

Master Curve and Time–Temperature–Transformation Cure Diagram of Lignin–Phenolic and Phenolic Resol Resins

M. V. Alonso,¹ M. Oliet,¹ J. García,¹ F. Rodríguez,¹ J. Echeverría²

¹Departamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Avda de la Complutense s/n. 28040 Madrid, Spain

²Hexion Specialty Chemicals Ibérica S. A., Carretera a Navarra, Epele 39. E-20120 Hernani (Guipúzcoa), Spain

Received 21 March 2006; accepted 19 September 2006

DOI 10.1002/app.25497

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The aim of this work is to generate both a master curve of resol resins based on the time–temperature superposition principle and their TTT cure diagrams. The samples used for this purpose were lignin–phenolic and phenol–formaldehyde resol resins. A TMA technique was employed to study the gelation of resol resins. In addition, a DSC technique was employed to determine the kinetic parameters through the Ozawa method, which allowed us to obtain isoconversional curves from the data fit to the Arrhenius

expression. Establishing the relationship between the glass-transition temperature and curing degree allowed the determination of the vitrification lines of the resol resins. Thus, using the experimental data obtained by TMA and DSC, we generated a TTT cure diagram for each of resins studied. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3362–3369, 2007

Key words: phenolic resin; lignin; curing kinetics; glass-transition temperature; TTT cure diagram

INTRODUCTION

Phenol–formaldehyde (PF) resol resins are used predominantly as adhesives in plywood panels, flakeboards, and particleboards.^{1–3} These resins provide excellent properties due to their high strength and extreme resistance to moisture. The phenolic resins are expensive as a result of the rising costs of petroleum-based materials. Extensive studies have been performed on the utilization of natural products, such as lignin, tannin, and vegetable extracts, which can be fillers or coreactants in the formulation of the PF resins.^{4–9} The lignosulfonates are one of the natural products that are most studied as partial substitutes of phenol in the formulation of the resol resins. The chemical modification of lignin by methylation or phenolation is necessary to improve its reactivity towards the formaldehyde during the polymerization reaction.^{4,6,10–12} The preparation of the resins and the chemical structure of the polymer have a great influence on their curing temperatures. Additionally, the curing stage has a great influence on the application of resol resin, since it determines the quality of final product. Thus, knowledge of the cur-

ing stage of phenolic resins is of great importance; however, it has not been studied much.

In addition to the reasons mentioned earlier, the curing of phenolic resins is complex due to the existence of changes in the gelation and vitrification steps during their chemical transformations. Gelation occurs when the average molecular weight of a material becomes infinity due to crosslinking; moreover, the material becomes nonfusible and insoluble. Therefore, gelation is a critical point, since the polymer does not flow and is no longer processable beyond this stage. This state is dependent on the functionality, reactivity, and stoichiometry of reactants. Nevertheless, the gelation does not inhibit the curing process. Beyond the gel point, the reaction continues towards the formation of a network with a high crosslink density. Vitrification is another phenomenon that may occur during the resin's curing process. In this case, there is a transformation from a viscous liquid or elastic gel to a glass, which occurs when the glass-transition temperature (T_g) coincides with the curing temperature (T_c). Vitrification is a transition that causes a change from a chemical reaction to diffusion control of the curing kinetics of the overall process.¹³ This phenomenon can be observed by a progressive decay of the reaction rate. Devitrification of the polymer occurs when the glass-transition temperature decreases as a result of the thermal degradation at a given temperature. The time–temperature–transformation (TTT) cure diagram is a

Correspondence to: M. V. Alonso (valonso@quim.ucm.es).
Contract grant sponsor: Ministerio de Ciencia y Tecnología.

