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Effect of halogen-free nanoparticles on the mechanical, structural, thermal and flame retardant properties of polymer matrix composite

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ABSTRACT

In this work, polypropylene (PP) nanocomposites were reinforced with 30 wt% of halogen-free flame retardants, which were prepared by melt compounding in a twin-screw extruder followed by injection molding technique. It was aimed to produce flame retardant nanocomposites by reinforcing different halogen-free nanoparticles with various compositions and to investigate the usability of the nanocomposites in industrial applications. Within this scope, halogen-free nano sized huntite/hydromagnesite, antimony trioxide, bentonite and zinc borate particles were reinforced to polypropylene matrix. The influence of different mineral type/content was investigated for polypropylene nanocomposites containing halogen-free flame retardants on the structural, thermal, mechanical and flame retardant properties. The nanocomposites were analyzed with X-ray diffraction (XRD), scanning electron microscopy (SEM), thermo-gravimetric analysis (TGA), tensile and UL94 flame retardancy tests to characterize the structural, thermal, mechanical and flame retardant behaviour of the PP composites. TGA and flame retardant tests showed that the decomposition temperature was increased in the presence of huntite/hydromagnesite in comparison to neat PP and PP composites comprising other mineral types. It was concluded that the flame retardancy behaviour of PP composites was improved within creasing mineral content, indicating that the UL94 rating reached V-0 via a good compatibility between huntite/hydromagnesite and PP.

1. Introduction

Polypropylene (PP) is one of the most important widely used in various fields, such as electronics, automobiles, interior decorations, architectural materials and other areas for its superior mechanical properties, low cost, easy processing and chemical stability [1–4]. Nevertheless, its severely flammability due to its aliphatic hydrocarbon structure restricts its further applications. Therefore, many researchers have carried out intensive investigations in order to improve the flame retardant properties of PP [5–9]. The most widely used approach to enhance mechanical, thermal properties and flame retardancy is addition of reinforcing materials into PP matrix which result in high strength, high modulus and high flame retardant performance [10].

Several flame retardant compounds have been used to enhance the flame retardancy properties of polymeric materials [11]. That is to say, it can be achieved by adding halogen based additives or halogen-free hydrated inorganic fillers [12]. Nonetheless, the potential applications of halogen based flame retardants are limited owing to their hazardous effect on health and environments [13–15]. Therefore, several studies have been performed on non-halogen additives such as metal hydroxides, phosphorus, boron containing compounds and inorganic clay fillers [16–20]. There are also numerous research articles illustrating effectiveness of non-halogenated additives to improve mechanical strength and thermal stability as well as flame retardancy [21–23].

One of the common flame retardant reinforcing material is huntite ($Mg_3Ca(CO_3)_4$) which is mostly used together with hydromagnesite ($Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$) [24]. The attractive properties of these minerals are low smoke generation, environmentally safe, noncorrosive, and low combustion [25]. Besides, there are many studies have been reported using huntite and hydromagnesite as flame retardant additives due to their extraction from Greek and Turkish mines in large quantities with relatively low cost [25–28]. In spite of the fact that there are several mechanisms to explain flame retardancy in polymer/clay nanocomposites, the

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protective barrier effect of char [29] and the migration of clay mineral layers [30] have been confirmed by many researchers [31–33]. Thus, organo-bentonite has been studied in terms of the effects of inorganic additives on mechanical, thermal stability and flame retardancy mechanism by Du et al. [9].

In this study, four different types of flame retardant additives, namely, huntite/hydromagnesite, bentonite, antimony trioxide and zinc borate were used in PP. Effect of these additives type/amount on flame retardancy, thermal and mechanical properties of PP based composites have not been previously investigated, to the best of our knowledge, in the same study. The objective of this work is to evaluate the effects of halogen free flame retardant additives on flame retardancy as well as mechanical, structural and thermal properties of PP based composites. The effects of filler content on the flame retardancy, thermal and mechanical properties of the PP composites have also been studied in detail.

2. Experimental studies

2.1. Materials

Polypropylene (PP) pellets were used as a polymer matrix to produce huntite/hydromagnesite, bentonite, antimony trioxide and zinc borate reinforced nanocomposites. A mineral filler with 40% of hydromagnesite and 60% of huntite by weight was used as a flame retardant additive. PP with a melt flow index (MFI, 230 °C, ASTM D 1238) of 7–8 g/10 min and melting point of 168 °C was supplied by Petkim Petrochemical Co. (Izmir, Turkey). Physical densities of huntite ($Mg_3Ca(CO_3)_4$), hydromagnesite ($4MgCO_3.Mg(OH)_2{\cdot}4H_2O$), antimony trioxide ($Sb_2O_3$), bentonite ($(Na, Ca)(Al, Mg)_6(Si_4O_{10})_3(OH)_6{\cdot}nH_2O$) and zinc borate ($2ZnO.3B_2O_3{\cdot}3.5H_2O$) minerals are 2.70, 2.24, 5.2, 1.65 and 3.64 g/cm^3, respectively [34–37].

