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Thermal degradation and flame retardancy of hexaacrylated/hexaethoxyl cyclophosphazene and their blends with epoxy acrylate☆

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Abstract

Two kinds of cyclophosphazenes, bearing UV-reactive acrylic groups (HACP) and non-reactive ethyl groups (HECP), respectively, were synthesized, and characterized by FTIR, ^{1}H-, and ^{13}C-NMR. These compounds were used as flame retardants to blend with commercial UV-curable epoxy acrylate EB600. The thermal behavior and degradation mechanism were monitored by TGA, in-situ FTIR and apparent activation energy calculation. The UV cured blends showed better thermal stability at elevated temperature with higher char yields compared with pure EB600 sample. The flame retardancy of the blends was examined by LOI measurements, and has shown that the blends with HACP or HACP powder have higher LOI than that with HECP.

Keywords: Cyclophosphazene; Thermal degradation; Flame retardancy; UV curing

1. Introduction

UV-curable resins are widely used in various industries replacing conventional thermally cured and solvent-based coatings and adhesives, due to their high curing rate, environmental protection, and the saving of energy [1,2]. The main types of oligomers used in the field are acrylated epoxies, acrylated polyurethanes, unsaturated polyesters, and acrylated polyesters. However, these oligomers generally give final cured films which are flammable. To increase their flame retardancy, the incorporation of flame retardants is very necessary when they are used in some special applications such as matrix for optical fibres [3] and wood coatings [4]. In UV curing systems, there are two methods to incorporate flame retardants: chemically modified oligomers, and blended flame retardants with oligomers [5]. The latter is more simple and practical. Moreover, if the flame retardant contains UV-reactive groups, such as acrylate, mathacrylate, it can be covalent-bonded with the matrix after UV irradiation. Even the matrix is unreactive, the blend system might be stable without significant volatilization and leaching because of the formation of 3-dimensional networks.

Compared with halogen-based compounds, phosphorus-containing flame retardants are receiving much more interesting recently, since they generally give off non-toxic and non-corrosive volatile products during combustion [6]. Their effects on combustion of polymers are mainly attributed to the generation of polyphosphoric acid and subsequent char formation, or modification of the decomposition mechanism of polymers [7]. In some systems, nitrogen combined with phosphorus can improve their flame retardant performance drastically [8]. They often exhibit intumescent behavior, producing a foamed protective char on the surface of a polymer material at elevated temperature. Phosphazenes, with a backbond of alternative phosphorus and nitrogen, have excellent flame retardant properties [9]. A wide range of phosphazene structures are available for flame retardants, including linear polymers [10], cyclolinear polymers [11], cyclomatrix [12], and cyclic oligomers [13–15]. Cyclophosphazene trimer is one of cyclic oligomers, and has been used most frequently as a flame

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retardant. However, most of these compounds are solid powders. Chan-Yang has synthesized cyclophosphazene trimer through the direct reaction of 2-hydroxylethylmethacrylate with hexachlorocyclotriphosphazene, for using as a flame retardant UV curable oligomer in wood coating [4]. However, little study has been reported about the effect of cyclophosphazene on thermal degradation and its corresponding mechanism of UV curing systems. In the present work, we synthesized two kinds of cyclophosphazene trimers as flame retardants, bearing UV-reactive acrylic groups and non-reactive ethyl groups, respectively. These trimers were then blended with commercial epoxy acrylate oligomers. Thermogravimetric analysis and in-situ FTIR were used to examine the thermal degradation behavior in order to determine the influence, if any, of these phosphazenes on the thermal decomposition of the epoxy acrylate. The phosphorus content change generated during the thermal degradation was measured by Inductively Coupled Plasma-Atomic Emission Spectrometry. Their flame retardancy was determined by the limited oxygen index measurements.

2. Experimental

2.1. Materials

2-Hydroxyethyl-acrylate (HEA), tetrahydrofuran (THF), triethylamine, and ethanol were dried and distilled before use. All the above chemicals and solid sodium were purchased from the First Reagent Co. of Shanghai, China. Hexachlorocyclotriphosphazene was synthesized and purified according to the reported method [16]. 2-hydroxy-2-methyl-1-phenyl-1-propanone (Darocur 1173) was used as a photoinitiator for UV curing, kindly supplied as a gift by Ciba Specialty Chemicals, Switzerland. EB600, a bisphenol A epoxy diacrylate oligomer with a molar mass of 500 g/mol, was supplied by UCB Co., Belgium.

