

Flammability and Thermal Degradation of Epoxy Acrylate Modified with Phosphorus-Containing Compounds

Xilei Chen, Lei Song, Yuan Hu

State Key Lab of Fire Science, University of Science and Technology of China, Anhui 230026, People's Republic of China

Received 4 August 2008; accepted 25 March 2009

DOI 10.1002/app.30477

Published online 4 November 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of UV-curable flame-retardant resins was obtained by blending phosphate acrylate (BTP) in different ratios with epoxy acrylate resin (EA). The flammability was characterized by limiting oxygen index (LOI), UL 94 flammability rating and cone calorimeter, and the thermal degradation of the flame-retardant resins was studied using thermo gravimetric analysis (TGA), and real-time Fourier transform infrared (RTFTIR). The results indicated that the flame-retardant efficiency increases with the addition of BTP. The heat release rate with the addition of BTP decreases

greatly. The TGA data showed that EA/BTP blends have lower initial decomposition temperatures and higher char residues than pure EA, whereas BTP has the lowest initial decomposition temperature and the highest char residue. The RTFTIR study indicates that the EA/BTP blends have lower thermal oxidative stability than the pure EA. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3332–3338, 2010

Key words: phosphorus; flame retardant; thermal degradation; UV curing

INTRODUCTION

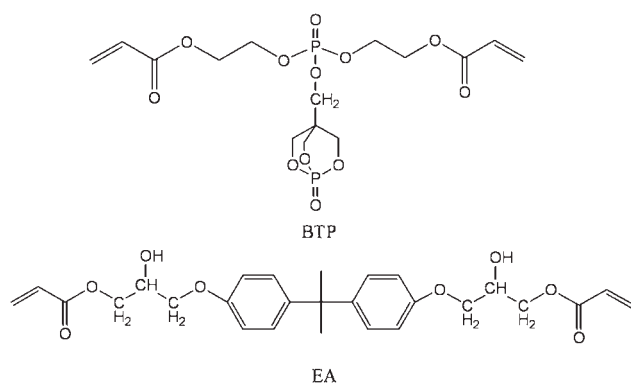
UV-curable coating applications have gained wide interests, because of their advantages such as lower energy consumption, less environmental pollution, lower process costs, high-chemical stability, and very rapid curing even at ambient temperatures.^{1–3} UV-curable coatings are continually being developed by many leading suppliers in an effort to reduce any detrimental effects to the environment and to meet high standards required by industry.⁴ Especially, in the field of UV curing industries, epoxy and epoxy acrylate derivatives have been widely used as coatings, structural adhesives, and advanced composite matrices.⁵ What distinguish epoxy acrylate resin from the other polymers are their excellent chemical and solvent resistance, good adhesion properties, and versatility in crosslinking. Therefore, UV-curable epoxy acrylate coatings are widely used for protective purposes. However, it is known that epoxy acrylate is highly combustible, and flame retardation is needed. Furthermore, few works has been reported to prepare flame-retardant epoxy acrylate resins used as UV-curable compositions, such as those used in wood⁶ and optic fiber coatings.⁷

With the increasing requirements on the fire safety of materials, searching for new flame-retardant epoxy acrylate resins and studying their flame-retardant mechanisms has attracted much attention. 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 conductivity⁸ and attenuate the transference of the heat. 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.^{9–14} When used in coatings, phase separation often takes place, which will cause cracks on the film surface.¹¹ Therefore, reactive-type flame retardants have received increasing attention to resolve these problems.

In this article, a new kind of UV flame-retardant curable acrylated phosphate (BTP) (Scheme 1) was blended with epoxy acrylate resin in different ratios to obtain a series of UV-curable flame-retardant resins. The flammability of the blends was tested using LOI, UL 94 flammability rating, and cone calorimeter.

Correspondence to: Y. Hu (yuanhu@ustc.edu.cn).

Contract grant sponsor: National Project of Scientific and Technical Supporting Programs, Ministry of Science & Technology of China; contract grant numbers: 2006BAK06B06, 2006BAK06B07, 2006BAK01B03.



Scheme 1 Molecular formula of BTP.

The thermal degradation behaviors of the cured films were studied using TGA and RTFTIR measurements.

