Synergistic Effect of Ammonium Polyphosphate and Expandable Graphite on Flame-Retardant Properties of Acrylonitrile-Butadiene-Styrene

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ABSTRACT: A new intumescent flame-retardant (IFR) system consisting of expandable graphite (EG) and ammonium polyphosphate (APP) was applied in acrylonitrile–butadiene–styrene (ABS) resin. A synergistic effect between EG and APP on the flame retardancy of ABS was observed. Fixing the total loading of flame retardant at 15 wt %, the limited oxygen index (LOI) could reach 31 vol % at a weight ratio of 3 : 1 for EG and APP. While LOI values of EG- and APP-filled ABS were only 26.0 and 21.5 vol % at the same loading, respectively. The UL-94 vertical burning test suggested that samples with different ratios of EG and APP could all pass V-0 rating while the samples containing EG and APP alone only passed V-1 rating. Thermogravi-metric analysis indicated that the addition of EG and APP (3 : 1 by weight) to ABS led to an increase in the amount of high-temperature residue by 11.8 wt %, and a decrease of mass loss rate by 0.7%/°C compared with pure ABS. Scanning electronic microscopy revealed a homogeneous compact intumescent char layer of ABS/EG/APP samples. Based on our experiment and combined with others' previous studies, the synergistic mechanism is inferred. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: acrylonitrile-butadiene-styrene; intumescent flame retardant; expandable graphite; ammonium polyphosphate; synergistic effect

INTRODUCTION

Acylonitrile–butadiene–styrene copolymer (ABS) is a versatile thermoplastic engineering plastic, which is extensively used in many fields, such as electronic and electric industry, traffic, construction, etc.[1–4] However, due to inherent flammability, its use is subjected to fire threat. The improvement of flame-retardant performance of ABS has reasonably become an important and urgent task.

Nowadays, among various flame-retardant methods, the halogen-free intumescent flame retardant (IFR) has been attracted increasing attention.[5–8] The conventional IFR system is usually composed of three active ingredients, including acid source, blowing agent, and carbon source. Upon heating, these three active ingredients form a multicellular swollen char layer, which slows down the heat and mass transfers to interrupt the degradation of a polymer. The mixture of ammonium polyphosphate (APP),

pentaerythritol (PER), and melamine is a typical IFR system,[7,9] which has been successfully used in fire-retardant intumescent coatings, due to its low smoke and toxic gases production during burning. Nevertheless, compared with bromine-containing flame retardants, it also has some shortcomings in flame retardancy of thermoplastics, such as lower thermal stability and lower water resistance.[10–12] When applied in ABS, it exhibits even lower flame retardancy. The limited oxygen index (LOI) is only 27.5 vol % even though the total amount of APP/PER is up to 30 wt %.[13] There is an increasing need to develop new IFR systems for ABS.

To solve the problems occurring in conventional IFR additives for ABS, some efforts have been taken. Xia et al.[13] obtained a synergistic effect by combination of PER/APP and zeolites on flame retardancy of ABS. Unfortunately, the mechanical properties of ABS were seriously sacrificed at the high content of flame retardants (30 wt %). Chen et al.[14] studied the IFR ABS system consisted of APP and Polyamide-6 (PA-6), where PA-6 was designed as the charring agent. As the weight ratio of PA6/ABS was fixed at 20/80, the LOI value reached 30 vol % at 25 wt % of APP content, but the UL-94 result only showed V-1 rating. Lee, et al.[15] employed tetra-2,6-dimethyl phenyl resorcinol diphosphate (DMP-RDP) as the flame

retardants for ABS resin with various novolac phenol resins (NP). The DMP-RDP/NP mixture exhibited upto 53 vol % of LOI value individually and highly enhanced thermal stability. Ma et al.[16] synthesized poly (4,4-diaminodiphenyl methane spirocyclic pentaerythritol bisphosphonate) (PDSPB), which reduced the peak heat release rate of ABS by 58.3% relative to pristine resin when adding 30 wt % PDSPB.

