

Kinetic Study of the Effect of Catalysts on the Curing of Biphenyl Epoxy Resin

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Received 12 June 1997; accepted 5 October 1997

ABSTRACT: The investigation of cure kinetics of biphenyl epoxy (4,4'-diglycidyl-3,3',5,5'-tetramethyl biphenyl)dicyclopentadiene type phenolic resin system with different kinds of catalysts was performed by a 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), 1-benzyl-2-methylimidazole (1B2MI), and tris(4-methoxyphenyl)phosphine (TPAP) as a catalyst proceeds through an n th-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 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. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1125–1137, 1998

Key words: biphenyl epoxy resin; dicyclopentadiene-type phenolic resin; catalyst; cure kinetics

INTRODUCTION

A high filler loading technique is very important to obtain a high reliable epoxy molding compound (EMC) for ultralarge-scale integrated circuits (ULSI) packaging. However, there are limitations to the development of the high filler EMC using normal *o*-cresol novolac epoxy resin, which is widely used as the base material of EMC for large-scale integrated circuits (LSIs), due to high viscosity. Hence, low viscosity epoxy resin such as biphenyl-type epoxy (4,4'-diglycidyl-3,3',5,5'-tetramethyl biphenyl) are required.¹ The biphe-

nyl type epoxy resin is of great advantage for good adhesion, high toughness, and the feasibility of high filler loading. But it has very low reaction rate, and thus EMC based on the biphenyl type epoxy could give rise to the molding problems.² To obtain the optimum curing condition and good moldability of such EMC, not only the most adequate catalyst should be selected, but the influence of the catalysts on the curing reaction of biphenyl epoxy resin compositions should be investigated.

In the previous study,² we investigated the curing characteristics of biphenyl-type epoxy resin with different phenolic-functional hardeners using the differential scanning calorimetric (DSC) technique, and reported that the curing reaction of formulation using phenol novolac with triphe-

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Journal of Applied Polymer Science, Vol. 68, 1125–1137 (1998)
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nylphosphine as a catalyst proceeds through an autocatalytic kinetic mechanism like the phenol novolac-cured *o*-cresol novolac epoxy resin,³ and the curing reaction of formulations using xylok or dicyclopentadiene-type phenolic resin (DCPDP) under the same catalyst proceeds by a first-order kinetic mechanism.

Among the above epoxy-hardener systems, the formulation with DCPDP is most expected to give a high reliable EMC because of the low moisture absorption and good adhesion. However, the investigations of a catalyst effect on cure properties for this system have not been carried out. In this study, therefore, the effects of catalysts on the curing characteristics of biphenyl-type epoxy reacted with the DCPDP curing agent were investigated using the DSC technique. The curing mechanism of the formulations with different catalysts was interpreted by means of an *n*th-order and an

autocatalytic mechanism,⁴⁻⁷ 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 the commercially available biphenyl epoxy resin (YX-4000H) obtained from Yuka Shell Epoxy Co. Hardener used was DCPDP obtained from Nippon Petrochemicals Co. Triphenylphosphine (TPP, Hokko Chemical Co.), 1-benzyl-2-methylimidazole (1B2MI, Nippon-Gosei Co.), tris(4-methoxyphenyl)phosphine (TPAP, Hokko Chemical Co.), diazabicycloundecene (DBU, SAN-APRO), and tetraphenyl phosphonium tetraphenyl borate (TPP-TPB, Hokko

Table I Description of Raw Materials Used in This Study

Materials	Structure
Biphenyl epoxy resin (YX-4000H)	
Dicyclopentadiene-type phenolic resin (DCPDP)	
Triphenylphosphine (TPP)	
1-Benzyl-2-methylimidazole (1B2MI)	
Tris(4-methoxyphenyl)phosphine (TPAP)	
Diazabicycloundecene (DBU)	
Tetraphenyl phosphonium tetraphenyl borate (TPP-TPB)	

Chemical Co.) as a catalyst were used as received. Detailed descriptions of chemical structures are summarized in Table I.

Sample Preparation

All epoxy resin compositions in this study contain the same equivalent weight ratio (1 : 1) of epoxy and phenolic group with 1.5 parts per hundred (phr) of each catalyst. Epoxy resin and hardener were well mixed at 120°C until a homogeneous solution was obtained. This mixture was cooled down to 80°C. The catalyst was added and the mixture was fully stirred for about 10 s. 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 -40–450°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 -10–300°C. A set of isothermal cure curves has been obtained 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.

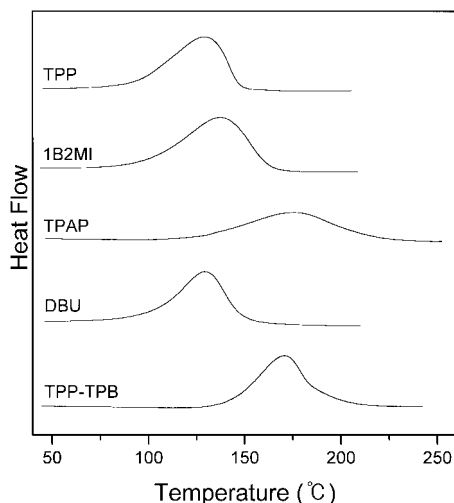


Figure 1 DSC thermograms in the dynamic mode of biphenyl epoxy resin with different catalysts.

