

# Analysis of the Crosslinking Process of a Phenolic Resin by Thermal Scanning Rheometry

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**ABSTRACT:** The curing reaction of a phenolic resin (resole type) carried out in the absence of an initiator was studied by thermal scanning rheometry under isothermal conditions at temperatures from 70 to 105°C. The same curing reaction was studied in the presence of an acid as a catalyst in the temperature range of 50–80°C. The gel time, which was defined by several criteria, was found to be a good parameter to determine the apparent activation energy of this process. An empirical model was used to predict the change in complex viscosity with time until the gel time was reached. If first-order kinetics were assumed, the apparent kinetic constant of the curing reaction could be obtained. Furthermore, the effect that the addition of water and free phenol had on the curing process of this type of resin was studied. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 57–65, 2002

**Key words:** crosslinking; thermoset

## INTRODUCTION

Thermosetting resins exhibit individual chains that are chemically crosslinked by covalent bonds during polymerization, which give rise to a final three-dimensional network that resists heating and solvent attack but cannot be thermally processed. Different kinds of resins belong to this group, for example, phenolic resins, which were studied in this work. Phenolic resins are thermosetting materials with very good resistance to fire and excellent insulation properties and that are

easily processable,<sup>1</sup> which leads to a wide range of applications, including foundry applications, coatings, and thermal insulation among others.<sup>2</sup>

Phenolic resins are of two main types:<sup>3</sup> novolacs and resols. Novolac resins are prepared by the reaction of an excess of phenol with formaldehyde under acidic conditions, whereas resols are prepared by the reaction of phenol with excess formaldehyde under basic conditions.

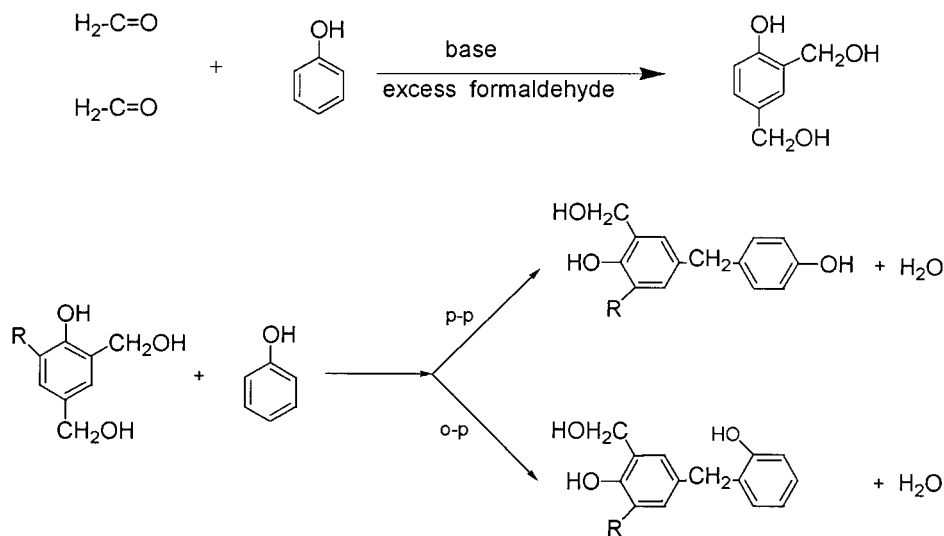
The first step in resole formation is the reaction of phenol and excess formaldehyde under basic conditions to form an addition compound followed by a condensation reaction of a methylol group in either the ortho or para position,<sup>3</sup> which produces methylene bridges:

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Due to the formation of water during the process and the difficulty of its elimination, all commercial phenolic resins contain water. Resin obtained in this way can be cured with different types of catalysts, including bases, acids, and amines, the process being complex because many different reactions are in competition, depending on the medium conditions.

The aim of this study was to analyze the rheological behavior and the kinetics of the curing process of a resole resin under isothermal conditions in the absence of an initiator and with an acid as a catalyst. The effect of changes in water and free phenol concentrations were also analyzed.

## EXPERIMENTAL

### Materials

The resin used was a commercial liquid phenolic-resole resin (pH = 8.7) supplied as TH-215 by Fers Resins (Barcelona, Spain) and containing 3 wt % of free phenol and 13 wt % of water. The phenolic resin was kept sealed at 4°C under nitrogen to avoid any possible water condensation.

