# Dynamic Mechanical Analysis Study of the Curing of Phenol-Formaldehyde Novolac Resins

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**ABSTRACT:** The curing reaction of typical commercial phenol-formaldehyde novolac resins with hexamethylentetraamine (HMTA) was followed by dynamic mechanical analysis. The evolution of the rheological parameters, such as storage modulus $G'$, loss modulus $G''$, and $\tan\delta$ ($G''/G'$), as a function of time, for samples of the phenolic resins on cloth, was recorded. The curing reaction, leading to the formation of a crosslinked structure, is described by a third-order phenomenological equation. This equation takes into account a self-acceleration effect, as a consequence not only of the chemical reaction of crosslinking after the gel point but of phase segregation as well. This rheokinetic model of the curing of phenolic novolac resins permits the determination of the numerical values of the kinetic equation constants. The influence of the composition, structure, and physical treatment on the curing kinetics of the novolac resins is evaluated. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1902–1913, 2001

**Key words:** novolac resins; curing reaction; dynamic mechanical analysis

## INTRODUCTION

Novolac phenol-formaldehyde resins belong to the important group of thermosetting polymeric materials. They are formed by the step growth polymerization of phenol and formaldehyde in acidic medium, at a molar ratio for phenol to formaldehyde of 1:0.75–1: 0.85. Novolac resins are mixtures of linear or slightly branched oligomer chains with a relatively low molecular weight of ≤2000. These resins are soluble and thermoplastic; i.e., they are permanently fusible. In the curing reaction, almost exclusively with hexamethylentetramine (HMTA), the oligomers are linked into a three-dimensional highly crosslinked network. They are used as thermal insulation materials, molding compounds, and coatings, as well as in the foundry and wood industry and in composite materials.[1]

Although phenolic resins were the first commercial synthetic polymeric materials, their synthesis, structure, and curing reaction are still a matter of great interest. The ability to analyze the structure and network formation of these resins using modern instrumental techniques increases the understanding of these phenomena and permits better product quality control. The structure, and consequently the properties, of novolac resins depend on the molar ratio of the reactants, as well as on the type and concentration of the catalyst.[2] If catalysts such as oxalic acid or sulfuric or *p*-toluene sulfonic acid are used, random or statistical novolacs are obtained with the $CH_2$ linkages randomly distributed in the *ortho-* and *para*-positions. High *ortho*-novolacs with the $CH_2$ linkages

predominantly in the *o-o'*-position are formed if salts or oxides of divalent transition metals are used as catalysts.

The kinetics of the curing reactions strongly depend on the nature and amount of reactive positions on the phenol rings. ^{13}C-NMR spectroscopy is very successful in the characterization of phenol-formaldehyde resins, especially because it enables the identification and quantification of the reactive sites on the phenolic rings.[3,4] ^{13}C-NMR is also used for the determination of the parameters that characterize the structure, including degree of polymerization, molar ratio of monomer residues in the products, and the degree of branching.

During the past 20 years, dynamic mechanical spectroscopy has been used intensively for the study of the curing reaction of thermosetting polymers and also for the determination of the viscoelastic properties and transition temperatures of the cured polymers. The formation of a polymer network can be evaluated from dynamic measurements by monitoring rheological parameters such as the storage modulus $G'$, loss modulus $G''$, and complex viscosity $\eta^*$ as a function of time. The entire process of polymer network formation can be divided into two parts separated by the point of gel formation. In the first phase, before the gel point, the reaction mixture shows remarkable viscosity changes. A great increase of the modulus which occurs after the gel point shows the formation of a rubbery or glassy state, characteristic of the second phase.

The gel point is one of the most important kinetic parameters characterizing a curing reaction. According to Flory's statistical theory of gel formation, a gel exists when the first indefinite molecular chain, i.e., $M_w \rightarrow \infty$ forms in the reaction mixture. The rheological parameters, such as viscosity and dynamic modulus, are very sensitive to molecular structure changes, albeit invoked by chemical reactions, phase separation, or phase and relaxation transitions. Rheological data can be used, in addition, to determine the gel point and to analyze the rheokinetics of curing of polymers, to estimate the extent of branching, the crosslinking density and the molecular weight.

The network formation and curing reaction of different phenolic resins has been studied using different dynamic mechanical measurements, such as rotational viscometry,[5] dynamic mechanical analysis,[6,7] and thermomechanical analysis (TMA).[8]

This article examines the influence of the composition, structure, and content of unreacted *ortho* and *para* positions in the phenol ring on the chemorheology and curing behavior of novolac phenol-formaldehyde resins, as well as the formation of crosslinked structure, studied by dynamic mechanical analysis.

## EXPERIMENTAL

The synthesis and structure of the phenol-formaldehyde novolac resins examined in this study have already been discussed in detail.[9] Briefly, six random novolac resins NLO 1–6, with decreasing molar ratio phenol-formaldehyde (1:0.85, 1:0.80, and 1:0.75 ) were prepared in the presence of two different concentrations of oxalic acid as catalyst. A high-*ortho*-novolac resin (NL-OO') was synthesized using zinc acetate, [Zn(Ac)$_2$], as the catalyst. The synthesized and physically treated (washing NLO-1W, NLO-3W and neutralization NLO-1N, NLO-3N) resins were characterized by standard analytical methods used for the quality control of commercial phenol-formaldehyde resins, i.e., viscosity of the solution, pH-value, softening point, flow distance, free phenol, and B time.

