

# Effect of Ulexite on Mechanical, Thermal, and Flame Properties of Halogen-Free Fire Retardant Polypropylene

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In this study it was aimed to improve the fire retardant performance of halogen free flame-retardant polypropylene by increasing limiting oxygen index value. Ammonium polyphosphate, pentaerythritol, and ulexite were used to improve flame retardancy of polypropylene. Ulexite powder filled (1, 2, and 4 wt%) polypropylene composites were obtained by using a twin-screw extruder and injection molding method. Thermal, mechanical, and flame retardant performances of polypropylene composites were investigated by several characterization techniques. Limiting oxygen index value was obtained higher than 45% when ulexite was added into polypropylene at 1–4 wt%. It was observed that flame retardant additives do not change the mechanical properties considerably. The effect of ulexite addition on melting and crystallization temperatures of polypropylene-based composite is not pronounced.

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## 1. Introduction

In recent years, demand for the development of safe and environmental flame retardant polymers has increased rapidly due to the requirement to fulfill fire resistance criteria for the production of new engineering materials. Polypropylene (PP) high flammability, with a limiting oxygen index (LOI) of around 17.5, restricts its range of industrial applications especially in electrical appliances for safety reasons [1, 2]. In order to improve fire retardancy of polymers, many types of flame retardants are added. Flame retardants are defined as chemical compounds that alter oxidation reactions emerged in the combustion by limiting or inhibiting them. They are mainly phosphorus, antimony, aluminum and boron-containing compounds, chlorides, and bromides [3, 4]. Among them, intumescent flame retardants (IFRs), the kind of halogen-free flame retardants, due to their low toxicity and low smoke production have become a topic of interest for the reduction of flammability of PP. In general, the intumescent systems contain three main ingredients, which are acidic source, carbonization agent, and blowing agent [5]. Ammonium polyphosphate (APP) which works as an acid source and blowing agent due to its high contents of phosphorus and nitrogen could be used as the filler for flame retardancy for PP [6]. For carbonization agent, pentaerythritol (PER) is usually preferred in an intumescent system. During the combustion process, the carbonization agent is helpful in charring

process under the catalytic effect of acid source. Ulexite with the chemical formula  $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 16\text{H}_2\text{O}$ , is one of the commercially important boron minerals because of its common use in the production of fire resistance materials [7]. In this paper effect of ulexite for use as a fire retardant additive in PP composites as synergists, which is used together with APP and PER, was investigated. The objectives of this paper is to improve the flame retardancy of the PP/APP+PER composites by the addition of ulexite and investigate the effects of the ulexite content on mechanical and thermal performance together with LOI, UL-94 flammability, tensile tests, and differential scanning calorimetry analyses.

## 2. Experimental

### 2.1. Materials and composite manufacturing

PP resin (co-polymer, melt flow rate: 8 g/10 min) used in this work was supplied by IMS Polymers. The combination of APP (Exolit APP 422 from Clariant) and PER (from MKS Marmara) were used as flame retardant additives in this study. The ratio of APP to PER was fixed at 3:1. Ulexite was supplied from Etimaden AS., Turkey. PP composites were prepared using the twin screw extruder. Their compositions are listed in Table I. PP-FR0, PP-FR1, PP-FR2, and PP-FR4 correspond to PP composites with ulexite at 0, 1, 2, 4 wt% respectively. Leistritz Extruder (Model ZSE 27) was used in the compounding process with a screw speed of 250 rpm and barrel temperature range 195–215 °C. Composites plates were produced by using injection molding machine (Bole, model BL90EK).

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TABLE I

Flammability behavior of PP and its composites

Samples	PP [wt%]	APP [wt%]	PER [wt%]	APP/PER	Ulexite [wt%]	LOI [%]	UL94 flammability category
PP	100	0	0	0	0	17	NA*
PP-FR	76	18	6	3	0	NA*	V2
PP-FR0	70	20	10	2	0	35.1	V0
PP-FR0	70	22.5	7.5	3	0	35.4	V0
PP-FR0	70	24	6	4	0	35.2	V0
PP-FR1	69	22.5	7.5	3	1	45.8	V0
PP-FR2	68	22.5	7.5	3	2	48.8	V0
PP-FR4	66	22.5	7.5	3	4	57	V0

\*NA: not available

## 2.2. Characterization

### 2.2.1. Flame retardancy testing

Flame retardancy of PP and ulexite filled PP composites was obtained according to ASTM D3801 by using Atlas HVUL2 Horizontal Vertical Flame Chamber. LOI value of PP and its composites was measured according to the ASTM D 2863-13 by using fire testing technology oxygen index apparatus.

