

Note

A NEW SYNERGIST FOR INTUMESCENT FLAME RETARDANT POLYPROPYLENE*

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Abstract The synergistic effects of silicotungstic acid (SiW_{12}) as a catalyst in the phosphorus-nitrogen compounds AM-based intumescent flame-retardant (IFR) polypropylene (PP) were studied using the limiting oxygen index (LOI), the UL-94 test, thermogravimetric analysis (TGA), real time Fourier transform infrared (FTIR), laser Raman spectroscopy (LRS). The LOI data show that SiW_{12} added to PP/IFR systems has a synergistic FR effect with an IFR additive named AM. The TGA data show that SiW_{12} apparently increases the thermal stability of the PP/IFR systems at high temperature ($T > 500^\circ\text{C}$). The FTIR results provide the positive evidence that IFR can improve the thermal stability of PP and SiW_{12} can induce a higher rate of formation of phosphoric acid and its derivatives. The LRS measurements provide useful information on the carbonaceous microstructures. In short, a suitable amount of SiW_{12} (1.5 wt%) exerts synergistic effects with the IFR by increasing the LOI value and the thermal stability at high temperature and promoting the formation of charred structures on the burning PP surface.

Keywords Silicotungstic acid, Synergistic effect, Intumescent flame retardant, Polypropylene

INTRODUCTION

Intumescent technology can provide fire protection for flammable polymeric materials^[1, 2]. Generally, intumescent formulations contain three active ingredients: carbonisation catalyst, char-forming agent, and a blowing agent. First, the acid source breaks down to yield a mineral acid, then it takes part in the dehydration to yield the carbonaceous char and the blowing agent decomposes to yield inert gaseous products. The proposed mechanism of intumescent flame retardant (IFR) materials is that the foamed cellular charred layers formed on heating act as a physical barrier on the surface of materials, a process that slows down heat and mass transfer between the gas and condensed phase and protects the underlying material from heat flux or a flame. Commercial inorganic fillers^[3, 4] (e.g. titanium dioxide, silicon dioxide and clay) used in intumescent flame retardant polymeric materials could increase the mechanical and thermal resistance of the char. Furthermore, they could lead to a control of the cells' size by acting as nucleation centers when the blowing gases are evolved in the charring matrix. The heteropolyacids are known to be effective acid and oxidation-reduction reaction catalysts^[5]. There are few reports about heteropolyacid being used in IFR polypropylene. The aim of this work is to study the synergistic effects of silicotungstic acid ($\text{SiO}_2 \cdot 12\text{WO}_3 \cdot 26\text{H}_2\text{O}$) with other IFR additives, such as phosphorus-nitrogen compounds AM, in the flame retardant properties, the formation of charred layers, and their microstructures in the PP/IFR blends.

Materials

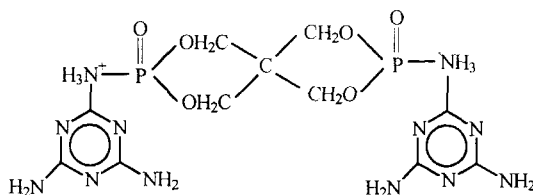
Commercial polypropylene (PP F401), from Yangtze Petro-Chemical Co., with a melt index of 2.0 g/min

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(230°C/2.16 kg) was used as the matrix. Silicotungstic acid ($\text{SiO}_2 \cdot 12\text{WO}_3 \cdot 26\text{H}_2\text{O}$ abbreviated as SiW_{12}) was from Taishan Chemical Plant. The main IFR additive named AM is a mixture of ammonium polyphosphate (APP) and CN329 with $\text{APP/CN329} = 1/4$. The molecular formula of CN329 is showed in Scheme 1.



Scheme 1 Molecular formula of CN329

Sample Preparation

All the PP/IFR samples were mixed for 10 min at 180°C in a Rheomixer XSS-300 (made in Shanghai) as 50 g batches of PP containing the desired amounts of IFR additives. After mixing, the samples were hot-pressed under 10 MPa for 5 min at 180°C into sheets of suitable thickness. Sheet size and thickness were dependent on the testing methods used in the present study.