EXPERIMENTAL

Materials

Epoxy acrylate (EA) was supplied by Tianjin Tianjiao Co., China. BTP was synthesized in our laboratory.¹⁵ Scheme 1 presents their chemical structures. 2-Hydroxy-2-methyl-1-phenyl-1-propanone (Darocur 1173), supplied as a gratis sample by Ciba-Geigy, Switzerland, was used as a photoinitiator.

Sample preparation

The ultraviolet light source used for irradiation is a lamp (80 mW/cm², Lantian Tedeng Cor., China), which emits light in the near UV (characteristic wavelength, 340–360 nm). The mixtures of EA with BTP in different ratios were stirred at 60°C for 20 min to get various homogenous blends. EA, BTP, and their blends were cured with UV in the presence of 2 wt % Darocur 1173. The formulations of blends are listed in Table I. The distance between samples and UV lamp was about 10 cm.

Measurements

Determination of conversion of unsaturated bond by FTIR

FTIR spectroscopy (EQUINOX55, Bruker Co. German) was used to determine relative conversion percentage (CP) of unsaturated bond during UV curing progress. The original resin and photoinitiator mixture (liquid) was spreading on the KBr plates and cured under UV irradiation directly. The relative CP of unsaturated bond in the UV-cured films was determined by using stretching vibration of the acrylate carbon-carbon double bond at 1635 cm⁻¹.¹⁶ The spectra were normalized with the carbonyl peak at 1723 cm⁻¹ as an internal standard to account for

variations in sample thickness and instrument recording.¹⁷ The unsaturated bond content (A_0) of the uncured sample added with photoinitiator was defined as 100%. If the sample was irradiated with t time, the unsaturated bond content would be defined as A_t , the CP of unsaturated bond could be calculated as follows:

$$\text{CP (\%)} = \left(\frac{A_0 - A_t}{A_0} \right) \times 100$$

Flame retardance

LOI was measured according to ASTM D 2863. The apparatus used was an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China). The specimens used for the test were of dimensions 100 × 6.5 × 3 mm³.

The vertical test was carried out on a CFZ-2-type instrument (Jiangning Analysis Instrument Company, China) according to the UL 94 flammability rating test standard. The specimens used were of dimensions 130 × 13 × 3 mm³.

The cone calorimeter (Stanton Redcroft, UK) tests were performed according to ISO 5660 standard procedures. Each specimen of dimensions 100 × 100 × 3 mm³ was wrapped in aluminium foil and exposed horizontally to an external heat flux of 35 kW/m².

Thermo gravimetric analysis

Thermo gravimetric analysis (TGA) was carried out in air on a STA 409C TGA apparatus (Netzsch Company, German) with crucible sample holders, at a heating rate of 10°C/min.

Real-time Fourier transform infrared spectra

Real-time fourier transform infrared (RTFTIR) spectra were recorded using a Nicolet MAGNA-IR 750 spectrophotometer equipped with a ventilated oven having a heating device. Powders of EA, BTP, or EA/BTP blends were mixed with KBr powders, and the mixture was pressed into a tablet, which was then placed into the oven. The temperature of the oven was raised at a heating rate of 10 °C/min.

TABLE I
Formulations of Flame Retardant EA resins

Formula	EA/g	BTP/g	P/%	LOI	UL 94 flammability rating
EA0	4.0	0	0	18	No rating
EA1	3.0	1.0	3.4	26.5	No rating
EA2	2.0	2.0	6.8	29.5	V0
EA3	0	4.0	13.6	39	V0

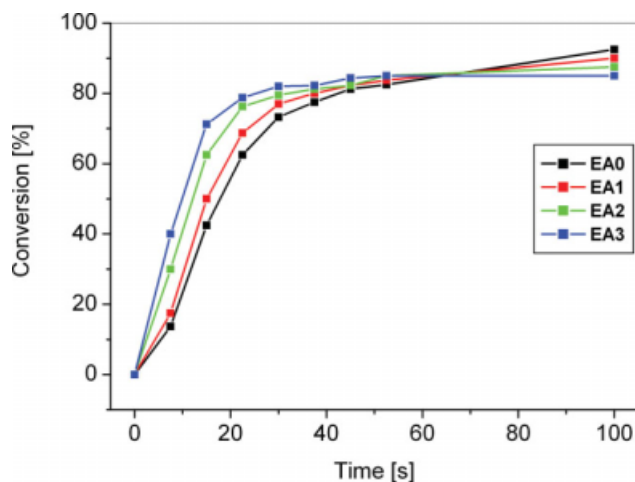


Figure 1 Unsaturation conversion versus the irradiation time of the resins. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSION

UV curing behaviors of flame-retardant EA

The properties of a UV-cured film, which are very important to its applications, depend not only on the resin's composition but also on its photopolymerization kinetics. The most important parameters characterizing the curing kinetics of a resin are the rate at the peak maximum (R_p max) and the final degree of double bond conversion (C_p). Figure 1 shows the unsaturation conversions of resins obtained from FTIR spectroscopy.