useful tool for studying these phenomenological changes of the polymers during their cure, gelation, and vitrification.^{13–17} Thus, this diagram can be expanded to include iso- T_g curves, which can be determined if a complete kinetic model of the resin curing process is known. Yang and Lee¹⁸ determined the gel point (t_{gel}) and curing degree (α_{gel}) of polyester resins by viscosity and calorimetric techniques, respectively. Riesen and Sommerauer¹⁹ determined the gel time and gel conversion of an epoxy resin through a thermomechanical analyzer (TMA) and differential scanning calorimetry (DSC), respectively. Hofmann and Glasser²⁰ also studied the curing of epoxy resins; in this case, they employed a dynamic mechanical analyzer (DMA) technique for measuring the gel time. However, Mijovic et al.²¹ utilized a FTIR technique based on Flory-Stockmayer's theory for measuring the α_{gel} value of an amine-epoxy system. One methodology employed to measure the glass-transition temperature is based on the polymer curing at different times and temperatures. In addition, the curing degree is determined by DSC from residual reaction heat. In this manner, the master curve of resol resins can be elaborated as a relationship between glass-transition temperature and curing degree. All these techniques have been widely utilized for studying epoxy resins.^{15,19,21} Furthermore, other techniques as torsional braid analysis (TBA), rheometrics dynamic analyzer (RDA), and size-exclusion chromatography (SEC) have been utilized for cure characterization and TTT cure diagram development.^{22–24} However, the applications of thermal analysis to elaborate TTT cure diagrams and/or master curves of phenolic resins yield unusual results. In the present work, the TMA and DSC techniques have been utilized for studying the gelation and vitrification phenomena of lignin-phenolic and phenolic resol resins during their cure. The experimental data obtained through these techniques allowed construction of the master curves and TTT cure diagrams of both resol resins.

EXPERIMENTAL

Materials

The phenol-formaldehyde (PF) commercial resol resin that was tested was supplied from Hexion Specialty Chemicals Ibérica, S.A. (Spain). This product was obtained by the polymerization between phenol and formaldehyde in alkaline medium (sodium hydroxide). The softwood ammonium lignosulfonate (Borregaard Deutschland) employed for the partial replacement of phenol in the lignin-phenol-formaldehyde resin was provided by BASF Curtex, S.A.

Preparation of lignin-phenolic resin

Lignin-phenol-formaldehyde resol resin was synthesized in the laboratory, with a 35% (w/w) methylolated softwood ammonium lignosulfonate. The optimal conditions for methylolation and formulation of lignin-phenolic resins were reported in previous work.^{9,11}

Techniques and procedure

The calorimetric measurements were performed on a Mettler Toledo DSC 821^e calorimeter, using medium pressure pans. The pans, with a volume of 120- μL , can withstand vapor pressures up to 10 MPa. Since it is difficult to weigh exactly the same amount of sample every time, different thermograms were normalized by the calorimeter software to 1 g.

The experimental work is divided in two sections. In the first section, dynamic DSC tests were completed for determining a kinetic model of the resin curing process and the relation iso- T_g , as mentioned before. In this case, Ozawa's isoconversional method was applied. The experimental data were obtained from nine heating rates (2, 4, 6, 8, 10, 12, 14, 16, and 20°C min⁻¹) in a scanning temperature range from 30 to 250°C. The data treatment of the dynamic curing processes by DSC begins with the calculations of conversion degree, which corresponds to the following expression:

$$\alpha = \frac{(\Delta H_p)_t}{\Delta H_0} \quad (1)$$

where $(\Delta H_p)_t$ is the heat released up to time t , and ΔH_0 is the total reaction heat associated with the resin cure process. The ΔH_0 value was calculated as the average value for total reaction heat obtained dynamically at the different heating rates.

In the second section, the isothermal curing of PF and LPF resol resins was carried out by DSC for different times at temperatures of 110, 120, 130, and 140°C, to establish the relationship between the glass-transition temperature and curing time. As the resin samples were not fully cured under these operating conditions, it was necessary to quench them at -80°C to keep them at their polymerization state. The samples were then scanned from -80 to 250°C at 10°C min⁻¹ to obtain the glass-transition temperature and residual heat for each sample. T_g was measured as the halfway point of ΔC_p , when the polymer passes from the glass to the rubber state. A typical thermogram of precured phenolic resol resin is shown in Figure 1. In the case of the isothermal curing processes, degree of conversion was determined as:

$$\alpha = 1 - \frac{(\Delta H)_{t,\text{res}}}{\Delta H_0} \quad (2)$$

where $(\Delta H)_{t,\text{res}}$ is the residual heat obtained after isothermal curing up to time t .

