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# PAPER



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## 1. Introduction

Ultraviolet (UV)-curing technology is widely used in many fields, ranging from polymeric coatings and composites to inks and adhesives, as a means of rapidly and efficiently converting liquid, multifunctional monomer resins into cross-linked polymer networks.<sup>1–3</sup> The advantages of photo-curable systems have been well documented, including environmental friendliness (without VOC emissions), a fast and controllable curing system, lower energy consumption than thermal curing, and the possibility of curing at room temperature.<sup>4,5</sup> Among UV-cured resins, much attention has focused on epoxy acrylates (EAS), due to their excellent adhesion, good chemical and corrosion resistance, and excellent electrical insulation. However, flammability is one of the principal disadvantages of EAs, restricting

# Thermal and flame retardant properties of transparent UV-curing epoxy acrylate coatings with POSS-based phosphonate acrylate

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A novel branched phosphonate acrylate monomer (BPA) containing phosphorus and polyhedral oligomeric silsesquioxanes (POSS) was successfully synthesized *via* thiol Michael addition of tri(acryloyloxyethyl) phosphate with octamercaptopropyl POSS, and then incorporated into epoxy acrylate (EA) resins in different ratios using ultraviolet curing technology. The structure of BPA was confirmed by Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance. The effects of BPA on the thermal stability, combustion performance, degradation process and transparency of EA were investigated. The modified EA (MEA) retained a high transparency and exhibited significantly enhanced flame retardancy, as evidenced by the increased limiting oxygen index values and greatly reduced peak heat release rate. The thermal properties of MEA indicated that the presence of BPA promoted the degradation of the EA matrix and produced additional char residues. The thermal degradation processes of the MEA were further investigated by real time FTIR. The char structure of MEA, investigated by Raman spectra, revealed that the addition of BPA increased the ratios of graphitized carbon in residual chars, thus enhancing the thermal stability of MEA.

the range of applications, especially where high flame retardancy is required. Thus, to widen the application of EAs, improving its flame retardancy and reducing the fire hazards are imperative.

Generally, incorporating phosphorus-,6 silicon-,7 nitrogen-8 and boron-containing compounds,9 nanoadditives,10 etc. into EA matrix is an effective way of improving its flame retardance. Of the different flame retardants (FRs) discussed in the literature, phosphorus-containing FRs, which promote char formation in the condensed phase through extracting water from the pyrolysis substrate, have been demonstrated to be effective flame retardants for most polymeric materials, such as polypropylene,<sup>11</sup> polystyrene,<sup>12</sup> and epoxy resins.<sup>13</sup> However, the incorporation of phosphorus-bearing FRs alone, especially organic phosphorus compounds, will lead to the formation of more unstable char residues, unable to resist the heat from fires. Therefore, synergistic combinations of phosphorus and other inorganic additives or organic-inorganic hybrids have been developed and reported to impart high thermal oxidation resistance to the resulting char layers.14,15

Polyhedral oligomeric silsesquioxanes (POSS), possessing a cage-like structure with 1–3 nm particle size, are a class of inorganic compounds. Their empirical formulas may be presented as  $(RSiO_{1.5})_n$ , where R may be hydrogen or any alkyl, alkylene, aryl, arylene or organo-functional derivative of alkyl, alkylene, aryl or arylene groups.<sup>16–18</sup> In prior work, POSS was demonstrated to improve the char yield, the oxidation

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resistance properties and flame retardancy of most polymers.<sup>14,19–21</sup> However, the effect of POSS on the thermal behavior and flame retardancy of the UV-cured epoxy acrylates have rarely been reported because of poor compatibility between EA matrices and POSS. In addition, most POSS with varied structures are additive, solid compounds and the presence of POSS may have a negative effect on the curing rate and degree of curing, as well as the transparency of the resultant cured films.

In this work, flame retardant and transparent UV-cured EA composites filled with different loadings of phosphorus- and silicon-containing compound (BPA) were prepared using UV-curing technology, where the compound was a liquid flame retardant synthesized *via* thiol Michael addition. The structure of BPA was characterized by Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR). The thermal degradation of the as-prepared films was investigated by thermogravimetric analysis (TGA), real-time Fourier transform infrared spectra (RT-IR) and thermogravimetric analysis/

infrared spectrometry (TG-IR). The combustion properties were evaluated by limiting oxygen index (LOI) and micro combustion calorimeter (MCC). The transparency and dynamic mechanical properties were investigated by UV-Vis spectra and dynamic mechanical analysis (DMA). This work describes a good reactive flame retardant for UV-cured transparent resins.

