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Novel phosphorous–nitrogen intumescent flame retardant system. Its effects on flame retardancy and thermal properties of polypropylene

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ABSTRACT

This paper describes the effectiveness of novel phosphorous–nitrogen intumescent flame retardant system (ammonium polyphosphate 202 and PPM Triazine HF – trademark, abbrev. IS) on fire retardancy and thermal stability properties of polypropylene (abbrev. PP) at incorporation level below the standard amount required for intumescent flame retardant system.

UL-94 vertical burning test revealed that the addition of 20 wt.% of IS into neat PP is enough to reach V-0 rating (short burn without dripping). Further, a higher increase of the oxygen concentration for ignition was also found with the addition of the novel intumescent flame retardant to neat PP; LOI value of neat PP by addition of 20 wt.% IS rose from 19 to 31 vol.%.

Finally, a remarkable decrease of peak heat release rate (PHRR: −91%), total heat release (THR: −42%), average of mass loss rate (AMLR: −92%), average of specific extinction aria (ASEA: −48%) and total smoke release (TSR: −58%) was revealed with increasing in IS content.

Novel intumescent flame retardant system showed good flame retardancy performance pointing out that the intumescent char formed resists oxidation; this aspect was also confirmed by the thermogravimetry analysis. Hence, it can be pointed out that the improvement of flame retardancy imparted by the novel intumescent flame retardant system at lower concentration enables on one side a lower cost material formulation and on the other side the impact on the mechanical properties of the polymer might be lower.

The thermo-oxidative data have revealed an enhancement of the thermal stability of the PP matrix by incorporation of IS (the PP/20IS composite showed a markedly increase in T_{onset}: 14 °C and T_{max}: 64 °C).

1. Introduction

Although halogen flame retardants deliver an excellent balance of performance, processability, and cost, due to the potential risk which they pose for environment as well as to human health [1–7], it has prompted the plastic industry to look for eco-friendly alternatives (Halogen-Free). One of the viable approach as a response to halogen-free retardants demand, beside of using inorganic filler (aluminum trihydrate, magnesium hydroxide, etc.) is the concept of intumescence. Intumescence comes from the Latin word “intumescere” which means “to swell up”, thereby the mechanism of an intumescent flame retardant refers to the formation of a foam, when the material is heated beyond a critical temperature, which acts as excellent insulation barrier against heat transfer from the heat flux/flame to the unburned fuel, diffusion of the volatile degradation products in the burring zone and diffusion of external oxygen into the degradation zone preventing, therefore, further decomposition [8,9]. As stated by the literature [10–12], a typical intumescent flame retardant system (IFRs) for polymers, development based on the experience required in coatings [13], should comprises:

- an inorganic acid, either free or formed *in situ* on heating by a suitable precursor, dehydration agent which promote charring (such as acids: phosphoric, sulfuric, boric; ammonium salts: phosphates, polyphosphates, sulfates; amine, amide phosphate: urea, guanylurea, melamine; organophosphorus compounds: tricresyl phosphate, alkyl phosphates, etc).
- carbon rich polyhydric compounds which are capable of supplying the char (such as starch, dextrin, sorbitol, pentaerythritol, phenol-formaldehyde resins, etc).
- organic amine or amide which release non-combustible gases for blowing the char to a foamed structure (such as urea, urea-formaldehyde resins, melamine, polyamides, dicyandiamide, etc.).

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According to the exhaustive research [[14–19] and references cited within], it was revealed that IFRs are efficient at large amounts (25–30 wt.%) which implicit entail a relatively high cost [20], therefore a continuous effort is carried out to develop new highly effective intumescent systems having impact not only on the fire properties of polymer materials but also, for instance, on the cost of material formulation, etc.

In this context, the main goal of this work is to investigate the effectiveness of novel phosphorous–nitrogen intumescent flame retardant system on the fire retardancy of polypropylene at incorporation level below the standard amount required for intumescent flame retardant system.

Furthermore, the flame retardancy performance of this novel intumescent flame retardant system was compared with that of traditional IFR system, such as Exolit AP760.

2. Experimental methods

2.1. Materials

Polypropylene used was a commercial grade product (Moplen HP 500N – trademark, abbrev. PP) supplied by Basell. Intumescent flame retardant system comprising: ammonium polyphosphate 202 – trademark and PPM Triazine HF – trademark (see Fig. 1 for its chemical structure) (abbrev. IS) supplied by MCA Technologies GmbH (Germany). Pentaerythritol (Charmor PM15 – trademark; abbrev. PER) supplied by Perstorp Winning Formulas (Sweden).

2.2. Sample preparation

All the PP/IS composites (PP/10 wt.% IS, PP/15 wt.% IS and PP/20 wt.% IS) were prepared via direct melt compounding using a Leistritz ZSE 18 HP (Brabender Technologies, Duisburg, Germany) co-rotating twin screw extruder (screw diameter = 18 mm, length/diameter = 40). The operating temperature of the extruder was maintained at 200-200-195-190-190-185-180-180 °C from the hopper to the die, respectively. The screw speed was maintained at 150 rpm and the throughput was 2 kg/h. The molten material was quenched in water and then pelletized.

