

Flame retardance of UV cured epoxy acrylate blended with different states of phosphated methacrylate

Shengwu Zhu, Wenfang Shi*

*State Key Laboratory of Fire Science and Department of Polymer Science and Engineering,
University of Science and Technology of China, Hefei, Anhui, 230026, PR China*

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Abstract

Methacrylated phosphate (MAP) and pulverized, UV-cured MAP were used as reactive and additive-type flame retardants in an epoxy acrylate prepolymer, EB600, to compare the difference of their flame retardance. The results from cone calorimetry show that the sample with the cured MAP as an additive-type flame retardant has higher flame retardance than that with MAP as a reactive-type flame retardant. The thermal degradation of UV cured MAP film was investigated with in situ Fourier transform infrared (FTIR). The phosphate unit in MAP degraded completely at 200–270 °C. The degraded products further react with aromatic polynuclear hydrocarbons formed above 270 °C to yield phosphorus–carbon complexes. To study the contributions of these phosphorus-containing complexes at different degradation stages to the flame retardance, the flammability of EB600 blended with MAP pre-treated at 270 and 400 °C, and EB600 blended with MAP without pre-treatment were compared. The results show that the flame retardance of MAP is mainly contributed by the phosphorus-containing degradation products formed at 270 °C.

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1. Introduction

With the increasingly stringent requirements on the fire safety of materials, searching for new flame retardant polymers and studying their flame retardant mechanisms has attracted much research activity. Besides inorganic flame retardants and halogen-containing flame retardants, phosphorus-containing compounds are another family of materials that can provide fire protection for flammable materials. In addition, they release less toxic gases and smoke during combustion compared with halogen-containing flame retardants. During combustion, they form expanding charred crusts on the surface of substrates, which have low thermal conductivity [1] and attenuate the transference of the heat.

UV curing technology is developing fast and being widely used in many fields. However, only a little work has been reported to prepare flame retardant resins used as 1UV curable compositions, such as those used in

wood [2] and optic fiber coatings [3]. A new kind of UV curable methacrylated phosphate (MAP) was synthesized in our laboratory [4]. This compound cured quickly under irradiation by UV light. The formed film has a limiting oxygen index of 26.8 and a char yield as high as 61.5 wt.% obtained from thermogravimetric analysis (TGA).

The traditional technique to prepare flame retardant materials is to blend additive-type flame retardants with matrices. However, the addition of a mass of flame retardant additives will adversely affect their mechanical properties. Moreover, a small quantity of flame retardants may be leached out or otherwise lost from the materials during using and aging, thus leading to the decrease of the flame retardant ability [5–10]. When used in coatings, phase separation often takes place, which will cause cracks on the film surface [7]. Therefore, reactive-type flame retardants have received increasing attention to resolve these problems. Price and coworkers have compared the flammability of poly(methyl methacrylate) (PMMA) with phosphorus-containing additives physically incorporated and PMMA copolymerized with phosphorus-containing monomers

* Corresponding author. Fax: +86-551-360-6084.
E-mail address: wfshi@ustc.edu.cn (W. Shi).

[11]. The copolymerized PMMA improved flame retardance much more significantly than the PMMA with phosphorus-containing additives incorporated. However, they compared the effects of these two types of flame retardants with different compositions. To compare the effects of reactive and additive flame retardants with the same molecular structure, MAP and the pulverized UV cured MAP were chosen as reactive and additive flame retardants used in epoxy acrylate, respectively, in this work.

The phosphate in UV cured MAP decomposed quickly at high temperature, then the degraded phosphorus-containing moieties form phosphorus-carbon complexes by grafting on, or linking different aromatic polynuclear hydrocarbons [12]. To learn the contributions of these phosphorus-containing moieties in different degradation stages to the flame retardance, the UV cured MAP films were pre-degraded at 270 and 400 °C before being blended into the epoxy acrylate, and the resins were then UV cured. The flammability of the resulting composites were tested by cone calorimetry and TGA as compared with the UV cured epoxy acrylate blended with MAP without pre-degradation.

