Cure behavior of paper–phenolic composite systems: assessment of the progress of cure by differential scanning calorimetry

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ABSTRACT: The cure behavior of phenolic-resin-impregnated kraft paper composites was studied by differential scanning calorimetry under dynamic and isothermal modes of operation. Procedures for establishing baselines, progress of cure, and fractional conversions as a function of time or temperature are presented. In dynamic experiments, the cure process was monitored up to 525 K. In isothermal experiments, curing was conducted at 430 K, 440 K, 450 K, 460 K, and 470 K. Heating rates were in the range 5–40 K/min. The exothermic heat of cure was found to be about 740 kJ/kg resin from both the dynamic and isothermal experiments. Results for isothermal experiments were adjusted to account for differences in the residual heat of cure at temperatures below 525 K.

KEYWORDS: Calorimetry, composites, curing, dynamics, isothermal process, polyphenolics, scanning.

Phenolic resins find a wide variety of uses, especially in coating applications, adhesives, carbonless copy paper, molding compounds, abrasives, laminates, air and oil filters, and other composites (*1*). Paper-phenolic composites, such as laminates, are manufactured by curing paper impregnated with phenolic thermosetting resins. Understanding the cure behavior and the cure kinetics is an important area of research for the manufacture of such composite materials.

Even though there is extensive literature on the cure behavior of epoxy systems and their composites with specialty fibers (*2, 3*), literature on the cure of phenolic systems and systems containing cellulosic fibers is limited. Furthermore, a close examination of the available literature on the curing of phenolics (*4–8*) reveals a number of unresolved issues regarding the nature of the cure reactions, i.e., whether they are endothermic or exothermic, the values of heat of cure, dependence on thermal history, and the mode of kinetics. The present study is aimed at clarifying these questions in a systematic manner. A critical evaluation of procedures to study the cure process and to determine the heat of cure and conversion as a function of time or temperature are presented in this paper. A future article will focus on the kinetic modeling of these reactions.

The literature includes several procedures for monitoring the progress of cure in composites and thermosetting systems (*9–11*). One way is to use chemical or spectroscopic procedures such as infrared or NMR (nuclear magnetic resonance) techniques (*12*) to monitor the depletion of reactant species or appearance of products that can be associated with the progress of cure. Another way is to monitor physical or thermal changes, such as changes in the viscosity, mechanical properties, glass-transition temperatures, heat capacity, or other heat effects associated with the reaction. Both approaches have advantages and limitations. Cure reactions of thermosets in composites are usually complex (*4*), and it is often easier to use changes in mechanical or thermal properties as a probe. In the present study we have used differential scanning calorimetry (DSC).

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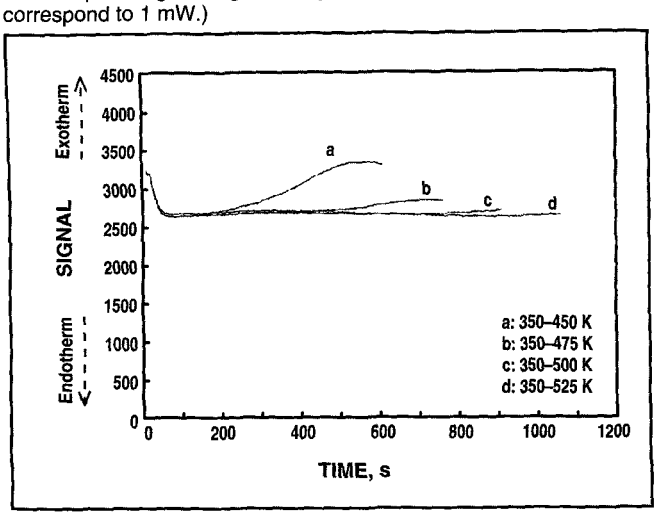
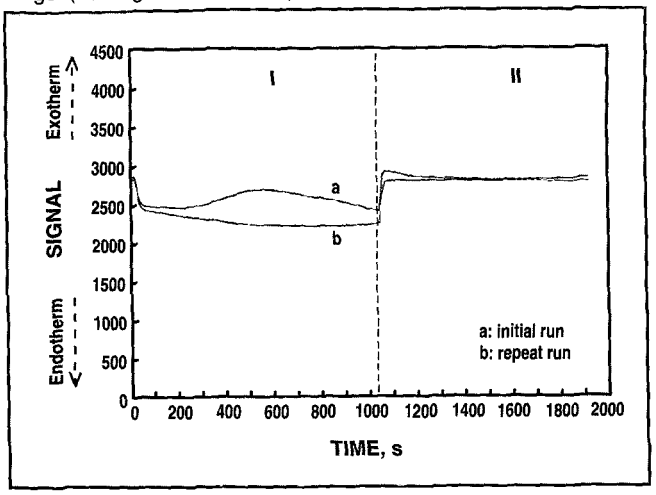
1. DSC scans during progressive heating of paper–phenolic composite. Sample weight 13 g; heating rate 10 K/min. (200 signal units correspond to 1 mW.)



