

Synergistic Effect of Zinc Oxide on the Flame Retardant and Thermal Properties of Acrylonitrile–Butadiene–Styrene/Poly(ethylene terephthalate)/Ammonium Polyphosphate Systems

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ABSTRACT: The influence of micrometric zinc oxide (micro-ZnO) and nanostructured zinc oxide (nano-ZnO) on the flammability and thermal properties of acrylonitrile–butadiene–styrene (ABS)/poly(ethylene terephthalate) (PET)/ammonium polyphosphate (APP) systems was investigated. When 1 wt % micro-ZnO (or nano-ZnO) was incorporated into the ABS/PET/APP systems, the best flame-retardancy rating of V0 was achieved during UL94 tests, and the limiting oxygen index value was 31 (or 30). The thermogravimetric analysis indicated that the addition of zinc oxide (ZnO) improved the thermal stability and the yield of char residues of the ABS/PET/APP systems.

Fourier transform infrared spectrophotometry showed that ZnO improved the efficiency of APP, and the char residues of the ABS/PET/APP + 2 wt % ZnO systems had higher phosphorus contents. Scanning electron microscopy showed that the surface of the char for ABS/PET/APP + 2 wt % micro-ZnO (or nano-ZnO) improved significantly with a cohesive and dense structure; however, that for ABS/PET/APP + 5 wt % micro-ZnO (or nano-ZnO) exhibited a looser char layer with bigger holes. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2338–2344, 2011

Key words: blends; flame retardance; FT-IR

INTRODUCTION

In recent years, acrylonitrile–butadiene–styrene (ABS)/poly(ethylene terephthalate) (PET) blends have been investigated a lot because of their many inherent advantages, such as a good corrosion resistance, a high heat deflection temperature, and excellent mechanical properties.^{1–4} However, fire hazards are inevitably associated with the use of ABS/PET blends. To meet wider application, the development of safe and environmental flame-retardant ABS/PET blends is of great importance. We demonstrated that an intumescent flame-retardant formulation containing ammonium polyphosphate (APP) as a carbonization catalyst and blowing agents and PET as carbonization agent could enhance the flame resistance of ABS/PET. However, a high loading (≥ 30 wt % APP) was required to achieve the appropriate flame retardancy. So, we needed to investigate the synergistic effect of other additives on ABS/PET/APP systems for good flame retardancy with low-load flame retardants.

Lewin and Endo⁵ demonstrated that zinc compounds could catalyze the flame-retardancy performance of intumescent systems based on APP and pentaerythritol in polypropylene. Also, Jiao and Chen⁶ investigated the synergistic effects of micrometric zinc oxide (micro-ZnO) with layered double hydroxides on ethylene vinyl acetate copolymer/layered double hydroxide composites. Zinc oxide (ZnO) and zinc salts were successfully used in halogen-containing polymeric compounds.⁷ However, Serge et al.⁸ reported that the flame retardancy of thermoplastic polyurethane/APP was not improved by the substitution of APP by nanostructured zinc oxide (nano-ZnO). As is known, nano-ZnO is different from micro-ZnO, which has a smaller size, larger specific area, and strong interfacial interaction between the organic polymer and inorganic nanoparticles because of the many hydroxyls on its surface.⁹ It was possible that nano-ZnO exhibited a different synergistic flame-retardant effect in ABS/PET/APP systems.

In this article, the synergistic effect of ZnO, including micro-ZnO and nano-ZnO, on the flame-retardant and thermal properties of ABS/PET/APP systems was investigated to provide theoretical guidance for the preparation of flame-retarded ABS/PET blends.

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EXPERIMENTAL

Materials

ABS (grade 0215A, Jilin Petrochemical Co., Jilin, China, melting flow rate = 20 g/10 min), PET (Yizheng Chemical Fibre Co., Ltd., Jiangsu, China, viscosity = 0.9 g/dL), and APP (Degree of polymerization $n = 1500$, Zhejiang Longyou Gede Chemical Factory, Zhejiang, China) were prepared. Micro-ZnO (200–400 nm) and nano-ZnO (20–40 nm) were supplied by Chengdu Kelong Co., Ltd., Chengdu, China and Nanjing High Technology Nano Material Co., Ltd. (Nanjing, China), respectively.