The catalyst used was *p*-toluensulphonic acid (6M) supplied as C.300 by Fers Co. The influence of water and free phenol concentrations on the curing process was studied by the addition of deionized water and solid phenol, respectively.

### Rheological Measurements

All the rheological measurements were carried out by means of a thermal scanning rheometer

(Rheometric Scientific, Epsom, Surrey, UK). This technique, already described,<sup>4,5</sup> allows measurement of the curing and rheological characteristics of a wide variety of materials and gives information about the viscoelastic behavior, especially the changes in rheological properties with time or temperature. The complex viscosity ( $\eta^*$ ) of a liquid is measured by the vertical oscillation of a spade-shaped probe below the liquid surface. The oscillatory motion of the probe is progressively damped by viscous drag, which allows for the monitoring of viscoelastic properties, such as viscosity and its components, the storage modulus ( $G'$ ), the loss modulus ( $G''$ ), and the loss tangent ( $\tan \delta$ ), during the curing process. The oscillation frequency is 2 Hz, and readings are obtained every second.

Table I shows the conditions used in the curing experiments; A experiments were carried out with fixed amounts of both water and phenol and different catalyst concentrations, B experiments were carried out with different water concentrations at fixed catalyst and phenol concentrations, and C experiments were carried out with fixed catalyst and water amounts at two different free phenol concentrations.

In all cases, the curing processes were carried out under isothermal conditions at the temperatures indicated in Table I. We always chose the isothermal cure temperatures below 100°C to avoid boiling the water condensed during the curing reaction because this would make it difficult to monitor the viscoelastic properties during the process. Only in the curing reactions carried out

**Table I** Conditions Used in the Curing Reactions

Run Type	C.300 (wt %)	Water (wt %)	Free Phenol (wt %)	$T$ (°C)
A	0.0	13	3	70, 75, 80, 85, 90, 95, 100, 105
	1.5	13	3	50, 60, 70, 80
	2.0	13	3	50, 60, 70, 80
	3.0	13	3	50, 60, 70
	4.0	13	3	50, 60, 70
B	1.5	17	3	50, 60, 70, 80
	1.5	19	3	60, 80
	1.5	21	3	60, 80
C	1.5	13	9	50, 60, 70, 80
	1.5	13	13	50, 60

in the absence of an initiator were the isothermal cure temperatures slightly above 100°C due to the slower rate of the curing reaction. On the other hand, in the absence of an initiator, no experiments were carried out below 70°C, as the curing reaction of the phenolic resin was too slow to be measured.

## RESULTS AND DISCUSSION

The cure of a thermosetting reactive prepolymer usually involves transformation of low-molecular-weight monomers from the liquid to the solid state as a result of the formation of a polymer network by the chemical reaction of the reactive groups of the system.<sup>6</sup> Two stages, which are divided by the gel point, are usually distinguished in this process. It is accepted that growth and branching of the polymer chains occur in the liquid state, where the reactive system is soluble and fusible. An infinite network of polymer chains appears and develops only after the gel time ( $t_g$ ). Then, the reactive system loses its solubility and fusibility, which leads to the final reactions, which take place in the solid state. The  $t_g$  is an important parameter to take into account as it determines at which point the resin becomes physically unprocessable.

Figure 1 shows a typical thermal scanning rheometry (TSR) response, and in it, three different regions are apparent. In the first region, the  $G'$  curve is parallel to the time axis, which corresponds to the region where the modulus is below the sensitivity of the instrument. In the second region, this modulus increases exponentially with time, and the  $t_g$  is reached. Finally, in the third

region, although some dispersion of data is obtained, the modulus appears to level off, which indicates that the resin has been cured.

