 30.4 kgf/cm² with respect to type of the polymer (Shenoy, 2013).

In this study, melt flow index was measured by Zwick Roell Mflow which is shown in Figure 3.17. While measurements were done with load 5 kg at 190 °C for polyethylene based blends, conditions for polyurethane based blends were 2.16 kg loads and 180 °C. Melt index which is defined by the sample weight passing through the die in 10 minutes was detected for all different compositions. The results were recorded as grams per ten minutes.



Figure 3.17 Zwick Roell Mflow

3.2.5 Scanning Electron Microscopy (SEM)

Scanning electron microscopy is the one of the oldest and widely used instrument for surface analysis. Qualitative analysis is comparatively easy because SEM supplies three-dimension image which is formed by scanning a focused electron beam probe across the specimen (Sperling, 2015).

Sample preparation is the most important step for SEM analysis. If the specimens which should be conductors are not conductor, the sample should be covered with a thin conductive layer. Unlike optical microscopes that use light, SEM uses electrons to create images. An electron beam is created in the electron gun on the microscope. When the electron beam strikes the sample, it emits backscattered and secondary electrons. These electrons which is collected by detector are transformed to signal. These signals are monitored by using television like device thus finally, image can be seen on the monitor (Miracle & Donaldson, 2003).

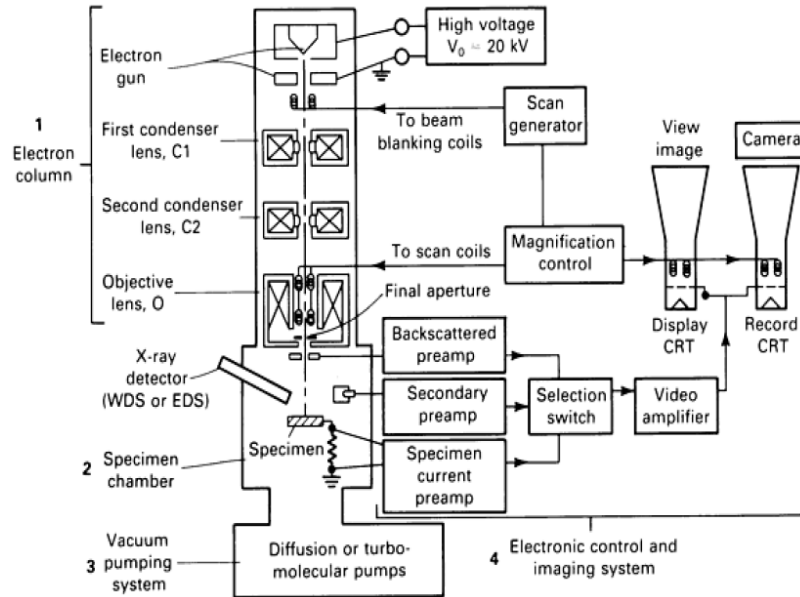


Figure 3.18 Schematic representation of SEM (Miracle & Donaldson, 2003)

SEM is a frequently used in polymer studies and applications to determine surface roughness, fractured surfaces, adhesive failures, phase boundaries and networks.

Liquids and temperature sensitive polymers can also be studied by using SEM. Thanks to energy dispersive x-ray spectroscopy (EDS), it is possible to make qualitative analysis during SEM analysis. Either identification and dispersive of inorganic fillers or inorganic impurities on surfaces can be determined by using SEM (Cengiz, 2008).

Scanning electron microscopy analysis was carried out by using FEI Quanta SEM FEG 650 at Çukurova University, shown in Figure 3.19. Various magnification was used in SEM photographs with an accelerating voltage of 20kV. Although surfaces of the samples could be coated with thin gold layer to get conductive layer, it wasn't done for not losing the background. This analysis was carried out to sight the dispersion of inorganic materials.



Figure 3.19 FEI Quanta SEM FEG 650

4. RESULTS AND DISCUSSION

4.1 Tensile Test

Mechanical properties of polymers alter in a great deal with respect to the amount of mineral filler within the system. The rationale behind using mineral filler is to improve rigidity values of thermoplastic, hence stiffness. Therefore, the first that need to be look at here ought to be elastic modulus values of any blend.

Table 4.1 Tensile properties of polyethylene based blends

	Ultimate Tensile Strength (MPa)	Elastic Modulus(MPa)	Elongation at Break (%)
PE	14.30	155.07	179.95
PE0	13.46	363.78	99.34
PE1	13.37	387.73	74.66
PE2	13.88	389.22	71.00
PE3	13.61	395.60	64.55
PE4	14.62	384.30	69.30
PE5	14.37	347.70	75.56
PE6	13.92	296.58	78.34
PE7	13.36	348.97	72.07
PE8	13.96	323.88	83.02
PE9	13.90	314.14	71.43

Table 4.1 demonstrates the mechanical data of different polyethylene blends. It is observed that an increase in colemanite content leads to a significant increase in stiffness values and the increase continues with an even more increasing colemanite content. However, the case appears to be different for ulexite filler. Although the immediate response to mineral filler input to system is to be an increase in stiffness, introducing a higher amount ulexite filler cause a slight drop

in the stiffness properties. Furthermore, with PE7, PE8 and PE9, the substitution of mineral fillers and its effect on stiffness is also examined. It is quite peculiar that increasing amount of colemanite in the colemanite/ulexite mix leads to a reduction in the stiffness of the polymer.

Table 4.2 Tensile properties of polyurethane based blends

	Ultimate Tensile Strength (MPa)	Elastic Modulus(MPa)	Elongation at break (%)
PUR	10.93	6.25	424.24
PUR1	14.12	6.34	532.81
PUR2	11.54	7.56	423.58
PUR3	11.78	10.49	371.06
PUR4	11.82	6.68	555.05
PUR5	10.66	7.81	548.75
PUR6	7.38	7.94	562.90
PUR7	10.76	6.68	449.39
PUR8	11.31	6.81	439.39
PUR9	11.85	6.57	465.21

Table 4.2 presents the mechanical properties of polyurethane based mixtures. Once more, the filler content has a strong effect on mechanical properties. To examine mechanical properties of these blends, elastic modulus values are chosen to understand the stiffness of the materials. Results reveal that increasing colemanite and/or ulexite filler content lead to an increase in the stiffness properties of the composite, even though somehow in varying degrees. Thermoplastic polyurethane is an extremely ductile material to work with at any rate, thus observing the effect of ulexite on polyurethane appear to be more straightforward than its effect on polyethylene. As to the substitution and its effect on the blend, it can be deduced from the results that there is not much a fluctuation

of results with an alteration in the mineral filler content. Therefore, it would be safe to say that the effect of boron-containing mineral filler substitution is not as clear-cut as other samples.

4.2 Impact Test

In order to interpret the results obtained from impact testing, there needs to be a few correlations that ought to be understood very well. As seen in Figure 4.1 and 4.2, it is undoubtedly clear that with increasing mineral filler input, there is a considerable reduction in the fracture toughness of the material of interest.