Preparation of the samples

ABS and PET, dried at 80°C for 4 h and 100°C for 12 h, respectively, with APP and ZnO (micro-ZnO and nano-ZnO), were extruded by a double-screw extruder (diameter = 25 mm, length-to-diameter ratio = 33, Chenguang Machine Research Institute, Chengdu, China) with a screw rotating rate of 100 rpm, and the barrel setting temperatures were 210, 235, 242, 245, 245, and 245°C. After the extrudate was pelletized and the blend was dried at 100°C for 12 h, all test specimens pertaining to GB/T standards were prepared by an injection-molding machine (PS40E5ASE, Nissei Plastic Industrial Co., Ltd., Nagano, Japan). The injection temperature profile was zone 1, 220°C; zone 2, 240°C; and zone 3, 250°C, and the mold temperature was between 30 and 35°C.

Flammability tests

The flammability of the 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 with a candle-type flammability tester (XYC-75, Chengde Jinjian Testing Instrument Co., Ltd., Chengde, China). Sample bars 3 mm thick were made by injection molding and then conditioned for 1 week at 23°C and 50% relative humidity. UL-94 tests were performed according to ASTM D 3801 procedures on a CZF-2 instrument (Nanjing Jiangning Analytical Instrument Factory, Jiangning, China) with samples of $127 \times 12.7 \times 3.2 \text{ mm}^3$.

Thermogravimetric analysis (TGA)

The weight loss during the thermal degradation of samples (6–10 mg) was measured on a WRT-2P thermogravimetric analyzer (Shanghai Precision and Scientific Instrument Co., Ltd., Shanghai, 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.

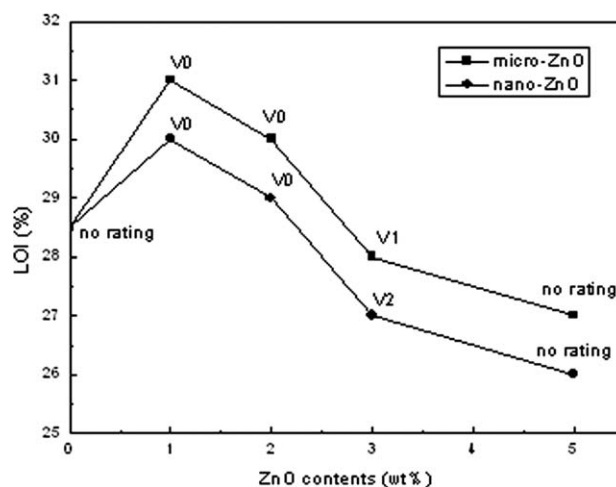


Figure 1 Flammability of the ABS/PET/APP/ZnO [micro-ZnO and nano-ZnO; 37.5/37.5/(25 - x)/x] systems. x is weight percent of ZnO

Fourier transform infrared (FTIR) spectrophotometry

The char residues on the surface of the flame-retarded ABS/PET systems after UL94 tests were characterized with an FTIR spectrophotometer (resolution = 4, Nicolet iZ10, Waltham) with KBr pellets.

Scanning electron microscopy (SEM)

The surface morphology of the char obtained after LOI tests was observed by a Hitachi X-650 scanning electron microscope (Japan). The sample was coated with gold to make the surface conductive.

