

Resin-Transfer Molding of Natural Fiber-Reinforced Plastic. I. Kinetic Study of an Unsaturated Polyester Resin Containing an Inhibitor and Various Promoters

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ABSTRACT: In this study an autocatalytic model was used to describe the cure of a polyester system containing various promoters and an inhibitor. The effect of the initiator concentration was investigated. Isothermal DSC measurements were used to determine the kinetic parameters for the curing reaction. The rate of curing increased with increasing initiator concentration. The parameters were found to be temperature dependent. The nonlinear regression analysis showed that by fixing one parameter at a constant value the temperature dependency of the other parameters was de-

scribed by simple relationships. The model was then compared to the experimental data. The reaction rate could be predicted fairly well in a wide range of temperatures. These results will be used to model the cure of this resin in a resin transfer-molding (RTM) process. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2553–2561, 2003

Key words: crosslinking; differential scanning calorimetry (DSC); polyesters; curing of polymers; inhibitors

INTRODUCTION

Unsaturated polyester resins are widely used in the composite industry because of their good mechanical properties, low cost, and low density. They are mainly used in closed-mold processes such as compression molding, injection molding, or resin-transfer molding (RTM), which is the process of interest in this study. The cure behavior of an unsaturated polyester/natural fiber system in an RTM mold will be predicted by use of a one-dimensional model. These results will be compared with those obtained for an unsaturated polyester/fiberglass system and will help to understand and optimize the manufacture of natural fiber composites. To develop this model a cure kinetics study of the unsaturated polyester resin was performed and is presented here.

The unsaturated polyester resin was prepared by the reaction of dibasic organic acids and diols. Depending on the reactants chosen, different types of resins with different properties can be manufactured. The most common general-purpose resins are referred to as orthophthalic, isophthalic, and BPA fumarate. They are sold in the form of solutions containing

40–70 wt % of the prepolymer mixed with a reactive solvent, usually styrene. Many other components can be found in the solution to enhance some key properties and stabilize the resin. Inhibitors, for instance, are usually present in the solution to prevent the polymerization of monomers and unsaturated resins. Promoters can be present as well to catalyze the reaction once the initiator is added.

The curing, or crosslinking, of unsaturated polyesters is a chain propagation reaction. In most cases a peroxide (radical initiator) is added to the resin and attacks the unsaturations in the polyester or the styrene vinyl groups to initiate the polymerization reaction. The styrene provides the crosslink between the polymer chains. Based on the knowledge of this reaction various studies proposed a mechanistic approach to describe the cure behavior of the resin.

Stevenson¹ presented a few models based on the kinetic mechanism for free-radical copolymerization. This mechanism is complex and involves many parameters such as the inhibitor and the initiator concentrations. The models were obtained by simplifying the mechanism with various assumptions and restrictions to simulate industrial processes. They showed good agreement with cure data obtained by isothermal differential scanning calorimetry (DSC). Ng and Manas-Zloczower² proposed a nonisothermal DSC study of the curing kinetics of an unsaturated polyester system based on a mechanistic approach. This work took into account the diffusion-controlled reaction. The evaluation of the kinetic parameters was

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performed by use of dynamic DSC scans. The results were in very good agreement with the experimental data. Once again this model assumed that the concentrations of the different constituents of the resin were known. More recently, Zetterlund and Johnson³ used a new method to determine the Arrhenius constants of an unsaturated polyester resin using dynamic DSC scans and a mechanistic model.

The cure reaction involves many parameters such as the styrene content, the promoter content, the initiator content, and the presence of other chemicals used to modify the properties of the final product. A mechanistic approach, like those described above, would be too complex as part of this investigation, given that the composition of the resin is not known. Numerous studies were conducted using an empirical model to describe the cure kinetics of unsaturated polyester resins.

Kamal and Sourour⁴ and Kamal⁵ showed that the following empirical model adequately represents the cure kinetics of unsaturated polyester resins:

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

where k_1 and k_2 are rate constants that follow an Arrhenius temperature dependency, α is the degree of cure, and m and n are the order of the reactions. More recently this equation was slightly modified by various researchers⁶⁻⁹ to satisfy the condition of zero curing rate at the maximum degree of cure:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(\alpha_{\max} - \alpha)^n \quad (2)$$

Vilas et al.⁶ evaluated the parameters of eq. (1), as well as other empirical relationships, using isothermal DSC measurements. The results showed a temperature dependency of all the parameters (including α_{\max}). The study was performed for three different initiator concentrations. The agreement between the experimental data and the models was found to be excellent, especially for vitrification < 0.6 .

The complexity of the reaction and the presence of many reactants require the temperature dependency of the parameters to predict properly the experimental data.⁷ Yousefi et al.^{8,9} presented the temperature dependency of the parameters in eq. (2) for an unsaturated polyester system using cobalt as a promoter. They expressed these parameters as a polynomial of the second or third order. The temperature dependency was explained by the presence of the promoter. A new procedure was implemented to analyze the isothermal DSC scans and to take into account any unrecorded extent of reaction. They also investigated the influence of glass fibers on the curing behavior of

the resin. The results showed that the fibers did not have a great influence on the parameters, even though the fiber acted as a heat sink that slowed down the reaction rate. Similar observations were made by McGee,¹⁰ who studied the effect of particulate fillers on the curing characteristics of a polyester resin. Increasing the filler content was shown to slow the rate of reaction.