As shown in Figure 1, the unsaturation conversion over 80% was obtained after a longer irradiation time for four resins. Their curves of C_p versus irradiation time illustrates that the more BTP content, the less is the unsaturation conversion. For the EA3 resin, the conversion is much higher than others before 60-s irradiation time because it has higher concentration of acrylic end groups. As a result, the curing reaction may result in low-unsaturation conversion. It is noticeable that for the resin EA0, the final unsaturation conversion becomes the highest after 100-s irradiation time. This can be interpreted that the network with lower crosslink density can easily release the polymeric radicals for further photopolymerization.¹⁸

LOI and UL 94 flammability rating

LOI, which is as a qualitative method to rank the flammability of materials, is the minimum oxygen concentration in an oxygen/nitrogen mixture that will just support the combustion. Table I presents the LOI values and UL 94 flammability ratings of the flame-retardant EA systems. It can be seen that

the LOI values of the blends increases as the BTP content increases. The LOI value of the flame-retardant EA containing 25% BTP is as high as 26.5, which is much higher than that of the pure EA. However, it does not pass the UL 94 flammability rating test. It is worthwhile to figure out that when 50% of BTP was blended into EA, the LOI rapidly increased to 29.5; furthermore, the resin passes UL 94 flammability rating test. Above results illustrate that BTP used alone in EA does have good flame retardancy.

Cone calorimeter study

Although the LOI and UL 94 flammability rating tests are widely used to evaluate the flame retardation of materials, especially for screening flame-retarded formulations of polymers, the cone calorimeter provides a wealth of information on the combustion behavior.¹⁹ Some cone calorimeter results have been found to correlate well with those obtained from large-scale fire tests and can be used to predict the behavior of materials in real fires.²⁰ For example, the peak heat release rate (PHRR) is an important parameter, which can be used to evaluate the intensity of fires.²¹

Figure 2 shows the HRR curves of the cured EA/BTP films with different BTP contents obtained from the cone calorimeter test. It can be seen that the pure EA resin burns very fast after ignition and a sharp HRR peak appears with a peak rate of heat release (PHRR) of 627 kW/m². In the case of the cured EA/BTP films, their PHRR values are greatly reduced and decrease with increasing the BTP content, as shown in Figure 2. Moreover, the combustion of the cured EA/BTP films is prolonged in comparison with that of EA. It is, however, noted that the ignition time (IT) of the EA/BTP films is lower than that

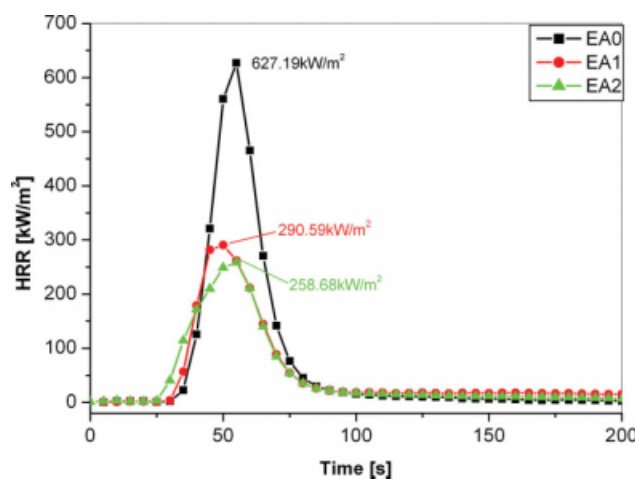


Figure 2 HRR vs. time curve for BTP series under a heat flux of 35 kW/m². [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of EA. The reason is due to the fact that BTP decomposes earlier than EA itself, and some small volatile molecules are produced from the decomposition of BTP.²²

From Figure 3, we can investigate that the EA0 has no char residue, and the char residue mass of EA1 and EA2 is higher than that of EA0. The more the amount of char residue, the more is the HRR decrease. The mechanism of this fire retardant is as follows: the char acts as a physical barrier against heat transmission and oxygen diffusion, thus preventing pyrolysis of the material to volatile combustible products.^{23,24}

Thermo gravimetric analysis

The thermal stability of a polymeric material is very important when used as a flame retardant, which mainly concerns the release of decomposition products and the formation of a char.

