

Halogen-Free Intumescent Flame Retardant Acrylonitrile-Butadiene-Styrene/Poly(ethylene terephthalate) Blends

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ABSTRACT: The influence of ammonium polyphosphate (APP) with and without synergistic agents — aluminum hypophosphite ($\text{Al}(\text{H}_2\text{PO}_2)_3$), epoxy resin (E-44), and Zeolite 4A — in acrylonitrile-butadiene-styrene/poly(ethylene terephthalate) (ABS/PET) blends was investigated. The limiting oxygen index (LOI) and UL94 tests were used to investigate flame properties. The results showed that APP with and without synergistic agents all improved the flame retardancy of ABS/PET systems. The ABS/PET/APP + 2 wt % $\text{Al}(\text{H}_2\text{PO}_2)_3$, ABS/PET/APP + 2 wt % E-44, and ABS/PET/APP + 3 wt % Zeolite 4A systems achieved the best flame retardancy rating of V0 and LOI values were 32, 34, and 30.5, respectively. The thermal degradation behaviors analyzed by thermogravimetric analysis

(TGA) indicated APP mainly accelerated the degradation of PET and led to the increase of charring residues. $\text{Al}(\text{H}_2\text{PO}_2)_3$ and E-44 resulted in synergistic effects on the charring process of ABS/PET/APP. SEM revealed that the intact, dense, and strong char layer formed on the surface of the ABS/PET/APP/ $\text{Al}(\text{H}_2\text{PO}_2)_3$ (or E-44) system, which was significantly different from the loose and porous char layer of ABS/PET and ABS/PET/APP systems. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1589–1597, 2010

Key words: acrylonitrile-butadiene-styrene/poly(ethylene terephthalate); ammonium polyphosphate; flame retardancy; synergistic agents

INTRODUCTION

Acrylonitrile-butadiene-styrene/poly(ethylene terephthalate) (ABS/PET) is a novel engineering polymer blend, which has many inherent advantages, such as good corrosion resistance, high heat deflection temperature, and excellent mechanical properties.^{1–4} However, fire hazards are inevitably associated with the use of ABS/PET blends, which are of particular concern among government regulatory bodies, consumers and manufactures alike. To meet the wider application, the development of safe and environmental flame retarded ABS/PET blends is of great importance.

A growing demand to avoid the generation of such toxic and corrosive gases during thermal degradation has led to the development of halogen-free flame retardants. And intumescent technology has found a place in polymer science as a method of providing flame retardancy to polymeric materials.^{5,6} In an intumescent materials formulation, usually there are carbonization agents, carbonization catalysts, and a blowing agent. On heating, intumescent

flame retardant (IFR) materials can form a foamed cellular charred layer on their surfaces, which protects the underlying materials from the heat flowing and flame.⁶ Ammonium polyphosphate (APP) is widely used as a part of intumescent materials formulation,^{6–8} which, to some extent, performs two roles as carbonization catalyst and blowing agents. The research from our laboratory⁸ indicated the IFR system of ABS/polyamide 6 (PA6)/styrene maleic anhydride (SMA)/APP not only obtained flame retardant properties of interest, but also avoided the problems of exudation and water solubility. Xinsheng Zhu et al.⁹ demonstrated APP/coal synergistically improved the flame retardancy of PET, and there existed some physical and chemical interactions among PET, APP, and coal during combustion process. Also, it has been reported that addition of APP enhanced the flame retardancy of Poly(butylene terephthalate) (PBT) and changed the composition of the solid, high and low boiling decomposition products as compared to those of neat PBT.¹⁰ Jang et al.¹¹ selected PET as char-source for ABS blends, and reported addition of small amounts of phenol novolac contributed to the enhancement of flame retardancy of ABS/PET blends.

In this work, an intumescent flame retardant system was selected for the purpose of increasing the flame resistance of ABS/PET. APP was used as carbonization catalyst and blowing agents, and without addition of other carbonization compounds, PET

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TABLE I
Flammability of ABS/PET Blends with APP and Different Synergistic Agents

Components wt %						
ABS/PET (50/50)	APP	Al(H ₂ PO ₂) ₃	E-44	Zeolite 4A	LOI (%)	UL-94 classes
100					21	No rating
85	15				25	No rating
80	20				27	No rating
75	25				28.5	No rating
70	30				31	V0
65	35				34.5	V0
60	40				40.5	V0
75		25			23	No rating
75	24	1			29	V1
75	23	2			32	V0
75	22	3			31.5	V0
75	21	4			29	V0
75			25		22	No rating
75	24		1		29.5	V1
75	23		2		34	V0
75	22		3		30.5	V0
75	21		4		31	No rating
75	19		6		32	V1
75				25	23.5	No rating
75	24			1	28	V1
75	23			2	30	V0
75	22			3	30.5	V0
75	21			4	29	V1
75	19			6	29	V1

was expected to be successfully used as carbonization agent in the intumescent system. ABS/PET (50/50) blends were prepared, which exhibited good mechanical properties.¹ Furthermore, aluminum hypophosphite (Al(H₂PO₂)₃), epoxy resin, and Zeolite 4A were used for their synergism with intumescent flame retardant materials.

