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Thermal Conductivity and Flammability of Ulexite Filled Rigid Polyurethane Materials

G. Gurlek, L. Altay* and M. Sarikanat
Ege University, Department of Mechanical Engineering, Izmir, Turkey

Polyurethane based materials are usually preferred due to thermal and electrical insulation, lightness, durability, ease of design and production, high compression strength and corrosion resistance in many industries such as heat insulation and automotive industry. In this study, ammonium polyphosphate and pentaerythritol was used as flame retardant additives for polyurethane based composite materials. Boron derivative, ulexite, was also added at 1, 3, and 5 wt% as a synergist to improve fire retardancy performance of polyurethane composites. It is aimed to examine thermal, mechanical, physical properties especially flammability, by adding ammonium polyphosphate, pentaerythritol, and ulexite with different weight ratios into the polyurethane. It is shown that thermal conductivity, density, compression strength, modulus and Limited Oxygen Index values increased in polyurethane based composites. Flame retardants and ulexite addition have improved flammability properties of polyurethane composites.

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PACS/topics: polyurethane, boron derivative ulexite, flame retardant, heat transfer coefficient, compression strength

1. Introduction

Due to the ease of production and the diversity of usage in different sectors especially such as heat insulation, wires and cables, conveyor belts, automotive, electrical and electronic industry the use of polyurethane based materials is increasing day by day [1]. Polyurethane based materials are usually preferred due to thermal and electrical insulation, combustion resistance, lightness, durability, ease of design and production, high compression strength and corrosion resistance in these areas. One of the characteristics of polyurethane materials that should be emphasized is its easy flammability. Depending on the properties of the polyurethane materials, the combustion reaction can spread heat, toxic gases and corrosive compounds [1, 2]. These harmful effects can be reduced by increasing the immunity of the polyurethane against burning by applying different techniques at the production stage. The most common practice among these techniques is to add flame retardant additives to the polyurethane during production [3–5]. Boron derivatives can be used as flame retardants in various polymers. Turkey has a total of 3.3 billion ton of boron deposits, which equates to about 73% of the total world reserves, and puts it in first place in this respect [6]. The consumption of boron products throughout the world is nearly 3.85 million tons. Approximately 57% of world boron demand in 2017 was met by Turkey. In the fields of healthcare, defense industry, space technology, energy, food, automotive, polymeric materials, nano-technologies, machine manufacturing and information communication technologies, potential to use of superior feature boron compounds produced with advanced technologies is high [6].

Various studies have been carried out at national and international level regarding the effects of flame retardant materials on the flammability of polyurethane foam [5]. Duquesne et al. [7], investigated the mechanism of fire retardancy of APP in PU. Their study showed that the presence of APP in polyurethane contributed to the fire retardancy process. Thirumal et al. [8], prepared rigid polyurethane foam with expandable graphite in two different particle sizes as flame retardant additive. The mechanical properties of polyurethane decreased and the flame-retardant properties improved with increasing expandable graphite loading. Usta [9] investigated the fire behaviors of rigid polyurethane foams containing a fly ash (up to 5% by weight) and an inflated flame retardant (up to 5% by weight) consisting of ammonium polyphosphate/pentaerythritol using a cone calorimeter. It has been demonstrated that fire resistance and thermal stability of the composites were improved. Czech-Polak et al. [10] studied polyurethane foams containing environmental sensitive flame retardants such as expanded graphite obtained by ammonium polyphosphate, melamine pyrophosphate, triethyl phosphate, bentonite and long fiber injection (LFI) method. Polyurethane foams containing flame retardants showed flammability class of V0 with acceptable mechanical properties. Yeler et al. [11] added boron oxide as filler to improve thermal degradation and combustion resistance of rigid polyurethane foam materials and showed that thermal conductivity of the composites were increased. Also, higher thermal stability and fire resistance was obtained. Zarzyka [12] investigated the application of boron-modified hydroxyethyl urea derivatives as polyol components to produce

*corresponding author; e-mail: lutfiyebulut@gmail.com

foamed polyurethane materials. This results showed better heat insulation properties and decreased flammability.

In this study, ammonium polyphosphate and pentaerythritol were used as flame retardant additives in polyurethane based composite materials. Also, one of the boron derivatives, ulexite, was added into polyurethane at different weigh fractions to investigate its synergistic effect on the flammability properties of composites. Ignitibility, limited oxygen index tests were performed to understand the fire retardancy performance of the composites. Thermal conductivity values and the density of the composites were measured, and compression tests were done for mechanical characterization.

