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A Kinetic Study of Biphenyl Type Epoxy-Xylok Resin System with Different Kinds of Catalysts

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The investigation of cure kinetics of biphenyl epoxy (4,4-diglycidyl-3,3',5,5'-tetramethyl biphenyl)-xylok resin system with four different catalysts was performed by differential scanning calorimeter using an isothermal approach. All kinetic parameters of the curing reaction including the reaction order, activation energy and rate constant were calculated and reported. The results indicate that the curing reaction of the formulations using triphenylphosphine (TPP) and 1-benzyl-2-methylimidazole (1B2MI) as a catalyst proceeds through a first order kinetic mechanism, whereas that of the formulations using diazabicycloundecene (DBU) and tetraphenyl phosphonium tetraphenyl borate (TPP-TPB) proceeds by an autocatalytic kinetic mechanism. To describe the cure reaction in the latter stage, we have used the semiempirical relationship proposed by Chern and Poehlein. By combining an *n*th order kinetic model or an autocatalytic model with a diffusion factor, it is possible to predict the cure kinetics of each catalytic system over the whole range of conversion.

Introduction

The biphenyl type epoxy resin is of great advantage to high reliable epoxy molding compound (EMC) for good adhesion, high toughness, and the feasibility of high filler loading. However, this resin system has very low reaction rate and it is difficult to control the curing reaction. Hence, EMC based on the biphenyl type epoxy could give rise to the molding problems. To obtain the optimum curing condition and good moldability of such EMC, the selection of the most adequate catalyst should be performed and it is very important to know the influence of the catalysts on the curing reaction of biphenyl epoxy resin compositions.

In the previous study,¹ we investigated the curing characteristics of the biphenyl type epoxy resin with different phenolic-functional hardeners using differential scanning calorimetric (DSC) technique and reported that the curing reaction of the formulation using phenol novolac with triphenylphosphine as a catalyst proceeds through an autocatalytic kinetic mechanism such as phenol novolac cured *o*-cresol novolac epoxy resin, and the curing reaction of formulations using xylok or dicyclopentadiene type phenol resin (DCPDP) under the same catalyst proceeds by a first order kinetic mechanism.

Although, recently, phenol novolac cured epoxy resin is most widely used for semiconductor encapsulation among the above epoxy-hardener systems,² it is expected that the formulation with xylok will be used for ultra large scale integrated circuit near future because of low moisture content, high heat resistance and good adhesion. However the in-

vestigations of catalyst effect on cure properties for this system have not been carried out. In this study, therefore, the effects of catalyst on the curing characteristics of the biphenyl type epoxy resin reacted with xylok curing agent were investigated using DSC technique. The curing mechanism of the formulations with different catalysts were interpreted by means of an *n*th order and an autocatalytic mechanism,³⁻⁷ and the curing kinetics in the overall conversion region have been analyzed using the kinetic and diffusion model.

Experimental

Materials. Epoxy resin used in this study was commercially available biphenyl epoxy resin (YX-4000H) obtained from Yuka Shell Co. Hardener used was xylok obtained from Mitsui Tohatsu Chemical Co. Triphenylphosphine (TPP, Hokko Chemical Co.), 1-benzyl-2-methylimidazole (1B2MI, Nippon-Gosei Co.), diazabicycloundecene (DBU, SAN-APRO), and tetraphenyl phosphonium tetraphenyl borate (TPP-TPB, Hokko Chemical Co.) as a catalyst were used as received. Detailed descriptions of chemical structures are summarized in Table 1.

Sample Preparation. All epoxy resin compositions in this study contain the same equivalent weight ratio (1:1) of epoxy and phenolic group, and the content of each catalyst is fixed to 1.5 parts per hundred resin (phr) to epoxy resin. Epoxy resin and hardener were well mixed at 120 °C until a homogeneous solution was obtained. This mixture cooled down to 80 °C. The catalyst was added and fully

Table 1. Description of Raw Materials Used in This Study

| Materials | Structure |
|--|-----------|
| Biphenyl Epoxy Resin (YX-4000) | |
| Xylok | |
| Triphenylphosphine (TPP) | |
| Tetraphenyl phosphonium tetraphenyl borate (TPB) | |
| Diazabicycloundecene (DBU) | |
| 1-Benzyl-2-methylimidazole (1B2MI) | |

stirred for about 10 seconds. Each sample was immediately quenched and stored in a refrigerator at 4 °C.