The influence of the promoter and of the inhibitor on the curing of an unsaturated polyester resin was investigated in two separate studies by Ramis and Salla.^{11,12} Their isothermal kinetic analysis, based on DSC measurements, was performed by isoconversional adjustment. The promoters were shown to influence the curing effect but not the final degree of cure. Similarly the inhibitor (hydroquinone) was shown to retard the curing effect and to slow the curing rate of the resin without changing the final degree of cure. In this last study an autocatalytic model similar to eq. (1) was also used. The parameters were found to have almost no temperature dependency. However, the rate constant was shown to depend on the concentration of inhibitor, decreasing with increasing inhibitor concentration. In a more recent investigation the same authors¹³ made a comparative study of an unsaturated polyester resin using different methods. Different procedures were proposed to calculate the degree of cure and the rate of cure using isothermal DSC measurements. One method was found to be more accurate to evaluate the parameters of an autocatalytic model.

In light of all the reviewed studies it can be concluded that DSC is the most reliable tool to study the curing kinetics of unsaturated polyester resins. The curing kinetic behavior of such systems was found to be complex¹⁴ and therefore the empirical model presented in eq. (2) seems the easiest and most reliable way to study this behavior. The first part of this work is therefore to determine the different parameters of eq. (2) by studying the cure kinetics of the chosen resin by isothermal DSC. The method proposed by Salla and Ramis¹³ seems very well adapted to this work and is described in the next section.

EXPERIMENTAL

In this study the commercial unsaturated polyester resin Stypol 040-8086 from Cook Composites and Polymers (Kansas City, MO) was chosen. This resin is manufactured for use in closed-mold processes such as RTM. It is a low-viscosity resin, which starts reacting by addition of an initiator. In this case the chosen initiator (promoter) was MEKP DDM-9 from ATOFINA (Philadelphia, PA). The resin manufacturer recommends the use of an initiator concentration between 0.9 and 2.3% by weight. Therefore concentrations of 1, 1.5, and 2% were investigated during the kinetic study. Like most commercial

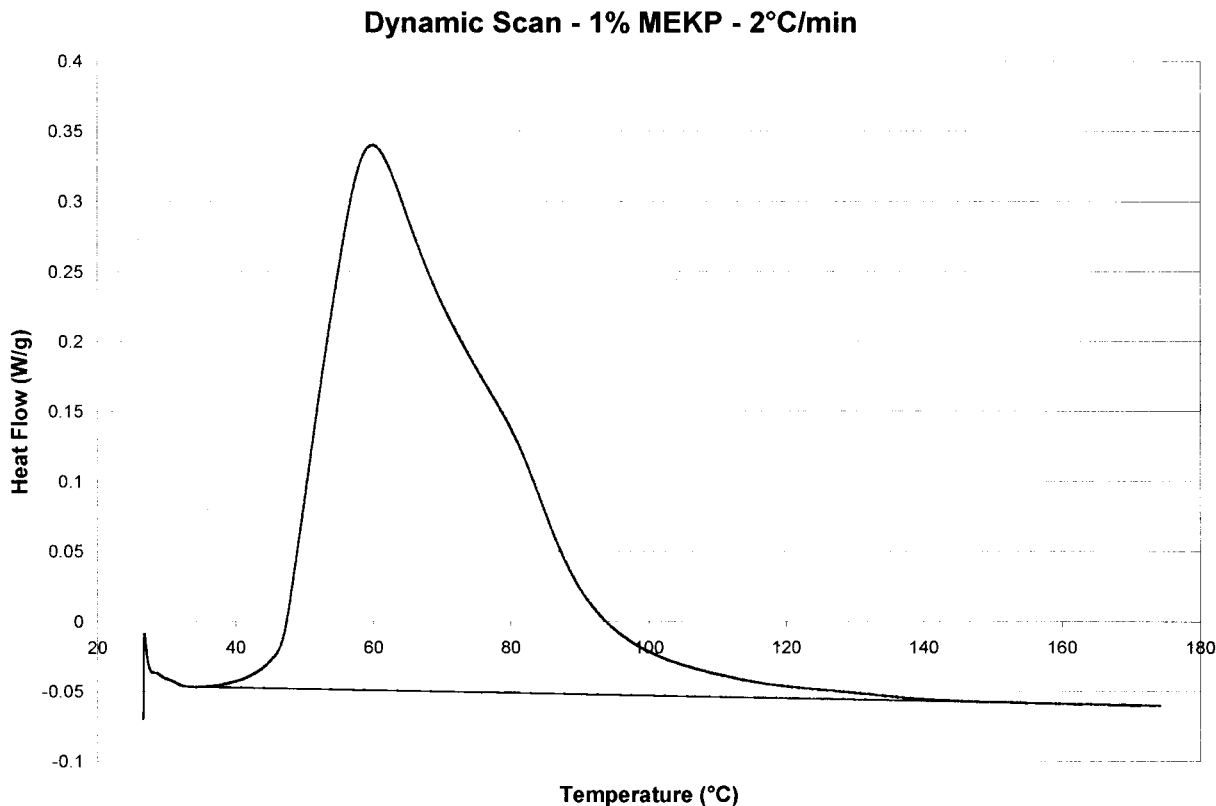


Figure 1 Dynamic DSC scan from 25 to 175°C at 2°C/min, for 1% MEKP concentration.

products this resin contains small amounts of inhibitor and promoters.