## 2. Experimental

### 2.1 Raw materials

Epoxy acrylate resin (EB600) was purchased from Cytec Industries Inc. Hydroxylethyl acrylate (HEA) was supplied by Beijing Orient Chemical Co. Ltd. (3-Mercaptopropyl) trimethoxysilane (MPTS) was obtained from Nanjing Shuguang Chemical Group Co., Ltd. 2-Hydroxy-2-methyl-1-phenyl-1-propanone (Darocur1173), supplied by Ciba Specialty Chemicals, was used as a photoinitiator. All the other chemicals were obtained from China National Pharmaceutical Group (Shanghai, China).



Scheme 1 Synthetic routes of (a) TAEP, (b) OMP-POSS and (c) BPA

Phosphorus oxychloride (POCl<sub>3</sub>) and MPTS were distilled prior to use. Triethylamine and HEA were distilled and dried over 4 Å molecular sieves before use. Other reagents were used asreceived without further purification.

# 2.2 Synthesis of POSS-based branched phosphonate acrylate (BPA)

Tri(acryloyloxyethyl) phosphate (TAEP) was prepared via substitution reaction between phosphorus oxychloride and hydroxyethyl acrylate in our laboratory,6 and OMP-POSS was synthesized by hydrolysis of 3-mercaptopropyl trimethoxysilane under acid conditions according to the method described in prior literature.<sup>22</sup> BPA was obtained in an 8:1 molar ratio of TAEP to OMP-POSS through Michael addition, using triethylamine as a catalyst. The synthetic route of (a) TAEP, (b) OMP-POSS and (c) BPA were presented in Scheme 1. The typical process for the preparation of BPA was as follows: TAEP (30.9 g, 78.7 mmol) and an appropriate amount of triethylamine (1 wt% as total weight) were dissolved in 120 ml of dichloromethane and then introduced into a 250 ml three-neck flask equipped with a dropping funnel, nitrogen inlet, condenser and mechanical stirrer. Afterward, a solution of OMP-POSS (10 g, 9.84 mmol) in dichloromethane (30 ml) was added dropwise at room temperature under magnetic stirring over a period of 1 h. After completion of the addition, the reaction was conducted at 40 °C under nitrogen for 24 h. Finally, the transparent and viscous liquid was collected by evaporation under reduced press to remove the solvent. (Yield: 98%).

OMP-POSS: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 0.65–0.85 (Si–CH<sub>2</sub>–), 1.33–1.47 (–SH), 1.72 (–CH<sub>2</sub>–), 2.50–2.60 (–CH<sub>2</sub>–S);

BPA: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 0.65–0.85 (Si–CH<sub>2</sub>–), 1.60–1.80 (–CH<sub>2</sub>–), 2.50–2.60 (–CH<sub>2</sub>–S), 5.8–6.5 (CH<sub>2</sub>==CH–), 4.0–4.55 (–OCH<sub>2</sub>CH<sub>2</sub>O–), 2.71–2.85 (–C(O)–CH<sub>2</sub>–), 2.60–2.71 (–C(O)CH<sub>2</sub>–CH<sub>2</sub>–);

#### 2.3 Preparation of UV-cured EA/BPA films

UV-cured epoxy acrylate with various amounts of BPA was designated as EAX, where *X*% represents the mass percentage of BPA. Briefly, the general procedure for preparing EA10 film was described below: BPA (2 g) was thoroughly dissolved in an appropriate amount of dichloromethane under sonication, and then introduced into a vial. Subsequently, EB600 (18 g) and Darocur1173 (0.4 g, 2 wt%) were added into this solution. After thorough stirring to form a homogeneous solution, the blended was cast onto glass plates and dried at 60 °C under vacuum to remove the solvent. The cured film was obtained when the mixture was exposed to UV irradiation ((80 W cm<sup>-2</sup>, Lantian

Sample	EB600 (g)	BPA (g)	1173 (wt%)
EAO	100		2
EAU EA10	100	 10	2
EA10 EA20	90 80	20	2
EA30	70	30	2

Co., China)). The formulations of the cured EA films with various BPA contents are shown in Table 1.

