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Research paper

Interactions between kaolinite and phosphinate-based flame retardant in Polyamide 6

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ABSTRACT

The interactions between kaolinite and a commercially available phosphinate-based flame retardant (Exolit® OP1311) were evaluated as flame retardant systems in Polyamide 6 (PA6). The thermal degradation and flammability of PA6 composites were studied by TGA and cone calorimeter tests. Characterizations were conducted using FTIR, EDX and XRD. Cone calorimeter results showed a reduction in peak heat release rate (pHRR) as a function of filler loading and type with a greater reduction for OP1311 containing composites. Interestingly, OP1311 can be partially substituted by kaolinite without detrimental effect on peak of release rate (pHRR) measured by cone calorimeter. FTIR, EDX and XRD analysis of cone calorimeter residues showed that kaolinite may trap some phosphorous compounds in condensed phase leading to the formation of a glassy structure on sample residue. To assess possible interactions between kaolinite and phosphinate, a controlled thermal degradation was carried out on kaolinite, OP1311 and kaolinite/OP1311 (50:50) blends. The residues were analyzed by EDX and XRD. Results showed that almost all phosphorous present in the initial sample remains in residue for Kaolinite/OP1311 blend versus only about 60% for OP1311 alone. Also, XRD results showed that during combustion, new crystalline phases can be formed in the sample when kaolinite is combined with OP1311. These results suggest that some interactions between both components may occur and could explain the observed fire behavior of the composites containing kaolinite and phosphinate.

1. Introduction

Polyamide 6 (PA6) is an important engineering polymer for electrical and electronic applications when flame retardancy is a major concern. Since it is quite often necessary to add flame retardant agents, they act, depending on their nature, chemically and/or physically in the solid or gaseous phase during the different stages of combustion. Hence, various flame retardant systems were proposed to improve polyamide fire retardancy, in particular nanoparticles (Pramoda et al., 2003; Samyn and Bourbigot, 2012; Weil and Levchik, 2004), mineral fillers (Batistella et al., 2015; Clerc et al., 2005) and phosphorous compounds (Braun et al., 2007; Braun and Schartel, 2004; Levchik et al., 1996a,b,c; Samyn and Bourbigot, 2012). Different mineral fillers at micronic and nanometric scale have attracted attention since they can impart advantageous mechanical (Batistella et al., 2015; Chow et al., 2003; Norris, 1990) and barrier properties (Alexandre and Dubois, 2000; Cabedo et al., 2004) as well as fire behavior (Beyer, 2006; Braun et al., 2007; Clerc et al., 2005; Vahabi et al., 2012). Generally, the addition of these mineral fillers reduces the total amount of fuel and the rate of diffusion of oxygen into the polymer. Also, the mineral fillers may accumulate on the surface of the decomposing polymer, shielding it from incoming radiation. Moreover, the addition of mineral fillers in the polymers can significantly change their combustion and thermal degradation pathway. The presence of these fillers will affect certain properties such as the heat capacity and the thermal conductivity of the material. Various mineral fillers received particular attention in literature such as hydrated mineral fillers and clay minerals. Hydrated fillers decompose at high temperature through endothermic release of water, slowing down the heating of the material. Considering the use of natural mineral-based nanoparticles, the use of clay minerals as components of flame retardant systems is being increasingly studied and many works have dealt with the use of organomodified montmorillonites (o-Mt) (Ramani et al., 2010; Sanchez-Olivares et al., 2008; Zhang et al., 2008), talcs (Clerc et al., 2005; Durin-France et al., 2000; Leong et al., 2004), halloysites (Hedicke-Höchstötter et al., 2009), sepiolites (Huang, 2010; Laoutid et al., 2013) or kaolinites (Batistella et al., 2016, 2014) as flame retardants.

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Generally speaking, the use of clay minerals alone is not enough to achieve acceptable levels of fire retardancy. Therefore, different compositions containing mineral fillers and phosphorous compounds were found to be efficient to reduce the heat release rate due to the formation of a protective surface barrier (Samyn and Bourbigot, 2012; Vahabi et al., 2013; Weil and Levchik, 2004). Consequently, efforts have been done to study the influence of phosphorous based additives in polyamide 6 and possibly synergies between phosphorous and mineral fillers (Braun et al., 2007; Braun et al., 2006; Levchik et al., 1996a,b,c). Inorganic and organic phosphorous compounds are extensively used to improve the fire behavior of many polymers. The range of phosphorous products is extremely broad and includes compounds of varied structure: phosphates, phosphonates, phosphinates and red phosphorus. The modes-of-action of these phosphorous compounds include flame inhibition in gas phase and char formation in condensed phase. The formation of a char layer during the fire test may protect the material and acts as a barrier to oxygen and heat of the flame. The flame retardant mechanism of the phosphorous compounds will depend on the type of compound used and the chemical structure of the polymer matrix to be flame retarded. The use of phosphinates has increased in the last years. Their beneficial impact on the fire performances has been studied either when used alone or in synergism with other components in various compounds as glass fibers reinforced polyamide 6 and 6,6 (Braun et al., 2007; Schartel et al., 2003), poly(methyl methacrylate) (Laachachi et al., 2007), poly (ethylene terephthalate) (Alongi, 2011), among others. Zhan et al. studied the synergistic effects of sepiolite and aluminum diethylphosphinate (AlPi) in PA66 (Zhan et al., 2015). Authors showed that the addition of 0.3 wt% of sepiolite allows reducing the amount of AlPi while maintaining a V-0 rating on UL-94 test and the same reduction in pHRR. Also, authors analyzed the char residues and showed that the incorporation of sepiolite changed the degradation process of the PA66/AlPi system and possibly formed diethylphosphinic acid, silicon-phosphate and magnesium-phosphate products in condensed phase, which enhanced the thermal stability and char yield of PA66 materials at high temperature.