RESULTS AND DISCUSSION

Flammability

The LOI and UL94 tests were used to investigate the flame retardancy of ABS/PET/APP systems with different ZnO contents. The results are shown in Figure 1. For all of the compounds, the amount of flame retardant was fixed at 25 wt %. It was clearly seen that the LOI values of ABS/PET/APP/micro-ZnO systems were all higher than those of the ABS/PET/APP/nano-ZnO systems, which meant that micro-ZnO and APP exhibited a better synergistic flame-retardant effect. However, with the increase of micro-ZnO or nano-ZnO content, the LOI values all decreased. When 1 wt % micro-ZnO (or nano-ZnO) was incorporated into the ABS/PET/APP systems, the best flame-retardancy rating of V0 was achieved during the UL94 tests, and the LOI value was 31 (or 30), respectively. Although the LOI value of the ABS/PET/APP system with 3 wt % micro-ZnO (or nano-ZnO) was 28 (or 27), respectively, lower than 28.5 of the ABS/PET/APP system, it was classified as V1 (or V2) during the UL94 tests. The mechanism

TABLE I
Synergistic Effect between APP and ZnO
(Micro-ZnO and Nano-ZnO)

Components (wt %)		Micro-ZnO	Nano-ZnO	LOI	$w_{(P+N)}$ (%)	EFF	SE
ABS/PET (50/50)	APP						
100				21	0		
75	25			28.5	12.19	0.62	
75	24	1		31	11.70	0.85	1.38
75	23	2		30	11.22	0.80	1.29
75	22	3		28	10.73	0.65	1.05
75	20	5		27	9.75	0.62	1
75	24		1	30	11.70	0.77	1.24
75	23		2	29	11.22	0.71	1.15
75	22		3	27	10.73	0.56	0.90
75	20		5	26	9.75	0.51	0.83

$w_{(P+N)}$ is the weight percent of phosphorus and nitrogen.

of the enhancement in UL94 rating was mainly due to the physical process in the condensed phase.^{10–12} However, the flame retardancy of ABS/PET/APP + 5 wt % micro-ZnO (or nano-ZnO) was much poorer. It was concluded that ABS/PET/APP + 1–2 wt % ZnO exhibited a good flame retardancy; however, the higher the ZnO content was, the poorer the flame retardancy of the ABS/PET/APP systems was.

To clearly show the synergistic effect between APP and ZnO, synergistic efficiency (SE) was used, which was defined as the ratio of the flame-retardant efficiency (EFF) of synergistic systems than that of non-synergistic flame-retardant systems. EFF was defined as the increase of LOI values by the unit mass of flame-retardant elements. The results are shown in Table I. We observed the fact that SE of ABS/PET/APP + 1, 2, and 3 wt % micro-ZnO systems was greater than 1, which indicated that 1, 2, and 3 wt % micro-ZnO exhibited synergistic effects with APP. Only 1 and 2 wt % nano-ZnO exhibited synergistic effects. However, 3 and 5 wt % nano-ZnO exhibited antagonism with APP. SE of micro-ZnO was greater than that of nano-ZnO (at the same loading). That also indicated that micro-ZnO showed a better synergistic flame-retardant effect.

At this moment, it was postulated that the improvement of flame retardancy resulted from the interaction of APP with ZnO. To examine the validity of the interaction between APP and ZnO, a mixture of APP and micro-ZnO (or nano-ZnO) at a 1 : 1 ratio was analyzed by TGA, as shown in Figure 2. The theoretical TG curves were calculated by the following equation:

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

where X is micro-ZnO or nano-ZnO, APP-X is a blend of APP and ZnO, $M_{\text{theo}}(T)_{\text{APP-X}}$ is the theoret-

ical residual mass of APP-X, wt % is the weight percentage of X (X mass/system mass), $M_{\text{exp}}(T)_X$ is the experimental residual mass of X, and $M_{\text{exp}}(T)_{\text{APP}}$ is the experimental residual mass of APP. The onset degradation temperature (T_{onset}) was defined as the temperature at which the weight loss of the sample reached 5 wt %.¹³ One could observe the remarkable difference between the experimental and theoretical TG curves of APP/micro-ZnO (or nano-ZnO). First, T_{onset} of the experimental curves of both the APP/micro-ZnO and APP/nano-ZnO systems was clearly lower than that of the theoretical curves. That indicated that ZnO accelerated the degradation of APP. Next, an interesting phenomenon could be seen; that is, the residues at 700°C of the experimental curves were not lower but higher than that of the theoretical curves, which meant that more thermally stable residues formed through the interaction between APP and ZnO. ZnO might have reacted with the two monomeric phosphate groups, released two ammonia and two water molecules, and produced a bridge between two APP chains. The formation of a