### 2.2.2. Mechanical properties

The tensile tests of PP, PP-FR0, PP-FR1, PP-FR2, and PP-FR4 composites were performed with a Shimadzu Autograph AG-IS Series universal testing machine at a crosshead speed of 50 mm/min at room temperature according to ASTM D638-10 standard.

### 2.2.3. Differential scanning calorimetry analysis

DSC analyses of the samples were made by using differential scanning calorimeter (DSC-Q20, TA Instruments Inc.) under nitrogen atmosphere with a heating rate of 10 °C/min in the temperature range 50 to 200 °C.

## 3. Results and discussion

### 3.1. Fire retardancy

Flame retardancy behavior of PP and ulexite filled PP composites was investigated by UL-94 and LOI tests. LOI values and UL-94 test results are shown in Table I. According to these test results, the LOI value of virgin PP was found to be 17%. When 24 wt% of APP and PER was added into PP, flammability of the composites was found to be V2 according to UL94 standard. When total weight fraction of APP and PER has been increased to 30%, the obtained LOI value is about 35. The APP/PER ratio was also investigated by changing the ratios to 2, 3 and 4 while total amount of APP and PER was kept the same at 30%. From Table I, It was observed that LOI values of the PP-FR0 composites were obtained to be 35.1, 35.4, and 35.2 when APP/PER ratios were 2, 3, and 4, respectively. The usage of different APP/PER ratios does not change V0 rating and LOI values to a significant extent. Therefore, from Table I, one can note that LOI value of PP increased from 17% to average of 35% when total 30wt% APP/PER was added. 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 [8]. Ulexite was added to the PP composites containing APP and PER at which ratio the highest LOI value was obtained. The flammability properties obtained by adding 1%, 2%, and 4% of ulexite into PP with 30 wt% of APP and PER are given in Table I. The addition of boron derivative, ulexite, causes sharp increase in LOI values of the PP composites. As can be seen from Table I, LOI values of the composites increase as the weight fraction of ulexite increases. According to the results the highest LOI value of 57 was achieved when 4 wt% of ulexite was used. Also, according to the UL-94 standards, all ulexite filled PP composites showed V0 class of flammability. It has been demonstrated in the literature that hydrated boron derivatives might compensate for the loss in gas phase fire retardancy by the endothermic dehydration reactions and fuel dilution or cooling by water vapor release [9]. The addition of inorganic fillers into thermoplastics with a combination of APP and PER leads to a significant improvement in their fire retardant performance [10].

### 3.2. Mechanical properties

The mechanical properties of PP and its composites are shown in Figs. 1 and 2. The tensile strength and modulus of the PP were 21.7 and 530 MPa, respectively. It can be seen that addition of APP/PER decreases the tensile strength of PP considerably. The APP and PER may not interfacially interact or adhere well with the matrix polymer, which will reduce the tensile strength of polymer. The poor interfacial interaction between APP and polymer matrix usually results in the deterioration of the mechanical properties of materials, which limits their application in many fields [11]. However, as the ulexite addition into PP was increased, tensile strength values slightly increased. These results could be explained by possible good interfacial adhesion between ulexite and the other components of the composite, which could provide a better stress transfer from the matrix to filling material. When APP and PER were added into PP, the tensile modulus increased by about 18%. The tensile

modulus of the PP composites considerably increased with ulexite loadings at 1–4 wt% compared to that of PP-FR0, which shows the dominant contribution of the ulexite to the moduli of the composites. This indicates that there is a certain stiffening effect of ulexite on the PP, which leads to the improvement of the stiffness of the PP composites [12].

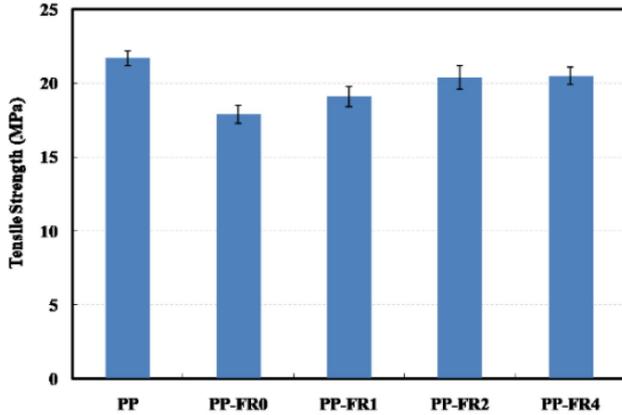


Fig. 1. Tensile strength of PP and its composites.