2. DSC scans on paper–phenolic composite. Sample weight 7.4 mg. Region I—dynamic heating range at 10 K/min. Region II—isothermal range. (200 signal units correspond to 1 mW.)



Experimental procedures

Samples

Phenolic-impregnated kraft paper composites were prepared using a generic phenol–formaldehyde resin in methanol–water solutions. The resin content of the composites was approximately 27% by weight.

Differential scanning calorimetry

A Perkin–Elmer DSC-2 differential scanning calorimeter, digitized in our laboratory (*13, 14*) for data collection and analysis, was used in all experiments. The digitization process involves only the digitization of the DSC signal and the corresponding temperature. An A/D (analog to digital) converter and the computer timer were used to collect data at discrete intervals.

Energy and temperature calibrations and evaluation of the dependence on sample mass or heating rate were conducted using the melting temperature and the heat of melting of indium. Accuracy of the instrument was then tested using the instrument calibration constant (K) to determine the melting transitions of zinc, tin, and lead. With this system, heats of transitions are determined with an accuracy better than ± 2.5%. Details are described elsewhere (*14*).

Sample pans

In the investigation of the paper-phenolic composites, Perkin–Elmer stainless steel Large Volume Capsules were used to suppress liberation of volatiles and loss of mass. These capsules are capable of withstanding pressures up to 350 psi (2.4 MPa), which limited the experiments in this study to temperatures below 525 K.

Assessment of baseline and peak areas

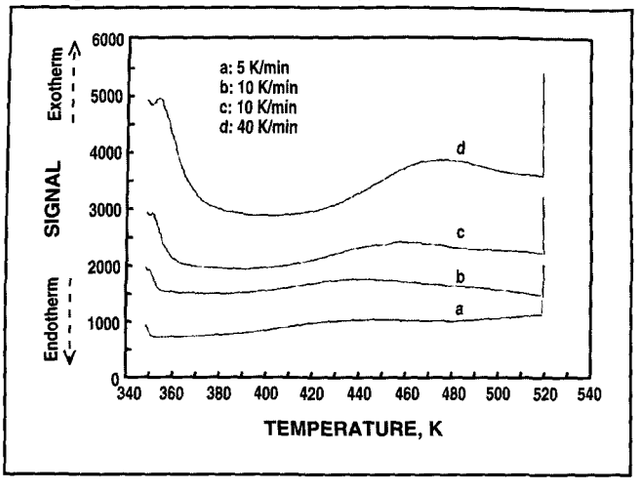
Two different procedures have been employed to establish a baseline. One of the procedures is applicable to systems that undergo physical transformations (i.e., melting of indium), and the other is applicable to systems that undergo chemical transformations (i.e., the curing of phenolics).

In the case of physical transformations, the start and the end of the thermal transition is established by the criterion of increasing slope (*14, 15*). In the present analysis, a deviation of 0.5% or greater of the signal value from the initial baseline for three sequential points is taken as the start of such a peak. The end of the peak is assessed by checking for a deviation of less than 0.5% for three consecutive points. The baseline is then drawn as a straight line between the start and the end of the peak.