Figure 4 shows the TGA curves of the blends of EA and BTP. It is clearly seen that all flame-retardant EA systems decompose early in comparison with pure EA. However, at a temperature higher than 450°C, the flame-retardant EA has more thermally stable than EA. For example, EA almost decomposes completely at 650°C, whereas the undecomposed parts at the same temperature for EA1 and EA2 are 30.6% and 40.3%, respectively.

The above phenomena can be explained as follows. The reduction of initial decomposition temperature is attributed to the fact that P—O—C is less stable than common C—C bond.²² The degraded phosphate group makes a big contribution to the formation of the compact char, which protects the sample from further degradation. As a result, the resin with high-phosphorus content is more stable at high

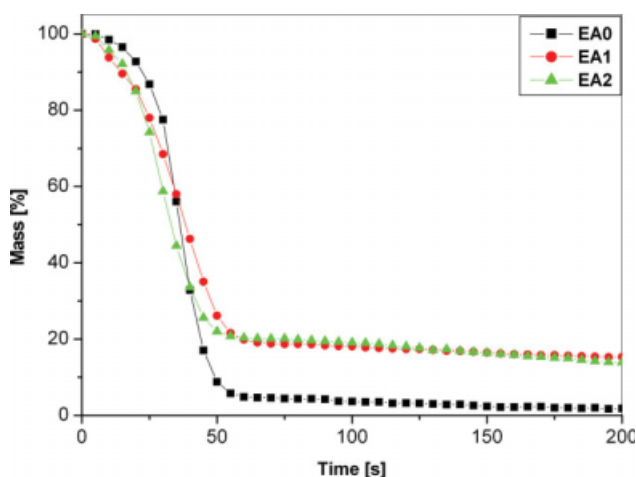


Figure 3 Mass loss vs. time curve for BTP series under a heat flux of 35 kW/m². [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

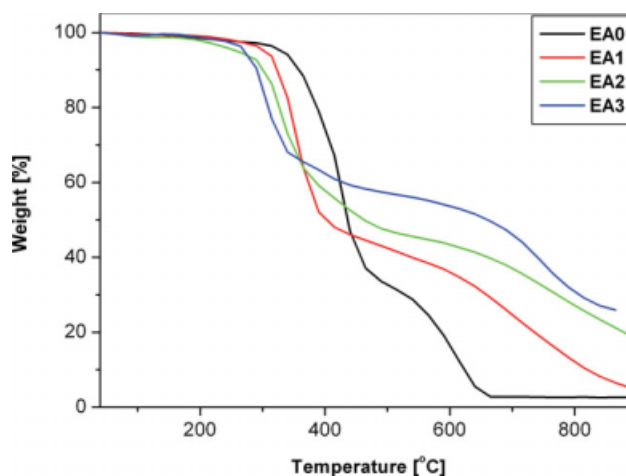


Figure 4 TGA curves of the UV-cured EA/BTP films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

temperature and yields more char at last. Furthermore, the big rigid PEPA group in BTP molecule also plays a crucial role in improving the char yield.

To further investigate the effect of BTP in EA/BTP blends on the formation of charred crust, the differential weight loss (DTG) of flame-retardant EA systems were given in Figure 5. It can be seen that the temperature of the maximum loss rate decreases with the addition of BTP. This can be illustrated as earlier.

