

Metal compound-enhanced flame retardancy of intumescent epoxy resins containing ammonium polyphosphate

Jun-Sheng Wang^a, Yun Liu^a, Hai-Bo Zhao^a, Jiang Liu^a, De-Yi Wang^a, Yan-Peng Song^a, Yu-Zhong Wang^{a,b,*}

^a Center for Degradable and Flame-Retardant Polymeric Materials (ERCEPM-MoE), College of Chemistry, Sichuan University, 29, Wangjiang Road, Chengdu 610064, Sichuan Province, China

^b State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, Sichuan Province, China

ARTICLE INFO

Article history:

Received 19 November 2008

Received in revised form

1 January 2009

Accepted 9 January 2009

Available online 18 January 2009

Keywords:

Ammonium polyphosphate

Epoxy resin

Intumescence

Flame retardance

Catalysis

ABSTRACT

A series of intumescent flame-retardant epoxy resins (IFR-EPs) were prepared only by adding a 5 wt% total loading of ammonium polyphosphate (APP) and metal compounds. All the samples could achieve V-0 rating and did not generate dripping during UL-94 testing. The limiting oxygen index (LOI) values of the samples with 4.83 wt% APP and 0.17 wt% CoSA increase from 27.1 to 29.4, compared with epoxy resin containing 5 wt% APP. The samples also showed excellent water resistance of flame retardancy in 30 °C and 70 °C water for 168 h. The LOI results show that the composition of metal compounds (metal ions and ligands/anions) and the mass ratios of APP to metal compounds affect the flame retardancy of the samples. TG results indicate that the catalytic effect of CoSA on the decomposition of both APP and the epoxy resins containing APP is better than that of CuSAO. The fire behavior of epoxy resin and epoxy resins containing APP with/without CoSA were investigated by cone calorimeter. Cone calorimeter parameters of the samples such as HRR, THR, TSP and COP indicate that the addition of APP and CoSA improves the fire safety of epoxy resin significantly, and CoSA shows an obvious catalytic effect.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Epoxy resins are widely used in laminating, adhesive, coating, and casting fields due to their dimensional stability, satisfactory mechanical properties, suitable weather, chemical and thermal resistance [1]. However, its lack of flame retardancy limits its more extensive applications where high thermal stability and flame retardancy are needed. The flame retardancy of epoxy resins can be improved by introducing flame-retardant elements such as halogen, phosphorus and silicon into epoxy resins or curing agents [2,3]. Halogen-containing flame retardants are reported to be effective flame retardants for various polymer materials including epoxy resins. However, some of them are restricted to use due to their generating dense toxic smoke and corrosive products during combustion [4]. Therefore, the preparation of halogen-free flame retardants is the subject of extensive investigations. A number of halogen-free flame retardants used for epoxy resin are reported, including epoxy monomers [5–10], cure agents [10–13] and additives [14–17].

Intumescent flame-retardant additives have aroused a great deal of attention. Generally, three kinds of components are incorporated into formulations to obtain intumescent flame retardancy: an acid source, a carbonization agent and a blowing agent [18,19]. Most of the epoxy resins with intumescent flame retardants are used as coatings [20–22], and they can also be used as thermoset plastics [9,14,23]. As we all know, epoxy resins cured with amidogen group contain a large number of hydroxyl (OH) groups and nitrogenous groups, which can be considered as both carbonization agent and blowing agent. In our previous work [24], we investigated a new intumescent flame-retardant epoxy resin system, in which epoxy resins cured with low-molecular-weight polyamide were used as carbonization agent and blowing agent, and ammonium polyphosphate was used as acid source.

However, the high loading level of flame retardants is the major problem for halogen-free flame-retardant system, especially for intumescent flame retardants. Recently, metal compounds were used as synergistic agents for improving flame-retardant efficiency of intumescent flame-retardant system [25]. Most of these investigations were still concentrated on flame retarded polyolefin with ammonium polyphosphate and pentaerythritol system [26–32]. Also, some of the reports related to synergistic effect between metal compounds and intumescent flame retardants for other polymer materials such as cotton fabric [33], polyvinyl chloride

* Corresponding author. Center for Degradable and Flame-Retardant Polymeric Materials, College of Chemistry, Sichuan University, 29, Wangjiang Road, Chengdu 610064, Sichuan Province, China. Tel./fax: +86 28 85410259.

E-mail address: yzwang@email.scu.edu.cn (Y.-Z. Wang).

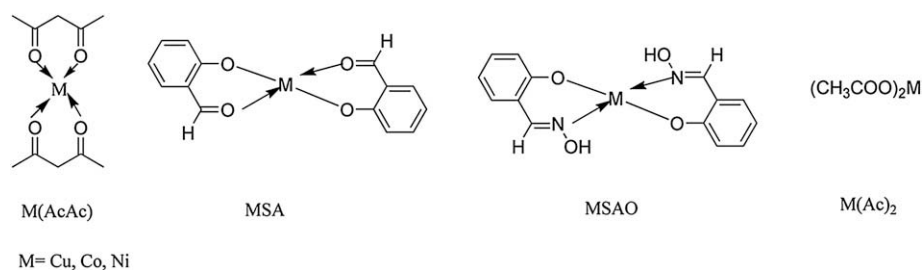


Fig. 1. Structure of metal compounds.

[34], polycarbonate [35], polyvinyl alcohol [36] and polyamide [37]. We also noticed that an easier approach for preparation of flame retarded epoxy resins had been reported recently. In these reports, ammonium polyphosphate [24,38] or melamine phosphate [39] was used as flame retardant for epoxy directly and acceptable flame retardancy was obtained.

However, to the best of our knowledge, there are few reports about the effect of metal compounds on flammability of flame-retarded cured epoxy resin by APP. In the present work, a series of intumescent flame-retardant epoxy resins have been prepared by using APP and metal compounds as flame retardants, and the total loading of flame retardants were kept at 5 wt%. Indeed, the focus in this investigation is to study the effect of APP and metal compounds on flame retardancy of cured epoxy. Herein, flammability and fire behavior of samples were evaluated by LOI, UL-94 vertical burning test and cone calorimeter, respectively. The thermal stabilities of the systems were also studied by thermogravimetric analysis (TGA).

