

Improving the Flame Retardancy of the Polypropylene/Aramid Fiber Composites by the Introduction of Decabromodiphenyl Ethane and Antimony Trioxide

Xiao-Sui Chen,¹ Guo-Zhi Xu,^{1,2} Sheng Zhang,^{1,2} Rong Zhang,³ Jun Sun,¹ Ming-Zhe Dong,¹ Xin-Jun Zhu,⁴ Wei Liu⁵

¹Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, China

²The Department of Materials Science and Engineering, Beijing Technology and Business University, Beijing 100037, China

³AVIC Aerospace Life-support Industries, Ltd., Xiangyang, Hubei Province 441003, China

⁴Heilongjiang Hongyu New Material of Short Fiber Limited Company, Heilongjiang Province 154004, China

⁵Sichuan Fire Research Institute of Ministry of Public Security, Dujiangyan, Sichuan Province 611830, China

Correspondence to: S. Zhang (E-mail: sheng1999@yahoo.com)

ABSTRACT: Our previous study showed that aramid fibers (AFs) could significantly enhance the mechanical properties of polypropylene (PP) composites; for example, the tensile strength of PP/AF composites with 30 wt % AF increased by 65.6%, whereas the Izod notched impact strength was almost five times that of pure PP. However, the fire performance of the PP/AF composites was not ideal. In this study, decabromodiphenyl ethane and antimony trioxide [Sb₂O₃; decabromodiphenyl ethane–antimony trioxide (D–S)] were introduced to improve the flame retardancy of PP/D–S/AF composites. Fourier transform infrared spectroscopy and scanning electron microscopy techniques were used to investigate the possible chemical reaction between the phosphate coupling agent and AFs. The mechanical properties of the PP composites were evaluated by tensile, flexural, and impact tests. The flame retardancy was characterized by limiting oxygen index and UL-94 burning tests. The thermal properties of the PP composites was also investigated by combined thermogravimetry–differential thermal analysis. The results show that good interfacial adhesion between the fibers and the PP matrix was formed in the presence of the phosphate coupling agent. The flame retardancy and mechanical properties of the PP/D–S/AF composites were significantly improved by the incorporation of AFs and D–S. The sample containing 30 wt % D–S and 20 wt % AF reached V-0 in the UL-94 test. The maximal char residue of PP/D–S/AF was up to 15.5%, which was 115% higher than that of PP/D–S. A possible synergism of the flame retardancy between the AFs and D–S is proposed and discussed. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: composites; degradation; flame retardance; high performance polymers; poly(propylene) (PP)

Received 9 September 2011; accepted 10 January 2012; published online

DOI: 10.1002/app.36789

INTRODUCTION

Polypropylene (PP) is a versatile polymer with good comprehensive properties and low cost, which has been widely used in the fields of household appliances, vehicles, packaging, architecture, and so on. However, its fire performance and mechanical properties are not good enough for use in fields with higher requirements.^{1–4} Many attempts have been made to improve its fire resistance and mechanical properties; these have included the addition of reinforcing agents and flame retardants to PP composites. Fiber is one of the most frequently used reinforcing materials for increasing the mechanical properties of PP because of its excellent mechanical properties and load capacity. Fibers

used as reinforcing materials include glass fibers (GFs),⁵ carbon fibers,^{6,7} aramid fibers (AFs),^{8,9} and various natural fibers.¹⁰ PP composites containing AFs usually have much better properties in both mechanical performance and flame retardancy compared with those with GFs and can be used in applications with higher requirements, such as vehicles, architecture, household appliances, and flight.

It was reported that polymer composites reinforced by fibers turn to be about four times stronger and stiffer than their unfilled equivalents.¹¹ However, the excellent mechanical properties of polymer/fiber composites depend not only on the inherent characteristics of the fiber and the matrix but also on the

interfacial properties.¹² The surface modification of fibers is one of the most effective treatments by which a good reinforcement can be achieved in fiber-reinforced composites.¹³ Surface modification can be classified into two categories: chemical modification and physical modification.¹⁴ The former is aimed at the introduction of active groups by chemical techniques to increase further the chemical reaction ratio between the fibers and the polymer matrix and, hence, improve the interfacial compatibility. Chemical modifications mainly include coupling agents, surface etching,^{15,16} and surface grating,¹⁷ although the latter is done to change the smooth surface of fibers into a rougher one to increase the contact area and friction between the fiber and matrix and, thus, enhance the interfacial adhesion. Physical modifications are mainly plasma,¹⁸ ultrasonic waves,^{19,20} and γ -ray radiation.²¹ Among these modification technologies, coupling agent treatment has several advantages, including a lower cost, shorter procession circle, and smaller harm to the fiber properties, and is rather suitable for industrial applications.

