

# An Improved Kinetic Model for the Autocatalytic Curing of Styrene-Based Thermoset Resins

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## Synopsis

The cure behavior of styrene-based thermosets such as orthophthalic polyester, isophthalic polyester, and vinyl ester resins is characterized using both isothermal and dynamic differential scanning calorimetry (DSC) techniques. In the conventional autocatalyzed kinetic model, it is assumed that the isothermal cure reaction of a thermoset goes to completion, which usually leads to a poor fit with the DSC kinetic data. It appears from the conversion-time profiles that the cure reaction reached a plateau value ( $\alpha_u$ ) less than unity. This is not unexpected, as the molecular mobility of the resin system decreases as the network cures. In this work, we have refined the model to remove this restrictive assumption by taking the total ultimate conversion ( $\alpha_u$ ) into account in the computation. This improved model permits us a better prediction of the course of the cure reaction of the styrene-based thermosets under isothermal and dynamic conditions. In addition, the cure kinetics of the three thermoset resins are studied and compared on the basis of several kinetic parameters including conversion, cure rate, reaction rate constant, heat of cure reaction, half-life, and Arrhenius parameters. The reactivity of these resins when arranged in ascending order is found to be: vinyl ester < orthophthalic polyester < isophthalic polyester.

## INTRODUCTION

The free radical crosslinking reaction of a styrene-based thermoset, such as unsaturated polyester, is a highly exothermic process. The heat generated during the isothermal cure reaction usually accelerates the addition polymerization. Horie, Mita, and Kambe<sup>1</sup> showed that the cure reaction of polyester fumarate with styrene monomer is accelerated by the gel effect about 10- to 50-fold and the autoacceleration is much enhanced for the systems with higher crosslinking densities. Since then, an autocatalyzed kinetic model has been proposed by several researchers<sup>2-7</sup> to elucidate the cure behavior of thermoset resins under isothermal conditions.

In the conventional autocatalyzed kinetic model, the total ultimate conversion of a thermoset is assumed to be unity. However, Horie et al.<sup>1</sup> indicated that the final conversion of isothermal cure decreases with increasing crosslinking density. Lee and Han<sup>8-10</sup> also suggested that the curing of unsaturated polyester was diffusion-controlled even at an early stage of the cure reaction; consequently, it was very difficult, or almost impossible, to achieve 100% conversion in the cure reaction of polyester resins. It is not unexpected that the molecular mobility of a thermoset resin decreases as the crosslinking density increases. As a result,

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a portion of the resin as well as some styrene monomer can be trapped in the network and is not able to participate in the cure reaction.

In this work, the cure kinetics of various styrene-based thermoset resins were monitored using differential scanning calorimetry (DSC), a technique considered to be the most effective method of obtaining complete qualitative and quantitative information on the curing process of thermosets. We also tried to improve the goodness of fit for the DSC kinetics data by incorporating one more kinetic parameter—the total ultimate conversion ( $\alpha_u$ )—into the conventional autocatalyzed kinetic model. It is hoped that in the improved model in conjunction with the DSC techniques can provide a simple, yet reliable, and informative means to assess the cure behavior of styrene-based thermoset resins.

The improved autocatalyzed kinetic model was also applied to study and compare the cure reactions of orthophthalic polyester, isophthalic polyester, and vinyl ester resins in terms of several kinetic parameters. The symbols used in the test are defined in the Appendix.

## EXPERIMENTAL

### Materials

Three different styrene-based thermoset resins were selected for this kinetics work. These resins were designated as:

1. Koppers orthophthalic unsaturated polyester B737-197 resin (39 wt % of styrene monomer)
2. Amoco isophthalic unsaturated polyester SG341A (30 wt % of styrene monomer)
3. Dow DERA KANE 411-45 vinyl ester (45 wt % of styrene monomer)

Lucidol *t*-butyl perbenzoate was used as an initiator for all the resins.

A catalyzed thermoset resin sample was freshly prepared before the kinetics experiment by mixing thoroughly in a vial, the styrene-based thermoset resin with 1 wt % of a *t*-butyl perbenzoate solution. About 10 mg of the resin sample was sealed in a hermetic sample pan and weighed before and after the experiment to ensure that there was no loss of styrene monomer during the cure reaction.

### Cure Kinetics

Cure kinetics of styrene-based thermoset resins were monitored using a DuPont Model 9900 thermal analyzer equipped with a differential scanning calorimetry cell and a computer. The DSC was calibrated using high-purity indium and an isothermal baseline was established at the preset cure temperature by means of two empty sample pans according to the procedure described in Ref. 7.

Isothermal kinetics experiments were performed at four different temperatures (90, 100, 110, and 120°C for both orthophthalic polyester and isophthalic polyester; and 100, 110, 115, and 120°C for vinyl ester) under a dry nitrogen atmosphere. A temperature scan from ambient to 250°C at 10°C/min was initiated to determine the residual activity of the sample after each isothermal

experiment. In the dynamic kinetics study, the samples were scanned at various heating rates (2.5, 5.0, 10.0, 12.5, and 15.0°C/min) from ambient to 250°C. The integral heat generated from the reaction, heat flow, and exothermic peak maximum temperature were analyzed using a computer.