To a certain extent, the above IFRs have overcome some deficiencies of the traditional IFR system. However, low efficiency, high loading and high cost still exist, so it is imperative to develop new efficient IFR system for ABS resin. As a new generation of intumescent additives, expandable graphite (EG) with high flame-retardant efficiency and low cost is used in a growing number of fire-retardant applications as a blowing agent and carbonization compound.[17–19] EG is an intercalated graphite compound in which some oxidants like sulfuric acid and potassium permanganate are inserted between the carbon layers of graphite. When exposed to heat, EG expands and generates voluminous insulating layers, thus improving fire-retardant effect of the polymeric matrix.[19,20] As reported by Camino et al.[21] the expansion of EG occurs by a redox reaction equation between sulfuric acid and graphite:

$$C + 2H_2SO_4 = CO_2 \uparrow + 2H_2O \uparrow + 2SO_2 \uparrow$$
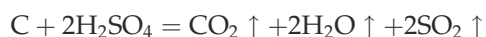
EG has been proved to present good fire-retardant properties for many polymers, such as polyolefins,[22] polyurethane foams.[23–27]

APP, usually associating with char-forming agents and nitrogen containing components, is one of the so-called IFRs and widely used as an acid source.[9,11,19,28] Phosphorus-containing compounds are involved in altering the pathway of the thermal degradation of the substrate by promoting carbonization with some other additives. Shih et al.[29] found a pronounced flame-retardancy effect as the phosphorous-containing additives was added to the unsaturated polyesters with EG, especially the APP-containing type. The synergistic effect between APP and EG on the rigid polyurethane foam (RPUF) has been systematically investigated in our previous study.[25] The results demonstrated that the mixture of APP and EG was an efficient fire-retardant additive for RPUF. They were also applied in polyethylene and polylactide polymers, where, usually, a prominent synergistic effect occurred.[30–33]

As part of our endeavor in pursuing effective flame-retardant system to reduce fire hazards and meet environmental protection standard for ABS, The aim of this work was to study the effects of APP and EG, whether or not they can synergistically improve the flame-retardant properties of ABS. IFR systems with different ratio of EG and APP for ABS were prepared, and the flame retardancy of ABS composites were investigated by LOI, UL-94 test, thus the optimal ratio was determined. The synergistic mechanism of APP and EG is illustrated by series of tests.

EXPERIMENTAL

Materials

All the starting materials were commercially available and were used without further purification. ABS resin (PA-757) was purchased from Chi Mei Corporation (Taiwan). APP was supplied by Chengdu Chuanke Chemical Company (China), with degree of polymerization > 1000. EG was bought from Qingdao Haida Graphite Company (China) and its main properties are as follows: ash, 1.0%; moisture, 1.0%; volatile, 15%; pH value, 3.0 and expansive volume, and 90 mL/g.

Sample preparation

ABS, APP, and EG were dried in an air oven at 80°C for 4 h. In this work, EG was selected as both char forming compound and blowing agent, APP was added as an acid catalyst. All the components were melt and mixed for 10 min at 180°C in an internal mixer with the roller speed of 60 rpm. The obtained mixture was hot-pressed into plates under a pressure of 10 MPa for 8 min at 180°C, and then the plates were cut into specimens for UL-94, LOI test.

Characterization

Flame-retardant testing

The UL-94 test was performed with a CTF-2 horizontal and a vertical burning instrument (made in Jiangning, China). The specimens for test were of dimensions of $130 \times 13 \times 4$ mm^3 according to IEC 60695-11-10. The LOI test was performed with an HC-2 oxygen index test instrument (made in Jiangning, China). The geometry of the sample sheet was $100 \times 10 \times 4$ mm^3 according to ASTM D 2863-97.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was conducted on an Q5000 WRT-2P thermogravimetric analyzer (Shanghai, China) at a heating rate of 10°C/min from 50 to 700°C under nitrogen.

Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectra were obtained with a Thermo Nicolet 6700 FTIR spectrometer, where the samples were prepared with KBr pellets to study the structure of char residues.

TABLE I
Composition and Flame Retardancy of the Samples

Sample	Component (wt %)			Flame retardancy	
	ABS	EG	APP	LOI	UL-94
1	100.00	0.00	0.00	19.0	No-rating
2	85.00	15.00	0.00	26.0	V-1
3	85.00	14.25	0.75	29.0	V-0
4	85.00	11.25	3.75	31.0	V-0
5	85.00	7.50	7.50	29.0	V-0
6	85.00	3.75	11.25	26.5	V-0
7	85.00	0.00	15.00	21.5	V-1

Scanning electron microscope observation

The morphology of the samples was examined by a JSM-5900LV (JEOL, Japan) scanning electron microscope (SEM) with an accelerating voltage of 20 kV.

