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**A KINETIC MODEL OF RESOL CURING IN THE PRODUCTION OF  
INDUSTRIAL LAMINATES**

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**Abstract**

The kinetics of resol resin cross-linking was investigated by a single-heating-rate DSC method. A simple kinetic model was developed, which predicts the behavior in the industrial impregnation process of laminate manufacture. It was found that the curing rate can be well described by a pseudo first-order kinetic model with apparent activation energy of 87.3 kJ/mol. The kinetic model was verified by comparing calculated and experimental conversions obtained in the run at the production line.

**Introduction**

Phenol-formaldehyde thermosetting resins have attracted special attention because of their wide range of industrial applications in adhesives, casting, molding, and in structural parts [1]. The chemistry of prepolymers such as novolac and resols has been studied in detail in the past decades [2–5]. The influence of a number of parameters on the synthesis and cure has been analyzed [6–8].

One of the possible applications of phenol-formaldehyde resins is in the production of industrial laminates. Laminates are multilayers of impregnated fibrous or other reinforcement sheets bonded together [9].

Reinforcing materials for laminates include glass, silica, asbestos, cotton fabric, kraft and cellulose paper. Reinforcement is impregnated by thermoreactive resins, which are cured at elevated temperature and pressure to produce a homogeneous duroplast. The thermoreactive resin may be an epoxide, silicone, melamine, or phenol-formaldehyde resin.

Industrial laminates made with phenol-formaldehyde resins are used primarily in electrical applications. Cellulose paper and nylon are used for the major part of electrical laminates, some of which are copper-clad for printed circuitry [9].

In the production of laminates, resins have to cure slowly in steps. Therefore, the most useful types are phenolic-resol resins with phenol : formaldehyde ratio above 1:1.5. These resins cross-link and form homogeneous duroplast at elevated temperatures.

Industrial processes of laminate production are already well established. A reinforced material impregnated with a resin passes through a continuous drying oven where volatiles are removed and the resin is advanced from the liquid A-stage to the rubber-like B-stage [1]. A commercial oven may be divided into three zones. The first zone is the drying zone, where all volatiles are removed, while in the second and third zones curing of the resin occurs.

The aim of the work was to formulate a simple kinetic model of resol curing. The model should well predict the behavior in an industrial impregnation process for the manufacturing of laminates for printed circuitry. A limited set of laboratory scale experiments were carried out by applying the differential scanning calorimetry (DSC) technique. The overall kinetic parameters for the curing reaction were estimated from data based on a single-heating-rate method. The kinetic model was then verified using data from an industrial process.

## Experimental

The resin used in this study was a mixture of proprietary commercial resol-type phenol-formaldehyde resins TL 706 and TL 706/3 (Fenolit, Borovnica). A dried mixture of resins was used for the estimation of kinetic parameters using differential scanning calorimetry (DSC).

DSC was performed with the Mettler DSC 27 HP differential scanning calorimeter at a nitrogen pressure of 20 bar in order to compensate for the evaporating effect of the water formed during polycondensation. The dynamic scans were taken at a heating rate of 10°C/min in a temperature range of 50–250°C. For DSC sample preparation, approximately 28 mg of the mixture was used in an aluminum crucible of 40 µl with a perforated lid. The heat flow data and the area under the curve obtained from the DSC exotherm were processed to obtain the extent of the reaction.

The kinetic model was validated in laboratory experiments of laminate preparation as well as in an industrial run. A laboratory simulation of the industrial process was performed with prepregs prepared with 100 g of  $\alpha$ -cellulose paper impregnated with the resol mixture (E6, E7, E8, E9). The validity of the proposed kinetic model in an industrial application was verified using a commercial laminate type Cu CART Fr2 (P1).

To remove the solvent, the prepregs (E6, E7, E8, E9) were dried in a vacuum to constant weight at a temperature of 132°C. It was found by the DSC method that about 4% of the prepolymer already reacted during the drying. The amount of the reacted prepolymer was taken into account when the data were analyzed.