The novolac resins were also analyzed by quantitative ^{13}C-NMR spectroscopy. All samples for nuclear magnetic resonance (NMR) spectroscopy were prepared by dissolving the novolac resins in *d*-pyridine. The ^{13}C-NMR spectra were obtained at 25°C, using a BRUKER MSL 400 (100.613 MHz ^{13}C-NMR) spectrometer. All ^{13}C-NMR spectra were recorded with inverse gated decoupling in order to obtain quantitative results. The relaxation delay was 25 s, the special width of 20,000 Hz, the number of scans 2048 and a 75° pulse (7.9 $\mu$s). Chemical shifts are given relative to the pyridine signal at 135.5 ppm. The degree of polymerization ($n$) of a novolac resin was calculated from the intensity ratio of the aliphatic to aromatic signals, using the following equation:

$$(n + 1)/(n + 2) = r \qquad (1)$$

where $r$ is the methylene/aromatic ratio [CH$_2$/(1/6 Ar)].

The number average molecular weight (Table I) was calculated from the degree of polymerization ($n$) according to the following equation[10]:

$$M_n = 106 \times n + 200 \qquad (2)$$

**Table I** $^{13}$C-NMR Characterization of the Composition and Structure of the Novolac Resins

| Sample | P/F Starting | P/F Found | $C_{1f}$, Free Phenol (%) | $M_n$ g/mol NMR | Degree of Polym. $n$ | Content of Isomer $o$-$o'$ % |
|---|---|---|---|---|---|---|
| NLO-1 | 1 : 0.75 | 1 : 0.75 | 3.77 | 406 | 1.95 | 26.05 |
| NLO-1W | 1 : 0.75 | 1 : 0.86 | — | 724 | 4.94 | 25.00 |
| NLO-1N | 1 : 0.75 | 1 : 0.77 | 2.58 | 444 | 2.30 | 25.86 |
| NLO-2 | 1 : 0.80 | 1 : 0.79 | 2.52 | 492 | 2.75 | 27.20 |
| NLO-3 | 1 : 0.85 | 1 : 0.87 | 3.55 | 813 | 5.82 | 30.61 |
| NLO-4 | 1 : 0.75 | 1 : 0.72 | 5.88 | 323 | 1.16 | 25.81 |
| NLO-5 | 1 : 0.80 | 1 : 0.78 | 5.73 | 412 | 1.93 | 25.64 |
| NLO-6 | 1 : 0.85 | 1 : 0.84 | 2.12 | 652 | 4.26 | 26.58 |
| NLOO'1 | 1 : 0.75 | 1 : 0.85 | 7.54 | 712 | 4.83 | 70.17 |
| NLOO'2 | 1 : 0.75 | 1 : 0.69 | 5.29 | 329 | 1.22 | 78.00 |

$C_{1f}$, from nuclear magnetic resonance (NMR).

Based on a maximum error of $\pm 2\%$ for the integration intensities, an absolute mean tolerance of 4.0% for the degree of polymerization can be expected. Thus, the experimental error in the NMR data does not influence significantly the conclusion about the molecular weight we draw from the results.

### Specimen Preparation

Specimens for the rheokinetical examinations were prepared by impregnating cotton strips with novolac resins. The novolac resins with 10% HMTA were first ground in a ball mill, and then 25% solutions in acetone were made. The cotton strips were soaked with the solutions and dried at room temperature and the procedure repeated. In order to obtain homogeneous and compact samples, the strips were heated in a mold at $\leq 70°C$ under a pressure of 5 bar. The content of phenolic resins in all samples was ~50 wt %.

### Rheological Measurements

The rheological measurements were performed by dynamic mechanical spectroscopy using a Rheometrics mechanical spectrometer RMS 605. The
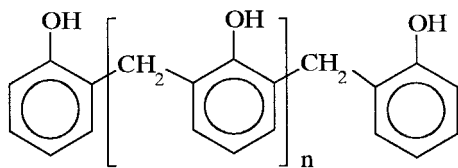


**Scheme 1**

specimens impregnated with novolac containing 10% HMTA, dimensions (25 × 12 × 0.5 mm), were submitted to rectangular torsional deformation in the Cure mode program (heating rate 50°C/min) at 180°C, at a constant frequency 6.28 rad/s and a strain of 0.1%. The rheological parameters, i.e., storage modulus $G'$, loss modulus $G''$, and tan$\delta$, were measured and recorded every 0.5 min for 45–60 min of isothermal heat treatment.

### Mathematical Analysis of the Results

The novolac resins were not crosslinked to the maximum extent after 45–60 min of heat treatment. In order to assess the maximum value of the storage modulus, $G'_\infty$, the experimental data obtained by plotting $G'$ vs. time were extrapolated by asymmetrical sigmoidal curves using Table Curve TM 2D Software. The kinetic parameters from the phenomenological equations were determined by fitting the experimental data, i.e., $d\beta/dt$ vs. $\beta$, using the same computer program.

## RESULTS AND DISCUSSION

The formation of the polymer network structure of the phenol-formaldehyde novolac resins by curing with HMTA can be evaluated from the dynamic rheological parameters, storage modulus $G'$, loss modulus $G''$ and tan$\delta$. The rheological parameters and the curing kinetics were determined during isothermal curing by applying torsion to the rectangular cotton strips impregnated with the novolac resins. The main interest of this
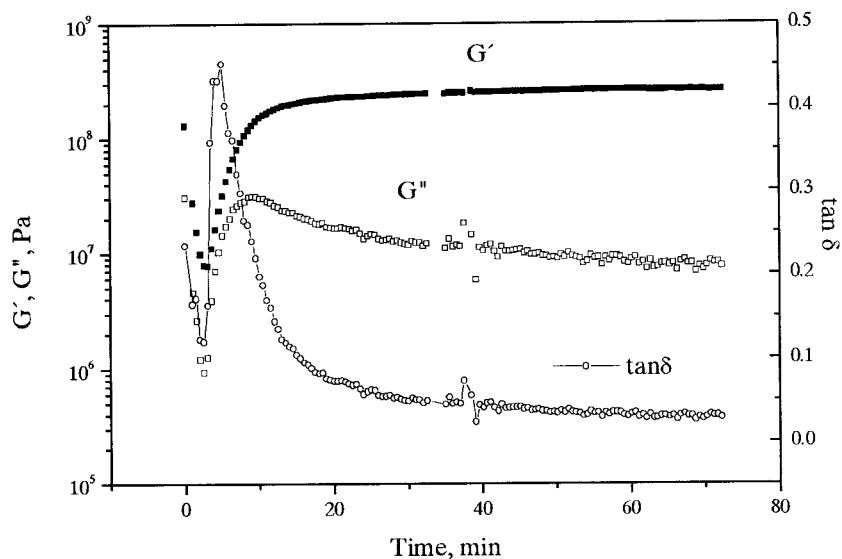
**Figure 1** Storage $G'$ and loss $G''$ dynamic moduli and tanδ for the reaction mixture NLO-3, plotted logarithmically as a function of reaction time at 180°C.