2. Materials and equipment

The polyurethane foam (PU) used in this work was obtained by using polyol/isocyanatemixture with a ratio of 100 g/134 g. The combination of ammonium polyphosphate (APP) (Exolit APP 422 from Clariant) and pentaerythritol (PER) (MKS Marmara) were used as flame retardant additives in this study. The ratio of APP to PER was fixed to 3:1. Ulexite was supplied from Etimaden AS., Turkey. Polyol-isocyanate, APP/PER (10 wt%) and ulexite were mixed with mechanical mixer at specified ratios, molded and test specimens were produced. Compositions of the test specimens are listed in Table I. PU + FR0, PU + FR1, PU + FR3, and PU + FR5 correspond to PU + APP/PER composites with ulexite at 0, 1, 3 and 5 wt% respectively. Ignitibility of specimens and Limited Oxygen Index (LOI) tests were investigated in accordance with ISO11925-2 and ASTM D 2863-13 standards respectively. Thermal conductivity value of PU and its composites was measured by FOX 314 Heat Flow Meter according to ISO 12667 standard with sample dimensions of 300 mm × 300 mm × 10 mm. During the thermal conductivity measurement, the Heat Flow Meterinstrument establishes steady state one dimensional heat flux through a test specimen between two parallel plates at constant but different temperatures. The Fourier law for heat conduction is used to calculate thermal resistance and thermal conductivity. Compression tests were performed according to ISO 826 standard with a Shimadzu Autograph AG-IS Series universal testing machine. Specimen dimensions were 50 mm×50 mm×20 mm. The stress/deformation relation were computer-recorded and processed using Trapezium software. The linear regression procedure was applied for determination of elasticity modules. Density measurement of the specimens was done according to the ASTM D792 using Densimeter MD-200S.

TABLE I

Flammability, LOI and density values of PU and its composites (composition in [%]).

Specimen	PU	APP	PER	Ulexite	Density [g/cm^3]	LOI	Flammability test
PU	100	0	0	0	0.052	21.6	failed
PU + FR0	90	7.5	2.5	0	0.057	22.4	pass
PU + FR1	89	7.5	2.5	1	0.059	22.0	pass
PU + FR3	87	7.5	2.5	3	0.063	22.8	pass
PU + FR5	85	7.5	2.5	5	0.069	23.1	pass

3. Results and discussion

3.1. Density

Density values of PU and its composites were given in Table I. As it is seen from Table I, density values of composites are higher than PU itself. The density of composites increased with an increase in weight fraction of fillers.

3.2. Flammability

Flame retardant behavior of PU and ulexite filled PU composites were investigated by ignitability and LOI tests. During ignitability test the flame was applied to the lower edge of the specimens for 15 s. Then the time for the flame to reach 150 mm over the point of application was recorded and the detachment of particles on fire during the 20 s which follow was measured. Ignitability test results are given in part A of Fig. 1. As can be seen, PU sample could not pass the test because the flames spread very quickly and the time to reach 150 mm line was very short. However, when flame retardants were added to the PU, composites showed improved flammability results as it is seen from Fig. 1A. Flame spread was the slowest as in the case of 5 wt% ulexite loading (Fig. 1Ae). Recorded times for the flame to reach 150 mm line was increased as flame retardants and ulexite were added to the composites.

The limiting oxygen index (LOI) test, shown in part B of Fig. 1, measures the minimum concentration of oxygen (O_2) in the flowing mixture of oxygen and nitrogen [O_2/N_2] that will support the combustion of material. The higher the LOI value, the better the flame retardancy of the material.

According to LOI test results, the LOI value of virgin PU was found to be 21.6. When 10 wt% of APP and PER was added into PU, LOI value increased to 22.4. APP acts as an acid source whereas PER acts as a carbonic source in the flame retardant system, and prevent the surface from heat and mass transfer by forming charred layer [10]. LOI values and flammability test results obtained by adding 1, 3, and 5 wt% of ulexite into PU with 10 wt% of APP and PER are given in Table I.

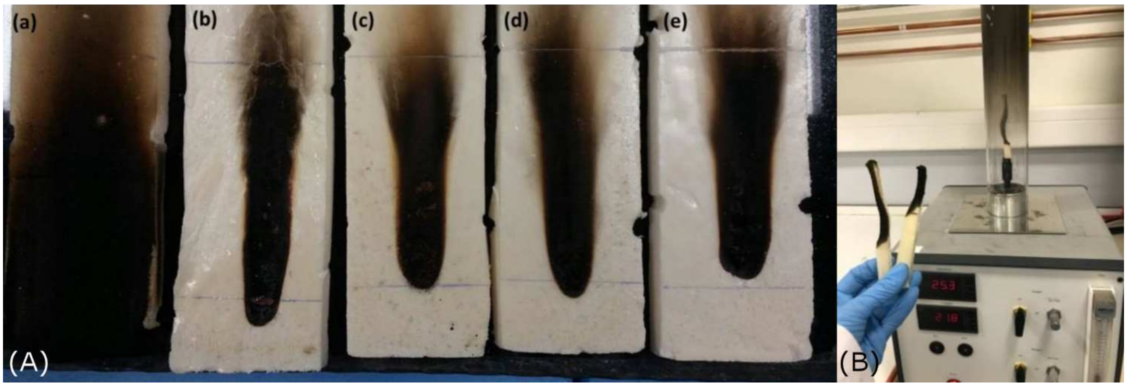

Fig. 1. (A): Ignitibility test results of (a) PU, (b) PU + FR0, (c) PU + FR1, (d) PU + FR3, (e) PU + FR5 (B): LOI test.

