# The Curing Reaction and Physical Properties of DGEBA/ DETA Epoxy Resin Blended with Propyl Ester Phosphazene

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ABSTRACT: The influences of different amounts of propyl ester phosphazene (FR) on the curing kinetics and physical properties of diglycidyl ether of bisphenol A (DGEBA) epoxy prepolymer cured with diethylenetriamine (DETA) were investigated with DSC, SEM, DMA, and tensile testing. The results revealed that FR could be a catalyst or a diluent depending on the FR content. In addition, the blending systems were partially miscible. The tensile strength and modulus of blends decreased with increasing amounts of FR, but the elongation increased with increasing FR. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 229–237, 1999

**Key words:** epoxy resin; curing kinetics; propyl ester phosphazene; mechanical properties

# INTRODUCTION

It is well known that the main structure of epoxy, a typical thermosetting resin, is formed through the reaction of epoxide groups and active hydrogen atoms (such as amine and acid). Epoxy resins are used in many fields such as printed circuit boards and aerospace, because it exhibits excellent mechanical properties, low shrinkage, and high performance. Studies<sup>1-6</sup> on the thermodynamics, kinetics, physical properties, and applications have been reported.

Recently, much work has been directed toward improving epoxy thermal stability by use of flame retardants or other modifications. There is a growing demand to avoid the generation of toxic and corrosive gases during thermal degradation. Therefore, halogen flame retardants have been gradually replaced by nonhalogen compounds such as propyl ester phosphazene (FR) that contained higher phosphorus and nitrogen elements. Because phosphazene compounds<sup>7-9</sup> contained tertiary amine and secondary amine structures at room temperature and during thermal degradation process, respectively, the curing kinetics of epoxy resin would be surely influenced by FR content. Therefore, the curing kinetics of epoxy resin blended with FR were studied using differential scanning calorimeter (DSC) by dynamic and isothermal scan method. Additionally, the degree of compatibility of blends was examined with a scanning electron microscope (SEM) and a dy-

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Code	Weight Ratio (DGEBA/DETA/FR)	P (wt %) <sup>a</sup>	$P \ ({ m wt} \ \%)^{ m b}$
Ep0f Ep1f Ep2f Ep3f FR	$\begin{array}{c} 89.37:10.63:0\\ 82.04:9.75:8.21\\ 75.82:9.02:15.16\\ 70.48:8.38:21.14\\ 0:0:100\end{array}$	$0.00 \\ 1.91 \\ 3.50 \\ 4.86 \\ 21.0$	< 0.01 1.86 3.47 4.60 21.0

Table ISymbol and Phosphorus Content ofBlended Samples

<sup>a</sup> Phosphorus content from composition calculation. <sup>b</sup> Phosphorus content by the colorimeter.

namic mechanical analyzer (DMA). The influence of FR on the thermal degradation behavior of diglycidyl ether of bisphenol A (DGEBA) cured with diethylenetriamide (DETA) will be discussed in another article.

## **Kinetic Background**

Based on the literature,<sup>10,11</sup> the possible mechanism of epoxy cured with amine curing agents is as follows:

$$\begin{array}{c} O & OH \\ H_2C - CH - + RNH_2 \rightarrow RNHCH_2CH - (1) \end{array}$$

$$\begin{array}{c} O \\ H_2C - CH - + RNHCH_2CH - \rightarrow \end{array}$$

$$\begin{array}{c} O \\ H_2C - CH - + RNHCH_2CH - \rightarrow \end{array}$$

$$\begin{array}{c} OH \\ H_2C - CH - + - CHOH - \rightarrow \end{array}$$

$$\begin{array}{c} O \\ H_2C - CH - + - CHOH - \rightarrow \end{array}$$

$$OH$$

| | --CH--O--CH<sub>2</sub>CH-- (3)

The extent of reaction depends on the reactivity of the amine, reaction temperature, and the ratio of epoxy equivalent mole to amine equivalent mole. Equations (1) and (2) occur under normal curing conditions. Equation (3) is an etherification reaction that can be neglected at molar stoichiometric conditions and when cur-



**Figure 1** Dynamic DSC thermograms of three epoxy blends at a heating rate of 10°C/min under nitrogen atmosphere.

ing temperature is below 150°C. This is especially true for aliphatic amines (such as DETA) cured with DGEBA. Here the etherification reaction based on the literature does not occur. For simplicity, the curing kinetics of epoxy resin blended with FR was analyzed using an *n*th-order model. The general kinetic equation for the *n*th-order reaction is given as follows<sup>12-14</sup>:

$$\frac{dX}{dt} = k(T)(1-X)^n \tag{4}$$

$$k(T) = Z \, \exp\!\left(\frac{-E_a}{RT}\right) \tag{5}$$

where *X* is the epoxy conversion, *t* is the reaction time, K(T) is the rate constant at temperature *T*, *Z* is the frequency factor, *n* is reaction order, and  $E_a$  is the activation energy.