2. Experimental

2.1. Materials

Diglycidyl ether of biphenol A (E-44) was provided by Wuxi Resin Factory of Xingchen New Chemical Material Co. Ltd (Wuxi, China). Low-molecular-weight polyamide (LWPA) was purchased from Haitian Chemical Reagent Co. Ltd (Hunan, China). Ammonium polyphosphate (APP) was supplied by Changfeng Chemical Corp. (Shifang, China), and the degree of polymerization of APP is

more than 50. Ni(II), Co(II) and Cu(II) complexes were synthesized in our laboratory [30–32,36,40]. Ni(II), Co(II) and Cu(II) acetate salts were supplied by Kelong Chemical Reagent Corp. (Chengdu, China). The metal compounds used in this paper are summarized in Fig. 1.

2.2. Preparation of flame-retardant epoxy resin samples

The cured epoxy resins were obtained by thermal curing. Intumescent flame retardants (IFR) were prepared by mixing ammonium polyphosphate with metal compounds in a certain weight ratio. Epoxy resin (E-44), low-molecular-weight polyamide and IFR were mixed together while the total content of IFR was kept 5 wt%. Finally, the composites were cured for 12 h at room temperature and for 5 h at 80 °C, and then the solid products were obtained.

2.3. Characterization

The limiting oxygen index (LOI) values were measured on an HC-2C oxygen index meter (Jiangning, China) with sheet dimensions of 130 mm × 6.5 mm × 3.2 mm according to ASTM D2863-97.

The vertical burning test (UL-94) of samples was conducted on a CZF-2 instrument (Jiangning, China) according to ASTM D 3801 testing procedure. The samples were made to a size of 125 mm × 12.7 mm × 3.2 mm.

Thermogravimetric analysis (TGA) was conducted on TAQ500 V6.4 Build 193 thermal analyzer at a heating rate of 10 °C/min. Samples were heated in the temperature range from room temperature to 700 °C under air at a flow rate of 60 ml/min.

Water resistance of flame-retardant epoxy resin was measured in an 800 ml beaker according to GB 11547-89.

The fire behavior of epoxy resins was characterized by cone calorimeter under a heat flux of 35 kW/m² with the sheet dimensions of 100 mm × 100 mm × 6.0 mm according to ISO 5660.

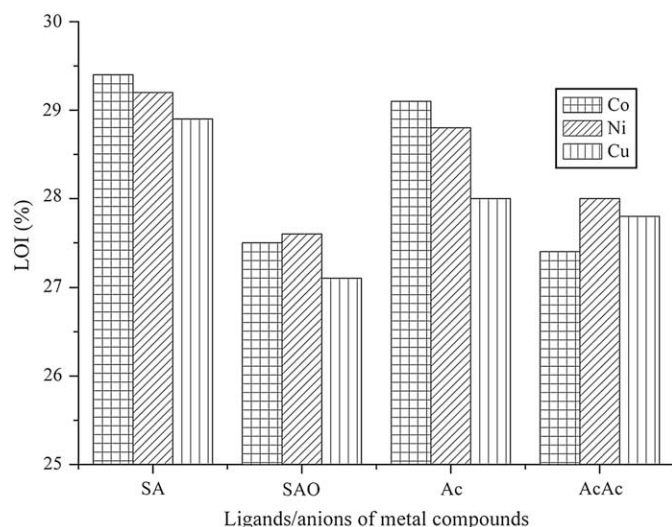


Fig. 2. The effect of different metal compounds on LOI values with APP.

Table 1
Effect of mass ratio of APP to CoSA on the flame retardancy of IFR-EPs with 5 wt% of total loading.

Sample	APP: CoSA ^a	Content of APP ^b (wt%)	Content of CoSA ^b (wt%)	LOI (%)	UL-94	Dripping
EP	–	0	0	19.6	N.R.	Yes
EP-APP	–	5.00	0	27.1	V-0	No
EP-APP-CoSA1	149:1	4.97	0.03	28.0	V-0	No
EP-APP-CoSA2	59:1	4.92	0.08	28.4	V-0	No
EP-APP-CoSA3	29:1	4.83	0.17	29.4	V-0	No
EP-APP-CoSA4	19:1	4.75	0.25	28.4	V-0	No
EP-APP-CoSA5	14:1	4.67	0.33	28.7	V-0	No
EP-APP2	–	12.50	0	28.9	V-0	No

^a Mass ratio.

^b Calculated based on the mass ratio of APP to CoSA.

Table 2
Flammability of IFR-EP samples dipped in 30 °C and 70 °C water for 168 h.

Sample	LOI (%)	Δ LOI (%)	UL-94	Dripping
EP-APP-CoSA3	29.4	–	V-0	No
EP-APP-CoSA3-30 °C	29.0	0.4	V-0	No
EP-APP-CoSA3-70 °C	28.7	0.7	V-0	No

3. Results and discussion

3.1. Flammability

The LOI values and UL-94 test are commonly used to estimate the ignition retardancy of materials. In this section, firstly we investigated the effect of different metal compounds and APP on LOI values, and the results are shown in Fig. 2. From these results, a noticeable case is that substrate structure of metal compound has a significant effect on flame-retardant efficiency. For example, LOI values of IFR-EPs-MSA and IFR-EPs-M(Ac)₂ are higher than those of IFR-EPs with M(AcAc) and MSAO, while the mass ratio of APP to metal compounds is kept constant (29:1). The reason for this case may be corresponding to the relationship between the structure and catalytic efficiency. Moreover, the metal element in the compound also affects flame retardancy of IFR-EPs with metal compounds. In fact, there are also some reports about this phenomenon in the literatures [25,26,30,31]. However, in this study, the case seems more complex, and has no regular sequence for the different compounds. The main reason, actually, is that there are two factors, metal elements and their chemical structures, that influence the catalysis of the compounds simultaneously. For vertical burning test, V-0 rating for all samples can be achieved easily and no dripping can be observed during testing.