work was to establish a general rheokinetic law that would describe the whole range of the change of the storage modulus $G'$ during isothermal curing of random and high-*ortho*-novolac resins. We were also interested in analyzing the influence of the composition, structure and physical treatment, like washing and neutralization, of the novolac resins on their curing behavior.

Rheokinetical examination were carried out (1) on two series random novolac, NLO 1-3 and NLO 4-6; (2) on two series washed and neutralized novolacs, NLO-1 (W or N) and NLO-3 (W or N); and (3) on two high *ortho*-novolac samples, NLOO′-1 and NLOO′-2.

### Structure and Composition of the Phenol-Formaldehyde Novolac Resins

The composition and number-average molecular weight of six typical commercial random novolac resins and two high-*ortho*-novolac resin are shown in Table I. In the random novolac resins there is almost equal amounts of *para-para* and *ortho-ortho*-methylene bridges, while in the high-*ortho*-novolac resins the *ortho-ortho* bridges (70%) dominate. This is reflected in an increased number of unreacted *para* positions. The predominance of *ortho-ortho* bridges and an increased number of unreacted *para* position are the main cause for the high curing rates of the novolac resins NLO-O′ and NLO-3, as was observed from the values of the gel-time and the rheological measurements.

### Crosslinking Behavior of the Phenol-Formaldehyde Resins from the Rheological Study

The crosslinking reaction of the novolac resins with HMTA was performed isothermally with torsional deformation of the rectangular samples at constant frequency. Typical plots of the dependencies of the storage modulus $G'$, loss modulus $G''$ and tanδ on reaction time, at 180°C for the sample of the random novolac resin NLO-3 are shown in Figure 1. The storage modulus $G'$ initially decreases because of softening, but afterward it increases, as a result of network formation, until it reaches its maximum value by entering a plateau. The loss modulus $G''$ also initially decreases because of softening, then increases, passes through a maximum, and again decreases. Tan δ shows two maxima during heating; the first is due to softening, and the second is linked to gel formation. The moment when the modulus $G'$ reaches a minimum was taken as zero time for the beginning of the curing reaction of the novolac resins. It is obvious that the increase of the modulus $G'$ during heating and later during isothermal curing could be related to network formation. A curing temperature of 180°C was chosen because it is close to the commercial condition of molding and due to fact that at this temperature the rate of decomposition of hexamethylentetramine (HMTA) is appropriate for monitoring the important transformations occurring during network formation.
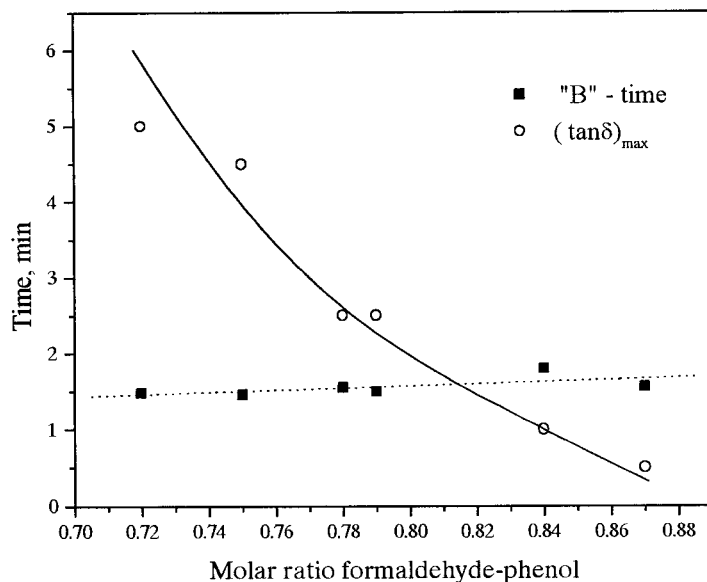
**Figure 2** Comparison between the gel time (B-stage) and gel-point for the series of random novolac resins.

## Determination of Gel Point Formation

The gel time of thermosetting polymers can be determined according to different criteria.[11–13] One criterion is the peak maximum in tangent angle of mechanical loss $(\tan\delta)_{max}$, where the difference between the elastic and viscous behavior of the reaction mixture is at its maximum. Another criterion is the crossover of $G' - t$ and $G'' - t$ curves, when the system shows the same level of elastic and viscous behavior, meaning that the same quantity of energy is stored and dissipated. The intersection point tangent on curve $G'$ (100 kPa) and base line ($G'' = 0$) on the curve $G'$ vs. time could be taken as the criterion.

The peak maximum in $\tan\delta$, where there is the maximum difference between the elastic and viscous behavior, was chosen as the criterion for the determination of the gel point for the curing of the phenol-formaldehyde novolac resins (see Table III). The second criterion, i.e., the crossover point of $G'$ and $G''$, which is not a general criterion, was impossible to apply because the intersection point appear very early in the phase of softening, i.e., before the reaction commences.

