

열가소성 폴리우레탄/콜레마나이트 복합재료의 모폴로지 및 기계적 성질

Ferhat Şen^{***}, Seyfullah Madakbaş^{*†}, Emre Baştürk^{*}, and Memet Vezir Kahraman^{*}

^{*}Department of Chemistry, Marmara University

^{**}Department of Food Processing, Bülent Ecevit University

(2017년 5월 30일 접수, 2017년 7월 3일 수정, 2017년 7월 6일 채택)

Morphology and Mechanical Properties of Thermoplastic Polyurethane/Colemanite Composites

Ferhat Şen^{***}, Seyfullah Madakbaş^{*†}, Emre Baştürk^{*}, and Memet Vezir Kahraman^{*}

^{*}Department of Chemistry, Marmara University, 34722 Istanbul, Turkey

^{**}Department of Food Processing, Bülent Ecevit University, 67900 Zonguldak, Turkey

(Received May 30, 2017; Revised July 3, 2017; Accepted July 6, 2017)

Abstract: The aim of this study was to improve thermal stability, mechanical and surface properties of thermoplastic polyurethane (TPU) with the addition of colemanite. The TPU/colemanite composites having various ratios of TPU and colemanite were prepared. The chemical structure of the prepared composites was investigated by Fourier transform infrared spectroscopy (FTIR). Thermal properties of the samples were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Mechanical properties of the samples were characterized with stress-strain test. Hydrophobicity of the samples was determined by the contact angle measurements. Moreover, the surface morphology of the samples was investigated by a scanning electron microscopy - energy dispersive spectrometer mapping (SEM-EDS). Finally, the obtained results prove that the prepared composites have good thermal, mechanical and surface properties and that they can be used in many applications such as the electronic devices, materials engineering and other emergent.

Keywords: thermoplastic polyurethane, colemanite, composites, differential scanning calorimetry, scanning electron microscopy.

Introduction

Thermoplastic polyurethanes (TPUs) because of its high strength, excellent abrasion resistance, chemical resistance as well as low smoke properties is being widely used as a sheathing compound in special purpose low voltage power cables as well as in profile extrusions.¹ TPUs are linear block copolymers consisting of alternating hard and soft segments. The hard segment is composed of alternating diisocyanate and chain-extender molecules (*i.e.* diol or diamine), whereas the soft segment is formed from a linear, long-chain diol. Phase separation occurs in TPUs because of the thermodynamic incompatibility of the hard and soft segments. The segments aggregate into micro domains, and this results in a structure

consisting of glassy or semi crystalline hard domains and rubbery, soft domains that are below and above their glass-transition temperatures (T_g 's) at room temperature, respectively. The hard domains act as physical crosslinks and impart elastomeric properties to the soft phase. Because of the absence of chemical crosslinking, TPUs are able to be processed via melt and solution methods.²

Colemanite is a natural rock that contains boron oxide. It is being used as raw material for instance in glass fiber. It is mainly found in Turkey and a few other places in the world. The typical constituents of colemanite are 44.5% B_2O_3 , 27.0% CaO , 2.0% MgO , 0.05% Fe_2O_3 , 4.5% SiO_2 .³ Commercially, the most-used compounds of boron are boric acid, boron oxides, and sodium perborate. In Turkey, in the production of these compounds, ulexite and colemanite are used as raw materials. There is an inverse proportion between scientific researches on boron and industrial interest in these researches.

[†]To whom correspondence should be addressed.

E-mail: smadakbas@marmara.edu.tr

©2017 The Polymer Society of Korea. All rights reserved.

While there are numerous studies on boron compounds such as metal borates, fluoroborates, borohydrides, carbon-boron compounds and these compounds have a share of approximately 99% of the scientific studies, the production of only four compounds of boron, borax, boric acid, calcium borate, and sodium pentaborate has a share of approximately 99% of industrial boron applications both quantitatively and economically.⁴

In the recent years, various composites studies have been done in order to improve the properties of TPUs. In one study, TPU/kenaf composites were prepared and the composites exhibited better mechanical properties in comparison with the TPU.⁵ In another study, novel thermoplastic composites elastomer material based on poly(styrene-butadiene-styrene) (SBS), ester-type polyurethane and ether-type polyurethane materials were prepared via melt blending and reported that the thermal resistance, dynamic damping and mechanical properties of SBS before and after thermal aging are improved as the amount of added TPU is increased.⁶ In another study, TPU/nanoclay composites were prepared and reported that the accelerated ageing process applied to the TPU composites led to an increase in the values for the mechanical properties, compared to samples without nanoclay.⁷