In addition, the effect of the mass ratio of APP to CoSA on LOI values is also investigated. The results of LOI values and UL-94 test of IFR-EPs are given in Table 1, in which the total amount of APP and CoSA is still 5 wt%. Compared with IFR-EP only containing APP, the LOI values of IFR-EPs containing CoSA increase from 27.1 to 29.4. However, the LOI values decrease while the mass ratio of APP to CoSA is lower than 29:1, indicating that there are synergistic effects between APP and CoSA and their optimal ratio is 29:1. It can be observed that the flame retardancy of EP-APP-CoSA is better than that of EP-APP2 containing 12.5 wt% APP from Table 1, indicating the synergistic effect between APP and CoSA is obvious. All samples of IFR-EPs could achieve V-0 rating and did not generate dripping

during UL-94 test. Therefore, the mass ratio of APP to metal compounds and the composition of metal compounds would affect flame retardancy of IFR-EPs.

3.2. Water resistance of intumescent flame-retardant epoxy resins

From Table 2, the flame retardancy of EP-APP-CoSA3 could satisfy the actual demand for applications. However, water solubility of IFRs (typically APP, melamine and pentaerythritol) leads to the leaching of IFRs from the polymer matrix for applications under moisture or in water condition, thus the reduction of properties of materials such as flame retardancy, electrical insulation cannot be avoided [41]. The water resistance of IFR-EPs containing APP and CoSA was investigated in 30 °C and 70 °C water for 168 h and the flammability test results are presented in Table 2. It can be seen that the LOI value of EP-CoAPP3 is 29.0 after treated in 30 °C water for 168 h and just decreases by 0.4 units. It is very surprising that the LOI value of EP-CoAPP3 is 28.7 in 70 °C water after 168 h and only decreases by 0.7 units. As we all know, crosslinked network structure of epoxy resins is formed during curing. Thus, it is not easy for APP and metal compounds to leach from epoxy resins, which may be the reason why flame retardancy of IFR-EP is still kept after treated in 70 °C water for 168 h. The results indicate that the flame retardancy of IFR-EPs can be kept under moist condition and IFR-EPs can be fitted to applications.

3.3. Thermal decomposition behaviors

TGA measurements can serve as useful indicators for polymer flammability [42]. Figs. 3 and 4 show TG and DTG curves of IFR-EPs and pure epoxy resin, and the main information of TG results is summarized in Table 3. Compared with TG curves of IFR-EPs and EP in Fig. 3, IFR-EPs show an obvious decrease in thermal stability below 413 °C and a significant increase in thermal stability over 413 °C. We can see that EP decomposes rapidly in the temperature range from 300 °C to 500 °C, generating an amount of fuel for combustion, which is the main reason for the flammability and large soot/smoke production of EP. However, the thermal decomposition rates of IFR-EPs are lower than that of EP, which could help to produce char to protect polymer matrix. From Fig. 4, it can be seen that the thermal degradation process of IFR-EPs and EP could be separated into two main steps. At the first step, APP could decompose under heat to yield polyphosphoric acid, water and

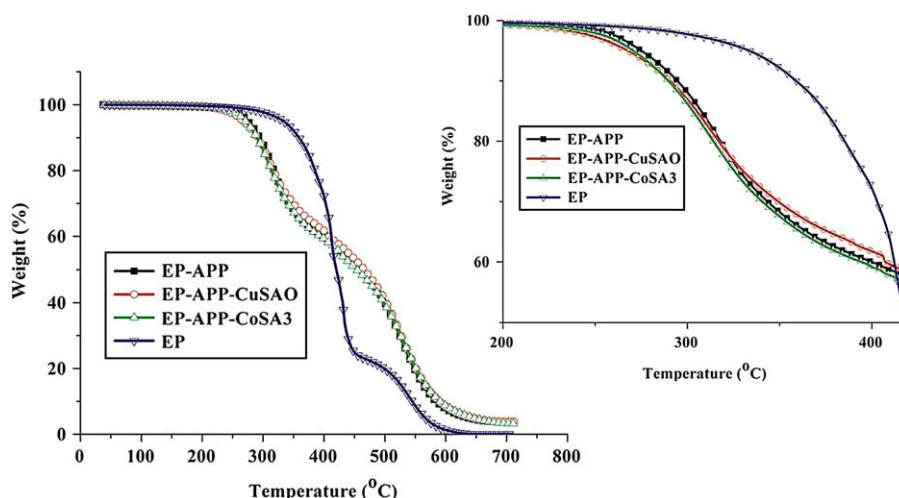


Fig. 3. TG curves of IFR-EPs and pure epoxy resin.

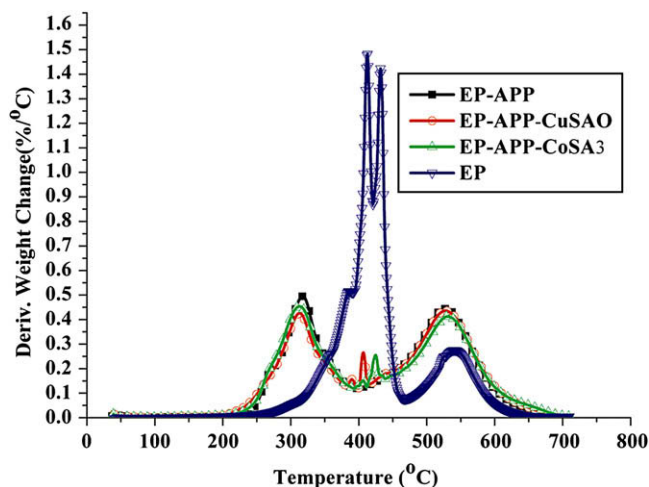


Fig. 4. DTG curves of IFR-EPs and pure epoxy resin.

ammonia; and polyphosphoric acid could react with the hydroxyl of cured epoxy resin to produce crosslinked phosphate ester. The resulting residues at the first step would decompose further to yield a lacunaris and compact char coating surface of the material, which can protect the polymer matrix effectively at the second step. We have discussed the thermal degradation mechanism of the reactions between EP and APP by TG, FT-IR and XPS in detail in our previous work [24].