EXPERIMENTAL

Materials

The flammability of ABS/PET blends, with APP and with and without the three synergistic agents - Al(H₂PO₂)₃, epoxy resin and Zeolite 4A - was investigated. ABS (0215A, Jilin petrochemical company, China, melting flow rate: 20 g/10 min) and PET (Yizheng Chemical Fibre Company Limited, China, viscosity: 0.9 g/dl) were prepared. And APP (*n* = 1500) was supplied by Zhejiang Longyou Gede Chemical factory (China); Al(H₂PO₂)₃ was provided by Qingzhou Yichao Chemical Company (China); bisphenol-A epoxy resin [epoxide value (eq/100 g): 0.41–0.47] (E-44) and Zeolite 4A were supplied by Chengdu Kelong Co. Ltd., (China).

ABS and PET, dried at 80°C/4 h and 100°C/12 h, respectively, with APP and with and without synergistic charring agents were extruded by a double-screw extruder (*D* = 25 mm, *L/D* = 33, Chenguang machine research institute) with screw rotating rate of 100 r/min, and the barrel setting temperatures were 210,

235, 242, 245, 245, and 245°C. And then the resulting pellets, dried at 100°C for 12 h, were injection-molded at 240–250°C into test samples for measurements of flame retardancy, using an injection-molding machine (PS40E5ASE, Nissei Plastic Industrial Co.).

METHODS

The flammability of flame retarded ABS/PET blends was evaluated by limiting oxygen index (LOI) and UL94 tests. LOI measurements were performed according to GB/T 2406-93, using the candle type flammability tester (XYC-75, Chengde, China). The sample bars with 3 mm thickness were made by injection molding, and then conditioned for one week under 23°C and 50% relative humidity. UL-94 tests were performed according to ASTM D 3801 procedures on a CZF-2 instrument (Jiangning, China) with samples of 125 × 12.7 × 3.2 mm³.

The weight loss during thermal degradation of samples (6–10 mg) was measured on the WRT-2P thermal gravimetric analyzer (Shanghai Precision and Scientific Instrument Co., China) at a heating rate of 10°C/min. Dynamic nitrogen was used as a carrier gas with a constant flow rate (50 mL/min) during analysis.

The surface morphology of char obtained after LOI test was observed by a HITACHI X-650 scanning electron microscope (SEM).

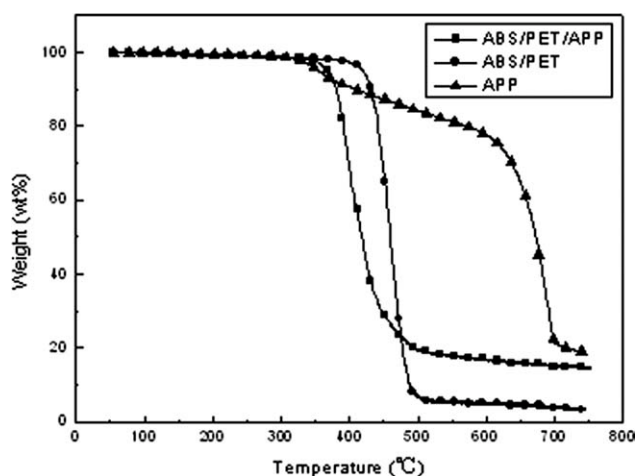


Figure 1 The TG curves of ABS/PET/APP (37.5/37.5/25), ABS/PET (50/50), and APP systems.

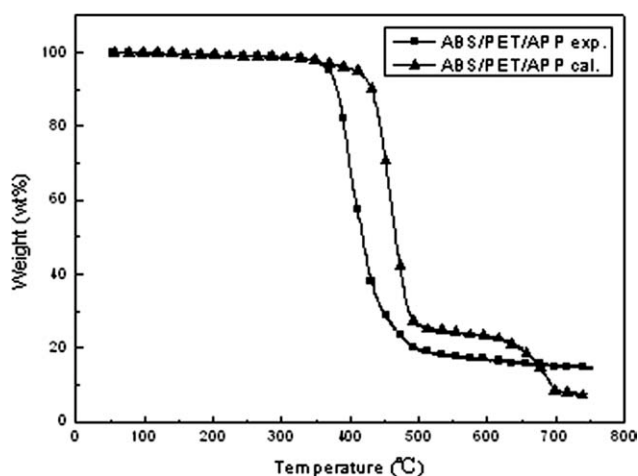


Figure 2 Experimental and theoretical TG curves of the ABS/PET/APP (37.5/37.5/25) system.

RESULTS AND DISCUSSION

Flammability

The flammability of the ABS/PET (50/50) blends with different APP contents was studied by the LOI values and UL94 tests, whose results were given in Table I. One could observe that the LOI value was increased with an increasing content of APP. When the APP content was 25 wt %, the LOI value of the ABS/PET/APP system was found to be 28.5, however, the system was not classified during UL-94 tests. When the APP content was 30 wt %, the ABS/PET/APP system achieved the best flame retardancy rating of V0, and the LOI value increased markedly to 31. The results indicated that APP improved the flame retardancy of ABS/PET blends. But high loading (not less than 30 wt % APP) were required to achieve appropriate flame retardancy.

To get better flame retardancy with less APP contents in ABS/PET blends, the three synergistic agents - $Al(H_2PO_2)_3$, E-44, and Zeolite 4A - were employed for investigating the synergistic effects on the flame retardancy of ABS/PET/APP systems. For all the compounds, the amount of flame retardant was fixed at 25 wt %. The different components, LOI values and UL-94 classes of ABS/PET/APP systems with different synergistic agents were listed in Table I.