The industrial reactor consisted of four consecutively placed ovens. Each oven was set at different temperature to obtain a desired end product. A prepregs passed through the ovens by means of continuously traveling belt. The residence time in an oven depended on the speed of the belt. To follow the process conditions at the production line, the curing program of the laboratory experiments was divided to four zones. Because the

laboratory preregs (E6, E7, E8, E9) were dried in vacuum, the first zone was eliminated in these experiments. The complete temperature-time program is shown in Table 1.

**Table 1.** The operating conditions for laboratory validation experiments (E6, E7, E8, E9) and industrial run (P1).

	<i>Zone 1</i>	<i>Zone 2</i>	<i>Zone 3</i>	<i>Zone 4</i>
<i>E6</i>				
Temperature (°C)	/	144	137	126
Residence time (s)	/	76	76	76
<i>E7</i>				
Temperature (°C)	/	144	137	126
Residence time (s)	/	50	50	50
<i>E8</i>				
Temperature (°C)	/	173	164	151
Residence time (s)	/	63	63	63
<i>E9</i>				
Temperature (°C)	/	115	110	101
Residence time (s)	/	63	63	63
<i>P1</i>				
Temperature (°C)	158	144	137	126
Residence time (s)	63	63	63	63

After the selected curing times in zones 2, 3, and 4, the preregs were removed from the oven. The remaining unreacted resin was extracted into tetrahydrofuran. The solvent was then evaporated under reduced pressure and the extent of reaction was determined by DSC analysis.

## Results and discussion

**Kinetic model development.** Curing of thermosetting materials generally involves transformation of low molecular weight monomers and prepolymers to high molecular weight amorphous solids by means of chemical reactions. The basic parameter governing the state of the material is the chemical conversion. Therefore, knowledge of the curing

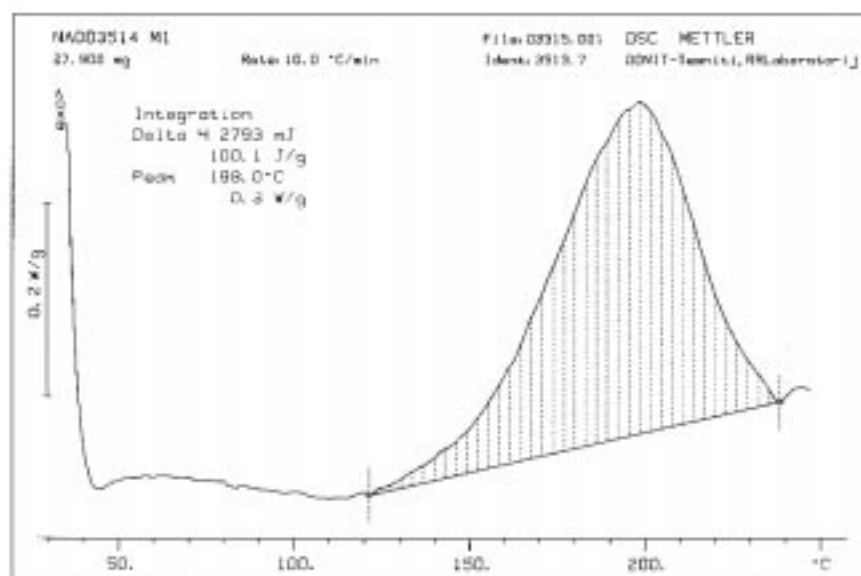
rate and how the rate changes with the cure temperature is important and useful for predicting the chemical conversion achieved after a cure schedule.

The chemical structure of resol prepolymers is very complex due to the many closely related isomers available. Therefore, the cure of resols is extremely complex involving a number of competing reactions each of which may be influenced by reaction conditions, and it is not easy to determine precisely what takes place [10]. Nevertheless, chemical reactions for the curing are basically divided into three stages [7].