Thus, we will mainly discuss the interaction between EP and the mixture of APP with metal compounds and synergistic effect between APP and metal compounds in this paper. From Table 3, we can see that the onset degradation temperatures (T_{onset}) of IFR-EPs containing metal compounds are lower than that of EP-APP and the T_{max1} (the temperature at the maximal degradation rate at the first step of thermal degradation) of IFR-EPs containing metal compounds decrease by about 5–11 °C compared with that of EP-APP. The results of T_{onset} and T_{max1} show that the addition of metal compounds could catalyze the degradation behavior of IFR-EP, which is an evidence for synergistic effect between APP and metal compounds. When TG curves of IFR-EPs in the temperature range from 200 °C to 420 °C are compared, the degradation rate of EP-APP-CoSA3 is quicker than that of EP-APP all through; the degradation rate of EP-APP-CuSAO is quicker than that of EP-APP firstly, and then the degradation rate of EP-APP-CuSAO is slower than that of the others, indicating that the catalytic effect of CoSA on degradation of EP-APP is better than that of CuSAO. The residues of EP-APP-CuSAO at 400 °C and 500 °C are more than that of EP-APP-CoSA, which also suggested that the addition of CuSAO could not catalyze the degradation of IFR-EP effectively. Relating with the results of LOI values, the degradation rate of EP-APP-CoSA3 with high LOI value is quicker than those of EP-APP and EP-APP-CuSAO. Therefore, the addition of CoSA affects the

char-forming process, which occurs at the first step. However, a regular rule could not be found from the degradation of IFR-EPs at the second step.

In order to investigate the synergistic effect between APP and metal compounds further, we examined the mixture of APP with CoSA or CuSAO by TG. Fig. 5 presents TG curves of APP, CoSA and the mixture of APP with metal compounds (APP-CoSA, APP-CuSAO). The calculated TG curve for APP-CoSA is given in Fig. 5. The mass loss of APP-CoSA for the calculated TG curve is calculated from the formula: mass loss of pure APP \times content of APP + mass loss of cured epoxy resin \times content of cured epoxy resin. It can be observed that TG curves of APP, APP-CoSA and APP-CuSAO are almost the same below 600 °C in Fig. 5. However, we can see that the decomposition rates of APP-CoSA and APP-CuSAO are quicker than that of APP in the temperature range from 150 °C to 420 °C. From comparison of TG curves between Cal-APP-CoSA and APP-CoSA, we can find that the addition of CoSA can catalyze significantly decomposition of APP. The different catalytic effects between CoSA and CuSAO on decomposition of APP can also be observed above 600 °C from Fig. 5. Compared with CuSAO, CoSA could accelerate the decomposition of APP obviously above 600 °C. More information of TG is summarized in Table 4. The T_{onset} s of APP-CoSA and APP-CuSAO decrease by about 24 °C compared with T_{onset} s of APP, which is an evidence for catalysis of metal compounds. The T_{max1} (the temperature at the maximal decomposition rate at the first step of thermal decomposition) of APP-CoSA (292 °C) is lower than that of APP (297 °C) while T_{max1} of APP-CuSAO (302 °C) is higher than that of APP. It suggests that the catalytic effect of CoSA on decomposition of APP is better than that of CuSAO, which may be one of the reasons that the flame retardancy of EP-APP-CoSA is better than that of EP-APP-CuSAO. However, at the second step of thermal decomposition, the temperatures at the maximal decomposition rate (T_{max2}) of these samples are almost the same as thermal decomposition of crosslinking of polyphosphoric acid formed at the first step takes place mainly. The order of the residues of APP-CoSA, APP-CuSAO and APP at 420 °C and 700 °C are the same: APP > APP-CuSAO > APP-CoSA, which indicates that the catalysis of CoSA on APP is better than that of CuSAO both at the step of decomposition of APP and further decomposition at the next step. Therefore, the catalysis of CoSA on the decomposition of APP is better than that of CuSAO from TG results, which is the reason that the flame retardancy of EP-APP-CoSA3 is better than that of EP-APP-CuSAO.

3.4. Fire behavior

The cone calorimeter was used to investigate the effects of APP and CoSA in various samples (EP, EP-APP and EP-APP-CoSA3) on the fire behavior of the composites. Cone calorimeter is one of the most useful bench-scale tests and provides a wealth of information to simulate real-world fire conditions [43,44]. Fire risk of materials can be investigated by cone calorimeter parameters such as time to ignition (TTI), heat release rate (HRR), total heat release (THR), smoke production rate (SPR), total smoke production (SPR), carbon monoxide (CO) production and carbon dioxide (CO₂) production.

HRR is one of the most important parameters for predictor of fire hazard [45]. Fig. 6 presents curves of heat release rate of EP, EP-APP and EP-APP-CoSA3. It can be observed that pure epoxy resin burns rapidly after ignition and HRR reaches a sharp peak with a peak heat release rate (PHRR) of 939 kW/m². It is very surprising that PHRRs of EP-APP and EP-APP-CoSA3 are reduced remarkably to 283 and 310 kW/m², respectively, with only 5 wt% of loading level. Based upon the shape of HRR curves of samples, it is indicated clearly that EP is a typical non-charring material and EP-APP and

Table 3
TG data of IFR-EPs and pure epoxy resin.