RESULTS AND DISCUSSION

Flammability

To evaluate flame-retardant properties of ABS resins, LOI and UL-94 tests were conducted. The data obtained are given in Table I, which indicates that pure ABS is an easily flammable polymeric material with the LOI value of only 19 vol %. LOI of ABS containing 15 wt % EG and that of 15 wt % APP are shown to be 26.0 vol % and 21.5 vol %, respectively, meaning EG alone turns out to be better than APP. When mixed together at 15% totally, the LOI of systems are remarkably enhanced above 26.0% as seen in Figure 1, where the maximum peak at 31.0 vol % can be seen when the mass ratio of EG to APP is 3 : 1.

Compared with the pure ABS resin, the maximum LOI value increases by 12.0 vol %. However, with the further increase of the APP content, the LOI value starts to decrease. As shown in UL-94 test in Table I, the pure ABS burns too fast to classify the level. When adding EG or APP alone, only V-1 rating can be achieved. However, all the samples with EG and APP mixture can pass V-0 rating. These results manifest that an obvious synergistic effect exists between EG and APP on enhancing the flame retardancy of ABS resin.
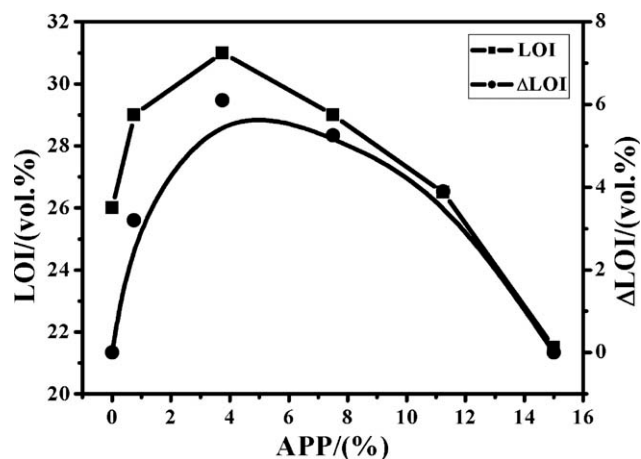

Figure 1 LOI and ΔLOI curves of ABS/EG/APP composites containing different ratios of EG and APP at 15 wt % total content.

To further demonstrate the mutual influences of EG and APP on the flame retardancy of ABS, we define the difference between the experimental LOI (LOI_e) and theoretical LOI (LOI_t), which can be estimated through linear combination between the LOI data of EG and APP according to eq. (1)–(2).[25]

$$LOI_t = \sum \%i \times LOI_e \qquad (1)$$

$$\Delta LOI = LOI_e - LOI_t, \qquad (2)$$

where i represents the flame-retardant additives, $\%i$ is the weight percentage of component i in the materials and LOI_e is the LOI value of 15 wt % i in ABS. If $\Delta LOI > 0$, it means a synergistic effect exists between EG and APP, and if $\Delta LOI < 0$, there is an antagonistic effect. As shown in Figure 1, the ΔLOI values of all samples are higher than zero, which indicates the synergistic effect of EG and APP on flame retardancy of ABS. We find that ΔLOI starts to increase with the APP content, then reaches a peak and decreases subsequently. The ΔLOI at 3.75 wt % APP is so near to the vertex, therefore, it is easy to conclude that the maximum synergistic effect can be obtained at this ratio (3 : 1 by weight) of EG and APP.

Figure 2 shows the photographs of the specimens obtained after combustion for 50 s in the atmosphere
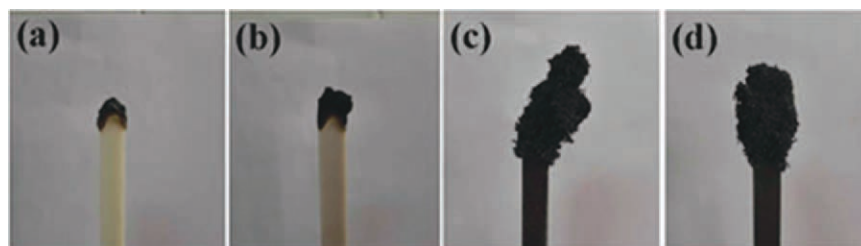