Table II Summary of Results Obtained from Dynamic-Heating Experiments

Catalyst Added	Exotherm Peak (°C)	Onset Exotherm (°C)	ΔH_{tot}
TPP	129	93	214
1B2MI	138	99	248
TPAP	176	125	192
DBU	131	102	210
TPP-TPB	170	143	197

RESULTS AND DISCUSSION

Figure 1 shows the DSC thermograms for dynamic cure of the biphenyl epoxy-DCPDP system with different catalysts at a heating rate of 5°C/min. The total heat of reactions (ΔH_{tot}) have been determined as the total area under the thermogram based on the extrapolated baseline at the end of reaction. Each experiment has been performed five times, and the average corresponding values of ΔH_{tot} are shown in Table II. The exotherm peak and onset exotherm are also summarized in Table II. The exotherm peak increases in the order of the system with TPP, DBU, 1B2MI, TPP-TPB, and TPAP. From Figure 1, it can be seen that the acceleration of the curing reaction of the system with TPAP or TPP-TPB is weak at lower temperature but strong at higher one. It can be assumed that TPAP and TPP-TPB have a latent acceleration of the cure reaction.

Figure 2 shows a series of isothermal reaction rate curves as a function of time for biphenyl epoxy resin compositions with different catalysts. For the formulation using TPP, 1B2MI, or TPAP, 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 conversions were calculated from Figure 2, and the conversion rate was plotted as a function of conversion in Figure 3. It can be seen that the curing reaction in the system using DBU and TPP-TPB proceeds through an autocatalytic kinetic mechanism with maximum conversion rate in 10–20% and 20–30% in conversion region, respectively. The other curing reactions proceed by an n th-order kinetic mechanism.

For thermosets that follow an n th-order curing reaction kinetics, the isothermal reaction conver-

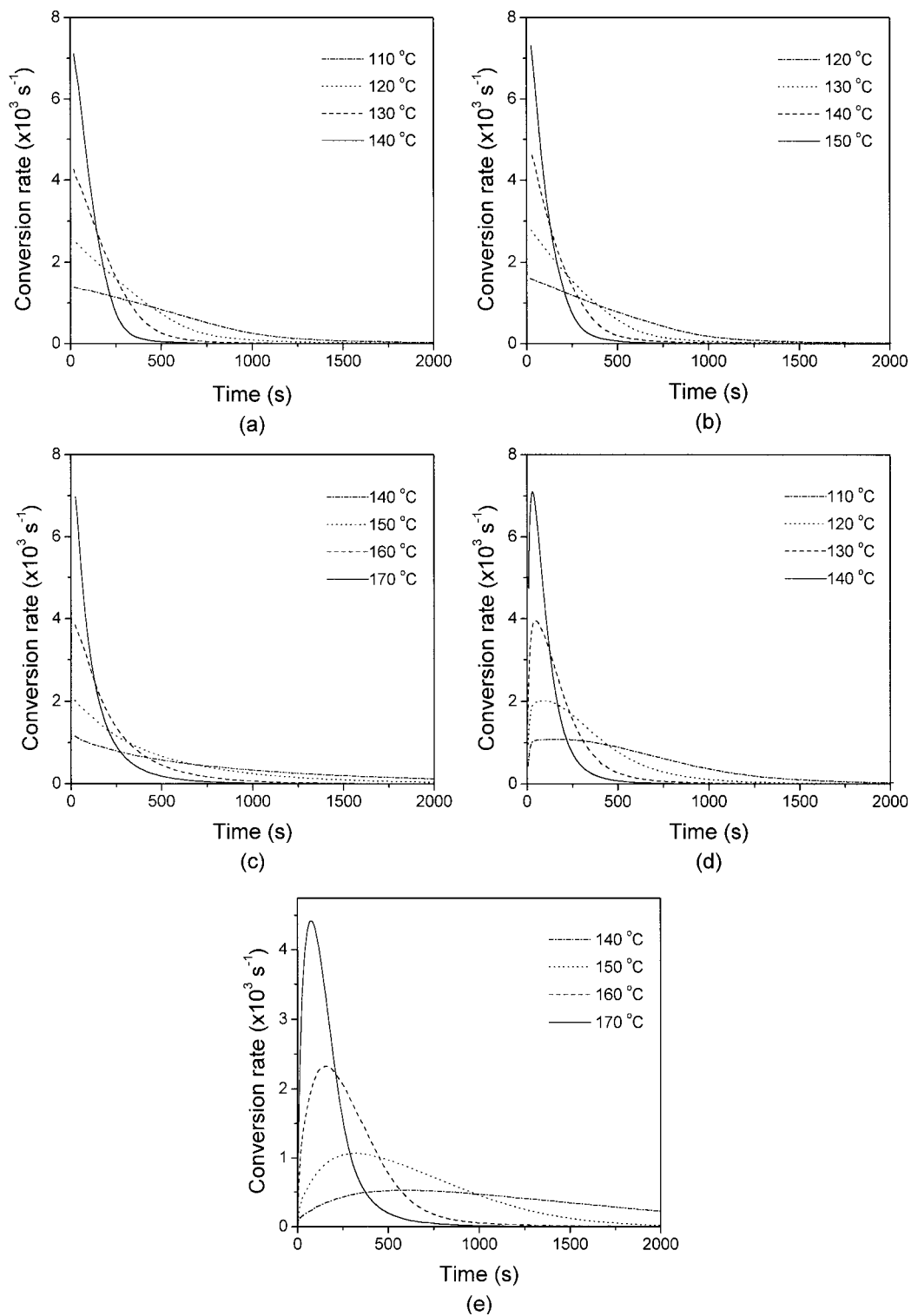


Figure 2 Conversion rate as a function of time at several isothermal temperatures of biphenyl epoxy resin composition with (a) TPP, (b) 1B2MI, (c) TPAP, (d) DBU, and (e) TPP-TPB.