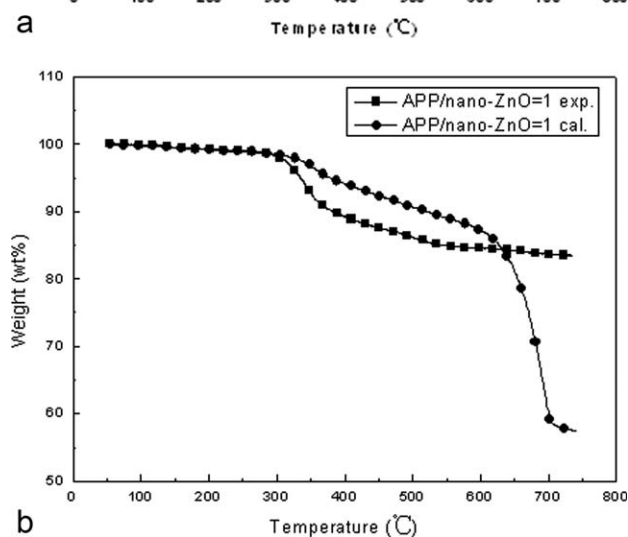
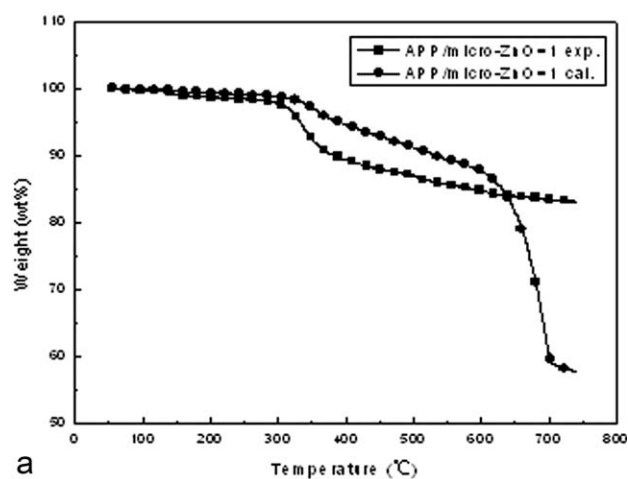


Figure 2 TG curves of the APP/ZnO mixture under nitrogen conditions: (a) APP/micro-ZnO and (b) APP/nano-ZnO.

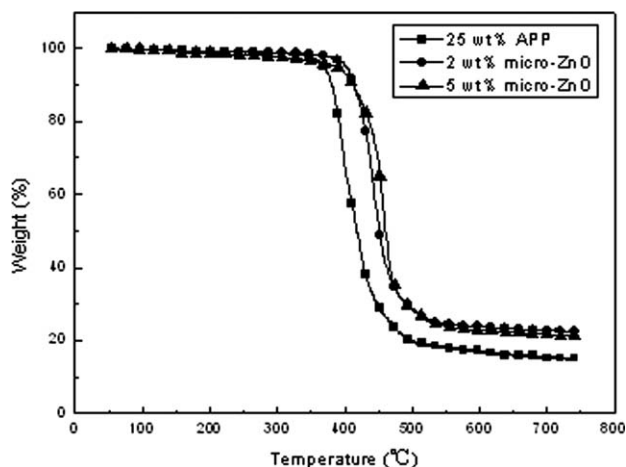


Figure 3 TG curves of the ABS/PET/APP and ABS/PET/APP/micro-ZnO systems.

small number of such bridges would have brought about the stability of APP and a decrease in the volatility of the phosphorus oxides during the pyrolysis, that is, more phosphorus would have been available for the phosphorylation and the char formation.⁵ From the results, it was postulated that the interaction between APP and ZnO, including the acceleration of degradation of APP and the production of higher thermally stable residues, influenced the flame retardancy of the ABS/PET systems, even though it is not clear at this moment.