The dependencies of the gel point as $(\tan\delta)$max and the B time measured in accordance to the standard method, on molar ratio of $F/P$ are shown in Figure 2. The curve obtained from the rheological measurements (tan $\delta$)max decreases with increasing molar ratio $F/P$, confirming the influence of $F/P$ on the reactivity of novolac resins. While

the rheological measurements showed satisfactory sensitivity towards gel-time analysis and its dependence on the reactivity of phenolic resins, the standards measurements were less successful. It can be concluded that dynamic mechanical measurements can be a powerful tool in the characterization of phenol-formaldehyde resins and other thermoreactive polymers.

A linear plot of $G'$ vs. time for the same novolac resin NLO-3 is shown in Figure 3. The curve obtained exhibits a characteristic autocatalytic S shape, which indicates that the rate of increase of the storage modulus with reaction time, $dG'/dt$, initially increases but after the inflection point decreases. Here it is important to note that the phenomenon of self-acceleration results from phase separation, which leads to an increase in the concentration of reactive groups in the separated microgel phase and, hence, reaction acceleration.

## Rheokinetic Model of Curing Phenol-Formaldehyde Novolac Resins

Rheokinetics models provide the opportunity to follow the entire process of network formation from the beginning to the end of the storage modulus $G'$, which is generally proportional to the density of the network formed by chemical bonds and physical entanglements, is used for the evaluation.

The rheokinetical model proposed by Malkin and Kulichikchin[14,15] for thermoreactive polymer
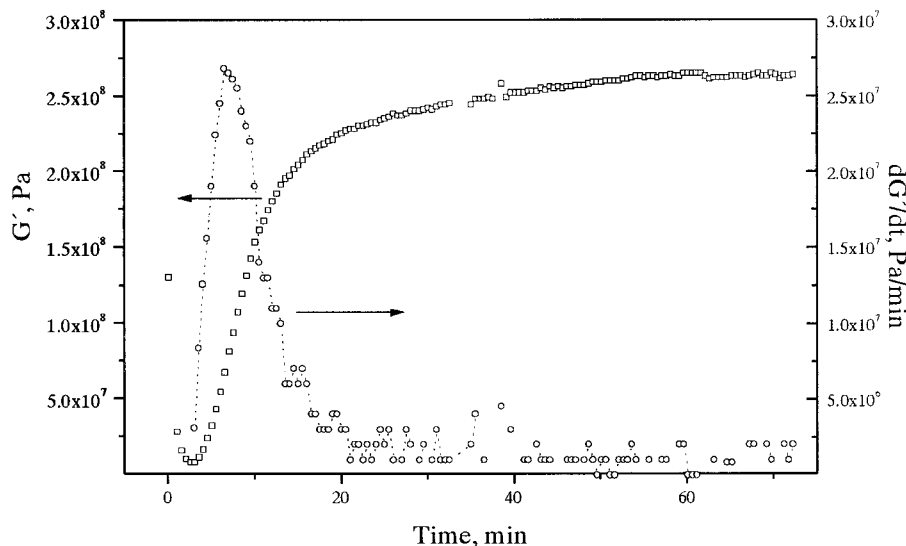
**Figure 3**  Storage modulus $G'$ and the rate of its change $dG'/dt$ for the novolac resin NLO-3 plotted linearly as a function of reaction time at 180°C.

curing was used for analyzing the curing reaction of phenol-formaldehyde resins. These investigators proposed a general phenomenological equation that contains a self-acceleration term $c$:

$$\frac{d\beta}{dt} = k(1 + c\beta)(1 - \beta)^n \tag{3}$$

where $\beta$ is the rheological degree of conversion, $t$ is time, $k$ and $c$ are temperature-dependent constants, and $n$ is the reaction order.

This kind of phenomenological equation has been employed successfully for analyzing the curing of thermoset polymers, such as epoxy,[16] silico-organic oligomers,[17] melamine-formaldehyde and carbamide resins,[18] unsaturated polyester,[19] and acrylate-terminated polyesters with styrene.[20]

Specifically for analyzing the obtained experimental data, the third-order equation (4) was used:

$$\frac{d\beta}{dt} = k(1 + c\beta)(1 - \beta)^2 \tag{4}$$

where $k$ is the initial reaction rate, i.e., the curing rate at $\beta \rightarrow 0$; and $n = 2$, i.e., a second-order reaction is being considered.

The rheological degree of conversion $\beta$ is defined on the basis of the change of the storage modulus $G'$ as

$$\beta = (G'_t - G'_0)/(G'_\infty - G'_0)$$

where $G'_\infty$ is the storage modulus of the completely cured resin, $G'_0$ is the storage modulus at the beginning of the reaction, and $G'_t$ is the storage modulus at time $t$.

Values for $k$ and $c$ were determined using Table Curve TM 2D software for analyzing the experimental data. The viability of fitting the experimental data, i.e., $d\beta/dt$ vs. $\beta$, by the selected form of kinetic expression, is confirmed by the correlation coefficients $r^2$ given in Table II.