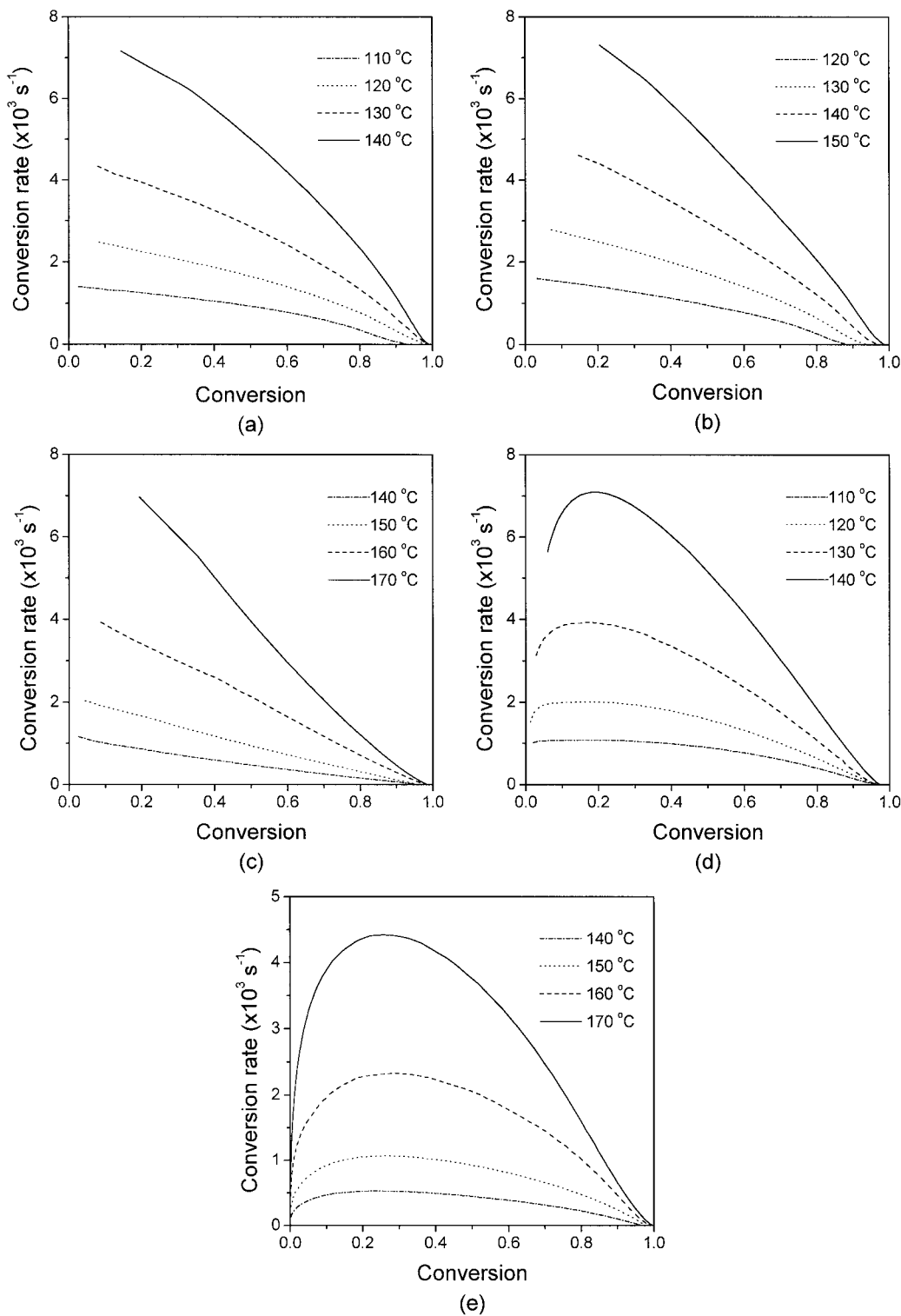


Figure 3 Isothermal conversion rate as a function of conversion of biphenyl epoxy resin composition with (a) TPP, (b) 1B2MI, (c) TPAP, (d) DBU, and (e) TPP-TPB.