TABLE II
Main Data Collected from TG Curves

Sample	T_{onset} (°C)	Weight at 700°C (%)
APP	354	21.2
ABS/PET	419	3.9
ABS/PET/APP	368	15.1
ABS/PET/APP/ $Al(H_2PO_2)_3$	361	20.7
ABS/PET/APP/E-44	358	17.9
ABS/PET/APP/Zeolite 4A	368	14.3

It has been reported that $Al(H_2PO_2)_3$ exhibited good flame retardancy in polyester.¹² It was observed that the LOI value of the ABS/PET/ $Al(H_2PO_2)_3$ system was only 23, however, the addition of $Al(H_2PO_2)_3$ to ABS/PET/APP systems led to the increase of LOI values in different degree and the achievement of V0 or V1 rating in UL94 testing. When the mixture of 2 wt % $Al(H_2PO_2)_3$ and 23 wt % APP was incorporated into ABS/PET, the best flame retardancy rating of V0 was achieved and LOI value was found to be significantly increased to 32.

E-44 was successfully used in the ABS/PA6/SMA/APP and ABS/TPP systems as a synergistic flame retardant.^{8,13} In our study, the addition of E-44 could not improve the flame retardancy of ABS/PET. But in the ABS/PET/APP systems, E-44 clearly improved the flame retardancy: the dramatic increase in LOI value and achievement of the ratings of V0 and V1. The possible reason for the fact was

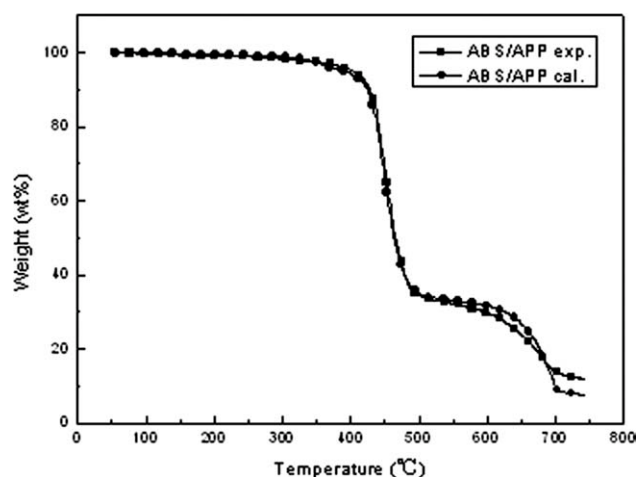


Figure 3 Experimental and theoretical TG curves of the ABS/APP (37.5/25) system.

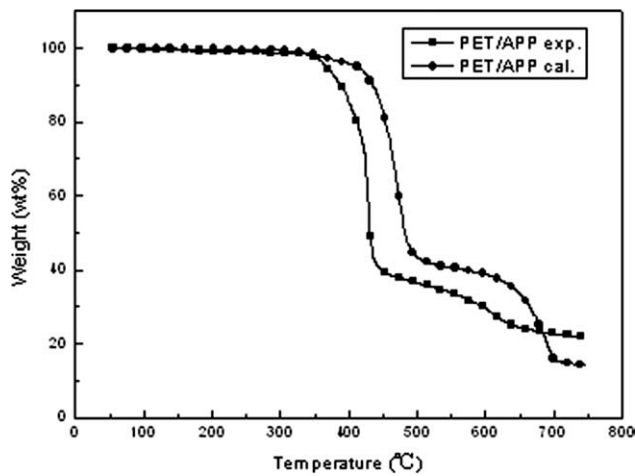


Figure 4 Experimental and theoretical TG curves of the PET/APP (37.5/25) system.

the interaction between phosphoric acid generated from APP and carboxylic acid generated from epoxy during thermal degradation.¹³ One observed the fact that the ABS/PET system containing 23 wt % APP and 2 wt % E-44 was identified V0 and the LOI value increased significantly to 34.

Zeolites can act as a catalyst for the development of the intumescent carbonaceous material and stabilize the carbonaceous residue resulting from degradation of the intumescent shield.¹⁴ So changing Zeolite 4A contents from 1 to 6 wt %, the synergistic flame retarded systems were classified during UL-94 tests, however, the LOI values did not increase markedly. It was observed that the LOI value of the flame retardant system containing 1 wt % Zeolite 4A was 28 lower than that of ABS/PET/APP system, but higher than that of the ABS/PET/Zeolite 4A system. When the mixtures with 22 wt % APP and 3 wt % Zeolite 4A were incorporated into the ABS/PET

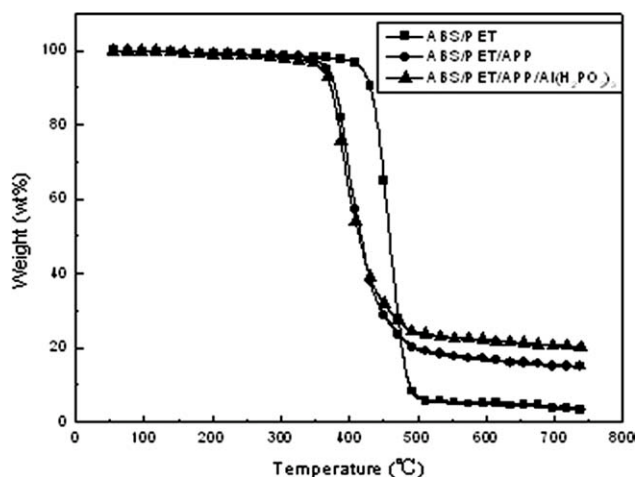


Figure 5 The TG curves of ABS/PET, ABS/PET/APP, and ABS/PET/APP/ $\text{Al}(\text{H}_2\text{PO}_2)_3$.