#### 2.4 Characterizations

FTIR spectra (KBr) were collected on OMP-POSS and BPA using a Nicolet 6700 FTIR spectrophotometer in the sample concentration range of 0.1–1.0 wt%.

<sup>1</sup>H NMR (400 MHz) spectra were measured with a Bruker AV400 NMR spectrometer, using chloroform- $d_6$  as solvent.

LOI measurement was performed on a HC-2 LOI testing device (Jiangsu, China) according to ASTM D2863 (the tested specimens:  $100 \times 6.5 \times 3 \text{ mm}^3$ ).

UL-94 vertical burning test was performed on a CZF-II horizontal and vertical burning tester (Jiang Ning Analysis Instrument Company, China). The specimens used were  $127 \times 12.7 \times 3 \text{ mm}^3$  according to the standard ASTM D3801-2010.

TGA of samples was conducted with a Q5000 thermal analyzer (TA Co., USA) from 50 to 700 °C at a heating rate of 20 °C min<sup>-1</sup>. The samples were run in triplicate: the temperature reproducibility of the instrument was 0.18 °C, while the mass reproducibility was 0.2%.

DMA was measured using a DMA Q800 apparatus (TA Instruments Inc., USA) from -65 to 150 °C at a heating rate of 5 °C min<sup>-1</sup>. The frequency of dynamic oscillatory loading was 10 Hz.

Small scale flammability tests were conducted on a pyrolysiscombustion flow calorimeter (PCFC, Model MCC-2, Govmark, Farmingdale, New York). The samples were tested according to ASTM D7309-07.

TG-IR of the samples was performed using a TGA Q5000 IR thermogravimetric analyzer that was interfaced to the Nicolet 6700 FTIR spectrophotometer. The sample was put in an alumina crucible and heated from 30 to 600 °C at a heating rate of 20 °C min<sup>-1</sup> under nitrogen. The stainless steel transfer pipe and gas cell were heated at 230 °C to avoid the condensation of volatile compounds.

RT-IR was recorded using the Nicolet 6700 FT-IR spectrophotometer, equipped with a ventilated oven with an additional heating device. The cured samples were mixed with KBr powder, and the mixture was pressed into a disc, which was then placed into the oven. The temperature of the oven was raised at a heating rate of 10 °C min<sup>-1</sup>.

Raman spectra in the range of  $500-2000 \text{ cm}^{-1}$  were conducted on a LabRAM-HR Confocal Raman Microprobe (Jobin Yvon Instruments, France) using a 514.5 nm argon ion laser.

The transparency of the cured films was evaluated with a DUV-3700 UV-Vis spectrometer (Sahimadzu, Japan) in transmission mode. The wavelengths studied were in the range of 400 to 800 nm.

## 3. Results and discussion

#### 3.1 Structural characterization

The structures of OMP-POSS and BPA were characterized by FTIR, and <sup>1</sup>H NMR spectra. Fig. 1 presents the FTIR spectra of OMP-POSS and BPA. In the prior literature, the absorption



Fig. 1 FTIR spectra of BPA and OMP-POSS.

bands may be observed in the FTIR spectra of OMP-POSS, namely alkyl C–H vibration (2927, 2853 cm<sup>-1</sup> for  $\nu$  C–H), S–H stretching vibration (2560 cm<sup>-1</sup>), Si–C asymmetric stretching vibration (1260 cm<sup>-1</sup>), Si–O–Si asymmetric stretching vibration (1120 cm<sup>-1</sup>), Si–C stretching vibration (694 cm<sup>-1</sup>), and POSS skeletal deformation vibrations (560 cm<sup>-1</sup>).<sup>22</sup> For BPA, the absorption peaks include some main peaks of TAEP and OMP-POSS. The peak at 1270 cm<sup>-1</sup> is attributed to P=O vibration; the peaks which appear at 1038 and 980 cm<sup>-1</sup> are attributable to P–O–C vibration; the peak at 1726 cm<sup>-1</sup> is assigned to C=O vibration, while the peaks at 1635, 1410 and 810 cm<sup>-1</sup> are ascribed to C=C vibration.<sup>6</sup> These results confirm the structure of BPA. Moreover, no peak at 2560 cm<sup>-1</sup> originating from the S–H vibration in OMP-POSS is visible, indicating the occurrence of thiol-acrylate Michael addition reaction.