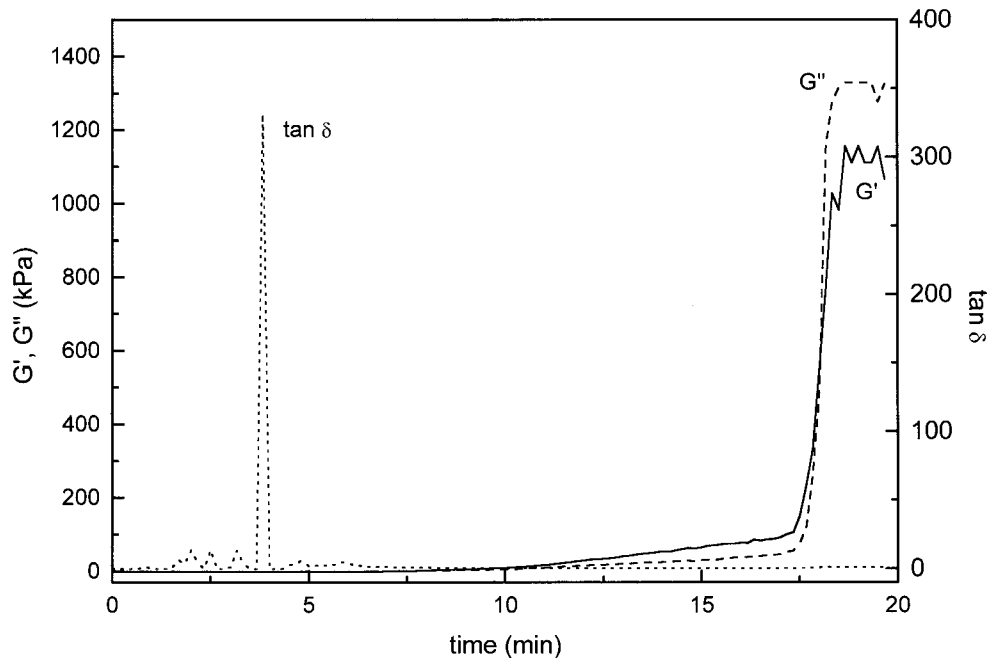
### $t_g$ Measurements

The change in dynamic-mechanical properties of a curing system is directly proportional to the extent of the reaction. From the study of these properties, a kinetic parameter such as the  $t_g$  can be determined. The  $t_g$  was determined according to several criteria:<sup>7</sup>

1. *Maximum peak in  $\tan \delta$* : based on the point where there was a maximum difference between the elastic and the viscous behavior of the system.
2. *Tangent line to the  $G'$  curve*: The  $t_g$  was taken at the point corresponding to the intercept between the base line ( $G' = 0$ ) and the tangent drawn at  $G'$  when  $G'$  reached a value close to 100 kPa.
3. *The crossover between the  $G'$  and  $G''$  curves*: At this point, the loss energy was equal to the energy stored.
4. *Viscosity*: At this point, the real dynamic viscosity ( $\eta'$ ) reached several determined values (1000, 2000, and 5000 Pa.s).

Table II shows the  $t_g$  values obtained according to the previous criteria for the curing reactions carried out under isothermal conditions in the absence of an initiator. From these data, some facts could be observed:

- The  $t_g$  decreased when the cure temperature increased; it can be explained by consider-



**Figure 1**  $G'$ ,  $G''$ , and  $\tan \delta$  versus cure time for the phenolic/C.300 system.

ation that an increase in temperature implies an increase in the mobility of the active chains, which leads to a faster curing reaction.

- No great variations were observed in the  $t_g$  values obtained for each experiment, although different criteria were used for their determination. On the other hand, when one considers that the gelification was not an instantaneous process but occurred during a period of time, it could be concluded that the  $t_g$  could be used as an adequate parameter to study the crosslinking process kinetics of the phenolic systems.

Table III shows the  $t_g$ 's obtained from the tangent line to  $G'$  curve for the cured phenolic resin/C.300 system under isothermal conditions (type A runs). In this case, some facts can be observed:

- The  $t_g$  decreased as the C.300 weight percent increased at a fixed cure temperature. This behavior can be explained by the increase in the number of functional groups as the catalyst concentration increased.
- The  $t_g$  decreased when the cure temperature increased at a fixed C.300 weight percent, this behavior being similar to that of the

**Table II**  $t_g$ 's (min) for the Systems Cured in the Absence of an Initiator

$T$ ( $^{\circ}\text{C}$ )	$t_{g1}$	$t_{g2}$	$t_{g3}$	$t_{g4}$	$t_{g5}$	$t_{g6}$
70	1049	1215	1300	1295	1369	1450
75	641.0	758.5	860	855.0	898.0	942.7
80	436.0	499.0	550	579.5	604.4	633.4
85	323.0	351.5	390	414.0	433.6	449.8
90	182.0	192.9	220	235.2	243.6	257.6
95	119.4	126.1	140	153.3	159.6	168.6
100	86.5	91.7	110	117.2	122.2	128.4
105	50.2	53.6	65.0	71.1	74.1	79.6

$t_{g1}$  = criterion of the maximum peak in  $\tan \delta$ ;  $t_{g2}$  = criterion of  $G' = G''$ ;  $t_{g3}$  = criterion of the tangent line to the  $G'$  curve;  $t_{g4}$ ,  $t_{g5}$ , and  $t_{g6}$  = criterion of viscosity for  $\eta' = 1000, 2000,$  and  $5000$  Pa.s, respectively.

