

# Photopolymerization and Properties of UV-Curable Flame-Retardant Resins with Hexaacrylated Cyclophosphazene Compared with Its Cured Powder

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**ABSTRACT:** Hexaacrylated cyclophosphazene (HACP) and its cured powder were blended with a commercial epoxy acrylate, EB600, to obtain UV-curable flame-retardant resins. The flame retardancy and the thermal stability of their cured films at elevated temperature were found to be improved from the measurements of limiting oxygen index and thermogravimetric analysis. Photopolymerization kinetics study showed that the photopolymerization rate increased with increasing amounts of HACP in EB600, whereas the unsaturation conversion decreased con-

versely. Dynamic mechanical thermal and mechanical properties showed that the addition of HACP had no influence, whereas adding HACP powder to EB600 had a negative effect, thus limiting its application in UV formulations. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1776–1782, 2005

**Key words:** thermogravimetric analysis (TGA); flame retardance; photopolymerization; resins; mechanical properties

## INTRODUCTION

Epoxy acrylates are widely used as oligomers in UV-curable coatings because of their low costs; fast cure rate; and the high gloss, hardness, and chemical resistance of the cured films. However, common epoxy acrylate products are highly flammable in air. In recent years, with the increasing requirements on the fire safety of polymer materials, increasing attention has focused on searching for new flame-retardant polymers and their acting mechanisms. In polymer materials, flame retardants are often incorporated either by reacting with resins as reactive components or blending with them as additives. The latter is simpler and more practical in conventional polymer systems, although there are some disadvantages that limit its usage in UV-curing systems.<sup>1</sup>

Although halogen-based compounds still play an important role in flame-retardant applications, halogen-free flame retardants, such as phosphorus-containing compounds, have become the focus of recent investigations because of the absence of toxic gases and corrosive volatile products during combustion.<sup>2</sup>

Phosphazenes, with a backbone of alternative phosphorus and nitrogen, provide a high level of phosphorus content. A series of phosphazene structures have been reported to be used as flame retardants,<sup>3–5</sup> including those used in UV-curing systems.<sup>6</sup> In our previous work,<sup>7</sup> hexaacrylated cyclophosphazene (HACP) was synthesized and then blended with a commercial UV-curable epoxy acrylate, EB600, which exhibited excellent flame-retardant properties. In the present study, HACP and the pulverized UV-cured HACP as a reactive and additive flame retardant, respectively, were used in EB600 resins. Besides the photopolymerization rate of resins, other properties, including the flame retardancy, thermal behavior, and dynamic mechanical thermal and mechanical properties of the cured films were evaluated, to compare the effects of the two types of flame retardants.

## EXPERIMENTAL

### Materials

2-Hydroxyethyl-acrylate (HEA), tetrahydrofuran (THF), and triethylamine were dried and distilled before use. All the above chemicals were purchased from the First Reagent Co. of Shanghai, China. Hexachlorocyclotriphosphazene was synthesized and purified according to the reported method. HACP was prepared as reported elsewhere.<sup>7</sup> The schematic outline for the synthesis is shown in Figure 1. 2-Hydroxy-2-methyl-1-phenyl-

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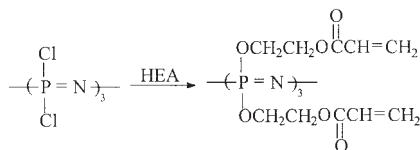


Figure 1 Schematic outline of the synthesis of HACP.

1-propanone (Darocur 1173, kindly supplied as a gift by Ciba Specialty Chemicals, Basel, Switzerland) was used as a photoinitiator for UV curing. EB600, a bisphenol A epoxy diacrylate oligomer (molar mass of 500 g/mol), was supplied by UCB N.V./S.A. (Brussels, Belgium). Its structure is shown in Figure 2.

### Sample preparation

The formulation containing HACP and/or EB600, and 3 wt % Darocur1173 (total amount) of the resin was poured into a cell with an ordered dimension, and then exposed to a UV lamp (80 W/cm; Lantian Co., Beijing, China) in air to form the cured film. For comparison, the blend containing EB600 and UV-cured HACP powder was also prepared and UV irradiated.

### Measurements

#### Limited oxygen index

The limited oxygen index (LOI) values of the cured samples were measured using a ZRY-typing instrument (made in China), using sheets of  $120 \times 6 \times 3$  mm<sup>3</sup>, according to ASTM D-2863-91.

#### Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out on a Shimadzu TG-50 (Shimadzu, Kyoto, Japan) at a heating rate of 10°C/min in air.