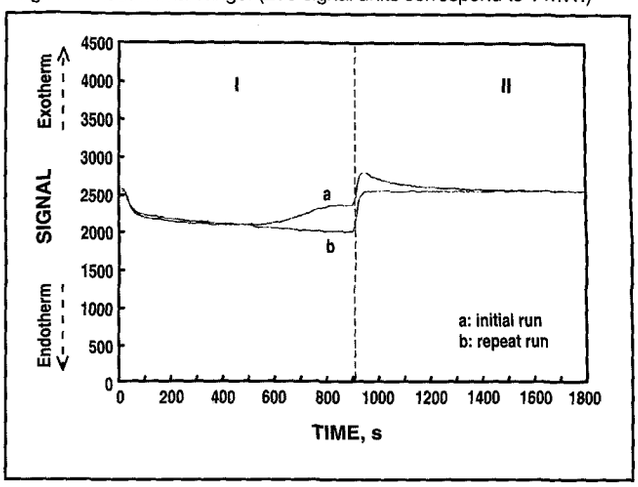
Once the baseline is constructed, the area calculation is performed by subtracting the peak signal from the baseline signal at discrete intervals and doing a summation of each subtraction across the peak region. The simple summation is permissible because the interval between two discrete data points is typically very small, and the number of data collected during an experiment (i.e., total time) is large enough to be assumed continuous. For example, in dynamic scans at 5 K/min and 10 K/min, a data collection interval of 1 s is used, while the duration of the experiment may be in the range of 2000–4000 s. At higher heating rates, such as 20 K/min and 40 K/min, data collection intervals are shortened to 0.5 s and 0.25 s, respectively.

In the case of chemical transformations, a different procedure is employed to establish the baseline. A different procedure is needed because, in reactive systems, there may be a change in the heat capacity of the initial reactants and the final products, so drawing a straight line as the baseline may not be an accurate description. To accommodate this, following the initial DSC scan during which the chemical transformations occur, a repeat scan is conducted. If thermal activity is still present, the scan is continued either to higher temperatures or for longer times until heat effects are no longer

3. Comparative plots of dynamic DSC scans from 350 K to 520 K. Sample weights normalized to 7.5 mg; heating rates are as indicated. (200 signal units correspond to 1 mW.)



4. Isothermal DSC scan at 450 K. Isotherm starts at 900 s. Sample weight normalized to 7.5 mg. Region I—dynamic heating range at 10 K/min. Region II—isothermal range. (200 signal units correspond to 1 mW.)



detectable. The final repeat scan devoid of any thermal activity is then used as the baseline for calculation of peak areas. It forms a natural baseline for cure reactions. The use of the repeat scan eliminates the need to define the start, the apex, and the end of the chemical transformations, which are not necessarily well defined as in the case of physical transformations. For area calculation, the computer reads the data files from the initial and repeat scans, subtracts the signals corresponding to the same time, and as before, does a summation of the difference over the interval of interest.

Determination of heat of cure

The peak areas are converted to the heat of transformation using the following relationship:

$$\Delta H = AE/mtK \qquad (1)$$

where

ΔH = heat of transformation

A = area between the initial and repeat scans

E = sensitivity setting of the instrument, 5 mcal/s in this study

m = mass of the sample, typically about 10 mg

t = the interval at which data are collected

K = instrument calibration constant, determined from heat of fusion of indium.

I. Heat of cure from dynamic experiments (kJ/kg resin)

Heating rate, K/min	Run no. 1	2	3	4	Average
10	796	815	755	751	777
20	748	748	862	718	766
40	615	703	766	637	681
			Overall average		740

II. Heat of cure from isothermal experiments (kJ/kg resin)

Isothermal temperature, K	Isothermal heat of cure	Residual heat of cure[a]	Total heat of cure
430	540	192	733
440	574	144	718
450	618	119	737
460	651	48	700
470	713	62	775

[a] Additional heat of cure measured when samples are heated to 520 K.

Determination of fractional conversions

Fractional conversion is determined by comparing the partial peak areas with total peak areas associated with the transformation, i.e.,

$$\alpha = A_t/A_T \qquad (2)$$

where

α = fractional conversion at time t

A_t = partial area at time t

A_T = total peak area.

Heating modes

Experiments were conducted either under dynamic heating modes of 5 K/

min, 10 K/min, 20 K/min, 40 K/min up to 525 K or isothermally at 430 K, 440 K, 450 K, 460 K, and 470 K. In isothermal experiments, the effect of each heating rate (i.e., 5, 10, 20, 40 K/min) used to achieve the selected isothermal-hold temperatures was evaluated.

