J Therm Anal Calorim (2011) 103:767–772
DOI 10.1007/s10973-010-1011-6

Effect of a novel charring agent on thermal degradation and flame retardancy of acrylonitrile–butadiene–styrene

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Received: 6 May 2010 / Accepted: 9 August 2010 / Published online: 2 September 2010
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Abstract A novel charring agent poly(*p*-propane terephthalamide) (PPTA) was synthesized by using terephthaloyl chloride and 1,3-propanediamine through solution polycondensation and it was used together with ammonium polyphosphate (APP) to prepare a novel intumescent flame retardant (IFR) for ABS. The thermal degradation behaviour and flame retardancy were investigated, the results showed that PPTA could be effective as a charring agent, the flame retardancy of ABS and the mass of residues improved greatly with the addition of IFR. When the content of APP was 22.5 mass% and PPTA was 7.5 mass%, the limiting oxygen index (LOI) value of IFR-ABS system was found to be 32.4, and class V-0 of UL-94 test was passed. Moreover, the synergistic effects of two different adjuvants AlPi and MnO_2 in IFR-ABS system have been studied.

Keywords Charring agent · Intumescent flame retardant · Thermal behaviour · TG

Introduction

Acrylonitrile–butadiene–styrene (ABS) is widely used as a thermoplastic material because of its good mechanical properties, chemical resistance and processing advantages [1–3]. However, easy combustibility and melt dripping limit its applications; so it is necessary to construct a flame-retarded composition for ABS resin. Bromine-containing compounds, such as decabromodiphenyloxide (DBDPO) and tetrabromobisphenol (TBBPA), are very effective and show a good ratio of property to price in flame retardancy of ABS resin [4]. However, the uses of these halogen-containing flame retardants have been limited because they lead to environmental problems by generating great quantities of toxic and corrosive fumes during combustion. Accordingly, to develop non-halogenated flame-retardant system becomes an attractive and emergent subject. Amongst non-halogenated flame retardants, intumescent flame retardants (IFR) with particular char-yielding properties have been widely used in various polymeric materials [5–8].

One characteristic of IFR systems is their formation of insulative foamed carbonaceous chars. It is reported that the char acts as a barrier between fire and polymer, and results in the extinguishment of combustion; thereby the flame retardancy of the underlying polymers is improved [9–11]. The carbonization agents commonly used in intumescent formulations are polyols, such as pentaerythritol, mannitol or sorbitol [12, 13]. These additives are confronted with the problems of exudation and water solubility. Furthermore, they are not compatible with the polymeric matrix, which weakens the mechanical properties of the material.

Using charring polymers as the carbonization agents can not only avoid the problems of exudation and water solubility, but also improve mechanical properties of the material. Nylon-6 is a well-known char-forming polymer, and the mechanism of thermal decomposition of nylon-6, especially in the presence of melamine, has been given in the literature [14–19]. However, the disadvantage of nylon-6 lies in its relatively strong polarity that leads to the poor compatibility with ABS [20, 21]. Therefore, this study was to prepare a high melting point, char-forming polymer which cannot melt during process and disperse in ABS like

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inorganic and rigid particles. On heating, this char-forming polymer could react with the acid source rapidly to form a uniform and compact intumescent charred layer to protect the underlying materials from the action of heat and flame.

In this article, a novel charring agent PPTA was synthesized (Scheme 1) and it was used together with ammonium polyphosphate (APP) to prepare a novel intumescent flame retardant (IFR) for ABS. The melting point of PPTA was higher than its initial decomposition temperature (266 °C), it could not melt during process and disperse in ABS like inorganic particles. The thermal degradation behaviour and flammability properties of IFR-ABS were investigated by thermogravimetric analysis (TGA), limiting oxygen index (LOI) and vertical burning test (UL-94). The structures of residues were investigated by scanning electron microscopy (SEM). In addition, two different adjuvants AlPi and MnO_2 were employed to investigate the synergistic effect on the thermal stability and flame retardancy of ABS/APP/PPTA blends.

Experimental

Materials

Acrylonitrile–butadiene–styrene (ABS) copolymer (0215-A) was supplied by Jilin Petrochemical Co. (Jilin, China). Ammonium polyphosphate (APP) was obtained from Zhejiang Longyou GD Chemical Industry Corp. (Longyou, China). Manganese dioxide was purchased from Kelong Chemical Reagent Corp. (Chengdu, China). Aluminium phosphinate $\{Al(H_2PO_2)_3\}$ was supplied by Qingzhou Yichao Co., Ltd (China).

