Curing Behavior of a Novolac-Type Phenolic Resin Analyzed by Differential Scanning Calorimetry

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ABSTRACT: Curing of a novolac-type phenolic resin was studied by DSC. The kinetic analysis was performed by means of the dynamic Ozawa method at heating rates of 5, 10, 15, and 20°C/min. This analysis was used to determine the kinetic parameters of the curing process. The activation energy was found to be 144 kJ/mol. It was found that the Ozawa exponent values decreased with increasing reaction temperature from 3.5 to 1, suggesting a change in the reaction mechanism from microgel growth to diffusion-controlled reaction. The reaction rate constant was found to range from 123.0 to 33.6 $(°C/min)^n$. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1678–1682, 2003

Key words: kinetics; differential scanning calorimetry (DSC); phenolic resins; Ozawa method; microgels

INTRODUCTION

Phenolic resins are widely used condensation polymers because of their high chemical resistance, electrical insulation, and dimensional stability. Their main applications include molding materials, laminates, and adhesives in the manufacture of plywood.[1]

There are two major categories of phenolic resins that are classified by their structures and curing properties as resole or novolac. The essential characteristics of both cured resole and novolac-type phenolic resins are almost identical (e.g., mechanical properties, chemical resistance, etc.). The synthesis of phenol–formaldehyde in the presence of alkaline catalyst and with an excess of formaldehyde yields a soluble and fusible prepolymer called resole, which contains reactive methylol groups in its structure and, upon heating, condense together to give a network formation.[2,3] In contrast, in the presence of acid catalysts, and with the mole ratio of formaldehyde to phenol less than unity, a condensation reaction takes place between these two chemicals, producing a fusible and soluble linear low polymer called novolac, which does not itself react further; therefore, a curing agent such as hexamethylenetetramine (HMTA) must be added to produce a crosslinked structure.[4]

The properties of the cured resin are significantly dependent on the extent of cure. Therefore, an understanding of the curing reaction is very important for process control and optimization.[5] In this study, the curing behavior of a novolac-type phenolic resin was analyzed by nonisothermal measurements using Ozawa's approach.

EXPERIMENTAL

The resin used in this study was a commercial novolac-type phenolic resin (CR-4871) supplied by Crios Resinas Ltd. (Rio Claro, Brazil), with HMTA content of about 7%.

DSC measurements were conducted on a Shimadzu DSC-50 differential scanning calorimeter (Shimadzu, Kyoto, Japan). Dynamic scans were conducted in a temperature range of 25–250°C, at constant heating rates of 5, 10, 15, and 20°C/min, under nitrogen atmosphere at a flux rate of 50 mL/min. For sample preparation, about 6 mg of the resin was used in an aluminum crucible of 40 μL with a perforated lid. The DSC curves were analyzed according to Ozawa's theory to obtain the kinetic parameters and the total heat of reaction.

TABLE I
Peak Temperature and Its Corresponding Total Heat of Reaction Obtained from Dynamic Method at Heating Rates of 5, 10, 15, and 20°C/min

Heating rate β (°C/min)	Peak temperature T_p (°C)	Heat of reaction ΔH (J/g)
5	147.7	63.4
10	155.2	56.8
15	159.6	39.2
20	162.2	44.5

RESULTS AND DISCUSSION

Curing of thermosetting materials generally involves transformation of low-molecular monomers and prepolymers to high molecular weight amorphous solids by means of chemical reactions.[6–8] It is assumed that the exothermic heat liberated during isothermal cure is proportional to the chemical conversion (i.e., the number of bonds that have reacted in the system). Based on these considerations, the relative degree of conversion or cure (α) is normally defined as

$$\alpha = \frac{\Delta H_p}{\Delta H_0} \tag{1}$$

where ΔH_p denotes the partial heat of reaction up to time t and ΔH_0 denotes the total heat of the reaction.

The most common approach used to describe the overall isothermal curing of thermosetting materials is the Johnson–Mehl–Avrami equation[5,8–15]:

$$\alpha(t) = 1 - \exp(-kt^n) \tag{2}$$

where $\alpha(t)$ is the relative degree of cure as a function of time, k is the effective overall reaction rate (a cluster of numerical and growth constants that is different in detail for each reaction), t is the time taken during the curing process (the incubation time t_0 is excluded), and n is the Avrami exponent or reaction order that depends on the mechanism of growth. Both k and n are constants, typical of a given polymerization mechanism and nucleation and growth processes.[12] The parameters n and k can be obtained from the least-squares line fit to the double-logarithmic plot of $\ln\{-\ln[1 - \alpha(t)]\}$ versus $\ln(t)$, where k is taken as the antilogarithmic value of the y-intercept and n is the slope of the obtained line.