### Data Analysis

Based on the DSC data, the relative degree of cure ( $\alpha_t$ ) at time  $t$  is given by

$$\alpha_t = Q_t / (Q_T + Q_R) \quad (1)$$

where  $Q_T$  = heat of isothermal cure reaction,  $Q_t$  = heat evolved at any time, and  $Q_R$  = the heat of residual reaction. The cure rate ( $d\alpha_t/dt$ ) in the DSC experiments is defined as

$$d\alpha_t/dt = (dQ_t/dt) / (Q_T + Q_R) \quad (2)$$

where  $dQ_t/dt$  = heat flow into or out of the sample. Isothermal curing of a styrene-based thermoset resin has been described previously as a simplified autocatalyzed second-order kinetic equation<sup>2,5,7,11</sup>:

$$d\alpha_t/dt = k \cdot \alpha_t^m \cdot (1 - \alpha_t)^n \quad (3)$$

where  $m + n = 2$  and  $k$  is the reaction rate constant. Typically,  $k$  usually follows an Arrhenius equation:

$$k = A \cdot \exp(-E/RT) \quad (4)$$

where  $A$  = preexponential factor and  $E$  = activation energy. The integrated form of eq. (3) is

$$\alpha_t = C / (1 + C) \quad (5)$$

where  $C = [k \cdot (n - 1) \cdot t]^{1/(n-1)}$ . As the reaction approaches completion, the extent of reaction does not approach unity as would be expected from eq. (5).

Rather, the reaction reaches a plateau value markedly less than unity, and this value is referred to as the ultimate conversion. This value may be incorporated into the model quite easily in the following ways:

$$d\alpha_t/dt = k \cdot \alpha_t^m \cdot (\alpha_u - \alpha_t)^n \quad (6)$$

The integrated form is similar to eq. (5):

$$\alpha_t = \frac{\alpha_u [k \cdot t \cdot \alpha_u \cdot (n - 1)]^{1/n-1}}{1 + [k \cdot t \cdot \alpha_u \cdot (n - 1)]^{1/n-1}} \quad (7)$$

Estimates of  $\alpha_u$  may be obtained using

$$\alpha_u = Q_T / (Q_T + Q_R) \quad (8)$$

Equation (7) is in same form as proposed by Gordon and McMillian<sup>12</sup> for the autocatalyzed reaction. By rearranging eq. (7), both reaction order ( $n$ ) and reaction rate constant ( $k$ ) can be determined from the following equation using least squares linear regression:

$$\ln[\alpha_t / (\alpha_u - \alpha_t)] = (n - 1)^{-1} \cdot \ln t + (n - 1)^{-1} \cdot \ln[k \cdot \alpha_u \cdot (n - 1)] \quad (9)$$

The half-life ( $t_{1/2}$ ) of the resin is computed by setting  $\alpha_t = 0.5$  in eq. (7).

The variations of conversion at peak maximum ( $\alpha_p$ ) are taken into account in the dynamic DSC study. The exothermic peak temperatures ( $T_p$ ) are measured as a function of heating rates ( $\beta$ ). Both activation energy of the cure reaction ( $E$ ) and preexponential factor ( $A$ ) are estimated in accordance with the dynamic kinetic eq. (7):

$$\ln \beta + \ln \mathbf{f}(\alpha_p) = \ln \frac{(A \cdot E)}{R} - 5.33 - \frac{1.05E}{R \cdot T_p} \quad (10)$$

where  $\mathbf{f}(\alpha_p) = [\alpha_u \cdot (n - 1)]^{-1} \cdot [\alpha_p / (\alpha_u - \alpha_p)]^{n-1}$ .

## RESULTS AND DISCUSSION

### Consistency of Improved Kinetic Model

The values of  $\alpha_u$  were determined from the residual reactivity. The results (Fig. 1) show that  $\alpha_u$  varies with the cure temperature and polymer type (vinyl ester vs. phthalic type ester). These values were then substituted into eq. (9) to accommodate linear regression for estimation of the remaining reaction parameters.

The typical S-shape conversion-time profiles at 110°C are shown in Figure 2 for the orthophthalic polyester, Figure 3 for the isophthalic polyester, and Figure 4 for the vinyl ester. The computed results based on the conventional model [eq. (5)] and the improved model [eq. (7)] are substantially different, especially at high conversion, for all three styrene-based thermoset resins. A much better fit is observed with the new model as the constraint of the reaction going to completion is lifted.

The cure rate-conversion profiles at 110°C for the three different thermoset resins are shown in Figures 5-7. Again, the improved kinetic model provides results which are in good agreement with the experimental data in most cases. The results obtained from the conventional model deviate significantly from the experimental data at  $\alpha_t \geq 0.6$  for both orthophthalic polyester (Fig. 5) and isophthalic polyester (Fig. 6) and at  $\alpha_t \geq 0.45$  for the vinyl ester (Fig. 7). The reason for the discrepancy of the results in Figures 4-6 for the conventional model at high conversion is the same as that for the conversion-time profiles (Figs. 2-4). The kinetic results in Figures 2-7 do reveal the consistency of the improved autocatalyzed second-order kinetic model for the curing of styrene-based thermoset resins.