The experimental and calculated TGA curves of EA2 are shown in Figure 6. The calculated curve is a linear combination of the TGA curves of the individual components of the mixture; therefore it is representative of a noninteracting behavior. The EA2 (the experimental curve) actually decomposes earlier and produces more residue than that calculated. This result shows that there is an interaction between EA

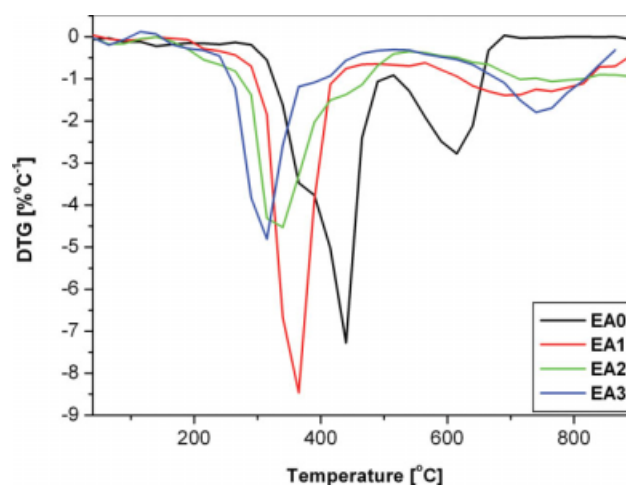


Figure 5 DTG curves of the UV-cured EA/BTP films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

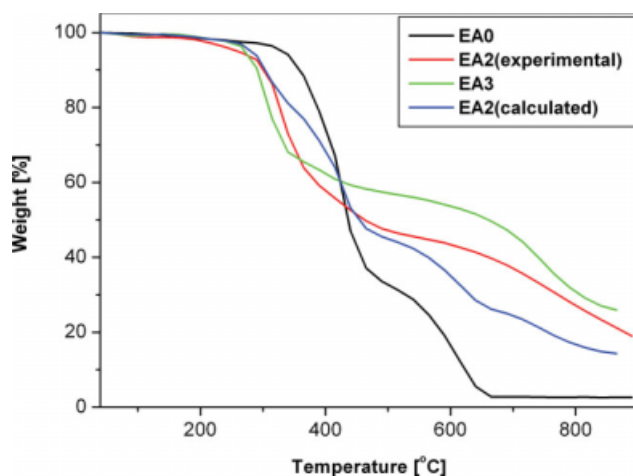


Figure 6 TGA curves of the UV-cured EA0, EA2, and EA3 films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and BTP on pyrolysis. The chemical structural changes of EA, BTP, and their blends during the thermodegradation are demonstrated by the following real-time FTIR measurements.

Thermal oxidative degradation

The thermal oxidative degradation (TOD) of EA, BTP, and EA2 films were monitored by RTFTIR. Figures 7–9 show the changes in the dynamic FTIR spectra obtained from EA, BTP, and EA2 at different pyrolysis temperatures.

The changes in C–H absorption intensities of aliphatic groups in the 2500–3200 cm^{-1} region are generally used to evaluate the thermal stability of polyolefins during the TOD study.²⁵ Figure 7 shows the real-time FTIR spectra of the degradation process of EA. The sample gave little changes in the FTIR spectra before being heated to 320°C. This result is in accord with the fact that there was no notable weight

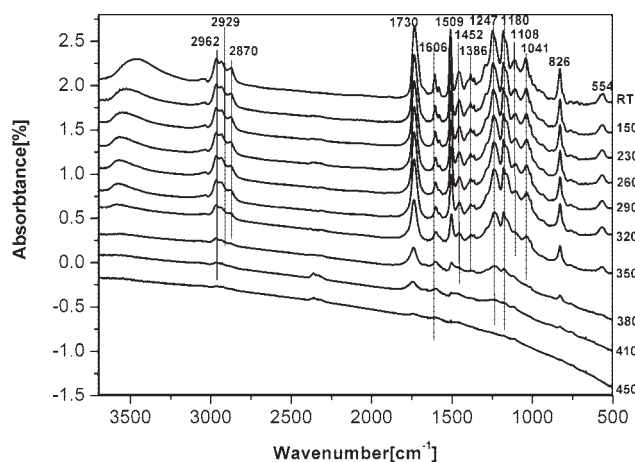


Figure 7 Dynamic FTIR spectra of EA0.