There are considerable studies regarding the evaluation of boron compounds in the literature. Korkut *et al.*⁸ studied neutron shielding properties colemanite, ulexite and tincal based on number of boron atoms by using experiment and simulation process. Binici *et al.*⁹ used colemanite, barite, ground basaltic pumice and ground blast furnace slag as additives in the production of mortars and determined mechanical and radioactivity shielding performances of the mortars. Kaynak *et al.*¹⁰ utilized colemanite as flame retardant in high-impact polystyrene containing brominated epoxy and antimony oxide. Isitman *et al.*¹¹ purposed to enhance flame retardancy of low-density polyethylene with adding combination of aluminum hydroxide and colemanite. Baştürk *et al.*¹² tried to improve mechanical, thermal and surface properties of bisphenol A dicyanate ester with bisphenol P dicyanate ester and colemanite. In the grand scheme of these studies mentioned above, boron compounds are especially effective to improve thermal stability and prevent radiation transmission with important lightweight and cost benefits. However, certain percentages of boron compounds can cause a decrease in mechanical strength of the materials.¹³

With this article, TPU/colemanite composites are reported for the first time. In this study, TPU/colemanite composites

having different ratios of TPU and colemanite were prepared and characterized. Thermal stability, mechanical properties and hydrophobicity of the samples were determined. The surface morphology of the samples was investigated.

Experimental

Materials. TPU used in the study was a adipate ester polyurethane (LARIPUR® LPR6325), kindly donated by local supplier. Colemanite was donated from Eti Maden (Turkey). It mainly comprises 40% B₂O₃, 27% CaO, 6.5% SiO₂ and the particle size of ≈45 microns. Dimethylformamide was purchased from Merck. All chemicals were high grade reagents and were used as they were received.

Preparation of TPU/Colemanite Composites. The TPU/colemanite composites having different ratios of TPU and colemanite were prepared. Table 1 shows the composition of the composites. Samples were designated as FX where X stands for the weight fraction of colemanite. For example, F3 means that the weight fraction of colemanite is 3%. The calculated amount of TPU, colemanite and 70 mL of dimethylformamide were stirred for 4 h by using magnetic stirrer at 80 °C under reflux. Then, the mixture was left in the ultrasonic bath for 30 min. The resultant mixture was poured into a mold and then dried at 60 °C under vacuum for 24 h. The composites were obtained as films with a thickness of 0.1 mm.

Measurements and Characterization. FTIR spectrum was recorded on Perkin-Elmer spectrum 100 FTIR spectrophotometer. The parameters of the device for the analysis were as follows: Resolution 2 cm⁻¹ and a frequency range of 400-4000 cm⁻¹.

The thermal decomposition behavior of composites was determined by using Perkin-Elmer thermogravimetric analyzer Pyris 1 TGA model. The composites were heated at 10 °C min⁻¹ to 750 °C under nitrogen atmosphere.

Glass transition temperature of the composites was determined by DSC analysis using Perkin-Elmer Pyris Diamond

Table 1. Formulations of the Composites

Sample	TPU (g)	Colemanite (g)	Colemanite (wt%)
F0	2	-	-
F1	2	0.02	1
F3	2	0.06	3
F5	2	0.10	5
F7	2	0.14	7

differential scanning calorimeter. Samples were heated from -30 to 200 °C, both at a heating rate of 5 °C min⁻¹, and cooled at the same rate under nitrogen flow (flow rate 25 mL min⁻¹).

Mechanical properties of the composites were determined by standard tensile stress-strain tests to measure the modulus (E), ultimate tensile strength (δ) and elongation at break (ϵ). Standard tensile stress-strain experiments were performed at room temperature on a materials testing machine Z010/TN2S, using a crosshead speed of 2 mm/min. Standard of ASTM D3039 was used in the testing of mechanical properties of composites. The test specimen size 60×10×1 mm.

Wettability characteristics of composites were performed on Kruss (Easy Drop DSA-2) tensiometer. A sessile drop method was used to measure a contact angle (θ) with a 3-5 μ L distilled water drop, which was applied to the surface by a pipette. The image of the liquid drop was captured by a video camera and then transferred to a computer screen.

The composites' morphology was determined by SEM using Phillips XL 30 ESEM-FEG microscope.

Results and Discussion

FTIR Spectroscopy of the Composites. Figure 1 shows the infrared spectra of TPU and TPU/colemanite composites.