The reaction order, frequency factor, and activation energy can be obtained from the following equations:

Table IICuring Temperature Characteristicsof Various Epoxy Blend Systems

Code	$T_{\rm ini}(^{\rm o}{\rm C})$	$T_p \;(^{\circ}\mathrm{C})$	$T_{\rm end}~(^{\rm o}{\rm C})$
Ep0f Ep1f Ep2f	37 30 30	100     85     87	$163 \\ 145 \\ 149$

$$\ln \frac{dX}{dt} = \ln k(T) + n \ln(1 - X) \tag{6}$$

$$\ln k(T) = \ln Z - \frac{E_a}{RT}$$
(7)



**Figure 2** Extent of reaction as a function of time at four different isothermal temperatures for (a) Ep0f, (b) Ep1f, (c) Ep2f.



**Figure 3** The reaction order of epoxy blend determined from the logarithmic value of the reaction rate versus logarithmic uncured mole fraction, (a) Ep0f, (b) Ep1f, (c) Ep2f.

# **EXPERIMENTAL**

## **Materials**

The epoxy prepolymer in this study was DGEBA (DER 331, from Dow Chemical Company, USA)



**Figure 4** Activation energy and frequency factor of the epoxy blend determined from the logarithmic value of rate constant versus inverse temperature, (a) Ep0f, (b) Ep1f, (c) Ep2f.

with an epoxide equivalent weight equal to 190 g/eq, determined by acid titration.<sup>11</sup> A stoichiometric amount of DETA (Janssen Chimica Company, Japan, amine equiv wt = 20.63 g/eq) was used as a curing agent. FR was supplied by Chung Shan Institute of Science and Technology (Taiwan). The chemical structure of these materials is shown below.



The composition of epoxy/FR blends are shown in Table I. These epoxy/FR blends are referred to as Ep0f, Ep1f, Ep2f, and Ep3f.

#### **DSC Sample Preparation**

OC<sub>3</sub>H<sub>7</sub>

The DSC samples were prepared by following the formulation in Table I; the samples weighed from 5 to 10 mg and were enclosed in aluminum pans and stored in a vessel full of liquid nitrogen until used.

The curing kinetics of epoxy blends were determined by a DSC (DuPont Model 910) coupled with a thermal analyzer computer Model 9900. Tests were run according to the dynamic and isothermal method. The thermal program used in the dynamic scan was from ambient temperature  $(25^{\circ}C)$  to 200°C at a heating rate of 10°C/min under nitrogen atmosphere. The isothermal temperatures were determined by the dynamic result. In isothermal experiments, the conversion (x) of epoxide at any time was assumed proportional to the heat of reaction and was calculated from



**Figure 5** The ratio of curing rate constant of epoxy blend relative to pure epoxy resin as a function of FR content.

$$x(t) = \frac{\Delta H_{\rm iso}(t)}{\Delta H_T} = \frac{\Delta H_{\rm iso}(t)}{\Delta H_{\rm iso} + \Delta H_{\rm resi}} \tag{8}$$

where x(t) is the conversion of epoxy at any time t,  $\Delta H_{\rm iso}(t)$  is the accumulated heat of isothermal reaction at any time t,  $\Delta H_{\rm iso}$  is the overall heat of reaction during the isothermal scan,  $\Delta H_{\rm resi}$  is the postcure heat of reaction during redynamic scan, and  $\Delta H_T$  is total heat of reaction.

# **Measurement of Phosphorus Content**

The phosphorus content of the epoxy blends was determined using a colorimeter.<sup>15</sup> The results are listed in Table I.

#### Morphology

The morphology and compatibility of epoxy blends were examined with a Jeol JSM-T100 SEM using an accelerating voltage of 20 kV.

## The Interaction Between Epoxy and FR

The interaction between epoxy resin and FR was investigated by using a Biorad 3240 + FTS-40 fourier transform infrared spectrometer (FTIR).

# **Dynamic Mechanical Spectra**

The glass transition temperatures  $(T_g)$  of the epoxy blends were obtained from tan  $\delta$  using a Du-



Figure 6 Scanning electron micrographs of epoxy blends. (a) Ep0f, (b) Ep1f, (c) Ep2f, (d) Ep3f (magnification,  $\times 10,000$ ).



Figure 7 FTIR spectra of FR and various epoxy blends.

Pont DMA 983. The sample sizes were  $30 \times 10 \times 2$  mm and the heating rate was 5°C/min under nitrogen atmosphere.

### **Mechanical Properties**

The mechanical properties of the epoxy blends were measured using a RTM-IT universal tensile test instrument at a speed of 2 mm/min.