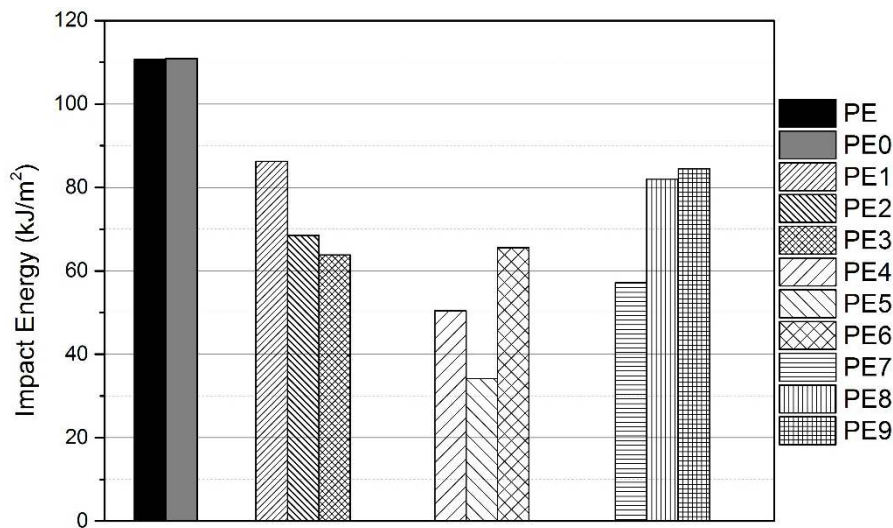


Figure 4.1 Impact energy of polyethylene based mixtures

Furthermore, there needs to be another distinction between the type mineral filler and its effect on the fracture toughness. Results reveal that the usage of colemanite as a filler has less of a detrimental effect compared to ulexite in terms of fracture toughness properties of the material. To monitor this behavior, one needs to inspect the fracture toughness properties of blends that contain both colemanite and ulexite. As seen in Figure 4.1 and 4.2, for samples coded with

number of 7,8,9 (increasing amount of colemanite, respectively), with an increasing colemanite content in the material structure, there is quite a noticeable boost in the fracture toughness properties of the sample.

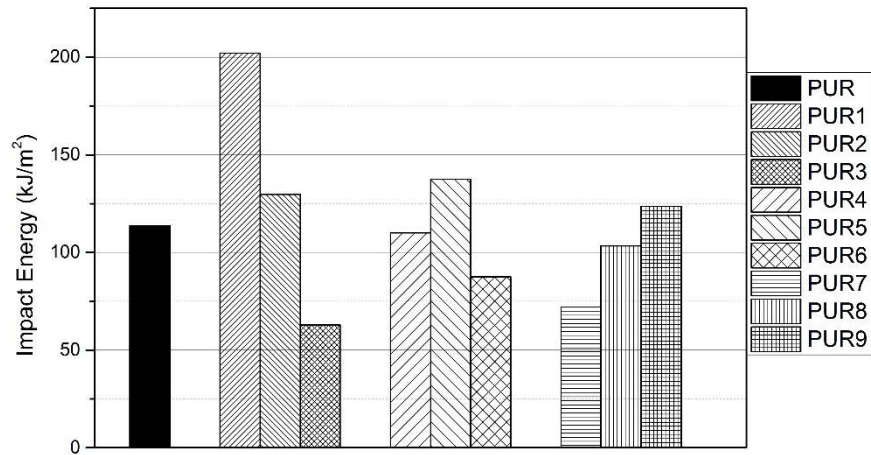


Figure 4.2 Impact energy of polyurethane based mixture

It should also be noted that there is some fluctuation in the data provided by Figure 4.1 and 4.2. This is thought to be due to non-homogeneous dispersion of mineral filler in the structure. Therefore, any fluctuations, such as seen at PE 6 and PUR 5, appear to be due to the inhomogeneity.

4.3 Hardness

Hardness of a given material is a very significant parameter in terms of the mechanical behavior. It can also provide insight towards the composition characteristics of polymer blends for homogeneous dispersion of mineral filler is one of the major concerns of this study.

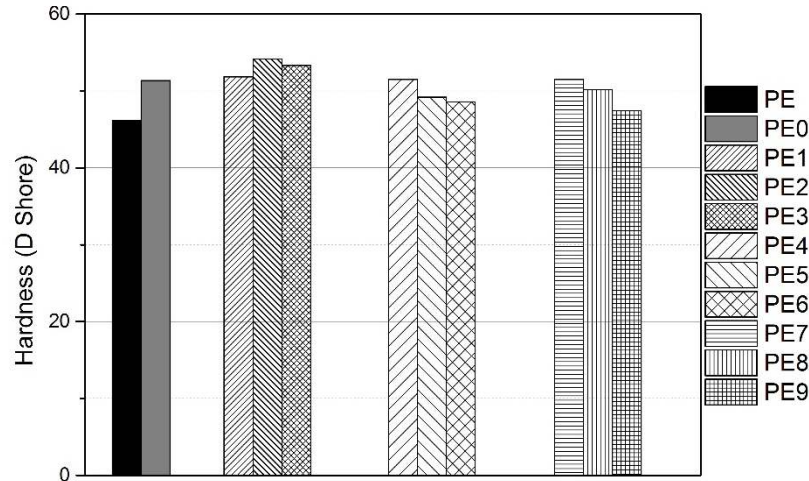


Figure 4.3 Hardness of polyethylene based mixtures

It is known that the hardness of mineral fillers is generally higher than of polymers'. However, it must be perceived that this study's concern is not the comparison of individual polymer and mineral filler in terms of their hardness values. Having said that, Figure 4.3 provides data that is correlative to the assumptions made before.

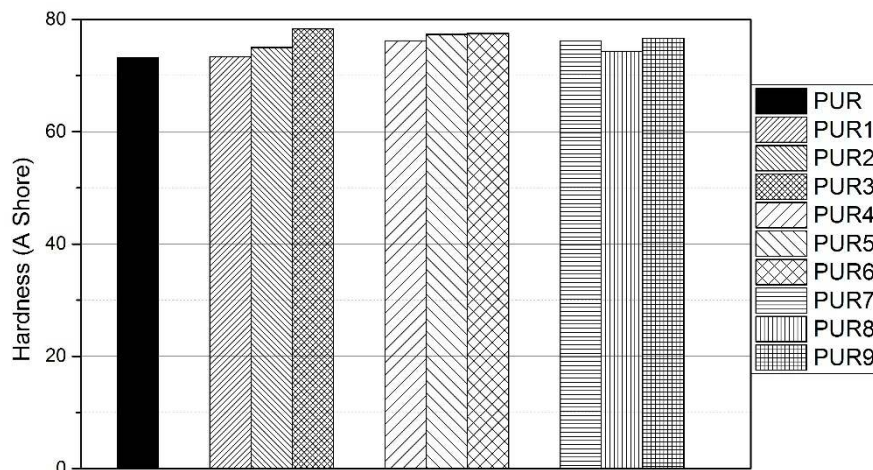


Figure 4.4 Hardness of polyurethane based mixtures

The hardness data chart, in Figure 4.4, shows that indeed there is a steady increase in specimen hardness with respect to increasing mineral filler content, with minor fluctuations for some specimens. Once again, comparison between colemanite and ulexite is drawn, showing that the effect of colemanite on hardness appears to be more dominant than ulexite's, although data is not very consistent and exhibit some vacillations.