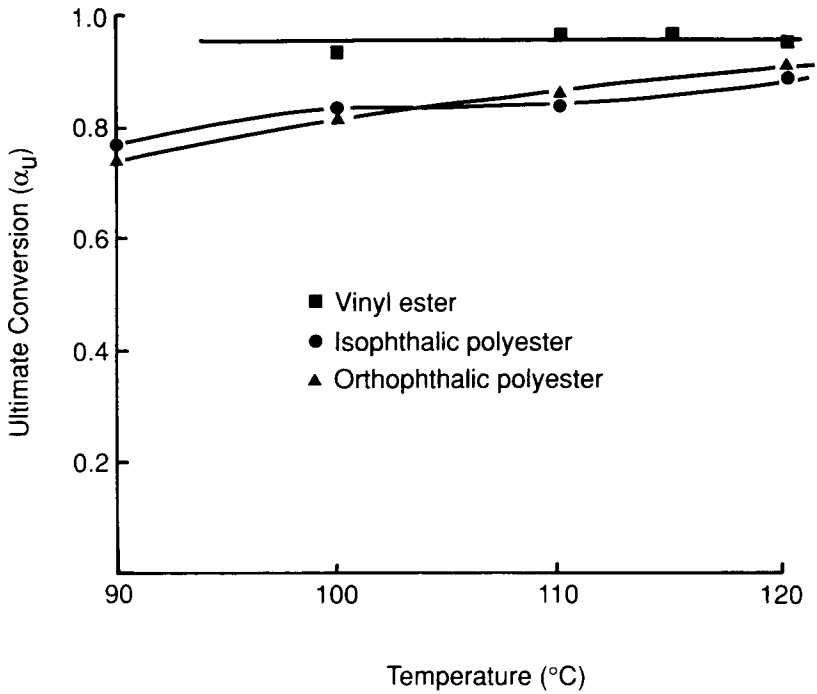


Fig. 1. Total ultimate conversion of styrene-based thermoset resins vs. curing temperature.

Both reaction rate constant ( $k$ ) and reaction order ( $n$ ) can be determined according to either eq. (6) (differential form) or eq. (7) (integrated form) using cure rate-conversion data or conversion-time results respectively. In this text, we refer to  $n_{DIF}$  (or  $k_{DIF}$ ) and  $n_{INT}$  (or  $k_{INT}$ ) to the kinetics parameters that are determined from the differential equation and the integrated equation, re-

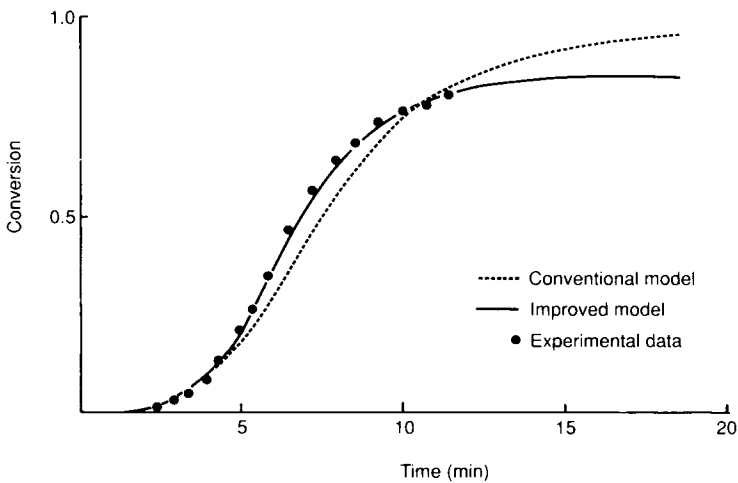


Fig. 2. Conversion-time profile of orthophthalic polyester at 110°C.

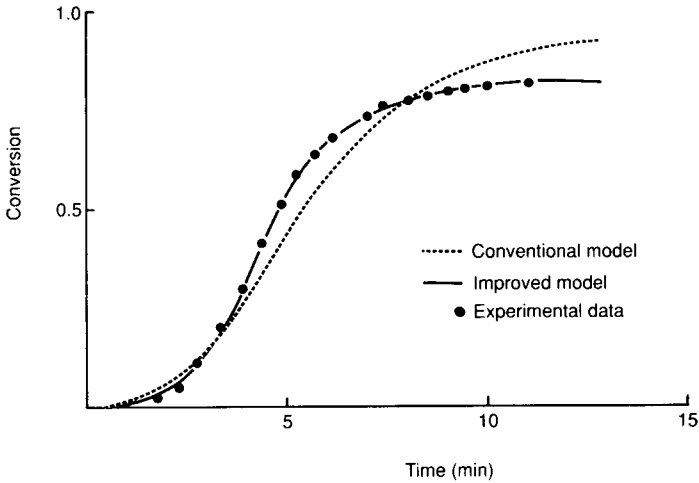


Fig. 3. Conversion-time profile of isophthalic polyester at 110°C.

spectively. In theory, a mathematical model implements a perfect fit for the kinetic data only if the ratios of  $n_{DIF}/n_{INT}$  and  $k_{DIF}/k_{INT}$  are equal to unity. In this work, we utilize the ratios of these two kinetic parameters obtained from the differential equation and the integrated equation as one of the measures for the reliability of the kinetic models (Figs. 8 and 9).