Our previous work has shown that although AFs can significantly improve the mechanical properties of PP/AF composites, the flammability does not meet the requirements of commercial applications.^{22,23} The sample PP/AF composite with 40 wt % AFs failed in the UL-94 rating test with a limiting oxygen index (LOI) value of 18.4%.²³ Therefore, it is of great importance to produce multifunctional composites with both good mechanical properties and flame retardancy.²⁴ Different flame retardants, such as those containing halogen or phosphorus,^{24,25} intumescent systems,²⁶ metal hydroxides and oxides,²⁷ and nanocomposites,²⁸ are usually synergistically applied in PP composites to improve their flame retardant efficiency.²⁹ Liu et al.²⁴ reported long-glass-fiber-reinforced PP composites with intumescent flame retardants composed of a charring agent, ammonium polyphosphate, and organically modified montmorillonite. Dvir et al.³⁰ used GFs, pentabromobenzyl acrylate, and magnesium hydroxide as flame retardants to improve the mechanical and flame-retardance properties of PP composites. Ferry et al.³¹ prepared a flame-retardant PP/GF composite with a brominated acrylate as both the monomer (pentabromobenzyl monoacrylate, PBB-MA) and polymer (pentabromobenzylester polyacrylate, PBB-PA), associated with Sb_2O_3 (Sb/Br) and $\text{Mg}(\text{OH})_2$, which reached a V-0 rating with a LOI value of 31.8%. However, efforts to improve the flame retardancy of AF-reinforced PP composites have not been reported so far.

Decabromodiphenyl ethane (DBDPE), which has equivalent effects on flame retardancy as decabromodiphenyl oxide, has better properties for recycling and environmental compatibility. It has replaced decabromodiphenyl oxide with a wide consumption in current industrial merchandise, especially in China.^{32–34} In this article, we report the introduction of DBDPE/ Sb_2O_3 to improve the flame-retardant properties of PP/AF composites. The thermal behavior, mechanical properties, and microstructure of the composites were analyzed and are discussed.

EXPERIMENTAL

Materials

The isotactic PP, with a melt flow index of 3.0 g/10 min (trade name K1001, weight-average molecular weight = 300,000, density = 0.90 g/cm³), used in this study was purchased from Yan

Shan Petroleum (Beijing, China). The antioxidant B225 was obtained from Beijing Dilong Chemical Industry Co., Ltd. (Beijing, China). The chopped AFs (AF 1414), with an LOI value of 28% (diameter = 12 μm , length = 3 mm, density = 1.44 g/cm³, high modulus = 85 GPa, and tensile strength = 19.4–23 cN/dtex), were purchased from Heilongjiang Hongyu New Material of Short Fiber Co., Ltd. (Heilongjiang, China). The phosphate coupling agent (DN-27) was supplied by Nanjing Daoning Co., Ltd. (Nanjing, China). DBDPE, with a Br content of 81.5% and an average size of 5.0 μm , was purchased from Shandong Runke Co., Ltd. (Shandong, China). Ethanol, acetone, and antimony trioxide (Sb_2O_3), which were pure chemical grade, were from Tianjing Hedong Hongyan Chemical Reagent Factory (Tianjing, China).

Modification of AF

To remove the impurities, AFs were first immersed into a 0.5 wt % sodium hydroxide solution for about 1 h, then placed in acetone for approximately 12 h, and then dried in an oven at 80°C for 12 h. The clean and dried fibers were put into a 1 wt % phosphate coupling agent solution with a mass ratio of ethanol to water of 9 : 1 for 2 h and were then dried in an oven at 110°C for 4 h to form a firm chemical bond between the coupling agent and the AFs (see Scheme 1) to improve the compatibility among the PP chains and AFs.

Preparation of the PP Composites

The dried pelletized PP was melt-blended with modified AFs, decabromodiphenyl ethane–antimony trioxide (D–S; the mass ratio of DBDPE to Sb_2O_3 was 3 : 1), and other processing agents in a twin-screw extruder (nominal diameter = 20 mm, length-to-diameter ratio (L/D) = 32, model SHJ35, Nanjing Teya Rubber and Plastic Equipment Factory, Nanjing, China) at 160–200°C with a screw speed of 100 rpm. The product was quenched in a water bath, cut into pellets, and then dried in an oven at 80°C for 12 h. Finally, the obtained pellets were shaped into the required specimens in a plastic injector at 190–200–190°C for mechanical and flammability property testing.

Fourier Transform Infrared (FTIR) Analysis

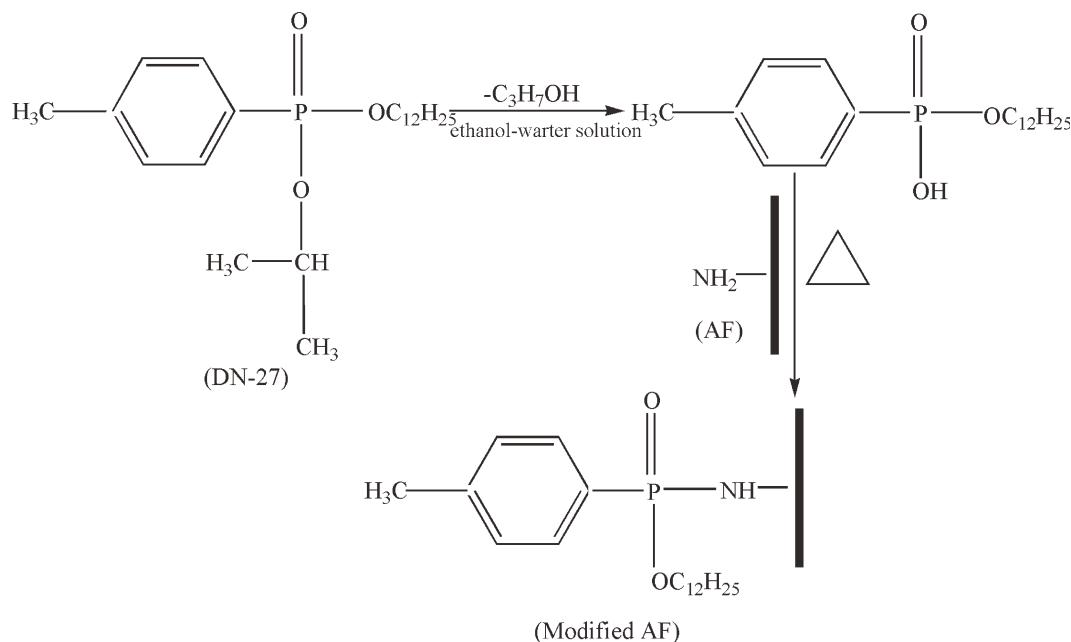
The chemical structure of the modified AF surface was characterized with a FTIR spectrometer (Nexus 670, Thermo-Nicolet, Thermo Electron Co., Madison, WI, USA).