Sample	T_{onset} (°C)	T_{max1} (°C)	T_{max2} (°C)	Weight of residue (%)				
				300 °C	400 °C	500 °C	600 °C	700 °C
EP-APP	275	318	528	88.1	60.0	40.0	7.7	3.8
EP-APP-CuSAO	268	313	527	86.9	61.8	40.9	8.5	3.9
EP-APP-CoSA3	271	313	531	86.2	59.2	39.5	8.7	3.4
EP	333	413	541	97.8	72.2	19.8	1.3	0.1

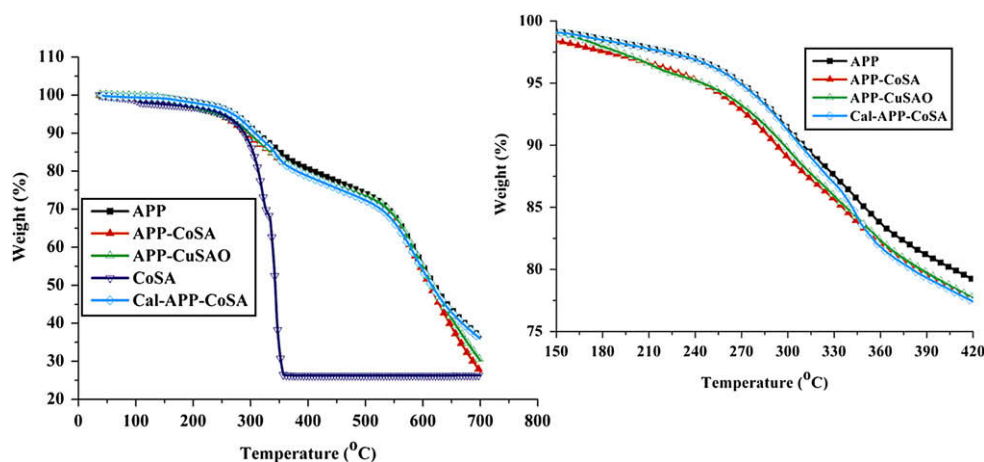


Fig. 5. TG curves of APP, the mixture of APP and metal compounds and CoSA.

EP-APP-CoSA3 are typical charring materials [43]. The results suggest that the addition of APP with/without CoSA can improve the flame retardancy of epoxy resin significantly. Fig. 7 presents curves of total heat release of the samples. It can be seen that THR values of samples containing APP with/without CoSA are lower than that of EP during testing, which is in accordance with the results of HRR.

However, HRR curves of EP-APP-CoSA3 and EP-APP are almost the same during the first 390 s, and then HRR values of EP-APP-CoSA3 are lower than that of EP-APP obviously as shown in Fig. 6. We can also observe that THR values of EP-APP-CoSA3 are almost the same as that of EP-APP during the first 450 s, but the THR values of EP-APP-CoSA3 are lower than that of EP-APP clearly after the 450th second. Thus, the fire behavior of EP-APP and EP-APP-CoSA3 can be separated into two steps. It is known that intumescent flame-retardant materials can produce gas, water and intumescent char under heat or combustion, which can protect the underlying materials [18]. For IFR-EPs with/without CoSA, the process of charring is almost the same, and this is why the HRR and THR curves of EP-APP and EP-APP-CoSA3 are almost the same at the first step. However, the quality of char formed at the first step may be different; the char of EP-APP-CoSA3 may be more compact than that of EP-APP due to the synergistic effect between CoSA and APP, which can protect underlying materials more effectively. That is the reason for the lower HRR and THR values of EP-APP-CoSA3 than that of EP-APP. Therefore, the effect of CoSA on fire behavior can be observed clearly at the second step.

Cone calorimeter parameters are summarized in Table 5. The order of time to peak HRR (TTPHRR) of samples is as follows: EP (265 s) < EP-APP (325 s) < EP-APP-CoSA (355 s), which shows the addition of APP and CoSA can delay TTPHRR. The average HRR (Av-HRR) of EP-CoSA is lower than that of EP-APP though PHRR of EP-CoSA is a little higher than that of EP-APP from Table 5, indicating that there exists the synergistic effect between APP and CoSA for flame-retardant epoxy resin.

Table 4
TG data of APP, the mixture of APP and metal compounds and CoSA.

Sample	T_{onset} (°C)	T_{max1} (°C)	T_{max2} (°C)	Weight of residue (%)		
				200 °C	420 °C	700 °C
Pure APP	269	297	589	98.1	79.2	36.4
APP-CoSA	244	292	590	97.0	77.5	27.4
APP-CuSAO	245	302	590	97.1	77.6	30.2
Pure CoSA	251	319	342	97.0	22.3	26.3
Cal-APP-CoSA	268	–	–	98.0	77.3	36.1

The smoke and toxic gases such as carbon monoxide generated during combustion are the other two most important factors concerning fire hazard. The higher smoke production is attributed to the dehydrogenation effect leading to aromatic volatiles in the flame, which results in a soot increase [46,47]. Fig. 8 presents total smoke production (TSP) of the samples. TSP values of EP-APP and EP-APP-CoSA are much lower than that of EP, which indicates the intumescent char acts as a physical barrier in preventing soot/smoke from being formed underlying materials. The TSP value of EP-APP-CoSA is lower than that of EP-APP, which shows that the physical barrier of the intumescent char of EP-APP-CoSA is more effective than that of EP-APP, suggesting that the char of EP-APP-CoSA is more compact than that of EP-APP. The results of total smoke production (TSP) are according to the results of THR and Av-HRR, which shows that there are the synergistic effects between APP and CoSA. The reduction of smoke production suggests that more carbonaceous material remains as char.

The curves of CO and CO₂ production of samples are shown in Figs. 9 and 10, respectively. Comparing CO production (COP) curves of EP-APP with that of EP-APP-CoSA3 in Fig. 9, it can be found that CoSA can reduce CO production after 360th second and that the CO productions of EP-APP and EP-APP-CoSA are lower than that of EP, indicating that addition of APP and CoSA can reduce both flammability and fire toxic gases of epoxy resin.

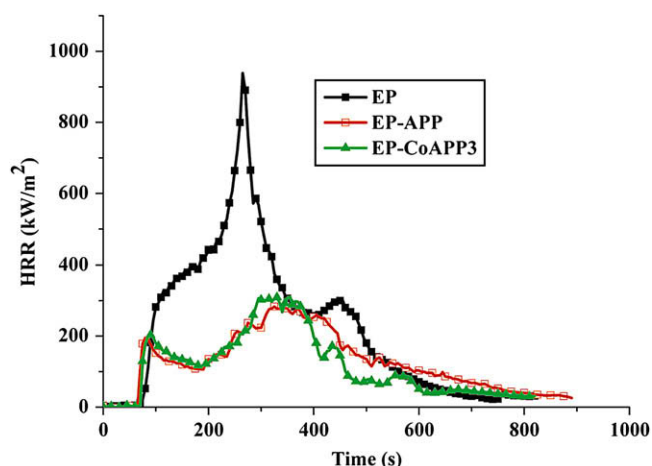


Fig. 6. Heat release rate curves of IFR-EPs and pure epoxy resin.