Figure 2 Photographs of the specimens after LOI tests: (a) pure ABS, (b) 15 wt % APP/ABS, (c) 15 wt % EG/ABS, and (d) 15 wt % (EG + APP)/ABS, EG : APP = 3 : 1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
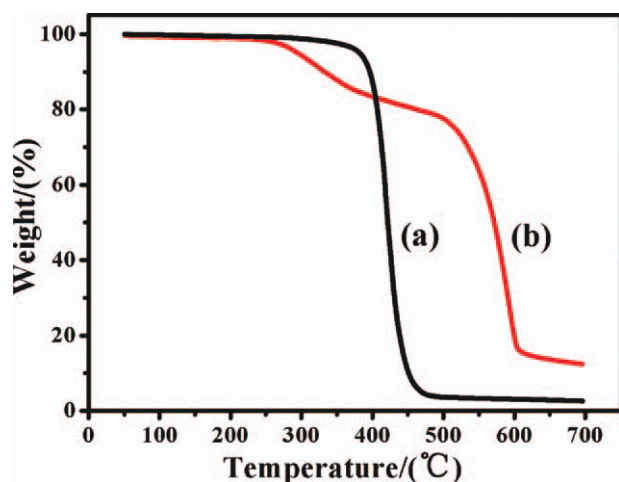
Figure 3 TG curves of components (a) ABS and (b) APP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with an oxygen concentration of 2 vol % higher than their LOI. It can be seen that pure ABS produces little char after combustion. The sample of 15 wt % APP/ABS leaves a little more char than that of pure ABS sample, but it is not intumescent while the char of 15 wt % EG/ABS is intumescent, but fluffy and brittle. The intumescent char layer is also formed for 15 wt % (EG + APP)/ABS, which is obviously much denser and more compact than that of 15 wt % EG/ABS. The high-quality char layer can more efficiently protect the remaining polymeric materials from further burning.

Thermal stability

The thermal stability of ABS samples is related to flame-retardant additives. TGA is used to study the thermal degradation properties of pure ABS, EG, and APP, as shown in Figure 3 and Table II. The pure ABS resin decomposes from 270°C and shows only one-step decomposition around 270 to 500°C leaving negligible char (2.0 wt %) above 500°C. The

degradation course of APP could be divided into two stages. The first one occurs from about 250 to 350°C with a peak at 325.1°C representative of the loss of NH_3, H_2O, and some volatile free radicals like PO•, PO2•. The second stage appears from 480 to 620°C with a peak at about 592.2°C, due to the generation of polyphosphoric acid and phosphoric acid by APP. Based on the previous studies,[17,34] EG begins to degrade from 200°C and the maximum weight loss occurs in the range of 200–300°C accompanied with expansion of the char. EG and APP decompose at relatively lower temperatures than pure ABS. This proper gap of initial degradation temperature between polymers and IFRs is necessary because the expanded char layer and phosphoric polyphosphoric acids have to be produced at the beginning of combustion.

It is noteworthy that the TGA curve of EG is not given here, since the final residual of EG at 700°C is only 6.2 wt % by the TGA test, far below the conventional results.[17,34] The reason for the less residual char is that the EG sample is only several milligrams, and the formed char is physically extremely soft even a puff of nitrogen flow could blow away the loose carbon char. To verify this, we carried out an additional experiment using a Muffle furnace. Initially, 1 g of EG was put into the Muffle furnace, then gradually heated it to 700°C and held at this temperature for 3 min; finally, we weighted the residual and found out 0.8 g char could be obtained. Based on this, 80 wt % can be considered as the residual char after pyrolysis.