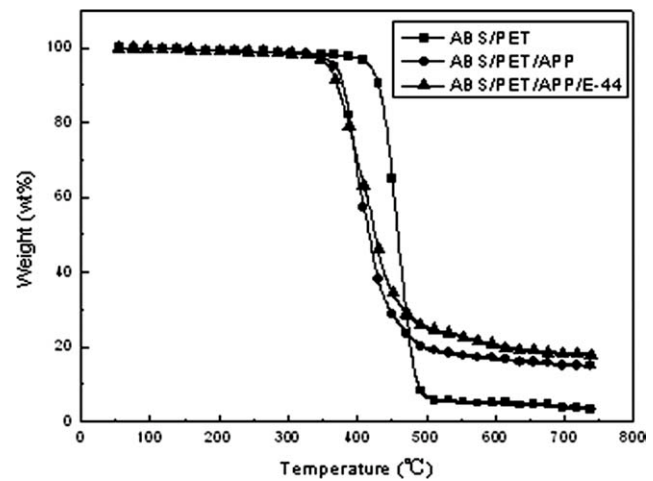


Figure 6 The TG curves of ABS/PET, ABS/PET/APP, and ABS/PET/APP/E-44.

blend, the LOI value was founded to be 30.5 and the flame retarded system was identified as V0.

From the above results, it can be concluded that the three synergistic agents - $\text{Al}(\text{H}_2\text{PO}_2)_3$, E-44, and Zeolite 4A - all exhibit a significant and beneficial synergism-flame-retardant effect with APP on ABS/PET blends.

Thermal degradation behaviors

The thermal degradation behaviors of flame retarded ABS/PET systems were investigated by TGA. Figure 1 showed the TG curves of ABS/PET/APP (37.5/37.5/25), ABS/PET (50/50), and APP systems in N_2 , and main data collected from TG curves was shown in Table II. The onset degradation temperature (T_{onset}) was defined as the temperature at which the weight loss of sample reaches 5 wt%.¹⁵ It was seen that the T_{onset} of the ABS/PET/APP system was 368°C,

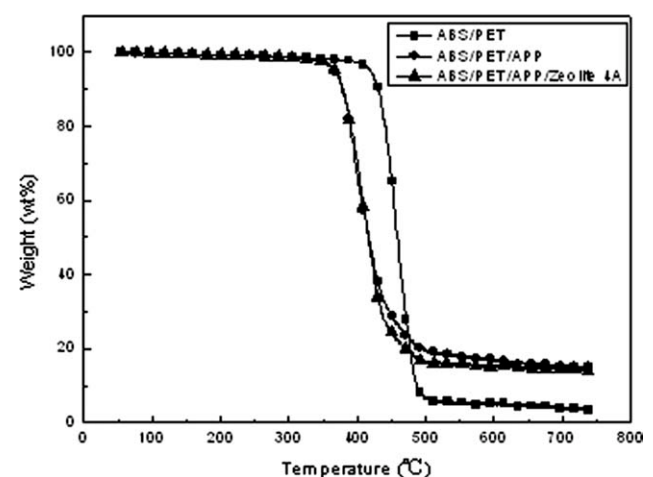


Figure 7 The TG curves of ABS/PET, ABS/PET/APP, and ABS/PET/APP/Zeolite 4A.