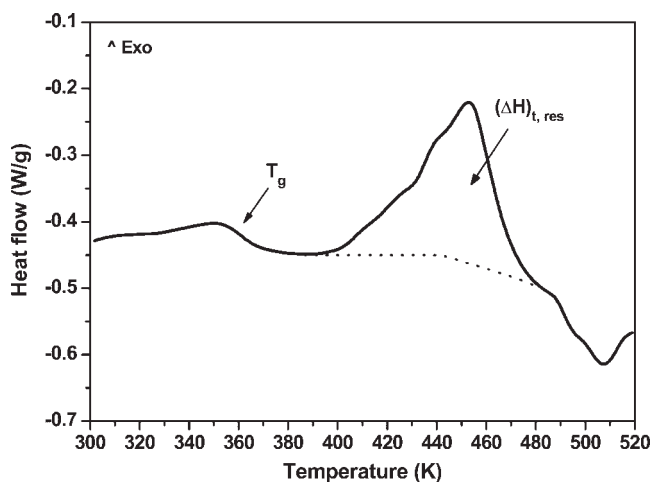


Figure 1 Typical thermogram by dynamic DSC for pre-cured phenolic resin ($T_{\text{cure, isothermal}} = 110^{\circ}\text{C}$, $t = 10$ min).

To characterize the change of resin from liquid to solid (gelation), the TMA technique (Mettler Toledo TMA 840^e analyzer) was used. The liquid resin was placed between two silica disks. The temperatures tested to reach the gel time were 110, 120, 130, and 140°C. A periodic force (cycle time = 12 s) of ± 0.03 N was automatically applied to the samples.^{25,26} Because of this force, the probe is moved up and down while the resin is still liquid. When the material reaches its gelation, the TMA measuring sensor is unable to respond to the force applied. At this moment, the sudden decrease in the amplitude of the oscillations reveals that the sample has attained gelation. Gelation was determined from the steepest initial slope of the dL/dt versus time curve, as shown in Figure 2. Then, the sample is cooled and a dynamic scan by DSC is performed at a heating rate of $10^{\circ}\text{C min}^{-1}$ to determine the glass-transition temperature at gel point ($_{\text{gel}}T_g$), residual heat ($\Delta H_{t, \text{res}}$), and gel conversion (α_{gel}) by eq. (2).

Kinetic method

The isoconversional method employed in this work is based on dynamic analysis by DSC. The reaction rate equation utilized to study the resin's curing kinetics can be expressed, in general, as follows:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (3)$$

where $d\alpha/dt = \beta(d\alpha/dT)$, and β is the heating rate (K/min), k is rate constant that depends on temperature, and $f(\alpha)$ is function of the curing degree of the polymer. Considering that dependence of the rate constant on temperature follows the Arrhenius expression, eq. (3) can be rewritten as:

$$\beta \frac{d\alpha}{dt} = Ae^{(-E/RT)}f(\alpha) \quad (4)$$

where T is the temperature, A is the pre-exponential factor, E is the activation energy, R is the gas constant, and α is the resin cure degree. In this way, the integral form of the rate equation [eq. (4)] can be expressed as:

$$g(\alpha) = \frac{A}{\beta} \int_0^{T\alpha} e^{(-E/RT)} dT = \frac{A}{\beta} P(E, T\alpha) \quad (5)$$

where $g(\alpha) = \int_0^{\alpha} d\alpha/f(\alpha)$ is the integrated form of the reaction model. To compute the dynamic conditions of Arrhenius parameters, there are several relationships to consider, each of which is based on an approximate form of the temperature integral [eq. (5)]. We can assume that $P(E/RT)$ can be expressed in the 20–60 E/RT range as follows^{26,27}:

$$\log P(E/RT) = -2.315 - 0.4680cE/RT \quad (6)$$

where c is initially 1.052; however, this value has been recalculated in an iterative procedure after the activation energy is estimated. To determine the kinetic parameters, eqs. (5) and (6) can be combined and rearranged as:

$$\log \beta = A' - 0.4567 \frac{E}{RT} \quad (7)$$

where $A' = \log(AE/g(\alpha) \cdot R) - 2.315$. The expression (7) is known as Ozawa's method, which can be applied to different degrees of conversion.^{28,29} Thus, for a given conversion degree of resin curing, according to eq. (7), the activation energy and the constant A' can be calculated from the slope and the origin ordinate, respectively, of the linear relationship $\log \beta$ versus $1/T$.

