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Investigation of Mechanical and Thermal Properties of Boron Minerals Doped Plastic Materials

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Abstract

In this study, mechanical and thermal properties of boron containing polyethylene and polyurethane was investigated. Manufacturing and characterization are main parts of the experimental study. Samples are manufactured by extruder, then tensile and impact tests samples is obtained by injection molding. Data showed that there is no significant decrease in tensile strength and a notable increase in stiffness. In addition, elongation at break decreases for polyethylene based whereas there is a variety of results obtained from polyurethane samples. While there was a notable decrease in impact resistance of polyethylene-based materials, contrary to expectation there is an increase in some polyurethane based samples. Results obtained in thermo gravimetric analysis (TGA) are lower than expected, however there is a noticeable improvement in the thermal properties of both materials.

Keywords: Colemanite, Ulexite, Polyethylene, Polyurethane

Bor Mineralleri Katkılı Plastik Malzemelerin Mekanik ve Termal Özelliklerinin İncelenmesi

Öz

Bu çalışmada, bor mineralleri içeren polietilen ve poliüretan malzemelerin mekanik ve termal özellikleri incelenmiştir. Deneysel çalışma, malzemelerin üretimi ve karakterizasyonu olmak üzere iki ana bölümden oluşmaktadır. Numuneler ekstrüderde üretilmiş sonrasında ise enjeksiyon kalıplama yöntemi ile çekme ve darbe test çubukları elde edilmiştir. 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 konusuyken, poliüretan malzemeler için beklenenin aksine bazı örnekler için artış gözlenmiştir. Termal özellikler beklendiği kadar olmasa da her iki malzeme için artış göstermiştir.

Anahtar Kelimeler: Kolemanit, Üleksit, Polietilen, Poliüretan

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1. INTRODUCTION

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 [1].

The properties of the polymers can be changed by fillers. Fillers that increase hardness in general increase wear resistance and reduce shrinkage of molded parts. The disadvantages of fillers are the difficulty of processing, reducing the toughness. In particular, polyolefins, which are nonpolar, are incompatible with the common hydrophilic fillers. So the adhesion between the filler surface and the matrix is weak. However, in order to provide some properties such as color, conductivity and flame retardancy, it is generally necessary to use high concentration filler materials [2,3].

Thanks to its versatile properties, polyethylene can be used in many applications. However, its use in applications where flame resistance is important is severely limited. Mineral filler is introduced to polyethylene to overcome this limitation. After the prohibition of halogen-containing flame retardants which are quite effective, halogen free flame retardants such as zinc borate are getting important [4].

Polyurethane used in various sectors such as biomedical, construction, textile and automotive is one of the important polymer class [5]. The properties of the polyurethane can be changed during chemical synthesis or by various additives [6]. Despite disadvantages in degradation under some conditions, easy flammability and thermal stability, polyurethane has good properties for special applications [7].

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 in 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 used in order to analyze and interpret the data in terms of mechanical and thermal properties.

2. MATERIALS AND METHOD

2.1. Material

Polyethylene with a trade name Petilen F2-12 was used in this study. It was supplied from Petkim Petrochemical Holding Inc. in a 5 kg polyethylene bag. The commercial thermoplastic polyurethane (Ravathane ® R130A65) was procured from Ravago Petrochemistry Inc. in a 5 kg polyethylene bag. Colemanite and ulexite are supplied from Bigadiç Boron Works of Eti Maden in a 10 kg bags.

Compositions of all samples which are prepared for this study and their notations are given in Tables 1 and 2.

Table 1. Compositions of samples for PE materials

	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 2. Compositions of samples for PUR materials

	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

2.2. Method

A co-rotating twin screw extruder which is Gülnar Makina 12 mm twin screw was used to produce samples. Although screw speed which is 100 rpm 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. Molten products were cooled by air. Then they were passed through the pelletizer.

Just after extrusion of the samples, they are molded by using laboratory scale injection molding machine which is Xplore IM 12. Granules was placed into cylinder 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.

Tensile tests of all sample were conducted under favor of Shimadzu AGS-X tensile tester. 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.

TE Common Non-Metallic Pendulum Impact Testing machine was used to perform un-notched charpy impact test. 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.

TGA was carried out to determine thermal stability of the samples by using Hitachi STA7000. Tests were performed from room temperature to 1000 °C with a heating rate 20°C/min under nitrogen flow of 50 ml/min.

3. RESULTS AND DISCUSSION

Table 3 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/ulexit mix leads to a reduction in the stiffness of the polymer.

Table 3. 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 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 deducted 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.

Table 4. 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

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 1 and 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.