Thermal stability

The influence of micro-ZnO and nano-ZnO on the thermal properties of the ABS/PET/APP systems was investigated by TGA, as shown in Figures 3 and 4, and the main data collected from TG curves are listed in Table II. It was clearly seen that the addition of micro-ZnO or nano-ZnO improved the ther-

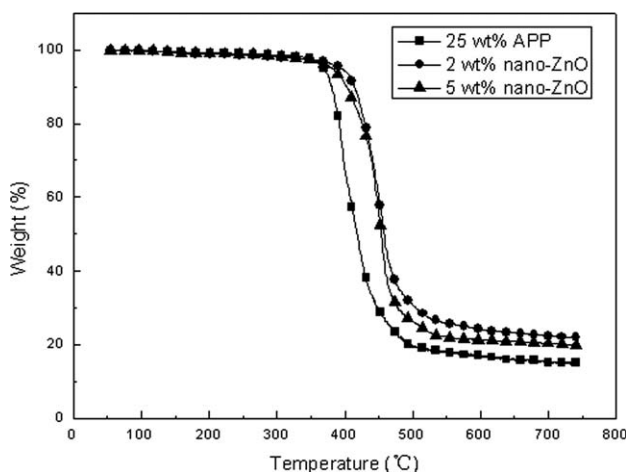


Figure 4 TG curves of the ABS/PET/APP and ABS/PET/APP/nano-ZnO systems.

TABLE II
Main Data Collected from TG Curves

Components (wt %)				T_{onset} (°C)	Weight at 700°C (%)
ABS/PET (50/50)	APP	Micro- ZnO	Nano- ZnO		
75	25			368	15.1
75	23	2		401	22.7
75	20	5		387	21.5
75	23		2	396	22.5
75	20		5	382	20.4

mal stability of the flame-retarded systems, and T_{onset} was on the order of 2 wt % micro-ZnO (401°C) > 2 wt % nano-ZnO (396°C) > 5 wt % micro-ZnO (387°C) > 5 wt % nano-ZnO (382°C) > APP (368°C). The lower T_{onset} of ABS/PET/APP + 5 wt % ZnO probably resulted from the stronger acceleration of the degradation of APP. This means that greater amounts of polyphosphoric acid, NH_3 , and H_2O were generated from APP at 260–420°C,¹⁴ and simultaneously catalyzed a higher degradation of PET on heating, which probably had a bad effect on the formation of the intumescent char layer. However, there was another insignificant difference that T_{onset} of the micro-ZnO systems was higher than that of the nano-ZnO systems; this probably resulted from the process progress, during which the hydroxyl on nano-ZnO surface led to the degradation of PET. Maybe this was the reason for the low LOI values of the nano-ZnO systems compared with the micro-ZnO systems. The char residues at 700°C of the ABS/PET/APP/ZnO systems were significantly higher than those of the ABS/PET/APP system, and the higher the ZnO content was, the lower the char residues at 700°C of the ABS/PET/APP/ZnO systems were. However, there was no significant

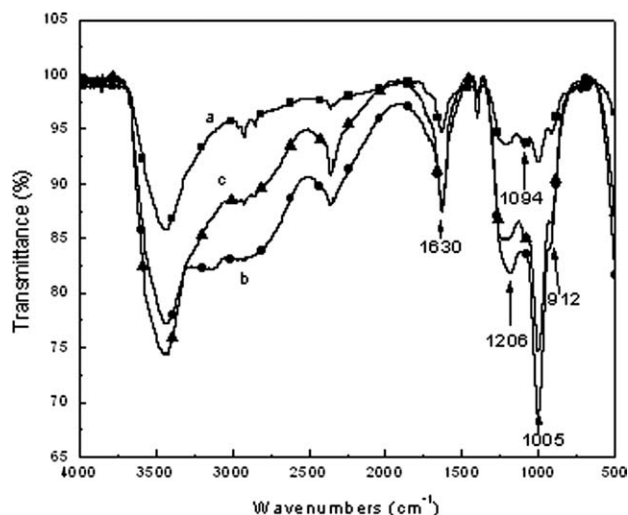


Figure 5 FTIR spectra of char residues of the (a) ABS/PET/APP, (b) ABS/PET/APP + 2 wt % micro-ZnO, and (c) ABS/PET/APP + 2 wt % nano-ZnO systems.