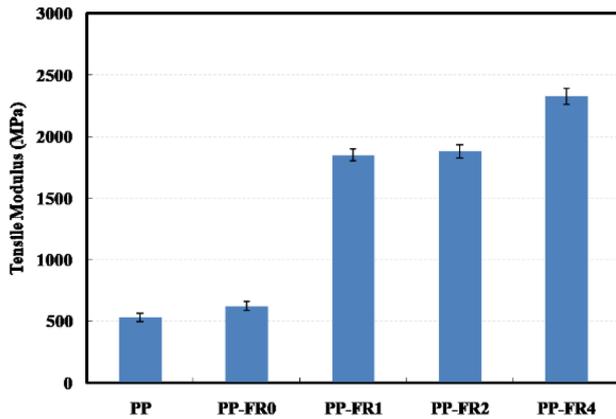


Fig. 2. Tensile modulus values of PP and its composites.

### 3.3. DSC analysis

The data obtained from DSC analysis, such as the melting temperature  $T_m$ , crystallization temperature  $T_c$ , melting enthalpy  $\Delta H_m$ , crystallization enthalpy  $\Delta H_c$ , and degree of crystallinity  $X_c$  are summarized in Table II. The degree of crystallinity of PP and its composites were obtained by using the following Eq. (1) [13].

$$X_c = \frac{\Delta H}{\varphi_P \Delta H_0} \times 100\% \quad (1)$$

where  $\varphi_P$  is weight fraction of PP in the composite and  $\Delta H_0$  is the melting enthalpy of the 100% crystalline polypropylene (209 J/g) [14]. While flame retardant loadings into PP have not changed the melting temperature, the crystallization temperature of PP slightly increased. Flame retardants loading into PP

has decreased the crystallization enthalpies. Besides, APP and PER loading has led to considerable increase in the crystallinity from 40 to 59%. However, ulexite loadings into APP and PER mixture decreased the crystallinity of PP.

DSC data for the samples

TABLE II

Sample	$T_m$ [°C]	$T_c$ [°C]	$\Delta H_m$ [J/g]	$\Delta H_c$ [J/g]	$X_c$ [%]
PP	166	118	78.9	82.9	40
PP-FR0	166	126	86.2	73.1	59
PP-FR1	166	123	62.4	55.6	43
PP-FR2	165	125	53.6	55.9	38
PP-FR4	165	125	50.1	53.5	36

## 4. Conclusion

The objective of this work is to investigate the effects of ulexite content on flammability of PP without degrading the thermal and mechanical properties. With the addition of flame retardants, LOI values increased considerably. The optimum flame retardant composition for PP was determined according to the LOI response. Highest LOI value of 57% was obtained at 30 wt% APP/PER and 4 wt% ulexite combination. Besides, PP filled with flame retardants showed V0 class of flammability according to ASTM D3801 standard. Mechanical and thermal performances of composites with flame retardants were comparable to those of PP. From DSC analyses, it is seen that APP/PER addition into PP increased the crystallinity of PP. However, ulexite addition into APP/PER filled PP composite decreased the crystallinity considerably.

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## References

- [1] P.A. Song, Y. Shen, B.X. Du, M. Peng, L. Shen, Z.P. Fang, *Acs. Appl. Mater. Inter.* **1**, 452 (2009).
- [2] Z. Qin, D. Li, R. Yang, *Polym. Degrad. Stabil.* **126**, 117 (2016).
- [3] A.F. Grand, C.A. Wilkie, *Fire retardancy of polymeric materials*, CRC Press, Boca Raton 2000.
- [4] J. Troitzsch, *International plastics flammability handbook: principles-regulations-testing and approval*, Hanser, Munich 1983.
- [5] X.Y. Wang, Y. Li, W.W. Liao, J. Gu, D. Li, *Polym. Advan. Technol.* **19**, 1055 (2008).
- [6] W.Z. Jiang, J.W. Hao, Z.D. Han, *Polym. Degrad. Stabil.* **97**, 632 (2012).

- [7] Y. Kar, N. Şen, A. Demirbaş, *Minerals & Energy-Raw Materials Report* **20**, 2 (2006).
- [8] P. Wei, H.X. Li, P.K. Jiang, H.Y. Yu, *J. Fire Sci.* **22**, 367 (2004).
- [9] C. Kaynak, N.A. Isitman, *Polym. Degrad. Stabil.* **96**, 798 (2011).
- [10] U. Atikler, H. Demir, F. Tokatli, F. Tihminlioglu, D. Balkose, S. Ulku, *Polym. Degrad. Stabil.* **91**, 1563 (2006).
- [11] H.J. Lin, H. Yan, B. Liu, L.Q. Wei, B.S. Xu, *Polym. Degrad. Stabil.* **96**, 1382 (2011).
- [12] J.Z. Liang, R.K.Y. Li, *Polym. Composite.* **19**, 698 (1998).
- [13] C. Wang, S. Ying, *Polymers & Polymer Composites* **21**, 65 (2013).
- [14] Q. Yuan, R. Misra, *Polymer* **47**, 4421 (2006).