Results and discussion

Assessment of completion of cure

The use of DSC to follow the cure reactions in paper–phenolic composites is illustrated in **Fig. 1**. The figure shows four different scans on the same graph. Scan A corresponds to the first heating of the composite sample from 350 K to 450 K at 10 K/min, at which point the scan was immediately stopped and the sample was cooled back to 350 K. It shows the initial step change in the DSC signal arising from the heat capacity and the mass differences between the sample and reference pans, followed by a steady signal that is, in turn, followed by a significant exothermic departure. Scan B corresponds to the repeat heating of the same sample, now to a higher temperature of 475 K, still at a 10-K/min heating rate, after which the sample was again cooled back to 350 K. This scan is different from Scan A in that the exothermic activity is much smaller, but still observable. Scan C is a repeat scan up to 500 K following Scan B, and finally Scan D is a repeat run to 525 K. Temperatures higher than 525 K were not scanned because of the pressure limitations of the capsules and also because of the possibility of the onset of decomposition reactions (*1*).

As seen in Fig. 1, with heating to higher and higher temperatures, signals that can be associated with thermal reactions decrease and finally disappear. Such a series of repeat scans allows one to establish that the cure reaction is indeed complete, and the final scan provides the baseline for further calculations on the system.

Figure 2 shows the DSC scans for a sample that was heated from 350 K to 520 K at 10 K/min and then, instead of being cooled back immediately, was held isothermally at 520 K for an additional period of about 15 min (Scan A). The sample was then cooled back to 350 K and a repeat run was conducted (Scan B) following a heating profile identical to that of the first scan. This figure has been plotted on the time domain instead of the temperature domain in order to show the progress of cure in the isothermal stage of the scan. The location of the isothermal hold is shown by the dotted vertical line. Region I is the dynamic heating step, and Region II is the isothermal-hold step. When the mode changes from dynamic to the hold mode, there is first the typical shift in the DSC signal, followed by a decaying signal (in Scan A), which indicates that cure reactions are still continuing. In the repeat scan (Scan B), both the dynamic and isothermal regions are free of detectable thermal activity. Even though the isothermal range has been monitored for about 15 min, the conclusion of further cure occurs after about 3 min. This figure also illustrates the procedure to establish the baseline in experiments in which the run has been terminated at some specified temperature. What needs to be done is to continue the run in the isothermal mode at that temperature until baseline stability is attained.

Figures 1 and 2 also illustrate the two possible procedures to investigate curing reactions in a given system. One procedure is to heat the sample under dynamic mode to the highest possible temperature, and the other is to heat it to some selected temperature under dynamic mode and then hold it isothermally until the cure is completed.

Effect of heating rate

Figure 3 shows the DSC scans obtained by heating to 520 K at different heating rates. After reaching 520 K, all the samples were held isothermally for 3 min, which is indicated by vertical displacement in the signal at 520 K. All scans have been normalized with respect to the sample mass and shifted vertically for clarity. Even though the exotherm is more visible in the runs with higher heating rates, as will be discussed under the heading "Heat of cure," total areas under each curve with respect to its corresponding baseline are found to be similar. What is different, however, is that the location of the maximum of the exotherm shifts to higher temperatures with increasing heating rate.

Isothermal scans

The essential features of an isothermal scan have already been shown in connection with Fig. 2. However, realizing that the maximum of the exothermic peak occurs around 450 K under 10-K/min heating conditions (see Fig. 1 or 3), additional isothermal scans were conducted at 430 K, 440 K, 450 K, 460 K, and 470 K. **Figure 4** shows the results at 450 K. The isothermal-hold temperature was attained at a heating rate of 10 K/min (Region I), and then the isothermal conditions were maintained for 15 min (Region II). The figure shows the repeat run (Scan B) that forms the baseline also. Comparison of Fig. 4 with Fig. 2 shows that, as would be expected, contribution to the area between the initial and repeat scans is greater in the isothermal experiments conducted at lower temperatures. Even though not shown, the relative proportions of enclosed areas become even greater (in favor of the isothermal range) as the isothermal-hold temperature is lowered towards 430 K.

Heat of cure

Total heat-of-cure values were evaluated from peak areas enclosed by the dynamic and isothermal portions of each scan and the baseline, using Eq. 1. **Table I** shows the results from dynamic experiments. They are given for each heating rate corresponding to Fig. 3. The values are reported for four repeat experiments at each heating rate. An average value of 740 kJ/kg resin has been established. This value is comparable with those reported in the literature (*5–8*). As already pointed out, Table I shows that there is no significant effect of heating

rate on the total heat of cure, especially at heating rates below 40 K/min.