Figure 8 indicates that both improved and conventional kinetic models achieve a slightly better fit for the DSC data of the orthophthalic polyester and the isophthalic polyester at higher curing temperatures because the ratio of  $n_{INT}/n_{DIF}$  is closer to unity as the temperature increases. However, the two kinetic models provide almost the same goodness of fit for the kinetic data of vinyl ester at different curing temperatures. The results in Figure 8 point out the merits of using the improved model over the conventional model to assess

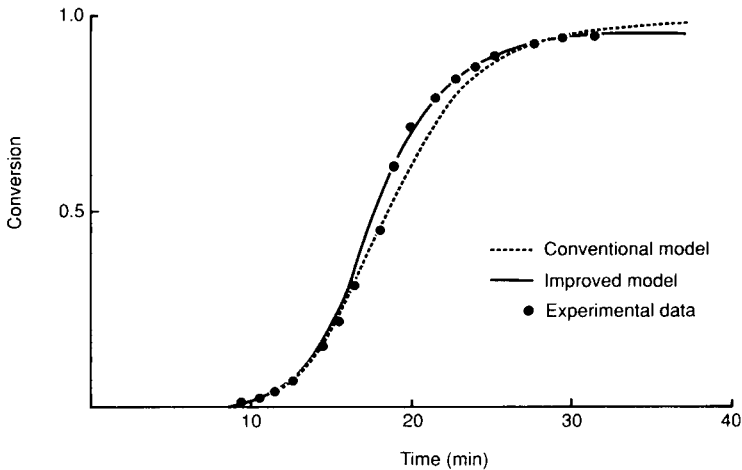


Fig. 4. Conversion-time profile of vinyl ester at 110°C.

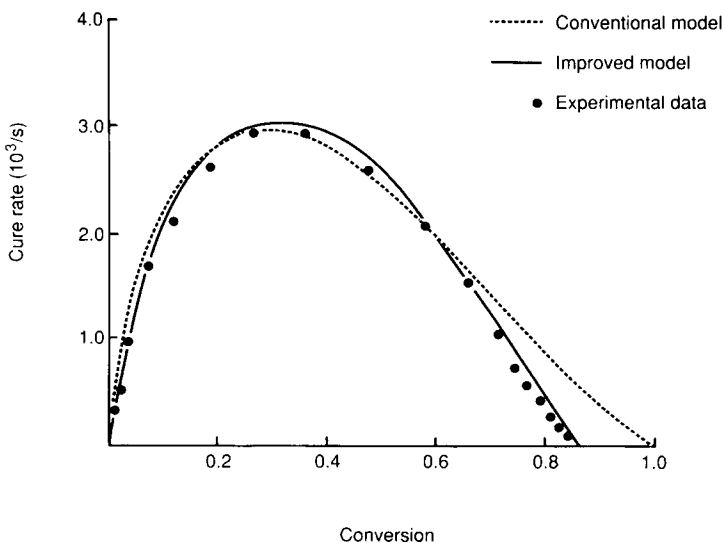


Fig. 5. Cure rate versus conversion of orthophthalic polyester at 110°C.

the cure kinetics, at least of the two unsaturated polyesters. The reaction orders of the unsaturated polyesters estimated from the integrated equation are smaller than those from the differential equation, while the vinyl ester produces opposite results.

The correlation between the reaction rate constants of these thermoset resins obtained from the integrated equation and the differential equation is shown in Figure 9. The dashed line is set for  $k_{INT} = k_{DIF}$ . In spite of different kinetic models, the integrated equation yields smaller values of reaction rate constant than the differential equation does in all cases. The improved model obviously imparts a better fit for the DSC data than the conventional model does because

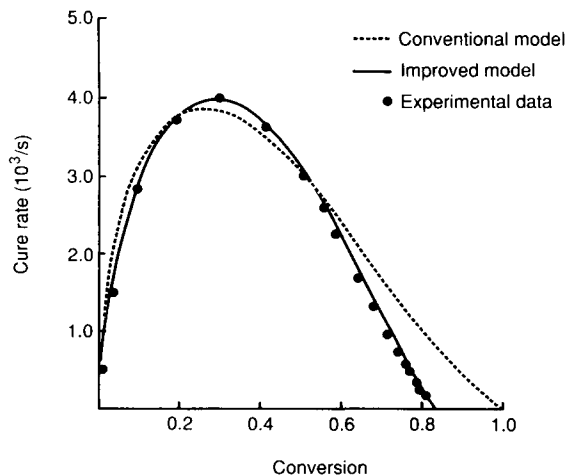


Fig. 6. Cure rate versus conversion of isophthalic polyester at 110°C.