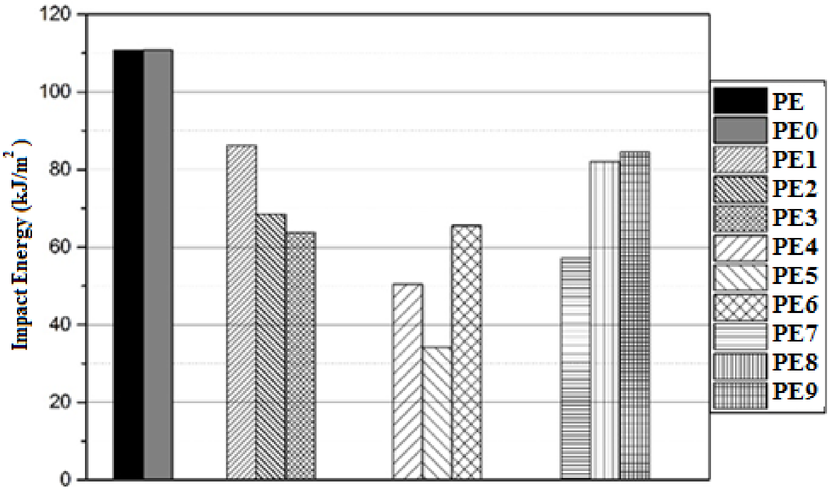

Figure 1. Impact energy of polyethylene based mixtures

Furthermore, there needs to be another distinction between the type mineral filler and its effect on the fracture toughness. Results reveal that the use colemanite as a filler has less of a detrimental effect compared 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 1 and 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.

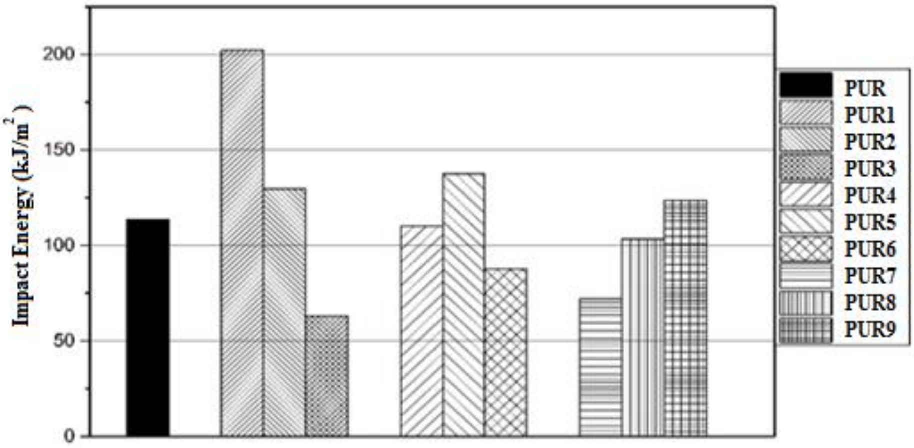

Figure 2. Impact energy of polyurethane based mixture

It should also be noted that there is some fluctuation in the data provided by Figure 1 and 2. This is thought be due to non-homogeneous dispersion of mineral filler in the structure. Therefore, any fluctuations, such seen at PE6 and PUR5, appear to be due to the inhomogeneity.

Thermo gravimetric analysis data are shown in Table 5. $T_{5\%}$ 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. 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 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 400-420°C for PE matrix systems, and 280-320°C for PUR matrix systems as shown in Figures 3 and 4. Furthermore, 400°C is a very crucial temperature both for mineral fillers used in this study and the polyethylene.

Table 5. Thermo gravimetric analysis data (PE)

	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	Char Yield (%)
PE	441.87	478.77	0.96
PE0	415.75	484.30	15.92
PE1	408.37	468.64	20.65
PE2	415.56	483.58	21.37
PE3	409.86	484.85	24.24
PE4	430.29	484.01	13.69
PE5	430.70	482.59	17.97
PE6	419.41	480.34	21.14
PE7	428.46	485.11	21.65
PE8	423.21	479.66	19.69
PE9	425.75	484.89	20.61
PUR	280.43	375.39	2.76
PUR1	280.94	364.38	13.51
PUR2	276.06	368.74	10.06
PUR3	282.47	373.95	16.93
PUR4	275.73	358.96	4.01
PUR5	276.15	351.82	11.54
PUR6	272.44	350.42	12.04
PUR7	273.86	354.12	11.86
PUR8	275.67	354.84	5.39
PUR9	279.09	360.94	14.73

