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Effect of microcapsulated red phosphorus on flame retardant, thermal and mechanical properties of thermoplastic polyurethane composites filled with huntite&hydromagnesite mineral

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ABSTRACT

The effect of microcapsulated red phosphorus (mRP) was studied on the flame retardant, thermal and mechanical properties of thermoplastic polyurethane (TPU) composites containing Huntite&hydromagnesite (HH). The flame retardant properties of TPU based composites were investigated using limiting oxygen index (LOI), vertical burning test (UL 94), thermogravimetric analysis (TGA) and mass loss calorimeter. The mechanical properties of composites were studied using tensile test and dynamic mechanical analysis (DMA). According to the test results, the adjuvant effect of mRP was observed in terms of both flammability and mechanical properties of composites. The highest LOI value (32.5), the highest UL-94 rating (V0) and the lowest pHRR (155 kW/m^2) value were observed with the partial substitution of 7 wt% mRP with HH. The tensile strength also increased at about 60% with respect to TPU/50HH. The mRP showed the synergistic effect by increasing the barrier effect of residue in the condensed phase and the formation of active radicals in the gas phase. The mRP showed adjuvant effect on mechanical properties due to the plasticizing and compatibilizer effect of low molecular weight epoxy resin carrier.

1. Introduction

Thermoplastic polyurethane (TPU) has desirable properties including excellent mechanical properties, chemical resistance and easy processability for many applications. However, its wider application is restricted due to the easily combustible character with melt dripping [1–3]. In the literature, the flame retardant properties of TPU were improved using various kinds of flame retardant additives [4–10].

Huntite&hydromagnesite (HH), naturally occurred mixed mineral, is mineral based flame retardant like aluminum hydroxide (ATH) and magnesium hydroxide (MH) [11,12]. HH is used as flame retardant additive in various polymers like ethylene vinyl acetate (EVA) [13–19], polypropylene (PP) [17], polyethylene (PE) [20], ethylene propylene copolymer [21], vinyl ester resin [22] and poly vinylchloride [23]. The general flame retardant mechanism of HH resembles to the ATH and MH [11,12,24]. HH has advantageous point of higher onset decomposition temperature (220–240 °C) than ATH (180–200 °C) whereas the decomposition enthalpy of HH (990 J g^{-1}) is lower than that of ATH (1300 J g^{-1}) [24]. Accordingly, to increase the flame retardant effect of HH with synergistic effect studies leads to wider use of it in various polymers and applications. Thus, commercial microcapsulated red phosphorus (mRP) is chosen as synergistic additive in the current study.

In the previous studies, the interaction between red phosphorus (RP) and mineral based flame retardants was investigated in various polymers [25–34]. Braun and Schartel investigated the synergistic interaction between MH and RP in high impact polystyrene (HIPS). A slight anti synergistic effect was observed in the limiting oxygen index (LOI) test results, whereas the synergistic interaction was observed in cone calorimeter studies due to the formation of magnesium phosphate in the condensed phase [25]. On contrary to the findings in the study made by Braun and Schartel, Liu et al. observed synergistic interaction between MH and RP in HIPS in terms of flammability test results. They found that the solely 50 wt% MH and RP containing composites failed in UL-94

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test. When MH and RP were used together, the highest UL-94 rating (V0) was achieved and the highest LOI value was observed at the highest concentration of RP (10 wt%) [26]. Du et al. investigated how RP affected the flammability properties of hydrotalcite containing EVA based composites. They observed synergistic interaction between RP and hydrotalcite. The solely 50 wt % hydrotalcite containing composite failed in UL-94 test and had LOI value of 35. The highest UL-94 rating (V0) and the highest LOI value of 39 were achieved with the addition of 5 wt% RP [32]. Zhuo et al. investigated the synergistic interaction between ATH and RP in silicone rubber composites. The LOI value of silicone rubber increased to 45 with the addition of 39 wt % ATH. With the partial substitution of ATH to RP (5 wt%), the highest LOI value of 52 was achieved. They proposed that the compact and homogeneous char formation with the inclusion of RP was the reason of synergistic interaction [34].

The main purpose of present work is to investigate the combustion and thermal degradation characteristics of flame retardant TPU based composites containing HH with and without RP. The combustion and the thermal degradation characteristics of composites are investigated by LOI, UL-94 standard, thermogravimetric analysis (TGA) and mass loss calorimeter. Char residues remained after mass loss calorimeter test are investigated by conducting attenuated total reflectance – Fourier-transform infrared spectroscopy (ATR-FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis. The mechanical properties of composites including tensile and dynamic mechanical analysis (DMA) are also examined.