The cure kinetics was studied by use of a TA Instruments DSC 2010 apparatus (TA Instruments, New Castle, DE) following well-established procedures.¹⁵ It was assumed that the exothermic enthalpy generated during the curing is proportional to the change in the resin’s degree of cure. The reaction rate was also assumed to be directly proportional to the rate of enthalpy generation dH/dt . The calibration of the apparatus was established by use of indium. First, dynamic scans in the range 25 to 175°C at 2°C/min were performed at the different initiator concentrations. From these dynamic scans the ultimate enthalpy of cure of the reaction H_u was obtained by calculating the area under the curve. These dynamic scans were used as well to have an initial idea of the speed of reaction of the resin.

Then isothermal scans at different temperatures were performed for each initiator concentration to determine the parameters of eq. (2). For each of these scans the isothermal enthalpy of cure H_{iso} was obtained by calculating the area under the curve. After each isothermal scan the sample was cooled to 25°C and a dynamic scan at 10°C/min in the range 25 to 200°C was performed. The area under the curve of this last scan was defined as the residual enthalpy of reaction H_r . The total enthalpy of reaction was therefore given by

$$H_{tot} = H_r + H_{iso} \tag{3}$$

The degree of cure α was then obtained for each experiment as a function of time using

$$\alpha(t) = \frac{H(t)}{H_u} \tag{4}$$

where $H(t)$ is the enthalpy of reaction at time t . The rate of reaction $d\alpha/dt$ as a function of time was obtained as well:

$$\frac{d\alpha}{dt}(t) = \frac{(dH/dt)_t}{H_u} \tag{5}$$

However, recent publications^{8,9,13} showed that $H_{tot} \neq H_u$. This is attributed to a low enthalpy generation, which is beyond the values detectable by DSC. A method was introduced¹³ to take into account the unrecorded part of the isothermal DSC thermogram. The corrected extent of cure and rate of cure are given by

$$\alpha^c = \alpha \left(\frac{H_u - H_r}{H_{iso}} \right) \tag{6}$$

$$\left(\frac{d\alpha}{dt} \right)^c = \frac{d\alpha}{dt} \left(\frac{H_u - H_r}{H_{iso}} \right) \tag{7}$$

TABLE I
Ultimate Enthalpy of Cure for Unsaturated Polyester Resin Obtained by Different Investigators

Author(s)	Q_u (J/g)
Ng and Manas-Zloczower ²	415
Zetterlund and Johnson ³	374
Vilas et al ⁶	231
Yousefi, Lafleur, and Gauvin ⁸	316
Ramis and Salla ¹¹	350
Salla and Ramis ¹³	345
Cuadrado, Borrajo, and Williams ¹⁴	243
This study	345

In the rest of this report all the data mentioned as extent of cure or rate of cure are corrected values. For the same reason the maximum degree of cure is given by

$$\alpha_{\max} = \frac{H_u - H_r}{H_u} \quad (8)$$

In the isothermal experiments the heat capacity of the reactants can be assumed to be constant, as explained by Richter and Macosko.¹⁶ The enthalpy of decomposition of the initiator was neglected as well because the quantities added to the resin were negligible. The resin samples used in the DSC experiments were in the range 8 to 16 mg.

The parameters of eq. (2) were determined with the isothermal scans using Sigmaplot 2000 software (SPSS Inc., Chicago, IL) which performed nonlinear regressions, based on the Marquardt–Levenberg algorithm. To obtain reliable results at least three scans were performed for each temperature. The same comment applies for the dynamic scans. All the results presented are average values over these three scans.

RESULTS AND DISCUSSION

Dynamic scans

Figure 1 shows a typical dynamic scan obtained with a concentration of 1% by weight of initiator. The baseline used to calculate the area under the curve is drawn on the graph. At 2% initiator concentration the resin starts to cure immediately at room temperature. Therefore this curve cannot be used to calculate the ultimate enthalpy of cure because some of the reaction takes place before introducing the sample into the DSC instrument. Another comment is that if the resin starts to cure as soon as the initiator is introduced this could cause a poor wetting of the fibers in the mold. Analysis of this first set of scans shows that a kinetic study of the resin with a 2% initiator concentration is not necessary.

At 1% MEKP concentration the curing reaction starts around 40°C (Fig. 1). The ultimate enthalpy of reaction was evaluated by calculating the area under the dynamic curve. The result obtained is the average over the all range of experiments: $Q_u = 345$ J/g. This value is in agreement with the results found in the literature (see Table I). This result gives the enthalpy of reaction per gram of mixture, resin plus initiator. The contribution of the enthalpy of decomposition of the initiator is neglected since it is used in very small quantities.

At 1 and 1.5% MEKP concentrations isothermal scans at five different temperatures (25, 35, 45, 55, and 65°C) were performed to study the resin kinetics.