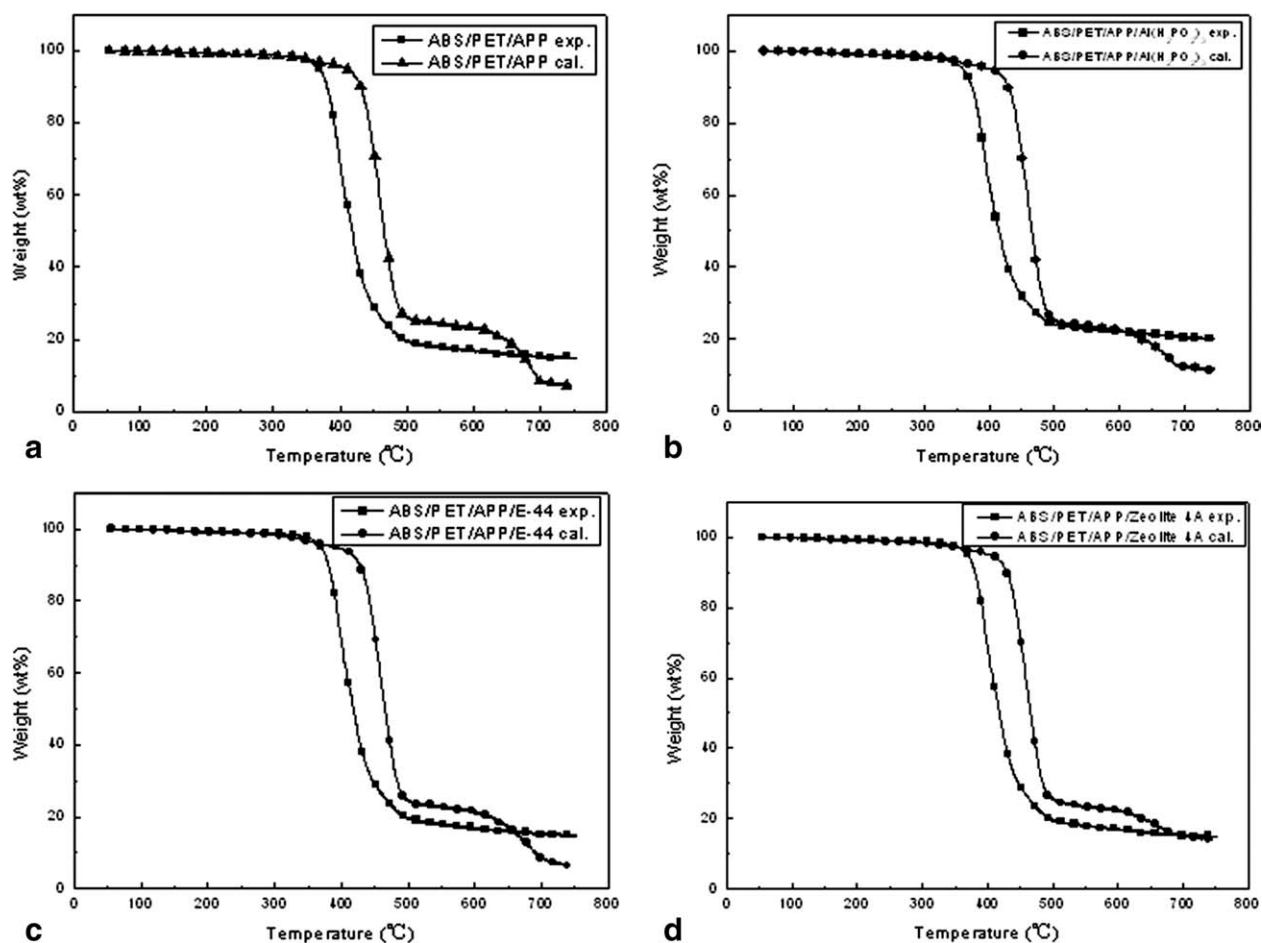


Figure 8 Experimental and theoretical TG curves: (a) ABS/PET/APP; (b) ABS/PET/APP/ Al(H₂PO₂)₃; (c) ABS/PET/APP/E-44; (d) ABS/PET/APP/Zeolite 4A.

significantly lower than that of ABS/PET (419°C) and nearly close to that of APP (354°C). It was concluded that APP promoted the degradation of ABS/PET blend, which was further supported in later discussion. ABS/PET/APP and ABS/PET systems were degraded into thermally stable charring at about 500°C. The residual mass of the ABS/PET/APP system at 700°C was 15.1 wt %, higher than that of ABS/PET. Figure 2 shows the experimental and theoretical TG curves of ABS/PET/APP, and theoretical TG curves are calculated by the equation:

$$M_{\text{theo}}(T)_{X\text{-APPi}} = \text{wt \%} \times M_{\text{exp}}(T)_X + (1 - \text{wt \%})M_{\text{exp}}(T)_{\text{APPi}} \quad (1)$$

where X is polymer material without retardant; APPi is the blend of APP and synergistic agents; $M_{\text{theo}}(T)_{X\text{-APPi}}$ is the theoretical residual mass of X-APPi; wt % is the weight percent of X (X mass/system mass); $M_{\text{exp}}(T)_X$ is the experimental residual mass of X; $M_{\text{exp}}(T)_{\text{APPi}}$ is the experimental residual mass of APPi. The remarkable differences between experimental and theoretical TG curves, for example,

the T_{onset} and the charred residues at 500–680°C and 700°C, were observed. The difference of T_{onset} was further in agreement with the indicated fact of APP accelerating the initial degradation of ABS/PET

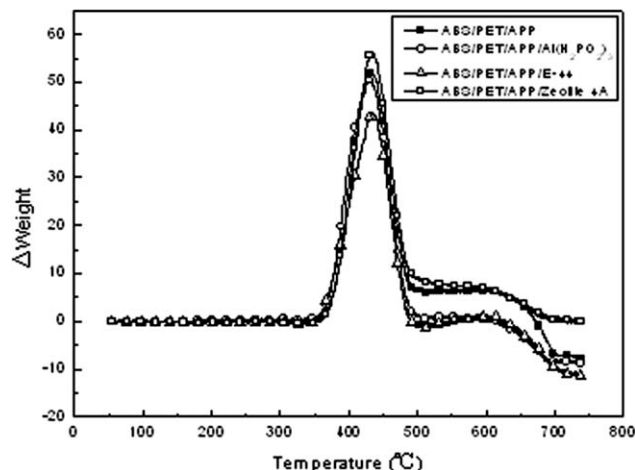


Figure 9 $\Delta M(T)$ versus T diagrams of ABS/PET/APP, ABS/PET/APP/ Al(H₂PO₂)₃, ABS/PET/APP/E-44, and ABS/PET/APP/Zeolite 4A systems.