2. Experimental

2.1. Materials

TPU (Pearlthane® ECO D12T85) was supplied from Merquinsa (Barcelona, Spain). It has a density of 1.15 g/cm^3 and hardness of 85 (Shore A). HH with a trade name of Ultracarb LH-15 was supplied from Likya Madencilik, Turkey. It has density and surface area of 2.5 g/cm^3 and 11–13 m^2/g, respectively. Exolit RP 6500, a blend of micro encapsulated RP in an epoxy resin carrier, was kindly obtained from Clariant (Frankfurt, Germany). The encapsulation of RP is quite common and crucial to reduce the intrinsic problems with respect to hydrolysis and phosphine formation. Exolit RP 6500 has the RP and the epoxy resin content of 43–47% and 52–57% by weight, respectively.

2.2. Sample preparation

TPU, HH and mRP were mixed in counter rotating twin screw microextruder (15 ml microcompounder®, DSM Xplore, Netherlands) at 100 rpm at 200 °C for 5 min. The extrudate was chopped into small pellets and was stored in desiccators for molding processes. The samples for thermal and flammability tests were produced using laboratory scale hot-press (Pneumo Hydraulic Press, AtsFaar, Italy) at 210 °C for 3 min. The specimens for mechanical tests were molded by a laboratory scale injection molding machine (Microinjector, Daca Instruments) at the barrel temperature of 210 °C and the mold temperature of 30 °C. The total amount of flame retardant additives was kept constant at 50 wt% by weight and the added amount of mRP was removed from the HH content. The highest adjuvant effect of mRP was observed at 7 wt% loading. Thus, pristine 7 wt% mRP containing composite was also produced and characterized for better understanding the interaction between mRP and HH. For sample coding, the abbreviations TPU, HH and mRP are used for thermoplastic polyurethane, huntite&hydromagnesite and microcapsulated red phosphorus, respectively. The sample coded as TPU/45HH/5 RP refers to the composite which contains 45 wt % HH and 5 wt% mRP.

2.3. Characterization methods

LOI values were measured using Fire Testing Technology Limiting Oxygen Index Analyzer instrument on test bars of size 130 × 6.5 × 3.2 mm^3, according to the standard oxygen index test ASTM D2863. Vertical burning tests (UL 94) were also conducted to investigate the flammability properties of composites on the test bars of 130 × 13 × 3.2 mm^3 according to ASTM D3801. TGA tests were carried out using Hitachi-High Tech STA-7300 instrument with a heating rate of 10°C/min from room temperature up to 800 °C under nitrogen flow of 50 ml/min. The mass loss calorimeter test was carried out following the procedures in ISO 13927 using Mass Loss Cone with thermopile attachment (Fire Testing Technology, U.K). Square specimens (100 × 100 × 3 mm^3) were irradiated at a heat flux of 35 kW/m^2, corresponding to a mild fire scenario. The microstructures of the residual chars remained after mass loss calorimeter test were examined with SEM (FEI Quanta 400F). All samples surfaces were coated with a thin layer of gold with a sputter-coater to provide the conductivity. Attenuated Total Reflectance - Fourier transform infrared spectroscopy (ATR-FTIR) was used to characterize char residues remained after mass loss calorimeter test at an optical resolution of 4 cm^{-1} with 32 scans. XRD data were collected on a Bruker AXS D8 diffractometer using Cu K_α radiation ($\lambda = 0.150595$ nm) with a 0.04 2θ step size and a 3 s count time. Tensile measurements were performed using Lloyd LR 5K universal tensile testing machine which equipped with 5 kN load cell at room temperature according to the ASTM D 638 standard. Tension tests were conducted on dog-bone shaped samples (7.4 × 2.1 × 80 mm^3) at a crosshead speed of 5 mm/min. Tensile strength, percentage elongation at break and modulus values were recorded. All the results were calculated with an average value of five samples with standard deviations. DMA experiments were carried out using Perkin Elmer DMA 8000 in dual cantilever bending mode at a frequency of 1 Hz to determine elastic modulus and tan δ of the composites. The test was taken place in the temperature sweep mode from −50 to 150 °C at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Thermal decomposition

Thermal properties of pristine TPU, HH, mRP and their composites are investigated by TGA under nitrogen atmosphere. TGA data of all compositions are given in Table 1. The related TGA and DTG curves are shown in Fig. 1. Thermal decomposition of TPU occurs through double step with maximum rates at 347 °C and 411 °C and two shoulders are seen at 300 °C and 466 °C with leaving 1.3% carbonaceous char. The first and second degradation stages are related with the urethane bond decomposition in the hard segments and the fragmentation of polyols in the soft segments, respectively [4,9,35]. HH decomposes in four steps at 268 °C, 445 °C, 556 °C and 693 °C with leaving 45.2% inorganic residue mainly based on magnesium oxide and calcium oxide. The first and second decomposition of steps are related with the loss of water and CO_2 from hydromagnesite in HH, respectively. The third and fourth degradation steps are related with the loss of CO_2 from huntite in HH [11,12,14].

The 50 wt% HH containing composite degrades mainly into three steps. The peak related with the initial loss of CO_2 from huntite at around 555 °C is not shown in the DTG curve of TPU/50HH. It is thought that this observed trend stems from the early decomposition of huntite which is masked with T_{max2}. The similar