Isothermal scans at 1 and 1.5% initiator concentrations

A typical isothermal DSC scan is shown in Figure 2(a). The associated dynamic scan used to evaluate the residual enthalpy of reaction is presented in Figure

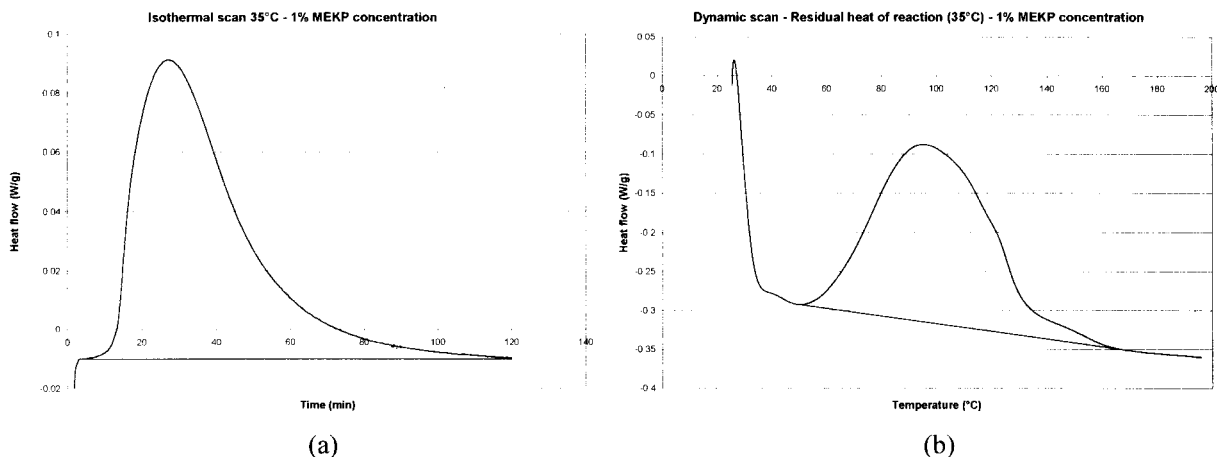


Figure 2 Isothermal DSC scan at 1% MEKP concentration (a) and the associated dynamic scan (b).

TABLE II
Enthalpy Obtained from Isothermal and Dynamic Residual Curves

Temperature (°C)	1% MEKP			1.5% MEKP		
	Q_{iso} (J/g)	Q_r (J/g)	Q_{tot} (J/g)	Q_{iso} (J/g)	Q_r (J/g)	Q_{tot} (J/g)
25	231	80	311	221	76	297
35	229	64	293	258	51	309
45	276	46	322	277	34	311
55	290	25	315	302	19	321
65	304	16	320	302	13	315

2(b). The baselines for these two curves are drawn on the graph.

The isothermal enthalpy of cure and the residual enthalpy of cure were calculated for each experiment by evaluating the area under these curves. The total enthalpy of cure, which is equal to the sum of these two data, was then calculated at each temperature. The results are given in Table II. The total enthalpy of cure H_{tot} is not constant with temperature and the values are always below the ultimate enthalpy of cure obtained by dynamic DSC. As explained earlier, this difference could be explained by low enthalpy generation at the start and the end of the reaction. In these zones the calorimeter is not sensitive enough to detect any enthalpy. This is why the method described in the Experimental section was chosen.

The first step of the isothermal study was to evaluate the maximum degree of cure at each temperature and each concentration by use of eq. (8). The results are summarized in Figure 3. As expected, the maximum degree of cure increases with increasing temperature and initiator concentration. Yousefi et al.⁸ proposed that the temperature dependency of the maximum degree of cure could be presented in the form of a third-order polynomial expression. However, this equation was valid only in the range of temperature studied. This study will be used to simulate the curing behavior of this resin in an RTM mold; thus the maximum extent of cure will have to be predicted outside the temperature studied. To fit the experimental data a sigmoid equation was thus chosen with the condition that α_{max} tends toward 1 at high temperatures.