4.4 Thermogravimetric Analysis (TGA)

To obtain an appropriate view of thermal properties and characteristics of the samples, thermogravimetric analysis is carried out on the samples, as pointed out in the previous chapter. There are different values and indicatives that needs explaining in the tables presented in this section. Therefore, it would be sensible to examine these abbreviations.

Table 4.3 TGA data of polyethylene based blends

	T _{5%} (°C)	T _{50%} (°C)	T _{max} (°C)	Char Yield (%)
PE	441.87	478.77	668.54	0.96
PE0	415.75	484.30	979.59	15.92
PE1	408.37	468.64	829.16	20.65
PE2	415.56	483.58	959.47	21.37
PE3	409.86	484.85	979.42	24.24
PE4	430.29	484.01	846.46	13.69
PE5	430.70	482.59	883.69	17.97
PE6	419.41	480.34	830.61	21.14
PE7	428.46	485.11	861.47	21.65
PE8	423.21	479.66	780.91	19.69
PE9	425.75	484.89	790.15	20.61

Table 4.4 TGA data of polyurethane based blends

	T _{5%} (°C)	T _{50%} (°C)	T _{max} (°C)	Char Yield (%)
PUR	280.43	375.39	976.70	2.76
PUR1	280.94	364.38	975.68	13.51
PUR2	276.06	368.74	976.42	10.06
PUR3	282.47	373.95	975.24	16.93
PUR4	275.73	358.96	982.88	4.01
PUR5	276.15	351.82	975.97	11.54
PUR6	272.44	350.42	977.00	12.04
PUR7	273.86	354.12	975.68	11.86
PUR8	275.67	354.84	975.68	5.39
PUR9	279.09	360.94	977.53	14.73

T_{5%} signifies the temperature where 5% of the sample is lost. The rationale behind this abbreviation is the same for T_{50%} (°C) which is the temperature where 50% of the sample weight is lost whereas T_{max} (°C) is the maximum decomposition temperature. Finally, Char Yield (%) is the amount of sample materials left in the crucible that is usually in the form of ashes.

In order to interpret the data obtained from TG-DTA analysis, one needs to figure out some thermal characteristics and expected from the samples examined in this study. The theory of thermal property improvement is based on the relatively better thermal properties of mineral fillers doped in the polymer matrix. Therefore, it is expected that with an increasing mineral content, there should be an advancement in the values explained above.

The main trouble with the values shown in tables which are given above may be rooted in the homogeneity and incompatibility problems in the composite structure. Typically, the values indicate that an increase in mineral filler content

reveals itself in Char Yield (%) values, which proves a point that there is indeed the amount of mineral filler targeted in the first place.

The examination of TG-DTA curves affirm that there is sharp loss in weight around 400°C-420°C for PE matrix systems, and 280°C-320°C for PUR matrix systems. Figure 4.5 shows that around 320°C-340°C there is a loss in the $\text{Mg}(\text{OH})_2$. It can be stated that this loss is not observed for samples that contain a certain amount of $\text{Mg}(\text{OH})_2$. Furthermore, 400°C is a very crucial temperature both for mineral fillers used in this study and the polyethylene.

It is thought that at 400°C, the crystallized chemical water in the mineral structure of any decomposes leading a sharp decline in the sample weight. To prove this, one needs to examine polyurethane samples where the polymer properties are not resistant enough to reach 400°C. There is again a decomposition mechanism at work, exposing itself on the curve. All in all, it can be deduced that there is a degree of improvement, however small it might be, in the thermal properties of these samples. TGA curves can be seen below in Figure 4.6 to 4.11.