Two main regions are of interest in this study, -NH absorption and -C=O stretching. It is seen in Figure 1 that the -NH absorption peak at 3325 cm⁻¹ was due to hydrogen-bonded -NH groups of urethane linkages. In this case, such hydrogen bonding can be formed with hard segment carbonyl and with soft segment ether linkages. The peak at 1727 cm⁻¹ is assigned to free urethane carbonyl, while the peak at 1697 cm⁻¹ is due to hydrogen bonded carbonyl. The peaks at 2917 cm⁻¹ and 2959 cm⁻¹ in the spectra can be attributed to the asymmetric and symmetric stretching vibrations of -CH bonds. In addition, urethanes are observed band features of the isocyanates at 1520 and 1080 cm⁻¹. These bands are typical of the bending N-H and stretching C-N bonds.¹⁴

Thermal Properties of the Composites. The thermal stability of polymeric materials is very important when they are used as flame retardant systems, which mainly concerns the release of decomposition products and the formation of char. Many authors suggest that urethane group is unstable at high temperature and that, depending on the type of diisocyanate, the structure of the hard segment and the composition of polyurethane, thermal degradation reactions can occur during heating.¹⁵ Thermal properties such as thermal stability and glass transition temperatures of TPUs is being developed by adding various inorganic additives.¹⁶ TGA technique was used to

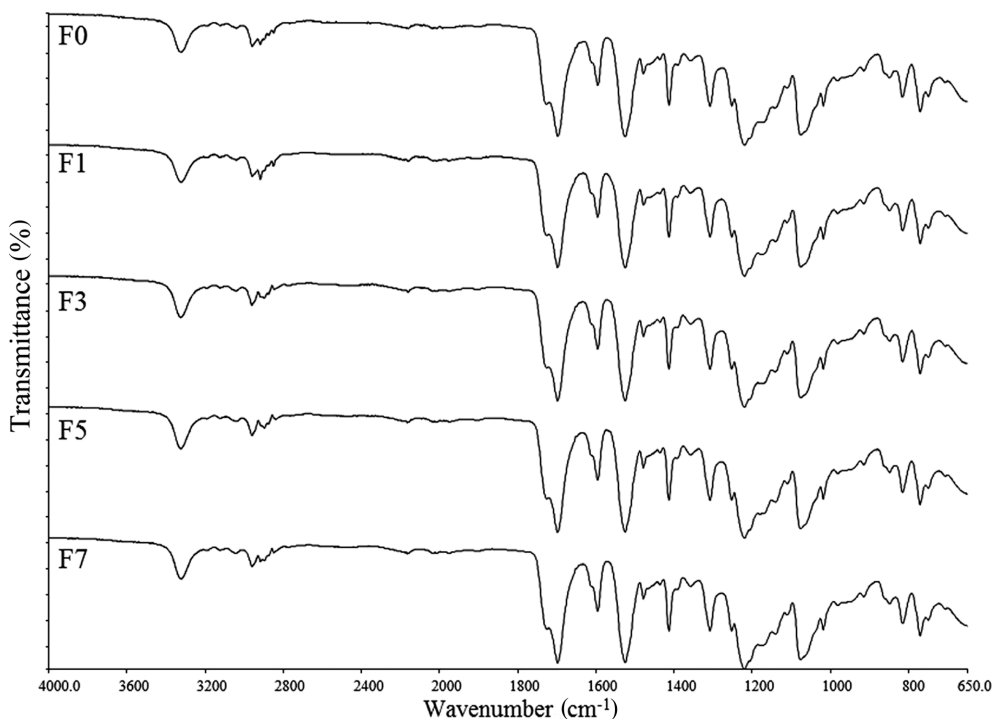


Figure 1. FTIR spectra of the composites.