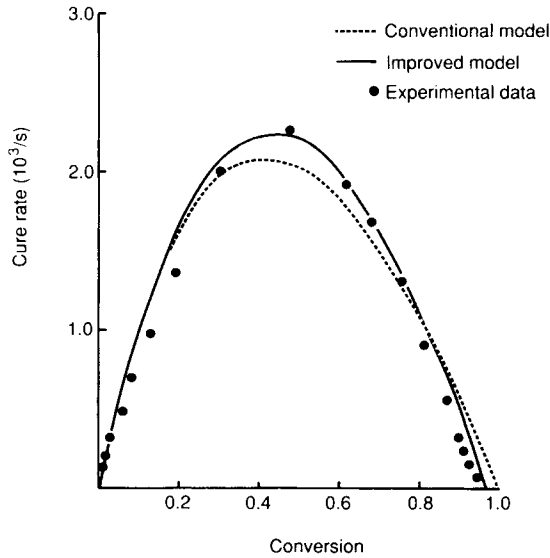


Fig. 7. Cure rate versus conversion of vinyl ester at 110°C.

the ratios of  $k_{\text{INT}}/k_{\text{DIF}}$  (slope of the curves) derived from the improved model are closer to the theoretical values (the dashed line) than those from the conventional model. The discrepancy of two sets of kinetics results ( $n_{\text{INT}}$  vs.  $n_{\text{DIF}}$  in Fig. 8 or  $k_{\text{INT}}$  vs.  $k_{\text{DIF}}$  in Fig. 9) is believed to be associated with the fact that  $\alpha_t$ , which is not an independent kinetic variable in eq. (5), possibly induces as much experimental error as  $d\alpha_t/dt$  does in estimating the kinetic parameters

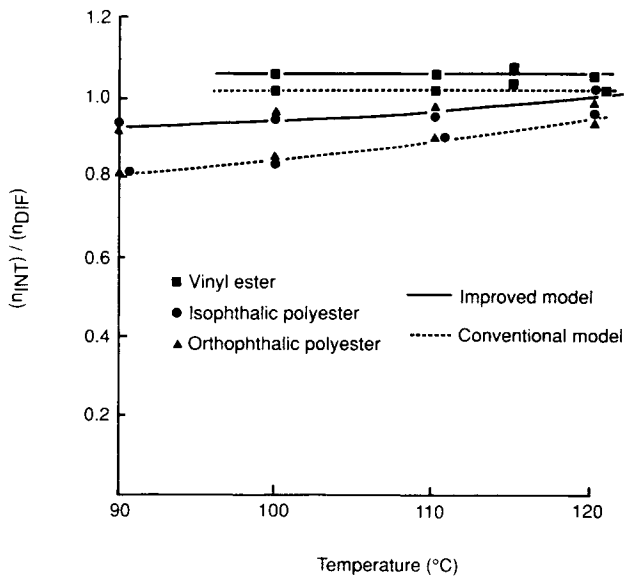


Fig. 8. Ratio of  $n_{\text{INT}}/n_{\text{DIF}}$  vs. temperature for styrene-based thermoset resins under isothermal conditions.



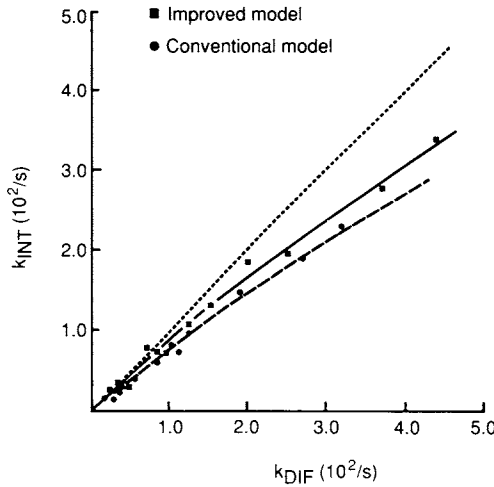


Fig. 9.  $k_{INT}$  vs.  $k_{DIF}$  for styrene-based thermoset resins under isothermal conditions.

$n_{DIF}$  and  $k_{DIF}$ . Since time  $t$  is an independent variable, it is recommended that the reaction order and reaction rate constant using the integrated equation [eq. (7) or eq. (9)] be assessed.

The correlation coefficient, which is obtained from the least square linear regression, may also be used as an indication of the goodness of fit of the DSC kinetics data. Table I shows the correlation coefficients for the kinetic parameters determined from the two kinetic models based on eq. (9) at different curing temperatures. The correlation coefficients generated by the improved model are, in general, greater than those by the conventional model. In the

TABLE I  
Correlation Coefficients for the Kinetic Parameters Obtained from Isothermal Kinetic Models at Different Temperatures

Resin	Temperature (°C)	Correlation coefficient	
		Conventional model	Improved model
Orthophthalic polyester B737-187	90	0.9495	0.9921
	100	0.9767	0.9984
	110	0.9835	0.9981
	120	0.9876	0.9946
Isophthalic polyester SG341A	90	0.9667	0.9980
	100	0.9774	0.9987
	110	0.9833	0.9959
	120	0.9904	0.9979
Vinyl ester 411-45	100	0.9953	0.9941
	110	0.9941	0.9984
	115	0.9926	0.9951
	120	0.9874	0.9982

case of the conventional model, the correlation coefficients for the orthophthalic polyester and isophthalic polyester seem to increase with the curing temperature, whereas those of vinyl ester are almost independent of the curing temperature. For the improved model, the curing temperature does not have any significant effect on the correlation coefficients for these resins.