## **RESULTS AND DISCUSSION**

### Kinetic Analysis of Curing

Figure 1 shows the DSC thermograms for three uncured epoxy blends at a heating rate of 10°C/min under nitrogen atmosphere. Table II presents the results of DSC analysis including the initiated  $(T_{\rm ini})$ , peaked  $(T_p)$ , and completed  $(T_{\rm end})$  temperatures for various epoxy blends. The

results indicated that the curing reaction of the epoxy blend was accelerated by blending with FR. The reaction speed for three epoxy blends was Ep1f > Ep2f > Ep0f. Possible explanations for this phenomenon were (1) the reaction was catalyzed because of FR, tertiary amine structure, and (2) FR could act as a diluent. However, its diluent effect was less important than its catalyst effect. Additionally, the isothermal experiments were conducted at 50, 60, 70, and 80°C for comparison with the above dynamic results. Figure 2(a-c) shows the curing extent (X) versus curing time (t) at various isothermal curing temperatures for three epoxy blends. The kinetic parameters such as frequency factor (Z), activation energy  $(E_a)$ , and reaction order (n) for curing reaction of three epoxy blends determined during the isothermal experiments are shown in Figures 3 and 4. These were obtained with Figure 2 using eq. (6)–(7) under consideration far from diffusion control. From the results of three epoxy blends, both frequency factor (Z) and activation energy  $(E_a)$  decreased with increasing FR content. In addition, the reaction order (n) of three epoxy blends all appear between 1.0 and 1.40. The ratios of curing rate constants of various epoxy blends relative to pure epoxy at four different temperatures are shown in Figure 5. These results revealed that the effect of FR as a catalyst was obviously greater than its effect as a diluent, when temperature was  $<70^{\circ}$ C and the FR content < 10 phr. Other cases showed the reverse trend.

# Miscibility Between FR and Epoxy Resin by SEM, FTIR, and DMA

The SEMs of the fracture surface, under liquid nitrogen, of epoxy blends are shown in Figure 6. EpOf showed only one phase that was very smooth in the fracture surface as shown in Figure 6(a). The apparent cavitated holes of the epoxy blends in Figure 6(b–d) corresponded to the contribution of FR particles, and the number of these holes increased with increasing FR content. However, the hole size remained about 0.5  $\mu$ m and there were no obvious whiskers in the fracture surface of epoxy blends. The FTIR spectra and functional group frequencies characteristic of FR and various epoxy blends are shown in Figure 7 and Table III, respectively. Here, the change of chemical shifts or the production of new chemical bonds due to the addition of FR were not observed, which suggested that only weak interaction ex-

Functional Group	Wavenumber $(cm^{-1})$	Type
ОН	$\sim 3500{-}3200$	$\mathbf{S}$
$\langle \bigcirc \rangle$	3060	С—H, S
$\begin{array}{c} \mathbf{CH}_3 \\ \mathbf{CH}_2 \end{array}$	2980, 2960 2880	S S
$\langle \bigcirc \rangle$	1600, 1580	C==-C, S
$\langle \bigcirc \rangle$	1510, 1468	C==-C, S
С—О	1250	S
0	1040	S
CH <sub>2</sub> —CH <sub>-</sub>	$\sim 3050{-}2990$	С—Н, S
CH <sub>2</sub> —CH <sub>-</sub>	880	Ring vib.
CH <sub>2</sub> —CH	916	S
-	820	В
$N \underbrace{\overset{CH_2}{\underset{CH_2}{\longleftarrow}}_{CH_2}}_{CH_2}$	880	C—N, S
$(P \rightarrow O - C$ P - O - (C) N = P	$\sim 1050-970\ \sim 830-740\ \sim 1440-1170$	S S
H O      NP	1400	s
P-O N-H P-N P=O	$\sim 1040-910$ $\sim 850-700$ $\sim 1100-930$ $\sim 1250-1150$	S B S S

Table III Characteristics of FTIR for Epoxy and Propyl Ester Phosphazene

S, stretching vibrations; B, bending vibrations.

isted in the epoxy blends. Figure 8 shows  $tan\delta$ as a function of temperature for various epoxy blends. The results showed that  $T_g$  decreased with increasing FR content but did not obviously obey the Fox equation. Therefore, the SEM, FTIR, and DMA evidence could explain how the epoxy blend systems were partially miscible.



**Figure 8** The tan $\delta$  as a function of temperature for various epoxy blends.

#### **Tensile Properties**

The relationship between mechanical properties and FR content of epoxy blends, with cure cycles of: 70 and 95°C/1 h, are shown in Figure 9. The results showed that the tensile strength and modulus of epoxy blends decreased with increasing FR content, but the elongation of epoxy blends increased with increasing FR content. These results agreed with the SEM observation. The fracture of material often occurs at the weakest points, the interface between epoxy resin and FR. Therefore, with increasing FR content, corresponding to increasing interface area, the tensile



**Figure 9** Mechanical properties of various epoxy blends as a function of FR content.

strength of epoxy blend decreased. Because FR could also act as a plasticizer, the modulus decreased with increasing FR content, and the elongation increased with increasing FR content.

# CONCLUSIONS

From the studies of the curing kinetics, it was found that FR accelerated the curing reaction when the temperature was  $<70^{\circ}$ C and FR content was <10 phr. In other cases, the diluent effect was greater than the effect of catalyst. Only partial miscibility was found in epoxy resins blended with FR using SEM and DMA. Additionally, the modulus decreased with increasing the FR content but the elongation increased.

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