2.2. Synthesis

2.2.1. Hexaacrylated cyclophosphazene (HACP)

A 150 ml of freshly distilled HEA (18.56 g), triethylamine (16.16 g), and cuprous chloride (0.1 g) solution in THF was poured into a 500 ml three-necked flask with a stirrer, a reflux condenser, and a nitrogen inlet, in an ice bath. A 100 ml of hexachlorocyclotriphosphazene (6.96 g) solution in THF was added dropwise into the above solution through a dropping funnel. The reaction mixture was kept with agitation at 60 °C for 48 h under nitrogen atmosphere. White triethylamine hydrochloride salt as a precipitate produced from the reaction was filtered. THF was removed under reduced pressure distillation. The obtained resultant was then dissolved in dichloromethane, washed with water, and dried over magnesium sulfate. A viscous yellowish liquid was finally obtained after removed dichloromethane under a vacuum system, with a yield of about 62%.

2.2.2. Hexaethoxyl cyclophosphazene (HECP)

A 150 ml of sodium (4.6 g) solution in THF was poured into a three-necked flask with a stirrer, a reflux condenser, and a nitrogen inlet, in an ice bath. Ethanol (9.2 g) was added dropwise into the above solution with continuously stirring until sodium was completely consumed to form a sodium salt. A 100 ml of hexachlorocyclotriphosphazene (6.96 g) solution in THF was then added dropwise into above sodium salt solution. The reaction mixture was kept with agitation at 60 °C for 48 h under nitrogen atmosphere. The sodium salt was filtered out from the mixture and the solvent was removed under distillation. The obtained resultant was then dissolved in dichloromethane, washed with water, and dried over magnesium sulfate. After removed dichloromethane by distillation, a viscous yellowish liquid was obtained with a yield of 67%.

2.3. Sample preparation

The formulations containing HACP or HECP, and/or EB600, and 3 wt.% Darocur1173 (total amount) were poured into a cell with an ordered dimension, and then exposed to a UV lamp were (80 w/cm, made by Lantian Co. Beijing) in air to form the cured film. For comparison, the blend containing EB600 and UV cured HACP powder was prepared, and UV irradiated.

2.4. Measurements

2.4.1. FTIR spectra

FTIR and in-situ spectra were recorded with a MAGNA-IR 750 spectrometer (Nicolet Instrument Co., U.S.A.). The KBr method was used for measuring the in-situ FTIR spectra in the range of room temperature to 400 °C with a heating rate of 2 °C/min.

2.4.2. ^1H- and ^{13}C-NMR spectra

The ^1H- and ^{13}C-NMR spectra were obtained with a DMX-500MHz apparatus, Bruker, Switzerland, using $CDCl_3$ as a solvent. The ^1H- and ^{13}C-NMR spectra were referenced to TMS.

2.4.3. Flammability test

The vertically suspended sample of $127\times12.7\times12.7$ mm^3 was ignited by a Bunsen burner. The burning time and the extent of combustion were recorded.

2.4.4. The limited oxygen index (LOI)

The LOI values of the cured samples were measured using a ZRY-typing instrument (made in China) with the sheets of $120\times6\times3$ mm^3 according to ASTM D-2863-91.

2.4.5. Thermogravimetric analysis (TGA)

The TGA was carried out on a Shimadzu TG-50 using a heating rate of 10 °C /min in air.

2.4.6. Phosphorus and chlorine contents

The sample was ignited in an oxygen bottle, using Pt as a catalyst. A 2% NaOH aqueous solution was used as received system. The phosphorus and chlorine contents were determined with Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) (Atomsian Advantage Thermo Jarrell Ash Co., U.S.A.) and by titration, respectively.

3. Results and discussion

3.1. Characterization of HACP and HECP

The schematic outlines for the synthesis of HACP and HECP were presented in Fig. 1. FTIR, and ^{1}H- and ^{13}C-NMR spectroscopy were used to characterize their chemical structures. The assignments of the related peaks in the FTIR and NMR spectra for HACP are given in Table 1.