2. Experimental

2.1. Materials

MAP was synthesized by the reaction of diethylphosphoric acid with glycidyl methacrylate, and the experimental detail was reported elsewhere [4]. The schematic outline of the synthesis is shown in Fig. 1. 1-Hydroxycyclohexylphenylketone (Irgacure 184), kindly supplied as a gratis sample by Ciba Specialty Chemicals, Switzerland, was used as the photoinitiator. EB600, with a molar mass of 500 g mol⁻¹, was supplied by UCB Co., Belgium.

2.2. Sample preparation

A mixture of 6.0 g MAP, 34.0 g EB600 and 1.3 g Irgacure 184 was heated at 60 °C and stirred for 20 min, then poured into a cell with dimensions 100×100×3 mm. The sample was UV cured with a UV lamp (1 kW, made by Lantian Co., Beijing) in air. The specimen obtained was denoted as MAP-r.

The pure MAP was UV cured in the presence of 3 wt% Irgacure 184 and then ground to powder. Six grams were used to replace the MAP in MAP-r, and the specimen was prepared as above and denoted as MAP-a.

Another two 6.0 g samples of UV cured MAP were heated at 270 and 400 °C respectively for 20 min. The residues were ground to powder and used to replace the MAP in MAP-r, giving two specimens denoted as MAP-270 and MAP-400, respectively.

2.3. Measurements

2.3.1. Cone calorimetry

A cone calorimeter (Stanton Redcroft type, UK) was used to measure the combustion characteristics under a heat flux of 25 kW m⁻² according to ASTM E-1356-90. The experimental error of cone calorimeter data from the instrument is about 5%.

2.3.2. TGA

TGA was carried out on a Shimadzu TG-50 using a heating rate of 10 K min⁻¹ in air.

2.3.3. FTIR

The in situ FTIR spectra were recorded with a Nicolet MAGNA-IR 750 spectrometer using the KBr disk method in the range of 200–320 °C with an interval of 10 °C and a heating rate of 2 °C min⁻¹.

3. Results and discussion

3.1. Comparison of the flame retardance of reactive-type and additive-type MAP in EB600 resins

The flammability of the EB600 resin copolymerized with MAP and that blended with pre-cured MAP was

Table 1
Data from the cone calorimetric measurements

| | MAP-r | MAP-a | MAP-270 | MAP-400 | EB600 |
|--|-------|-------|---------|---------|-------|
| Time to ignition (s) | 175 | 142 | 274 | 240 | 260 |
| Peak HRR (kW m ⁻²) | 508 | 443 | 313 | 621 | 916 |
| Average HRR (kW m ⁻²) | 358 | 265 | 190 | 373 | 597 |
| Average SEA (m ² kg ⁻¹) | 438 | 420 | 313 | 461 | 421 |
| Residue (%) | 30.7 | 22.7 | 32.5 | 28.7 | 14.3 |

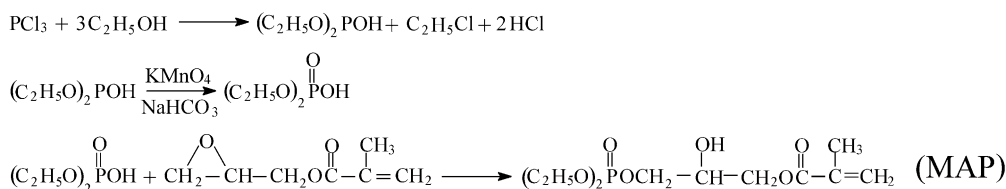


Fig. 1. Schematic outline of the synthesis of MAP.

assessed by cone calorimetry, and the results are given in Table 1 and shown in Figs. 2–4.

The MAP added in either way can effectively lower the flammability of EB600 resin.