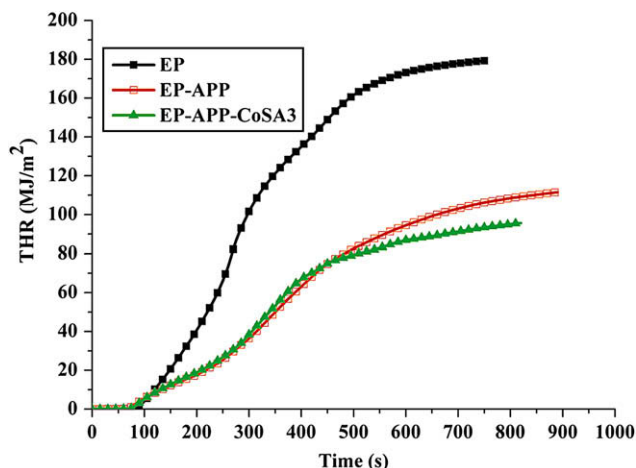


Fig. 7. Total heat release curves of IFR-EPs and pure epoxy resin.

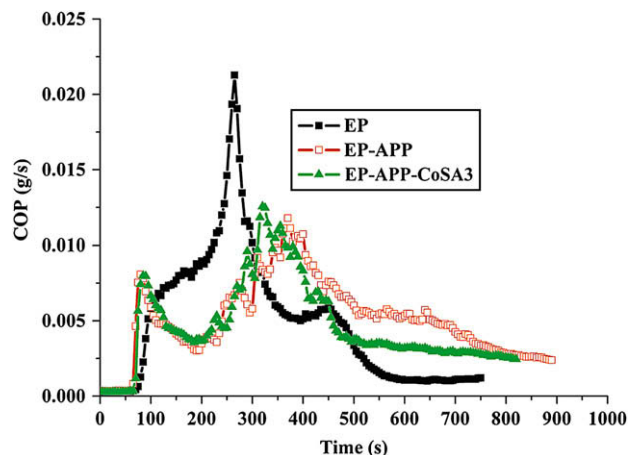


Fig. 9. CO production curves of IFR-EPs and pure epoxy resin.

Table 5

Cone calorimeter parameters of IFR-EP and pure epoxy resin.

Sample	TTI (s)	PHRR (kW/m ²)	TT-PHRR (s)	Av-HRR (kW/m ²)	THR (MJ/m ²)	Mass loss (%)	TSP (m ² /m ²)
EP	64	939	265	261	179	95.6	58.1
EP-APP	61	283	325	134	111	63.5	25.6
EP-APP-CoSA3	65	310	355	126	95	52.1	23.4

A similar conclusion can be achieved for CO₂ production (CO₂P) of samples from Fig. 10. Lower CO₂P and COP suggest that more residual mass remains during testing [48], or in other words, mass loss becomes smaller. Fig. 11 presents the curves of the ratio of CO₂P to COP of samples. The curves of ratio of the CO₂ to CO production are gotten by CO₂P/COP, which are presented in Fig. 11. It can be observed that the values of EP-APP and EP-APP-CoSA3 are significantly lower than that of EP from Fig. 11, suggesting that the more incomplete combustion of EP-APP or EP-APP-CoSA occurred than that of EP, which is the result of protecting char formed [43]. It is known that incomplete combustion leads to more CO production, which is very dangerous in fire. However, COP of EP-APP or EP-APP-CoSA3 is lower than that of EP from Fig. 9, which is also the result of protecting char formed. From Table 5, it can be seen that mass losses of EP-APP-CoSA3 (52.1%)

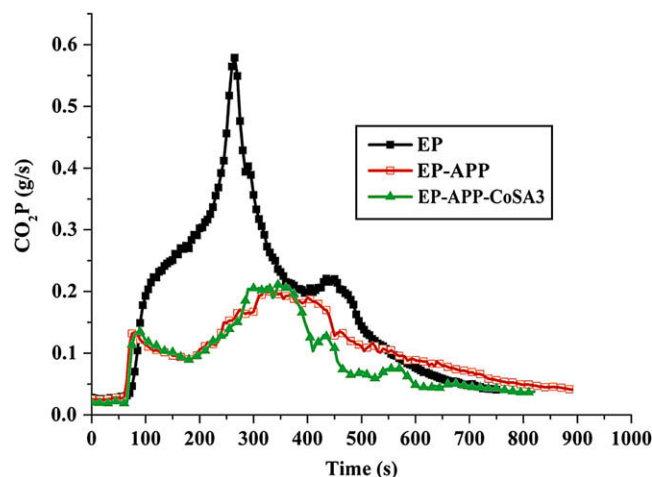


Fig. 10. CO₂ production curves of IFR-EPs and pure epoxy resin.

and EP-APP (63.5%) are much lower than that of EP (95.6%), and mass loss of EP-APP-CoSA is lower than that of EP-APP, indicating that the addition of APP and CoSA can greatly enhance the char yield of the flame-retardant epoxy resin and that CoSA has an obvious catalyzing-charring effect.

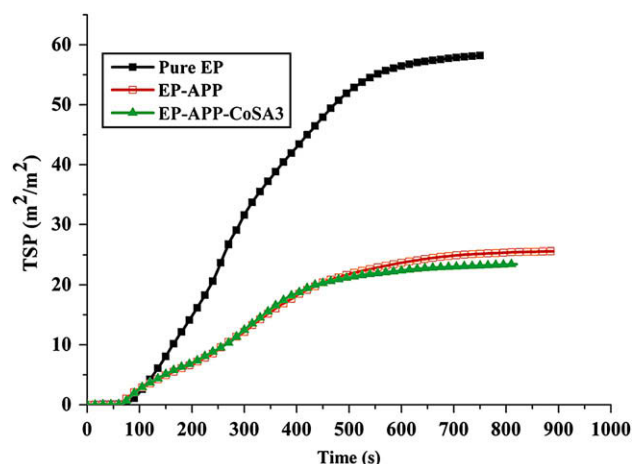


Fig. 8. Total smoke production curves of IFR-EPs and pure epoxy resin.