TGA and DTG curves of ABS samples are separately shown in Figures 4 and 5, and some important data are tabulated in Table II. The thermogram of samples containing EG alone exhibits two main pyrolysis peaks at about 250 and 420°C, respectively. The first step is an intumescent process of EG appearing in the temperature range of 200 to 300°C. The second one occurs in the range of 400–500°C and can be assigned to thermal degradation of ABS. While the thermogram of sample with APP alone

TABLE II
Thermal Degradation Data Under Pure Nitrogen by TGA

Sample	$T_{initial}$[a] (°C)	T_{max}[b] (°C) Stage 1	Stage 2	R_{max}[c] (%/°C)	Residue at 700°C (wt %)
ABS	270.0	431.1	–	2.4	2.0
APP	267.5	325.1	592.2	–	12.4
EG	200.4	223.5	–	–	6.2
15 wt % EG/ABS	227.4	255.1	419.9	1.9	13.2
15 wt % APP/ABS	240.0	–	421.2	1.9	14.4
15 wt % (EG + APP)/ABS EG : APP = 3 : 1	230.8	254.3	420.3	1.8	15.2

[a] $T_{initial}$ is the initial degradation temperature (temperature at 2.0% weight loss).
[b] T_{max} is the maximum-rate degradation temperature.
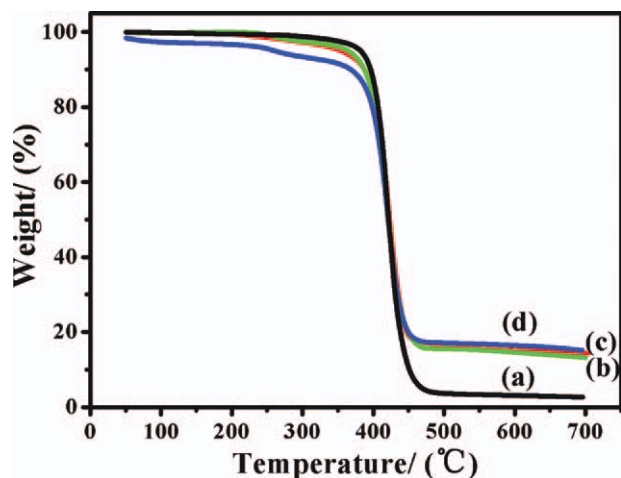[c] R_{max} is the maximum rate of decomposition.

Figure 4 TG curves of (a) pure ABS, (b) 15 wt % APP/ABS, (c) 15 wt % EG/ABS, and (d) 15 wt % (EG + APP)/ABS, EG : APP = 3 : 1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

exhibits only one main pyrolysis peak at 421.2°C with a char yield of 14.4 wt % at 700°C. The char residues of (EG + APP)/ABS system at 700°C are about 15.2 wt %, which is more than that of pure ABS. The maximum decomposition rates (R_{max}) of different samples are listed in Table II. Comparing to the R_{max} of pure ABS, one can conclude that the samples containing EG or APP make R_{max} decrease, thus indicating improved thermal stability when flame retardants are added. It should be noted that $T_{initial}$ of ABS sample containing flame-retardant additives is below that of pure ABS. The earlier decomposition of the flame retardants (APP or EG) may explain this point.

The above results show that combination of EG and APP can not only increase the charred residue
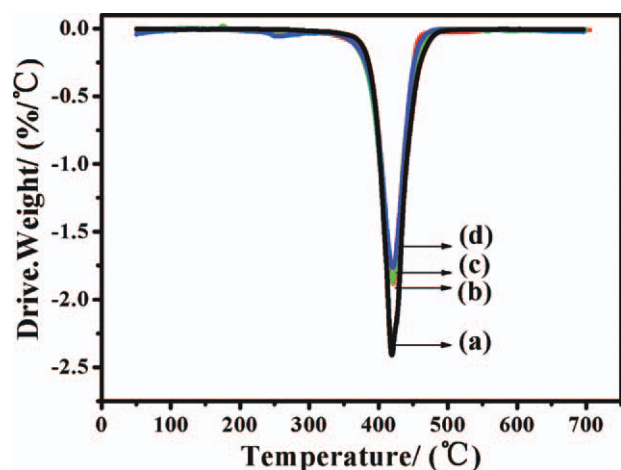
at high temperature but also slow down the mass loss rate compared with original ABS resin, and stabilize the char layer, which could act as protective shield against combustible gases during combustion, thus the flame-retardant property has been highly enhanced. Generally, a close connection exists between weight percent of char residue and LOI value, for example increase of weight percent of char residue always accompanies with improvement in LOI value.[5,9,11,35] Since residue content is similar for EG/ABS, APP/ABS, and (EG + APP)/ABS, the above view could not explain the variation in LOI values. Residue structure is another important factor,[15,16,22] and based on this, the following experiment was carried out to confirm it better.