The heats of cure from isothermal experiments were also calculated in a manner similar to that used for dynamic experiments. The values obtained were between 540–750 kJ/kg resin, depending on the isothermal-hold temperature. These are lower than those obtained from dynamic experiments. This stems from reaction quenching at isothermal-hold temperatures below 520 K. These samples cured isothermally at temperatures below 520 K. When heated to 520 K, all show residual exotherms. When contributions from the residual exotherms are added to the isothermal heat of cure, the total heat of cure becomes comparable with that obtained from the dynamic experiments. The heat-of-cure values determined from isothermal experiments are shown in **Table II.**

Fractional conversions

Using fractional areas and total peak areas, fractional conversions were evaluated and conversion-time–temperature data were generated for dynamic experiments, and conversion-time data were generated for the isothermal experiments. **Figures 5 and 6** show the conversion-time plots for dynamic and isothermal experiments, respectively. **Figure 7** illustrates the conversion-vs.-time data for isothermal experiments conducted at 450 K at 10-K/min, 20-K/min, and 40-K/min heating rates of approach to the isothermal temperature. The isothermal regime starts at 900 s for 10-K/min approach, 450 s for 20-K/min approach, and 225 s for 40-K/min approach. As would be expected at lower rates of approach, considerable cure occurs before the isothermal-hold temperature is reached. Figure 7 shows that for the 10-K/min, 20-K/min, and 40-K/min approach rates to isothermal temperatures, respective conversions of 55%, 31%, and 15% occur by the time the isothermal temperature is attained. Higher heating rates of approach would therefore be preferable in order to confine the major part of the cure to the isothermal regime. These conversion-time data are the key to evaluating the kinetics of these reactions and testing the various kinetic models.

Kinetic analysis

Kinetic models may be phenomenological or mechanistic. Phenomenological models relate to the main features of the reaction kinetics and do not take into account individual reactions, whereas mechanistic models are obtained from balances of species involved in the reaction.

A phenomenological approach to kinetic modeling has been used in this study because the curing process is very complex, and it is very difficult to identify each and every reaction. Phenomenological reaction rate can be expressed either in the differential form of Eq. 3 or in the integrated form of Eqs. 5 and 6:

$$d\alpha/dt = kf(\alpha) \qquad (3)$$

where

$$k = A\, e^{-E/RT} \qquad (4)$$

or

$$\int_0^{\alpha} d\alpha/f(\alpha) = \int_0^{t} k\,dt \qquad (5)$$

or

$$g(\alpha) - g(0) = A\int_0^{t} \exp(-E/RT)dt \qquad (6)$$

where

α = fractional conversion at any time t

k = Arrhenius rate constant

E = activation energy

R = gas constant

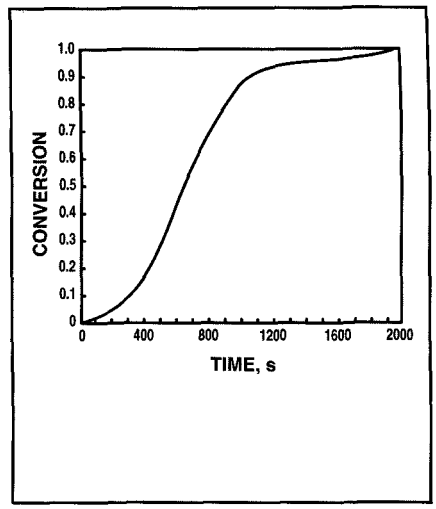
T = temperature

$f(\alpha)$ = a function of conversion α and depends on the reaction mechanism

$g(\alpha) = \int d\alpha/f(\alpha)$.

The functional form of $f(\alpha)$ depends on the reaction mechanism. For example, for first-order homogeneous reactions $f(\alpha) = (1 - \alpha)$ and for nth order homogeneous reactions, it is expressed as $(1-\alpha)^n$. Autocatalytic reactions are represented by $\alpha^m(1 - \alpha)^n$, where m and n are reaction-order parameters.