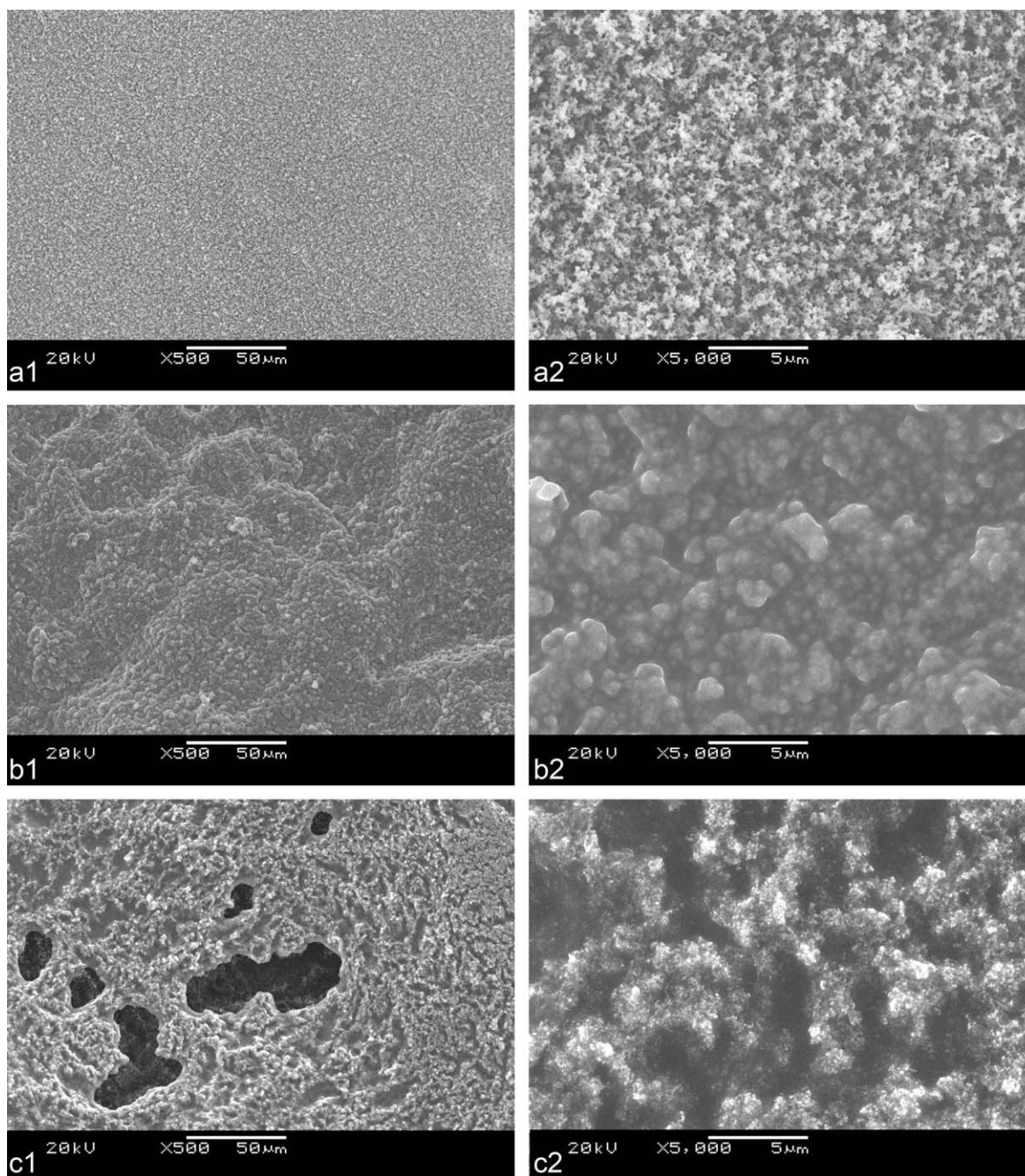


Figure 6 SEM of the charred surface structure of the flame-retardant systems: (a) ABS/PET/APP, (b) ABS/PET/APP + 2 wt % micro-ZnO, (c) ABS/PET/APP + 5 wt % micro-ZnO, (d) ABS/PET/APP + 2 wt % nano-ZnO, and (e) ABS/PET/APP + 5 wt % nano-ZnO.