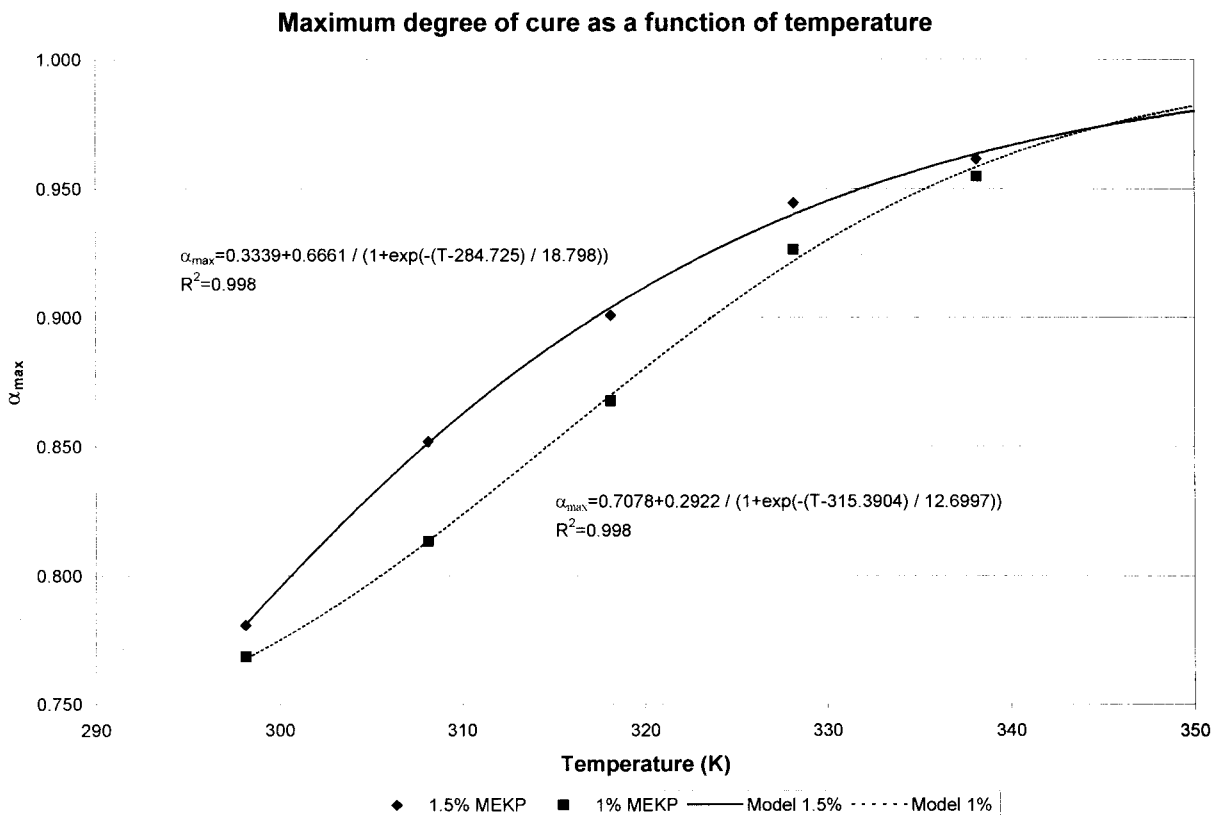


Figure 3 Maximum degree of cure as a function of absolute temperature.

TABLE III
Kinetics Parameters Obtained by Application of Eq. (2) (neglecting k_1)

Temperature (°C)	1% MEKP				1.5% MEKP			
	k_2	m	n	$m + n$	k_2	m	n	$m + n$
25	1.13×10^{-3}	0.71	1.28	1.99	1.58×10^{-3}	0.67	1.33	2.00
35	1.87×10^{-3}	0.63	1.25	1.87	3.01×10^{-3}	0.68	1.57	2.25
45	2.47×10^{-3}	0.59	1.37	1.96	4.09×10^{-3}	0.56	1.65	2.21
55	3.23×10^{-3}	0.45	1.53	1.98	4.05×10^{-3}	0.38	1.63	2.01
65	2.87×10^{-3}	0.26	1.45	1.71	4.48×10^{-3}	0.25	1.63	1.88

The correlations at the two different concentrations are shown on Figure 3.

The extent of cure and rate of cure for each isothermal experiment were then calculated by use of eqs. (4) and (5), and corrected by use of eqs. (6) and (7). The rate of cure was then plotted versus the degree of cure and the parameters of eq. (2) were determined with Sigmaplot 2000 software.

All the experimental curves were fitted by use of eq. (2) with a high degree of accuracy. The nonlinear regressions were performed with the condition $k_1 > 0$. From Figure 2(a) it can be seen that the initial rate of cure is very small. The curve-fitting results confirm this observation and show that k_1 does not have a major effect on the results. If k_1 is neglected, the values obtained for k_2 , m , and n are not changed. In the rest of this study k_1 will therefore be neglected in eq. (2). The

curve-fitting results are summarized in Table III for both initiator concentrations and at each temperature.

All the parameters were found to be temperature dependent. The values of m at 1% and 1.5% MEKP concentration are very close and do not seem to be influenced by the initiator concentration. On the other hand, the results for n and k_2 are significantly higher at 1.5% MEKP. Even though m and n are temperature dependent, it is interesting to notice that the sum of these two parameters varies only slightly and is roughly equal to 2 in the range of temperature studied. In their study of the influence of a cobalt promoter on the curing of an unsaturated polyester resin Yousefi et al.⁸ proposed that the temperature dependency of m and n could be presented in the form of a second-order polynomial expression. However, the results obtained here do not show any clear trend, es-