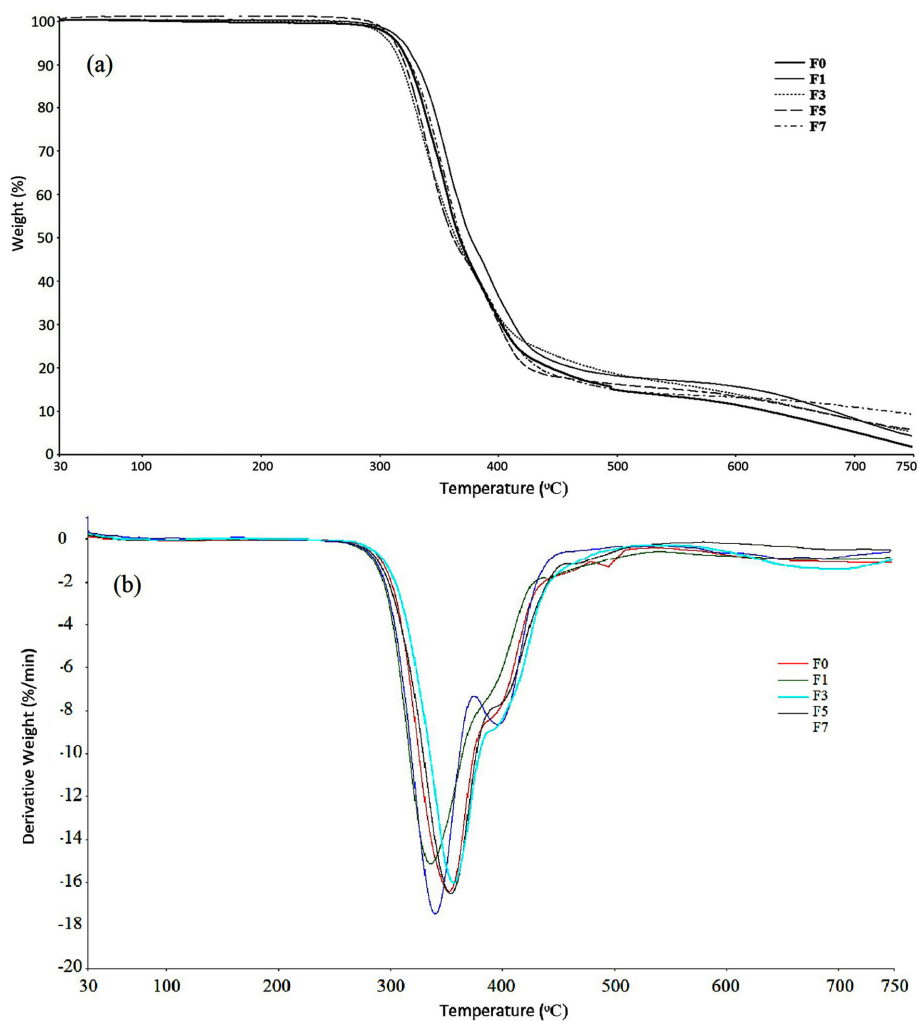


Figure 2. (a) TGA thermograms of composites; (b) derivatives of the TGA thermograms.

investigate the thermal oxidative stability of composites. In Figure 2 the TGA thermograms and derivatives can be seen and the evaluated char yield (%) data were listed in Table 2. Results of the TGA experiments indicate that all composites began to lose weight above 300 °C. This was followed by a rapid thermal decomposition with further heating. It can be seen that the temperature corresponding to 5 wt% loss and the

temperature of maximum weight loss for the composites are about 310 and 345 °C, respectively. As a result of the further degradation process, the char yield increased when colemanite content were increased. The char yield increased 7.57% with the addition of 6.54% colemanite to the formulations. The char formation is very important for flame resistance. It isolates polymer, prevents feeding the flame, and the air inlet in the polymer.

Figure 3 shows the DSC thermograms of TPU and TPU/ colemanite composites. Glass transition temperatures of the composites are given in Table 2. DSC results indicate that with the addition of colemanite, it causes T_g values of the composites to increase. While neat TPU has a T_g value of -1 °C, the glass transition temperature of F7 raised to 32 °C. This situation can be attributed to the loss of mobility of the polymer chains of composites due to the decrease in the free volume.¹⁷⁻¹⁹

Table 2. Thermal Properties of the Composites

Sample	Char yield (%)	T_g (°C)
F0	1.74	-1
F1	4.30	4
F3	5.32	13
F5	5.86	17
F7	9.31	32