The <sup>1</sup>H NMR spectra of OMP-POSS and BPA are presented in Fig. 2. The absence of the peaks around 1.33–1.47 ppm, which



Fig. 2 <sup>1</sup>H NMR spectra of OMP-POSS and BPA.

are assigned to the protons of thiol groups, reveals the successful reaction of the thiol groups. Moreover, two new signals in the range of 2.71–2.85 and 2.60–2.71, corresponding to the protons of the methylene groups in  $-C(O)-CH_2$ - and  $-C(O)CH_2$ -CH<sub>2</sub>-, respectively, occur in the <sup>1</sup>H NMR spectrum of the BPA. The above results clearly support that all thiol moieties of OMP-POSS have participated in the thiol-acrylate reaction and BPA was successful synthesized.

# 3.2 Thermal and flame retardant properties of composite films

Thermogravimetric analysis (TGA) is a widely used tool to evaluate the thermal degradation behaviors of polymeric materials. The TGA curves of the cured films under nitrogen and air atmosphere are shown in Fig. 3 and 4, respectively, and the corresponding data are listed in Table 2. The initial degradation temperature  $(T_{0,1})$  of the samples is the temperature where 10% mass loss occurs, and T<sub>max</sub> represents the temperature of the maximum mass loss rate. As can be seen from Fig. 3, the control EA film exhibits a one-step degradation process in the temperature range of 350–500  $^{\circ}$ C, with a  $T_{\text{max}}$  of 424 °C, which can be attributed to the degradation of the principal EA chains. The initial degradation temperature and char yields at 700 °C of EA0 were 371 °C and 12.9 wt%, respectively. With the incorporation of BPA, all the composites exhibit similar decomposition behaviors to that of pure EA, but the  $T_{0.1}$  and  $T_{max}$  are both lower than those of EA0. Moreover,  $T_{0.1}$  gradually decreases with an increase in BPA content. A



Fig. 3 TGA curves of the cured films under nitrogen atmosphere.



Fig. 4 TGA curves of the cured films under air atmosphere.

Table 2 TGA data for the cured films

	$T_{0.1}$ (°	$T_{0.1}$ (°C)		$T_{\max}$ (°C)		Char (700 °C, wt%)	
Sample	$N_2$	Air	$N_2$	Air	$N_2$	Air	
EA0	371	360	424	424, 601	12.9	0.46	
EA10	354	360	378	379, 621	26.5	6.29	
EA20	336	339	347	347,651	33.2	13.86	
EA30	323	325	328	329, 652	34.8	16.16	

similar phenomenon has been observed in prior research and this decrease in  $T_{0.1}$  may be explained by the early degradation of unstable P-O-C bonds of BPA, along with the formation of some acid derivatives.<sup>22,23</sup> These acid derivatives will catalyze polymer degradation to produce additional char residues. Additionally, the aliphatic chains, which radiate out from the POSS core and relatively poor thioether linkages lead to the low thermal stability of MEA, while OMP-POSS degrades to form a ceramic-like layer, which reinforces the forming char.24 In Table 2, the char formation in nitrogen of the cured film gradually increases as the BPA content increases from EA0 to EA30. For example, the char yield of EA30 is as high as 34.8%, higher than that of EA0, suggesting the improved thermal stability of EA30 at high temperature. The significant increase in char yield is due to the synergistic effect of phosphorous and silicon, where phosphorous promotes char formation, while silicon reinforces the char retarding further degradation of char residue. In the DTG curves, the mass loss rate exhibits the same reduction

trend as the char yields do, due to the formation of increased char and the barrier effect of char layer, which reduces the release of combustible gases, thus reducing the heat release rate.