However, a lumped kinetic equation may be employed for the prediction of individual parameters which affect the extent of the reaction. For that purpose, the curing rate in terms of the extent of the reaction is assumed to be adequately described by a power-law kinetic model [11]

$$\frac{d\alpha}{dt} = k_0 \exp\left[-\frac{E_{app}}{R \cdot T}\right] (1 - \alpha)^n$$

where  $\alpha$  is the extent of the reaction,  $E_{app}$  is the apparent activation energy in J/mol,  $k_0$  is the preexponential factor in  $s^{-1}$ ,  $n$  is the reaction order, and  $T$  is temperature in K.



**Figure 1.** DSC dynamic scan for the determination of kinetic parameters ( $m_{resol} = 27.9$  mg;  $\beta = 10$  K/min).

Assuming the heat of reaction released at any time is proportional to the number of moles reacted at that time in a DSC experiment, the extent of the curing reaction at any time may be defined as [11,12]

$$\alpha = \frac{\Delta H(t)}{\Delta H_T} \quad (2)$$

where  $\Delta H(t)$  is the partial area under the DSC curve up to the time  $t$  and  $\Delta H_T$  is the total heat released during curing reaction determined by DSC. By integrating the reaction peak acquired from the DSC dynamic scan of completely cross-linked original resol mixture (Figure 1)  $\Delta H_T$  was found to be of 100.1 J/g.

To determine the kinetic parameters in Eq. 1,  $E_{app}$ ,  $k_0$ , and  $n$  a single-heating-rate method was performed by DSC. This method is attractive because it can, in principle, provide from one experiment what would otherwise require three or more lengthy experiments [11]. The method, while valuable, is not consistently reliable when used to predict the course of a reaction over a wide time-temperature range. The criterion for judging the dynamic experiment is usually its ability to describe and predict accurately the isothermal behavior [11].

Differentiation of Eq. 1 by time considering temperature change gives

$$\frac{d}{dt} \left( \frac{d\alpha}{dt} \right) = k_0 \exp \left[ -\frac{E_{app}}{R \cdot T} \right] (1 - \alpha)^n \frac{E_{app}}{R \cdot T^2} \frac{dT}{dt} - k_0 \exp \left[ -\frac{E_{app}}{R \cdot T} \right] (1 - \alpha)^{n-1} n \frac{d\alpha}{dt} \quad (3)$$

Combining Eqs. 1 – 3 and rearranging the expression the final relationship in terms of measurable quantities in the single-heating-rate method may be expressed as

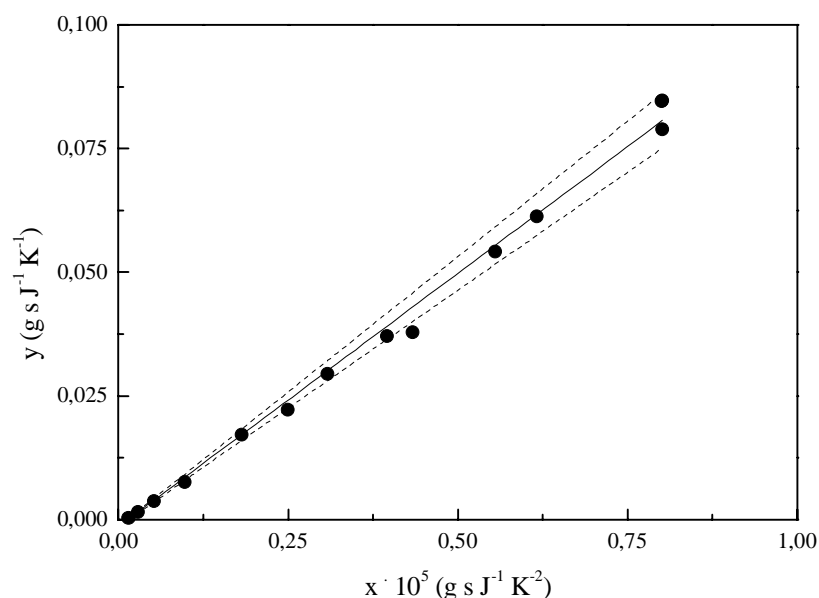
$$\frac{(1 - \Delta H(t)/\Delta H_T) d/dt (d\Delta H(t)/dt)}{\beta (d\Delta H(t)/dt)^2} = \frac{E_{app}}{R} \frac{(1 - \Delta H(t)/\Delta H_T)}{(d\Delta H(t)/dt) T^2} - \frac{n}{\beta \Delta H_T} \quad (4)$$

where  $\beta = \frac{dT}{dt}$  is the heating rate in K/s.