Mechanical Properties

The tensile properties of the PP composites (dumbbell-shaped, span length = 50 mm, width = 10 mm, thickness = 4 mm) was evaluated according to GB/T1040-1992 by a computerized universal testing machine (LR 30 K Plus, Lloyd Instruments Ltd., Hampshire, UK) at a speed of 100 mm/min. The sample's flexural properties were estimated according to GB/T1449-2005 with dimensions of 80 × 10 × 4 mm³ with the same machine at a speed of 10 mm/min. The Izod impact test was performed according to GB/T1843-1996 with dimensions of 80 × 10 × 4 mm³ by a Resil impactor (P/N 6957, CEAST, Pianezza, Italy) under an impact power of 25 J. All of the data were averaged from six to eight measurements with an accuracy of $\pm 5\%$.

Flammability Properties

The LOI test was carried out according to GB/T 2406-1993 by a LOI Instrument (Type JF-3, Jiangning Analysis Instrument



Scheme 1. Reaction mechanism of DN-27 on the AF surface.

Factory, Nanjing, China)) with dimensions of $120 \times 6.5 \times 3 \text{ mm}^3$ and showed a fluctuation of $\pm 1\%$. The vertical burning test (UL-94) was measured according to GB/T 2408-1996 with a CZF-3 instrument (Nanjing Jiangning Analytic Instrumental Factory, Nanjing, China) with dimensions of $125 \times 12 \times 3 \text{ mm}^3$. All samples were tested at least five times.

Scanning Electron Microscopy (SEM)

SEM (S-4700, Hitachi Co., Tokyo, Japan) was conducted to observe the micromorphology of modified AFs and the fracture surface of the PP composites with a beam voltage of 20 kV. The samples were coated with a conductive carbon layer before observation.

Thermogravimetry (TG)–Differential Thermal Analysis (DTA)

TG and DTA analysis were evaluated with a TG–DTA analyzer (HENVEN HCT-1, Beijing Hengjiu Instrument, Ltd., Beijing, China) in a temperature range of $50\text{--}800^\circ\text{C}$ under a static air atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. The mass of each sample was approximately 5–6 mg.

RESULTS AND DISCUSSION

Modification of AF

FTIR Analysis. FTIR spectroscopy was conducted to investigate the possible chemical reactions between the AFs and phosphate coupling agent (DN-27), and the FTIR spectrum curves of DN-27, pure AFs, and modified AFs are shown in Figure 1. The characteristic absorption peaks of pure AF at 3314 cm^{-1} ($\nu_{\text{N-H}}$), 1647 cm^{-1} ($\nu_{\text{C=O}}$), 1536 and 1512 cm^{-1} ($\delta_{\text{N-H}}$), and 1303 cm^{-1} ($\nu_{\text{C-N}}$) could be clearly seen in Figure 1(b), whereas the absorption peaks at 1464 cm^{-1} [$\nu_{\text{P-C}}$ (carbon in aromatics)], 1380 cm^{-1} ($\nu_{\text{isopropyl}}$), 1212 cm^{-1} ($\nu_{\text{P=O}}$), and 1034 cm^{-1} [$\nu_{\text{P-O-C}}$ (carbon in aliphatics)] in Figure 1(a) were the characteristic peaks of the coupling agent DN-27. However, the stretching vibration absorption peak of isopropyl ($\nu_{\text{isopropyl}}$) at 1380 cm^{-1} vanished, whereas the absorption peaks at 889 cm^{-1} ($\nu_{\text{P-O-C}}$) and 1034 cm^{-1} ($\nu_{\text{P-O-C}}$) appeared in Figure

1(c); this indicated that the phosphate coupling agent was successfully grafted onto the AF surface. The detailed chemical reaction process is described in Scheme 1. The phosphate coupling agent DN-27 in ethanol–water solution could be easily hydrolyzed to a medium compound with an active function group ($-\text{OH}$), which could react with amino groups ($-\text{NH}_2$) on the AF surface, form a strong chemical bond, and result in good interphase compatibility between PP and AF.³⁵

Micromorphology of Modified AF. The surface micromorphologies of the pure AFs and modified AFs are shown in Figure 2. It was obvious that the surface of the pure AFs in Figure 2(a) was relatively flat and smooth, whereas a regular cobblestone shape could be seen on the surface of the modified AFs in Figure 2(b); this was more evidence to prove the successful grafting reaction between the AFs and DN-27. The surface roughness