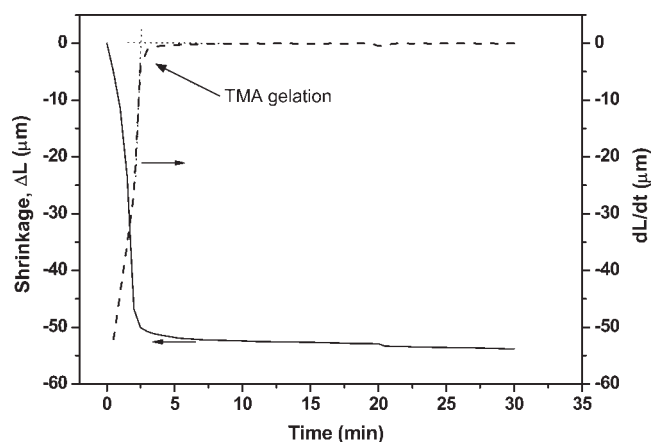


Figure 2 Typical shrinkage curves by TMA for phenolic resin.

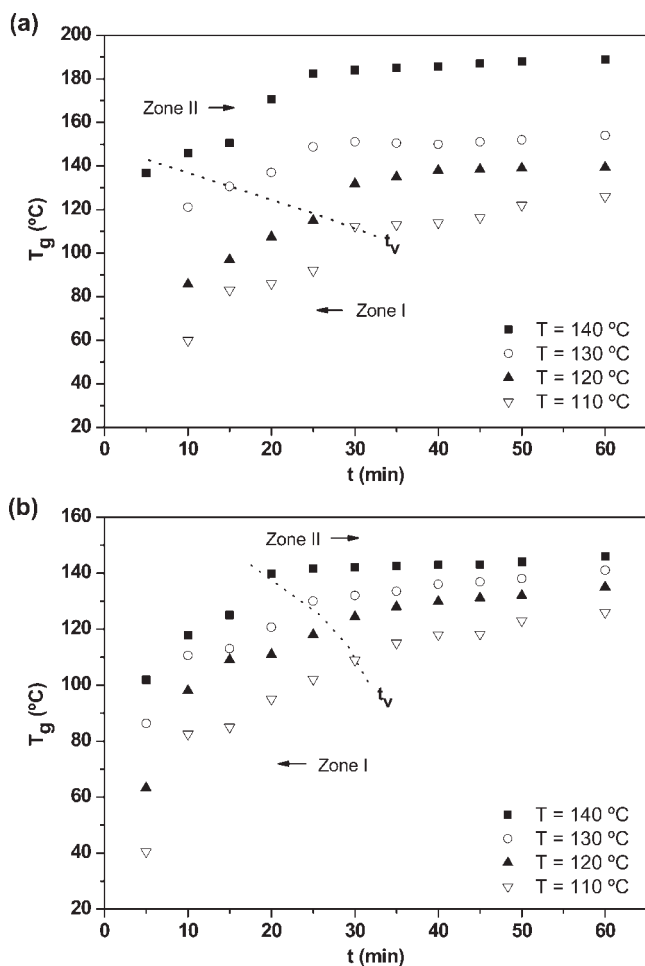


Figure 3 Iso- T_{cure} curves. (a) lignin-phenolic resin and (b) phenolic resin.

RESULTS AND DISCUSSION

Iso- T_c diagrams of lignin-phenolic and phenolic resin resins are shown in Figure 3, which displays the change of glass-transition temperature with the curing time as a function of curing temperature. Two stages can be observed during the curing process, which correspond to zones I and II (Fig. 3). First, when the curing temperature is found in zone I, the crosslinking of resin is controlled by the chemical reactivity of functional groups; therein, the resin initially exhibits a liquid state up to T_g equal to T_c , where the sample enters the sol/gel glass state. The reaction time required to reach $T_g = T_c$ is called the vitrification time, t_v (Fig. 3). The second stage, when the curing temperature is found in zone II, occurs when the resin resin starts to vitrify. In this case, the reaction rate decreases due to the resin curing kinetics of the overall process becoming controlled by diffusion of the components.³⁰ Therefore, the progress of the crosslinking reaction becomes very restricted.

