



The combined effect of organic phosphinate/ammonium polyphosphate and pentaerythritol on thermal and fire properties of polyamide 6-clay nanocomposites

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ABSTRACT

The PA6/organoclay nanocomposites with organic phosphinate (OP) or ammonium polyphosphate (APP) and pentaerythritol (PER) flame retardant additives were prepared by melt blending process using a twin screw extruder. The structure and morphology of nanocomposites formed were studied by X-ray diffraction and transmission electron microscopy, which indicated that the clay (Cloisite 30B) was intercalated and/or exfoliated into the PA6 matrix. Thermal behaviour was evaluated by thermogravimetric analysis. The small shift in TG curve to lower temperature in the initial stage of degradation on addition of OP to PA6 shows the mild catalysing effect of OP on degradation of PA6 in the presence of clay whereas the onset temperature of degradation of PA6 on addition of equal amount of APP is found to be decreased by about 100 °C due to decomposition of APP and strong catalysing effect of phosphoric acid released from APP. The cone calorimeter test showed that on addition of 15% OP and 5% 30B to PA6 have reduced the PHRR by 77%. From thermal and combustion behaviour, PA6/OP/30B sample having 5% 30B and 15% OP is found more effective in reducing burning propensity of PA6.

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1. Introduction

The development of flame retardant polymeric materials has become the necessity with the increasing use of flammable polymers in domestic, transport, military and industrial applications [1]. Polymer-clay nanocomposites have been developed and studied because of the tremendous increase in their many important properties such as mechanical, barrier and thermal [2–8]. Moreover, the existing melt blending technique for synthesis of polymer-clay nanocomposites is commercially viable, cost effective, easy and environmental friendly which has facilitated further advancement in research and development of flame retardant materials.

Polyamide 6 (PA6) is one of the developed engineering thermoplastic with especially attractive dynamic properties and can readily form nanocomposites with clays by melt blending technique [9,10]. PA6 as sheet/bulk, fibres and films is widely utilized in

many industrial and textile applications due to its high mechanical strength and durable properties but shows unsatisfactory flame retardancy due to serious flammable dripping and low limiting oxygen index [11]. The montmorillonite (MMT) clay is the most promising material of the layered silicates owing to its natural abundance and high aspect ratio. It is reported in case of PA6-clay nanocomposites that clay on dispersion in polymer matrix not only improves mechanical properties, thermal stability and barrier properties but also influences the degradation path of polymer due to interchain interactions of degrading polymer molecules enclosed in well-dispersed clay [3,7].

Addition of clay alone in polymers mainly decreases the peak heat release rate (PHRR) as one of the flame retardant property in cone calorimeter study but when flame retardancy is evaluated using LOI and UL 94 test, clays do not show any enhancement. Therefore, recent trend is to use conventional flame retardants (FRs) along with clay to achieve better flame retardant properties. This way, amount of conventional FRs added to polymer to achieve reasonable flame retardancy can be reduced significantly and hence, processing is easy. Halogen flame retardant additives are often used in industry to decrease combustibility and prove to be

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very effective [12,13]. But they cause corrosion to the processing equipment and generate corrosive and toxic products. Therefore, phosphorus and phosphorus-nitrogen based FRs are preferred and considered environmental friendly. Many workers [14–20] have studied the thermal degradation mechanism of PA6 and also reported the products released such as monomer, cyclic or linear oligomers and volatile gases during degradation.

Bourbigot et al. [21] investigated the reaction to fire of polymer nanocomposites (thermoplastic polyurethane and PA6) containing organoclay and nanotubes. Nanocomposites exhibit significant reduction of PHRR but the nanomorphology (exfoliation, intercalation and presence of tactoids) does not play any significant role. They reported that nanocomposite approach gives the best results combined with conventional FR Exolit OP 1311 (a mixture of aluminium diethyl phosphinate and melamine polyphosphate) or Exolit APP 422 (ammonium polyphosphate) and leads to synergistic effects. The nanoparticles act mainly in a physical way reinforcing the intumescent char. Ramani et al. [22] investigated the thermal degradation behaviour of a PA6 nanocomposite with FR (OP 1311). They reported that the inclusion of FR changes the degradation behaviour by lowering the degradation temperature and a lot of FR goes to the gas phase as diethylphosphinic acid. Braun et al. [23] investigated the fire retardancy mechanism of aluminium diethyl phosphinate (OP 1311) and combination with melamine polyphosphate in glass-fibre reinforced PA6. Aluminium diethyl phosphinate partly vaporizes as it and partly decomposes to volatile diethylphosphinic acid and aluminium phosphate residue. The aluminium phosphate acts as a barrier for fuel and heat transport, whereas the melamine release results in fuel dilution and the phosphinic acid formation in flame inhibition.