difference in the char residues at 700°C between the ABS/PET/APP/micro-ZnO and ABS/PET/APP/nano-ZnO systems.

Evidence for the synergistic effect of ZnO by FTIR

In an attempt to elucidate the synergistic effect between APP and ZnO on the ABS/PET blends, the char residues on the surface of the flame-retarded ABS/PET systems after UL94 tests were analyzed by FTIR spectroscopy, and the results are presented in

Figure 5. It was seen that the absorption peaks of the ABS/PET/APP + 2 wt % micro-ZnO and ABS/PET/APP + 2 wt % nano-ZnO systems were significantly stronger than that of the ABS/PET/APP system. The band at 1630 cm^{-1} was ascribed to the β_{OH} in the P—OH group. The absorption of P=O appeared at 1206 and 1094 cm^{-1} , and the absorption band at 912 cm^{-1} was assigned to the P—O vibration in the P—O—P group, whereas that at 1005 cm^{-1} was attributed to the stretching mode of the P—O—C group.¹⁵ The results show that the char residues of

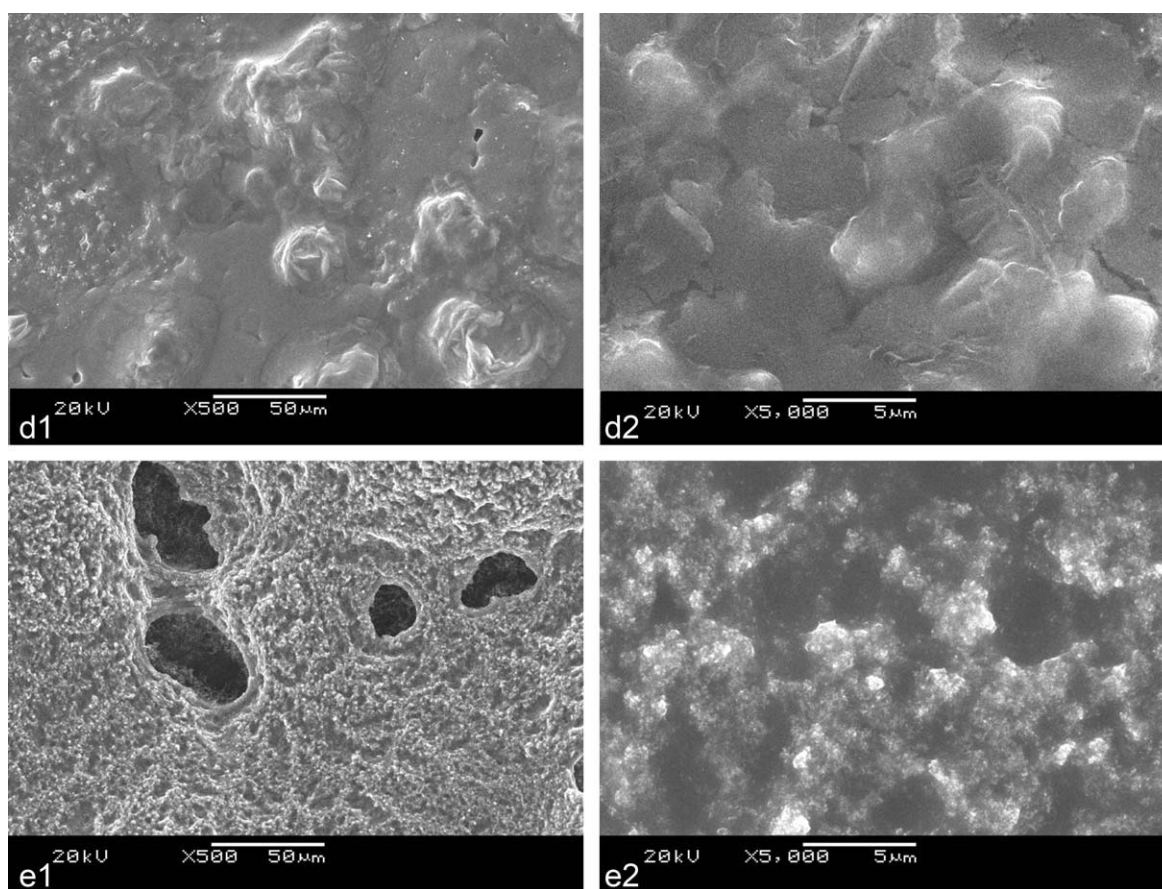


Figure 6 (Continued)

the ABS/PET/APP + 2 wt % micro-ZnO and ABS/PET/APP + 2 wt % nano-ZnO systems had a higher phosphorus content. This indicated that the addition of ZnO improved the efficiency of APP, which contributed to the increase of char residues of ABS/PET/APP/ZnO. Therefore, this char formulation was helpful for the enhancement of flame retardancy.

SEM analysis

Figure 6 shows the scanning electron micrographs of chars from the surfaces of the ABS/PET/APP, ABS/PET/APP + 2 wt % micro-ZnO (or nano-ZnO), and ABS/PET/APP + 5 wt % micro-ZnO (or nano-ZnO) systems. One could observe a loose and porous char layer formed on the surface of ABS/PET/APP. However, the surface of the char for ABS/PET/APP + 2 wt % micro-ZnO (or nano-ZnO) was significantly improved with a cohesive and dense structure, which could have acted as a barrier to shield the underlying polymer from heat and air,^{16–18} in agreement with the improvement of flame retardancy. The char layer for the nano-ZnO system was smoother compared with that of the micro-ZnO system. This may have been due to the smaller size of