**Table III**  $t_g$ 's According to the Criterion of Tangent Line to  $G'$  Curve for the Systems Cured in the Presence of an Acid as a Catalyst

$T$ ( $^{\circ}\text{C}$ )	C.300 (wt %)	$t_g$ (min)
50	1.5	89.2
	2.0	57.0
	3.0	31.5
	4.0	22.1
60	1.5	37.4
	2.0	22.1
	3.0	10.1
	4.0	8.6
70	1.5	12.5
	2.0	9.5
	3.0	6.1
	4.0	5.6
80	1.5	7.0
	2.0	5.3

phenolic resin cured in the absence of an initiator.

The behavior of these systems was similar to that already described for epoxy and vinyl ester resins.<sup>4,5,8</sup>

### Apparent Activation Energy ( $E_a$ )

At the first stage of the reaction, before the  $t_g$ , the kinetic equation for the system could be described as:

$$\frac{d\alpha}{dt} = k' \cdot (1 - \alpha)^n \quad (1)$$

where  $\alpha$  is the chemical conversion,  $k'$  is the apparent kinetic constant, and  $n$  is the kinetic order.

If the chemical conversion at  $t_g$  is considered constant for a given system,<sup>6</sup> the relation between the  $t_g$  and the apparent kinetic constant ( $k'$ ) of the reaction can be expressed as:

$$tg \propto \frac{1}{k'} \quad (2)$$

If it is assumed that the apparent kinetic constant of the reaction ( $k'$ ) is related to the temperature by an Arrhenius relationship:

$$\ln tg = C + \frac{E_a}{R} \cdot \frac{1}{T} \quad (3)$$

where  $C$  is a constant related to the chemical conversion at  $t_g$ . A linear relationship was observed between  $\ln t_g$  (min) and the inverse of temperature for isothermal curing reactions carried out in the absence of an initiator. From the slope of this relationship,  $E_a$  could be obtained (see Fig. 2 and Table IV). From these values, an average  $E_a$  of 91.2 kJ/mol was obtained.

The  $E_a$ 's obtained from all criteria were in agreement with those obtained by other authors with different analysis techniques such as differential scanning calorimetry,<sup>9,10</sup> so we could conclude that TSR is an adequate technique to measure  $E_a$  of the curing reaction of phenolic resins in the absence of an initiator.

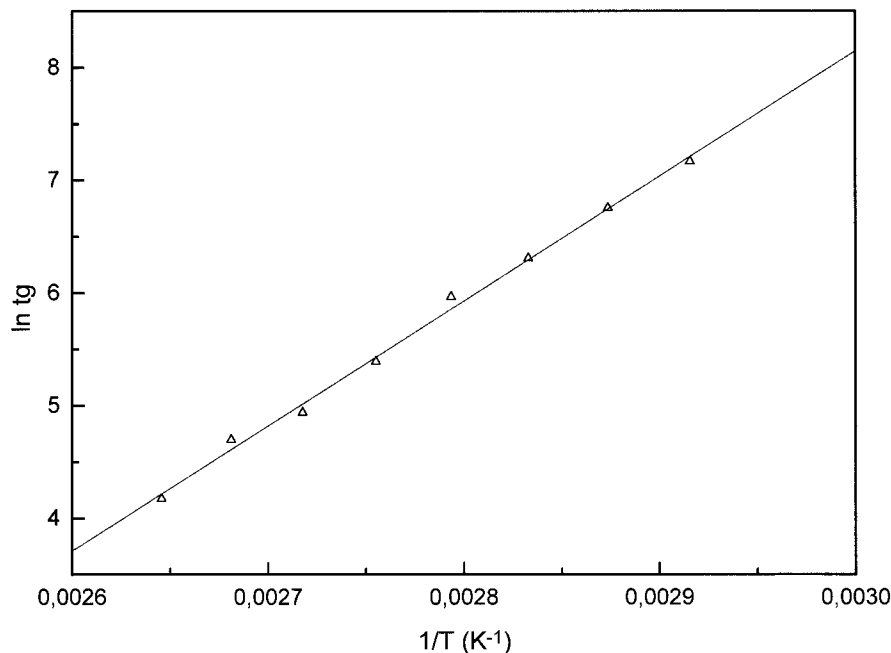
A similar linear relationship was obtained for those systems in which an acid was utilized as a catalyst; the  $E_a$  values are given in Table V.  $E_a$  tended to decrease as C.300 weight percent increased, and from that dependency, an  $E_a$  value for C.300 weight percent = 0 of 92.9 kJ/mol (with the criterion of the tangent line to the  $G'$  curve) was estimated. This value was similar to that obtained previously (Table IV) for the curing reactions of the phenolic resin in the absence of an initiator, with the same criterion (92.2 kJ/mol). This fact seems to indicate that the curing reaction was the same either in the absence of an initiator or in its presence and was a function of the hydrogen ion in the medium.