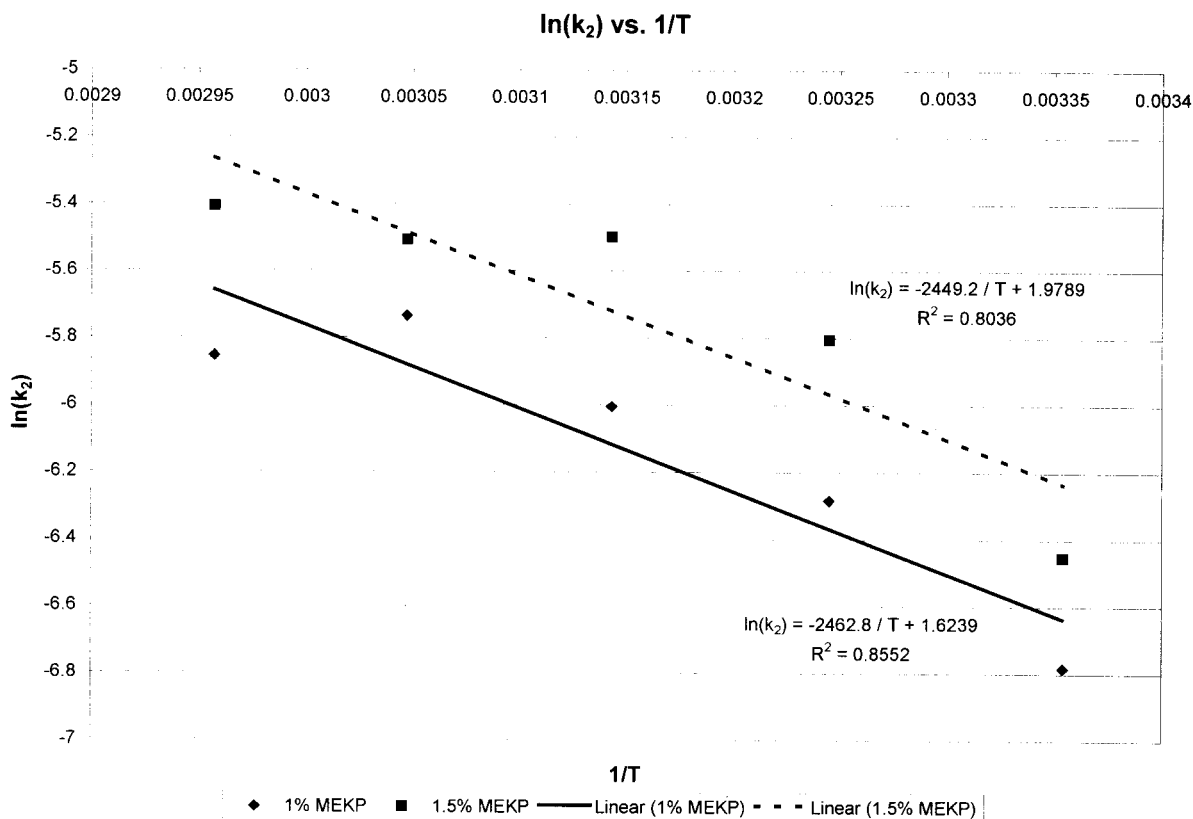


Figure 4 Logarithm of the rate constant k_2 as a function of reciprocal absolute temperature.

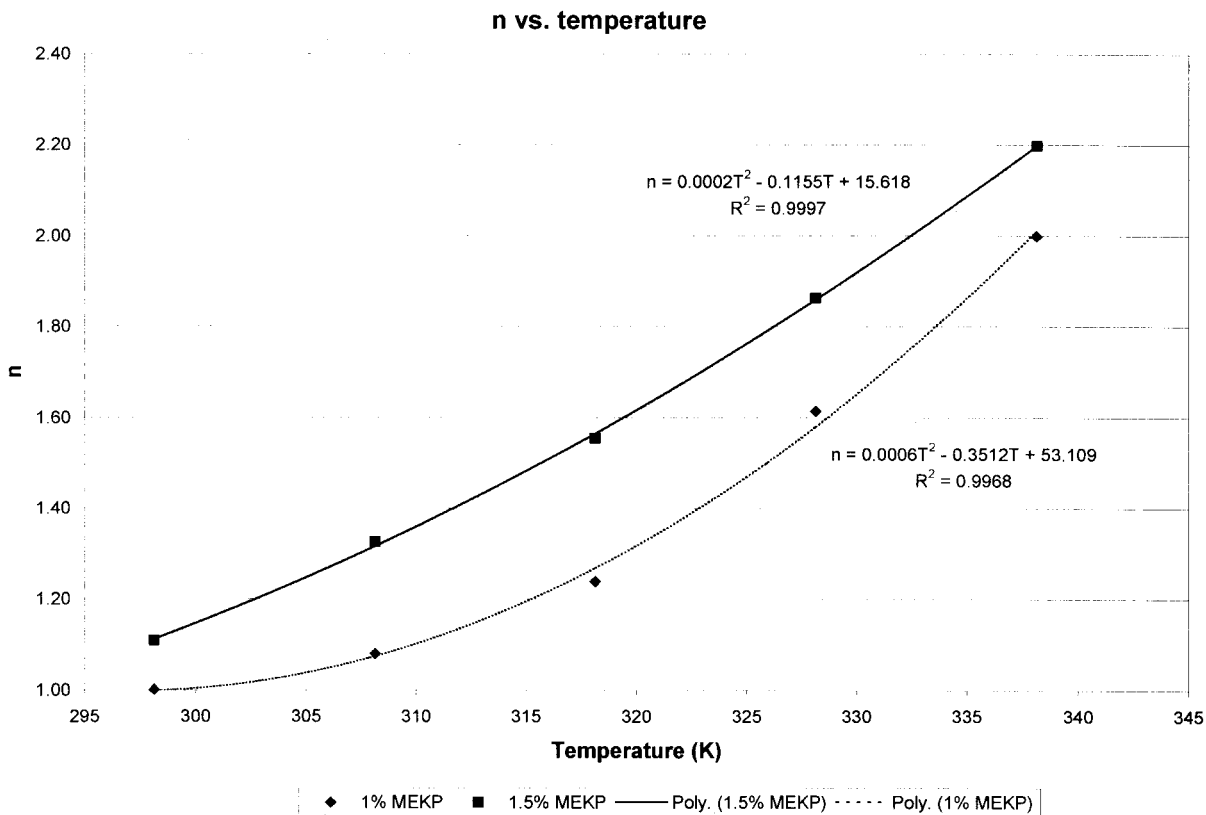


Figure 5 Parameter n as a function of absolute temperature.