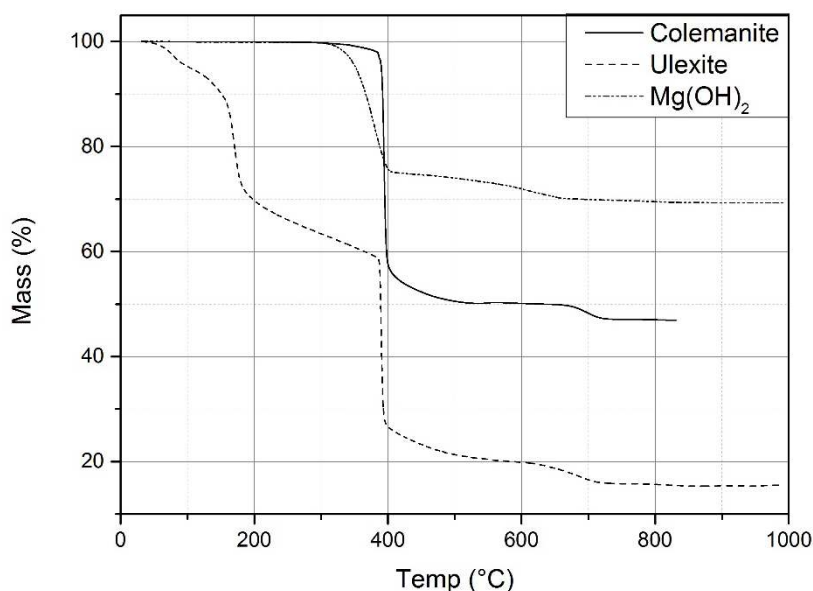


Figure 4.5 TGA curves of colemanite, ulexite and $\text{Mg}(\text{OH})_2$

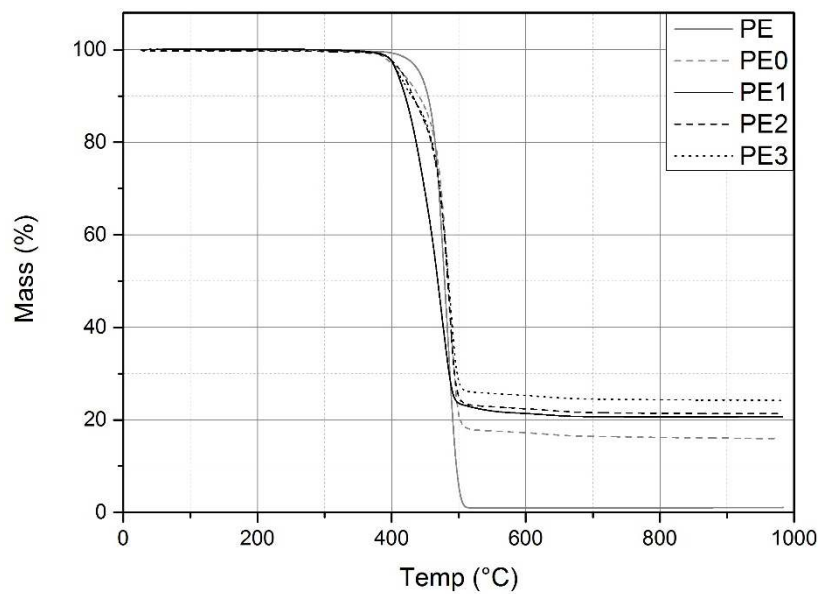


Figure 4.6 TGA curves of chosen compositions

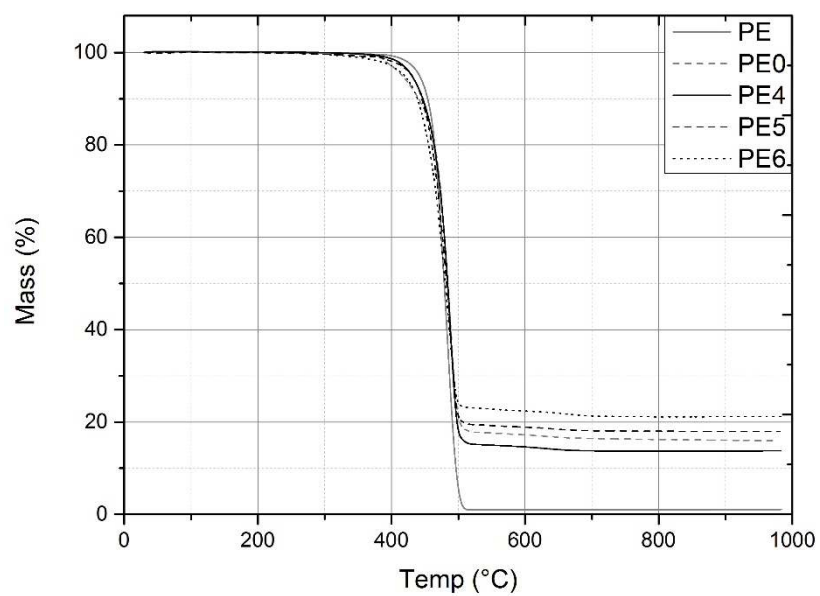


Figure 4.7 TGA curves of chosen compositions

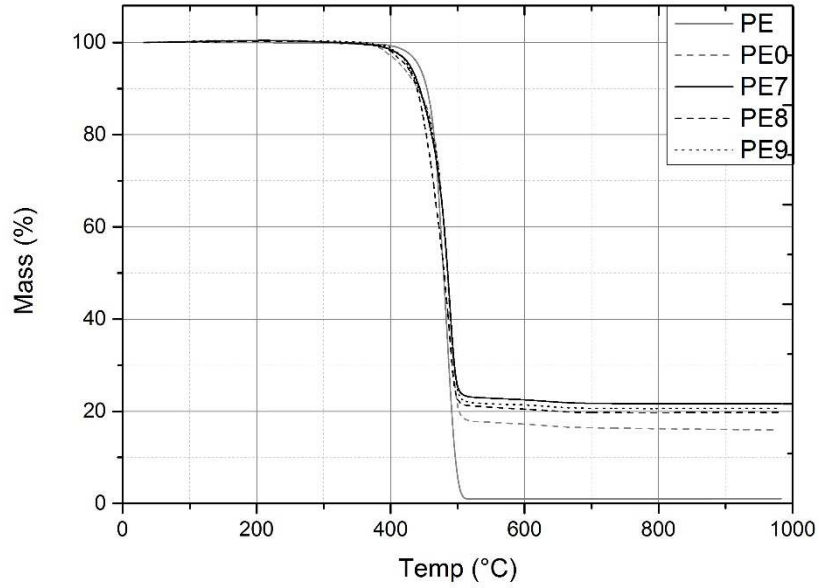


Figure 4.8 TGA curves of chosen compositions

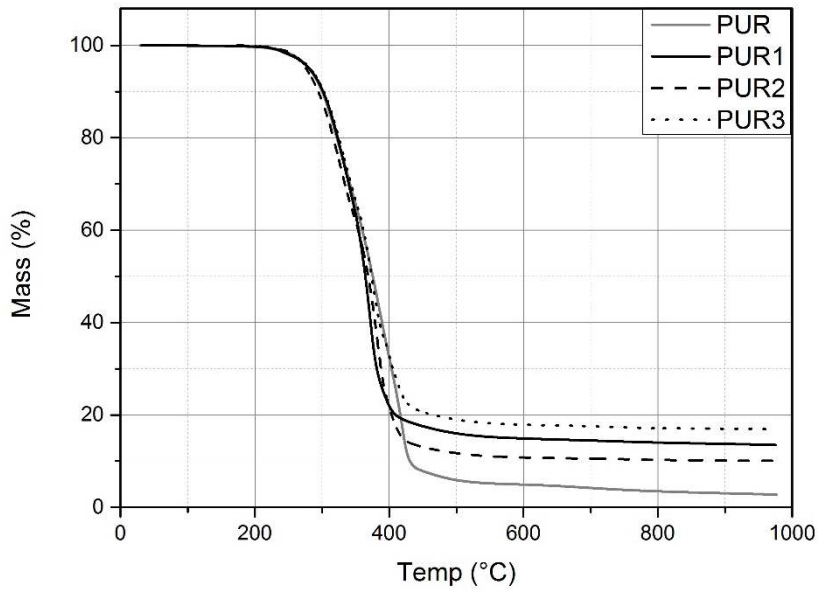


Figure 4.9 TGA curves of chosen compositions

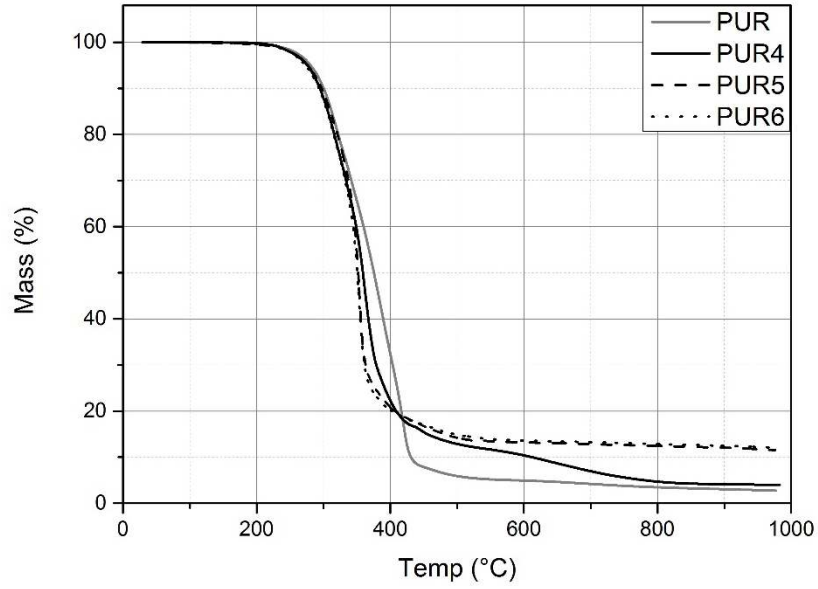


Figure 4.10 TGA curves of chosen compositions

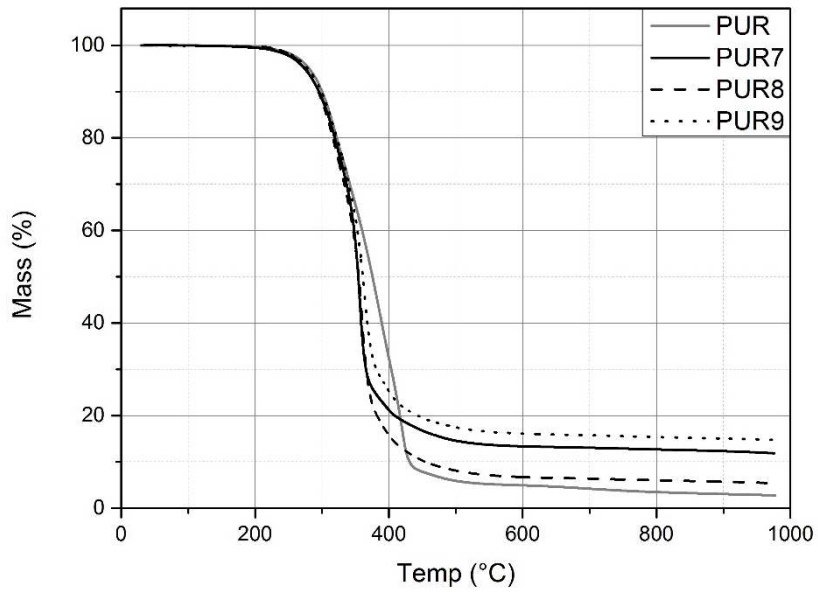


Figure 4.11 TGA curves of chosen compositions

4.5 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is an important tool to investigate different thermal characteristics of polymers such as glass transition temperature (T_g), degree of crystallinity, degree of cure, decomposition kinetics, melting temperature and different first/second order phase transitions.