**Table II  Rheokinetic Parameters of the Novolac Resins Cured at 180°C Obtained by Fitting the Experimental Data With the Expression $d\beta/dt = \mathbf{k}(1 + \mathbf{c}\beta)(1 - \beta)^2$**

| | Kinetical Parameters | | | |
| | | | Molar Ratio | Correlation |
| Sample | $k$, min$^{-1}$ | $c$ | Formaldehyde/ Phenol | Coefficient, $r^2$ |
|---|---|---|---|---|
| NLO-1 | 0.023 | 13.74 | 0.73 | 0.979 |
| NLO-2 | 0.025 | 15.32 | 0.80 | 0.969 |
| NLO-3 | 0.042 | 10.27 | 0.85 | 0.980 |
| NLO-4 | 0.021 | 12.24 | 0.70 | 0.987 |
| NLO-5 | 0.025 | 13.79 | 0.78 | 0.976 |
| NLO-6 | 0.034 | 13.42 | 0.85 | 0.980 |
| NLOO'1 | 0.069 | 5.32 | 0.85 | 0.95 |
| NLOO'2 | 0.106 | 3.95 | 0.69 | 0.93 |
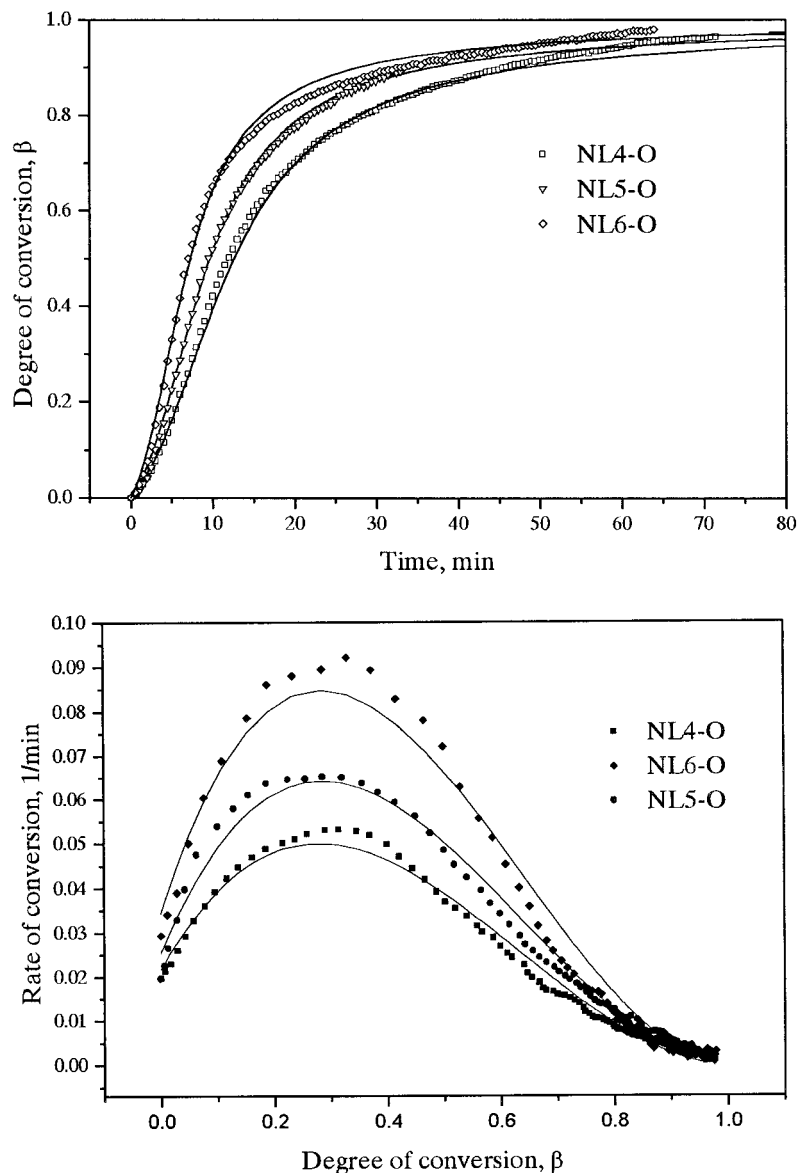
**Figure 4** (a) Degree of rheological conversion $\beta$ versus time for the novolac series NLO 4-6 at 180°C. (b) Rate of change of the rheological conversion $d\beta/dt$ versus the rheological degree of conversion $\beta$ for the NLO-4, NLO-5, and NLO-6 reaction mixtures at 180°C. Symbols, experimental values of $\beta$; curves, calculated values.

The integral of equation (4) gives the dependency $\beta = f(t)$ in the implicit form:

$$\frac{\beta}{\beta + 1} + \frac{c}{1 + c} \ln \frac{1 + c\beta}{1 - \beta} = (1 + c)kt \qquad (5)$$

It can seen in Figure 4(a)(b) that good agreement between the experimental and calculated dependencies of the degree of conversion on time and on the rate of conversion over the entire conversion is obtained. This confirms that the proposed rheo-

kinetic model is good and that the self-acceleration character of these process is a consequence of the chemical reaction of crosslinking and of morphological changes.

**Influence of the composition and structure of phenol-formaldehyde novolac resins on the curing reaction**

Even though the random novolac resins were synthesized within a very narrow range of molar
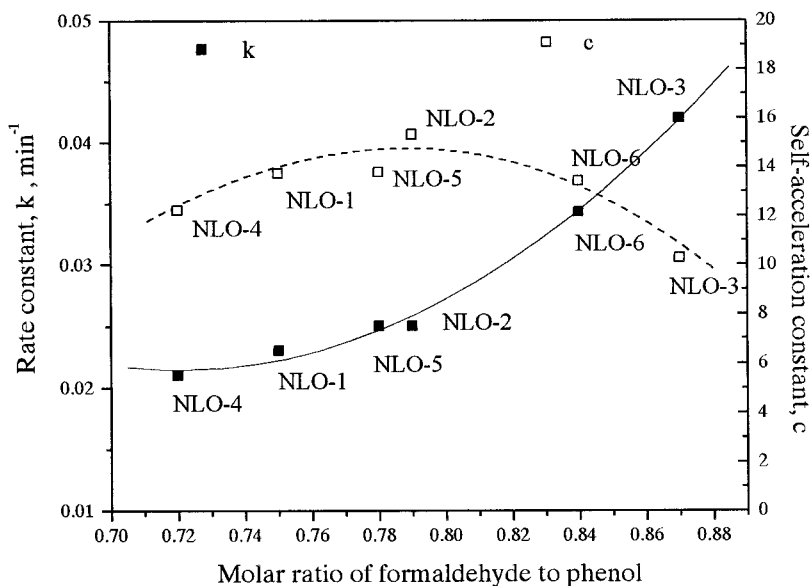
**Figure 5**   Effect of the novolac composition on the rate constant of curing $k$ and the self-acceleration constant $c$ for the series NLO 1–6 (Table II).