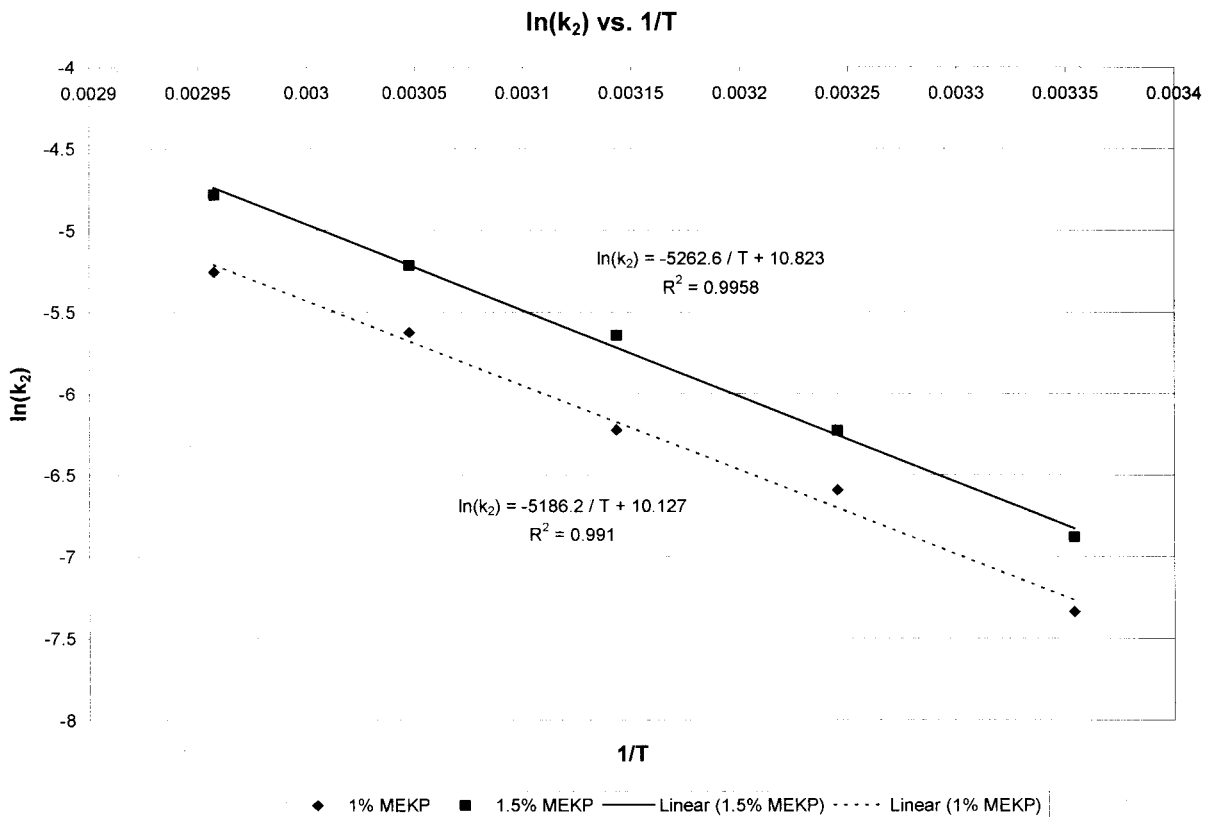


Figure 6 Logarithm of the rate constant k_2 as a function of reciprocal absolute temperature for $m = 0.5$.

TABLE IV
Arrhenius Constants for k_2

1% MEKP		1.5% MEKP	
A (s^{-1})	E (J/mol)	A (s^{-1})	E (J/mol)
25008	43120	50148	43755

pecially for n , which shows a slightly different behavior at 1% MEKP concentration and 1.5% concentration. Moreover, the parameter k_2 , which was shown to follow an Arrhenius relationship in previous works,⁴⁻¹⁴ cannot clearly be described by such a relationship (Fig. 4).

$$k_2 = A \exp\left(-\frac{E}{RT}\right) \quad (9)$$

where A is a constant, E is the activation energy, R is the perfect gas constant, and T is the temperature in Kelvin.

Because these results will be used to predict the curing behavior of this resin in an RTM mold filled with natural fibers, accurate correlations should be determined to describe the parameters' variations. More nonlinear regressions were performed by use of Sigmaplot 2000 software with different imposed conditions. First, the condition $m + n = 2$ was fixed. The curve-fitting results were not very accurate for most of the temperatures studied. Conditions of $n = 1.5$ at 1.5% MEKP concentration and $n = 1.4$ at 1% MEKP concentration were chosen in a second attempt to fit the experimental curves. These choices were based on the average value for this parameter over the range of temperatures studied. The experimental curves were fitted with good accuracy. The parameter m was found to have a linear relationship with T , very similar at both concentrations. The rate constant k_2 , however, cannot be fitted properly with an Arrhenius relationship, especially at 1% MEKP concentration.