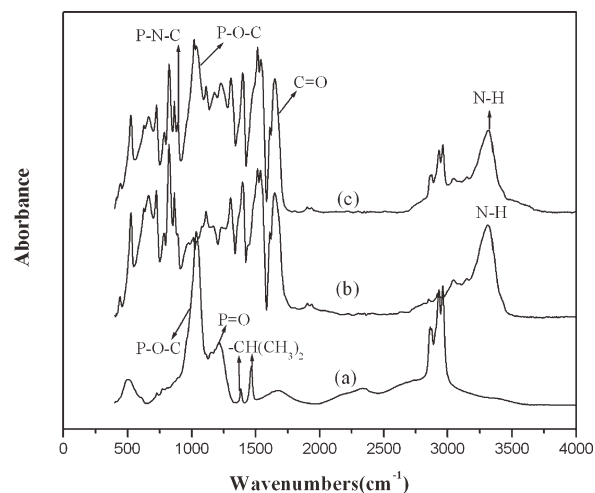


Figure 1. FTIR spectrums of (a) DN-27, (b) pure AF, and (c) modified AF.

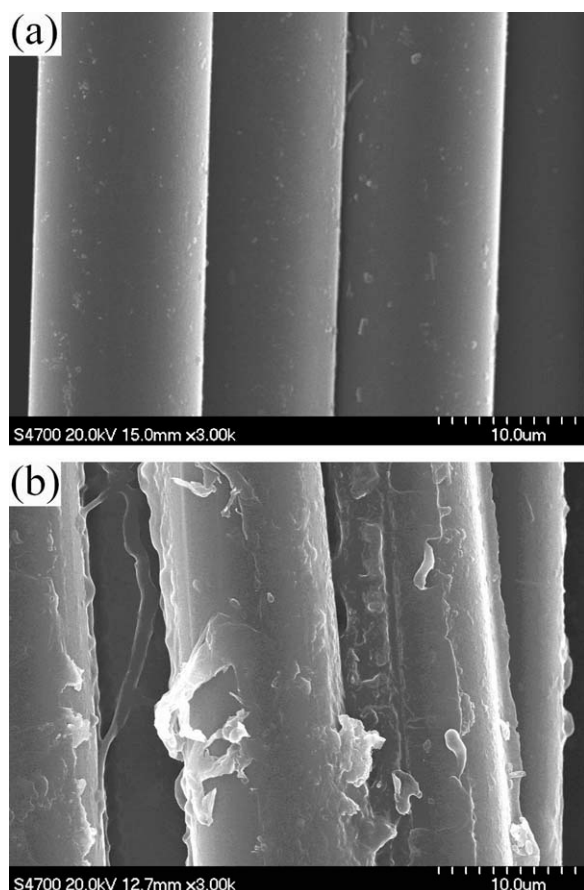


Figure 2. SEM photographs of (a) pure AF and (b) modified AF.

and friction of the modified AFs were increased by the grafted DN-27 chains; this could improve the physical adhesion between PP and the AFs. It was suggested that physical entanglements among the long aliphatic chains (e.g., $-C_{12}H_{25}$) in DN-27 and PP chains also improved the interfacial compatibility between the AFs and PP matrix.

Characterization of the PP Composites

Mechanical Properties. The effect of the D-S content on the mechanical properties of the PP/D-S composites without AF is shown in Table I. With the increase in the D-S content, the mechanical properties of the composites presented a great decrease-

Table I. Influence of D-S on the Mechanical Properties of the PP/D-S Composites

D-S content (%)	Tensile strength (MPa)	Elongation at break (%)	Flexural strength (MPa)	Izod notched impact strength (kJ/m ²)
0	32.0	88.7	76.2	8.63
20	31.2	39.3	78.3	7.66
25	29.2	27.2	82.7	7.57
30	28.7	23.2	86.3	7.12
35	26.8	20.8	88.4	6.38

Table II. Influence of D-S on the Mechanical Properties of the PP/D-S/AF Composites with 20 wt % AFs

D-S content (%)	Tensile strength (MPa)	Elongation at break (%)	Flexural strength (MPa)	Notched impact strength (kJ/m ²)
0	67.8	7.9	98.8	31.2
20	52.3	3.2	94.2	19.40
25	49.3	2.8	102.3	19.01
30	45.2	2.1	95.8	18.76
35	41.5	1.3	85.7	15.81

ing trend in tensile strength, elongation at break, and notched impact strength with maximum drop percentages of 16.3, 22.4, and 26.1%, respectively, except for the flexural strength. This demonstrated that the addition of flame retardant had a negative effect on the mechanical properties of the PP/D-S composites. This was attributed to the poor compatibility of D-S with the PP matrix because of the relatively more polar character of the flame-retardant component.²⁶ Therefore, the increase in D-S content improved the flame retardancy of the PP composites but at the expense of the mechanical properties.