The peak and average heat release rates (HRR) decreased to nearly half compared with bulk EB600. However, the time to ignition decreased from 260 s for EB600 to 175 and 142 s for MAP-r and MAP-a, respectively. This is because the phosphate units of MAP begin to degrade at lower temperature than EB600. These degraded phosphate groups have a major contribution to formation of compact chars for protecting the resin from further degradation. As a result, the peak and average HRRs decreased greatly compared with that of EB600, more residues remaining after combustion.

There is only a small difference between MAP-r and MAP-a. The former has a little higher peak and average HRRs than the latter. The possible reason is suggested as follows. The polymer chain of MAP-r is composed of MAP and epoxy acrylate segments, alternately, and the former begins to degrade at lower temperature than the latter. If the temperature rises high enough to make the MAP units degrade, the polymer chain will be cut to short segments. In contrast, MAP-a is composed of MAP chains and epoxy acrylate chains, separately. The degradation of MAP units will not promote the degradation of polymer chains of epoxy acrylate. As a result, the MAP-r degrades faster than MAP-a at the same heat flux, making the HRR higher and the burning time shorter. As the phosphorus-containing units in MAP-r distribute more homogeneously in the material than those in MAP-a, they can more effectively form non-flammable phosphorus–carbon complexes. The amount of residue of MAP-r after combustion is more than that of MAP-a. The mass loss in Fig. 3 and the TGA in Fig. 5 show the same trend. The MAP-r degraded faster than MAP-a at the beginning of combustion or thermal degradation, then slowed and more residues remained at the end.

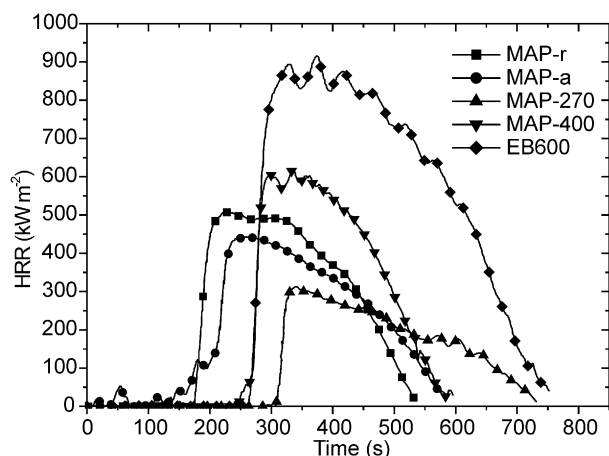


Fig. 2. HRRs of the different UV cured samples.

Both MAP-r and MAP-a have similar smoke extinction area (SEA) shown in Fig. 4. However, the peak values are a little higher than that of EB600.

3.2. Contribution of phosphorus-containing degradation products in different thermal degradation stages to flame retardance

The FTIR spectra of the UV cured MAP at the temperatures of 200–320 °C with an interval of 10 °C are shown in Fig. 6. The peaks at 1262 and 1038 cm^{-1} can be assigned to the stretching vibration of P=O bond [13] and the stretching vibration of P–O–C bond [14], respectively. The intensity of the P–O–C peak decreased quickly between 200 and 220 °C. Only 21.6% of the absorbance remained, which implies that most P–O–C bonds decomposed below 220 °C. It disappeared completely when the temperature was raised to 270 °C. The absorbance for P=O vibration at 1262 cm^{-1} decreased at temperatures above 280 °C. On the other hand, two new peaks at 1274 and 1300 cm^{-1} appeared. They can be assigned to C–O stretching vibration [15,16] and