The poor fit of kinetic data in the conventional model is due to the fact that the assumption of  $\alpha_u = 1$  is overly simplified, as indicated in Figure 10. The correlation coefficients for the conventional model appear to increase with the total ultimate conversion and then approach the values for the improved model asymptotically. Since the total ultimate conversion is determined experimentally in the improved model, the correlation coefficients of curve fitting are found to be independent of the total ultimate conversion (Fig. 10). The results in Figure 10 certainly reveal that the reliability of the kinetic model for the styrene-based thermoset resins can be greatly improved simply by taking the total ultimate conversion into account in computation.

### Cure Behavior of Styrene-Based Thermosets

The heat of isothermal cure reaction of styrene-based thermosets varies slightly with the curing temperatures (Fig. 11). The heat of cure reaction under isothermal conditions is about 220–240 J/g for both orthophthalic polyester and isophthalic polyester, and about 260 J/g for the vinyl ester. The cure reaction of vinyl ester seems to be slightly more exothermic than that of unsaturated polyesters. The total ultimate conversion of unsaturated polyesters, which ranges from 0.75 to 0.90, tends to increase with curing temperature as shown in Figure 1. For the vinyl ester, the ultimate conversion is greater than that of the unsaturated polyesters and is almost independent of the temperature. It is likely that the greater values of heat of cure reaction and total ultimate conversion of vinyl ester, compared to the unsaturated polyester, are attributed to the difference in molecular structure and the reactivity of vinyl functional

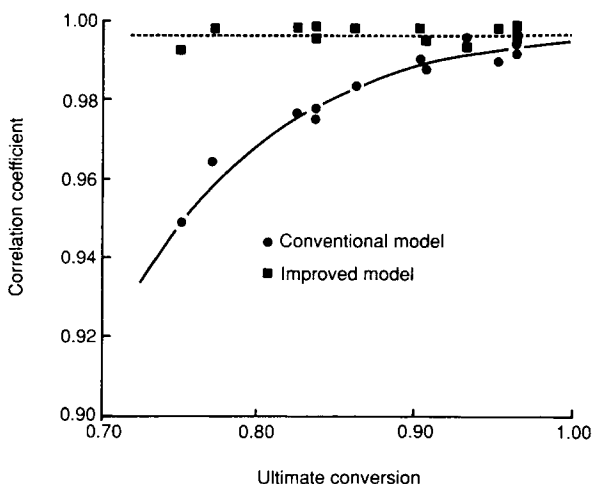


Fig. 10. Correlation coefficient of curve fitting vs. total ultimate conversion of styrene-based thermoset resins under isothermal conditions.

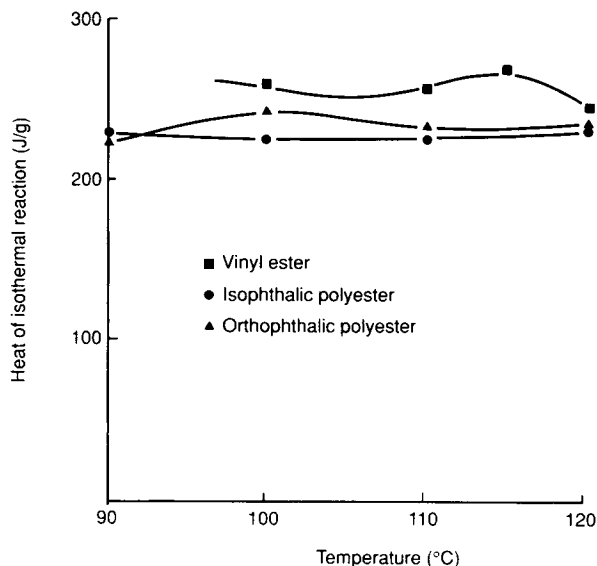


Fig. 11. Heat of isothermal cure reaction of styrene-based thermoset resins vs. curing temperature.

groups, and the amount of styrene monomer in the resin. In this paper, we do not attempt to explore the cure kinetics of the resins in terms of their chemistry.

The reaction orders ( $n$ ) for the isothermal cure reaction of two unsaturated polyesters and vinyl esters are found to be independent of the curing temperatures (Fig. 12). In spite of the difference in the resin chemistry, these styrene-based thermosets have almost the same values for the reaction order at different curing temperatures. The average value of the reaction order is about 1.15 for all the resins.

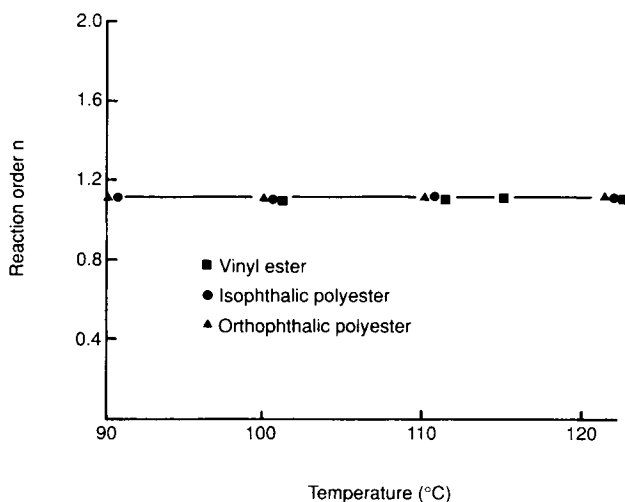


Fig. 12. Reaction order of styrene-based thermoset resins vs. curing temperature.