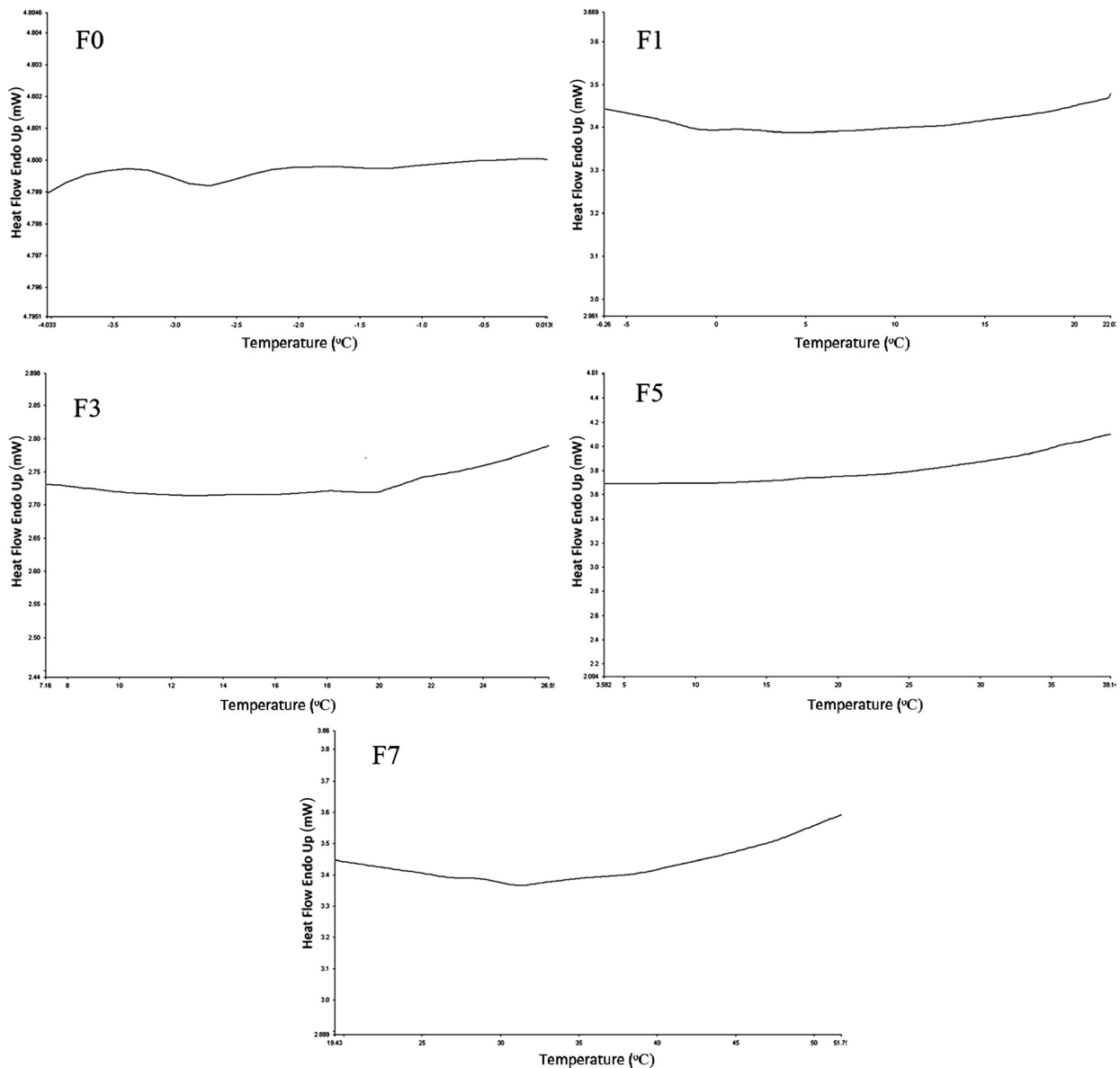


Figure 3. DSC thermograms of the composites.

The melting point (T_m) of the composites in DSC results was not observed.

Mechanical Properties of the Composites. It was reported that TPUs show good mechanical properties and these properties increase by adding various inorganic additives.²⁰ In Figure 4 the stress-strain curves can be seen and the evaluated data were listed in Table 3. Table 3 shows the mechanical properties of the TPU/colemanite composites. Results indicate that modulus, tensile strength, strength at break, tensile elongation and elongation at break increased by increasing the content of colemanite. Especially, there is a significant increase in tensile elongation and elongation at break. This increase is due

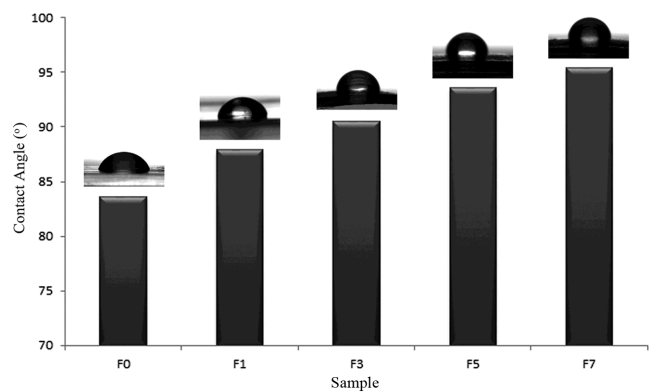


Figure 4. Contact angle values of the composites.