Structural analysis of combustion residue

As mentioned above, the char residues play a significant role in improving flame retardancy of ABS, thus, the observation of morphology and structure of the combustion residues could help to a better understanding the synergistic effect of EG and APP in the flame-retardant system. Figure 6 presents the FTIR spectrum of the residues obtained from the samples treated for 5 min at 700°C in the Muffle furnace. The absorption band at 1152 cm^{-1} is assigned to the stretching mode of P=O group, and the peaks at 1002 cm^{-1} are attributed to the symmetric vibration of P—O (P—O—C) group.[36–38] Improvement in the intensity of these peaks is observed as APP content increases. The FTIR spectrum confirms the existence of P—OH, P=O, and P—O in the charred layers, suggesting polyphosphoric acid generated at

Figure 5 DTG curves of (a) pure ABS, (b) 15 wt % APP/ABS, (c) 15 wt % EG/ABS, and (d) 15 wt % (EG + APP)/ABS, EG : APP = 3 : 1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
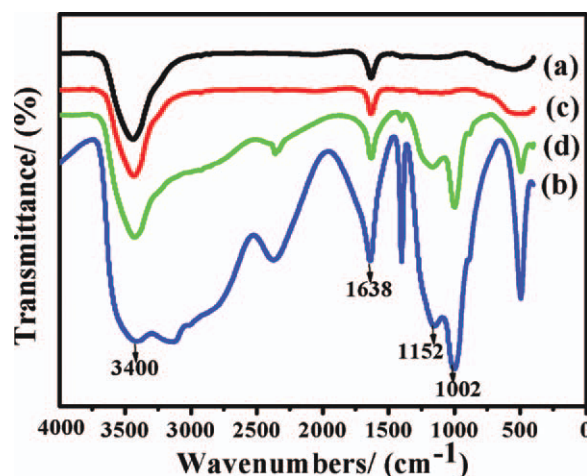

Figure 6 The FTIR spectra of ABS samples' char obtained after combustion for 5 min in the muffle at 700°C: (a) pure ABS, (b) 15 wt % APP/ABS, (c) 15 wt % EG/ABS, (d) 15 wt % (EG + APP)/ABS, EG : APP = 3 : 1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
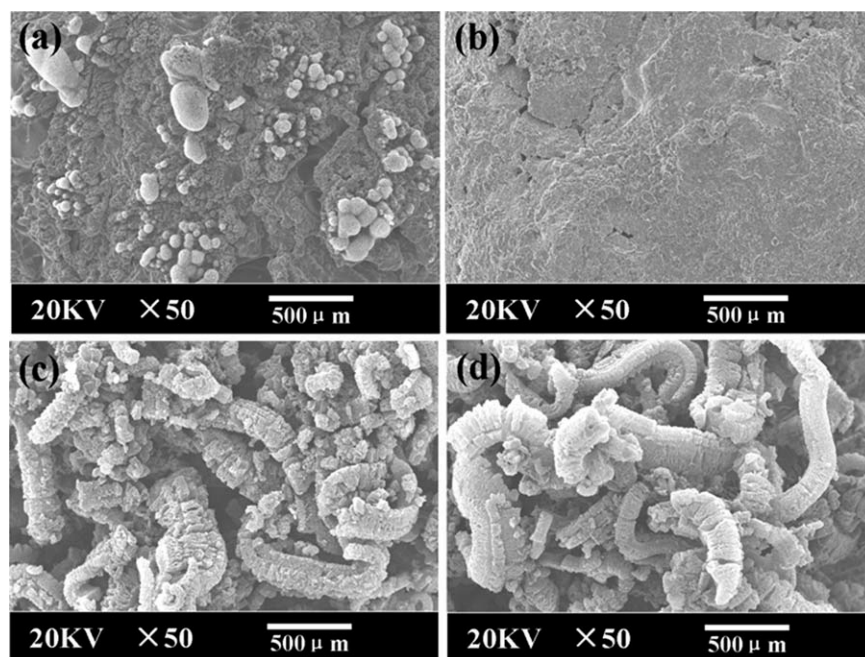
Figure 7   SEM morphology of the char samples obtained from ABS composites after LOI tests: (a) pure ABS, (b) 15 wt % APP/ABS, (c) 15 wt % EG/ABS, and (d) 15 wt % (EG + APP)/ABS, EG : APP = 3 : 1.

high temperature. Moreover, it can also be observed that the peaks appear at around 1638 cm^{-1} in all spectra which refers to the stretching vibration for carbon duplet bond (C=C).[39] This indicates the generation of amorphous carbon and it forms protective char layer for samples containing EG and APP during combustion.