ratios of formaldehyde to phenol (0.75–0.85) with two different concentrations of catalyst, the real composition of the novolac resins were within the range $F/P$ 0.72–0.87. The novolac resins synthesized with the higher concentration of oxalic acid were of higher molecular weight, larger polydispersity, and more reactive than those prepared with the lower concentration. This difference in reactivity was ascertainable from rheokinetical analysis. Thus, the reaction rate constant $k$ from the phenomenological expression increases regularly with increasing molar ratio of formaldehyde to phenol, going from 0.023 to 0.042 min$^{-1}$ for the series of random novolac NLO 1–6 (Table II). The values of the self-accelerating constant $c$ varies between 10 and 15 for the series of novolac NLO 1–6 and does not show any apparent dependency on the molar ratio (Table II and Fig. 5).

However, it is possible to see that in the region of low molar ratio ($\leq$0.8) of formaldehyde to phenol, the self-acceleration constant $c$ increases with increasing molar fraction of formaldehyde. In the region of higher molar ratio in the case of the more reactive novolac resins, such as NLO-3 and NLO-6, the value of the self-acceleration constant $c$ decreases. This is especially pronounced with the novolac NLO-3, which from all the random samples has the highest number of $o$-$o'$ methylene linkages (Table I) and the highest reactivity.

One of the aims of this work was to quantify the differences in the reactivity between random

and high-$ortho$-novolac resins. The rate constant $k$ of curing high-$ortho$-novolac resins were 1.6–2.5 times higher compared with the most reactive random novolac resin NLO-3, while the values of the self-acceleration constant $c$ were the lowest for the novolac resin with the highest content of $o$-$o'$ methylene bridges.

The characteristic parameters of curing novolac resins at 180°C, such as the time of gel point, i.e., the time of the maximum of $\tan\delta$, $t$ $(\tan\delta)_{\mathrm{max}}$, the time of the attainment of the inflection point $t$ $(\beta_{\mathrm{infl}})$, the rheological conversion $(\beta\mathrm{infl})$, and its rate at the inflection conversion $(d\beta/dt)_{\mathrm{infl}}$, are presented in Table III and in Figure 6. It may be noted that the gel time, as well as time and conversion at the inflection point, are dependent on both the novolac composition, i.e., the molar ratio of formaldehyde to phenol, and the content of the $o$-$o'$ isomer. It can also be seen that the curing rate maximum is higher and the conversion at the curing rate maximum is lower for the high-$ortho$ than for the fastest random novolac NLO-3. Figure 7 also shows that the $dG'/\mathrm{dt}$ maximum for the high-$ortho$-novolac is reached before that for the fastest random novolac resin NLO-3.

The self-acceleration model $d\beta/dt = k(1+c\beta)(1 - \beta)^2$ can be used when the maximum reaction rate appears at around 30% conversion, as is the case in the curing reaction of random novolacs. The reason for the derivation of the calculated from the experimental data in the curing reaction

**Table III   Characteristic Rheological Parameters of the Curing Novolac Resins at 180°C**

| Sample | Gel Point $(\tan \delta)_{max}$ (min) | Characteristics of the Inflection Point | | | $G'_{\infty}$ (Pa) |
| | | $t_{infl}$, min | $\beta$ | $d\beta/dt$, min$^{-1}$ | |
| --- | --- | --- | --- | --- | --- |
| NLO-1 | 4.4 | 6.5 | 0.29 | 0.061 | 4.43 10$^8$ |
| NLO-2 | 2.5 | 5.15 | 0.30 | 0.071 | 6.99 10$^8$ |
| NLO-3 | 0.5 | 3.9 | 0.26 | 0.093 | 6.12 10$^8$ |
| NLO-4 | 5.0 | 7.7 | 0.31 | 0.052 | 4.75 10$^8$ |
| NLO-5 | 2.5 | 5.8 | 0.30 | 0.064 | 3.00 10$^8$ |
| NLO-6 | 1.0 | 4.1 | 0.29 | 0.092 | 6.36 10$^8$ |
| NL-OO'1 | 1.0 | 3.0 | 0.25 | 0.107 | 3.75 10$^8$ |
| NL-OO'2 | 0.5 | 3.0 | 0.26 | 0.125 | 3.74 10$^8$ |

of high-*ortho*-novolac resins (Table II, correlation coefficient, $r^2$) may be that the reaction at 180°C is very fast without an induction time, so that the maximum of the curing rate occurs at ~25% conversion.

The molar ratio formaldehyde to phenol (fraction of formaldehyde) appears to be the main variable that governs the reactivity of novolac resins, especially random ones (Fig. 5). On the contrary, it can be seen that the rate constant values of high-*ortho*-novolac resins are higher than expected on the base of molar fraction of formaldehyde. From the dependency of the rate constant on the content of *o-o'* isomer, which is an indirect measure of the unsubstituted *para* positions per phenolic ring, it can be seen that random novolacs

with a greater content of the *o-o'* isomer show higher values of the rate constant. For high-*ortho*-novolac resins, this is even more pronounced, which is obviously the influence of the high fraction of free *para* positions, which are more reactive than the *ortho* position in the curing reaction (Fig. 8).