For HECP sample, the absorption bands at 1010–1030 cm^{-1} and at 1240 cm^{-1} in the FTIR spectrum indicate the presence of P-O-C (aliphatic) and P=N groups, respectively. The chemical shifts at 1.0 and 4.2 ppm in the ^{1}H-NMR spectrum are assigned to CH_3 and P-O-CH_2 groups, respectively. Its chemical shifts at 9.9 ppm and 69.2 ppm in the ^{13}C-NMR spectrum are assigned to CH_3 and CH_2 groups, respectively.

The chlorine contents in two products are measured to be not over 0.1%. This implies that the syntheses proceeded completely and the residual chlorine exists in the products only as a trace.

The compatibility between individual components in a UV formulation is very crucial, because it strongly affects the chemicophysical and mechanical properties of the cured film. In order to obtain homogeneous systems, blending EB600 with two cyclophosphazene oligomers was performed at 50 °C, leading to two transparent viscous liquids HECP/EB600 and HACP/EB600. However, blending EB600 with the UV irradiated HACP powder formed an opaque HACP/EB600 blend. These results indicate that HACP and HECP can be blended well with UV-curable oligomers. Compared with their polymeric counterparts such as polyphosphazenes, formulating conditions for two products are moderate due to the nature of liquids with lower viscosities. Moreover, their higher molecular weights make volatilization and leaching not significant during the use. All those formulations HACP/EB600, HECP/EB600 and HACP powder/EB600 were found to polymerize rapidly in the presence of Darocur 1173, at room temperature in air. This will be presented in another paper.

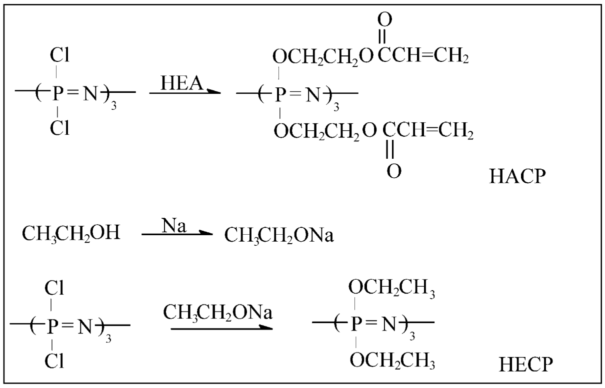


Fig. 1. Schematic outline of the synthesis of HACP and HECP.

Table 1
Assignments of the peaks in FTIR and NMR spectra of HACP

FTIR (cm$^{-1)}$	^{1}H-NMR (ppm)	^{13}C-NMR (ppm)
2850–2980 (CH)	3.9 (CH_2)	62.0 (CH_2)
1723 (C=O)	4.2 (P–O–CH_2)	66.3 (P–O–CH_2)
1636 (C=C)	5.8 (CH–CH=CH_2)	128.0 (CH–CH=CH_2)
1220–1250 (P=N)	6.1 (CH–CH=CH_2)	131.0 (CH–CH=CH_2)
1170, 1240 (O–C=O)	6.4 (CH–CH=CH_2)	166.0 (C=O)
980, 1030–1050 (P–O–C)		
810 (C=C)		

3.2. Thermal behavior

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

Fig. 2 shows the TGA curves for the UV cured EB600 and HACP, and their blends HACP/EB600, and HACP powder/EB600 and also HECP/EB600. The pure EB600 film began to lose its weight at about 300 °C and degraded in two steps. The first step occurred in the range of 300–450 °C with around 50% weight loss. In the second step, EB600 degraded slowly, and little residue remained at above 640 °C. The HACP and its blend films have a lower initial decomposition temperature of around 160 °C, and the first small degradation steps occurred in the range of 160–260 °C with about 10% weight loss. This is attributed to the less stable P-O-C bond linkage. This result is the same with that reported in the previous study [16]. For HECP/EB600 film, the weight loss at 260 °C reached to 15% due to its more volatile side ethyl group. HACP film has the slowest degradation rate in the second step and the highest residue at the end. HACP/EB600 film and HACP powder/EB600 film have the same degradation behavior in the range of 260–470 °C. However, the former remained more residue, due to its compatibility and higher cross-linking density compared with the latter. Pure HACP film has a faster degradation rate in the first step and the highest char yield. This is attributed to the easy decomposition of aliphatic chains and the highest phosphorus content in HACP molecule. The char yield of HECP/EB600 at 650 °C is higher than those of HACP/EB600 and HACP powder/EB600 because of its higher phosphorus content. With increasing the loading of cyclophosphazenes, the TGA curves for HACP(20)/EB600 and HACP(40)/EB600 show significant difference over 380 °C. The former presents a faster mass loss rate and a lower char yield due to the lower phosphorus content.