In this study, PA6 nanocomposites were prepared using organoclay (Cloisite 30B), ammonium polyphosphate (Exolit AP 422), organic phosphinate (Exolit OP 1230 i.e. only aluminium diethyl phosphinate) and pentaerythritol by the most conventional processing method, melt blending, which is based on a direct dispersion of clays into the polymer during the melt. The PA6 nanocomposites structures thus prepared were characterized by XRD and TEM techniques. Thermal and flammability properties of the polyamide 6 nanocomposites were studied using TG and cone calorimeter. The purpose of this paper was to study the comparative effects of conventional flame retardants such as OP (containing phosphorus only) and APP (containing both phosphorus and nitrogen) with pentaerythritol as carbonizing agent on PA6 nanocomposites.

2. Experimental

2.1. Materials

Polyamide 6 (Ultramid B 3 BASF, Germany) was used as provided. Cloisite 30B (sodium montmorillonite modified with methyl bis-(2-hydroxyethyl) tallow ammonium cation) (30B) was supplied by Southern Clay Products Inc. Ammonium polyphosphate (Exolit AP 422, $(\text{NH}_4\text{PO}_3)_n$, $n > 1000$) (APP) and Exolit OP 1230 (aluminium diethyl phosphinate) (OP) were obtained from Clariant Inc. Pentaerythritol (PER) was supplied by Sigma Aldrich Co. All these commercial materials were used as received without further purification. For Cloisite 30B, the cation exchange capacity and percent weight loss on ignition were about 90 meq/100 g and 30, respectively.

2.2. Preparation of nanocomposites

All the samples were prepared by melt blending PA6 with different additives (see Table 1) in a co-rotating, twin screw

Table 1

TG data of clay and flame retardant additives in He.

Material	Composition (%)	$T_{10 \text{ wt\%}}$ (°C)	$T_{50 \text{ wt\%}}$ (°C)	DTG peak (°C)	Residue at 600 °C (%)
Cloisite 30B (30B)	100	305	—	293, 397	78.0
Exolit OP 1230 (OP)	100	431	471	—	15.0
Exolit AP 422 (APP)	100	382	630	350, 640	65.3
Pentaerythritol (PER)	100	231	264	272	0.3

extruder (Coperion Zweischncken Laborextruder, L/D = 40) with a feed rate of 5 kg/h. The screw speed was 300 rpm in order to have high shear stress. The temperature range from feed end to die end in different zones was 220–240 °C. The composition of samples is given in Table 2. The extrudates thus obtained were then pelletized. These samples in pellet form were dried at 80 °C for 10 h. Cone samples were prepared by injection moulding machine at 240 °C into square plaques of size 75 mm × 75 mm × 3 mm.

2.3. Characterization by XRD and TEM

The dispersibility of the silicate layers in the PA6 was investigated by X-ray diffraction (XRD) technique. XRD determines the d_{001} spacing in the modified clay and provides information on the degree of hybrid structure generated. Diffraction peaks in the low angle region indicate the d-spacing (basal spacing) of ordered intercalated and ordered delaminated nanocomposites. Disordered nanocomposites show no peak in this region due to loss of structural registry of the layers and/or the large d-spacing. The XRD spectra of PA6 samples were obtained with instrument Bruker D8 Advance using $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) to determine d-spacing between the clay layers. The voltage and the current of the X-ray tube were 40 kV and 40 mA, respectively. Transmission electron microscopy (TEM) images of PA 6 and composites were obtained with instrument Philips CM 200 FEG at 200 kV accelerator voltage. The cloudy dispersions of samples were prepared and particles were deposited from solution onto the mica sheet and then solvent was evaporated. After shadowing carbon coating, the film was floated-off the mica and retrieved on to copper grids.

2.4. TG analysis

The thermal stability of PA6 and its nanocomposites was tested by thermogravimetry analysis (TG). The thermal degradation in the TG was carried out using a DuPont 951 Thermogravimetric analyzer at a heating rate of 10 °C/min under He atmosphere with flow rate of 100 ml/min. In each case, a 5–10 mg sample was examined in the range of ambient temperature to 700 °C.

2.5. Cone calorimetry

The fire properties of polyamide and its nanocomposites were characterized by a cone calorimeter, Fire Testing Technology

Table 2

TG data of PA6 and its composites with 30B, OP, APP and PER in He.

Material	Composition (%)	$T_{10 \text{ wt\%}}$ (°C)	$T_{50 \text{ wt\%}}$ (°C)	DTG peak (°C)	Char at 600 °C (%)	Calculated char at 600 °C (%)
PA6	100	436	466	468	2.2	2.2
PA6/30B	95 + 5	436.5	478	482	5.9	5.9
PA6/OP	80 + 20	432.4	470	472	4.8	4.7
PA6/30B/OP	80 + 5 + 15	425	470	475	7.7	7.9
PA6/30B/OP/PER	80 + 5 + 10 + 5	393	463	467	8.7	7.2
PA6/APP	80 + 20	334	386	391	13.1	14.8
PA6/30B/APP	80 + 5 + 15	335	392	391	17.2	15.4
PA6/30B/APP/PER	80 + 5 + 10 + 5	335	406	405	17.7	12.2

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