2.2. Nano grinding process and particle size distribution

The huntite/hydromagnesite, antimony trioxide, bentonite and zinc borate powders were separately milled to obtain nano-scale particles using a high energy ball milling machine (Fritsch, Pulverisette 7) at the rate of 700 rpm at room temperature for 20 min in air. In this process, a powder mixture placed in the ball mill was subjected to high-energy collision from the balls. This method could successfully produce fine and uniform dispersions of oxides. To understand the effect of grinding process, a particle size analysis was carried out using a particle size measurement machine (Malvern, Zetasizer Nano ZS).

2.3. Production of composites

In the production of polymeric composite materials, extrusion and injection molding techniques were used for flame retardant applications. A co-rotating twin screw extruder (Thermo-Fisher, Eurolab 16) with screw diameter of 16 mm and L/D ratio of 40 was utilized for production of the composites by adjusting 70% by weight of PP (pellets form) and 30% by weight of halogen-free inorganic nanoparticles. We also produced 40 and 50 wt% huntite/hydromagnesite reinforced PP composites in order to investigate the effects of filler content on the flame retardancy, thermal degradation behaviour and mechanical properties of the PP composites. The screw speed was set at 300 rpm and the barrel temperatures of the zones were 160, 170, 180, 190, 200 and 180 °C, from the feeding zone to the die zone. An injection molding machine (Permak Co.) equipped with a self-designed mold was used to prepare specimens. Injection process was carried out at a melting temperature of 185 °C, a molding temperature of 25 °C and an injection pressure of 960 kg/cm^2. Sample code and composition of PP and PP composites were listed in Table 1.

2.4. Characterization of composites

The crystallinity of huntite/hydromagnesite, antimony trioxide, bentonite and zinc borate reinforced composites was characterized by X-ray Diffraction (XRD) analysis using Thermo-Scientific, ARL K_α diffractometer with Cu K_α as a radiation source. Diffraction patterns were collected in the range of 8°–60° with a scanning rate of 2°/min and X-ray radiation of Cu-K_α was set at 45 kV and 44 mA. Fourier transform infrared spectroscopy (FTIR) (Thermo-Scientific, iS10) absorption spectra of the PP and PP composites were measured between the range of 4000–650 cm^{-1} at room temperature. FTIR spectra of the samples were recorded to determine the organic components in the samples. The surface morphology and microstructure of the powders and PP composites were characterized by a scanning electron microscope (SEM, COXEM EM 30 Plus).

Thermo-gravimetric analysis (TGA) was performed for the all samples in order to determine the effective content of inorganic phase and the degradation behaviour by using a TGA analyzer (Perkin Elmer, STA 6000). The TGA curves were recorded from 25 °C to 600 °C at a heating rate of 10 °C/min under a nitrogen flow (flow rate = 20 ml/min).

Tensile properties of PP and PP composites were tested using a universal testing machine (Shimadzu, AG-50kNG) with a crosshead speed of 5 mm/min according to ASTM D638. Tensile strength and Young's modulus of PP and PP composites were measured to use in industrial applications.

Flammability of PP and PP composites were studied by a vertical burning test with the sample dimensions of 125 × 13 × 3.2 mm^3, angular radius 1.3 mm, in accordance with the American National Standard UL-94 standard. Limiting oxygen index (LOI) tests were performed according to ASTM D2863.

3. Results and discussion

3.1. Measurement of particle size distribution

Particle size distribution of all fillers was shown in Fig. 1. As calculated from Fig. 1, the mean particle size of huntite/hydromagnesite, antimony trioxide, bentonite and zinc borate powders were 121, 141, 380 and 426 nm respectively, which are reasonable

Table 1
Designation and composition of PP and PP composites.

Sample code	PP (wt%/vol%)	Antimony trioxide (wt%/vol%)	Bentonite (wt%/vol%)	Zinc borate (wt%/vol%)	Huntite/Hydromagnesite (wt%/vol%)
PP	100/100	–	–	–	–
PP/30A	70/93.06	30/6.94	–	–	–
PP/30B	70/80.97	–	30/19.03	–	–
PP/30Z	70/90.37	–	–	30/9.63	–
PP/30H	70/86.43	–	–	–	30/13.57
PP/40H	60/80.37	–	–	–	40/19.63
PP/50H	50/73.19	–	–	–	50/26.81

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