In this study, DSC is mainly utilized to understand the degree of endothermic decomposition and double-check that it is indeed a decomposition where there is a loss in weight in the thermogravimetric analysis. Another aspect of the examination is to see the T_g for polyurethane samples since the T_g temperature of polyurethane samples is well within the range of the cooler used in this study.

Results indicate that a thermal decomposition takes place starting approximately at the temperature of 300°C as seen in Figure 4.12 to 4.14. Furthermore, the T_g temperature of polyurethane is seen in Figure 4.15 to 4.17 as a small peak as it's a second order transition and could be detected rather difficultly.

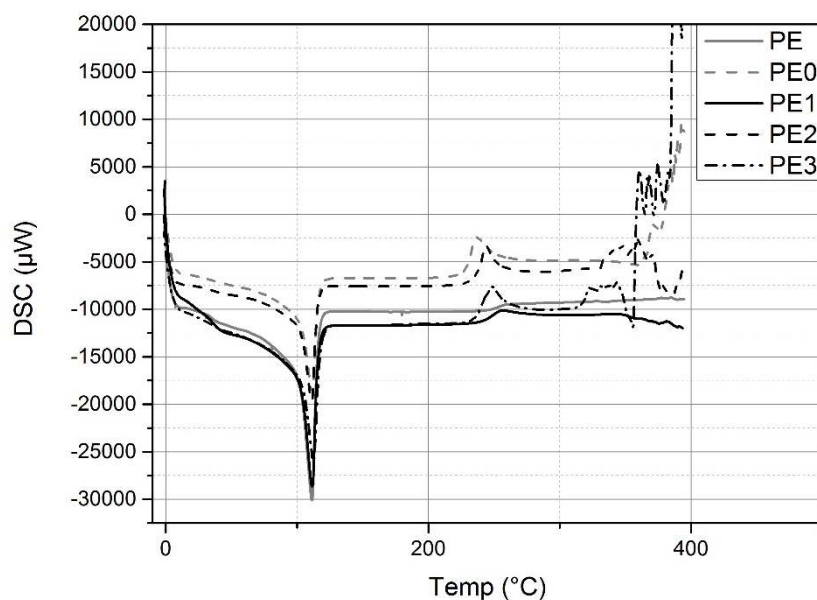


Figure 4.12 DSC curves of chosen compositions

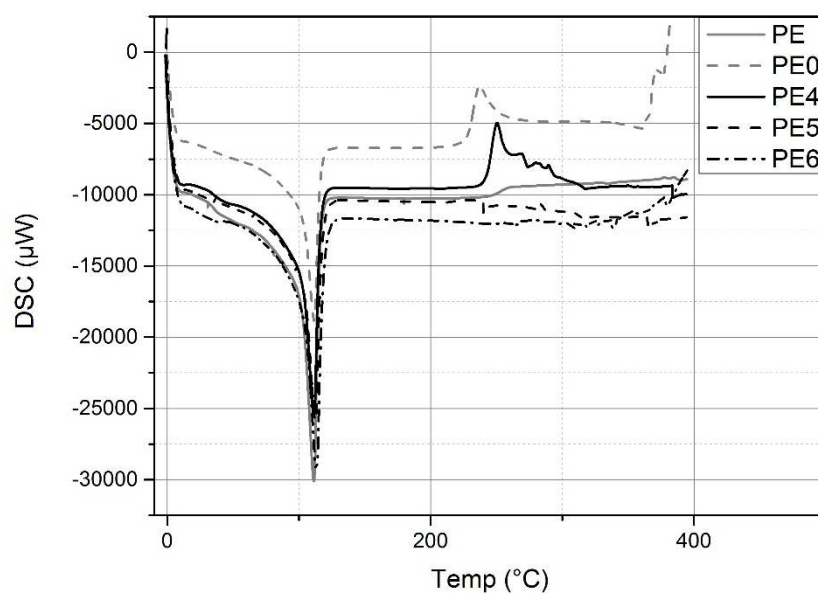


Figure 4.13 DSC curves of chosen compositions

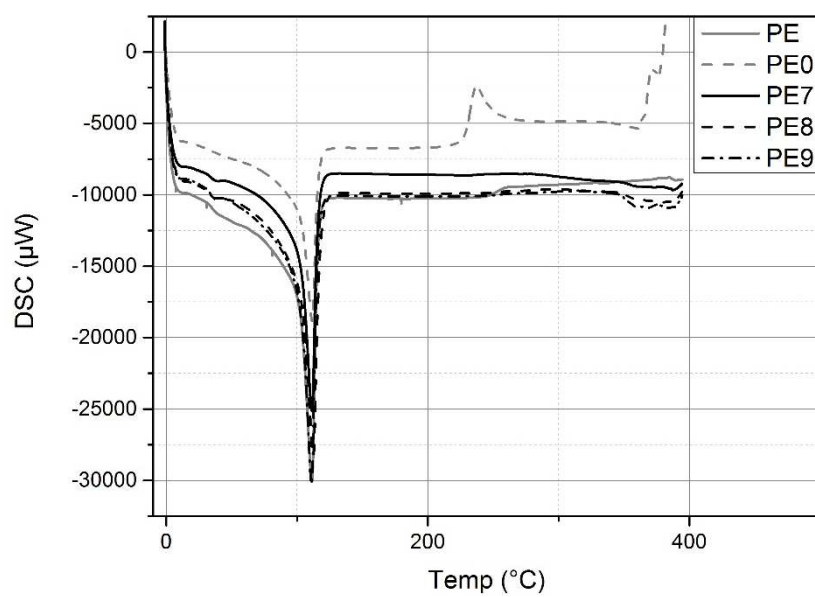


Figure 4.14 DSC curves of chosen compositions

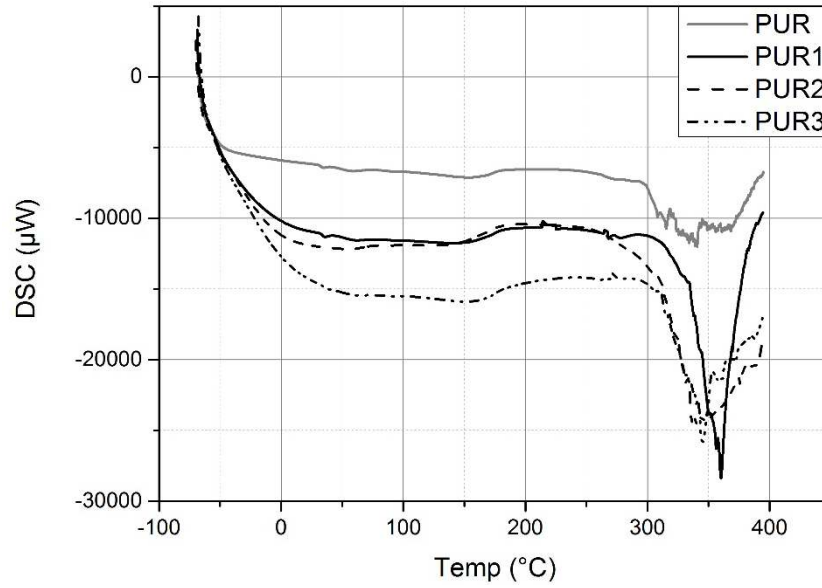


Figure 4.15 DSC curves of chosen compositions

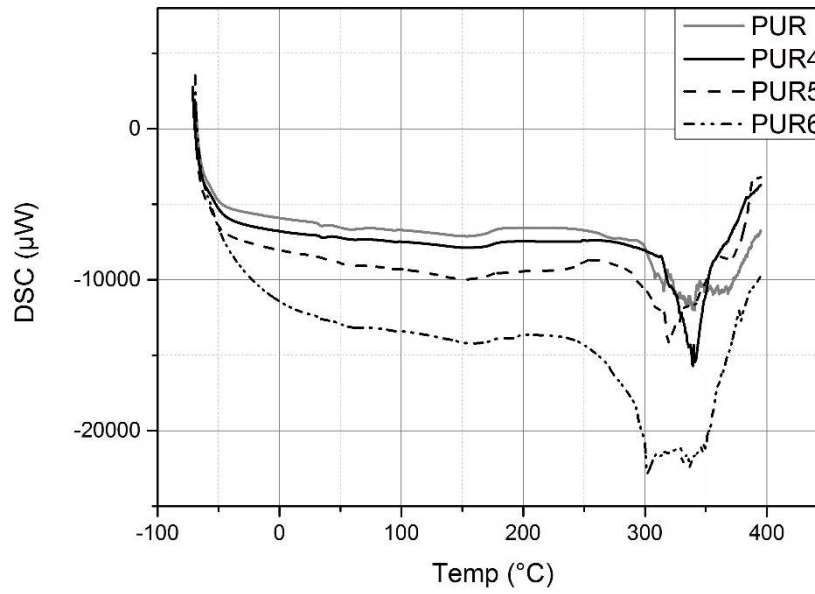


Figure 4.16 DSC curves of chosen compositions

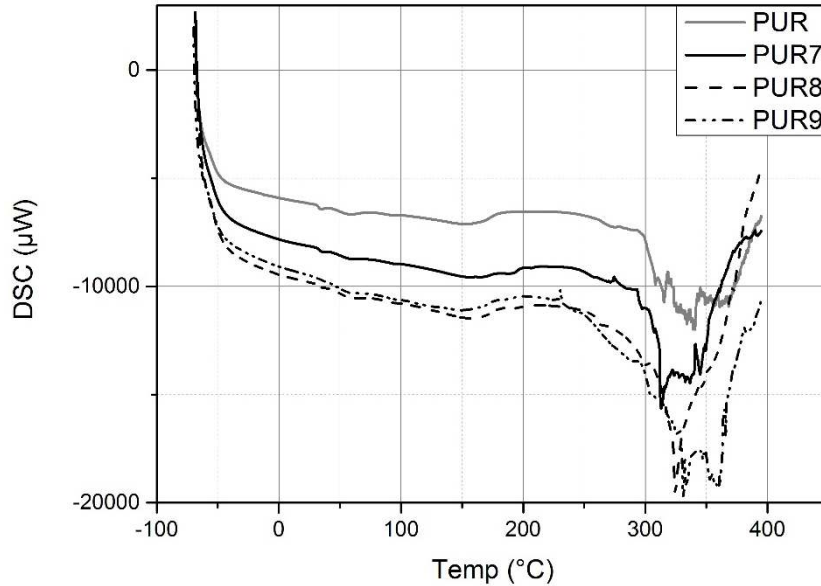


Figure 4.17 DSC curves of chosen compositions

4.6 Melt Flow Index (MFI)

The rheological behavior of polymer melts constitutes a major place in thermoplastic composites manufacturing. Therefore, the melt viscosity of polymer blends is an important parameter in the event of examining manufacturing characteristics of thermoplastic systems. MFI values change with many different parameters such as molecular weight of the polymer, degree of branching, presence of additives and processing methods.