The effect of the D-S content on the mechanical properties of the PP/D-S/AF composites containing 20 wt % AF is shown in Table II. It can be seen that the addition of the flame retardant D-S showed a similar decreasing trend in the mechanical properties; however, the actual mechanical values were much higher than those in Table I. For example, the tensile strength, flexural strength, and notched impact strength of the sample containing 30 wt % D-S and 20 wt % AFs were 45.2 MPa, 95.8 MPa, and 18.76 kJ/m², respectively; these values were 57.5, 11.0, and 66.3% higher, respectively, than those of the sample with the same D-S content (see Tables I and II). It was suggested that the presence of AFs had a positive effect on the mechanical properties of the composites, which could have been due to the excellent properties of the AFs themselves and the good interfacial compatibility between the PP matrix and AFs. It has been reported that the external power can be transferred and passed along the fiber weave from the contact point into the whole volume and, thus, can enhance the bearing capability of external pressure and lead to better

Table III. Influence of AF on the Mechanical Properties of the PP/D-S/AF Composites Containing 30 wt % D-S

AF content (%)	Tensile strength (MPa)	Elongation at break (%)	Flexural strength (MPa)	Izod notched impact strength (kJ/m ²)
0	28.7	23.2	86.3	7.12
10	38.1	4.2	88.0	16.43
15	42.2	3.6	90.2	17.68
20	45.2	2.1	95.8	18.76
25	47.4	1.3	98.7	20.24
30	44.3	1.0	105.5	17.43

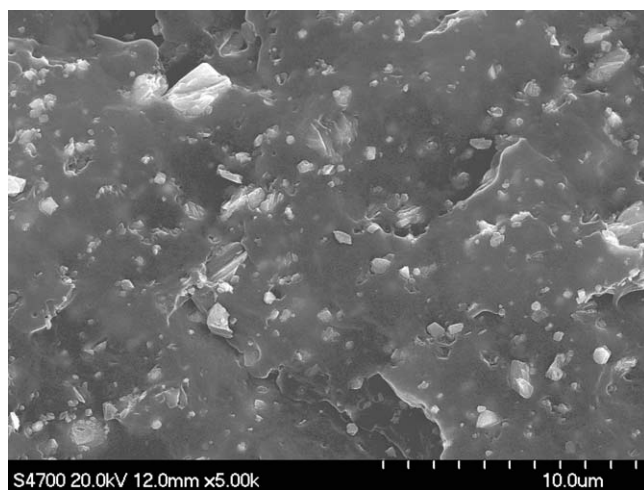


Figure 3. SEM photograph of the PP/D-S composites containing 30 wt % D-S.

mechanical properties.^{36,37} However, the 3-mm length of AFs dramatically reduced the extensibility of the PP matrix and, hence, decreased the elongation at break of the composite.

Table III shows the effect of the AF content on the mechanical properties of the PP/D-S/AF composites. It was seen that with the increase in AFs, the tensile strength, flexural strength, and notched impact strength of the composites increased first and then decreased slightly, whereas the elongation at break decreased straightly. The sample containing 25 wt % AFs had the best comprehensive mechanical properties, with a tensile strength of 47.4 MPa, a flexural strength of 98.7 MPa, and a notched impact strength of 20.24 kJ/m². It has been demonstrated that AFs cannot be impregnated completely and/or evenly in the matrix when its content is too high; this can weaken the interface adhesion and generate stress concentration and, thus, could lead to worse mechanical properties.³⁷

Morphology Analysis. Figure 3 shows the SEM photograph of PP composites with 30 wt % D-S, whereas Figure 4 shows the SEM photographs of PP composites with 30 wt % D-S and 20 wt % AF at different magnifications. The white spots in the SEM photographs correspond to the flame retardant D-S. The fractured surface of the PP/D-S composite shown in Figure 3 was even and smooth, and a small amount of D-S was partially exposed. These observations reflect that the flame retardance of D-S had poor compatibility with the PP matrix; this could have been responsible for the poor mechanical properties of the PP/

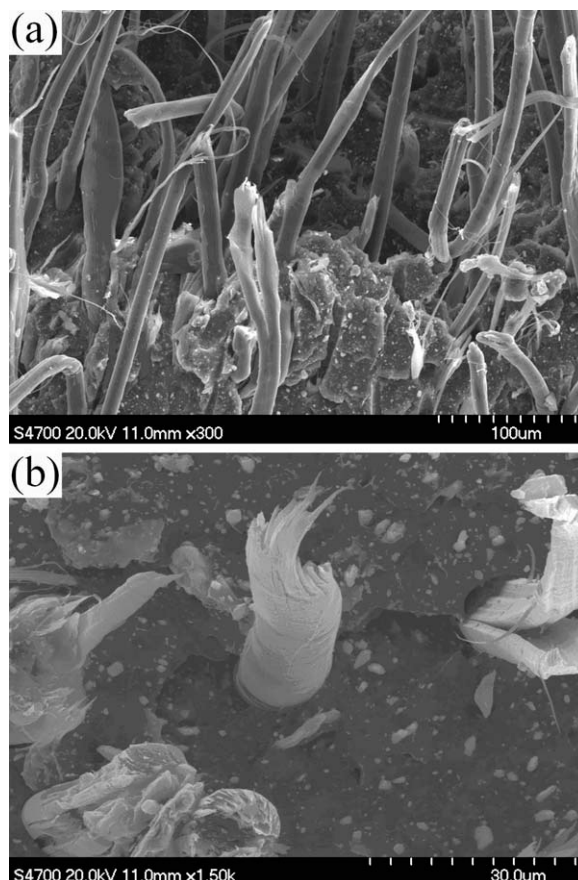


Figure 4. SEM photographs of the PP/D-S/AF composite containing 30 wt % D-S and 20 wt % AF at magnifications of (a) 300 and (b) 1500 \times .

