

## Synthesis of halogen free flame retardant and its application on polypropylene

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*Received 23 December 2011; accepted 10 December 2012*

The present work is aimed at synthesizing halogen free, ecofriendly phosphorous based flame retardant (FR) for polypropylene (PP). Polypropylene is highly flammable at room temperature and leaves almost no char. The synthesised FR enhances the LOI values of polypropylene and also arrests the antidripping properties of the polymer. However, the breaking strength of flame retardant polypropylene filaments is found to be decreasing with increasing concentration of FR compound. Thermal stability of the PP increases with the increase in degradation temperature.

**Keywords:** Flame retardant, Polypropylene, Phosphorous based flame retardant, Thermal stability

### 1 Introduction

A major virtue of polypropylene is its ability to be used in a wide range of fibrous forms in general and nonwovens in particular. The low melting point of polypropylene (160-170°C) is an advantage in many nonwoven processing steps. Polypropylene is extremely difficult to flame retard<sup>1-3</sup>. Pure polypropylene is highly flammable at room temperature and leaves almost no char<sup>4</sup>. Its flammability, a very low limiting oxygen index (LOI) value (17.4), has limited its applications in some important fields<sup>5</sup>. When ignited, polypropylene burns with a hot smoke-free flame without leaving a char residue. The burning is accompanied by dripping and flowing of the flaming polymer which is a considerable hazard in itself. Therefore, a flame retardant should not only cause extinction of the burning polymer, but also prevent the flaming drip<sup>6</sup>. Thus, flame retardant polypropylene material is a requirement of many fields for their development<sup>7</sup>.

Traditionally, halogen-containing compounds with antimony trioxide as a synergistic agent are the main flame retardants of PP. However, as far as the safety aspects and environmental problems are considered, the use of some of these flame retardants is limited because of the evolution of toxic gases and corrosive smoke during combustion<sup>8</sup>. Chiu and Wang<sup>9</sup> have studied the dynamic flame redundancy of polypropylene (PP) filled with ammonium polyphosphate.

Now halogen-free compounds are regarded as promising flame retardants because of their environment-friendly properties. Metallic hydroxides and oxides are kinds of flame retardant additives used in polypropylene, but the high loading seriously destroys the mechanical properties of polymeric material<sup>10</sup>. Chen *et al.*<sup>11</sup> have studied the effect of magnesium hydroxide on mechanical properties and thermal behavior of polypropylene.

Intumescent flame retardant (IFR) systems have been used recently in flame retardant polypropylene (FRPP) as a kind of halogen-free flame retardant<sup>12</sup>. Intumescent flame retardant compounds are usually composed of an acid source, a carbon source and a gas source, such as ammonium polyphosphate (APP), pentaerythritol (PER) and melamine respectively. Ammonium polyphosphate (APP) is commonly used acid source in intumescent fire retardant systems<sup>13,14</sup>. On heating, it forms polyphosphoric acid which is a well-known acid catalyst for organic reactions. The thermal behavior of PP improves by introduction of a phosphorus-nitrogen intumescent flame retardant. Besides being halogen free, the intumescent flame retardant systems have the advantage of low toxicity, low corrosion and absence of melt dripping<sup>15-17</sup>.

Considering the toxicological concerns regarding FRs, the present work is aimed at synthesizing an ecofriendly phosphorous-based flame retardant for polypropylene. The synthesized FR is compounded into the PP matrix and its flammability performance in terms of LOI (limiting oxygen index) has been studied.

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## 2 Materials and Methods

### 2.1 Materials

Polypropylene chips REPOL H200FG with melt flow index 20 were obtained from Reliance Industries, Mumbai. Phosphorous oxychloride (Sandhya Group of Companies, Mumbai) was used as a main FR compound, Neopentyl glycol (SD Fine Chemicals, Mumbai) was used to prepare a stable intermediate compound before the final FR compound is synthesized using thermally stable compound 4-phenyl phenol or P-hydroxyl diphenyl (SD Fine Chemicals, Mumbai). Solvent used was toluene (SD Fine Chemicals, Mumbai). Triethylamine (SD Fine Chemicals, Mumbai) played role of acid scavenger and magnesium chloride (SD Fine Chemicals, Mumbai), a catalyst.

### 2.2 Reaction Scheme

Neopentyl glycol reacts with phosphorous oxychloride to form neopentyl Glycol phosphonyl chloride (NGPC) which further reacts with 4-phenylphenol to finally form a FR compound (Scheme 1).