5. Fractional conversion based on dynamic data at 10-K/min heating rate to 520 K (time domain)



The conversion-vs.-time data generated under either isothermal or dynamic heating conditions such as those shown in Figs. 5–7 can be used to select the reaction mechanism that best describes the progress of the cure reactions. The procedure involves assuming a model and then testing the suitability of the model using either the derivative or the integral relationships characterized by Eqs. 3 and 5. For example, if the assumed model is the first-order homogeneous reaction model, then the derivative relationship becomes

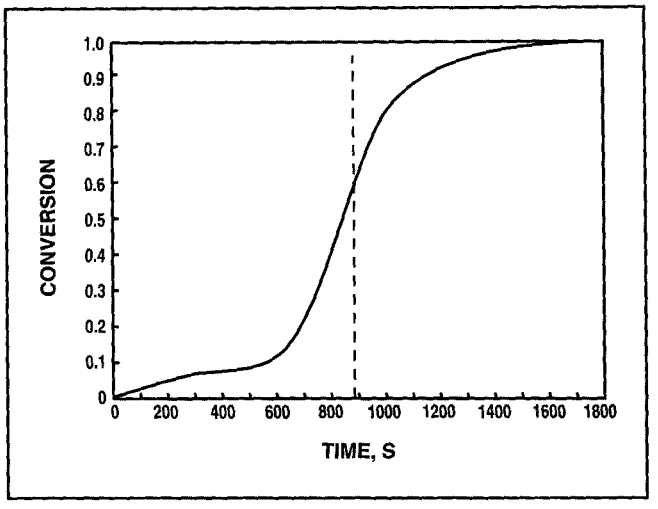
$$d\alpha/dt = k(1 - \alpha) \qquad (7)$$

which, after substituting for k and rearranging, can be expressed as

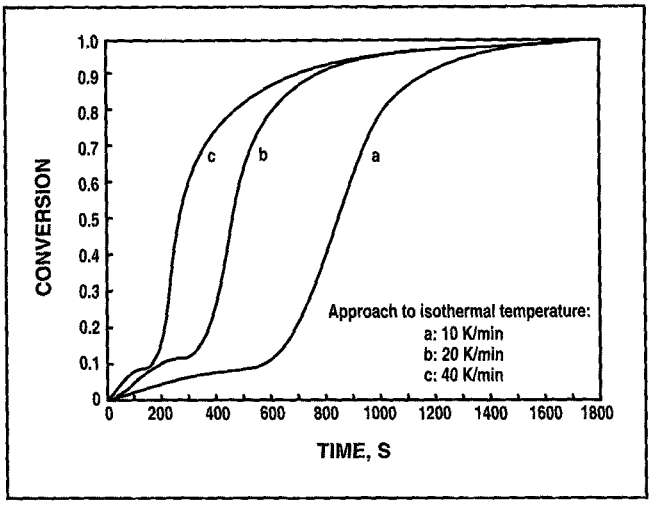
$$\ln[(d\alpha/dt)/(1 - \alpha)] = \ln A - E/RT \qquad (8)$$

From the conversion-vs.-time data, at each conversion α, the numerical value of $d\alpha/dt$—and hence the left-hand side of the equation—can be evaluated. If the assumed model is correct, for conversion data obtained under dynamic heating conditions, a plot of the left-hand side as a function

6. Fractional conversion during isothermal cure at 450 K. Isotherm starts at 900 s. Region I—dynamic heating range at 10 K/min. Region II—isothermal range.



7. Comparative plots of fractional conversion during isothermal cure at 450 K approached at different heating rates. Isotherm starts at 900 s (10-K/min approach), 450 s (20 K/min), and 225 s (40 K/min).



of $1/T$ will yield a straight line with a slope equal to $-E/R$. For conversion data obtained under isothermal conditions, the rate constant k being constant and hence the parameters A and E being fixed, the left-hand side should assume the same value at all conversions.

In the integral analysis of the data, use is made of Eq. 5. For the homogeneous reaction model, it becomes

$$\int d\alpha/(1-\alpha) = \int k dt \qquad (9)$$

or after substitution for k and integration between conversions zero and α

$$-\ln(1-\alpha) = A\int_0^t \exp(-E/RT)dt \qquad (10)$$

Here again, from the conversion-vs.-time data, the left-hand side of the equation can be evaluated. For isothermal conversion data, k being a constant, plotting the left-hand side with time will yield a straight line passing through the origin. If the conversion data are based on a dynamic run, then the plot of the left-hand side with

$$\int_0^t \exp(-E/RT)dt$$

should yield a linear line passing through the origin.