3.3. Degradation mechanism

The TGA results indicated that cyclophosphazenes play important roles to increase the thermal stability of EB600 at elevated temperature. However, its stability at lower temperatures decreases. To further investigate their influence, in-situ FTIR was used to monitor the thermal degradation of EB600, HACP and the blends from room temperature (RT) to 400 °C.

Fig. 3 shows the FTIR spectra of residual products of EB600 film degraded at different temperatures. There was little change in the absorption peaks of the FTIR spectra before 300 °C which is consistence with the TGA result. The absorption of ester group (1170 cm^{-1} and 1240 cm^{-1}) is still rather strong at 350 °C. No new absorption bands have been found during the thermal degradation period. However, in the FTIR spectra of HECP/EB600 (Fig. 4) and HACP/EB600 (Fig. 5), the absorption peaks at 1030 cm^{-1} and 980 cm^{-1} due to P-O-C bond decrease with the increasing temperature and disappear at 250 °C. The characteristic absorption peaks for P = N at about 1240 cm^{-1} and for ester group at 1170 cm^{-1}, 1240 cm^{-1} also disappear at elevated temperatures. Compared with those in EB600 film, the absorption peaks at 2850–2980 cm^{-1} (C–H) and 1723 cm^{-1} (C=O) in the spectra of HACP/EB600 blend decrease more quickly with the increasing temperature. Moreover, a few new peaks at 1090 cm^{-1} and 880 cm^{-1}, which might be ascribed to the generation of P-O-P, and

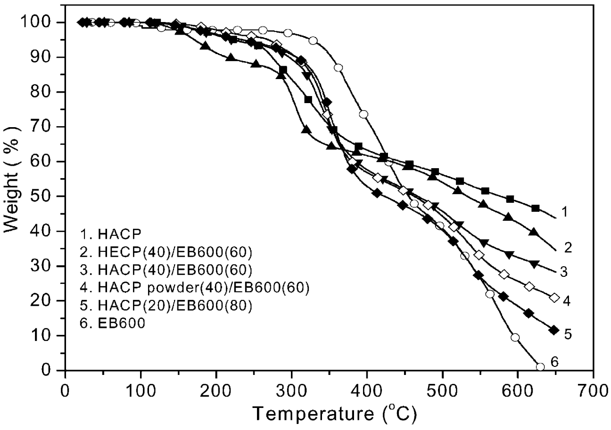


Fig. 2. TGA curves of EB600 and its blends with HACP, HECP or HACP powder in air.

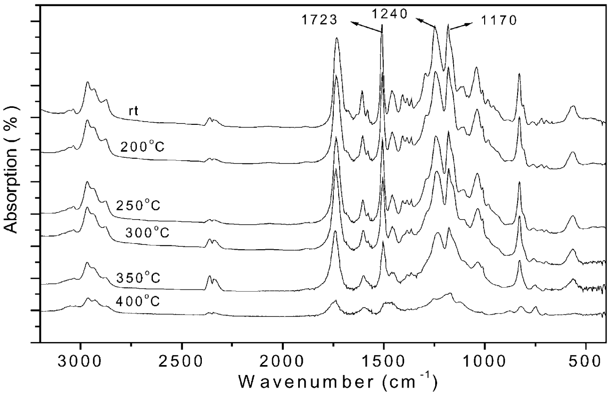


Fig. 3. FTIR spectra of EB600 film during the thermal degradation in the range of RT—400 °C.