DSC Measurement. Calorimetric measurements were performed using a TA Instruments differential scanning calorimeter (TA-2020). This was calibrated in the -40 °C-450 °C region. Isothermal and dynamic-heating experiments were conducted under a nitrogen flow of 60 mL/min. For dynamic cure, the sample was heated at a rate of 5 °C/min from -10 to 300 °C. A set of isothermal cure curves has been obtained in order to evaluate the kinetic parameters for the curing reactions. To measure glass transition temperature during curing reaction, each sample was quenched to -40 °C after isothermal curing in the range from 5 to 60 min, and subsequently scanned at a heating rate of 5 °C/min up to 300 °C.

Results and Discussion

Figure 1 shows a series of isothermal reaction rate curves as a function of time for biphenyl epoxy resin compositions with different kinds of catalysts. For the formulation using TPP or 1B2MI, maximum reaction rate occurs at time zero. However, for the formulation using DBU or TPP-TPB, the peaks were found, and the value of the peak was increased and shifted to shorter time with increasing temperature. Fractional conversion were calculated from Figure 1 and the conversion rate was plotted as a function of conversion in Figure 2. It can be seen that the curing reaction in the system using DBU and TPP-TPB proceeds through the autocatalytic kinetic mechanism with maximum conversion rate in 10-20% and in 20-30% conversion region. The other curing reactions proceed by an n th order kinetic mechanism.

For thermosets that follow an n th order curing reaction, isothermal reaction conversion rate is proportional to the fraction of material unreacted ($1-\alpha$), as expressed in the form shown below:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \quad (1)$$

where n is the reaction order and k is the rate constant.

The kinetic parameters of epoxy resin compositions with TPP and 1B2MI were obtained by fitting the experimental

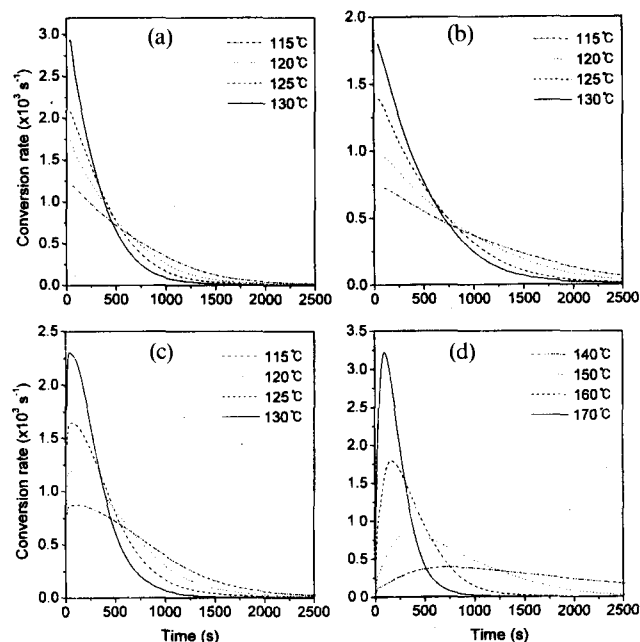


Figure 1. Conversion rate as a function of time at several isothermal temperatures of biphenyl epoxy resin composition with (a) TPP, (b) 1B2MI, (c) DBU, and (d) TPP-TPB.