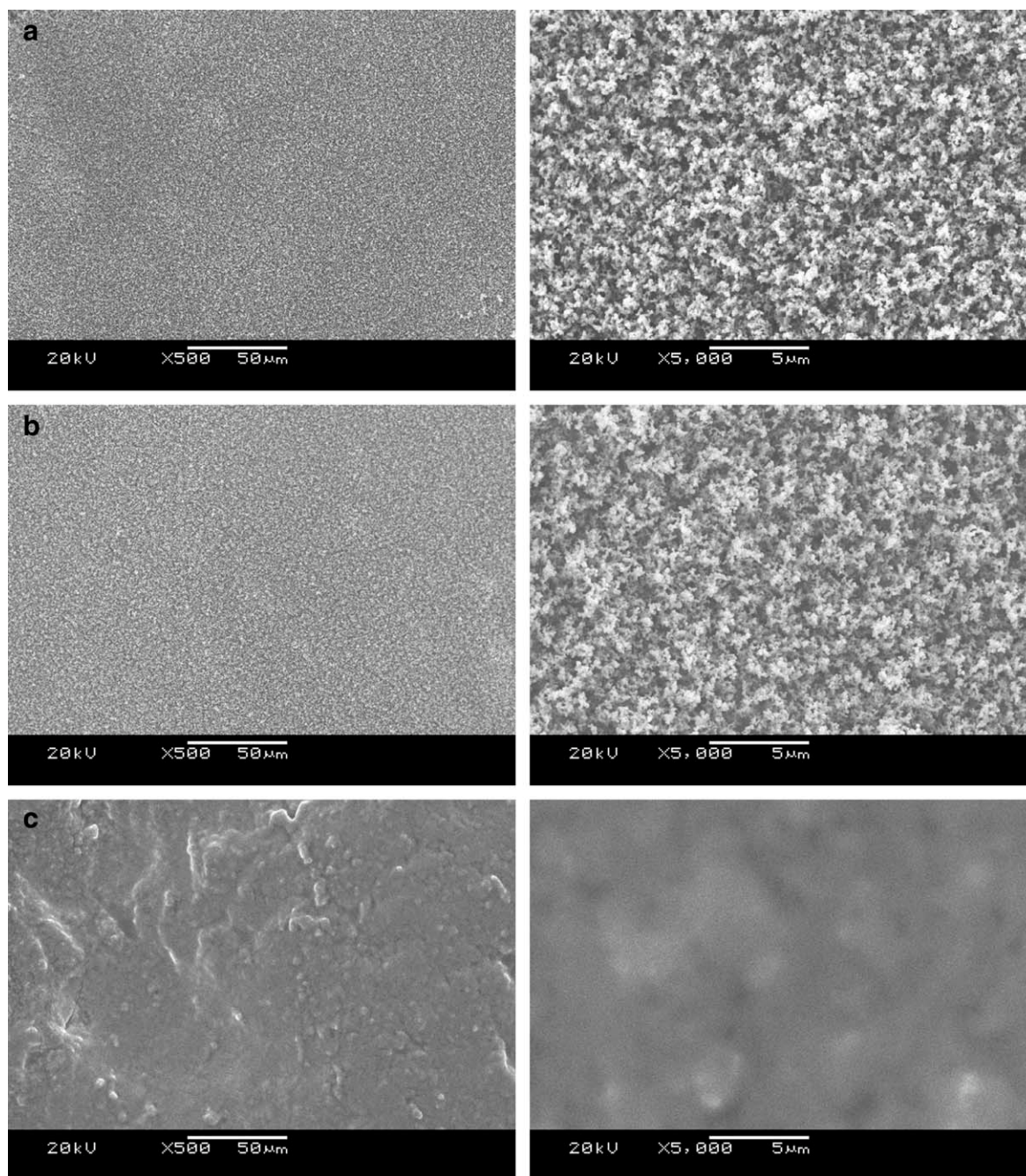


Figure 10 SEM of the charred surface structure of flame retardant systems: (a) ABS/PET; (b) ABS/PET/APP; (c) ABS/PET/APP/ $\text{Al}(\text{H}_2\text{PO}_4)_3$; (d) ABS/PET/APP/E-44; (e) ABS/PET/APP/Zeolite 4A.

blends. The theoretical residual mass of ABS/PET/APP was higher than experimental residual mass at 500–680°C. It was possible that APP promoted the emission of a large amount of volatile low molar mass compounds. However, at 700°C the TG curve of experimental ABS/PET/APP exhibited higher charring residues. That was because “high temperature” stable residue formed in the ABS/PET/APP system at about 500°C, which prevented the weight loss even at higher temperature. Taken as a whole, APP not only promoted the degradation of the

ABS/PET blends, but also contributed to the charring process of ABS/PET with the increase of charring residues.