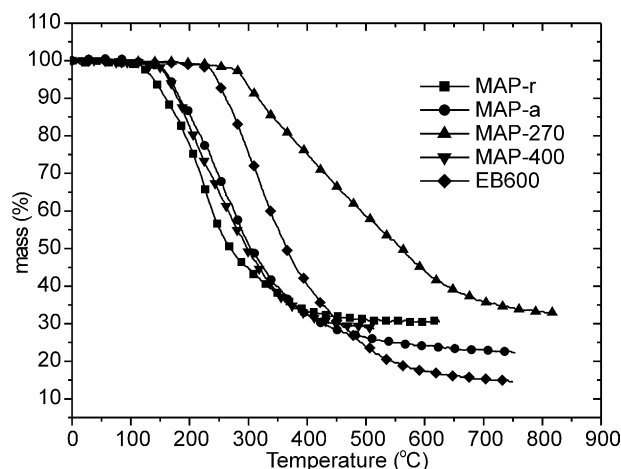


Fig. 3. Mass loss of the different UV cured samples.

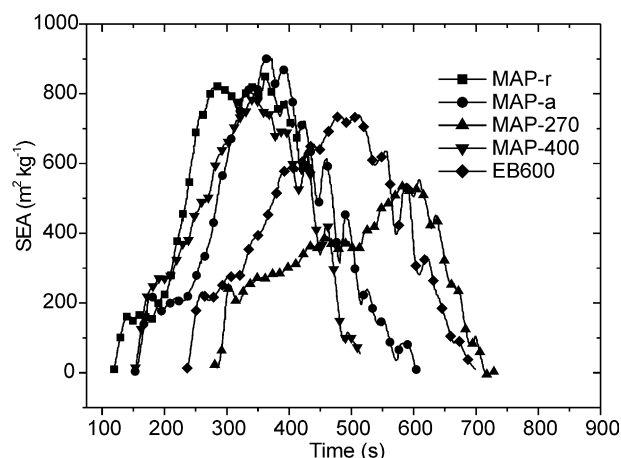


Fig. 4. SEAs of the different UV cured samples.

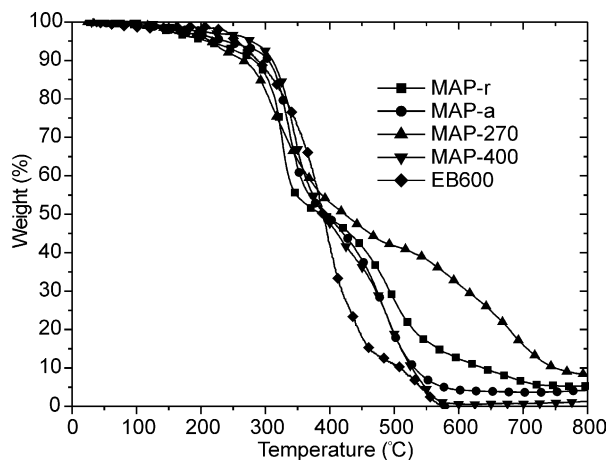


Fig. 5. TGA thermograms of the different UV cured samples.

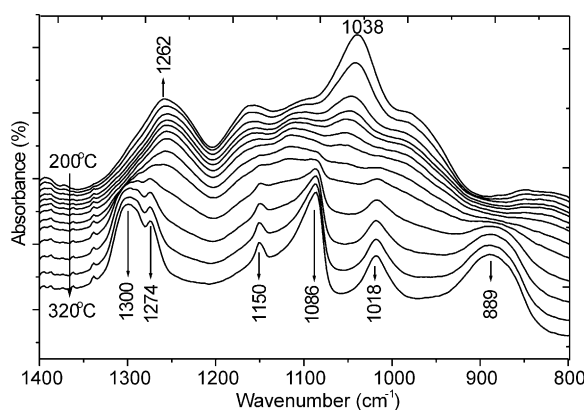


Fig. 6. FTIR spectra of UV cured MAP at the temperatures of 200–270 °C with an interval of 10 °C.