## Influence of Physical Treatment on the Curing of Novolac Resin

Rheokinetic studies of the influence of physical treatment on the novolac resins was performed on two series of novolac resins, NLO-1 and NLO-3. Physical treatment, such as washing and neutralization, changes the composition of phenolic resin
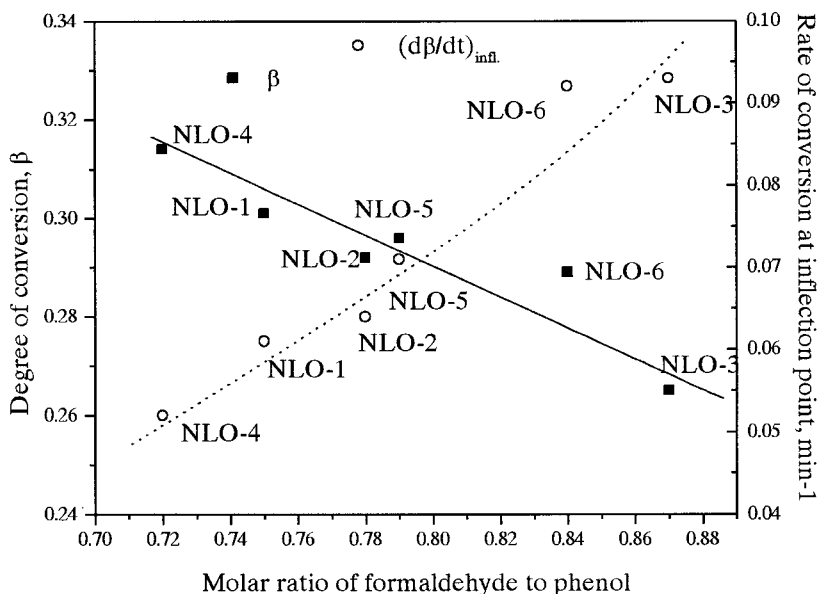


**Figure 6** Degree of rheological conversion $\beta$ and its rate $d\beta/dt$ at the inflection point as a function of the novolac composition (mole ratio of formaldehyde to phenol.
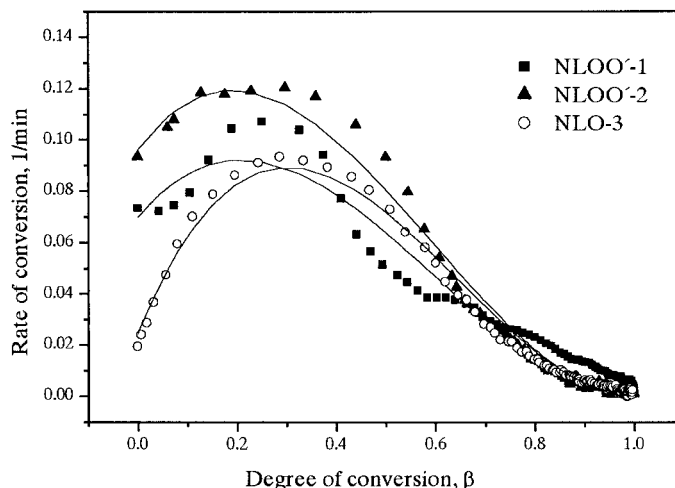
**Figure 7** Rate of change of the rheological conversion $d\beta/dt$ versus the rheological degree of conversion $\beta$ for the random novolac NLO-3 and the high-*ortho*-NLOO'-1 and NLOO'-2 novolac resins at 180°C. Symbols, experimental values; curves, calculated values.

by elimination of lower molecular fractions and free phenol. They also affect the reactivity of novolac resins in the curing reaction by changing the pH values. These, to a great extent, change the rheokinetical and rheological characteristics of the novolac resins (Table IV). Washing the novolac resins increases the curing rate constant $k$ due to changes in composition, i.e., increased $F/P$ ratio (Table I). The increase in reactivity of washed novolac resins was confirmed by the shorter time to the gel point and assessment of the inflection point. While neutralization, as expected, decreases the curing rate constant. The curing rate constant as well as the curing rate at the inflection point are diminished on neutralization by the factors 0.6 and 0.8, respectively, of that of the starting novolac resin due to the change of pH.

### Effect of Temperature

The influence of temperature on the curing behavior of the novolac resins was studied on samples NLO-4 and NLO-6 at four temperatures (140, 160,180, and 200°C). The increase of the curing rate with increasing temperature is shown in Figure 9. The activation energy of the curing process, $E_a$, was determined by applying the Arrhenius
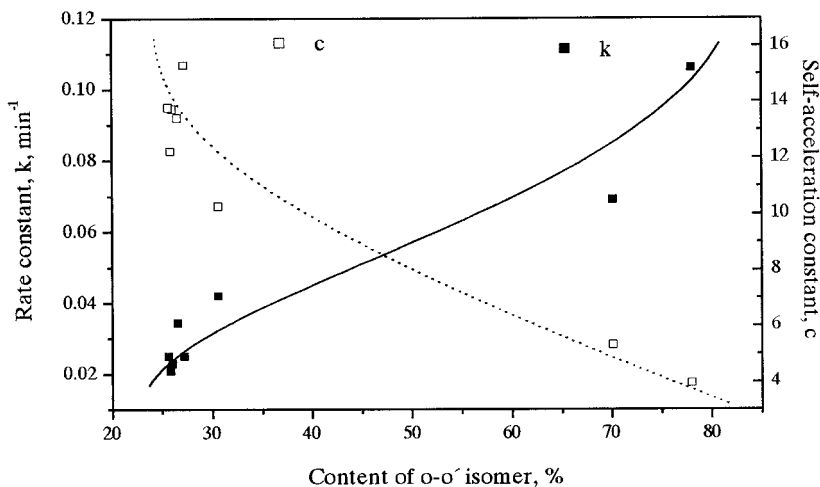


**Figure 8** Effect of the novolac composition, i.e., content of the *o-o'* isomer, on curing rate constants $k$ and self-acceleration constant $c$ for the novolac resins (Table II).