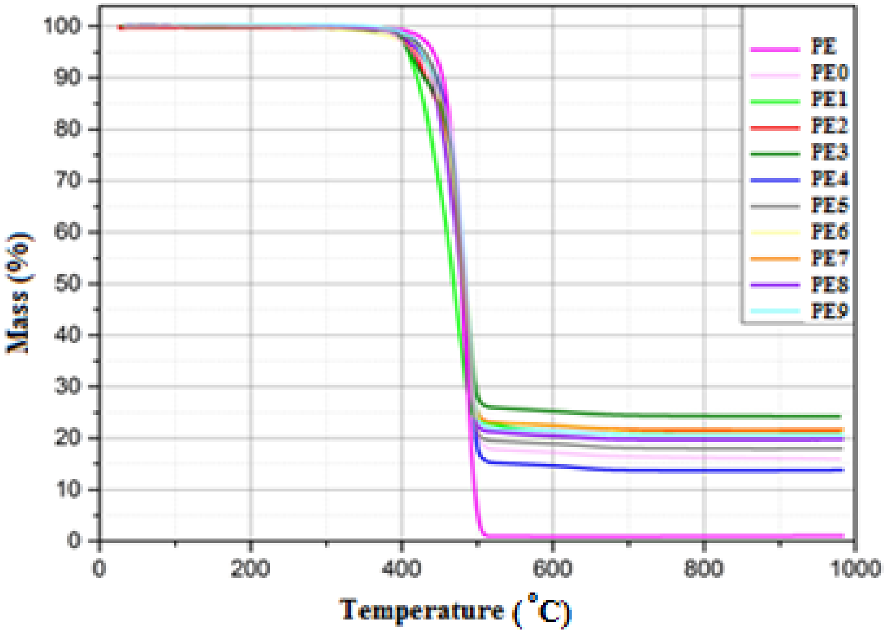

Figure 3. TGA curves of polyethylene based samples

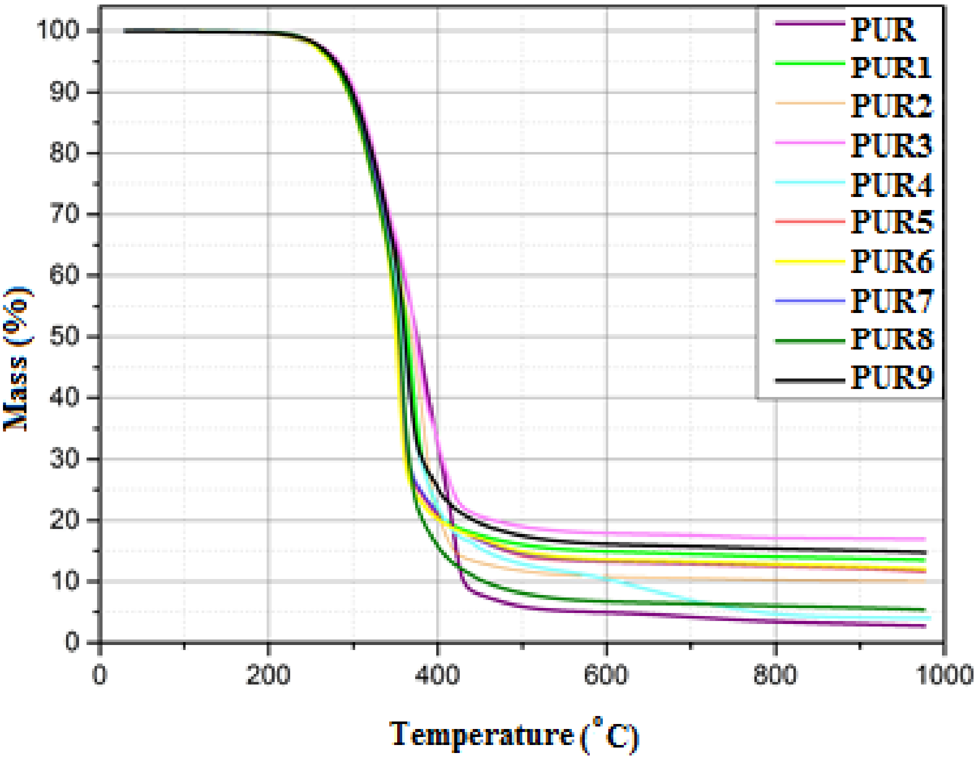

Figure 4. TGA curves of polyurethane based samples

4. CONCLUSIONS

Preparation and manufacturing of the blends is obtained via an extruder. 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. 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 $Mg(OH)_2$ 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. Thermal properties of the blends are investigated using TG analysis. It is found that the shift in total decomposition of the polymer is not as expected as it to be.

For further study, 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. In addition, other boron-containing minerals that contain a higher amount of boron such as boracite ($Mg_3B_7O_{13}Cl$) and nobleite ($CaB_6O_{10}.4H_2O$) can be used as mineral fillers and their influence on mechanical and thermal properties can be investigated.

5. ACKNOWLEDGEMENT

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