D-S composites. The fractured surface of the PP/D-S/AF composite shown in Figure 4 looked rather rough, and some traces of the matrix distortion could be seen; this showed that an elastic breakdown occurred in the composite. Fibers were dispersed evenly, and their orientation was consistent and regular. Moreover, very few holes caused by the AF pullout were left in the fractured surface of the PP/D-S/AF composite; this indicated that a good interfacial adhesion was formed among the modified AFs and the PP matrix; this positively promoted the improvement of the mechanical properties.³⁵

Flame Retardancy. Table IV shows the comparative effect of the D-S content on the flame retardancy of the PP/D-S and PP/D-S/AF composites with 20 wt % AFs. The LOI value of the

Table IV. Effect of D-S on the Flame Retardancy of the PP/D-S and PP/D-S/AF Composites with 20 wt % AFs

Sample name	D-S content (wt %)	0	20	25	30	35
PP/D-S	LOI (%)	18.0	23.8	24.6	25.2	26.3
	UL-94	No rating	No rating	No rating	No rating	V-2
	Dripping	Yes	Yes	Yes	Yes	Yes
PP/D-S/AF	LOI (%)	18.3	21.2	22.2	23.1	23.8
	UL-94	No rating	No rating	V-1	V-0	V-0
	Dripping	No	No	No	No	No

Table V. Effect of AFs on the Flame Retardancy of the PP/D-S/AF Composites Containing 30 wt % D-S

	AF content (wt %)						
	0	5	10	15	20	25	30
LOI (%)	25.2	22.0	22.4	22.8	23.1	23.6	23.4
UL-94	No rating	No rating	V-1	V-1	V-0	V-0	V-0
Dripping	Yes	No	No	No	No	No	No

PP/D-S composites was improved from 18.0 to 26.3% with the increase of D-S; however, flame dripping still existed even with 35 wt % D-S in the composite; this resulted in only a V-2 rating in the UL-94 vertical burning test. To achieve a better UL-94 rating, a higher content of D-S is required; however, a greater addition of flame retardant can worsen the mechanical properties. Therefore, a multifunctional PP composite with better both flame retardancy and mechanical properties is of great challenge and importance, whereas AFs with excellent flame retardancy and high mechanical properties are good candidates for achieving these requirements. The flame retardancy of the PP/D-S/AF composites with 20 wt % AFs is also list in Table IV. It is reported²⁴ that GFs have a candlewick effect in fiber-reinforced polymer composites, which can make the reinforced materials more combustible, and AFs may have a similar effect on the flammability of PP composites. Comparing the LOI data in Table IV, we found that the LOI value of the PP/D-S/AF composites decreased with the addition of AF, as was expected. For example, the LOI value of the sample with 35 wt % D-S was 23.8%; this was 2.5 units lower than that of the PP/D-S composite with the same D-S content. However, the presence of AFs could provide resistance to flame dripping and increase the char residue of the PP/D-S/AF composites; this could improve the UL-94 rating. It is clearly shown in Table IV that the sample of the PP/D-S/AF composite containing about 20 wt % or more D-S had no flame dripping, and it could reach a V-0 rat-

ing in the UL-94 test when the D-S content was increased to 30 wt %. However, the sample of the PP/D-S composite with 35 wt % D-S only reached a V-2 rating because of flame dripping. This indicated that the AFs improved the dripping resistance and enhanced the UL-94 classification.

The effect of the AF content on the flame retardancy of the PP/D-S/AF composites containing 30 wt % D-S is shown in Table V. The flame retardancy of this composite improved with increasing addition of AFs. Their LOI value of rose slightly from 22.0 to 23.4%. Moreover, the sample with only 5 wt % AFs prohibited flame dripping, and when the AF content equaled or exceeded 20 wt %, it reached a V-0 rating in the UL-94 test. This demonstrated an obvious improvement in the vertical burning classification. This could be attributed to the excellent thermal stability of AFs, which can act as the framework and make PP chains adhere to its surface through good interfacial adhesion. On the one hand, AFs covering the PP chains could hinder the chain segment movement and thus improve the thermal stability of the composite; on the other hand, the AFs aggregated on the surface of the composites gradually along with increasing temperature as the PP chains decomposed; this formed a char layer of protection in the condensed phase and prevented heat and volatile gas from transferring and exchanging, whereas the D-S provided a flame-retardant effect in the gaseous phase. Finally, the flame retardancy of PP/D-S/AF was significantly improved by the synergistic effect between D-S and AF. Further analysis will be discussed in the next section.

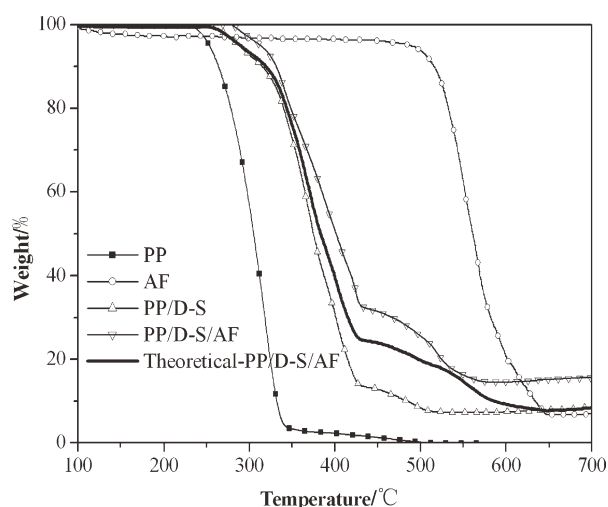


Figure 5. TG curves of (■) pure PP, (○) pure AF, the (△) PP/D-S composite containing 30 wt % D-S, (▽) the PP/D-S/AF composite containing 30 wt % D-S and 20 wt % AF, and (—) the theoretical PP/D-S/AF composite containing 30 wt % D-S and 20 wt % AF.