Table 3. Mechanical Properties of the Composites

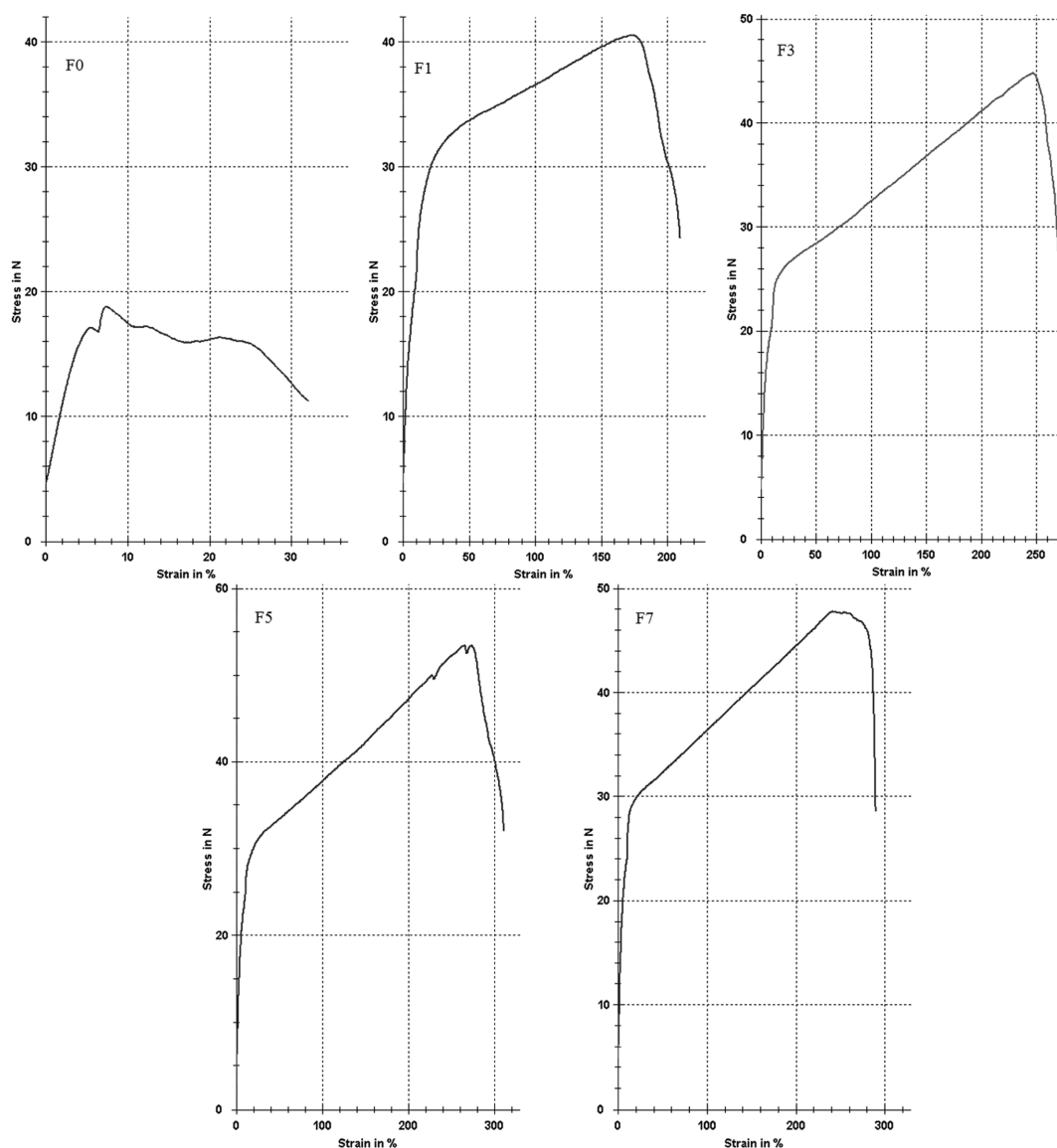
Sample	Modulus (MPa)	Tensile strength (MPa)	Tensile elongation (%)	Strength at break (MPa)	Elongation at break (%)
F0	39.3	2.9	7.4	17.7	32.1
F1	48.9	6.2	172.5	38.2	209.8
F3	50.4	6.9	247.4	42.2	270.7
F5	60.9	8.2	265.5	50.3	310.9
F7	58.9	7.4	241.3	44.9	289.6

to the structural character of colemanite. These results prove that the mechanical properties of the TPU were increased with the addition of the colemanite. Colemanite contributed pos-

itively to the mechanical properties of composites.²¹ It was observed a decrease in the mechanical properties of the F7 sample. This situation can be explained that colemanite has been agglomerated in a high concentration.