As can be seen from Table I, LOI values of the composites increased as the weight fraction of ulexite was increased. According to the results the highest LOI value of 23.1 was achieved when 5% of ulexite was used.

3.3. Thermal conductivity

Thermal conductivity values of PU and its composites are shown in Fig. 2. Thermal conductivity of PU was obtained to be 0.049 W/mK. After addition of flame retardants and ulexite, thermal conductivity values of 0.061, 0.063, 0.067, 0.078 were obtained for PU + FR0, PU + FR1, PU + FR3, and PU + FR5, respectively. The addition of APP, PER and ulexite reduces the amount of polyurethane foam raw materials, so the decrease in the number of cells are expected condition. The number of cells decreases with the amount of increasing filler material, which might cause an increase in the thermal conductivity of the foam material.

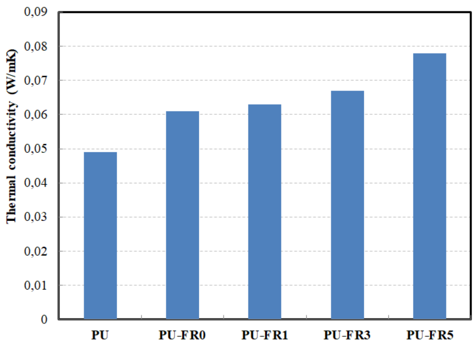

Fig. 2. Thermal conductivity results of PU and its composites.

3.4. Compression tests

The compression properties of PU and its composites are given in Fig. 3a, b. Compression strength increased from 1.21 to 2.18 MPa with the addition of APP + PER. It can be seen that addition of APP/PER significantly increases the compressive strength of PU. The compressive strength values were decreased when ulexite was used in PU composites. These results could be explained by changing of cell morphology in the PU foam in the case of ulexite addition. When APP and PER was added into PU, the compressive strength was increased by about 80%. Similarly, when APP and PER was added into PU, the compression modulus was increased by about 65%. The compression modulus of the PU-FR composites considerably increases with ulexite loadings at 1–5 wt% compared to that of PU-FR0, which shows the dominant contribution of the ulexite to the moduli of the composites. It is believed that ulexite, which has maximum H_2O content respect to other fillers, consumed more isocyanate during preparation of the foam. This may affect total properties of ulexite filled polyurethane foam.

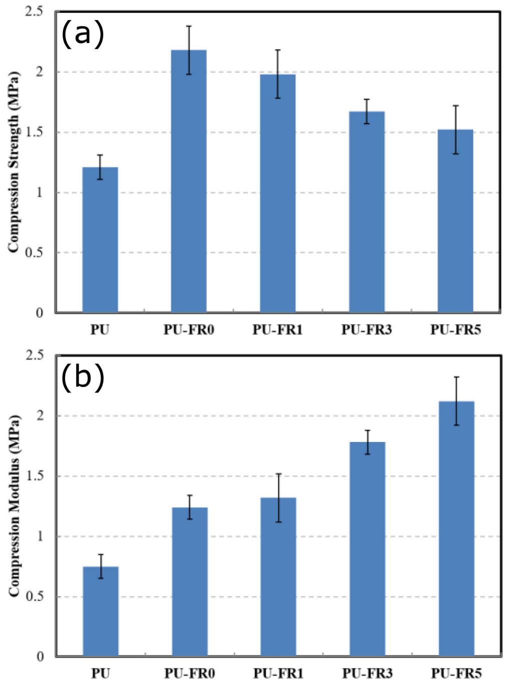

Fig. 3. (a) Compression strength of PU and its composites, (b) compression moduls of PU and its composites.

4. Conclusion

The effect of flame retardant additives and ulexite on flammability, thermal, and mechanical properties of polyurethane foam was investigated. The main results obtained from this study are as follows:

- Density of the composites increased via incorporation of flame retardants and ulexite into PU.
- According to the ignitability tests, flame retardants improved the flammability properties of the PU foam as flame spread was decreased with APP/PER and increasing ulexite content.
- Flame retardants increased LOI values of the PU foam. The highest LOI value of 23.1 was obtained when 5 wt% ulexite was used.
- Flame retardant additives increased the thermal conductivity of PU indicating worse insulating properties.
- Although the addition of ulexite decreased the compression strength, increased compression strength and modulus values were obtained in PU composites compared to that of pure PU foam.

Acknowledgments

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