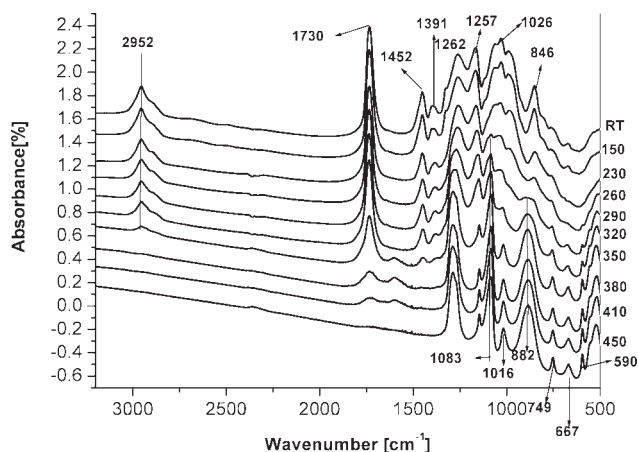


Figure 8 Dynamic FTIR spectra of EA3(BTP).¹⁵

loss in the TG investigation before 320°C. The absorption at 1180 cm^{-1} and 1247 cm^{-1} for ester group is still rather strong at 350°C. With the further increase in pyrolysis temperature, the relative intensity of the absorption peaks continues to decrease. At 450°C, all peaks nearly disappear, meaning that EA decomposes completely. No new absorption bands were found during the thermal degradation process.

To explain the changes in absorption bands of the flame-retardant EA during the heating, it is worthwhile to understand the absorptions from BTP during the degradation process. Figure 8 shows the real-time FTIR spectra of BTP (EA3).¹⁵

As seen in Figure 8, the quick decrease in relative intensities at 1026 cm^{-1} and 980 cm^{-1} at above 150°C and then the complete disappearance at above 260°C clearly indicate the complete degradation of P–O–C functionality. Furthermore, the peaks at 1083 cm^{-1} and 1016 cm^{-1} assigned to the stretching vibration of P–O–P and PO_2/PO_3 in phosphate-carbon complexes, respectively,²⁶ and the peaks at 1083 cm^{-1} and 882 cm^{-1} assigned to the symmetric and asymmetric stretching vibration of P–O–P band^{26,27} appear

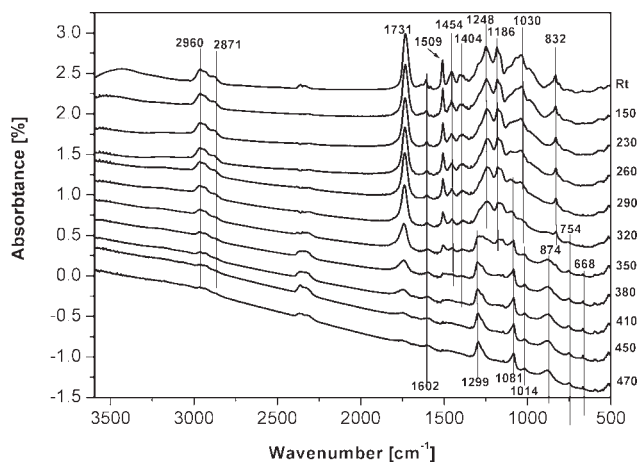


Figure 9 Dynamic FTIR spectra of EA2.

above 260°C. This indicates that some phosphate groups link to each other by sharing one oxygen atom, leading to the formation of poly(phosphoric acid), which can further decompose to form phosphorus oxides, such as P₂O₅.

The disappearance of strong peak at 1257 cm⁻¹ and 1262 cm⁻¹ and the appearance of two new peaks at 1283 cm⁻¹ and 1149 cm⁻¹ in the FTIR spectra imply that the phosphate group deviates from the aliphatic structure and forms poly (phosphoric acid) or relinks to the aromatic structures at the temperatures over 270 °C.²⁸ The formation of aromatic structures is approved by the appearance of two new peaks at 749, 667, and 590 cm⁻¹.²⁹