Ramani et al. also studied synergistic effects of organomodified montmorillonite (Cloisite 30B) and OP1311 in PA6 by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Ramani and Dahoe, 2014). In their study, the weight of final residue of o-Mt and OP1311 containing composites was higher compared to a simple mixture rule of additives. Using TGA coupled with FTIR analyses, the authors showed that, at higher temperatures (above 400 °C), a water release is produced by the degradation of hydroxyl groups of the clay mineral layers, leading to a collapse of the crystal structure of melamine polyphosphate and the formation of an amorphous phase composed of metal oxides. Samyn et al. studied interactions between aluminum phosphinate, melamine polyphosphate and o-Mt in PA6 and PA66 (Samyn and Bourbigot, 2012). Authors showed that, under nitrogen, the presence of o-Mt decreases the initial decomposition temperature of aluminum phosphinate/melamine polyphosphate but the decomposition products are the same indicating that no interaction takes place between the additives. However, under air, the combined action of o-Mt and oxygen converts all the phosphinates into aluminophosphate species which contribute to an improvement in fire behavior measured by cone calorimeter for PA66 composites.

Braun et al. studied the effect of addition of a zinc borate in combination with aluminum phosphinate and melamine polyphosphate in glass fiber reinforced PA66 (Braun et al., 2007). The authors showed that the reactivity of the phosphorous additive with the polymer matrix influences not only the gas or condensed phase, but also the interaction with other additives. Also, the authors showed that the main flame-inhibition effect of the phosphinates in glass fiber PA66 is replaced by a strong barrier effect when the zinc borate is added to the formulation with a reduction in the flame inhibition effect.

Other layered silicates than o-Mt, which can be combined with phosphorous FRs, like kaolinite, have received less attention. Kaolinite is an aluminosilicate with theoretical formula $Al_2Si_2O_5(OH)_4$ and basal interlayer space of 7.1 Å. Kaolinite is a 1:1 or tetrahedral/octahedral (TO) type clay mineral, since it is formed by combining clay mineral layers of Si tetrahedra (T) and Al octahedra (O), in 1:1 proportion. The layers remain attached to each other because they share common oxygen atoms, giving rise to the structure of the clay mineral (Brindley, 1986; Giese Jr. and Giese, 1973). In a previous work, our group studied the influence of surface treatment of kaolinite in mechanical and fire properties of PA6 compounds. It was shown that surface treatment leads to different microstructures that influence fire properties measured by cone calorimeter. Kaolinite with surface modified with (3-glycidoxypropyl)trimetoxysilane decreased pHRR by about 70% compared to neat polymer and about 40% compared to PA6 filled with untreated kaolinite (Batistella et al., 2015).

Therefore, in this study, the effect of incorporation of kaolinite and a phosphinate-based flame retardant (Exolit® OP1311) on the fire reaction of PA6 is studied and interactions between components were evaluated in order to understand the mechanisms of fire retardancy and to establish possible synergistic effects.

2. Materials and methods

Commercial polyamide (PA6, Technyl® C206-Rhodia), phosphinate-based flame retardant (Exolit® OP1311-Clariant) and kaolinite (Paralux – Vale with a mean diameter of 0.8 µm and a surface specific area of 12.2 $m^2 \cdot g^{-1}$ measured by B.E.T.) were used as received. Characteristic dimensions of kaolinite layers are showed in Fig. 1. Prior to compounding, neat PA6 and PA6 composites were dried under vacuum at 80 °C. Previous studies showed that OP1311 is an aluminum diethylphosphinate enriched with nitrogenous compounds such as melamine polyphosphate, acting as synergistic agents. The elementary analysis showed that phosphorus is about 20 wt% and nitrogen about 14 wt% (Laachachi et al., 2007).

2.1. Compounds preparation

Blends of fillers and polymers were prepared by melt compounding in a twin screw extruder (Clextral, Firminy-France). The rotation speed was kept at 150 rpm, temperature ranged between 200 and 240 °C and polymer output was 4.5 kg/h. Square sheets specimens were prepared with dimensions of 100 × 100 × 4 mm^3 by injection molding using a 50 ton Krauss-Maffei equipment (Munich, Germany) and temperature range from 200 to 260 °C. The formulations are showed in Table 1.

2.2. Characterization

XRD patterns were obtained using a Bruker AXS D8 Advance diffractometer with CuKα radiation and a Vantec detector. The scanning

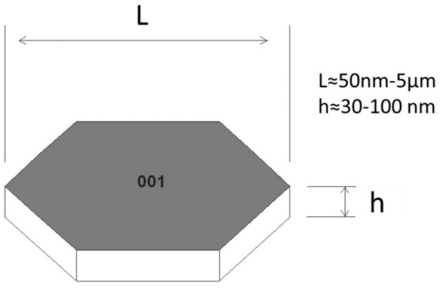

Fig. 1. Characteristic dimensions of kaolinite used in this study.