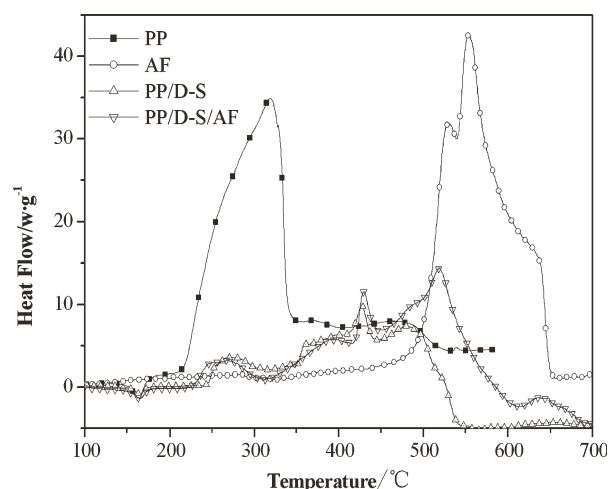


Figure 6. DTA curves of (■) pure PP, (○) pure AF, (△) the PP/D-S composite containing 30 wt % D-S, and (▽) the PP/D-S/AF composite containing 30 wt % D-S and 20 wt % AF.

Thermal Analysis. The TG curves of pure PP, pure AF, the PP/D-S composite with 30 wt % D-S, and the PP/D-S/AF composite with 30 wt % D-S and 20 wt % AFs, together with the theoretical TG curve of the PP/D-S/AF composite with 30 wt % D-S and 20 wt % AFs, are shown in Figure 5. The pure PP decomposed in a single step between 215 and 350°C with little char residue left. The AFs started to decompose at 475°C and stopped at 645°C with a char yield of 7.0%. The sample of the PP/D-S composite decomposed at 241–429 and 429–530°C, whereas the sample of the PP/D-S/AF composite degraded at 264–430 and 432–595°C; this showed a similar decomposition pathway. However, the onset and ending decomposition temperatures of the PP/D-S/AF composite were respectively, 23 and 65°C higher than that of the PP/D-S composite. Moreover, the temperature at 50% decomposition of the PP/D-S/AF composite was 402°C, which was, respectively, 32 and 92°C higher than that of PP/D-S composite (370°C) and pure PP (310°C). This indicated that the incorporation of AF and D-S significantly improved the thermal stability of the PP/D-S/AF composite. The char residue of the PP/D-S composite at 700°C was only 7.2%; this was because D-S belonged to a halogen-containing system that mainly took effect in the gaseous phase and did little to promote char formation. However, the experimental char formation of the PP/D-S/AF composite increased up to 15.5%; this was 7.3% higher than the theoretical char formation, with an actual value of 8.2%. These results reveal that the AFs and D-S had a synergistic effect on improving the thermal stability and char formation in the PP composites.

The theoretical char formation could be calculated according to the following formula:

$$R_{PP/D-S/AF} = X_{AF}R_{AF} + X_{D-S}R_{PP/D-S}$$

where X_{AF} and X_{D-S} are the mass fractions of AFs and D-S in the PP/D-S/AF composite, respectively; R_{AF} , $R_{PP/D-S}$, and $R_{PP/D-S/AF}$ are the char residues of the AFs, PP/D-S composite, and PP/D-S/AF composite samples; and $X_{AF} = 2/15$ and $X_{D-S} = 13/15$ in the previous discussion.

Figure 6 shows the DTA curves of the pure PP, pure AFs, PP/D-S composite with 30 wt % D-S, and PP/D-S/AF composite with 30 wt % D-S and 20 wt % AFs. Pure PP had a single heat-release peak at 317°C, and it had degraded completely at 348°C. However, the AFs started to degrade around 450°C, with two heat-release peaks at 530 and 553°C; they showed excellent thermal stability. The sample of the PP/D-S composite had two small heat-release peaks occurring at 270 and 427°C, respectively, whereas the PP/D-S/AF composite had an additional peak appearing at 520°C, which could be assigned to the degradation of AF. It was obvious that the total heat release of the PP/D-S/AF composite was a great deal smaller than that of the pure PP and AFs. This suggested that the incorporation of D-S and AFs not only delayed the decomposition of the PP composites (246°C) compared with pure PP (215°C) and but also decreased the heat release by D-S trapping the combustion radicals and the dilution effect of HBr over samples in the gaseous phase and by the increased char layers in the condensed phase covering the PP composites and providing further protection by inhibiting the transfer of heat and volatile gas.

CONCLUSIONS

The flame retardancy and mechanical properties of PP composites were both improved by the incorporation of D-S and AFs. The presence of AFs increased the flame-dripping resistance and UL-94 rating. It was found that 5 wt % AFs were enough to prohibit the flame dripping and at least 20 wt % AFs was required for the composite to reach the V-0 rating. Moreover, the presence of both AFs and D-S significantly increased the thermal stability and char formation in the PP composites. The AFs showed a good synergistic effect with D-S in promoting char formation. The introduction of AFs also improved the tensile strength, flexural strength, and Izod notched impact strength.