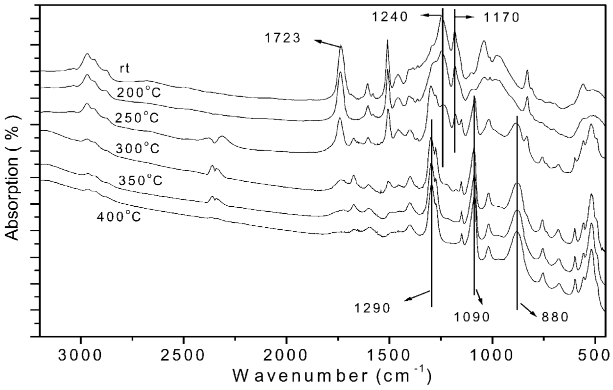


Fig. 4. FTIR spectra of HECP/EB600 film during the thermal degradation in the range of RT—400 °C (HECP/EB600 = 40/60).

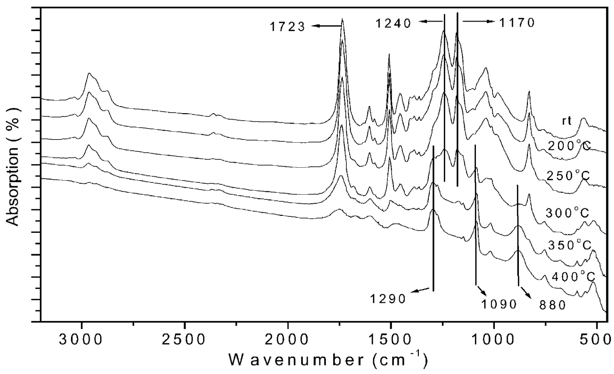
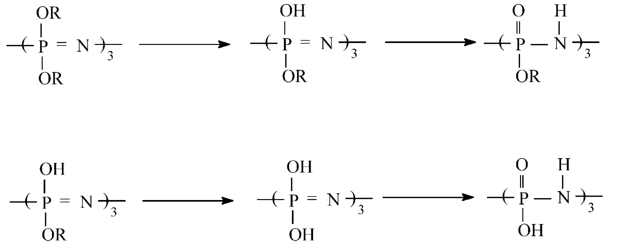


Fig. 5. FTIR spectra of HACP/EB600 film during the thermal degradation in the range of RT—400 °C (HACP/EB600 = 40/60).

at 1290 cm^{-1} for P=O appear over 250 °C, and become rather strong up to 400 °C [17,18]. These evidence suggest that a different thermal degradation mechanism for HECP/EB600 and HACP/EB600 blends occurs compared with pure EB600 samples. Similar to the mechanism which has been reported [19,20], one possible reason for the result is that cyclophoshazenes could experience the reactions as follows while heating:



$$-\!\left(\underset{OR}{\overset{OR}{P}}=N\right)_3\!- \longrightarrow -\!\left(\underset{OR}{\overset{OH}{P}}=N\right)_3\!- \longrightarrow -\!\left(\underset{OR}{\overset{O}{\overset{\|}{P}}}-\overset{H}{N}\right)_3\!-$$

$$-\!\left(\underset{OR}{\overset{OH}{P}}=N\right)_3\!- \longrightarrow -\!\left(\underset{OH}{\overset{OH}{P}}=N\right)_3\!- \longrightarrow -\!\left(\underset{OH}{\overset{O}{\overset{\|}{P}}}-\overset{H}{N}\right)_3\!-$$

The obtained structure could act as an acid catalyst, which would accelerate the cleavage of side groups and the breaking of ester groups in EB600. Then the degradation products reacted with the residue of EB600 and formed more stable structures. The appearance of P-O-P group can be considered as a crosslinker linking to different species, resulting in the formation of complex phosphorus structures [18]. This is why the thermal degradation of the blends containing cyclophosphazenes is much slower than EB600 at above 400 °C (Fig. 2).