The Surface Wettability Properties of the Composites.

The surface wettability properties of the composites were investigated by water contact angle measurements. Contact angles are very sensitive to the surface composition changes. Each contact angle value is given in Figure 5 which represents an average of 5 readings. As it can be seen from the Figure 5, when colemanite was added into TPU, the contact angles have the tendency to increase the hydrophobic behavior on the surface. The high values of the contact angle that was measured

**Figure 5.** Stress-strain curves of the composites.

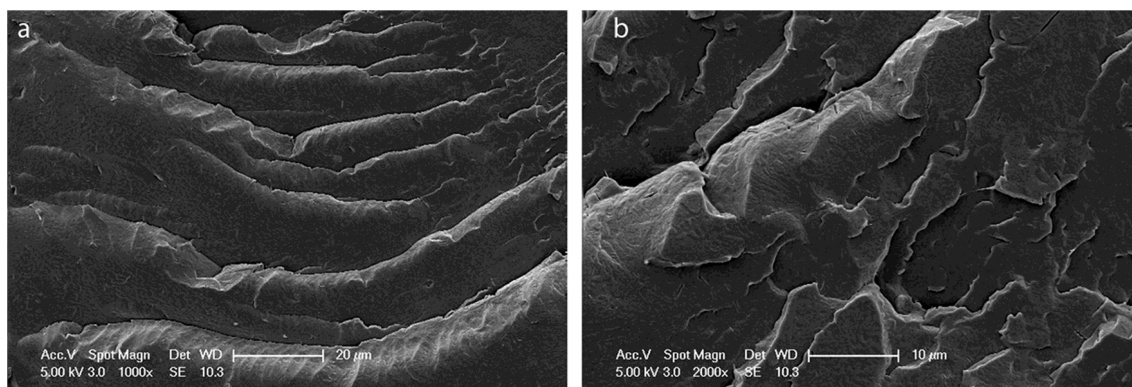


Figure 6. SEM images of the fractured surface of (a) F1 ($\times 1000$); (b) F5 ($\times 2000$).

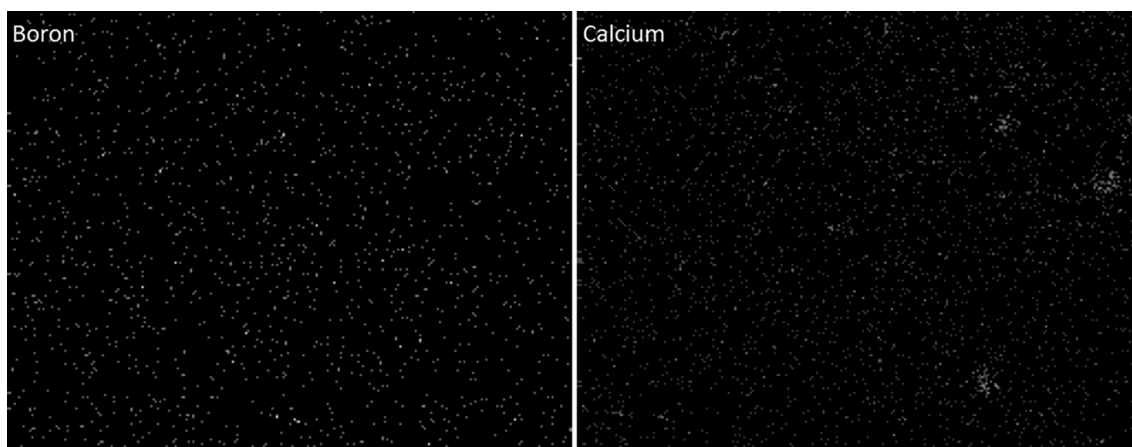


Figure 7. SEM-EDS mapping images of F1 sample (boron and calcium particles on colemanite).

for the composites can be attributed to inorganic structure of colemanite.

Morphology of the Composites. SEM image of composites were obtained using a Phillips XL 30 ESEM-FEG scanning electron microscope, after coating gold under reduced pressure. Figure 6 show SEM images of the fractured surface of F1 and F5 ($1000\times$ and $2000\times$). It can be seen that colemanite particles were buried inside TPU. As it can be seen in Figure 6, the samples have a smooth, homogeneous surface.