Concerning thermal analysis of EB600 blended with HACP or HACP powder, the curves of weight difference between the experimental and theoretical TG curves are computed as follows<sup>8</sup>:

- $W_{\text{exp}}(T)_{\text{EB600}}$ : TG curve of the UV-cured EB600
- $W_{\text{exp}}(T)_{\text{HACP}}$ : TG curve of the UV-cured HACP
- $W_{\text{exp}}(T)_{\text{blend}}$ : TG curves of the UV-cured blends (EB600/HACP or EB600/HACP powder)

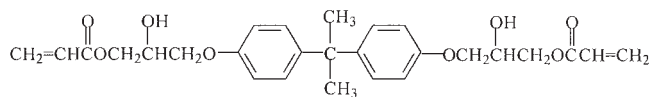


Figure 2 Chemical structure of EB600.

- $W_{\text{th}}(T)_{\text{blend}}$ : theoretical TG curves computed by linear combination between the TG curves of EB600 and HACP
- $W_{\text{th}}(T)_{\text{blend}} = xW_{\text{exp}}(T)_{\text{EB600}} + yW_{\text{exp}}(T)_{\text{HACP}}$ ;  $x + y = 1$ , where  $x$  and  $y$  are the weight percentages of EB600 and HACP or HACP powder in the blend, respectively
- $\Delta(T)_{\text{blend}}$ : curve of the weight difference

Therefore,  $\Delta(T)_{\text{blend}} = W_{\text{exp}}(T)_{\text{blend}} - W_{\text{th}}(T)_{\text{blend}}$

The  $\Delta T$  curve indicates the effect of a flame retardant on the thermal stability of a blend theoretically compared to the combination of a component.

### Viscosity

The viscosity was measured with a QNX Model spinning viscometer (Tianjin Instrument Co., Tianjin, China) at a speed of 750 rpm at 60°C.

### Photopolymerization kinetics

The photopolymerization rate ( $R_p$ ) was monitored by a modified CDR-1 differential scanning calorimeter (DSC; Shanghai Balance Instrument Co., Shanghai, China). Photopolymerization was carried out in N<sub>2</sub> atmosphere with a UV spotcure system BHG-250 (Mejiro Precision Co., Tokyo, Japan). The incident light intensity at the sample pan was measured to be 2.14 mW cm<sup>-2</sup> with a UV power meter. The unsaturation conversion ( $P_t$ ) was calculated by the formula,  $P_t = H_t/H_{\infty}$ , where  $H_t$  is the heat effect within  $t$  seconds and  $H_{\infty}$  is the heat effect of 100% unsaturation conversion. The DSC curves were unified by the weights of samples (g). The polymerization rate is defined as the variation of unsaturation concentration (mmol<sub>C=C</sub> g<sup>-1</sup>) per second. To calculate the polymerization rate and  $H_{\infty}$ , the value for the heat of polymerization  $\Delta H_0 = 86$  J mmol<sup>-1</sup> (per acrylic unsaturation), was taken.<sup>9</sup>

TABLE I  
Viscosity of EB600 and Its Blends with HACP and HACP Powder

EB600 (wt %)	HACP (wt %)	HACP (powder) (wt %)	Viscosity (cps)
100	0	0	3000
90	10	0	2800
80	20	0	2550
60	40	0	1800
0	100	0	100
90	0	10	4000
80	0	20	5000
60	0	40	8400

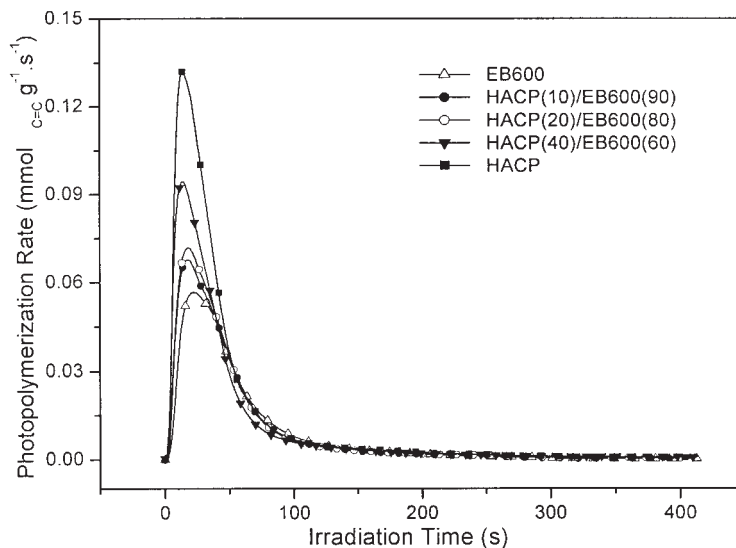


Figure 3 Photopolymerization rates of EB600, HACP, and their blends.