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

Catalyst Added	Temperature (°C)	k	n	Temperature Dependence of the Rate Constant	Average n Value
TPP	110	1.45×10^{-3}	0.66	$3.60 \times 10^7 \exp(-76248/RT)$	0.7
	120	2.64×10^{-3}	0.71		
	130	4.63×10^{-3}	0.73		
	140	8.31×10^{-3}	0.75		
1B2MI	120	1.66×10^{-3}	0.78	$4.84 \times 10^7 \exp(-78749/RT)$	0.8
	130	2.99×10^{-3}	0.81		
	140	5.29×10^{-3}	0.85		
	150	9.17×10^{-3}	0.89		
TPAP	140	1.14×10^{-3}	1.26	$4.55 \times 10^{10} \exp(-107924/RT)$	1.2
	150	2.19×10^{-3}	1.24		
	160	4.46×10^{-3}	1.13		
	170	9.49×10^{-3}	1.26		

sion 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, 1B2MI, and TPAP were obtained by fitting the experimental data in the first portion of cure to eq. (1), and they are summarized in Table III. The average value of n obtained from all isothermal experiments and the temperature dependence of the rate constant are also shown in Table III. It can be considered that the curing process of the formulations using TPP, 1B2MI, and TPAP is a first-order kinetic mechanism, and thus the rate-determining step could be the unimolecular reaction.⁵ Typical comparisons between experimental and an n th-order model of the formulation with TPP, 1B2MI, and TPAP with previously determined model parameters are shown in Figure 4. The curing temperature was 140°C. Good agreement is observed up to 70–80% in the formulations with TPP and 1B2MI, beyond which 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 chemical factors.⁸ Whereas, in the formulation with TPAP, the good linear relationship is found in the entire range of conversion, which could be

assumed that the onset of gelation is shifted to a higher conversion than that of the composition with TPP or 1B2MI. To verify this phenomenon, the glass transition temperatures were measured at a certain fractional reaction conversion. Figure 5 shows the experimental results of T_g versus α change. At the same conversion, the values of T_g were higher in the order of the formulation with 1B2MI, TPP, and TPAP. It could be considered that the mobility of reacting groups of the system with 1B2MI is hindered at lower conversion compared to the system with TPP or TPAP.

To consider diffusion effect more precisely, we

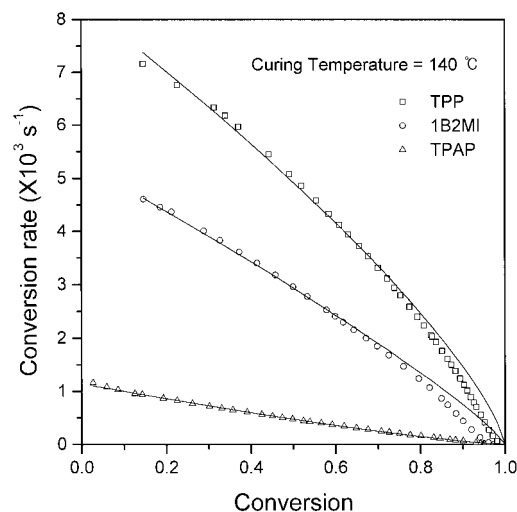


Figure 4 Comparisons of experimental data with an n th-order cure model for biphenyl epoxy resin composition with (\square) TPP, (\circ) 1B2MI, and (\triangle) TPAP.

have used a 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. For $\alpha \ll \alpha_c$, $f(\alpha)$ approximately equals to unity and the effect of diffusion is negligible, so that the reaction is kinetically controlled. As α approaches α_c , $f(\alpha)$ begins to decrease and approaches 0.5 when $\alpha = \alpha_c$. Beyond this point, it continues to decrease and approaches zero, which means that the reaction becomes very slow and effectively stops. 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 an n th-order cure kinetic model in eq. (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 Table IV. As shown in other studies,^{8,10,11} α_c increased with temperature but C has not discernible trend. At the same curing temperature, the α_c value of the formulation with TPP is higher than that of the formulation with 1B2MI. As shown in Figure 5, it could be considered that this result would be due to the higher cross-

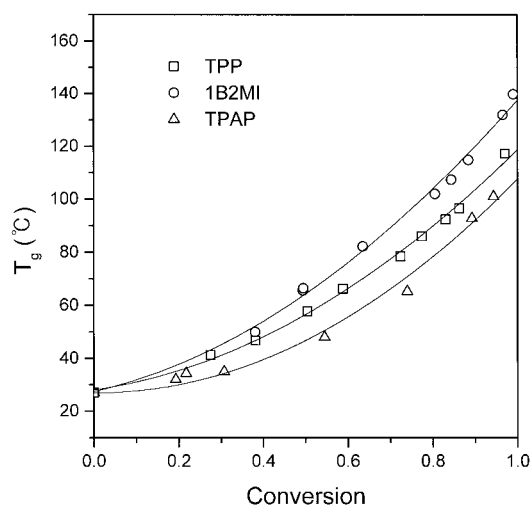


Figure 5 Relationships between T_g and reaction conversion of biphenyl epoxy resin with (\square) TPP, (\circ) 1B2MI, and (\triangle) TPAP.

Table IV Values of the Constant C and Critical Conversion at Different Temperatures for the Formulation Following n th-Order Cure Reaction

Catalyst	Temperature (°C)	C	α_c
TPP	110	23	0.84
	120	19	0.93
	130	18	0.95
	140	18	0.96
1B2MI	120	20	0.81
	130	26	0.86
	140	30	0.91
	150	39	0.94

linking network of the system using 1B2MI catalyst than that using TPP. Figures 6 and 7 show the comparisons between the experimental values of $d\alpha/dt$ with these values calculated using an n th-order cure kinetic model and that model coupled with the diffusion factor for the composition with TPP and 1B2MI at each curing temperature. Good agreement was found over the whole curing temperature range.