The conversion and cure rates of the three different resins at 110°C are shown in Figures 2–7. The magnitude of conversion or cure rate at any time for the resins, when arranged in ascending order, appears to be: vinyl ester < orthophthalic polyester < isophthalic polyester. Although vinyl ester has a lower conversion or smaller cure rate than the other two unsaturated polyesters it attains the highest total ultimate conversion under isothermal conditions. It was suggested by Kubota<sup>13</sup> that the total ultimate conversion of the unsaturated polyesters is determined by the amount of styrene monomer in the resins. Lee and Han<sup>14</sup> also pointed out that a thermoset resin which cured faster than others did not necessarily give rise to a larger value of  $\alpha_u$ . The cause of this peculiar cure behavior of styrene-based thermosets is not known at present.

The reaction rate constants ( $k$ ) of the resins follow the Arrhenius eq. (4) as represented by the solid curves in Figure 13. The reaction rate constants increase quite rapidly with the curing temperatures. The unsaturated polyesters have greater reaction rate constants than the vinyl ester in the temperature range of 50–150°C. The reaction rate constant of isophthalic polyester is slightly greater than that of orthophthalic polyester at temperatures greater than 100°C.

The half-lives of the thermoset resins at various temperatures are computed on the basis of eq. (7) and the results are shown in Figure 14. The unsaturated polyesters possess a shorter half-life than the vinyl ester especially when the temperature is below 150°C. Isophthalic polyester seems to be the most reactive resin among the three styrene-based thermosets because it has the shortest half-life over a broad temperature range. These results are consistent with those in Figures 2–7 and Figure 13.

The reactivity of a thermoset resin can be also interpreted in terms of the Arrhenius parameters. Table II shows the results of the activation energy and

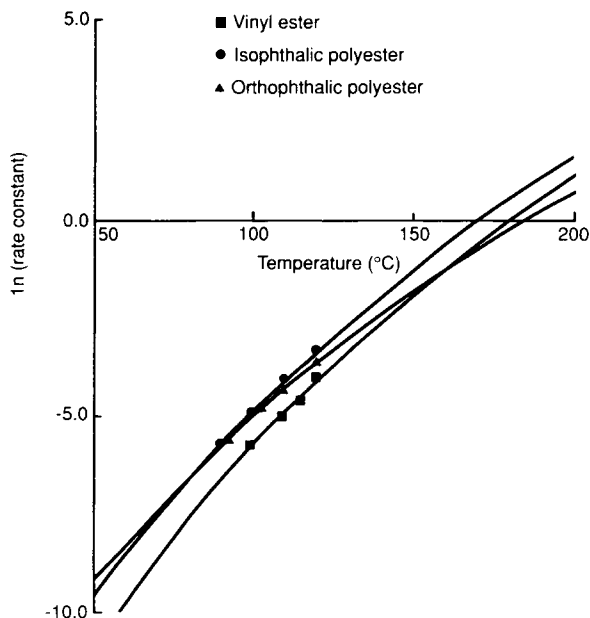


Fig. 13. Reaction rate constant of styrene-based thermoset resins vs. curing temperature.

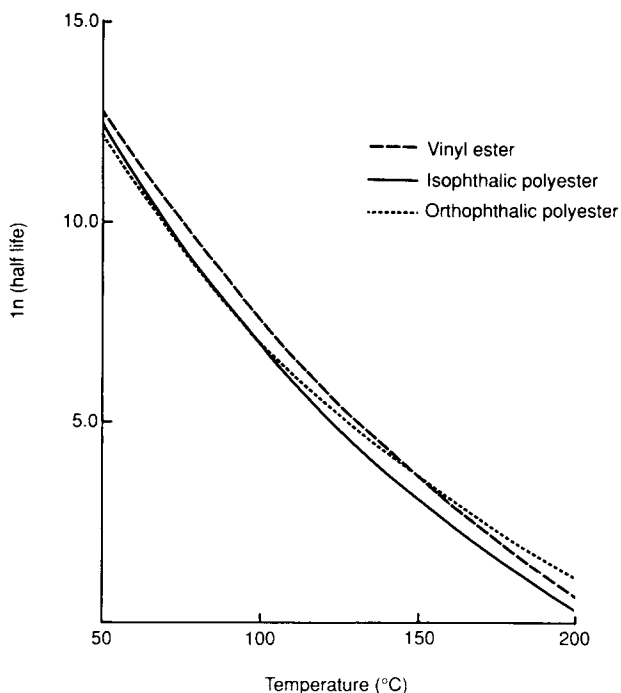


Fig. 14. Half-life of styrene-based thermoset resins vs. temperature.

preexponential factor obtained from the isothermal and the dynamic DSC experiments. For the isothermal experiments, the two Arrhenius parameters are determined using the Arrhenius plots [eq. (4)]. The dynamic kinetic plots which are derived from eq. (10) are shown in Figure 15. All the styrene-based thermoset resins follow the dynamic kinetics equation nicely.