### Kinetic Analysis from Viscosity Data

There are different treatments for the quantitative viscosity data obtained for thermosetting systems cured under isothermal conditions. Most are mainly based on the Williams-Landel-Ferry equation:<sup>11,12</sup>

$$\log a_T = -C_1 \cdot \frac{T - T_S}{C_2 + (T - T_S)} \quad (4)$$

where  $a_T$  is the shift factor;  $T_S$  is a reference temperature; and  $C_1$  and  $C_2$  are two universal constants with values 17.44 and 51.6, respectively, only if  $T_S$  is the glass-transition temperature ( $T_g$ ) of the material. This equation was considered exclusively to observe the dynamic-me-



**Figure 2** Arrhenius plot for type A runs.

chanical relaxation times in the  $T_g$  to  $T_g + 50^\circ\text{C}$  zone.

Viscosity data can also be treated by fitting them to empirical equations, where the dependency of the viscosity on temperature and conversion is separated into two independent terms:

$$\eta(T, \alpha) = \eta(T) \cdot \eta(\alpha) \quad (5)$$

If it is assumed that the reaction in the liquid state follows first-order ( $n = 1$ ) kinetics until the  $t_g$  and it is taken into account that for a fixed temperature,  $\eta(T)$  can be considered a constant,  $\eta_0$ :

$$\ln \eta = \ln \eta_0 + k_\eta t \quad (6)$$

where  $\eta$  is the viscosity, which is a function of temperature and conversion;  $\eta_0$  is the viscosity at  $t = 0$ ; and  $k_\eta$  is the apparent kinetic constant.

From TSR measurements, the dependence of the  $\eta^*$  with time,  $\eta^*(t)$ , could be obtained. By plotting  $\ln \eta^*$  versus time, according to eq. (6), a linear relationship was observed only during the gelation stage (Fig. 3), which corresponded to the second region observed in Figure 1. This study was carried out for all runs made in the absence of an initiator, whereas it was only made at 50 and 60°C for runs carried out in the presence of the catalyst.

Table VI shows the  $k_\eta$  values obtained from eq. (6) for the curing reaction of the phenolic resin in the absence of an initiator. The value of  $k_\eta$  increased as the curing temperature increased; some dispersion in the values was observed for temperatures above 100°C, which could indicate that the kinetic treatment of these systems became difficult above this temperature, probably due to the influence of water or changes in the reaction mechanism.

**Table IV**  $E_a$ 's (kJ/mol) for the Phenolic Resin Cured in the Absence of an Initiator

$E_{a1}$	$E_{a2}$	$E_{a3}$	$E_{a4}$	$E_{a5}$	$E_{a6}$	$\overline{E}_a$
91.7	95.2	92.2	89.3	89.7	89.3	91.2

$E_{a1}$  = criterion of the maximum peak in  $\tan \delta$ ;  $E_{a2}$  = criterion of  $G' = G''$ ;  $E_{a3}$  = criterion of the tangent line to the  $G'$  curve;  $E_{a4}$ ,  $E_{a5}$ ,  $E_{a6}$  = criterion of viscosity for  $\eta' = 1000$ , 2000, and 5000 Pa.s, respectively;  $\overline{E}_a$  = average  $E_a$ .