The phosphorus contents of blends at various temperatures were measured with ICP-AES, and are listed in Fig. 6. While heating the blends from room temperature to 200 °C, the phosphorus contents in both blends increased steadily. To further investigate the change of phosphorus contents during the thermal degradation, the weight loss of the phosphorus element was calculated from the above results (Fig. 7). The weight loss of phosphorus contents is 17% for HECP(40)/EB600(60) and 10% for HACP(40)/EB600(60) at 450 °C. However, the weight loss of samples have reached to 42.3% and 48.0%, respectively at the same temperature (Fig. 2). The results indicate that phosphorus element, unlike other elements, could remain exclusively in the residue during the thermal degradation. Combined with the results from FTIR analysis, the formation of new structures with rich phosphorus in the blends is crucial, which are more stable and act as a protective layer at elevated temperature.

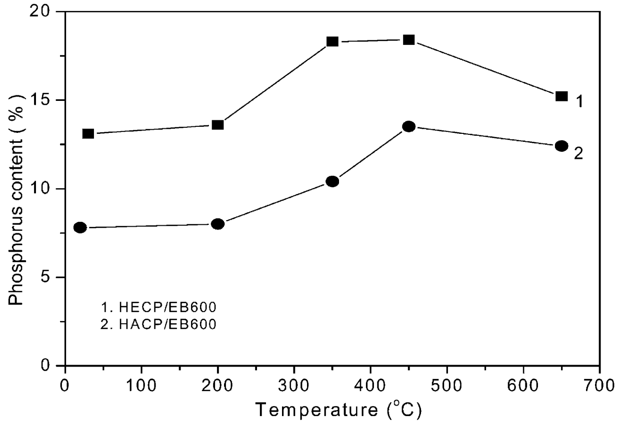


Fig. 6. Phosphorus contents in HECP and HACP at various temperatures (HECP/EB600 and HACP/EB600 = 40/60).

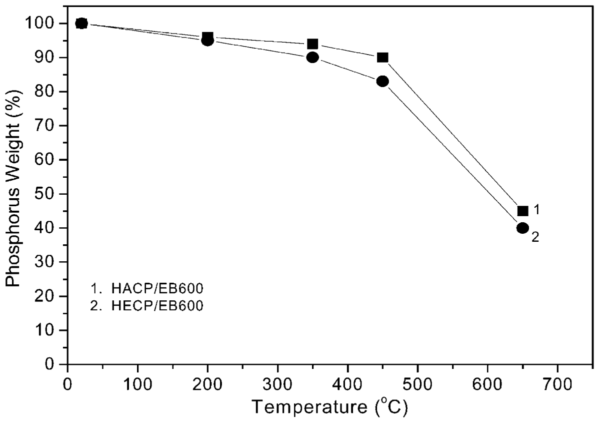


Fig. 7. Phosphorus weight loss of the blends during the thermal degradation (HECP/EB600 and HACP/EB600 = 40/60).

The phosphorus loss in HECP/EB600 sample was higher than that in HACP/EB600 sample. However, 83% phosphorus still remained in the residue of the blend at 450 °C. This result is different from that in other system, which the cyclophosphazene trimers bearing methoxy and ethoxy side groups were degraded and extracted from the the system [21]. It might ascribe to the formation of crosslinking network after UV cured. The network can prevent this cyclophosphazene extracting and volatilizing from the system.

The apparent activation energies for the thermal degradation of EB600 and the blends with HACP and HECP were determined from the TGA curves. The method used was described by Broido [22]. The equation could be written as the follows:

$$\ln[\ln[1/(1-\alpha)]] = -E_a/RT + \ln\left[(R/E_a)(Z/U)T_m^2\right]$$

α is the extent of conversion and is given by:

$$\alpha = W_e/W_o$$

where W_e is the mass of sample evolved as volatile fragments and W_o is the original mass. R is the gas constant. Z is a constant. T_m is the temperature for the maximum reaction velocity, and U is the rate of heating.

The plots of $\ln[\ln[1/(1-\alpha)]$ versus 1/T in the temperature range 300–500 °C are shown in Fig. 8. The apparent activation energies, E_a, are determined from the slopes of these plots. The slope of the plot for EB600 film is nearly a constant during 300-500C, as shown as the curve 3 in Fig. 8. However, the slope of HECP/EB600 becomes slower at 330 °C, while the same change also occurs in the slope of HACP/EB600 at 360 °C, as shown as curve 1 and curve 2 in Fig. 8, respectively. The results further indicate that the degradation of the blends is slower than that of EB600 film.