The FTIR spectra of residual products for EA2 are shown as Figure 9. As the pyrolysis temperature increases, the 1262 cm⁻¹ peak assigned to P=O moves gradually to a higher wave number, whereas the 1108 cm⁻¹ band attributed to P(=O)—O—C shifts to a lower wave number. The reason for the movement is the scission of P—O—C in phosphoric esters, which decompose at about 320°C and form P—O—P bond.²⁶ On the other hand, the band at 2850–2980 cm⁻¹ and the peak at 1731 cm⁻¹ corresponding to C—H and C=O absorption, respectively, are not changed before 290°C. These results indicate that the degradation of EA/BTP blends before 290°C proceeded mainly via the destruction of P—O—C groups in the films. Comparing with those in EA, the TOD processes of the flame-retardant EA are much more complicated. The absorption peaks at 2850–2980 cm⁻¹ (C—H) and at 1723 cm⁻¹ (C=O) decreased more quickly with increasing temperature. However, some new absorption peaks appear simultaneously. The absorption peaks at 1150 cm⁻¹ and 1014 cm⁻¹ might be assigned to the stretching vibration of P—O—C and PO₂/PO₃, respectively, in phosphate-carbon complexes.²⁶ The peaks at 1081 cm⁻¹ and 874 cm⁻¹ might be attributed to the symmetric and asymmetric stretching vibration of P—O—P band.^{26,27,30} At temperatures up to 350°C, the 1262 cm⁻¹ peak moves to 1299 cm⁻¹, and 1108 cm⁻¹ moves to 1081 cm⁻¹. Moreover, a new band at 874 cm⁻¹ appears at this temperature. The bands at 1081 and 874 cm⁻¹ are attributed to symmetric and asymmetric stretching vibration of P—O—P.^{26,30} The two bands and the peak 1299 cm⁻¹ are attributed to phosphoric ester (P(=O)—O—P) species.³¹ These new peaks are rather strong even at 470°C. These evidence suggest that there is a difference in the thermal degradation mechanisms of EA and its blends with BTP. P—O—C groups in the blends can degrade at lower temperature to form poly(phosphoric acid), which catalyzes the degradation of EA and then reacts with the decomposition products of EA to decrease the production of flammable volatile compounds and promote the formation of crosslinked char at higher temperature.

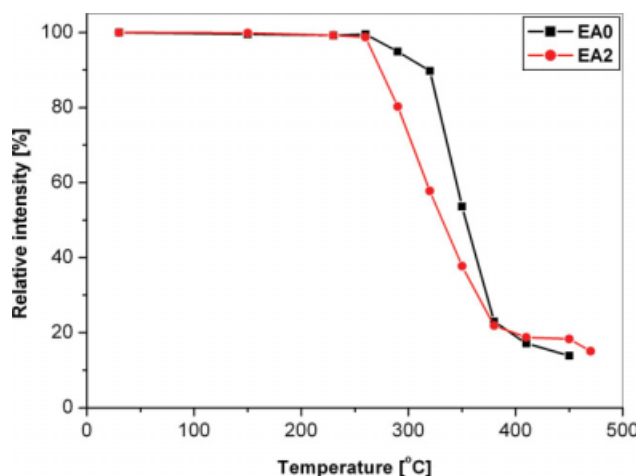


Figure 10 Relative peak intensity between 2800 cm⁻¹ and 3020 cm⁻¹ for C—H bond in the FTIR spectrum of UV-cured EA0 and EA2 films at various temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 10 shows the relative intensity of the peak between 2800 cm⁻¹ and 3020 cm⁻¹ in the FTIR spectrum of cured EA0 and EA2 films for C—H bond in CH₂ and CH₃ groups with temperature raising from 30 to 470°C. It is very clear that the C—H bond of EA2 film decreases rapidly with increasing temperature from 260°C to 380°C, whereas the absorbance between 2800 cm⁻¹ and 3020 cm⁻¹ for UV-cured EA film decreases slowly with increasing temperature from 260°C to 380°C. The sharp decrease of C—H bond of EA2 film can be interpreted as due to the fast decomposition of unstable P—O—C at lower temperatures. It is worthwhile to note that the absorbance for UV-cured EA film decomposed fast when the temperature is raised to 400°C. This can be attributed to the char residue isolating under material from heat and oxygen.

CONCLUSIONS

The BTP can polymerize rapidly with EA under UV irradiation. Their P^f are in the order of EA3 > EA2 > EA1 > EA0. The LOI, UL 94 flammability rating and cone calorimeter data illustrate that BTP used alone in EA dose have good flame retardancy.

The results indicate that the thermal oxidative degradation mechanism of EA is greatly changed by BTP addition. P—O—C groups in the cured films could degrade at lower temperature and form poly (phosphoric acid), which catalyzes the degradation of EA, and further react with the decomposition products of EA to form thermally stable compounds in the condensed phase.

The Program for New Century Excellent Talents in University is gratefully acknowledged.