**Table V**  $E_a$ 's According to the Criterion of the Tangent Line to the  $G'$  Curve for the Phenolic Resin Cured in the Presence of the Catalyst

C.300 (wt %)	$E_a$ (kJ/mol)
1.5	83.3
2.0	76.1
3.0	75.8
4.0	63.5

When one considers that the temperature dependence of the  $k_\eta$  is given by an Arrhenius relationship:

$$\ln k_\eta = \ln k_{\eta^\infty} - \frac{E_a}{R \cdot T} \quad (7)$$

and the plotting of  $\ln k_\eta$  versus the inverse of temperature for the curing reaction of the phenolic resin in the absence of an initiator, a linear relationship was obtained (Fig. 4) from which an  $E_a$  value of 124 kJ/mol was obtained. This value was higher than that obtained from  $t_g$  values; this behavior was similar to that observed for other systems.<sup>4,13,14</sup> The  $E_a$  value obtained from viscosity data may be considered as representative of

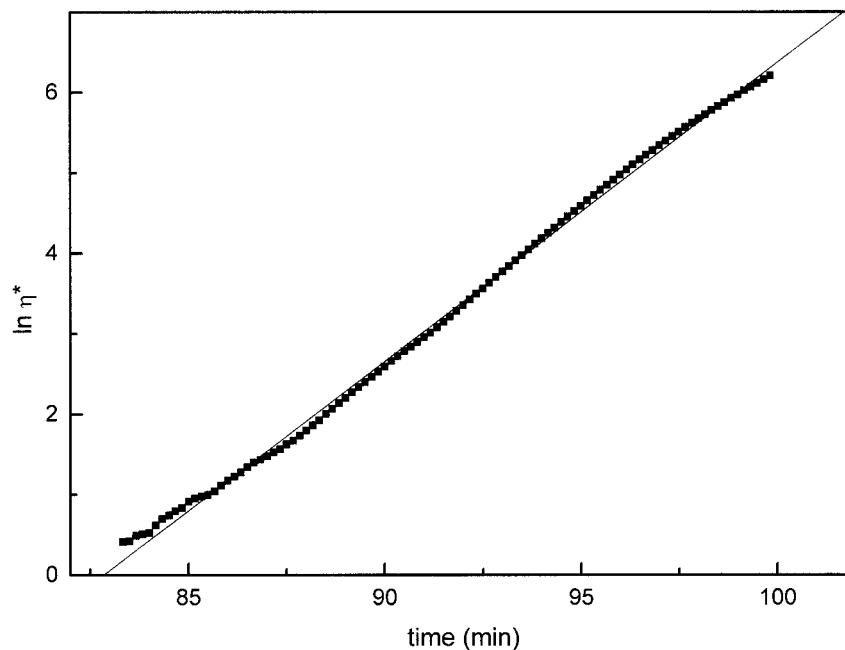
**Table VI**  $k_\eta$  Values for the Phenolic Resin Cure in the Absence of an Initiator

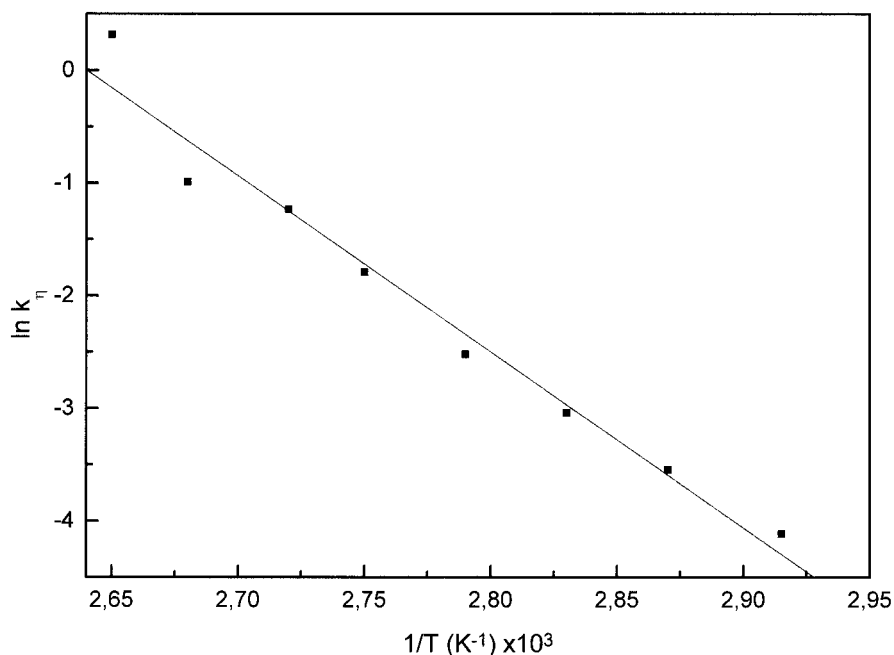
$T$ ( $^\circ\text{C}$ )	$k_\eta$ ( $\text{min}^{-1}$ )
50	0.00081 <sup>a</sup>
60	0.0035 <sup>a</sup>
70	0.016
75	0.029
80	0.048
85	0.080
90	0.17
95	0.29
100	0.37
105	1.4