It is expected that a mineral filler to a thermoplastic matrix system would increase the viscosity of the melt and cause the polymer flow to disrupt due to the very nature of these blends. However, the degree of this disruption for PE/PUR – Boron containing filler are yet to be pondered upon.

Figure 4.18 and 4.19 demonstrate that there is an immediate rise in the viscosity of the blends. Even for $\text{Mg}(\text{OH})_2$ -containing polyethylene sample (PE0) there is an increase in viscosity, which is expected. Furthermore, for colemanite/ulexite containing samples of polyethylene, it becomes apparent that

there is indeed an increase in the viscosity of polymer/mineral filler systems with an exception of sample PE2 which might be due to irregularity of homogeneity. For samples PE7, PE8 and PE9 it is expected that the melt viscosities should be roughly the same. Figure 4.18 presents that such case is taken place as samples of question approximately have the same MFI values.

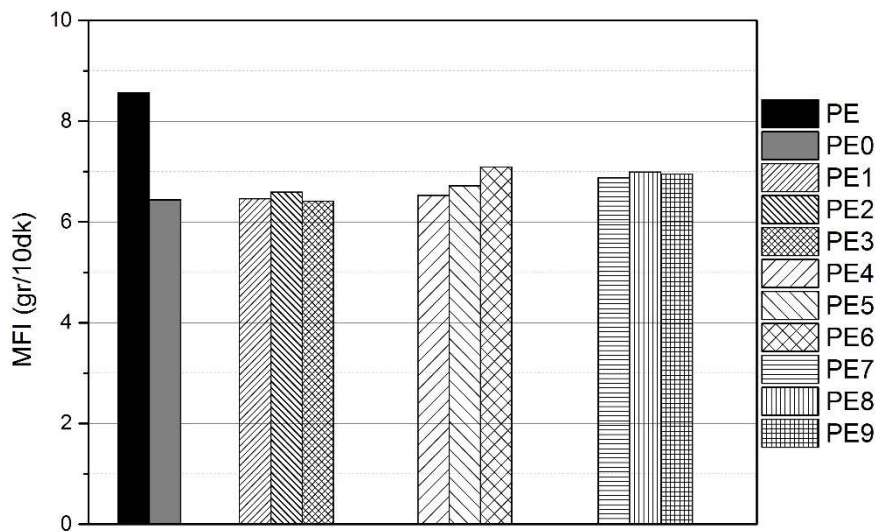


Figure 4.18 MFI test results of polyethylene based samples

Figure 4.19 exhibits the MFI values PUR/Mineral Filler systems. Once again, there is a noticeable decrease in MFI values as the mineral content increases. There is a fluctuation of data in the values of PUR2 and PUR6 which are thought to be due to heterogeneous nature of the blend for PUR2. There is a very extreme behavior on PUR6's part that the viscosity of the blend is even lower than the unreinforced original polymer. There thought to be only one explanation for this phenomenon. During the experimental stages, it is observed that there is a substantial amount of water disintegrated from the ulexite structure. This water could be trapped in some of granules of PUR6 samples and this could be very well the reason why MFI values of PUR6 samples are much higher than its counterparts.