It is convenient to simplify Eq. 4. The left term of the Eq. 4 is represented by  $y$  and the first term on the right side excluding  $E_{app}$  and  $R$  is represented by  $x$ . It follows

$$y = \frac{E_{\text{app}}}{R} x - \frac{n}{\beta \Delta H_T} \quad (5)$$

The objective of the kinetic analysis, however, is to confront the experimental data obtained by the DSC dynamic scan represented in Figure 1 with the expression given by Eq. 5. From the given set of data the apparent activation energy,  $E_{\text{app}}$ , and the reaction order,  $n$ , can be determined. Performing the linear regression method on the experimental data (Figure 2) the  $E_{\text{app}}$  was calculated from the slope of the regression line. A confidence interval of 95% was calculated by the regression technique. The apparent activation energy was found to be  $87.3 \pm 2.6$  kJ/mol.



**Figure 2.** Linear regression of the experimental data according to Eq. 4 with 95% confidential intervals.

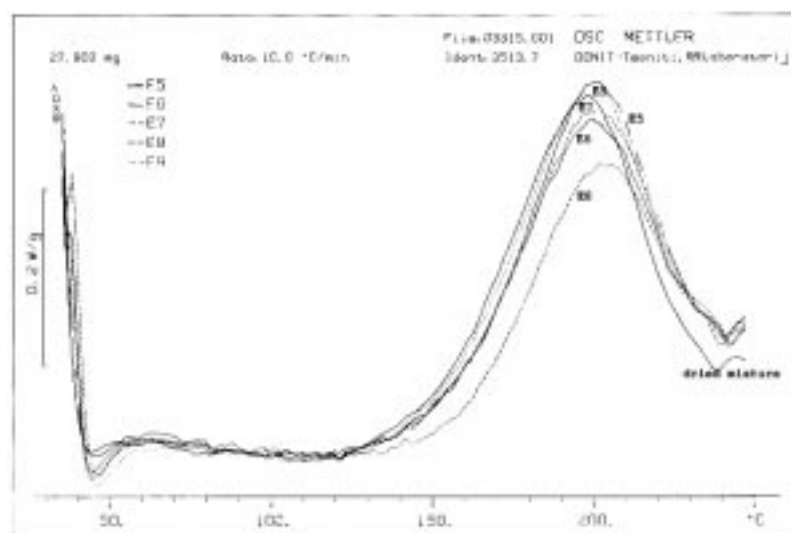
From the intercept of the regression line in Figure 2 the reaction order was found to be  $1.1 \pm 0.04$ . According to the statistically obtained value of the reaction order it was assumed that the kinetic model (Eq. 1) could be well approximated by a first-order reaction rate. Therefore, the parameter  $n$  in Eq. 1 was fixed at value 1.

Knowing the  $E_{app}$ , the preexponential factor,  $k_0$ , was calculated from the integrated Eq. 1 for different conversions at a given temperature. The evaluated mean value of  $k_0$  was equal to  $(4.0 \pm 0.36) \times 10^7 \text{ s}^{-1}$ . The similar order of magnitude for the values of the apparent activation energy and preexponential factor were found in the study of curing behavior of epoxy resins [13, 14].

**Model validation.** The kinetic parameters obtained by the analysis of the curing process in the dynamic scan were verified by curing the prepregs E6, E7, E8, and E9, as well as by curing a sample P1 at the industrial production line. The operating conditions shown in Table 1 were employed in the simulations. The extent of reaction,  $\alpha_v$ , was determined from residual resin in a sample. DSC run employing the same conditions used for the determination of kinetic parameters was performed. From the heat released  $\alpha_v$  may be calculated from the expression

$$\alpha_v = 1 - \frac{\Delta H(t)}{\Delta H_T} \quad (2)$$

Typical DSC curves of the residual resin from the laboratory samples are shown in Figure 3.