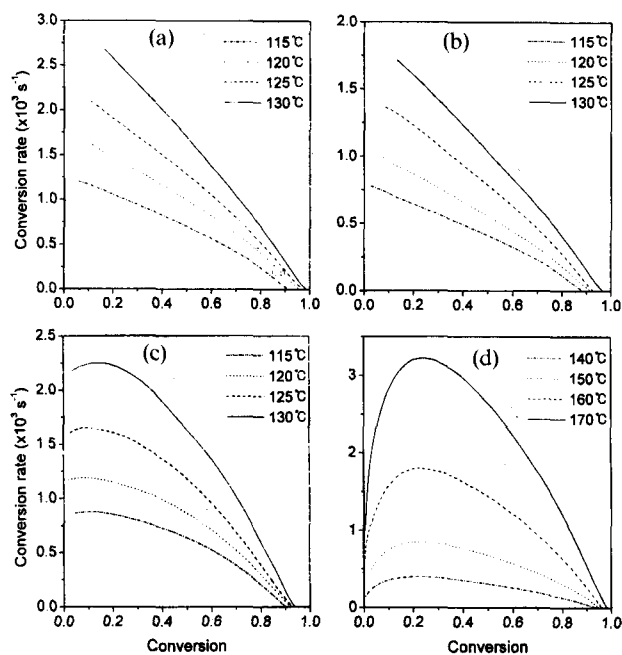


Figure 2. Isothermal conversion rate as a function of conversion of biphenyl epoxy resin composition with (a) TPP, (b) 1B2MI, (c) DBU, and (d) TPP-TPB.

data in the first portion of cure to equation (1) and they are summarized in Table 2. It can be considered that the curing process of the formulations using TPP and 1B2MI is a first-order kinetic mechanism. Typical comparisons between experimental and an n th order model of the formulation with TPP and 1B2MI with previously determined model parameters are shown in Figure 3. The curing temperature was 120 °C. Good agreement is observed up to 70-80% in the for-

Table 2. Kinetic Parameters of Epoxy Resin Compositions Following n th Order Cure Reaction Obtained from Each Isothermal Test

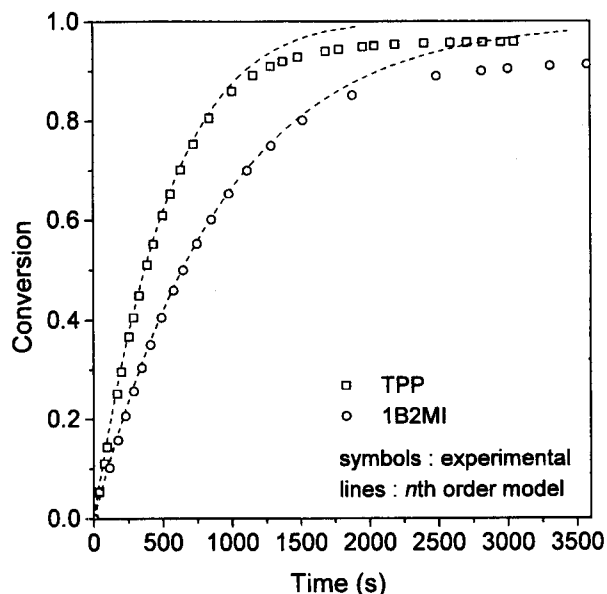
| Catalyst added | Temperature (°C) | k | n |
|----------------|------------------|-----------------------|------|
| TPP | 115 | 1.28×10^{-3} | 0.89 |
| | 120 | 1.79×10^{-3} | 0.86 |
| | 125 | 2.32×10^{-3} | 0.87 |
| | 130 | 3.17×10^{-3} | 0.92 |
| 1B2MI | 115 | 0.80×10^{-3} | 0.96 |
| | 120 | 1.07×10^{-3} | 0.97 |
| | 125 | 1.52×10^{-3} | 0.97 |
| | 130 | 1.98×10^{-3} | 0.95 |

mulations with TPP and 1B2MI, beyond that region deviations are observed. The deviations observed are attributed to the gelation where the mobility of the reacting groups is hindered and the rate of conversion is controlled by diffusion rather than by kinetic factors.⁸

To consider diffusion effect more precisely, we have used semiempirical relationship, based on the free volume considerations proposed by Chern and Poehlein.⁹ In this relationship, a diffusion factor, $f(\alpha)$, has been defined with two empirical parameters as follows;

$$f(\alpha) = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (2)$$

where C is the constant and α_c is the critical conversion. The effective reaction rate at any conversion is equal to the chemical reaction rate multiplied by $f(\alpha)$. In this study, $f(\alpha)$ was determined as the ratio of experimental reaction rate to the reaction rate predicted on the basis of the n th order cure kinetic model in equation (1). The values of C and α_c were obtained by fitting $f(\alpha)$ versus α at various temperatures for the system with TPP and 1B2MI. They are summarized in