#### Mechanical properties

The tensile tests were carried out on a DECS-5000 instrument (Shimadzu Co., Tokyo, Japan) with the UV-cured films ( $80 \times 5 \times 1 \text{ mm}^3$ ) according to GB 1447. The final data were obtained after averaging the results from the five samples.

#### Dynamic mechanical thermal analysis (DMTA)

DMTA was carried out on the sheets ( $20 \times 5 \times 1 \text{ mm}^3$ ) using a dynamic mechanical thermal analyzer (Rheome Tric; SCI Systems, Inc., Hunstville, AL) at a frequency of 1 HZ and a heating rate of  $2^\circ\text{C min}^{-1}$  in the range of  $-20$  to  $200^\circ\text{C}$ .

## RESULTS AND DISCUSSION

### Photopolymerization kinetics

For a UV-curable formulation, viscosity is an important parameter that will substantially affect the processability, cure rate, and the properties of the cured film. HACP has a lower viscosity than that of EB600, as listed in Table I. With the addition of HACP, the viscosity of blends decreases sharply. Therefore, it is possible to adjust the viscosity of a blend through the addition of HACP. However, adding HACP powder, which is insoluble in EB600, causes the viscosity of the blends to increase, which affects the photopolymerization kinetics together with the functionality of resins.

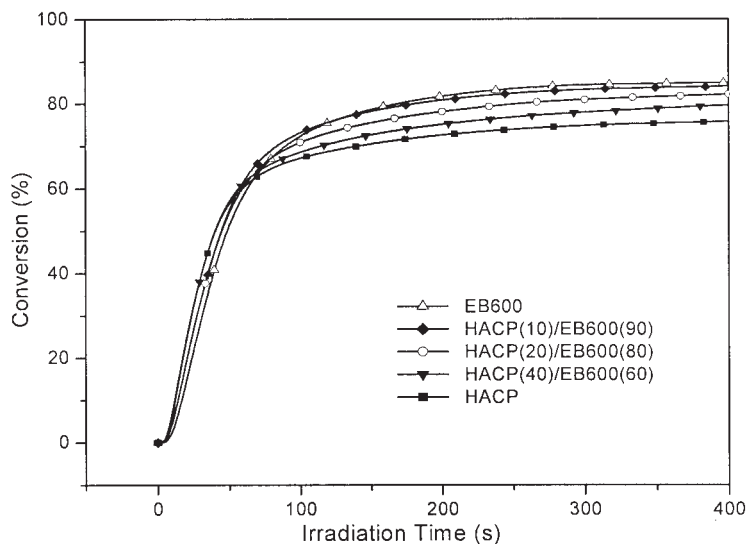


Figure 4 Unsaturation conversion of EB600, HACP, and their blends.

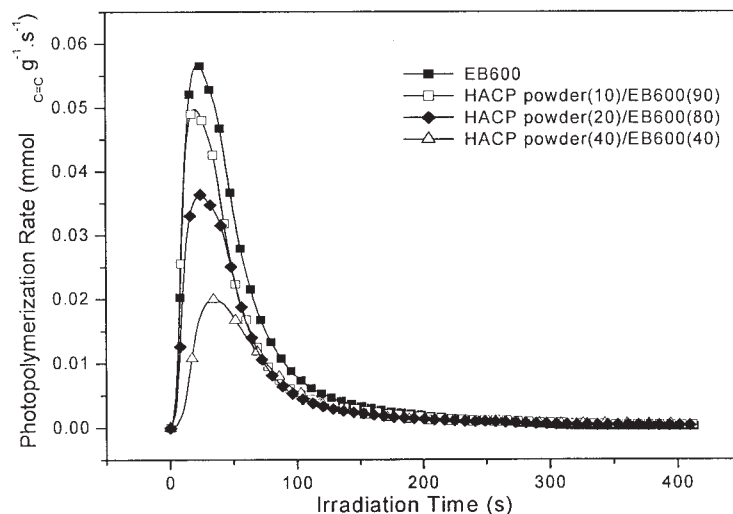


Figure 5 Photopolymerization rates of EB600 and its blends with HACP powder.