We have conducted detailed kinetic modeling studies using conversion data obtained from both the isothermal and dynamic experiments and tested the suitability of homogeneous, autocatalytic, phase-boundary movement and diffusion, and nucleation and growth-type reaction models (*14, 16*). The results from such analyses show that at low conversions (<30%), the progress of cure can indeed be described by a simple homogeneous first-order reaction model [with $f(\alpha) = (1-\alpha)$]. At high conversions, three-dimensional diffusion models—in particular the Jander-type diffusion model (for which $f(\alpha) = 3/2\,(1-\alpha)^{2/3}\,[1-(1-\alpha)^{1/3}]^{-1}$)—are observed to describe the progress of the cure better.

Figures 8 and 9 show the results using the integral form of the kinetic expression on dynamic data (at 10 K/min) in the respective conversion ranges using the two models. As shown, the data are described well with the proposed models. Using these models, activation energies are found to be in the range 30–40 kJ/mole.

Conclusions

Differential scanning calorimetry (DSC) is a convenient tool for assessing the cure behavior of phenolic composites. In this study, consistent and reliable DSC procedures were developed in an effort to facilitate assessment of cure behavior. DSC was operated in both the dynamic and isothermal modes. The effects of different heating rates of approach to target temperatures in isothermal experiments, different target temperatures, and different sample weights were investigated.

The cure reactions were, in general, found to be unaffected by rate of approach to target temperatures in both the isothermal and dynamic cases, evidenced by the consistent and similar heat-of-cure values. For isothermal experiments, the cure reactions were quenched at temperatures below 520 K. When the isothermally cured samples were heated to 520 K, they exhibited residual exotherms which, when taken into account, yielded heat-of-cure values comparable with those from dynamic experiments. A heat-of-cure value of 740 kJ/kg resin has been determined for these phenolic systems. Fractional areas calculated from the cure curves yield conversion-time–temperature data, which are needed to establish kinetic parameters for the cure reactions. ■

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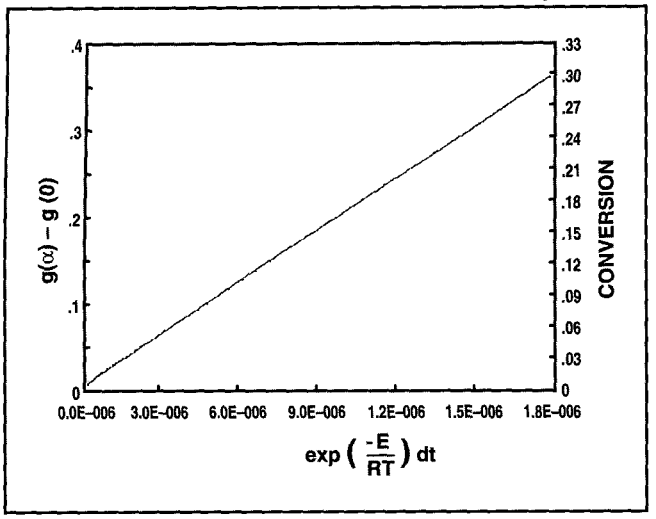
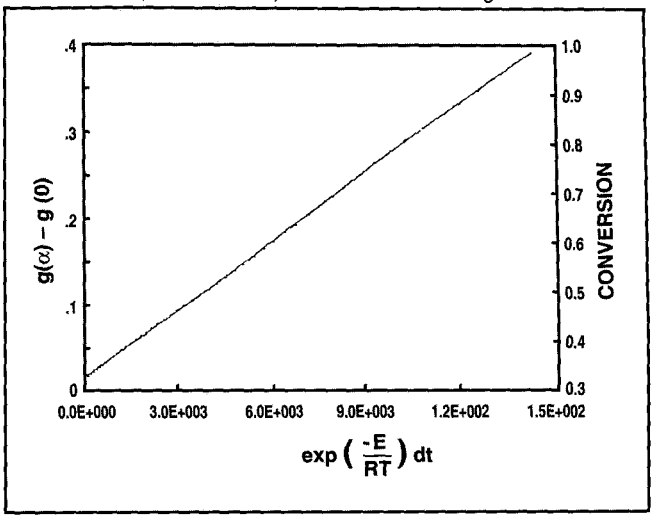


9. Integral analysis of dynamic data obtained at 10 K/min. Three-dimensional diffusion (Jander kinetics) model. Conversion range 30–95%.



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