**Table IV  Influence of Physical Treatment (Washing and Neutralization) on the Rheological Parameters of Curing of Novolac Resins NLO-1 and NLO-3**

| Sample | Gel Point $(\tan \delta)_{max}$ (min) | Inflection Point Characteristics | | | Rheokinetical Parameters | |
|---|---|---|---|---|---|---|
| | | $t_{infl}$ | $\beta$ | $d\beta/dt$ min$^{-1}$ | $k$ (min$^{-1}$) | $c$ |
| NLO-1 | 4.5 | 6.5 | 0.30 | 0.061 | 0.023 | 13.74 |
| NLO-1W | 1.5 | 5.4 | 0.26 | 0.068 | 0.032 | 10.30 |
| NLO-1N | 4.2 | 7.9 | 0.29 | 0.051 | 0.014 | 18.47 |
| NLO-3 | 0.5 | 3.9 | 0.26 | 0.093 | 0.042 | 10.27 |
| NLO-3W | 1.4 | 3.5 | 0.29 | 0.101 | 0.047 | 9.29 |
| NLO-3N | 2.0 | 5.0 | 0.30 | 0.078 | 0.028 | 13.94 |

equation. Activation energies of 60.8 kJ/mol and 33.24 kJ/mol were found for NLO-4 and NLO-6, respectively. These results confirm that the value of the activation energy of the curing process decreases with increasing reactivity of novolac resin. Also, as can be seen from Table V, not only the rate constant, but also the self-acceleration constant, depends on temperature. The rheokinetic parameters obtained by this analysis could permit the simulation of the curing process both inside and outside the experimental range of temperatures. The dependency of gel time on curing temperature is shown in Table V. The time to the gel point, as well as the time to the inflection point, were shorter with increasing temperature.

These results indicate that dynamic mechanical measurements on cotton strips impregnated with phenol-formaldehyde resins, followed by careful rheological analysis, can be a powerful tool in the characterization and design of thermosetting resins and in the determination of the properties of the final products. They could also play an important role in the better understanding of structure-properties relationships.

## CONCLUSIONS

The curing reaction of novolac phenol-formaldehyde resins with hexamethylentetramine (HMTA) is described by a third order phenomenological equation, which takes into account the self-acceleration effect that arises from the superposition of both the chemical reaction and the phase separation. The results
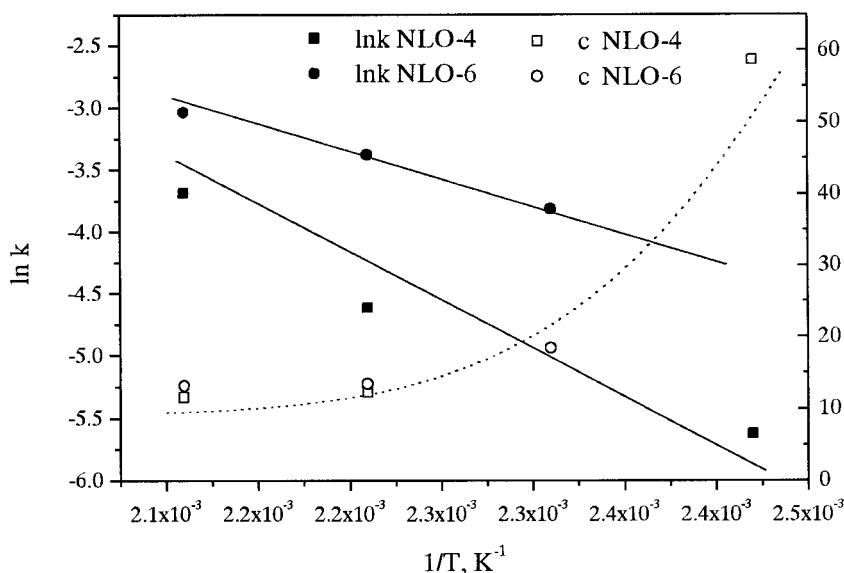


**Figure 9**  Dependence of curing rate constant **k** and the self-acceleration constant $c$ on curing temperature for the reaction mixtures NLO-4 and NLO-6.

**Table V   Rheokinetic Curing Parameters of NLO-4 and NLO-6 Novolac Resins at Different Temperatures**

| Sample | Temperature (°C) | Gel Point (tan δ) (min) | Kinetical Parameters | |
|---|---|---|---|---|
| | | | $k$ (min$^{-1}$) | $c$ |
| NLO-4 | 140 | 9 | 0.0037 | 58.64 |
| NLO-4 | 180 | 5 | 0.021 | 12.24 |
| NLO-4 | 200 | 1 | 0.035 | 11.53 |
| NLO-6 | 160 | 2.5 | 0.022 | 18.33 |
| NLO-6 | 180 | 1 | 0.034 | 13.42 |
| NLO-6 | 200 | 0 | 0.048 | 13.16 |

from the rheokinetic model demonstrate good agreement with the experimental data over the entire conversion. The constants of the curing reaction follow an Arrhenius type temperature dependence. The influence of the composition and physical treatment was shown by comparing the values of the rate constant and the self-acceleration constant from the phenomenological equation describing the curing reaction. It was shown that the characteristic parameters, such as the time of gel formation, the time to the inflection point, and the rheological degree of conversion at the inflection point, all decrease with an increasing molar ratio of formaldehyde to phenol. At the same time, the rate of the rheological conversion, $(d\beta/dt)_{\text{infl}}$ increases.

Among the physicochemical methods for studying curing process, calorimetry is the closest to rheokinetics, both yielding combined characteristic of the chemical reaction and morphology changes. The curing behavior of these random and high-*ortho*-novolac resins by DSC analysis will be discussed in a further report.

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