The photopolymerization process of UV-curable systems often shows a complex behavior that influences the properties of cured films. The two most important parameters characterizing the curing kinetics of these systems are the maximum polymerization rate ( $R_p^{\max}$ ) and the final double-bond conversion ( $P^f$ ).

The UV-curing kinetics of EB600 and its blends with HACP are shown in Figures 3 and 4. HACP gives the highest  $R_p^{\max}$  because of its higher unsaturation concentration ( $7.27 \text{ mmol}_{\text{C}=\text{C}} \text{ g}^{-1}$ ) and higher molecular mobility, which is attributed to the lower viscosity. With decreasing loading of HACP, the  $R_p^{\max}$  of the blend correspondingly decreases. However, the cured EB600 film has the highest  $P^f$  value, whereas the HACP has the lowest. It can be explained that HACP,

having high reactivity once exposed to UV light, is highly crosslinked to form a dense polymeric network, which traps residual unreacted double bonds, resulting in a lower  $P^f$  value than that of EB600 and its blends with HACP.

Different results were obtained from the photopolymerization of EB600 blends with HACP powder, as shown in Figures 5 and 6. With increasing loading of HACP powder, both  $R_p^{\max}$  and  $P^f$  decrease. Besides the effects of unsaturation concentration and viscosity, the cured HACP powder plays a rather important role. These solid particles absorb the UV light during UV curing, which influences the efficiency of photopolymerization, indicating that the high loading of additives would lead to difficult curing in UV systems.<sup>10</sup>

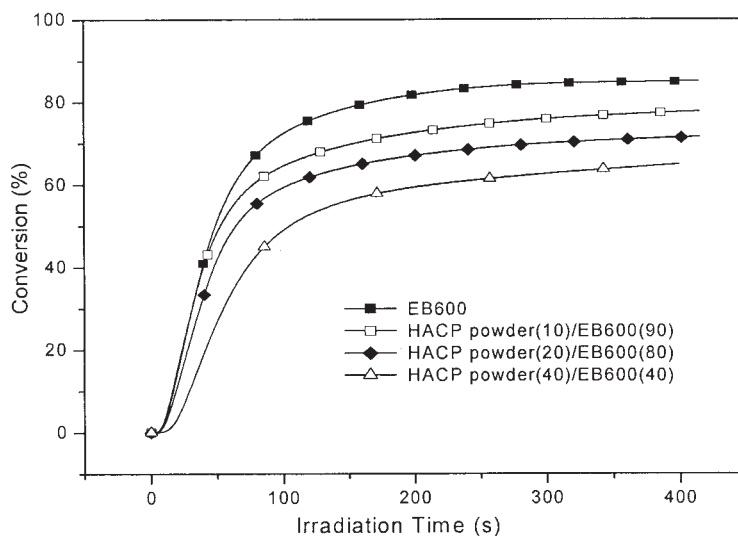


Figure 6 Unsaturation conversion of EB600 and its blends with HACP powder.

TABLE II  
LOI Values of EB600, HACP, and Their Blend Films

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
HACP powder/EB600	21.0	21.0	22.0	23.5	25.0	26.0	—

### Flame retardancy

It was found in the combustion tests that the cured EB600 film burned rapidly in air, and is completely consumed within 60 s, to leave a little black char. However, the blended films containing HACP and HACP powder exhibited flame retardancy. A loading of 20% caused the samples to self-extinguish in air. After burning, in the middle of the HACP/EB600 and HACP powder/EB600 charred areas, there were some internal regions that remain unchanged, without any evidence of combustion. The cover layer formed a black glassy char, which apparently provided a protective layer over the bulk of the sample and prevented further combustion.

The LOI measurement, a qualitative method for determining the flammability of blends, showed the same trend, as listed in Table II. The LOI values of samples increase with increasing loading of cyclophosphazene. Moreover, the LOI values of HACP/EB600 blends are generally higher than those of HACP powder/EB600 blends, especially in the high loading of cyclophosphazene.

### Thermal behavior

Figure 7 shows the TGA curves for the UV-cured EB600, HACP, HACP/EB600, and HACP powder/EB600 films. Compared with EB600 film, HACP and

its blend films have a lower initial decomposition temperature, which is attributed to the less stable P—O—C bond linkage. However, they prove to be more stable at elevated temperatures (>450°C). HACP/EB600 and HACP powder/EB600 films have exactly the same degradation behavior in the range of 260–470°C, although the former retains more residue because of its compatibility and higher crosslinking density compared with that of the latter. It might also account for the difference in the LOI values of two kinds of blends.