2.3. Characterization techniques

2.3.1. Thermal analysis

Thermogravimetric (TG) analyses were performed with a Q 500 thermal analyzer (TA Instruments, Chicago, Illinois, USA) at a heating rate of 10 °C/min from 50 to 800 °C under air flow (60 mL/min). The samples (ca. 10 mg) were placed in open alumina pans. From TG curves, the parameters T_{onset} (the temperature at which the sample lost 5 wt. % of its original mass) and T_{max} (the temperature at which the maximum rate of mass loss occurred) were evaluated to characterize the thermal stability of the neat polymer matrix and the composites. Furthermore, the synergistic effect between APP and PPM Triazine HF (IS) as well as APP and PER during their pyrolysis was investigated by comparing the experimental TG curves of the mixtures with the calculated ones. The calculated mass loss ($M_{calculated}$) curves were calculated by the linear combination of the experimental TG curves of each compound taken individually: APP, PPM Triazine HF and PER, (Equation (1)); in other words, the calculated curves, calculated by additives rules, represent the degradation of the mixtures when no chemical or physical interaction between the compounds takes place.

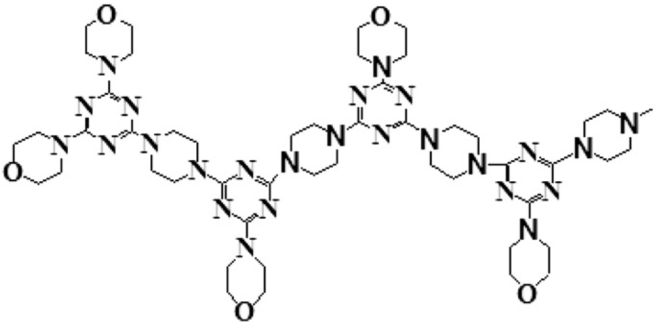

Fig. 1. Chemical structure of PPM Triazine HF.

$$M_{\text{calculated}}(T) = xM_{\text{APP}}(T) + yM_{\text{PPM Triazine HF or PER}}(T) \quad (1)$$

where M_{APP} is the mass loss of APP, $M_{\text{PPM Triazine HF or PER}}$ is the mass loss of PPM Triazine HF or PER and T is the temperature of degradation (50–800 °C), $x + y = 1$, x and y are the mass percentages of APP, PPM Triazine HF and PER in the mixture; $\Delta(T)$: curve of weight difference: $\Delta(T) = M_{\text{experimental}}(T) - M_{\text{calculated}}(T)$, which allows the observation of eventual synergy and/or antagonism during degradation between APP–MMP Triazine HF and APP–PER; synergism refers to the combined effect of two or more additives, which is greater than the sum of their individual effects, while antagonism effect means that the observed effect is less than the sum of the individual effects.

2.3.2. Scanning electron microscopy (SEM)/energy-dispersive X-ray spectroscopy (EDS)

The microstructural and elemental analyses of the cross-sectional sample as well of the residues obtained at the end of the cone calorimeter test were done with a scanning electron microscope (LEO 1450 VP, Oberkochen, Germany) with an energy-dispersive X-ray probe (INCA Energy Oxford, UK) attachment. The cross-sectional sample was prepared by cryogenic fracture in liquid nitrogen and then sputter-coated with gold for 27 s at a working pressure of 0.1 mbar before the SEM/EDS measurements.

2.3.3. Fire tests

The limiting oxygen index (LOI) test was carried out with a Fire Testing Laboratories (Fire Instrumentation & Research Equipment Ltd, Kent, UK) instrument according to the standard oxygen index test UNI EN ISO 4589-2. This test is a procedure for measuring the minimum oxygen concentration in a flowing mixture of oxygen and nitrogen that supports combustion in a candle like configuration of a top-ignited vertical test specimens as follows: a Bunsen burner propane flame is applied on the top of a vertical orientated test specimen for up to 30 s, removing it every 5 s, just briefly, to observe whether or not the entire top surface of the specimen is burning. The higher the LOI value, the better is the flame retardancy (air contains approximately 21 vol.% oxygen and therefore any material with an LOI of less than 21 will probably support burning in an open-air situation). The dimensions of the specimens used for this test were 75 × 6 × 3.2 mm^3.

The UL-94 vertical burning (UL-94 V) test was carried out according to ASTM D 3801-00 standard procedure. A Bunsen burner methane flame is applied at the bottom end of a vertical orientated test specimen for 10 s, two times, with an interval made by the time that it takes for flaming combustion to stop after the first application. This test classified the materials as V-0, V-1, V-2 or not classifiable according to the time period needed for extinguishment of the flame after each ignition and whether combustion occurs with dripping of flaming particles which are capable of igniting surgical cotton placed underneath the specimen. V-0 is the most required classification. The dimensions of the specimens were 125 × 12.5 × 3.2 mm^3.