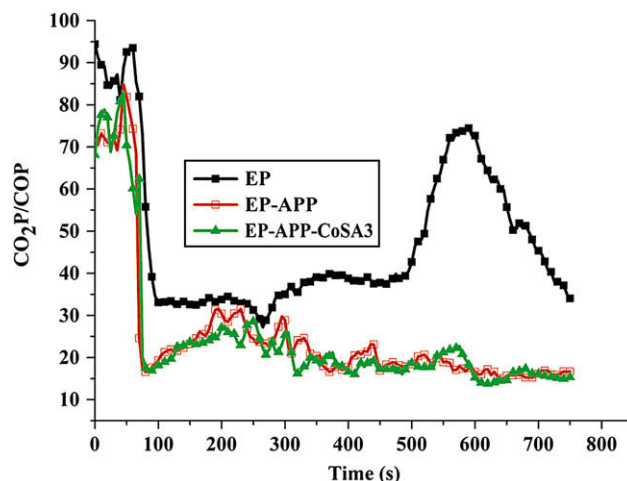


Fig. 11. CO₂ production/CO production curves of IFR-EPs and pure epoxy resin.

4. Conclusion

Flame retardancy of epoxy resin could be improved by adding APP and metal compounds. The LOI values of flame-retardant epoxy resins increase about 0–2.3 unit while total loading of APP and metal compounds is 5 wt%. The highest LOI value of all samples is 29.4 (EP–APP–CoSA3) while the mass ratio of APP to CoSA is 29:1. It can be found that there are two important factors affecting flammability of IFR-EPs from results of LOI testing: composition of metal compounds including metal elements and ligands/anions, and mass ratio of APP to metal compounds. The IFR-EP containing APP and CoSA has good water resistance after treated in both 30 °C water and 70 °C water for 168 h, and the LOI values of samples decrease slightly (about 0.4 and 0.7 units). The comparison with TG results between EP–APP and IFR-EPs indicates that addition of metal compounds can catalyze decomposition of EP containing APP to produce noncombustible volatile gas in initial stage. The TG results of APP, CoSA and mixture of APP and CoSA show that CoSA has catalytic effect both in initial decomposition stage of APP and later crosslinking of polyphosphoric acid. Thus, metal compounds can enhance flame retardancy of epoxy resin containing APP. Most of the cone calorimeter parameters of IFR-EPs with 5 wt% of total loading of APP and CoSA are improved significantly compared with those of pure epoxy resin. Those parameters such as HRR, THR, TSP, TTPHRR and mass loss of EP–APP and EP–APP–CoSA3 indicate that CoSA can enhance the flame retardancy of epoxy resins containing APP.

Acknowledgement

This work was supported by the National Science Fund for Distinguished Young Scholars (50525309).