For thermosets following an autocatalytic curing reaction kinetics, the isothermal reaction rate is expressed as shown below:

$$\frac{d\alpha}{dt} = k' \alpha^m (1 - \alpha)^n \quad (3)$$

where m and n are the reaction order and k' is the kinetic rate constant.

To take into account the autocatalytic reaction where the initial reaction rate of an autocatalytic reaction is not zero, Kamal¹² proposed the generalized expression

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

where k_1 and k_2 are kinetic rate constants.

As previously described, the curing reaction of the formulation using DBU or TPP-TPB proceeds by an autocatalytic cure kinetics. However, the composition with DBU and TPP-TPB could be employed somewhat different reaction step. As seen from Figure 2, because the initial reaction rate of the system with DBU is not zero, the non-zero initial reaction rate should be considered to compute kinetic parameters. In the system with

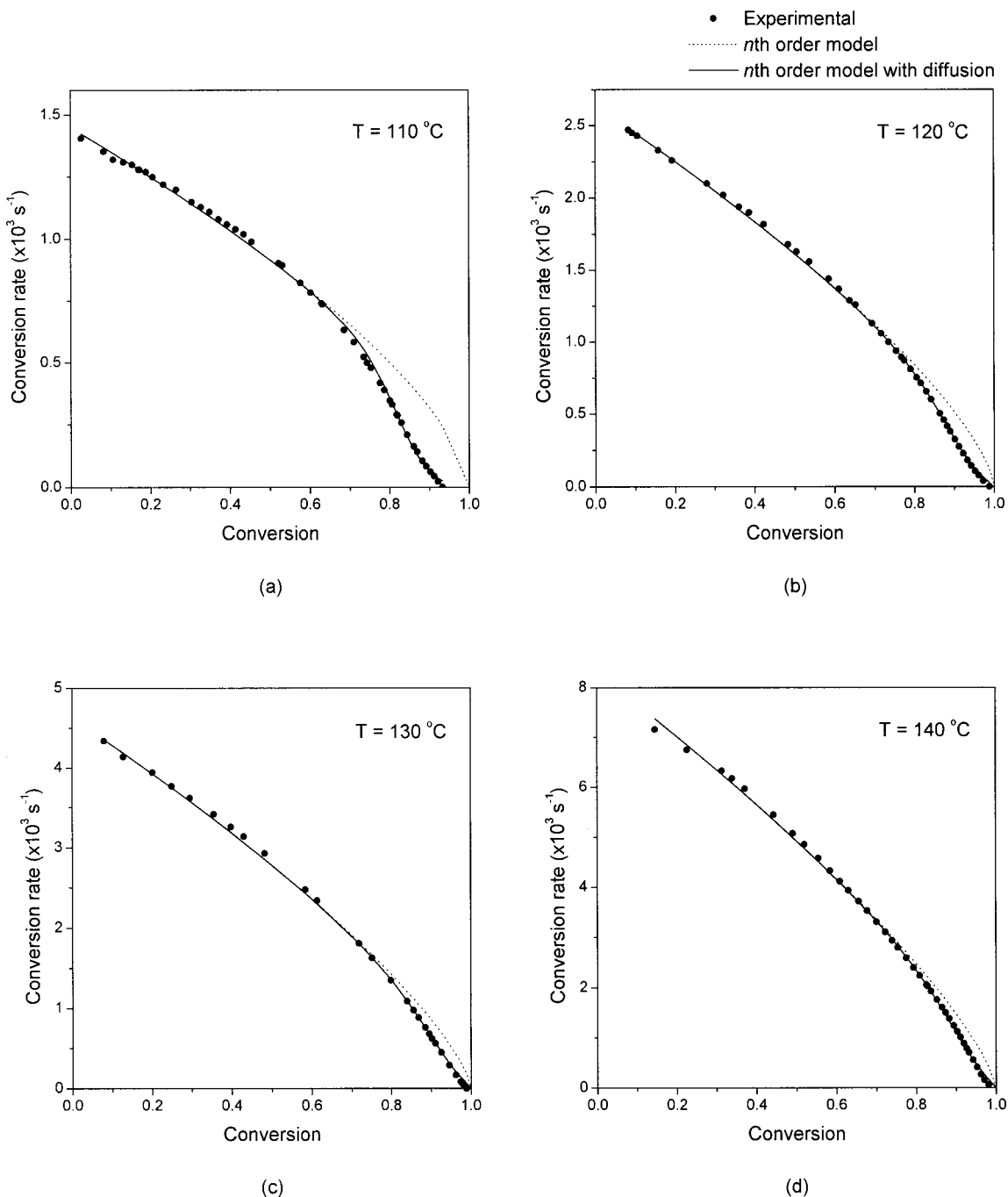


Figure 6 Comparisons of experimental data with an *n*th-order cure model coupled with a diffusion factor for the formulations with TPP.

TPP–TPB, the initial reaction rates observed at each curing temperature were so negligibly small that k_1 in eq. (4) could be considered to be zero.