3.4. Flame retardancy

When pure EB600 film was ignited vertically in air, it burned rapidly and was completely consumed within 60 s to leave a little black char. The addition of HECP into EB600 had little effect on the overall combustibility of the blends until the loading reached to 40%. Moreover, the HECP/EB600 sample extinguished slowly after the flame was removed. The residual char obtained expanded drastically. The blends containing HACP and HACP powder exhibited better flame retardancy. A loading of 20% could make the samples self-extinguished in air. After burned, in the middle of HACP/EB600 and HACP powder/EB600 charred area, there were some internal regions which remained unchanged with no evidence of combustion. The cover layer formed a black glassy char. It apparently provided a protective layer over the bulk of sample and prevented further combustion.

The LOI measurements as a qualitative method for determining the flammability of blends have shown the same trend. LOI, which ranks the flammability of materials, is the minimum concentration of oxygen in an oxygen/nitrogen mixture that will just support combustion. Table 2 lists the LOI values of the samples having different ratios of EB600 to HACP, HECP or HACP powder. The LOI values of samples increase with increasing the loading of cyclophosphazene. However, a lower limit of addition was necessary to impart the meaningful flame retardancy to the blends. Moreover, the LOI values of HACP/EB600 blends are generally higher than those of HACP powder/EB600 blends, especially in high loading of cyclophosphazenes. It can be interpreted by the difference in the char yield at 650 °C. The LOI results of HECP/EB600 blends are not encouraging. Even adding a loading of 40% HECP, the LOI value of the blend was only 23.5, which was only 2.5 units higher than that of EB600, although HECP/EB600 showed the highest char yield at 650 °C. A possible reason for the result is the influence of its side ethyl group. When the blend containing HECP was applied to the flame, small molecules such as ethylene, ethane, would be formed due to the breaking of P-O-C in HECP at lower temperature. These small molecules are volatile and become fuel for the flame. Because of escaping of the small molecules, the char layer obtained becomes more porous. It also deteriorates the protective effect of char.

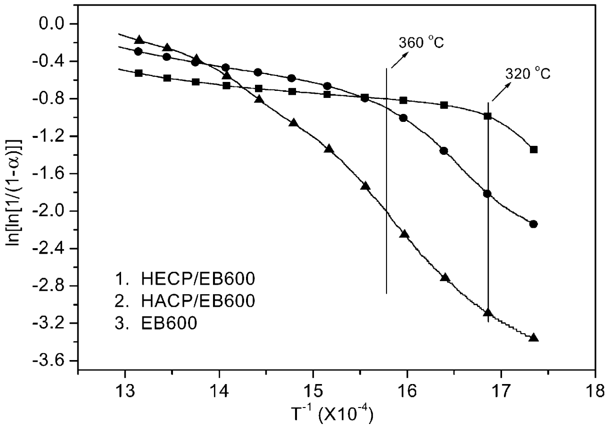


Fig. 8. ln[ln[1/(1−α)]] vs T^{-1} by Broido method during thermal degradation of EB600 and the blends (HECP/EB600 and HACP/EB600 = 40/60).

Table 2
LOI values of EB600 and its blends with HECP, HACP and HACP powder

Sample	0/100	5/95	10/90	20/80	30/70	40/60	100/0
HACP/EB600	21.0	21.0	22.0	24.0	26.5	28.5	33.0
HECP/EB600	21.0	21.0	20.5	21.5	22.0	23.5	–
HACPpowder/EB600	21.0	21.0	22.0	23.5	25.0	26.0	–

4. Conclusions

The addition of HECP and HACP can effectively improved the thermal stability of EB600 blends at elevated temperatures. However, the initial decomposition temperatures of the blends decreased due to the breakage of P-O-C group. The presence of HACP and HACP powder in the blends had positive effect on overall flammability. At the levels of greater than 20% HACP and HACP powder in the blends, there was evidence of significant flame retardancy. It was believed to result from the production of a protective char layer which inhibited the overall combustion of the blend. No obviously improved flammability was found in the blends containing HECP.

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