The degradation behaviors of all the cured films under air (Fig. 4) are different from those under nitrogen. The control EA film exhibits a two-stage degradation process in the temperature ranges of 300-400 °C and 600-700 °C. The first stage is attributed to the degradation of the main EA chains and the second is the oxidation of the unstable char residues. After the incorporation of BPA, the  $T_{0.1}$  of the composite films shifts to a lower temperature and is gradually reduced with an increase in additives. Moreover, the temperature of maximum degradation rate at the first stage  $(T_{max1})$  displays a similar change trend to the  $T_{0,1}$  of the cured films. However, the incorporation of BPA enhances the temperature of the second-stage maximum degradation rate  $(T_{max2})$  and the char yields at 700 °C of cured films. For EA30 containing 30 wt% of BPA, the  $T_{\text{max}}$  and char yields are 652 °C and 16.12 wt%, respectively, much higher than those for EA0 (601 °C, 0.46 wt%). These results indicate that the degradation products of flame retardant in the condensed phase improve the thermal oxidative resistance of residual chars, thus enhancing the flame retardancy of the cured films.

DMA was used to study the dynamic mechanical properties of the UV-cured flame retardant coatings. Fig. 5 presents (a) storage modulus and (b) tan  $\delta$  curves of the cured EA coatings. The storage modulus of the cured flame retardant coatings shows gradually increasing trend with increasing the concentration of BPA. The storage modulus at 30 °C for pure EA film is



Fig. 5 (a) Storage modulus and (b) tan  $\delta$  curves of the cured EA films.

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around 1890 MPa. With adding 30 wt% BPA, the storage modulus of EA30 is improved by 56.6%, compared to that of pure EA film, due to the nanoreinforcement of the POSS cages in the crosslinked polymer networks since the POSS cages were covalently bonded with the crosslinking networks of the epoxy acrylate.<sup>25,26</sup> Glass transition temperature ( $T_g$ ) is determined from the peak maximum of the tan  $\delta$  curve. The incorporation of BPA has little effect on the  $T_g$ s of the cured EA films. The reason for this phenomenon is that the flexibility of organic branches present in the POSS structure and the decrease in the crosslink density leads to the decrease of  $T_g$ s, whereas the nanoreinforcement of POSS cages restricting the movement of the molecule chains in the matrix, thus increasing the  $T_g$ s.

To estimate the flame retardancy of composite films, MCC was performed on a series of cured films. Fig. 6 presents the heat release rate (HRR) curves of various cured films *versus* temperature. The detailed data obtained from the MCC curves, including the peak heat release rate (PHRR), total heat release (THR) and heat release capacity (HRC), are summarized in Table 3. Neat EA film is highly flammable with high PHRR and THR values, which are 296 W g<sup>-1</sup> and 20.5 kJ g<sup>-1</sup>, respectively. Incorporating BPA into EA remarkably reduces the PHRR and THR values. With the addition of 30 wt% BPA, the PHRR and THR of the cured film are decreased by 50.8% and 29.8%, respectively, relative to those of pure EA. Moreover, it is worth noting that the heat for the composite films starts to release at a relatively low temperature, and the temperature to peak heat



Fig. 6 HRR curves of various cured films versus temperature.

 Table 3
 MCC and UL-94 test results and LOI values of various cured films

Sample	HRC $(J g^{-1} K^{-1})$	$^{\rm PHRR}_{\rm (W~g^{-1})}$	THR (kJ g <sup>-1</sup> )	LOI (%)	UL-94
EA0	294	296.0	20.5	22.0	NR
EA10	251	252.5	19.0	27.0	NR
EA20	226	226.2	17.3	28.5	NR
EA30	145	145.7	14.4	29.0	NR

release rate (PHRR) is lower than that of pure EA film. This result is caused by the early degradation of the relatively weak phosphate moieties, which promotes the formation of more stable phosphorus-carbon-silicon complexes in the solid phase.<sup>23</sup> Thus, the formation of more stable char layers helps decrease the release amounts and release rate of evolved combustible gases, thus contributing to the low THR and PHRR. The flame retardancy of cured films is further investigated by LOI and UL-94 tests, and the resulting values are listed in Table 3. Owing to the easy burning of virgin EA, a low LOI value of 22.0% is obtained. As the BPA increases to 30 wt%, the LOI of the cured films is gradually increased to a maximum of 29.0%, which is in agreement with the increased char residues under nitrogen. However, no ratings (NRs) in the UL-94 tests are observed for the FR EA systems. Consequently, the additive loading level can not improve the vertical burning rating of the system effectively.