<sup>a</sup>  $k_\eta$  value extrapolated.

the whole process, whereas the value derived from the  $t_g$  considers only a given point of the process.

Table VII shows the  $k_\eta$  values for the isothermal curing reaction carried out in the presence of an acid as a catalyst at 50 and 60 $^\circ\text{C}$ . At a fixed temperature,  $k_\eta$  increased when C.300 weight percent increased, and the values estimated at both temperatures when C.300 weight percent went to zero were consistent with those obtained from extrapolation of the data in Figure 4, in the

**Figure 3**  $\eta^*$  dependency with time from TSR measurements without a catalyst at 100 $^\circ\text{C}$ .



**Figure 4** Plot of  $\ln k_{\eta}$  versus  $T^{-1}$  for the system cured in the absence of an initiator.

absence of a catalyst. This demonstrates the correlation between the catalyzed and uncatalyzed experiments.

#### Water and Free Phenol Addition

To determine the influence of the addition of either water or free phenol on the phenolic system  $t_g$ 's, several experiments were carried out with different amounts of both water (type B) and phenol (type C). Table VIII shows  $t_g$ 's, according to the criterion of the tangent line to the  $G'$  curve for type B and type C runs. The curing process was significantly influenced by the proportion of water

added, which led to an increase in  $t_g$ 's with water content. A similar effect was observed for the addition of phenol.

Table IX shows  $E_a$ 's, calculated from data in Table VIII, for systems with added water or phenol. These results show that these variables must be considered in the curing reaction to design the

**Table VII**  $k_{\eta}$  Values Obtained for the Catalyzed Curing Process

$T$ ( $^{\circ}\text{C}$ )	C.300 (wt %)	$k_{\eta}$ ( $\text{min}^{-1}$ )
50	1.5	0.085
	2.0	0.093
	3.0	0.16
	4.0	0.24
60	1.5	0.29
	2.0	0.43
	3.0	0.58
	4.0	0.52

**Table VIII**  $t_g$ 's According to the Criterion of the Tangent Line to the  $G'$  Curve for B and C Runs

$T$ ( $^{\circ}\text{C}$ )	Water (wt %)	Free Phenol (wt %)	$t_g$ (min)
50			146.3
60	13	9	59.4
70			18.4
80			7.0
50	13	13	245.0
60			74.4
50			108.0
60	17	3	49.6
70			25.1
80			9.6
60	19	3	55.8
80			10.1
60	21	3	68.3
80			10.7



**Table IX**  $E_a$ 's According the Criterion of the Tangent Line to the  $G'$  Curve for B and C Runs

C.300 (wt %)	Water (wt %)	Free Phenol (wt %)	$E_a$ (kJ/mol)
1.5	17	3	74.8
1.5	13	9	97.4

adequate conditions for processing these materials.

## CONCLUSIONS

The results obtained in the study of the crosslinking process of phenolic resins by TSR allows us to conclude that this is an adequate technique to study rheological properties during the curing process of thermosetting resins.

The curing reaction of the phenolic resin has similar characteristics in the presence or in the absence of a catalyst, as deduced from the apparent kinetic constants obtained from both kind of experiments.

The  $t_g$  values decreased when temperature and C.300 weight percent increased (at a fixed C.300 weight percent and temperature, respectively) as a consequence of an increase in the mobility of active centers and the presence of a higher number of them, which gives rise to a faster curing process.

$E_a$  obtained from  $t_g$  data was different than that derived from viscosity data, probably due to the fact that in the later case, the full gelation process was considered.

The water and phenol concentrations influenced the cure process as derived from the  $t_g$  values obtained, so these variables should be considered when these resins are processed.

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