Synthesis of PPTA

A 150 mL three-necked round bottom flask equipped with a stirrer charged with 3 g $CaCl_2$, 3.7 g (0.05 mol)1,3-propanediamine and 100 mL *n*-methyl-pyrrolidone(NMP). Then the mixture was stirred, when the $CaCl_2$ dissolved completely, the flask was cooled to 0–10 °C. After that, 10.15 g (0.05 mol) TPC was added slowly to the flask within about 0.5 h, and the reaction temperature was kept at 0–10 °C. Then the flask was heated up to 45–50 °C and the reaction would be completed after 2 h. Successively the reaction mixture was cooled to room temperature, then the mixture poured into distilled water and filtered. The white solid was washed with water and dried in a vacuum at 80 °C to constant mass. (product yield: 78.4%).

FTIR (KBr) (cm^{-1}): 1540, 1492 and 3067 (benzene ring), 2927 and 2872 ($-CH_2-$), 1632 (C=O), 3300 (N–H). ^1H NMR (400 MHz, CF_3COOD) (ppm): 7.85 (d, benzene, 4H), 3.66 (m, $-CH_2-C-CH_2-$, 4H), 2.05 (m, $-C-CH_2-C-$, 2H).

Preparation of flame-retardant ABS samples

PPTA, APP, ABS and various adjuvants were dried in vacuum at 100 °C for 24 h before use. ABS resins with different APP, PPTA and the adjuvants content were prepared via a twin screw extruder (TSSJ-25, Chengguang, China) at a temperature range of 200–230 °C. Then the extruded composites were injected into standard testing bars for the tests of combustibility.

Methods

IR spectroscopy was applied with a Nicolet IS10 FTIR spectrometer using KBr pellets. ^1H NMR (400 Hz) spectra were recorded on a FT-80A NMR by using CF_3COOD as a solvent. LOI data of all samples were obtained at room temperature on an oxygen index instrument (XYC-75) produced by Chende Jinjian Analysis Instrument Factory, according to ASTM D2863-77 standard. The dimensions of all samples are 130 × 6.5 × 3 mm. Vertical burning rates of all samples were measured on a CZF-2 instrument produced by Jiangning Analysis Instrument Factory, with sample dimensions of 125 × 12.5 × 3.2 mm, according to UL-94 test ASTM D635-77. Thermogravimetry analysis was performed on a WRT-2P Thermal Analyser at a linear heating rate of 10 °C min^{-1} under pure nitrogen. The surface morphology of the char obtained after the LOI test was observed by using a HITACHI X-650 scanning electron microscope (SEM).

Results and discussion

Flame retardancy

Table 1 gives the effect of PPTA on flame retardancy of IFR-ABS systems. It could be seen that single use of APP with a 30 mass% addition showed low efficiency in flame retardancy on ABS. However, the LOI value increased

Scheme 1 Synthesis of PPTA

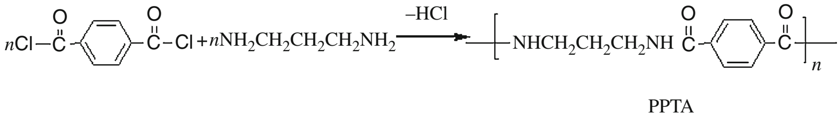

Table 1 Effect of PPTA on flame retardancy of IFR-ABS systems

Sample	Components/mass%			LOI	UL-94
	ABS	APP	PPTA		
1	100	0	0	18.9	Failure
2	100	30	0	25.6	Failure
3	70	25	5	30.5	V-1
4	70	22.5	7.5	32.4	V-0
5	70	20	10	32.2	V-1

rapidly with the addition of PPTA. When 5.0 mass% PPTA was added to the flame retardant ABS, whilst maintaining 30 mass% loading of flame retardant, the LOI value increased from 25.6 to 30.5. When the mass ratio of PPTA to APP increased to 1:3, LOI value of IFR-ABS system reached a maximum of 32.4 and class V-0 of UL-94 was passed. These results demonstrated that PPTA could obviously enhance the flame retardant efficiency of IFR and this novel IFR was very effective in ABS.

Table 2 gives the effect of adjuvants on flame retardancy of IFR-ABS systems. As can be seen, when the addition of IFR (APP/PPTA = 3:1) was 25 mass%, the LOI value of IFR-ABS increased to 27.8 but failed in the UL-94 test. For obtaining better flame retardancy of the flame-retarded IFR-ABS, AlPi and MnO_2 were added as the synergistic charring agents into this system. When 2 mass% AlPi was incorporated into IFR-ABS, the LOI value of the system increased to 30.4 and class V-0 of UL-94 was passed. When 2 mass% MnO_2 was added, the LOI value increased to 30.8 and V-1 rating obtained. This experiment result proved these two synergistic charring agents were very effective in enhancing the flame retardancy of IFR-ABS system.