References

1. Valet, A. *Prog Org Coat* 1999, 35, 223.
2. Maag, K.; Lenhard, W.; Loffles, H. *Prog Org Coat* 2000, 40, 93.
3. Randoux, T.; Vanovervelt, J. C.; Van Den Bergen, H.; Camino, G. *Prog Org Coat* 2002, 45, 281.
4. UV-Curable Coatings-Generic Testing and Quality Assurance Protocol. Operated by Concurrent Technologies Corporation; National Defense Center for Environmental Excellence (NDCEE); Johnstown, USA, 1998.
5. Kim, J. W.; Suh, K. D. *Colloid Polym Sci* 1998, 276, 342.
6. Chen-Yang, Y. W.; Chuang, J. R.; Yang, Y. C.; Li, C. Y.; Chiu, Y. S. *J Appl Polym Sci* 1998, 69, 115.
7. Timothy, E.; Erwin, S. WO 9502004, 1995.
8. Xie, R. C.; Qu, B. J. *J Appl Polym Sci* 2001, 80, 1190.
9. Hsiue, G. H.; Shiao, S. J.; Wei, H. F.; Kuo, W. J.; Sha, Y. A. *J Appl Polym Sci* 2001, 79, 342.
10. Price, D.; Pyrah, K.; Hull, T. R.; Mimes, G. J.; Wooley, W. D.; Ebdon, J. R. *Polym Int* 2000, 49, 1164.
11. Park, H. S.; Kim, D. W.; Hwang, K. H.; Yoon, B. S.; Wu, J. P.; Park, J. W. *J Appl Polym Sci* 2001, 80, 2316.
12. Chen-Yang, Y. W.; Lee, H. F.; Yuan, C. Y. *J Polym Sci Part A Polym Chem* 2000, 38, 972.
13. Guo, W. J. *J Polym Sci Part A Polym Chem* 1992, 30, 819.
14. Ebdon, J. R.; Hunt, B. J.; Joseph, P. *Polym Degrad Stab* 2000, 70, 425.
15. Chen, X. L.; Hu, Y.; Jiao, C. M.; Song, L. *Prog Org Coat* 2007, 59, 318.
16. Goddard, R. J.; Cooper, S. L. *Macromolecules* 1995, 28, 1390.
17. Larkin, P. J.; Makowaki, M. P.; Colthoupe, N. B. *Spectrochim Acta A* 1999, 55, 1011.
18. Chen, X. L.; Hu, Y.; Song, L.; Xing, W. Y. *J Fire Sci* 2008, 26, 93.
19. Price, D.; Liu, Y.; Hull, T. R.; Milnes, G. J.; Kandola, B. K.; Horrocks, A. R. *Polym Degrad Stab* 2002, 77, 227.
20. Babrauskas, V. SFPE Technology, Report 84-10; Society of Fire Protection Engineers: Boston, 1984.
21. Hirschler, M. M. In *Heat Release in Fires*; Babrauskas, V.; Grayson, S., Eds. Elsevier: London, 1992, 375.
22. Huang, Z. G.; Shi, W. F. *Polym Degrad Stab* 2006, 91, 1674.
23. Dabrowski, F.; Le Bras, M.; Cartier, L.; Bourbigot, S. *J Fire Sci* 2001, 19, 219.
24. Chiu, S. H.; Wang, W. K. *Polymer* 1998, 39, 1951.
25. Xie, R. C.; Qu, B. J.; Hu, K. L. *Polym Degrad Stab* 2001, 72, 313.
26. Bugajny, M.; Bourbigot, S.; Le Bras, M.; Delobel, R. *Polym Int* 1999, 48, 264.
27. Le Bras, M.; Bourbigot, S.; Revel, B. *J Mater Sci* 1999, 34, 5777.
28. Zhu, S. W.; Shi, W. F. *Polym Degrad Stab* 2003, 2, 233.
29. Setnescu, R.; Jipa, S.; Setnescu, T.; Kappel, W.; Kobayashi, S.; Osawa, Z. *Carbon* 1999, 37, 1.
30. Levchik, S. V.; Camino, G.; Costa, L.; Levchik, G. F. *Fire Mater* 1995, 19, 1.
31. Levchik, S. V.; Balabanovich, A. I.; Levchik, G. F.; Costa, L. *Fire Mater* 1997, 21, 75.