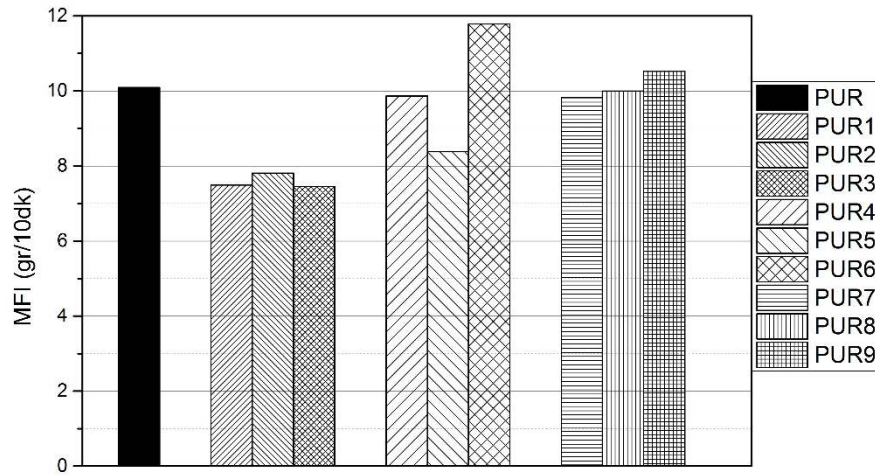


Figure 4.19 MFI test results of polyurethane based samples

4.7 Scanning Electron Microscopy (SEM)

SEM and EDX are often used to justify elemental configuration and morphology of polymer blends. Figure 4.20 illustrates that the mineral filler is not very well dispersed within the structure in terms of the size and distribution of the mineral. The images are complementary to the results obtained with almost all of other tests as there is a significant degree of fluctuation in the results.

Even though, there is a problematic aspect to the distribution of mineral filler within the structure, it's noted that the targeted amount of mineral filler is fulfilled. The EDX results reveal that the boron containing minerals and $Mg(OH)_2$ content is well satisfied and the presence of these is prevalent.

Furthermore, crack surfaces of different samples that represents polyethylene and polyurethane are investigated. The investigation of Figure 4.21 indicates a no noticeable difference in the surface roughness characteristics of samples aforementioned. Due to the ductile nature of polyurethane samples a substantial amount of elongation during the deformation is observed whereas polyethylene specimens appear to be less ductile in terms of surface morphology as seen in Figure 4.21.