To further investigate the thermal degradation of ABS and PET with APP, the experimental and theoretical TG curves of ABS/APP (37.5/25) and PET/APP (37.5/25) were analyzed respectively, as shown in Figures 3 and 4. In Figure 3, it was clear that there was no clear difference between experimental and theoretical TG curves, which indicated there was no obvious catalysis of APP for ABS. However,

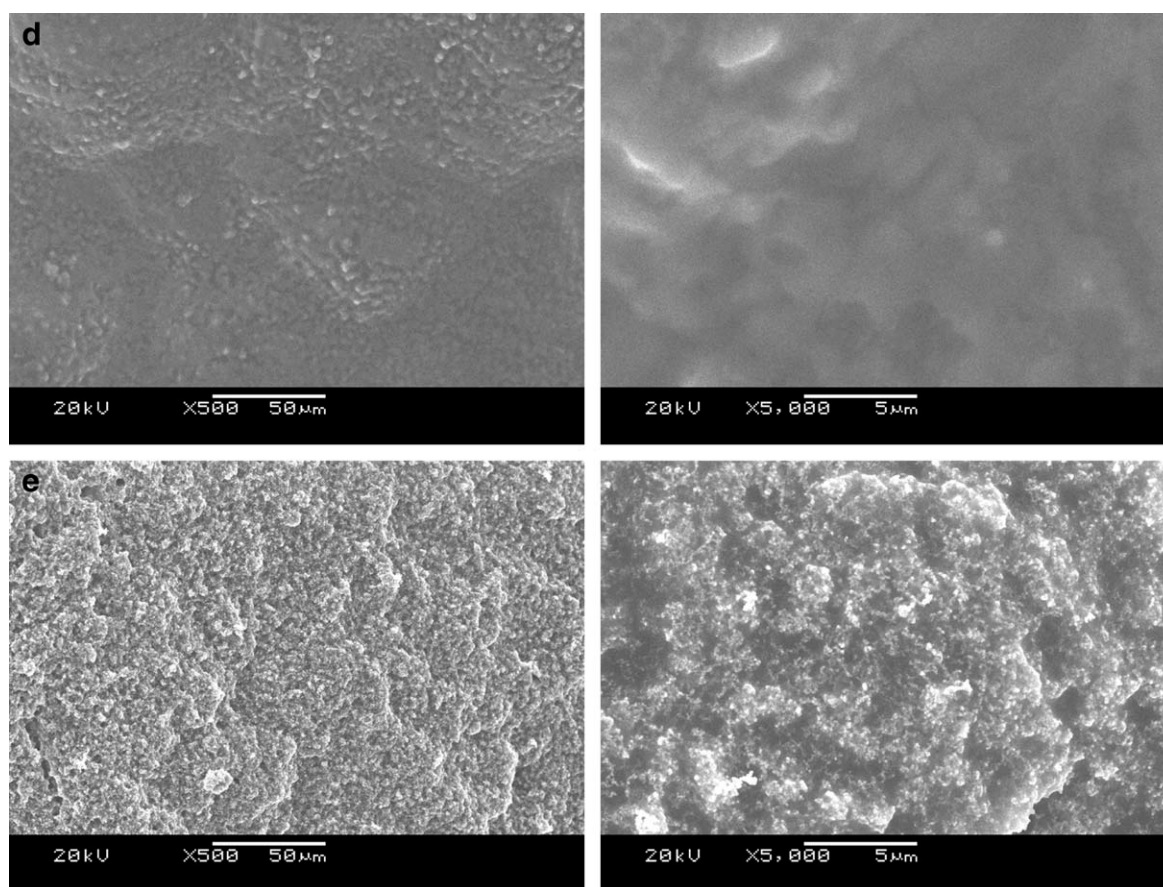


Figure 10 (Continued from the previous page)

the higher residual mass of experimental TG curve of the ABS/APP system at 700°C indicated the little effect of APP on the charring process of ABS. Figure 4 showed the great differences between experimental and theoretical TG curves of PET/APP, such as the T_{onset} and charring residues at 500–680°C and 700°C. It was concluded that APP catalyzed PET degradation on heating, as reported in recent article,⁹ due to the interaction between polyphosphoric acid, NH_3 and H_2O generated from APP at 260–420°C¹⁶ and PET. And the emission of a large amount of possible low molecule mass compounds associated with thermal reaction between APP and PET led to the lower residual mass of experimental TG curve at 500–680°C. However, an interesting phenomenon can be observed, that is, the experimental residual mass at 700°C is not lower but higher than theoretical residual mass, which means the charring residue that APP catalyzes PET to degrade into can prevent weight loss with temperature increasing. In conclusions, APP mainly catalyzed PET in ABS/PET blends thermal degradation. As we expected, a novel intumescent flame retardant system containing APP (acid source and blowing agents) and PET (carbon source) was obtained, avoiding the problems caused by adding other carbon sources.

The thermal degradation behaviors of flame retarded ABS/PET systems with 23 wt % APP and 2 wt % synergistic agents - $\text{Al}(\text{H}_2\text{PO}_2)_3$, E-44 and Zeolite 4A - were analyzed by TGA. The thermograms of different samples were shown in Figures 5–7 and main data was further summarized in Table II. The T_{onset} of all synergistic flame retardant systems was about 360°C, which was almost completely close to that of the ABS/PET/APP system, however, the charring residues of all synergistic flame retardant systems at 700°C were significantly different from that of the ABS/PET/APP system. The charring residues of ABS/PET/APP/ $\text{Al}(\text{H}_2\text{PO}_2)_3$ and ABS/PET/APP/E-44 systems were clearly higher, which were 20.7 and 17.9%, than 15.1% of ABS/PET/APP system. However, the residual mass of ABS/PET/APP/Zeolite 4A system was only 14.3%, slightly lower than that of the ABS/PET/APP system.