Thermal behaviours

Figure 1 shows the TG and DTG curves of PPTA. It could be seen that the PPTA was thermally stable below 250 °C and its thermal degradation occurred through two steps. The decomposing temperature in the first step was between 270 and 300 °C; the second was ranging from 400 to 450 °C and the most of the mass loss occurred in the second stage. After the first degradation, PPTA could form a relatively stable chemical structure and this structure had a high degradation activation energy, which slowed down the rate of mass loss between 300 and 400 °C. As the temperature continued to increase, the structure collapsed and the mass loss rate started to speed up, then the second thermal degradation appeared. The maximum mass loss rate of the first step was at 288.3 °C and the second was at 411.6 °C. When the temperature reached 700 °C, PPTA almost decomposed completely and only 10.51% char residue existed.

Table 2 Effect of adjuvants on flame retardancy of IFR-ABS systems

Sample	Components/mass%					LOI	UL-94
	ABS	APP	PPTA	AlPi	MnO_2		
1	75	25	0			24.0	Failure
2	75	18.75	6.25			27.8	Failure
3	75	18.75	6.25	2		30.4	V-0
4	75	18.75	6.25		2	30.8	V-1

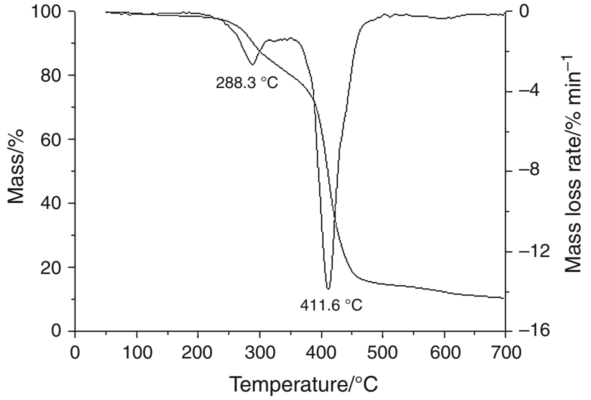

Fig. 1 TG and DTG curves of PPTA

Figure 2 shows TG curves of experimental and calculated APP/PPTA (3/1) mixture, and Table 3 lists the data from the curves. According to Table 3 and Fig. 2, there was a decrease in the mass loss onset (T_{onset}) and an obvious increase in the solid residue at high temperatures in experimental TG curve. However, when temperature was between 250 and 540 °C, a higher amount of residue was obtained in calculated TG curve. It was possible to infer that there was an interaction between APP and PPTA when the temperature was above 250 °C. APP possibly

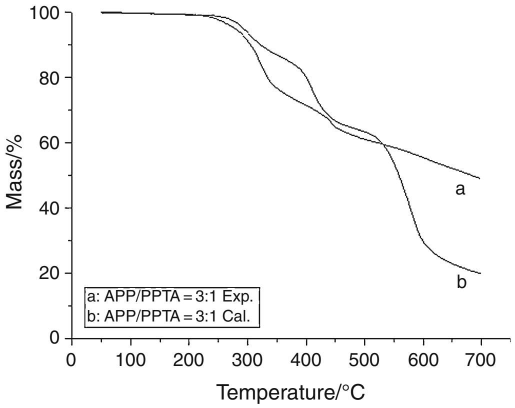

Fig. 2 TG curves of experimental and calculated APP/PPTA (3/1) mixture

Table 3 TG data for different systems

Sample	T_{onset}/°C	Char residue/%		
		500 °C	600 °C	700 °C
APP	304.3	79.5	35.6	23.0
PPTA	266.4	14.9	12.4	10.5
APP/PPTA (3/1)	278.5	61.1	55.5	49.0
APP/PPTA (3/1) (cal.)	292.7	63.4	29.8	14.1
ABS/APP (75/25)	449.0	61.8	19.4	10.9
ABS/APP/PPTA (75/18.75/6.25)	374.9	32.0	16.7	13.6
ABS/APP/PPTA/AlPi	321.4	23.1	18.0	16.0
ABS/APP/PPTA/MnO_2	341.2	20.4	16.1	14.7

T_{onset} represents the temperature at which mass loss is 5%

catalysed the PPTA decompose, changed the thermal degradation behaviour of PPTA and promoted char formation of PPTA at high temperature. The char formation efficiency of APP/PPTA was much stronger at 700 °C than that of PPTA at even 500 °C. The char residue of APP/PPTA was 49.0% at 700 °C, whilst it was only 14.13% based on calculation.