REFERENCES

1. Chen, X. S.; Yu, Z. Z.; Liu, W.; Zhang, S. *Polym. Degrad. Stab.* **2009**, *94*, 1520.
2. Maity, J.; Jacob, C.; Das, C. K.; Alam, S.; Singh, R. P. *Compos. A* **2008**, *39*, 825.
3. Zhang, S.; Horrocks, A. R.; Hull, R.; Kandola, B. K. *Polym. Degrad. Stab.* **2006**, *91*, 719.
4. Zhang, S.; Hull, T. R.; Horrocks, A. R. *Polym. Degrad. Stab.* **2007**, *92*, 727.
5. Gullu, A.; Ozdemir, A.; Ozdemir, E. *Mater Des.* **2006**, *27*, 316.
6. Klein, N.; Marom, G. *Polymer* **1996**, *37*, 5493.
7. Walker, L.; Hu, X. Z. *Scr. Mater* **1999**, *41*, 575.
8. Arroyoa, M.; Zitzumbob, R.; Avalosc, F. *Polymer* **2000**, *41*, 6351.
9. Wu, C. M.; Chen, M.; Kocsisb, K. J. *Polymer* **2001**, *42*, 199.
10. Spoljaric, S.; Genovese, A.; Shanks, R. A. *Compos. A* **2009**, *40*, 791.
11. Kukureka, S. N.; Hooke, C. J.; Rao, M.; Liao, P.; Chen, Y. K. *Tribology* **1999**, *32*, 107.
12. Nuriela, H.; Kozlovich, N.; Feldmanb, Y.; Maroma, G. *Compos. A* **2000**, *31*, 69.
13. Kitagawa, K.; Hayasaki, S.; Ozaki, Y. *Vib Spectrosc* **1997**, *15*, 43.
14. Wang, J. H.; Hu, Y. Y. *New Chem. Mater* **2009**, *37*, 24.
15. Maity, J.; Jacob, C.; Das, C. K. *Polym. Compos.* **2007**, *28*, 462.
16. Mukherjee, M.; Das, C. K.; Kharitonov, A. P. *Mater Sci. Eng. A* **2006**, *441*, 206.
17. Anongnuch, C.; Chakrit, S.; Taweechal, A. *J. Appl. Polym. Sci.* **1999**, *74*, 2414.
18. Ooij, J. W.; Luo, S. J.; Datta, S. *Plasmas Polym.* **1999**, *1*, 33.
19. Liu, L.; Huang, Y. D.; Zhang, Z. Q. *J. Appl. Polym. Sci.* **2001**, *81*, 2764.
20. Liu, L.; Huang, Y. D.; Zhang, Z. Q. *J. Appl. Polym. Sci.* **2006**, *99*, 3172.
21. Zhang, Y. H.; Huang, Y. D.; Liu, L. *J. Appl. Polym. Sci.* **2007**, *106*, 2251.
22. Toldy, A.; Szolnoki, B.; Marosi, G. *Polym. Degrad. Stab.* **2011**, *96*, 371.
23. Chen, X. S.; Zhang, S.; Xu, G. Z.; Zhu, X. J.; Liu, W. J. *Appl. Polym. Sci.* **2012**, *125*, 1166

24. Liu, Y.; Deng, C. L.; Zhao, J.; Wang, J. S.; Chen, L.; Wang, Y. Z. *Polym. Degrad. Stab.* **2011**, *96*, 363.
25. Braun, U.; Schartel, B.; Fichera, A. M.; Jager, C. *Polym. Degrad. Stab.* **2007**, *92*, 1528.
26. Chen, Y. H.; Wang, Q. *Polym. Degrad. Stab.* **2006**, *91*, 2003.
27. Sain, M.; Park, S. H.; Suhara, F.; Law, S. *Polym. Degrad. Stab.* **2004**, *83*, 363.
28. Isitman, N. A.; Gunduz, H. O.; Kaynak, C. *Polym. Degrad. Stab.* **2009**, *94*, 2241.
29. Zhang, S.; Horrocks, A. R. *Prog. Polym. Sci.* **2003**, *28*, 1517.
30. Dvir, H.; Gottlieb, M.; Daren, S.; Tartakovsk, E. *Compos Sci Technol* **2003**, *63*, 1865.
31. Ferry, L.; Lopez, C. J. M.; Chivas, C.; Mac, W. H. G.; Dvir, H. *Polym. Degrad. Stab.* **2001**, *74*, 449.
32. Ge, Y. X.; Tan, Z. Y.; Cao, C. L.; Gao, Y. L.; Ju, A. Q.; Zhang, H X. *China Plast* **2007**, *21*, 77.
33. Ru, S. G. *Shangdong Chem Ind* **2006**, *35*, 16.
34. Li, X.; Yan, G. L.; Huan, G. X.; Chen, Y. *China Plast* **2005**, *19*, 75.
35. Huang, J. X.; Chang, J. B.; Wang, X. M. The application of infrared spectrum on organic and pharmaceutical chemistry; Science Press: Beijing, 2002; Vol.1, Chapter 16, p 351–357.
36. Saikrasuna, S.; Amornsakchaia, T.; Sirisinhaa, C.; Meesirib, W. *Polymer* **1999**, *40*, 6437.
37. Maity, J.; Jacob, C.; Das, C. K.; Alam, S.; Singh, R. P. *Compos. A* **2008**, *39*, 825.