To further investigate the effects of HACP and HACP powder in the thermal degradation of blends, the curves of weight difference between the experimental and theoretical TG curves were computed and are shown in Figure 8. Both systems have strong destabilization zones between 300 and 450°C (with negative weight difference) and obvious stabilization above 580°C (with positive weight difference), which indicates that there are interactions between the different components in the blends during thermal degradation. This phenomenon can be explained as follows<sup>11</sup>: the phosphazene degrades first during heating and the obtained structure acts as an acid catalyst, which accelerates the cleavage of side groups and the breaking of ester groups in EB600 at 300–450°C. Then the degradation products react with the residue of EB600 and form more stable structures at elevated

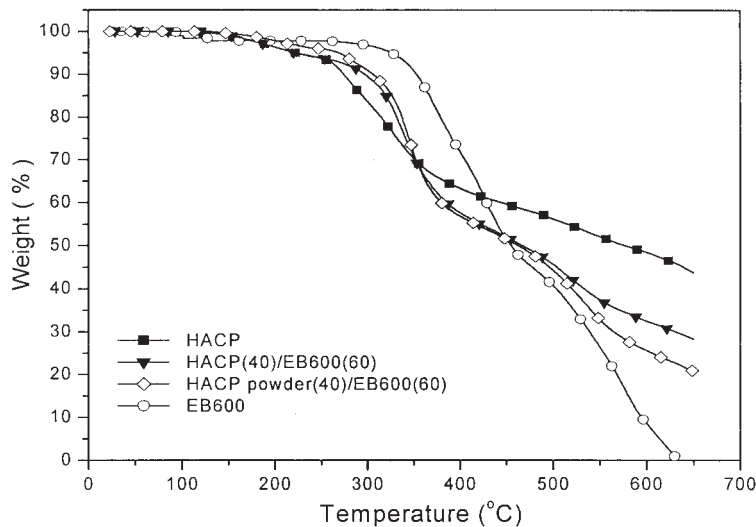


Figure 7 TGA curves of EB600 and its blends with HACP or HACP powder in air.

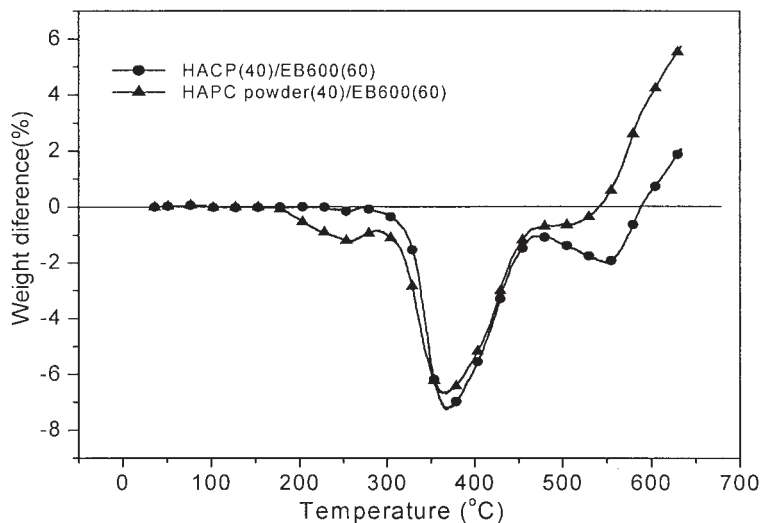


Figure 8 Curves of the weight difference for EB600 blends with HACP and HACP powder.

temperatures. This outcome is also coincident with the results previously obtained from the *in situ* FTIR measurements of these blends.<sup>7</sup>

**Dynamic mechanical thermal and mechanical properties**

The dynamic mechanical thermal properties of the UV-cured EB600 HACP and the blend films are shown in Figure 9. According to the definition,<sup>12</sup> the softening point ( $T_s$ ) is the temperature of extrapolated onset of the decrease of storage modulus, and the glass-transition temperature ( $T_g$ ) is defined as the peak position of the  $\tan \delta$  curve. The  $T_s/T_g$  ratio, which represents the width of the  $\tan \delta$  peak, is higher when the width is

narrower. It is believed that a more homogeneous film leads to a narrower  $\tan \delta$  peak, that is, a higher  $T_s/T_g$  ratio. DMTA also provides a direct means to determine the crosslink density of a highly crosslinked film by measuring the modulus at a temperature well above the  $T_g$ . If the bond angle bending and the bond breakage are eliminated by its small deformation, and the entanglements are also avoided by selecting components that give short network chains, the crosslink density ( $V_e$ ), that is, the molar number of elastically effective network chains per cube centimeter of a sample, could be calculated from the formula:  $V_e = E' / 3RT$ , where  $E'$  is the tensile storage modulus,  $R$  is the gas constant, and  $T$  is the Kelvin temperature.<sup>13</sup>