### 2.3 Synthesis of FR Compound

In a three-necked flask provided with a stirrer, a dropping funnel, a hydrochloric acid absorber device and a condenser, 1 mole of neopentyl glycol and toluene were fed. The resulting mixture was heated at 45-55°C. With stirring, 1 mole phosphorous oxychloride was added drop-wise to the mixture in an hour. The mixture was heated to 75°C in an hour, and then allowed to react at the same temperature (75°C) for an hour. The generated hydrogen chloride as a gas was absorbed or neutralized by using potassium hydroxide solution.

The resulting reaction mixture was cooled to room temperature to which 0.95 mole of 4-phenylphenol

(para-phenylphenol), 0.1 mole of magnesium chloride and 1.1 mole of toluene were added and the mixture was heated at 65-75°C. With stirring, 1.05 moles of triethylamine was drop-wise added to the mixture in an hour. Thereafter, the mixture was allowed to react at the same temperature (75°C) for an hour.

The obtained mixture was cooled to room temperature and neutralized by adding a hydrochloric acid solution which corresponds to an excess amount of triethylamine, and allowed to stand to separate an oil phase. Finally, the obtained oil phase was washed with water at approximately 85°C. The remaining liquid, if any, was removed by dehydration in oven and white solid was obtained as flame retardant compound.

### 2.4 Preparation of Flame Retardant Polypropylene

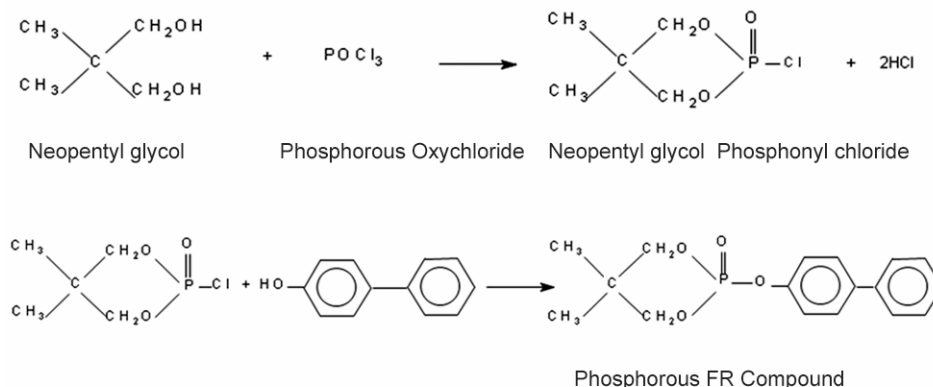
#### *Compounding of Polypropylene Chips with Phosphorous Flame Retardant*

The PP chips were dried in a vacuum dryer for 4 hours at 60°C to remove traces of moisture. Before melt spinning the PP pallets were compounded with phosphorous flame retardant (FR) in twin screw co rotating extruder where RPM of screw was 60-80.

The compounding of FR into PP was done using 5, 10 and 15% conc. of FR compound. The temperatures of five zones in extruder were 175, 185, 195, 210 and 220°C for zone 1, 2, 3, 4 and 5 respectively.

#### *Melt Spinning of FR Polypropylene Filaments*

The melt spinning of the PP pallets blended with FR was carried out on laboratory melt spinning machine supplied by Fair Deal Associates, New Delhi, India. The temperatures of this spinning extruder zones maintained were 190, 200 and 220°C for Zone-I, Zone-II and Zone III respectively. The temperatures were distinctly above the melting point of the PP pallets. The extruder zone was provided with a nitrogen gas to prevent oxidation of PP.



Scheme 1—Synthesis of phosphorus flame retardant compound

The pellets melt to form a molten mass, which moves further to metering pump and then to Die head zone. The filaments extruded from the spinnerets were cooled down by blowing cool air in 1.5 meter long quench duct. The filaments were guided to the godet roller subsequently and were taken over to the draw rollers. The drawing was carried out by two-stage drawing method at draw ratio of 3. The filaments were finally fed to the take up winder machine over the condenser arm wheel, which applies tension to the yarn and controls the speed of the spindle, ensuring that consistent package could be formed.

## 2.5 Characterization and Testing of FRPP

### *Analysis of FRPP by FTIR*

FTIR spectra of FRPP were obtained with Shimadzu IR Prestige 21 Spectrophotometer which gives an idea of induction of chemical or bonding with the parent material. FRPP filaments were cut into fine pieces, dried and the same were dispersed into dry KBr and made into pellets with hydraulic press and were immediately subjected to FTIR analysis

### *Evaluation of Tensile Strength of PP Filaments*

The tensile strength and elongation-at-break of polypropylene and FR polypropylene filaments were measured on Tinius Olsen MK supplied by Aimil Ltd. A single filament of test length (10 cm) was used at an extension rate of 50 mm/min. An average of 5-10 readings was noted and expressed in terms of kgf. Testing was carried out as per the test method ISO 5079 for breaking strength of filaments.