**Figure 3.** Comparisons of experimental data with n th order cure model for biphenyl epoxy resin composition with TPP (□) and 1B2MI (○).**Table 3.** Values of the Constant C and Critical Conversion at Different Temperature for the Formulation Following n th Order Cure Reaction

| Catalyst added | Temperature (°C) | C | α_c |
|----------------|------------------|------|------------|
| TPP | 115 | 27.5 | 0.85 |
| | 120 | 32.7 | 0.90 |
| | 125 | 33.6 | 0.92 |
| | 130 | 48.3 | 0.95 |
| 1B2MI | 115 | 29.5 | 0.83 |
| | 120 | 32.6 | 0.86 |
| | 125 | 36.2 | 0.88 |
| | 130 | 41.7 | 0.92 |

Table 3. From Table 3, it can be seen that the α_c value of the formulation with TPP is higher than that of the formulation with 1B2MI at the same curing temperature. It could be considered that this result would be due to the higher crosslinking network of the system using 1B2MI than that using TPP. To verify this phenomenon, the glass transition temperatures were measured at a certain fractional reaction conversion. Figure 4 shows the experimental results of T_g versus α change. At the same conversion, the values of T_g of the formulation with 1B2MI is higher than that of formulation with TPP. It could be concluded that the mobility of reacting groups of the system with 1B2MI is hindered at lower conversion compared to the system with TPP.

A more general model is necessary to predict the advance of cure at different temperatures. Considering diffusion effect, equation (1) can be rewritten as follows:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (3)$$

In this study, based on the assumptions proposed by Barral *et al.*,¹⁰ the generalized parameters in an n th order kinetic model in equation (3) were obtained and summarized in

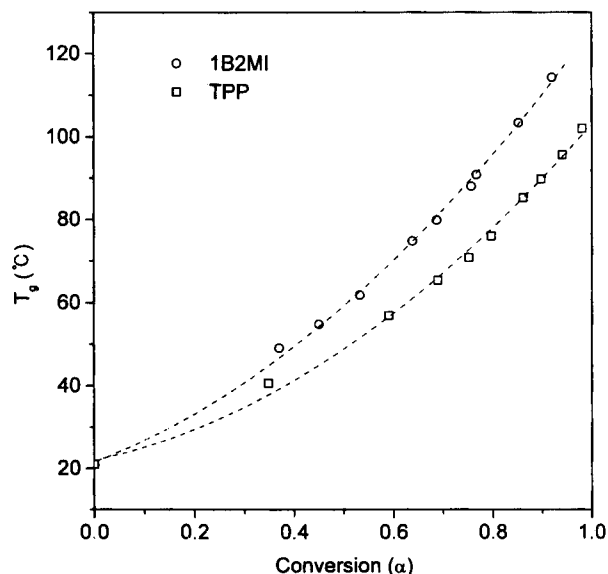
**Figure 4.** Relationships between T_g and reaction conversion of biphenyl epoxy resin composition with TPP (□) and 1B2MI (○).

Table 4. Generalized Kinetic Parameters for the Formulation Following n th Order Cure Reaction

| Catalyst Added | Generalized n th order Kinetic Model | value |
|----------------|--|------------------------------------|
| TPP | k | $3.13 \times 10^7 \exp(-77123/RT)$ |
| | n | 0.9 |
| | C | 36 |
| | α_c | $-1.6262 + 0.0064T$ |
| 1B2MI | k | $4.44 \times 10^7 \exp(-79823/RT)$ |
| | n | 1 |
| | C | 35 |
| | α_c | $-1.4214 + 0.0058T$ |

Table 4. Figure 5 show the comparisons between the experimental values of α with these values obtained from the generalized n th order cure kinetic model for the composition with TPP and 1B2MI at each curing temperature. Good agreement was found over the whole curing temperature range.

For an autocatalytic curing reaction, isothermal reaction rate is proposed by Kamal and expressed as shown below:

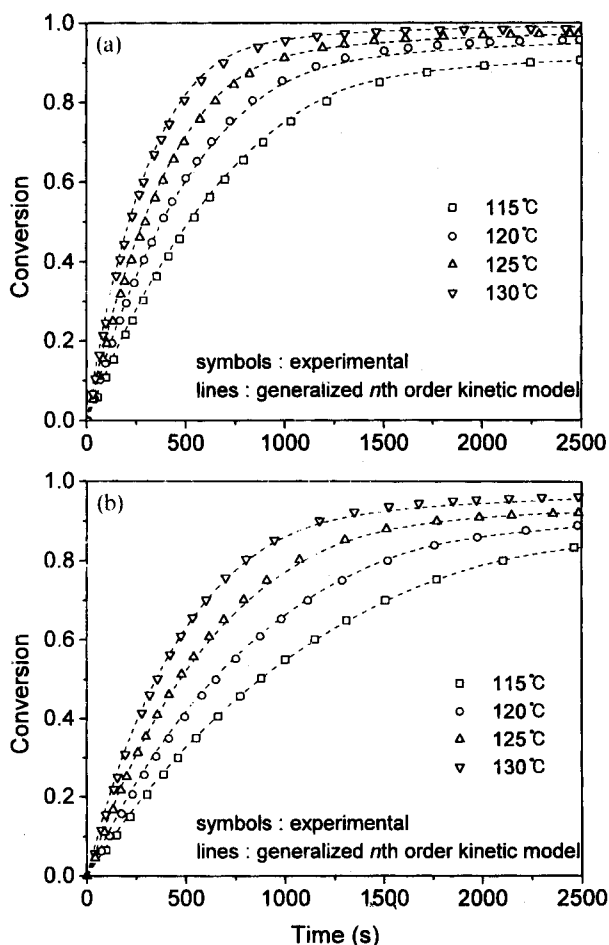


Figure 5. Comparison between the experimental values of α with these values obtained from generalized n th order cure model for the composition with (a) TPP and (b) 1B2MI at each curing temperature.

Table 5. Kinetic Parameters of the Formulation Following Autocatalytic Cure Reaction Obtained from Each Isothermal Test

| Catalyst added | Temperature (°C) | k_1 | k_2 | m | n |
|----------------|------------------|-----------------------|-----------------------|------|------|
| DBU | 115 | 0.88×10^{-3} | 1.15×10^{-3} | 1.10 | 1.16 |
| | 120 | 1.20×10^{-3} | 1.66×10^{-3} | 1.16 | 1.20 |
| | 125 | 1.58×10^{-3} | 2.19×10^{-3} | 0.99 | 1.21 |
| | 130 | 2.15×10^{-3} | 2.88×10^{-3} | 0.93 | 1.17 |
| TPP-TPB | 140 | — | 0.90×10^{-3} | 0.37 | 1.18 |
| | 150 | — | 1.88×10^{-3} | 0.36 | 1.10 |
| | 160 | — | 3.63×10^{-3} | 0.35 | 1.11 |
| | 170 | — | 7.54×10^{-3} | 0.38 | 1.12 |

$$\frac{d\alpha}{dt} = (k_1 + k_2 \alpha^m) (1 - \alpha)^n \quad (4)$$

where m and n are the reaction order and k_1 and k_2 are kinetic rate constants.

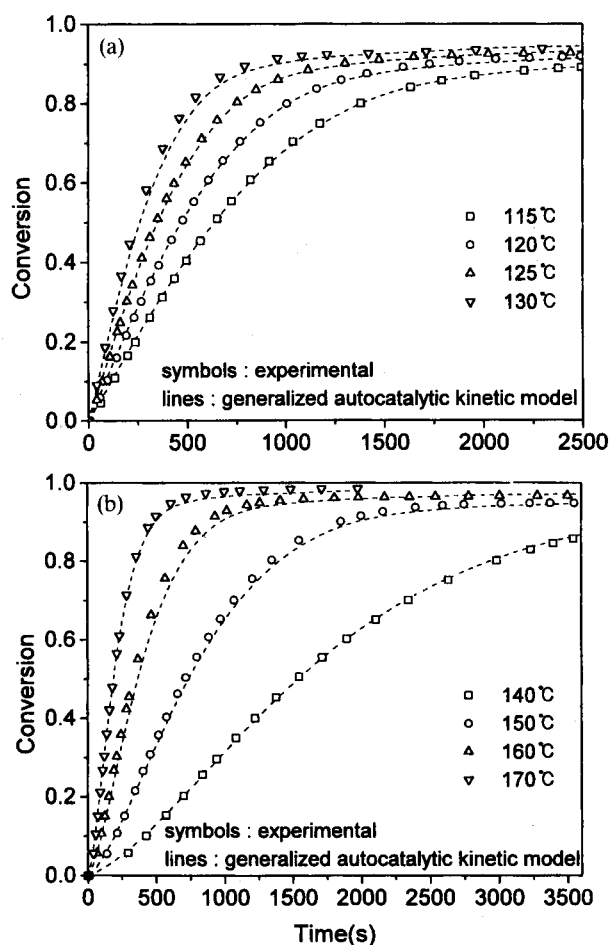
As previously described, the curing reaction of the formulation using DBU or TPP-TPB as a catalyst proceeds by an autocatalytic cure kinetics. But the composition with DBU and TPP-TPB could be employed somewhat different reaction step. As seen from Figure 2, since the initial reaction rate of the system with DBU is not zero, the nonzero initial reaction rate should be considered to compute kinetic parameters. In the system with TPP-TPB, the initial reaction rates observed at each curing temperature were so negligibly small that k_1 in equation (4) can be considered to be zero. In this study, without any constraints on the parameters k_1 , k_2 , m , and n , they were calculated by fitting the experimental data to equation (4) in the first portion of cure up to 70-90% cure depending on the composition and the curing temperature.^{7,11} The resulting data obtained from this method are summarized in Table 5 for all isothermal experiments of the composition with DBU and TPP-TPB. To predict precisely the cure kinetics over the whole range of conversion, modifications of an autocatalytic model were performed by introduction of a diffusion term as described in equation (2). $f(\alpha)$ at different temperature for the systems with DBU and TPP-TPB was obtained and the resulting are summarized in Table 6. As in the system following an n th order cure kinetics, the generalized kinetic parameters are obtained and summarized in Table 7. Figure 6 shows the comparison between the experimental values of α with