References

- Wang DZ. Production and application of epoxy resin. 2nd ed. Beijing: Chemical Industry Press; 2001.
- Levchik SV, Weil ED. Thermal decomposition, combustion and flame-retardancy of epoxy resins – a review of the recent literature. *Polym Int* 2004;53:1901–29.
- Weil ED, Levchik SV. A review of current flame retardant systems for epoxy resins. *J Fire Sci* 2004;22:25–40.
- Lu SY, Hamerton I. Recent developments in the chemistry of halogen-free flame retardant polymers. *Prog Polym Sci* 2002;27:1661–712.
- Schafer A, Sebald S, Walter O, Doring M. Novel high T_g flame retardancy approach for epoxy resins. *Polym Degrad Stab* 2008;93:557–60.
- Liu YL. Epoxy resins from novel monomers with bis-(9,10-dihydro-9-oxa-10-oxide-10-phosphaphenanthrene-10-yl) substituent. *J Polym Sci Part A Polym Chem* 2002;40:359–68.
- Ren H, Sun JZ, Wu BJ, Zhou QY. Synthesis and properties of a phosphorus-containing flame retardant epoxy resin based on bis-phenoxy(3-hydroxy) phenyl phosphine oxide. *Polym Degrad Stab* 2007;92:956–61.
- Kumar SA, Denchev Z, Alagar M. Synthesis and thermal characterization of phosphorus containing silicized epoxy resins. *Eur Polym J* 2006;42:2419–29.
- Gao LP, Wang DY, Wang YZ, Wang JS, Yang B. A flame-retardant epoxy resin based on a reactive phosphorus-containing monomer of DODPP and its thermal and flame-retardant properties. *Polym Degrad Stab* 2008;93:1308–15.
- Levchik S, Piotrowski A, Weil ED, Yao Q. New developments in flame retardancy of epoxy resins. *Polym Degrad Stab* 2005;88:57–62.
- Lin CH, Hwang TY, Taso YR, Lin TL. Phosphorus-containing epoxy curing agents via imine linkage. *Macromol Chem Phys* 2007;208:2628–41.
- Mercado LA, Ribera G, Galia M, Cadiz V. Curing studies of epoxy resins with phosphorus-containing amines. *J Polym Sci Part A Polym Chem* 2006;44:1676–85.
- Liu YL. Flame-retardant epoxy resins from novel phosphorus-containing novolac. *Polymer* 2001;42:3445–54.
- Chen GH, Yang B, Wang YZ. A novel flame retardant of spirocyclic pentaerythritol bisphosphorate for epoxy resins. *J Appl Polym Sci* 2006;102:4978–82.
- Peerez RM, Sandler JKW, Altstadt V, Hoffmann T, Pospiech D, Ciesielski M, et al. Novel phosphorus-modified polysulfone as a combined flame retardant and toughness modifier for epoxy resins. *Polymer* 2007;48:778–90.
- Zerda AS, Lesser AJ. Orgnophosphorus additive for fortification, processibility, and flame retardance of epoxy resins. *J Appl Polym Sci* 2002;84:302–9.
- Braun U, Knoll U, Schartel B, Hoffmann T, Pospiech D, Artner J, et al. Novel phosphorus-containing poly(ether sulfone)s and their blends with an epoxy resin: thermal decomposition and fire retardancy. *Macromol Chem Phys* 2006;207:1501–14.
- Camino G, Costa L, Martinasso G. Intumescent fire-retardant systems. *Polym Degrad Stab* 1989;23:359–76.
- Horrocks AR. Developments in flame retardants for heat and fire resistant textiles – the role of char formation and intumescence. *Polym Degrad Stab* 1996;54:143–54.
- Jimenez M, Duquesne S, Bourbigot S. Intumescent fire protective coating: toward a better understanding of their mechanism of action. *Thermochim Acta* 2006;449:16–26.
- Gu JW, Zhang GC, Dong SL, Zhang QY, Kong J. Study on preparation and fire-retardant mechanism analysis of intumescent flame-retardant coatings. *Surf Coat Technol* 2007;201:7835–41.
- Jimenez M, Duquesne S, Bourbigot S. Characterization of the performance of an intumescent fire protective coating. *Surf Coat Technol* 2006;201:979–87.
- Li X, Ou YX, Shi YS. Combustion behavior and thermal degradation properties of epoxy resins with a curing agent containing a caged bicyclic phosphate. *Polym Degrad Stab* 2002;77:383–90.
- Wang JS, Wang DY, Liu Y, Ge XG, Wang YZ. Polyamide-enhanced flame retardancy of ammonium polyphosphate on epoxy resin. *J Appl Polym Sci* 2008;108:2644–53.
- Lewin M. Synergism and catalysis in flame retardancy of polymers. *Polym Adv Technol* 2001;12:215–22.
- Lewin M, Endo M. Catalysis of intumescent flame retardancy of polypropylene by metallic compounds. *Polym Adv Technol* 2003;14:3–11.
- Chen XC, Ding YP, Tang T. Synergistic effect of nickel formate on the thermal and flame-retardant properties of polypropylene. *Polym Int* 2005;54:904–8.
- Song RJ, Zhang BY, Huang BT, Tang T. Synergistic effect of nickel catalyst with intumescent flame-retardants on flame-retardancy and the thermal stability of polypropylene. *J Appl Polym Sci* 2006;102:5988–93.
- Li YT, Li B, Dai JF, Jia H, Gao SL. Synergistic effects of lanthanum oxide on a novel intumescent flame retardant polypropylene system. *Polym Degrad Stab* 2008;93:9–16.
- Xie F, Wang YZ, Yang B, Liu Y. A novel intumescent flame-retardant polyethylene system. *Macromol Mater Eng* 2006;291:247–53.
- Wang DY, Liu Y, Wang YZ, Artilles CP, Hull TR, Price D. Fire retardancy of a reactively extruded intumescent flame retardant polyethylene system enhanced by metal chelate. *Polym Degrad Stab* 2007;92:1592–8.
- Wang DY, Liu Y, Ge XG, Wang YZ, Stec A, Biswas B, et al. Effect of metal chelates on the ignition and early flaming behaviour of intumescent fire-retarded polyethylene systems. *Polym Degrad Stab* 2008;93:1024–30.
- Davies PJ, Horrocks AR, Alderson A. The sensitization of thermal decomposition of ammonium polyphosphate by selected metal ions and their potential for improved cotton fabric flame retardancy. *Polym Degrad Stab* 2005;88:114–22.
- Tian CM, Qu HQ, Wu WH, Guo HZ, Xu JZ. Metal chelates as synergistic flame retardants for flexible PVC. *J Vinyl Addit Technol* 2005;11:70–5.
- Nodera A, Kanai T. Thermal decomposition behavior and flame retardancy of polycarbonate containing organic metal salts: effect of salt composition. *J Appl Polym Sci* 2004;94:2131–9.
- Wang DL, Liu Y, Wang DY, Zhao CX, Mou YR, Wang YZ. A novel intumescent flame-retardant system containing metal chelates for polyvinyl alcohol. *Polym Degrad Stab* 2007;92:1555–64.
- Levchik SV, Levchik GF, Camino G, Costa L, Lesnikovich AI. Mechanism of action of phosphorus-based flame retardants in nylon 6. III. Ammonium polyphosphate/manganese dioxide. *Fire Mater* 1996;20:183–90.
- Biswas B, Kandola BK, Horrocks AR, Price D. A quantitative study of carbon monoxide and carbon dioxide evolution during thermal degradation of flame retarded epoxy resin. *Polym Degrad Stab* 2007;92:765–76.
- Chen WY, Wang YZ, Chung FC. Thermal and flame retardation properties of melamine phosphate-modified epoxy resins. *J Polym Res* 2004;11:109–17.
- Cao HM. Handbook of inorganic compounds. 1st ed. Beijing: Chemical Industry Press; 1988.
- Wang Q, Chen YH, Liu Y, Yin H, Aelmans N, Kierkels R. Performance of an intumescent-flame-retardant master batch synthesized by twin-screw reactive extrusion: effect of the polypropylene carrier resin. *Polym Int* 2004;53:439–48.
- Hirschler MM. Thermal analysis and flammability of polymer. Effect of halogen-metal additive systems. *Eur Polym J* 1983;19:121–9.
- Schartel B, Hull TR. Development of fire-retarded materials – interpretation of cone calorimeter data. *Fire Mater* 2007;31:327–54.
- Morgan AB, Bundy M. Cone calorimeter analysis of UL-94 V-rated plastics. *Fire Mater* 2007;31:257–83.
- Babrauskas V, Peacock RD. Heat release rate: the single most important variable in fire hazard. *Fire Safety J* 1992;18:255–72.
- Wu Q, Zhang C, Liang R, Wang B. Fire retardancy of a buckypaper membrane. *Carbon* 2008;46:1164–5.
- Fina A, Abbenhuis HCL, Tabuani D, Camino G. Metal functionalized POSS as fire retardants in polypropylene. *Polym Degrad Stab* 2006;91:2275–81.
- Siat C, Bras ML, Bourbigot S. Combustion behaviour of ethylene vinyl acetate copolymer-based intumescent formulations using oxygen consumption calorimetry. *Fire Mater* 1998;22:119–28.