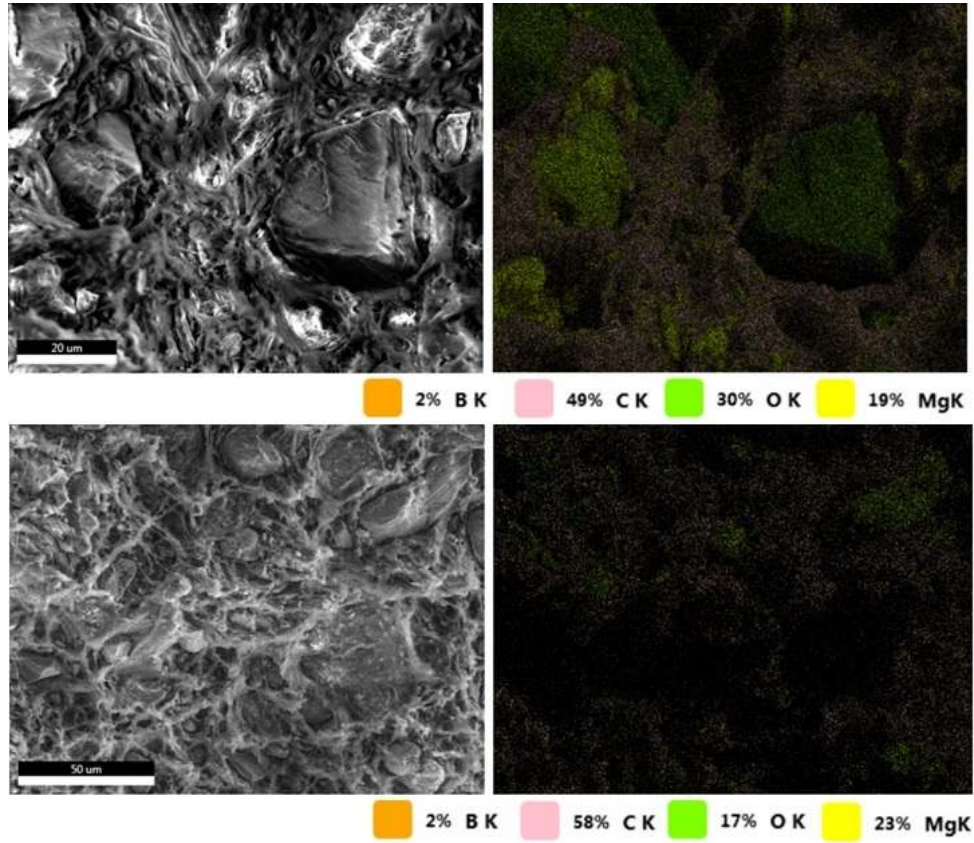


Figure 4.20 SEM images and EDX results

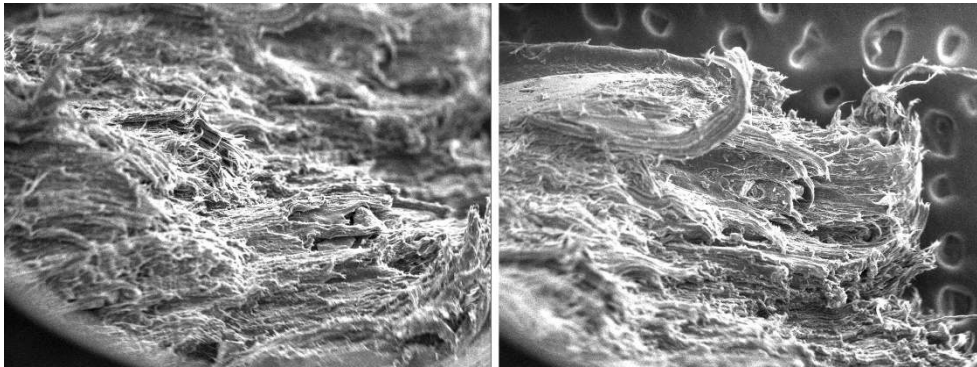


Figure 4.21 SEM image of crack surface of polyethylene and polyurethane

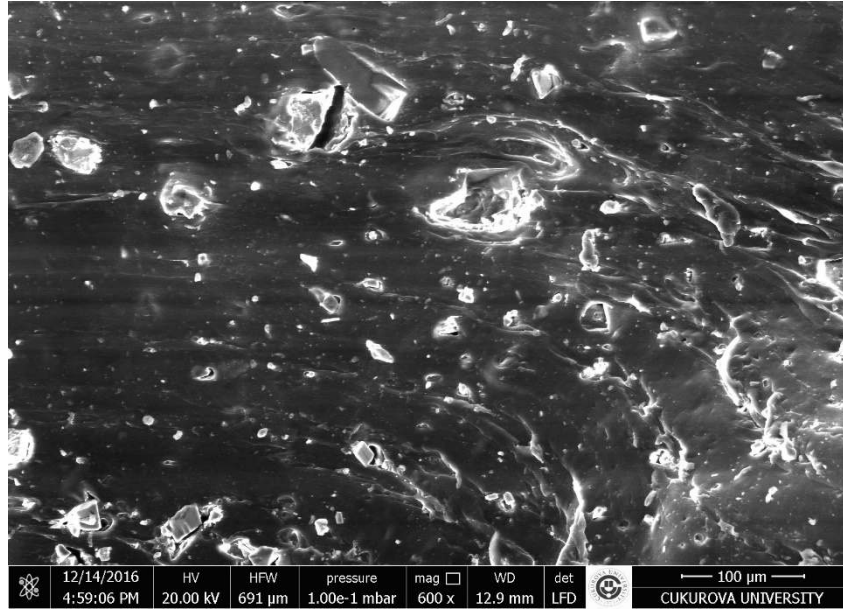


Figure 4.22 SEM image

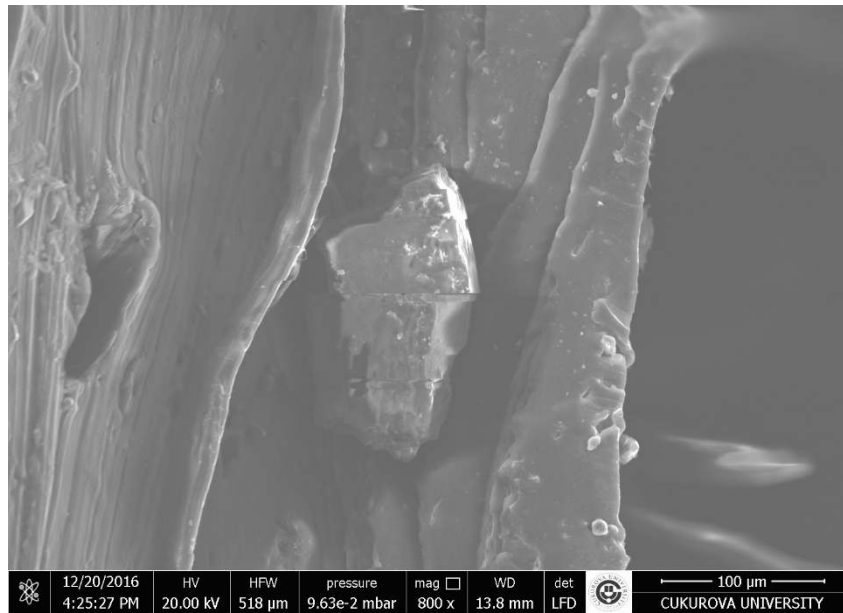


Figure 4.23 SEM image

5. CONCLUSION

In this study, the effects of boron-containing mineral fillers in polyethylene and polyurethane are investigated. The mineral filler content of polyethylene matrix system is reinforced with a $\text{Mg}(\text{OH})_2$ along with colemanite/ulexite to increase the thermal decomposition characteristics of the blend. For polyurethane matrix system, a sole utilization of boron-containing minerals is applied.

Preparation and manufacturing of the blends is obtained via an extruder. The specifications and process temperature of the extruder is given in Chapter 3. After the granulation of blends, an injection molding machine is used in order to attain samples for tensile tests (dog-bone specimens) and impact testing.

Tensile tests carried out on the samples to monitor any improvements on the mechanical properties of the blends. Results reveal that there is not a great change in the tensile strength of the blends, although there is clear improvement in the stiffness for polyethylene samples. It is observed that the elongation at break values for polyethylene samples drop with respect to increasing mineral content, whereas for polyurethane blends the data is not very consistent and a significant amount of fluctuations are observed in the data.

Introduction of mineral filler to polymeric materials usually end up in a sharp drop in impact toughness properties of the polymer. There is not a strong influence of $\text{Mg}(\text{OH})_2$ on the impact properties of the blend. On the other hand, it can be safely said that the impact properties of colemanite/ulexite polymer blends are strongly affected by the addition at a high degree, negatively. However, it should also be noted that there is a noticeable amount inconstancy in the results especially with PUR samples.

The examination of mechanical properties is continued with measurements of hardness. Initially, it should be pointed out that there seems to be not much different in terms of hardness of the samples, the difference being less than 10%.

Thus it's concluded that there is not a great deal of influence of mineral reinforcement in the polymer blend.

Thermal properties of the blends are investigated using TG analysis and Differential Scanning Calorimetry (DSC). It is found that the shift in total decomposition of the polymer is not as expected as it to be. Along with decomposition dynamics of the system, DSC data reveal that there is indeed a vast amount of multiple endothermic peaks around the temperatures where TG analysis indicate that there is a loss in the sample weight. Furthermore, glass transition temperature (T_g) is examined for polyurethane samples and found to be around -50°C. T_g temperatures could not be obtained for polyethylene due to the fact the cooler used in this study is only limited to approximately -70°C.

For thermoplastics, the melt viscosity constitutes a challenge in an aspect of manufacturing. It is thought that addition of mineral fillers would further increase the viscosity of the blends, therefore making the challenge even more difficult to overcome. MFI (Melt Flow Index) results indicate that this is, indeed, the case and the rheological behavior of the polymer melt shifts.

Finally, SEM (Scanning Electron Microscopy) images are collected to analyze the dispersion of mineral fillers in the polymer structure. Additionally, EDX (Energy Dispersive X-Ray Spectroscopy) analysis is obtained in order to gather the elemental configuration of the material, hence prove the presence of the minerals. Results show that mineral fillers are not very well dispersed and agglomeration is commonplace within the material.

The study acknowledges that there are a few challenges to overcome and these are as follows:

- The dispersion of the mineral filler can be achieved through utilization of compatibilizers. The introduction of compatibilizer could increase some of the properties in which there are not as sufficient improvements as targeted.
- The content of colemanite/ulexite can be used solely on their own rather than a combination with $\text{Mg}(\text{OH})_2$.
- The content of mineral fillers can be increased up to 30% for polyethylene and polyurethane polymers and effects can be examined.
- Other boron-containing minerals that contain a higher amount of boron such as boracite ($\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}$) and nobleite ($\text{CaB}_6\text{O}_{10}\cdot 4\text{H}_2\text{O}$) can be used as mineral fillers and their influence on mechanical and thermal properties can be investigated.

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CURRICULUM VITAE

He was born in Tarsus in 1990. He completed primary school in Tarsus and high school in Mersin Science School. He completed Metallurgical and Material Engineering in the Middle East Technical University, which he started in 2008, in 2014. In 2014, he gained experience in a leading company in the automotive industry. In 2015, he started to work as a research assistant in Adana Science and Technology University material engineering. He is still studying as master of science student at the Automotive Engineering Department of Çukurova University and Nanotechnology and Engineering Science of Adana Science and Technology University.