Samples of intumescent chars for measuring laser Raman spectra were prepared by heating with a flame the top of bar specimens of flame-retardant PP kept in a stream of nitrogen-oxygen in a ZRY-type oxygen index apparatus made in China. The volume percent of oxygen in the stream was 1 unit higher than that of the limiting oxygen index (LOI) value of sample following the method stated in the OI test of ASTM D2863-77. The charred layers were carefully removed from the specimen and examined without further treatment.

RESULTS AND DISCUSSION

Effect of SiW_{12} Concentrations on LOI Values of PP/IFR Blends

The data of limiting oxygen index (LOI) value in Fig. 1 show that the addition of 1.5 wt% SiW_{12} to PP/AM blend can increase its LOI value from 30.5 to 34.5 with the total amount of additives AM and SiW_{12} being kept constant (at 25 wt%). This result indicates that SiW_{12} has a distinct synergistic effect on AM by increasing the LOI value of PP/IFR blends, which might be due to the formation of charred layers from SiW_{12} as an acid catalyst.

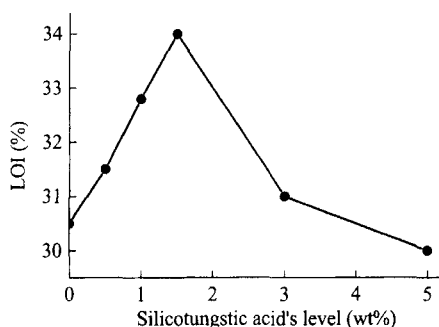


Fig. 1 Changes of LOI values with SiW_{12} 's level for PP/AM/ SiW_{12} with the total amount of 25 wt% additives kept constant

Thermogravimetric (TG) Behavior of PP and PP/IFR Blends

The TG data obtained by comparison of PP/AM and PP/AM/ SiW_{12} samples show that the charred layers formed on the PP/AM/ SiW_{12} sample remains stable up to 11% char residues in the temperature range of 500–800°C, while those formed on the PP/AM sample continue to degrade up to 4% char residues. This means that the PP/AM blended with SiW_{12} has higher thermal stability above 500°C resulting from the compact charred layers,

which are related to the nucleating behavior of oxides arising from the degradation of SiW_{12} ^[4].

Formation Rates of P–O–C and P–O–P Products

The changes of FTIR spectra for the two PP/IFR blends (PP/AM and PP/AM/ SiW_{12}) with increasing pyrolysis temperature have been studied in detail using real time FTIR spectroscopy, the results of which are shown in Fig. 2. The formation rates of the P–O–C, P–O–P, and PO_3 products can be expressed by the rates of change of the relative peak intensities at 1274, 1088, and 1018 cm^{-1} , respectively^[6]. In Fig. 2, the relative intensities of P–O–C, P–O–P, and PO_3 in the PP/AM/ SiW_{12} system are higher than those of the corresponding groups in the PP/AM system when the pyrolysis temperature is above 230°C. These results indicate that the formation rates of P–O–C, P–O–P, and PO_3 groups in the intumescent carbonaceous charred structures obtained from the PP/AM/ SiW_{12} system are higher than those of the corresponding groups in the PP/AM system. This is positive evidence that SiW_{12} as an acid catalyst has a synergistic effect on the formation of charred layers with the P–O–C, P–O–P, and PO_3 complex structures.