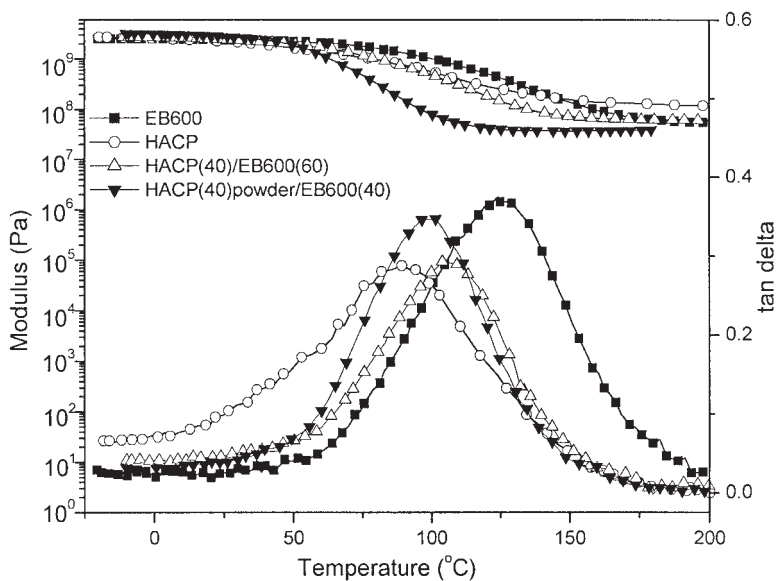


Figure 9 DMTA curves of EB600, HACP, and their blend films.

The DMTA results of the UV-cured films are listed in Table III. The addition of HACP or HACP powder causes the  $T_g$  of the blend film to shift to lower temperature, which might be explained by the incorporation of phosphorus units in polymer chains that significantly reduce the rigidity of cured films,<sup>14</sup> although the crosslinking density in the blend film increases compared with that of EB600. There is a little change in  $T_s/T_g$  ratio after adding 40% HACP, which implies that HACP has good compatibility with EB600; thus the cured film has a homogeneity similar to that of EB600. However, the addition of HACP powder decreases the  $T_s/T_g$  ratio of 0.92 for the cured EB600 film to that of 0.87 for the blend film, which suggests that the presence of HACP powder as an additive deteriorates the homogeneity of the cured film.

The tensile strength of the cured film is enhanced from 12.0 MPa of EB600 to 13.5 MPa of HACP(40)/EB600(60), whereas the elongation at break decreases slightly, from 16.4 to 15%. However the tensile strength decreases from 12.0 MPa of EB600 to 8.9 MPa of HACP powder(40)/EB600(60), and the elongation at break also decreases, from 16.4 to 12.1%, as listed in Table IV.

### CONCLUSIONS

Adding both HACP and HACP powder into EB600 can improve the flame retardancy and thermal stability at elevated temperature of the cured blend films.

**TABLE III**  
DMTA Results of EB600, HACP, and Their Blend Films

Sample	$T_s$ (°C)	$T_g$ (°C)	$T_s/T_g$	$V_e$ (mmol/cm <sup>3</sup> )
EB600	91	124	0.92	4.84
HACP	60	91	0.91	15.3
HACP(40)/EB600(60)	73	107	0.90	6.40
HACP powder(40)/ EB600(40)	50	99	0.87	3.60

**TABLE IV**  
Mechanical properties of EB600 and its blend films

EB600 (wt %)	HACP (wt %)	HACP (powder) (wt %)	Tensile strength (MPa)	Elongation (%)
100	0	0	12.0	16.4
90	10	0	12.4	16.0
80	20	0	13.1	15.3
60	40	0	13.5	15.0
90	0	10	11.5	16.1
80	0	20	10.4	15.0
60	0	40	8.9	12.1

Because of the compatibility of HACP with EB600, there is little negative effect either on the photopolymerization process or on the dynamic mechanical thermal and thermal properties of the blend films. However, the addition of HACP powder (as an additive flame retardant) into EB600 resin will deteriorate those properties of the UV-cured films because of its insolubility in EB600.

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