Finally, the parameter m was fixed at a value of 0.5 (once again based on the average value over the range of temperatures studied). Given that the parameter m is not influenced by the initiator concentration, this value is valid at 1 and 1.5% MEKP concentrations. The experimental curves were fitted with good accuracy. The parameter n is well described by a polynomial relationship of the second order, as shown in Figure 5. The n values increase with increasing temperature and increasing initiator concentration.

Moreover, the results obtained for the rate constant show that k_2 follows an Arrhenius relationship at 1 and 1.5% MEKP concentrations. Figure 6 presents $\ln(k_2)$ plotted as a function of $1/T$. The slopes of the two lines are almost identical, which means that the activation energy is not dependent on the initiator concentration, as expected. An increase in initiator concentration facilitates destruction of the inhibitor and therefore accelerates the reaction. However, the crosslinking reaction is not changed by this increase and therefore the activation energy also should not be changed. The parameters for eq. (9) describing k_2 are summarized in Table IV.

These last results give reliable correlations over the range of temperatures studied. Figure 7(a) and (b) show the plots of the isothermal curing rate versus the degree of cure for the two concentrations under study.

The trends are very similar at the two concentrations under study. The calculated rate of cure fits very well the experimental data, especially at the lower temperatures. At higher temperatures, for instance 65°C, the predicted results are shifted slightly to the right compared to the experimental results. At this temperature a difference of behavior in the last part of the curve can be observed between the model and the experiments. This could be explained by the addition of a thermally induced crosslinking reaction in the system or by the fact that above a certain degree of

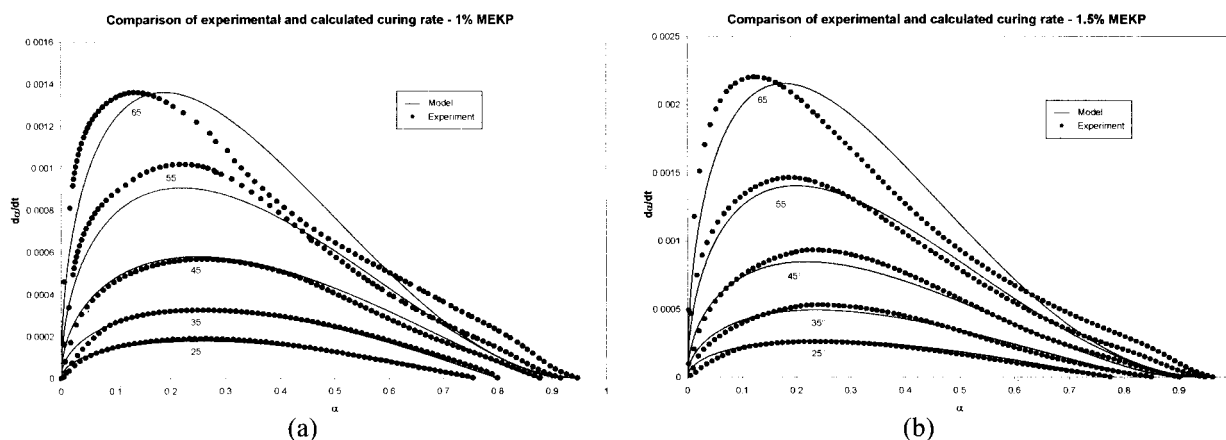


Figure 7 Comparison of experimental and calculated curing rate for (a) 1% MEKP and (b) 1.5% MEKP.

cure the curing reaction becomes diffusion controlled.^{8,14} This last mechanism occurs at all temperatures and therefore does not seem to be the cause of this difference of behavior. The lack of precision of the DSC apparatus at high reaction rates could as well explain these discrepancies. However, this model seems to predict fairly well the reaction rate of the resin over a wide range of temperatures, which is needed for the prediction of the curing behavior in an RTM mold. The curves giving the degree of cure as a function of time can be plotted as well by use of this model.

CONCLUSIONS

In this work a kinetic study of an unsaturated polyester resin was performed by use of isothermal DSC experiments. The results were fitted with a well-accepted autocatalytic model and the parameters determined using Sigmaplot 2000 software. The value found for the enthalpy of reaction was in very close agreement with values reported in previous studies.

The experimental curves were fitted with a high degree of accuracy and all the parameters were found to be temperature dependent. This time dependency was explained in previous works by the presence of promoter in the resin system. Because the initial rate of reaction was very small because of the presence of an inhibitor in the system, the rate constant was shown to be negligible. It was found that by giving a fixed value to one parameter, the experimental curves could be very well fitted. Moreover, the parameters left to vary were expressed as simple functions of the temperature. The best results were obtained by fixing $m = 0.5$ and determining n and k_2 ; n was expressed as a second-order polynomial relationship and k_2 followed an Arrhenius relationship. The rate constant k_2 increased with increasing initiator concentration and the activation was found to be constant.

The autocatalytic model obtained by fixing $m = 0.5$ gave more reliable results than any other regression

performed in this study. Some discrepancies were observed at the highest temperatures. The presence of thermally induced reactions, diffusion-controlled reaction, or lack of precision of the DSC apparatus at high reaction rates can explain these discrepancies. This model will be used to predict the curing behavior of this unsaturated polyester system mixed with natural fibers in an RTM mold. Finally, the DSC data provided useful heat flow data that will be used to design the mold's heating loop.

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