Microstructure Characterization of Carbonaceous Charred Layers

Raman scattering is especially sensitive to the structural disorder of graphite. Figure 3 shows the Raman diffusion spectra of the char residues obtained from the PP/AM and PP/AM/ SiW_{12} blends. Both spectra exhibit two broad bands around 1580 and 1350 cm^{-1} , similar to the graphite-like species^[6]. The peak observed at 1580 cm^{-1} (G peak) could be attributed to the C–C vibration in the aromatic layers, and the peak at 1350 cm^{-1} (D peak) to the so-called defect band^[7], from A_{1g} vibration mode of “unorganized” carbon in the sample. Tuinstra and Koenig (T-K)^[8] found that the relative intensity ratio R of the D peak to the G peak is inversely proportional to an in-plane microcrystalline size and/or an in-plane phonon correlation length obtained from Raman spectroscopy. Therefore, the T-K relation has frequently been used to evaluate in-plane microcrystalline size and to characterize the carbonaceous species. The spectrum of the PP/AM/ SiW_{12} system shows that the relative intensity of the D peak is higher than that of the G peak, while the intensities of the G and D peaks from the PP/AM system are almost the same. Therefore, the size of carbonaceous microstructures from the PP/AM/ SiW_{12} system might be smaller than that from the PP/AM system. These results are in good agreement with those reported in Bourbigot’s work^[6], in which the higher protective shield’s efficiency was related to the smaller size of carbonaceous microstructures. It is presumed that the SiW_{12} or its pyrolytic products inhibit the increase of the carbonaceous micro-domain in size during burning, which leads to the formation of more compact charred layers.

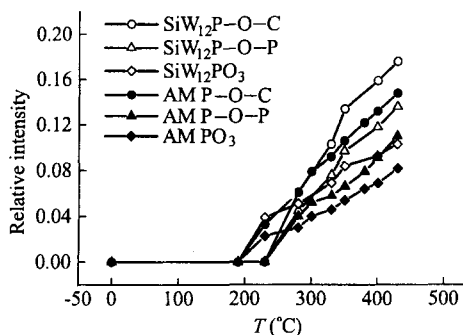


Fig. 2 Relative peak intensities of P–O–C, P–O–P, and PO_3 products obtained from real time FTIR versus different pyrolysis temperatures

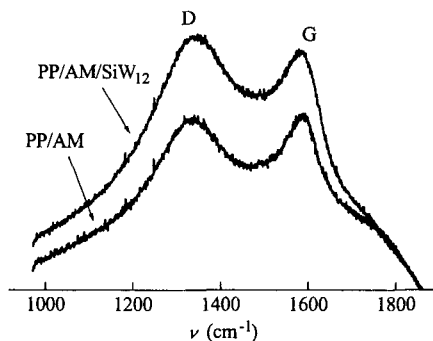


Fig. 3 Laser Raman spectra of the intumescent char residues obtained from PP/AM and PP/AM/ SiW_{12} blends

In short, a suitable amount of SiW_{12} as a new synergist added to the PP/IFR blend could play an important role in increasing the LOI value, improving the thermal stability, and promoting the formation of carbonaceous charred layers of PP/IFR materials.

REFERENCES

- 1 Weil, E. D., Zhu, W. and Patel, N., "Char-forming additive in flame retardant system", in: "Fire Retardancy of Polymers: The Use of Intumescence", ed. by Le Bras, M., Camino, G., Bourbigot, S. and Delobel, R., Royal Soc. Chem., London, 1998, p.35
- 2 Xie, R.C. and Qu, B.J., *J. Appl. Polym. Sci.*, 2001, 80: 1181
- 3 Scharf, D., Nalepa, R. and Heflin, R., *Fire Safety Journal*, 1992, 19: 103
- 4 Bourbigot, S., Bras, M.L., Delobel, R., Decressain, R. and Amoureux, J.P., *J. Chem. Soc. Faraday Trans.*, 1996, 92: 3435
- 5 Wu, Y., "Catalyst Chemistry" (in Chinese), Science Press, Beijing, 2000, p.1066
- 6 Xie, R.C. and Qu, B. J., *Polym. Degrad. Stab.*, 2001, 71: 395
- 7 Bourbigot, S., Bras, M. L. and Delobel, R., *Carbon*, 1993, 31: 1219
- 8 Tuinstra, F. and Koenig, J. L., *J. Chem. Phys.*, 1970, 53: 1126