### *Determination of Limiting Oxygen Index (LOI)*

The polypropylene pellets were compounded with flame retardant and then melt spun into filaments which were further subjected to compression moulding to form a sheet of FR polymer composite. The moulded sheet was used to find out limiting oxygen index (LOI) using the method ASTM D 2863. The sheet was clamped to holder in a chamber and ignited with fire source till it catches fire and burns entire length of specimen.

### *Thermogravimetric Analysis (TGA)*

TGA can serve as a useful indicator of polymer decomposition and flammability behavior. It is the most favoured technique for rapid evaluation in comparing and ranking the thermal stability of various polymers. The effect of FR when incorporated into polymer matrix on the thermal stability was studied

by TGA. The weight loss due to the formation of volatile products after degradation at high temperature was monitored as a function of temperature. TGA was done for pure PP and FRPP with DTG-60H Thermogravimetric Analyser, Shimadzu, Japan by heating the samples under nitrogen atmosphere at a heating rate of 5 °C/min from 40 °C to 500 °C.

### *Study of Morphological Features*

Scanning electron microscopy is a widely used microscopic technology to study the morphological features and surface characteristics of the polymeric materials. The FRPP and pure PP were studied for their morphology and surface characteristics. SEM analysis was carried out on a scanning electron microscopy of the make JEOL, JSM-6380, Japan. Samples were sputter-coated with platinum to increase surface conductivity. The SEM machine was operated at 10 kV for analysis of images.

## 3 Results and Discussion

FTIR plot of pure and flame retardant polypropylene is shown in Fig. 1 where the dominant presence of –CH groups in the linear chain of polypropylene at 2915  $\text{cm}^{-1}$  can be observed. The synthesized FR compound is melt blended with pure polypropylene. It is observed that the –CH groups at 2915  $\text{cm}^{-1}$  in PP and P=O bond in the FR compound at 1280  $\text{cm}^{-1}$  both are present in the spectrum of flame retardant polypropylene. Thus, spectrum shows that synthesized FR compound is well incorporated into polypropylene matrix.

The effect of loading of FR additive on thermal stability of the modified polymer is studied with thermogravimetric analysis (TGA), as shown in Fig. 2. It is observed from the figure that there is single stage degradation. When both the curves are compared, it is observed that with introduction of 10% FR compound into matrix, thermal stability of the FRPP increases significantly. Fifty per cent weight loss in pure PP is observed at 402.2 °C, while in case of FRPP it is seen at 448.7 °C. The difference in temperatures of 50% weight loss is quite considerable. The degradation in pure PP starts quite early at 391.64 °C and in FRPP the degradation starts at 436.92 °C. From the above temperature difference it is sure that FR plays its role in increasing thermal stability of the polymer.

Figure 3 shows the comparison of pure PP and FRPP for SEM analysis. The pure PP surface is

smooth and clean, while FRPP shows quite opened up cavited texture. The fractured, rough and bumpy surface of the FRPP further supports increase in accessibility or amorphous region as a result of FR addition into polymer matrix. Thus, SEM study also supports increase in amorphous region, leading to decrease in tensile strength of FRPP filaments.

The flame retardancy of the PP increases with increase in conc. of FR compounded into polymer. The LOI of the control PP is 18 and with the introduction of 5% FR compound into PP, LOI value reaches to 21 which is a considerable increase in flame retardancy. Similarly, when conc. of FR compound is increased to 10% and 15%, the LOI values obtained for FRPP increase to 24 and 26 respectively. The increasing flame retardancy of PP with increasing concentration of FR compound may be attributed to the higher amount of phosphorous content present in the polymer which acts in condensed phase. During burning, phosphorous decomposes relatively at

lower temperature due to weak phosphonate bond and forms a surface layer of char. This charred layer formed on the surface is itself difficult to burn and can insulate the underlying polymer against further thermal degradation, it acts as physical barrier restricting the oxygen access. From the data, a linear relationship between flame retardancy of PP and concentration of FR compound loaded can be observed.

Table 1 depicts the effect of loading of FR compound on the strength of FRPP filaments. The breaking strength of control PP filament is 0.207 kgf, whereas that of FRPP filament modified with 5% FR

Table 1—Effect of flame retardant on strength of FRPP filaments

Conc. of FR, %	Breaking strength kgf	Elongation %	Strength retention, %
0	0.207	414	100
500	0.192	340	92.7
1000	0.178	293	85.9
1500	0.165	280	79.7