Based on the mathematical derivation of Evans,[17] Ozawa[12,16] extended the Avrami[9–11] theory to describe the nonisothermal case. This method uses the relationship between the peak temperature of the reaction exotherms and the heating rates to determine kinetic parameters, that is, reaction order (n) and the effective reaction energy (E) of the transformation process.

If the sample temperature is changed by a controlled and constant heating rate, the variation in degree of cure can be written as a function of the heating rate according to

$$\alpha(T) = 1 - \exp\left(-\frac{k_0}{\beta^{n_0}}\right) \tag{3}$$

where $\alpha(T)$ is the relative degree of cure as a function of temperature; k_0 is the Ozawa reaction rate constant; n_0 is the Ozawa exponent, which is similar to the Avrami exponent; and β is the constant heating rate in °C min^{-1}.

The data analysis can be performed through a double-logarithmic plot of $\ln\{-\ln[1 - \alpha(T)]\}$ versus $\ln(\beta)$ for a fixed temperature. The parameter k is taken as the antilogarithmic value of the y-intercept and n_0 is the negative value of the slope calculated from least-square lines drawn through plots of at least three points; that is, at least three different heating rates should be used in DSC experiments to obtain the Ozawa parameters.

The area under the exothermal curves obtained by dynamic DSC tests, performed at heating rates of 5, 10, 15, and 20°C/min, were measured to calculate the total heat of reaction (ΔH_0) and peak temperatures. As shown in Table I, the ΔH_0 values decrease with increasing heating rates. Higher heating rates tend to abbreviate the time required for complete curing, decreasing the degree of conversion. As a result, a postcure peak appears at a temperature about 220°C to the heating rates of 10, 15, and 20°C/min (see Fig. 1).

Because the change in peak temperature in DSC experiments is closely related to the corresponding heating rates,[14,15] the kinetic parameters can be deter-
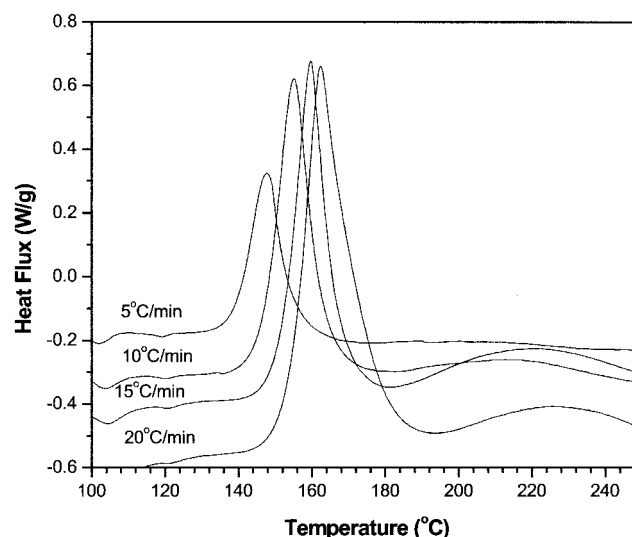

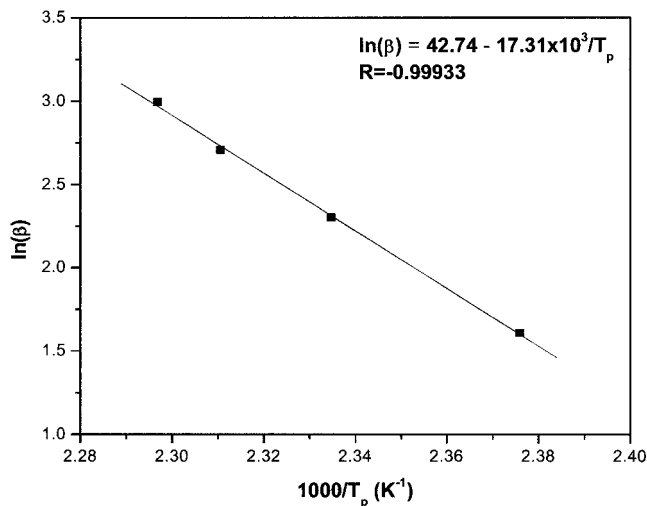**Figure 1** Dynamic DSC curves conducted at heating rates of 5, 10, 15, and 20°C/min.

Figure 2 Plot of $\ln(\beta)$ versus $(1/T_p)$ correlating the measured peak temperatures with the heating rates.