nano-ZnO. The surface of ABS/PET/APP + 5 wt % micro-ZnO (or nano-ZnO) exhibited a looser char layer with bigger holes compared with that of the ABS/PET/APP system. The poor char layer could not act as a barrier to shield the underlying polymer from heat and air, which led to the poor flame retardancy of the systems. Hence, observation of the morphological structures of the residual char of the previous systems could clearly be present whether the flame retardancy of the flame-retarded ABS/PET systems was good. However, the significant difference in char layer between the ABS/PET/APP + micro-ZnO and + nano-ZnO (the same loading) systems could not be seen by SEM, which resulted in the difference in the fire properties.

CONCLUSIONS

In this study, the synergistic effect of ZnO (micro-ZnO and nano-ZnO) on ABS/PET/APP systems was investigated. ABS/PET/APP + 1 or 2 wt % ZnO exhibited a good flame retardancy, and micro-ZnO exhibited a better synergistic effect with APP than nano-ZnO. When 1 wt % micro-ZnO (or nano-ZnO) was incorporated into the ABS/PET/APP systems, the best flame-retardancy rating of V0 was achieved,

and the LOI value was 31 (or 30), respectively. TGA showed that the addition of ZnO improved the thermal stability and the yield of char residues of the ABS/PET/APP systems. ZnO accelerated the degradation of APP. However, more thermally stable residues formed through the interaction between APP and ZnO. Also, the FTIR spectra showed that the char residues of the ABS/PET/APP + 2 wt % ZnO systems had higher phosphorus contents. The addition of ZnO improved the efficiency of APP. SEM showed that the surface of the char for ABS/PET/APP + 2 wt % micro-ZnO (or nano-ZnO) was significantly improved with a cohesive and dense structure; however, that of ABS/PET/APP + 5 wt % micro-ZnO (or nano-ZnO) exhibited a looser char layer with bigger holes.

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