#### 3.3 Gaseous and condensed phase analysis

TG-FTIR technique was used to investigate the evolved gas products of flame retardant EA coatings during thermal degradation process. The FTIR spectra of pyrolysis gaseous products of EA0 and EA30 at maximum degradation rate are presented in Fig. 7. The FTIR spectrum of EA30 is similar to that of EA0, implying similar volatile compounds. The absorption of gaseous products from the pyrolysis of BPA is not clearly observed, probably due to the overlapping of the absorptions of the degradation products from the EA matrix. The evolved volatile products of EA0 and EA30 are identified by the characteristic bands of water and/or phenol ( $3500-3750 \text{ cm}^{-1}$ ), various hydrocarbons ( $2950-2850 \text{ cm}^{-1}$ ), CO<sub>2</sub> (2250-2400 cm<sup>-1</sup>), CO ( $2100-2200 \text{ cm}^{-1}$ ), carbonyl-containing compounds ( $1700-1760 \text{ cm}^{-1}$ ) and aromatic compounds ( $1480-1650 \text{ cm}^{-1}$ ).<sup>27</sup>

The absorbance of selected pyrolysis products *vs.* temperature for EA0 and EA30 is presented in Fig. 8. It can be observed that all the pyrolysis products for EA30 begin to release earlier than that of pure EA, due to the low thermal stability of BPA.



Fig. 7 FTIR spectra of pyrolysis gaseous products of EA0 and EA30 at maximum degradation rate.



Fig. 8 Absorbance of selected pyrolysis products vs. temperature for EA0 and EA30

Moreover, BPA catalyzes the thermal degradation of the EA matrix. The absorbance intensity of the degradation products for EA30 is much lower than that for EA0, especially for these flammable gases (hydrocarbons, aromatic and carbonyl compounds). The reduction in the release of these organic volatiles is attributed to the formation of additional char residues. The reduced flammable gases will lead to a reduction of the heat release rate. Moreover, the absorbance intensity of toxic gas (CO) is remarkably decreased. The most important fire hazards are classified as heat, smoke and toxic gases. Therefore, the addition of BPA effectively reduces the fire hazards of EA coatings.

Real time FTIR was chosen to monitor the thermal oxidative degradation process of the cured films in an air atmosphere. Fig. 9 shows the RT-FTIR spectra of the sample EA0 at different



Fig. 9 RT-FTIR spectra of the sample EA0 at different pyrolysis temperatures.

pyrolysis temperatures. It may be seen that the cured EA film presents some characteristic absorption peaks at approximately 3450 cm<sup>-1</sup> (O–H stretching vibration), 2970 cm<sup>-1</sup> (stretching vibration of C-H), 1730 cm<sup>-1</sup> (C=O stretching vibration), 1610, 1510 cm<sup>-1</sup> (C-C stretching vibration of aromatic ring), 1460, 1380 cm<sup>-1</sup> (bending vibration of C-H), 1240 cm<sup>-1</sup> (stretching vibration of CO-O-C), 1180 cm<sup>-1</sup> (stretching vibration of C-O-C) and 830  $\text{cm}^{-1}$  (deformation vibration of H atoms in benzene).<sup>28,29</sup> As the pyrolysis temperature increases, the peak at 3450 cm<sup>-1</sup> shifts to higher wavenumbers and nearly disappears at a temperature of 420 °C, because of the release of water. The relative intensity of all the other bands nearly hardly alters before being heated to 300 °C. Upon the pyrolysis temperature above 400 °C, the relative intensity of the absorption peaks dramatically decreases, implying that the primary decomposition of EA occurs. When the temperature rises to 560 °C, no obvious absorptions are observed in the condensed phase of EA0, indicating complete decomposition of the EA matrix.