P=O [17] vibration for P–O– Φ structure, where Φ represents an aromatic group and its formation has been verified in our previous work [12]. This implies that the phosphate group dissociates from the aliphatic structure and re-links to the aromatic structure at temperatures above 270 °C. Moreover, all phosphate groups or their derivatives link to aromatic structures up to 320 °C. Another four new peaks at 1150, 1086, 1018 and 889 cm^{-1} appeared when raising the temperature over 27 °C. The peaks at 1150 and 1018 cm^{-1} can be assigned to the stretching vibration of P–O–C and PO_2/PO_3 in phosphate–carbon complexes, respectively [18]. The peaks at 1086 and 889 cm^{-1} can be assigned to the symmetric and asymmetric stretching vibrations of P–O–P bonds [19,20], respectively. This indicates that some phosphate groups link to each other by sharing one oxygen atom. Therefore, the P–O–P group can be considered as a crosslinker linking to different aromatic species, resulting in the formation of phosphorus–carbon complexes.

From the changes of FTIR spectra, it can be seen that the phosphorus is present in different form with the degradation of the material. The critical temperature at which all the P–O–C groups have degraded and remain

in the material as other kinds of phosphorus-containing compounds is 270 °C. At temperatures above 270 °C, these phosphorus-containing compounds further reacted with aromatic polynuclear hydrocarbons to form phosphorus–carbon complexes. MAP-a contains the phosphorus moieties in the form of P–O–C while MAP-270 and MAP-400 contain the phosphorus moieties as degradation products of MAP at 270 and 400 °C, respectively. Comparing the flammability of these three products can show the contribution of the phosphorus in different degradation stages to the flame retardance.

As shown in Fig. 2, MAP-a ignited in the shortest time and the peak and average HRRs are much lower than those of EB600. MAP-270 has the longest time to ignite and the HRRs are lower than those of MAP-a. MAP-400 has the similar time to ignite as EB600 and the HRRs are higher than those of MAP-a. These results show that the degradation products of UV cured MAP at 270 °C have the biggest contribution to flame retardance. The aliphatic phosphate structures have degraded at this temperature, phosphorus remaining in the material in other forms. They are more stable than UV-cured MAP, and will not release organic compounds such as ethene, a possible degradation product of ethyl phosphate [10], to support fire. As a result, MAP-270 has a longer time to ignite and lower HRRs than MAP-a. After ignition, the degradation products of UV cured MAP at 270 °C can react with EB600 and its derivatives to form stable phosphorus–carbon complexes to protect the material from fire. MAP-400 contains the degradation products of UV cured MAP at 400 °C. The phosphorus–carbon complexes have formed before preparing the MAP-400 sample. These complexes are stable and hard to react with EB600 and its derivatives, resulting in a low contribution to flame retardance.

From the mass loss tested by cone calorimeter and the thermal degradation test by TGA, it also can be seen that MAP-270 degraded slowly and has the biggest char yield after combustion or thermal degradation. This result is consistent with that of HRR.

The SEA of MAP-270 is also the smallest among the samples, as shown in Fig. 4. This may be because that more aromatic compounds which have high SEA remain in the residue by reacting with phosphorus-containing compounds.

4. Conclusions

The results indicate that the MAP incorporated in EB600, both in additive-type and reactive-type way, can improve the flame retardance of the final products. The sample with additive-type MAP has smaller fire intensity than that with reactive-type MAP because the degradation of MAP will not promote the degradation of EB600 polymer chains.

Phosphorus is present in the material in different forms during combustion. The phosphate groups in MAP degraded quickly at 200–270 °C. The degraded phosphorus-containing compounds further react with aromatic polynuclear hydrocarbons formed above 270 °C to give phosphorus–carbon complexes. The UV cured films of EB600 blended with MAP in different forms were compared to study the contribution of phosphorus in different degradation stages to flame retardance. The results show that the flame retardance of MAP is mainly contributed by the degradation products at 270 °C. However, the detailed structures of these degradation products are still unknown, and will be further studied.

Acknowledgements

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