Figure 4 Plots of $\ln\{-\ln[1 - \alpha(T)]\}$ versus $\ln(\beta)$ for temperatures ranging from 142 to 170°C.

mined assuming Arrhenius-type dependency of peak temperature for the heating rate constant (β):

$$\beta = A \exp\left(- \frac{E}{RT_p}\right) \qquad (4)$$

where A is the preexponential factor, E is the activation energy, T_p is the peak temperature obtained from multiple rate scans, and R is the gas constant.

By plotting $\ln(\beta)$ versus $(1/T_p)$ a straight line is obtained (see Fig. 2). The value of the slope yields $-E/R$ and the y-intercept yields the preexponential factor. The value of activation energy was found to be 144 kJ/mol, a value that is consistent with values reported in the literature.[6,14,18]

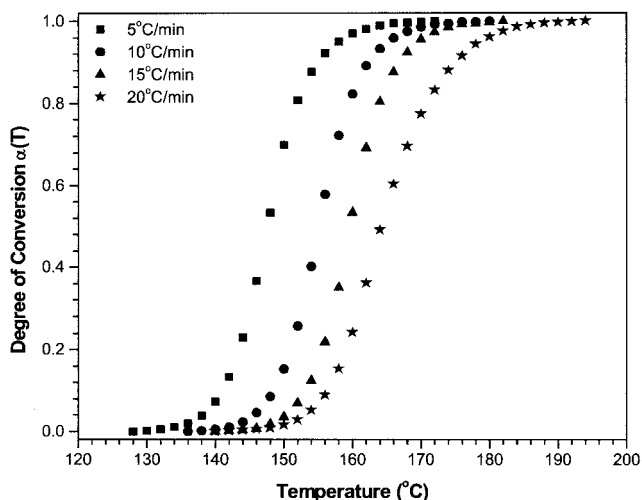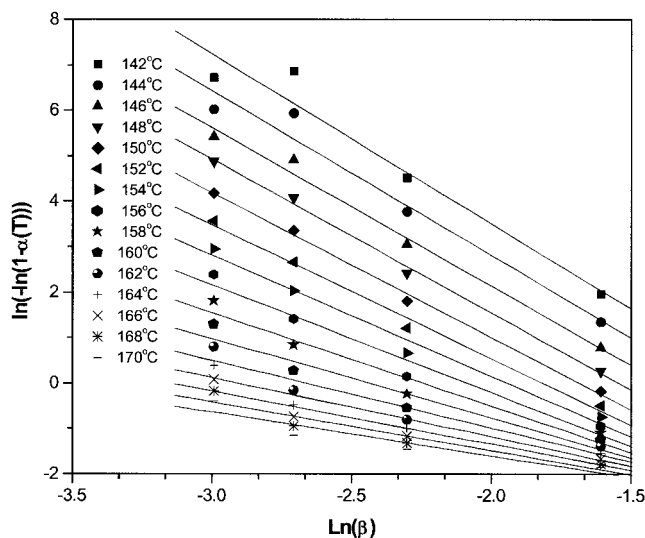From the plot of the relative degree of cure as a function of the temperature in Figure 3, a straight line

was obtained by plotting $\ln\{-\ln[1 - \alpha(T)]\}$ versus $\ln(\beta)$, as shown in Figure 4. The Ozawa exponent (n_0) was calculated from the negative value of the slope of the lines. Figure 5 shows the Ozawa exponent variation as a function of temperature.

It is observed that the Ozawa exponent decreases with increasing temperature from about 3.5 to 1, which implies that the fast initial stage of curing was replaced by a diffusion-controlled reaction by advance of curing reaction. As the curing temperature increases the curing reactions start and HMTA decomposes and reacts with phenol, forming various intermediates such as benzoxazine- and benzilamine-type molecules. These intermediates may decompose and further react to produce methylene linkages between phenolic rings for chain extension and crosslinking.
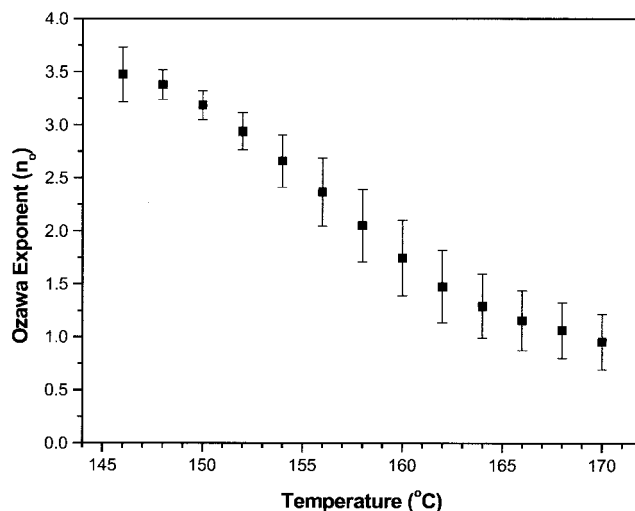

Figure 3 Relative degree of cure as a function of temperature and heating rates.