To understand the more detailed effect of different synergic agents on the thermal degradation behaviors of ABS/PET/APP systems, curves of weight differences between experimental and theoretical TG curves were calculated according to the eq. (1) and

$$\Delta M(T) = M_{\text{theo}}(T)_{\text{X-APPi}} - M_{\text{exp}}(T)_{\text{X-APPi}} \quad (2)$$

Figure 8 showed the experimental and theoretical TG curves of flame retardant systems. These curves demonstrated APP with or without synergistic agents all promoted the degradation of ABS/PET at lower temperature, and except for APP with Zeolite 4A, others led to produce much larger amount of charring residues that ABS/PET blends were degraded into. The weight difference curves ($\Delta M(T)$ versus T diagrams) of flame retardant systems were presented in Figure 9. A clear phenomenon can be observed, that is, the peaks of ABS/PET/APP/ $\text{Al}(\text{H}_2\text{PO}_2)_3$ and ABS/PET/APP/E-44 systems are smaller, however, the peak of ABS/PET/APP/Zeolite 4A system is larger than that of ABS/PET/APP system, which means that APP with $\text{Al}(\text{H}_2\text{PO}_2)_3$ and E-44 possibly slow down the degradation of ABS/PET, however, APP with Zeolite 4A accelerates the degradation of ABS/PET more, compared with APP. Another significant phenomenon also can be seen, that is, the $\Delta M(700^\circ\text{C})$ of ABS/PET/APP/ $\text{Al}(\text{H}_2\text{PO}_2)_3$ and ABS/PET/APP/E-44 systems are smaller, however, the $\Delta M(700^\circ\text{C})$ of ABS/PET/APP/Zeolite 4A system is larger than that of ABS/PET/APP, which means APP with $\text{Al}(\text{H}_2\text{PO}_2)_3$ and E-44 exhibit more significant charring effect for ABS/PET blends leading to the production of larger amount of charring residues, however, APP with Zeolite 4A decreases the charring yield that ABS/PET blends are degraded into, compared with APP. Therefore, 2 wt % $\text{Al}(\text{H}_2\text{PO}_2)_3$ and E-44 exhibited a good synergistic effect on charring process of ABS/PET, however, 2 wt % Zeolite 4A resulted in an antagonistic effect on the charring of ABS/PET+APP.

SEM analysis

Observation of the morphological structures of the residual char of the above systems possibly clearly presents whether the flame retardancy of the flame retarded ABS/PET systems is good. Figure 10 showed the scanning electron micrographs of chars from the surfaces of ABS/PET (50/50), ABS/PET/APP (37.5/37.5/25), and ABS/PET systems with 23 wt % APP and 2 wt % $\text{Al}(\text{H}_2\text{PO}_2)_3$ (or E-44 or Zeolite 4A). One could observe that a loose char layer with a lot of holes formed on the surface of ABS/PET. And a similar char layer, which was loose and porous with shallower holes, formed on the surface of the ABS/PET/APP system. The poor char layer could not act as a barrier to shield underlying polymer from heat and air in agreement with the fact of no rating in UL-94 tests. The surface of the char for ABS/PET/APP/ $\text{Al}(\text{H}_2\text{PO}_2)_3$ (or E-44) systems was significantly improved with a cohesive, strong, smooth, and dense structure without clear holes, which could serve as a barrier to heat, air and pyro-

lysis product.^{17–19} The charred surface of the ABS/PET/APP/Zeolite 4A system exhibited swollen char layer with few holes due to the bubble formation with incorporation of Zeolite in composites.⁶ Hence, the surface layer is a stable and dense char structure that plays an important role in improving flame retardancy of ABS/PET blends.

CONCLUSIONS

In this work, a novel intumescent flame retardant formulation containing APP acting as carbonization catalyst and blowing agents and PET as carbonization agent promoted the flame retardancy of ABS/PET (50/50) blends well. When APP content was 30 wt %, the ABS/PET/APP system achieved the best flame retardancy rating of V0, and the LOI value increased markedly to 31. Synergistic agents – $\text{Al}(\text{H}_2\text{PO}_2)_3$, E-44, and Zeolite 4A – all exhibited a significant and beneficial synergistic flame retardant effect with APP on ABS/PET blends. The ABS/PET/APP + 2 wt % $\text{Al}(\text{H}_2\text{PO}_2)_3$, ABS/PET/APP + 2 wt % E-44 and ABS/PET/APP + 3 wt % Zeolite 4A systems achieved the best flame retardancy rating of V0 and LOI values were 32, 34, and 30.5, respectively. TG analysis indicated APP mainly promoted the degradation of PET and led to produce much larger amount of charring residues. $\text{Al}(\text{H}_2\text{PO}_2)_3$ and E-44 could lead to the increase of charring residues of ABS/PET/APP system, however, Zeolite 4A led to the decrease of charring residues. SEM showed, the char structure of the ABS/PET/APP system was loose and porous with shallower holes, as shown in the ABS/PET system, however, the charred surface of the ABS/PET/APP/ $\text{Al}(\text{H}_2\text{PO}_2)_3$ (or E-44) system was cohesive, strong, smooth, and dense, and that of the ABS/PET/APP/Zeolite 4A system exhibited swollen char layer with few holes.

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