Figure 7 shows the SEM-EDS mapping images of boron and calcium (F1 sample). It can be seen that boron and calcium particles in colemanite were dispersed homogeneously and they were buried inside the composite matrix. Figure 7 also clearly shows that the colemanite particles are being surrounded by TPU.

Conclusions

The prepared composites showed high thermal stability, and

the char yield increased as colemanite content increased. The char formation isolates polymer, prevents feeding the flame, and the air inlet in the polymer. The glass transition temperatures of the composites rise with the addition of colemanite. It is due to the decrease in the segmental motion of the polymer chains. The mechanical properties of the TPU were increased with contribution of the colemanite. Especially, there is a significant increase in tensile elongation and elongation at break due to the structural character of colemanite. The contact angles have the tendency to increase the hydrophobic behavior on the surface, when colemanite were added into TPU. SEM-EDS mapping images showed that colemanite particles were dispersed homogeneously. Finally, the obtained results prove that the prepared composites have good thermal, mechanical and surface properties and that they can be used in many applications such as the electronic devices, materials engineering and other emergent.

Acknowledgment: This work was financially supported

by the Research Foundation of Marmara University, Turkey (BAPKO no: FEN-C-YLP-121114-0364).

References

1. D. Baral, P. P. De, and G. B. Nando, *Polym. Degrad. Stab.*, **65**, 47 (1999).
2. B. Finnigan, D. Martin, P. Halley, R. Truss, and K. Campbell, *J. Appl. Polym. Sci.*, **97**, 300 (2005).
3. K. Okuno, *Radiat. Prot. Dosim.*, **115**, 258 (2005).
4. C. Özmetin, M. M. Kocakerim, S. Yapıcı, and A. Yartaşı, *Ind. Eng. Chem. Res.*, **35**, 2355 (1996).
5. Y. A. El-Shekeil, S. M. Sapuan, K. Abdan, and E. S. Zainudin, *Mater. Design*, **40**, 299 (2012).
6. J. H. Wu, C. H. Li, Y. T. Wu, M. T. Leu, and Y. Tsai, *Compos. Sci. Technol.*, **70**, 1258 (2010).
7. L. Pizzatto, A. Lizot, R. Fiorio, C. L. Amorim, G. Machado, M. Giovanela, A. J. Zattera, and J. S. Crespo, *Mater. Sci. Eng.*, **29**, 474 (2009).
8. T. Korkut, A. Karabulut, G. Budak, B. Aygun, O. Gencel, and A. Hancerliogullari, *Appl. Radiat. Isotopes*, **70**, 341 (2012).
9. H. Binici, O. Aksogan, A. H. Sevinc, and A. Kucukonder, *Constr. Build Mater.*, **50**, 177 (2014).
10. C. Kaynak and N. A. Isitman, *Polym. Degrad. Stab.*, **96**, 798 (2011).
11. N. A. Isitman and C. Kaynak, *J. Fire Sci.*, **31**, 73 (2012).
12. E. Baştürk, F. Şen, M. V. Kahraman, and S. Madakbaş, *Polym. Bull.*, **72**, 1611 (2015).
13. G. Guzel, O. Sivrikaya, and H. Deveci, *Composites Part B*, **100**, 1 (2016).
14. A. Pattanayak and S. C. Jana, *Polymer*, **46**, 5183 (2005).
15. A. Eceiza, M. D. Martin, K. de la Caba, G. Kortaberria, N. Gabilondo, M. A. Corcuera, and I. Mondragon, *Polym. Eng. Sci.*, **48**, 297 (2008).
16. X. Wang, Y. Hu, L. Song, H. Yang, W. Xing, and H. Lu, *J. Mater. Chem.*, **21**, 4222 (2011).
17. S. Madakbaş, F. Şen, M. V. Kahraman, and F. Dumludağ, *Adv. Polym. Tech.*, **33**, 1 (2014).
18. F. Şen, S. Madakbaş, and M. V. Kahraman, *Polym. Compos.*, **35**, 456 (2014).
19. F. Şen and M. V. Kahraman, *Prog. Org. Coat.*, **77**, 1053 (2014).
20. U. A. Pinto, L. L. Y. Visconte, and R. C. R. Nunes, *Eur. Polym. J.*, **37**, 1935 (2001).
21. O. Gencel, W. Brostow, C. Özel, and M. Filiz, *Int. J. Phys. Sci.*, **5**, 216 (2010).