To further observe the microstructure of intumescent charred layer, the morphology of the charred layers were examined by SEM. As shown in Figure 7(a), many big holes and cracks exist in the residuals of pure ABS owing to insufficient char formation or less condensed char during combustion. When APP is added alone [Fig. 7(b)], a smooth thin film-like glassy coating forms on the surface as a result of the viscous phosphoric or polyphosphoric acid from the decomposition of APP. However, this char can not effectively prevent the ABS matrix from degradation. From Figure 7(c,d), one can observe the "worm-like" structure carbon layer is developed due to the expansion of EG. Comparing Figure 7(c,d), the char of 15 wt % EG/ABS in Figure 7(c) seems brittle and easy to collapse, while the char surface of ABS with both EG and APP [Fig. 7(d)] is compact, thick, tight, and with a large expansion volume. This char structure could suppress both mass and heat transfer, making char layer protect the matrix from heat for a long time at high temperature, which is effective in retarding the degradation of underlying material. Therefore, we can conclude that combination of EG and APP would endow ABS matrix with superior flame-retardant property.

Origin of the synergetic flame-retardant mechanism

From the LOI and UL-94 tests, the flame retardancy of ABS can be greatly improved by combination of EG and APP, showing a typical synergetic flame-retardant behavior. Through the analysis of TG, FTIR, and SEM, and combined with others' previous studies,[24,32] the synergistic mechanism was proposed for this flame-retardant system. In the gas phase, the nonflammable gases, such as CO_2, SO_2, NH_3, and H_2O released through decomposition of EG and APP can dilute the combustible gases. In the condensed phase, EG and APP play an important role in different time periods during combustion. Initially, the "worm-like" char was formed by the inflation of EG from 200 to 250°C, but the char could not effectively endure heat flux for a long time at high temperature. Then the polyphosphoric acid generated from APP increased the melt viscosity, which could strengthen the char barrier for its strong adhesion effect. The structure of char layer for 15 wt % (EG + APP)/ABS [Fig. 7(d)] was adjusted through the addition of APP, showing a thicker and denser char layer compared with the composite with EG alone [Fig. 7(c)]. In addition, the decomposition products of APP accelerated dehydration of the sample containing EG and APP, which is illustrated in Figure 5. Thus, the transfer of gas and heat was retarded by this insulative layer. Meanwhile, a certain amount of EG was needed to ensure a sufficient carbon source. There is therefore an optimal ratio of EG and APP. At this ratio, the superior quality of the

carbon layer formed, which could make the heat and mass transport achieve a balance, indicating the best flame-retardant efficiency.

CONCLUSIONS

A new IFR system containing EG and APP shows high efficiency in flame retardance of ABS, LOI value can reach 31 vol % and V-0 rating is obtained at the optimum ratio of EG : APP (3 : 1 by weight), keeping the 15 wt % total content of additives. While LOI value of EG- or APP-filled ABS is only 26.0 and 21.5 vol %. The results of TG and DTG demonstrate that the char residues can reach 15.2 for 15 wt % (EG + APP)/ABS : EG : APP = 3 : 1, which is more than that of pure ABS. The char residue content is similar for EG/ABS, APP/ABS, and (EG + APP)/ABS, The best properties presented by the sample of (EG + APP)/ABS are probably more due to the structure of residue than to the char residue content. SEM results show that a compact and thick char layer is formed in 15 wt % (EG + APP)/ABS system, because of the expansion of EG and the coverage adhesion effect of phosphoric acid generated from APP, which further certifies that there is a synergistic effect between EG and APP in improving the char morphology and promoting the thermal stability The char layer hinders the transfer of heat flow and combustible gases in the condensed phase. Meanwhile, in the gas phase, the nonflammable gas, such as NH_3, H_2O, CO_2, and SO_2 released by EG and APP can dilute the combustible gases. Thus, the combination of EG and APP has been proved to be a promising IFR system for ABS.

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