Figure 3 gives TG curves of ABS, ABS/APP (75/25) and ABS/APP/PPTA (75/18.75/6.25) systems, and the data from the curves also lists in Table 3. Previous studies showed that there was a chemical interaction between APP and PPTA and APP could catalyse PPTA decompose at relatively low temperature. Due to this fact, the onset temperature of thermal degradation (T_{onset}) of ABS/APP/PPTA decreased greatly compared with the other two systems. Also, we found that when the temperature rose from 600 to 700 °C,the char residue of ABS/APP decreased from 19.4 to 10.9%,with the smaller reduce of the ABS/APP/PPTA from 16.7 to 13.6%. This proved that with the addition of PPTA, the thermal stability of ABS/APP/PPTA system at high temperatures reinforced.

Figure 4 gives TG curves of ABS/APP/PPTA and ABS/APP/PPTA/AlPi systems. It could be seen from Table 3 and Fig. 4 that the T_{onset} of ABS/APP/PPTA/AlPi was lower than that of ABS/APP/PPTA, which indicated that the AlPi could promote the degradation of APP/PPTA, for the possible reason that AlPi could react with the carboxyl terminal of PPTA, forming phosphoric acid, aluminium phosphate and phosphine. The phosphoric acid could dehydrate the nylon molecular and form the char easily. Aluminium phosphate could act as an inorganic glass which improved the thermal shielding effect and created proper protection of the char at higher temperature. The char residue was 16.0% at 700 °C, whilst that of ABS/APP/PPTA was 13.6%. This demonstrated that AlPi could further promote char formation of ABS/APP/PPTA system.

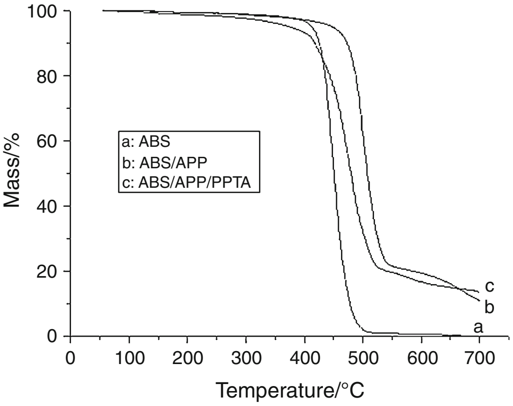

Fig. 3 TG curves of ABS, ABS/APP (75/25) and ABS/APP/PPTA (75/18.75/6.25) systems

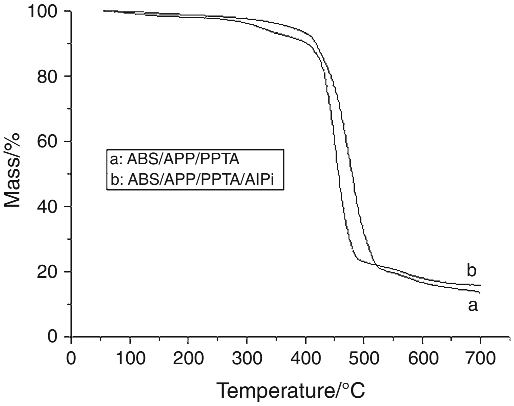

Fig. 4 TG curves of ABS/APP/PPTA and ABS/APP/PPTA/AlPi systems

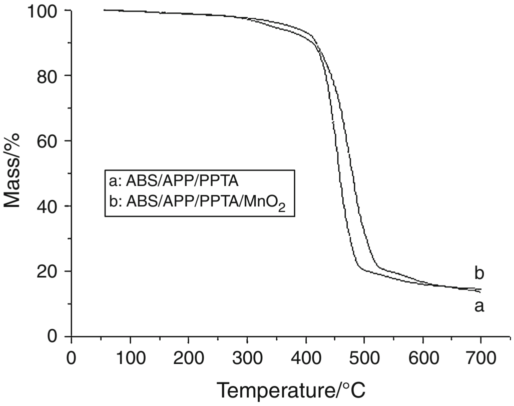

Fig. 5 TG curves of ABS/APP/PPTA and ABS/APP/PPTA/MnO_2 systems

Figure 5 gives TG curves of ABS/APP/PPTA and ABS/APP/PPTA/MnO_2 systems. Levchik [22] verified that there was a synergistic effect between MnO_2 and APP. The interaction between MnO_2 and APP started at 270–280 °C which corresponded to the beginning of thermal decomposition of APP. Pure $Mn^{IV}O_2$ lost O_2 into $Mn^{II}O$ at 470–530 °C, whereas APP or phosphorus acid species catalysed $Mn^{IV}O_2$ reduction, since at 350 °C Mn^{IV} already completely transformed to managanese(II)-ammonium polyphosphate $Mn(NH_4)_2(PO_3)_4$ and managanese(II)-ammonium cyclotriphosphate $MnNH_4P_3O_9$. On further heating, $Mn(NH_4)_2(PO_3)_4$ completely transformed to the $MnNH_4P_3O_9$ which was more thermostable, whereas above 570 °C managanese phosphate (inorganic) glass was formed. The inorganic glass improved the morphology of the char and its thermal shielding effect, and created proper protection of the char at higher temperature. Therefore, MnO_2 enhanced the flame retardancy of IFR-ABS system.