Table 6. Values of the Constant C and Critical Conversion at different temperature for the Formulation Following Autocatalytic Cure Reaction

| Catalyst added | Temperature (°C) | C | α_c |
|----------------|------------------|------|------------|
| DBU | 115 | 35.9 | 0.86 |
| | 120 | 40.2 | 0.87 |
| | 125 | 47.7 | 0.88 |
| | 130 | 41.5 | 0.88 |
| TPP-TPB | 140 | 49.2 | 0.92 |
| | 150 | 59.8 | 0.93 |
| | 160 | 53.7 | 0.95 |
| | 170 | 55.2 | 0.96 |

Table 7. Generalized Kinetic Parameters for the Formulation Following Autocatalytic Cure Reaction

| Catalyst Added | Kinetic parameter | value |
|----------------|-------------------|--|
| DBU | k_1 | $1.94 \times 10^7 \exp(-76825/RT)$ |
| | k_2 | $4.88 \times 10^7 \exp(-78867/RT)$ |
| | m | 1.0 |
| | n | 1.2 |
| | C | 35 |
| | α_c | $0.3188 + 0.0014T$ |
| TPP-TPB | k_1 | - |
| | k_2 | $3.03 \times 10^{10} \exp(-106976/RT)$ |
| | m | 0.4 |
| | n | 1.1 |
| | C | 54 |
| | α_c | $0.3408 + 0.0014T$ |

**Figure 6.** Comparison between the experimental values of α_c with these values obtained from generalized autocatalytic model for the composition with (a) DBU and (b) TPP-TPB at each curing temperature.

these values obtained from generalized autocatalytic model for the composition with DBU and TPP-TPB at each curing temperature. Good agreement was found over the whole curing temperature range.

Conclusions

The isothermal curing reaction of biphenyl type epoxy-xylok resin system was mostly dependent on the type of catalyst. The curing reaction of formulations using TPP or 1B2MI as a catalyst proceeds through a first-order kinetic mechanism, whereas the formulation using DBU or TPP-TPB proceeds by an autocatalytic kinetic mechanism.

The n th order cure model obtained from the experimental data of the formulations with TPP and 1B2MI agreed well with the experimental data in the first stages of cure up to onset of gelation, after which deviations are observed. The mobility of reacting groups of the system with 1B2MI is hindered compared to TPP due to the higher crosslinking network of the system using 1B2MI catalyst. As in the n th order cure model, the autocatalytic model obtained from the experimental data of the formulations with DBU and TPP-TPB agreed well with the experimental data in the first stages of cure.

To describe the cure in the latter stages of reaction of each catalytic system, we have used semiempirical relationship proposed by Chern and Poehlein.⁹ The corresponding model coupled with diffusion factor can predict all stages of reaction over the whole curing temperature range.

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