To compute kinetic parameters in eq. (4), several methods have been proposed.^{5,6,10,13} Usually, the constant k_1 was graphically calculated as the

initial reaction rate at $\alpha = 0$, given by the intercept of the conversion rate – fractional conversion plot, and the total reaction order ($m + n$) was assumed 2. 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 eq.

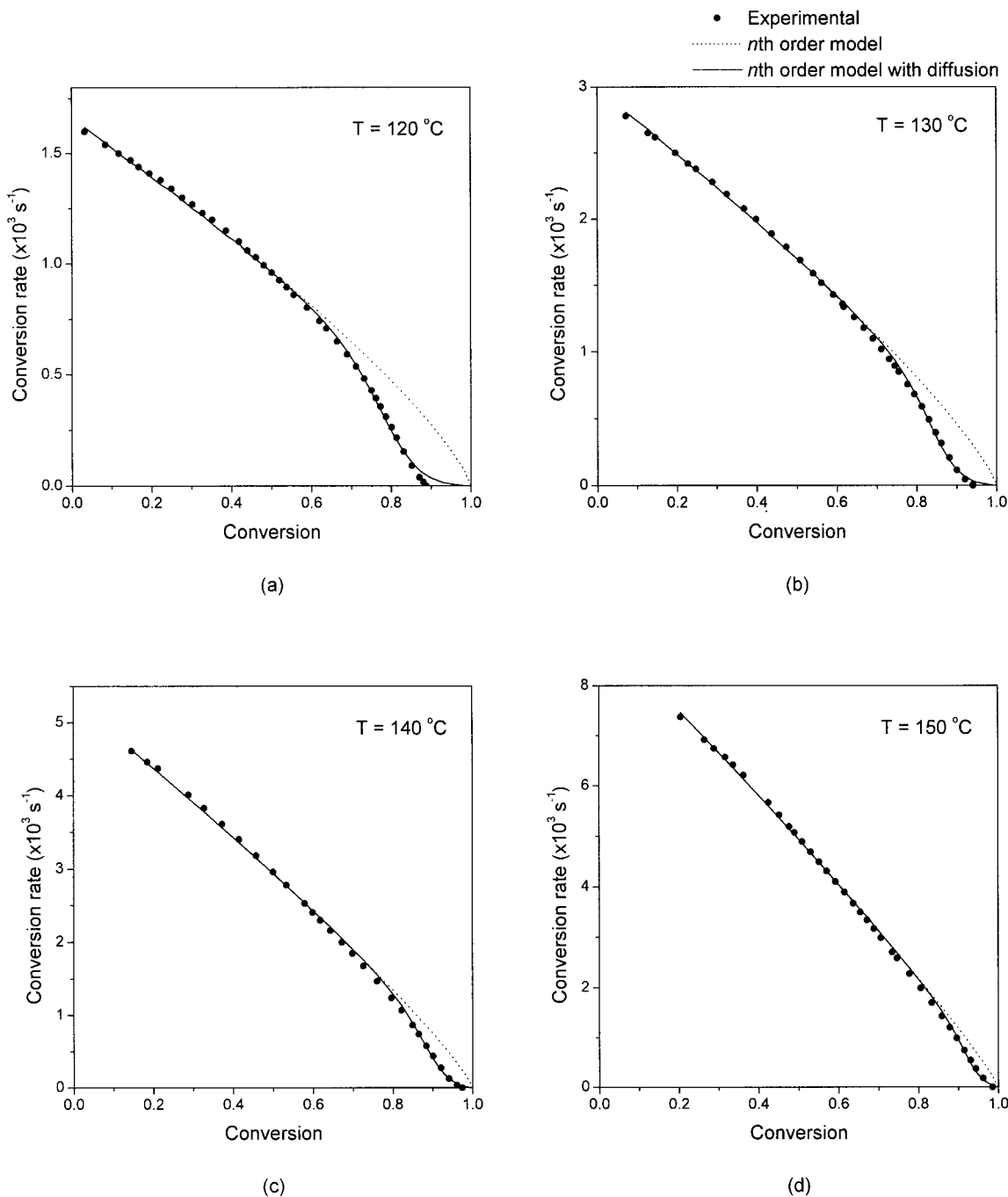


Figure 7 Comparisons of experimental data with an n th-order cure model coupled with a diffusion factor for the formulations with 1B2MI.

(4) in the first portion of cure up to 70–80% cure, depending on the composition and the curing temperature.¹¹ The resulting data obtained from this method are summarized in Table V for all isothermal experiments of the composition with DBU and TPP–TPB. Temperature dependence of rate

constant of epoxy resin composition with DBU and TPP–TPB can be determined with Arrhenius equation form from Table V. The resulting data were also summarized in Table V. The reaction orders were determined by averaging values of all isothermal experiments. Because the sum

Table V Kinetic Parameters of the Formulation following Autocatalytic Cure Reaction Obtained from Each Isothermal Test