Morphology of the residues' char

Figure 6 is the SEM micrograph of char residues of ABS/APP (70/30), ABS/APP/PPTA (70/22.5/7.5), ABS/APP/PPTA (75/18.75/6.25), ABS/APP/PPTA/AlPi, and ABS/APP/PPTA/MnO_2. From Fig. 6a for ABS with 30 mass% APP alone, there were many holes on the surface of the residue suggesting a poor char quality. However, the char surface of ABS with 22.5 mass% APP and 7.5 mass% PPTA illustrated on Fig. 6b was compact, smooth and tight. This structure of char could resist both mass and heat transfer, which is effective in retarding the degradation of underlying material. In addition, it could be seen that in Fig. 6c the char surface of ABS with 25 mass% IFR (APP/PPTA = 3:1) was alveolate and distributed with lots of cracks; thus, it failed in vertical burning test. From Fig. 6d and e, we found with the addition of AlPi and MnO_2 the char surface of ABS/APP/PPTA became continuous and dense, this char structure can offer a good shield to prevent melt ABS from dripping and this has been proved in vertical flammability tests.

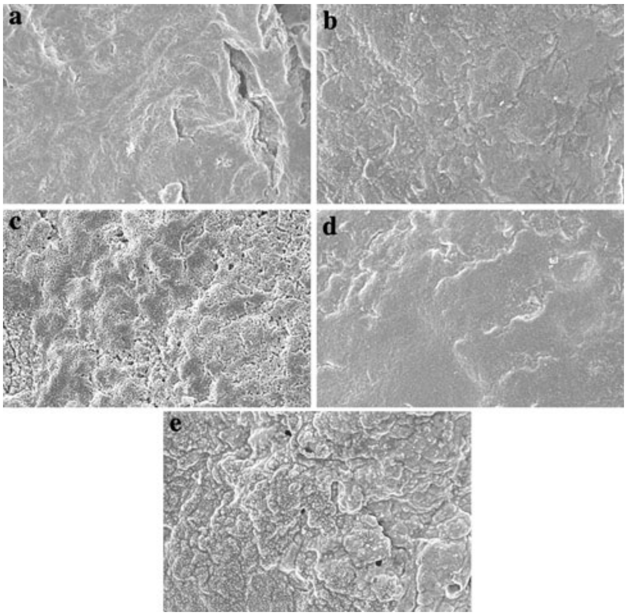

Fig. 6 SEM micrographs of residues of different systems (×300). **a** ABS/APP (70/30); **b** ABS/APP/PPTA (70/22.5/7.5); **c** ABS/APP/PPTA (75/18.75/6.25); **d** ABS/APP/PPTA/AlPi and **e** ABS/APP/PPTA/MnO_2

Conclusions

A novel charring agent poly(*p*-propane terephthalamide) (PPTA) was synthesized. It could act as a very efficient charring agent in intumescent flame retardants and APP could change its thermal degradation behaviour and obviously promote its char formation. The combination of PPTA and APP could form a very effective intumescent flame retardant (IFR). When the content of APP was 22.5 mass% and PPTA was 7.5 mass%, the limiting oxygen index (LOI) value of IFR-ABS system was found to be 32.4, and class V-0 of UL-94 test was passed. Two synergistic charring agents AlPi and MnO_2 were very effective in enhancing the thermal stability and flame retardancy of ABS/APP/PPTA. When the addition of IFR was 25 mass%, the mass ratio of APP to PPTA was still 3:1, the system's LOI value was only 27.8 and failed in UL-94 test. However, when 2 mass% AlPi and MnO_2 were incorporated into ABS/APP/PPTA system, the LOI value were both increased to 30, class V-0 and class V-1 in the UL-94 test were passed, respectively. The structure of char residues investigated by SEM also showed that AlPi and MnO_2 could promote the quality of the char, which was effective in preventing melt ABS from dripping.

Acknowledgements We would like to thank the generous financial support by the following grant: National Natural Sciences Foundation of China, Grant no. 50973066.

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