The FTIR spectra of the sample EA30 at different pyrolysis temperatures are shown in Fig. 10. There is no distinct difference of the absorption bands between EA0 and EA30, except for a peak at 988  $\text{cm}^{-1}$  (P–O–C), probably due to overlapping of the characteristic bands of BPA with those of EA0. The peak at 988 cm<sup>-1</sup> decreases quickly with increasing temperature and disappears completely above 300 °C due to the degradation of P-O-C bonds, which is consistent with the TGA results under air. Above 350 °C, the rapid decrease in all the peak intensities indicates that primary chain decomposition of EA occurs. Moreover, similar specific absorptions to those of EA0 are observed in the condensed phase of EA30 at 560 °C. The peak at 1290 cm<sup>-1</sup> is attributed to the P=O stretching vibration of the O=P-O- $\Phi$  structure, where  $\Phi$ represents a polynuclear aromatic structure.<sup>30,31</sup> The presence of an aromatic structure in char residues at 560 °C is further



Fig. 10 RT-FTIR spectra of the sample EA30 at different pyrolysis temperatures.

verified by the peaks at 1610 and 750 cm<sup>-1</sup>, ascribed to the stretching and deformation vibrations of the aromatic rings, respectively. Moreover, the appearance of peaks at 1084 and 880 cm<sup>-1</sup> resulting from symmetrical and asymmetrical stretching vibrations of P-O-P structure confirms the presence of pyrophosphate.<sup>30,32</sup> Hence, a char layer composed of phosphorus-carbon complexes forms during combustion, which acts as an effective barrier to protect the matrix beneath from decomposing at high temperature.

Raman spectra were employed to investigate the structure of char residues. The flame retardant efficiency of any flame retardant is dependent on the quality of char layers. Fig. 11 shows the Raman spectra of residual chars of the cured films heated in a muffle furnace at 600 °C for 10 minutes. These two samples present two principal peaks around 1360 and  $1600 \text{ cm}^{-1}$ . The former is called the D band, while the other is called the G band and these are attributed to the K-point photons of  $A_{1g}$  symmetry and the first order scattering of the  $E_{2g}$ phonon of sp<sup>2</sup> C atoms, respectively.<sup>33</sup> In general, the intensity ratio of the D to G bands  $(I_D/I_G)$  is used as a measure of the graphitization extent of the char. The lower the  $I_{\rm D}/I_{\rm G}$  values, the higher the extent of graphitization and thermal resistance of the

residual char. The char for neat EA has a high  $I_D/I_G$  value of 2.62. Adding 30 wt% BPA into EA reduces the  $I_D/I_G$  value of the char to 2.42, indicating the presence of more graphitized carbons in the residual char. From the TGA and Raman discussions above, we conclude that the phosphorus-silicon flame retardant not only increases the char residue, but also enhances the thermal stability of the residual char, suggesting significant improvement in the thermal properties of composite films.

#### 3.4 Transparency

Fig. 12 presents the UV-Vis transmittance spectra of the cured EA films over the visible wavelength range of 400-700 nm. The pure EA exhibits high optical transparency with transmittance of over 75% in the studied wavelength range. With the incorporation of flame retardant additives, the optical transparency of the composite film is slightly higher than that of neat EA film. For example, for 550 nm UV irradiation, the transmittances of the films containing 10 wt%, 20 wt% and 30 wt% of BPA FRs are 87.6%, 85.5% and 84.3%, respectively, as compared to 83.6% for neat EA. These enhanced optical transmittances of the composite films imply a good dispersion of the additive in the EA matrix. The attractive optical property can broaden the application of UV-curable coatings in some areas where high transparency is required.



Fig. 12 UV-Vis spectra of the cured films



Fig. 11 Raman spectra of residual chars of the cured films heated in muffle furnace at 600 °C for 10 minutes

# 4. Conclusions

A phosphorus- and silicon-containing branched compound with active double bonds was first synthesized by Michael addition reaction and then the well-characterized co-monomer was covalently incorporated into EA. The simultaneous presence of phosphorus and silicon elements significantly improved the flame retardancy and thermal properties of the EA. The flame retardant EA composites exhibited significantly improved LOI values, as high as 29%, while the PHRR and THR values of the composites were reduced by 50.8% and 29.8%, respectively. TGA, TG-IR and RT-IR results revealed that the incorporation of flame retardant accelerated the degradation of the EA matrix, reduced the flammable and toxic gases release and promoted char formation. Moreover, the formation of silicon dioxide originating from the degradation of BPA on the surface of the residual chars reinforced the char layer, thus enhancing thermal oxidative resistance. The production of additional graphitized carbon in char layers results in higher thermal stability. The improved flame retardancy of EA was responsible for a condensed phase flame retardant mechanism, including the catalyzing charring effect of phosphorus flame retardants and the char strengthening effect of silicon flame retardants, thereby forming a more effective protective barrier.

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