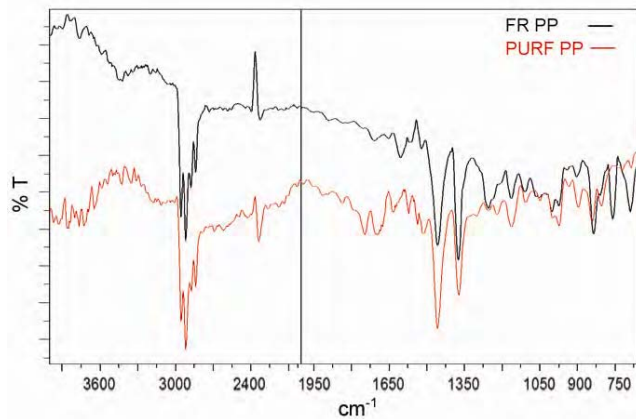


Fig. 1—FTIR plot of pure and flame retardant polypropylene

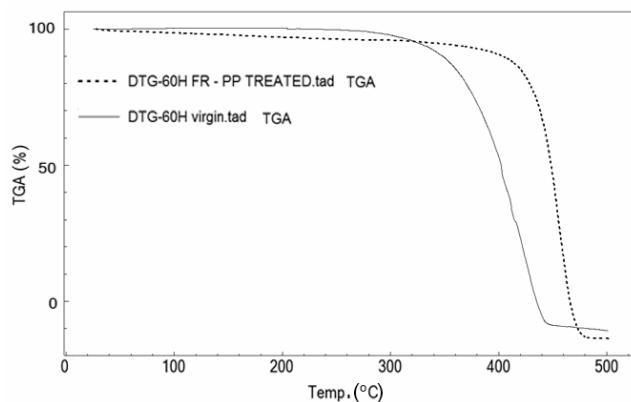


Fig. 2— Thermogravimetric analysis of pure(virgin) and flame retardant polypropylene

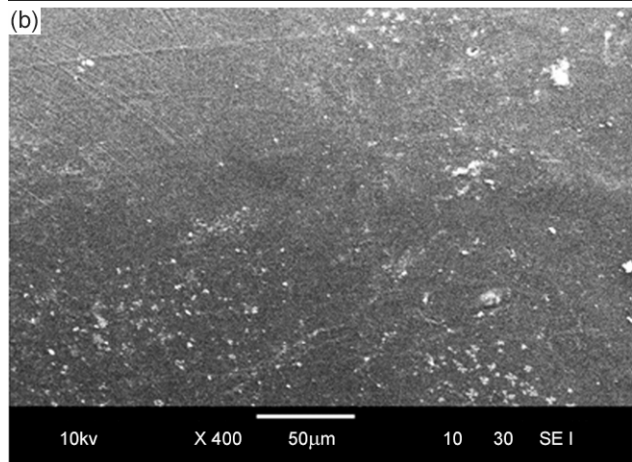
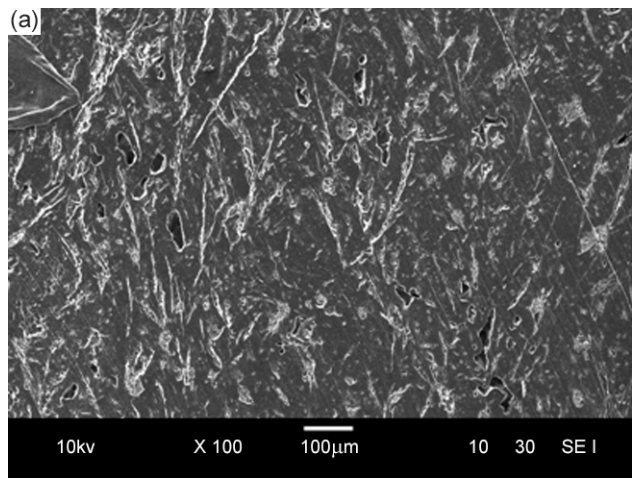


Fig. 3—Scanning electron microscopy of (a) pure polypropylene and (b) flame retardant polypropylene

compound is found to be 0.192 kgf which clearly indicates 8% strength loss of filament. A similar trend of decreasing strength of FRPP filaments with increase in conc. of FR compound is observed for 10% and 15% FR compound. As the conc. of FR compound increases, the number of amorphous regions in the polymer matrix also increases, disturbing the regular arrangement of macromolecular chains. Thus, decrease in crystallinity of the PP with increase in conc. of FR compound is supposed to be responsible for decrease in breaking strength of FRPP.

#### 4 Conclusion

Ecofriendly FR synthesized by using phosphorous oxychloride has imparted flame retardancy to polypropylene though with partial success. A linear relationship between flame retardancy of PP and concentration of FR compound loaded has been observed. The breaking strength of FRPP filaments is found to be decreasing with increasing concentration of FR compound. Thermal stability of the PP is increased with increase in degradation temperature from 391.64 °C for pure PP to 436.92 °C for FRPP using 10% of FR compound.

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