TABLE II  
Arrhenius Parameters of Styrene-Based Thermoset Resins Obtained from Isothermal and Dynamic DSC Methods

Method	Arrhenius parameter	Orthophthalic polyester B737-187	Isophthalic polyester SG341A	Vinyl ester 411-45
Conventional isothermal	$E$ (kJ/mol)	98.54	105.67	104.59
	$\ln A$	26.18	28.57	27.68
	$r^a$	0.9981	0.9939	0.9861
Improved isothermal	$E$ (kJ/mol)	91.21	93.82	104.68
	$\ln A$	24.56	25.39	28.01
	$r^a$	0.9978	0.9974	0.9905
Dynamic	$E$ (kJ/mol)	95.77	86.61	103.14
	$\ln A$	25.21	22.96	27.51
	$r^a$	0.9665	0.9847	0.9838

<sup>a</sup>  $r$  = correlation coefficient.

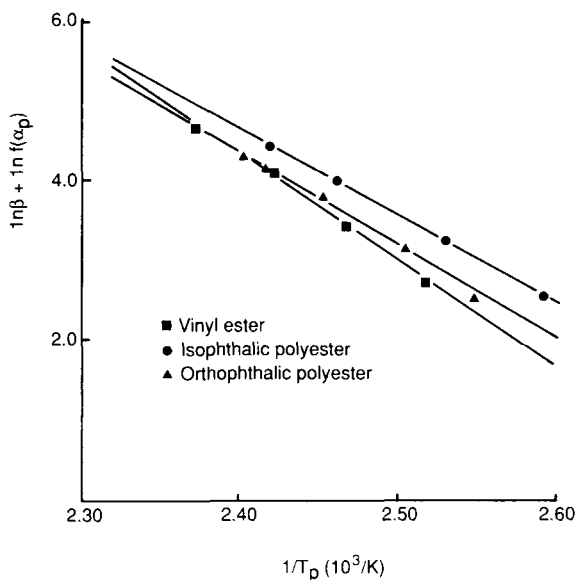


Fig. 15. Dynamic kinetics plots of styrene-based thermosets resins.

The Arrhenius parameters of the unsaturated polyesters obtained from the dynamic method are in better agreement with those from the improved isothermal kinetic model than those from the conventional model. For the vinyl ester, both isothermal and dynamic methods produce consistent results for the Arrhenius parameters. The activation energy of vinyl ester is slightly greater than those of the two unsaturated polyesters. This is another indication of lower reactivity of vinyl ester as compared to that of orthophthalic polyester or isophthalic polyester.

## CONCLUSION

It is demonstrated in this work that, by taking the total ultimate conversion into account, improved autocatalyzed kinetic model is possible. This offers a better fit with the DSC kinetic data of a styrene-based thermoset resin than the conventional model. The goodness of fit appears to be independent of the total ultimate conversion for the improved model (Fig. 10), yet greatly improved with increasing the total ultimate conversion for the conventional model. Apparently, the assumption of  $\alpha_u = 1$  in the conventional model is overly simplified because the molecular mobility of a thermoset system decreases as the network cures.

We also show that it is feasible to assess the cure behavior of styrene-based thermosets using the improved kinetic model. The reaction orders of isophthalic polyester, orthophthalic polyester, and vinyl ester are found to be almost the same, and independent of the curing temperature. Both isothermal and dynamic DSC methods produce consistent results for the Arrhenius parameters of the resins. The reactivity of the styrene-based thermoset resins can be interpreted in terms of the kinetic parameters including conversion, cure rate, reaction

rate constant, half-life, and activation energy of the cure reaction. The reactivity of these resins, when arranged in ascending order, appears to be

vinyl ester < orthophthalic polyester < isophthalic polyester

Although vinyl ester is rated as the least reactive resin among the three, it attains the highest total ultimate conversion under isothermal conditions.

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### APPENDIX: NOMENCLATURE

$\alpha_p$	conversion at peak maximum in the dynamic experiments
$\alpha_t$	conversion at time $t$ under isothermal conditions
$\alpha_u$	total ultimate conversion under isothermal conditions
$\beta$	linear programmed DSC heating rate
$A$	preexponential factor
$C$	Composite function of $k$ , $t$ , $\alpha_u$ , and $n$ [see eq. (5)]
$d\alpha_i/dt$	cure rate
$dQ_i/dt$	heat flow into or out of the sample
$E$	activation energy of cure reaction
$f(\alpha_p)$	composite function of $n$ , $\alpha_p$ , and $\alpha_u$ [see eq. (10)]
$k$	reaction rate constant
$k_{\text{INT}}, k_{\text{DIF}}$	reaction rate constants determined from eqs. (7) and (6), respectively
$m, n$	reaction orders
$n_{\text{INT}}, n_{\text{DIF}}$	reaction orders determined from eqs. (7) and (6), respectively
$Q_t$	heat which is evolved isothermally corresponding to a partial cure condition at time $t$
$Q_R$	heat evolved due to the residual isothermal reactivity of the sample
$Q_T$	total heat of cure reaction under isothermal conditions
$R$	gas constant
$t_{1/2}$	half-life of the resin
$T$	cure temperature
$T_p$	exothermic peak maximum temperature in the dynamic experiments

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