Catalyst	Temperature (°C)	Temperature Dependence of Rate Constant				Average <i>m</i> Value	Average <i>n</i> Value
		<i>k</i> ₁	<i>k</i> ₂	<i>k</i> ₁	<i>k</i> ₂		
DBU	110	1.02 × 10 ⁻³	1.71 × 10 ⁻³	2.35 × 10 ²	6.33 × 10 ⁹	0.7	1.2
	120	1.72 × 10 ⁻³	3.09 × 10 ⁻³	exp(-39059/RT)	exp(-92407/RT)		
	130	2.00 × 10 ⁻³	5.93 × 10 ⁻³				
	140	2.60 × 10 ⁻³	1.44 × 10 ⁻²				
TPP-TPB	140	—	1.11 × 10 ⁻³			—	2.56 × 10 ¹¹
	150	—	2.20 × 10 ⁻³				
	160	—	4.88 × 10 ⁻³				
	170	—	1.03 × 10 ⁻²				

Table VI Values of the Constant *C* and Critical Conversion at Different Temperatures for the Formulation Following Autocatalytic Cure Reaction

Catalyst	Temperature (°C)	<i>C</i>	<i>α</i> _{<i>c</i>}
DBU	110	30	0.92
	120	34	0.93
	130	21	0.94
	140	42	0.94
TPP-TPB	140	45	0.94
	150	40	0.96
	160	41	0.96
	170	42	0.97

of the exponent factors, total reaction order of the system with DBU is 2, it can be concluded that the curing process of the composition using DBU follows the commonly used empirical models (*m* + *n* = 2),^{14,15} whereas total reaction order of the system with TPP-TPB is 1.4. Although the data of our kinetic analysis in the system with TPP-TPB also represent an autocatalytic reaction, this system seems to contain the presence of more than one type of kinetic mechanism.

To precisely predict the cure kinetics over the whole range of conversion, modifications of an autocatalytic model were performed by the introduction of a diffusion term as described in eq. (2). *f*(*α*) at different temperatures for the systems with DBU and TPP-TPB was obtained and values of *C* and *α*_{*c*} were obtained by fitting *f*(*α*) versus *α*. The results are summarized in Table VI. As in the system following an *n*th-order cure kinetics, *α*_{*c*} increased with temperature but *C* has no discernible trend in the composition with DBU or TPP-TPB.

Figures 8 and 9 show the comparisons between the experimental values of *dα/dt* with these values calculated using the autocatalytic kinetic model and that coupled with the diffusion factor for the composition with DBU and TPP-TPB at each curing temperature. Good agreement was found over the whole curing temperature range.

CONCLUSIONS

The curing reaction of formulations using TPP, 1B2MI, or TPAP as a catalyst proceeds through a first-order kinetic mechanism, whereas the