Figure 5 Variation of Ozawa exponent as a function of temperature.

Initially these intermediates behave like microgels that grow without restraint during the initial stage of curing. As the reaction proceeds, microgel particles increase and become densely distributed. Eventually, they are forced to impinge on each other and the intermicrogel crosslinking becomes predominant, which results in a marked increase in viscosity. The curing process becomes diffusion controlled and the development of the microgels is restrained, thus decreasing the n value.[5] Zhang and coworkers,[19–24] who studied the curing mechanisms of phenolic resins by ^{13}C- and ^{15}N-NMR, provided an extensive and detailed description of the curing reaction mechanisms of the novolac resins. Figure 6 shows the curing reaction of the novolac resin with HMTA.

The values of the reaction rate constant obtained by Ozawa theory from antilogarithmic values of the y-intercept increase with temperature up to 150°C, decreasing thereafter at higher temperatures (see Table II). This behavior suggests that the initial curing stage processes occur at a higher reaction rate whereas the final stage processes occur at a lower reaction rate. As mentioned previously, the microgels grow without restraint at the beginning of the curing process until the impingement, reaching a maximum, and thereaf-

TABLE II
Reaction Rate Constant (k_0) Values Obtained by Ozawa Theory

Temperature (°C)	k_0 (°C/min)^n
146	123.0
148	182.7
150	213.8
152	207.3
154	175.4
156	140.2
158	99.9
160	70.8
162	51.2
164	43.2
166	38.5
168	37.1
170	33.6

ter the rate constant decreases when the curing reaction becomes diffusion controlled.

CONCLUSIONS

The kinetic behavior of the novolac-type phenolic resin was described by means of Ozawa's approach. The activation energy was found to be 144 kJ/mol. This value is consistent with values reported in the literature. The Ozawa kinetic parameters, which are closely related to Avrami parameters obtained under isothermal experiments, are strongly influenced by temperature and reaction time. The n_0 values decrease with increasing reaction temperature from 3.5 to 1. The k_0 values increased with temperature up to 150°C, reaching a maximum, and thereafter decreasing at higher temperatures. This behavior suggests that the initial curing stage is controlled by growth of microgels whereas the final curing reaction becomes diffusion controlled.

Figure 6 Curing reaction of the novolac resin with hexamethylenetetramine (HMTA).[19]

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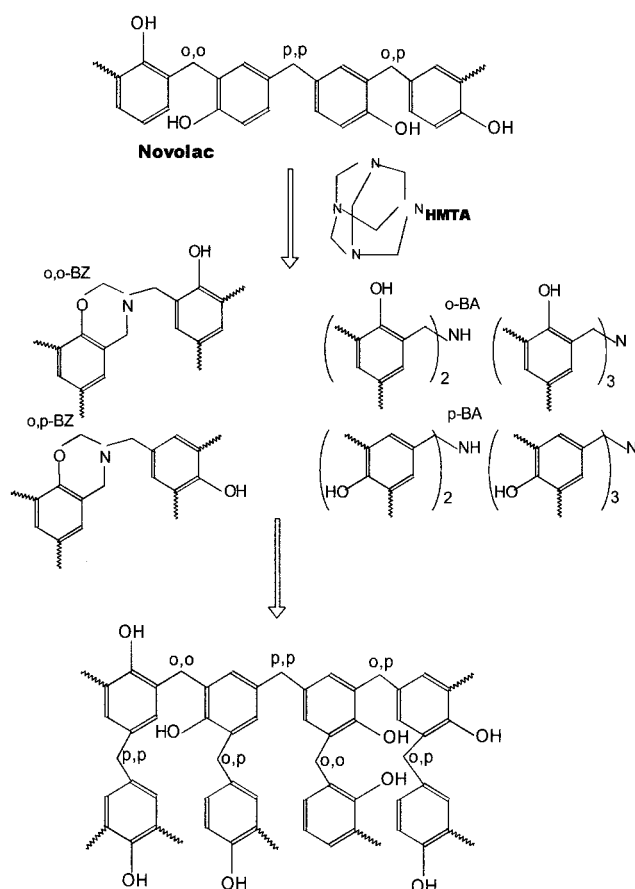6. Krajncatjaž, M.; Golob, J.; Podržaj, J.; Barborič, F. Acta Chim Slov 2000, 47, 99.

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