**Figure 3.** DSC scans of the laboratory validation experiments (E6, E7, E8, E9) and sample E5.



Table 2 shows the extent of reaction calculated from the developed kinetic model (Eq. 1) in each temperature zone separately and the final measured extent of reaction of samples which passed the temperature program. One can observe a good agreement between the calculated value and the measured extent of reaction in zone 4.

**Table 2.** Comparison of experimental and calculated extent of reaction for laboratory samples E6, E7, E8, and E9.

	kinetic model				experimental
	$\alpha_{v, cal}$ end of Zone 1	$\alpha_{v, cal}$ end of Zone 2	$\alpha_{v, cal}$ end of Zone 3	$\alpha_{v, cal}$ end of Zone 4	$\alpha_{v, exp}$ end of Zone 4
E6	0.04	0.08	0.10	0.11	0.12
E7	0.04	0.07	0.08	0.09	0.10
E8	0.04	0.18	0.25	0.28	0.33
E9	0.04	0.04	0.04	0.04	0.04

It can be considered that Eq. 1 is a kinetic equation that seems to describe quite reasonably the behavior of the resol curing in laminates at the conditions employed in the industrial process. Furthermore, the single-heating-rate method performed by DSC proved to be a useful and quite accurate method for the determination of kinetic parameters.

To confirm the validity of the proposed kinetic model in a continuous process, an industrial run was performed. However, at the production line the curing reaction in the first zone occurs in a solution, where the solvent evaporation takes place simultaneously. It was assumed that only the preexponential factor,  $k_0$ , was affected by the process in the solution. The change of the preexponential factor was determined only by processing a prepreg under conditions characterizing the first zone. After measuring the extent of reaction (E5; Figure 3), the value of  $k_0$  in the first zone was found to be  $1.51 \times 10^8 \text{ s}^{-1}$ . It was used in the conversion evaluation in the first zone for P1. The comparison of calculated and experimentally obtained data is shown in Table 3.

The results confirm that the kinetic model proposed in this work may be utilized in the production of laminates in order to predict the properties of final products as well as in the optimization process of temperature program in the continuous production line.

**Table 3.** Comparison of experimental and calculated extent of reaction for industrial sample P1.

	kinetic model				experimental
	$\alpha_{v, \text{cal}}$ end of Zone 1	$\alpha_{v, \text{cal}}$ end of Zone 2	$\alpha_{v, \text{cal}}$ end of Zone 3	$\alpha_{v, \text{cal}}$ end of Zone 4	$\alpha_{v, \text{exp}}$ end of Zone 4
P1	0.22	0.25	0.26	0.27	0.31

## Conclusions

The kinetic model obtained from the DSC dynamic scan obeys simple first order kinetics with an apparent activation energy of 87.3 kJ/mol. It may be used to predict the behavior of resol curing in an industrial process. Furthermore, also the quality and characteristics of the final product can be predicted by determining the degree of resol cross-linking in the laminates. The increase in temperature of the heating zone by 30°C results in five times shorter residence time with unchanged product quality and observable advance in production capacity.

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### **Povzetek**

Kinetiko reakcije polikondenzacije rezolne smole smo spremljali s pomočjo diferenčne dinamične kalorimetrije. Predpostavili smo preprost kinetični model za napoved dogajanja v industrijskem procesu izdelave laminatov. Ugotovljeno je bilo, da je mogoče hitrost zamreževanja preučevane rezolne smole matematično zapisati s kinetično enačbo psevdo prvega reda z navidezno aktivacijsko energijo 87.3 kJ/mol. Zanesljivost kinetičnega modela smo preverili v nizu eksperimentov, ki so potekali pri pogojih, enakih tistim v industrijskem procesu, kakor tudi s primerjavo izračunanih in eksperimentalno določenih konverzij, dobljenih med preizkusom na proizvodni liniji.