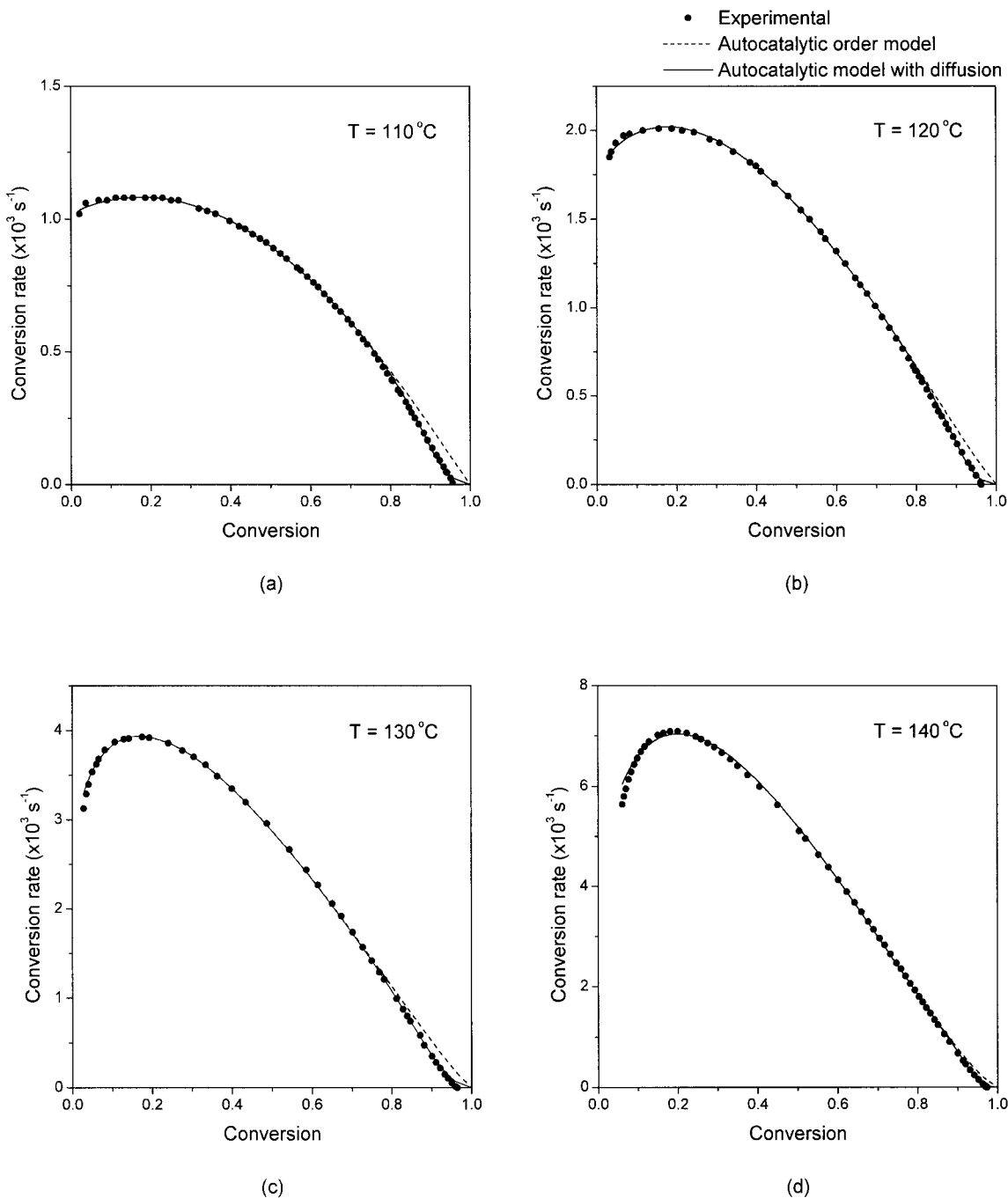


Figure 8 Comparisons of experimental data with an autocatalytic model coupled with a diffusion factor for the formulations with DBU.

formulation using DBU or TPP–TPB proceeds through 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. However the n th-order cure model obtained from the experimental data of the formulations with TPAP agreed well with the experimental data at almost conversion. As in

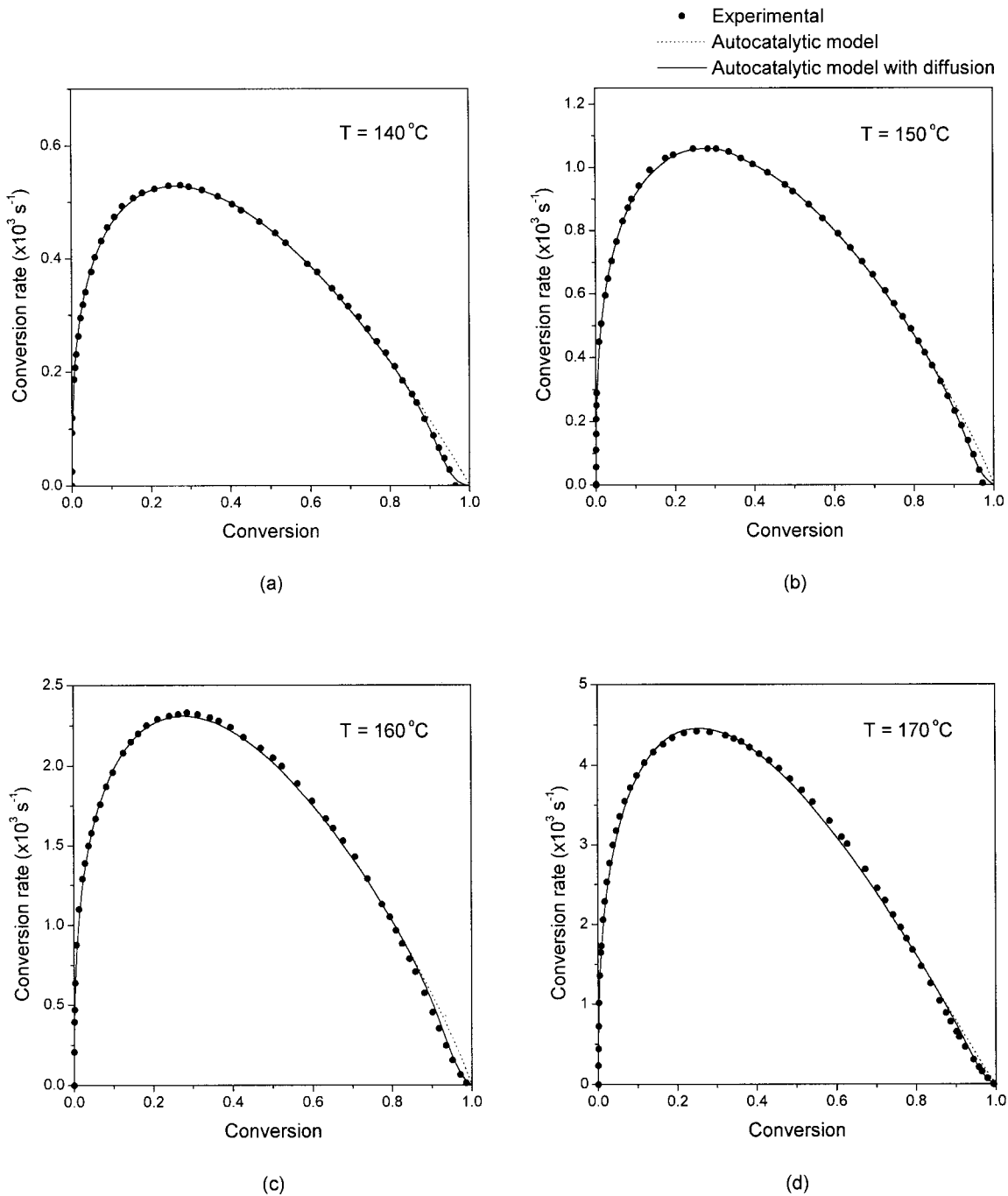


Figure 9 Comparisons of experimental data with an autocatalytic model coupled with a diffusion factor for the formulations with TPP-TPB.

an 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 reac-

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

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