TABLE I
Shift Factors a_T Employed to Elaborate the Master Curves of the LPF and PF Resins

T_c (°C)	Shift factor a_T	
	LPF resin	PF resin
110	-5.1	-9.5
120	1	1
130	15.5	3.6
140	26	8.7

$$T_{ref} = 120^\circ\text{C}.$$

A useful practice to elaborate the master curve of polymer curing is the representation of the T_g - t curves, which have been previously shifted along the logarithmic time scale by a factor " a_T " to superimpose them at a given reference temperature ($T_{ref} = 120^\circ\text{C}$). The shift factors a_T for obtaining the master curve are summarized in Table I. The values of a_T for the LPF and PF resins can be fitted to the Arrhenius expressions (8) and (9), respectively, as follows:

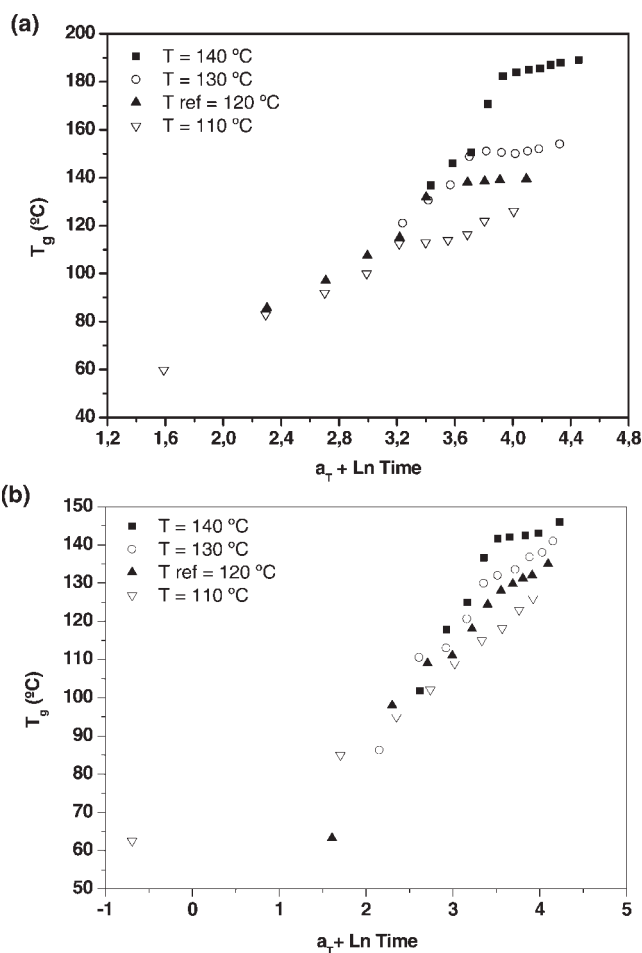


Figure 4 T_g vs. \ln time master curve at $T_{ref} = 120^\circ\text{C}$. (a) lignin-phenolic resin and (b) phenolic resin.

TABLE II
Kinetic Parameters of LPF and PF Resins Curing Determined by the Ozawa's Method at Different Conversion Degrees

α (%)	LPF resin				PF resin			
	A'	E (kJ/mol)	$*A$	R^2	A'	E (kJ/mol)	$*A$	R^2
2	707.54	2 258.2	–	0.997	9.46	58.42	–18.26	0.973
10	9.80	63.33	–18.96	0.989	9.54	61.42	–18.39	0.984
20	10.23	67.80	–19.88	0.995	9.71	64.25	–18.73	0.992
30	10.67	71.93	–20.83	0.994	9.88	66.61	–19.09	0.992
40	10.93	74.76	–21.38	0.992	10.32	70.80	–20.04	0.993
50	11.02	76.20	–21.58	0.995	10.48	72.90	–20.38	0.990
60	11.13	77.95	–21.81	0.994	10.36	72.90	–20.10	0.990
70	11.20	79.37	–21.96	0.994	10.60	75.84	–20.62	0.993
80	11.28	80.99	–22.12	0.987	11.18	81.71	–21.88	0.994
90	11.87	86.90	–23.41	0.990	12.07	90.30	–23.83	0.990
95	11.62	85.70	–22.84	0.993	11.68	88.05	–22.96	0.986
98	11.94	89.07	–23.54	0.991	11.18	84.79	–21.84	0.983
100	11.72	89.74	–23.04	0.959	11.23	88.61	–21.91	0.948

$$A' = [\log(k_0 E / g(\alpha) R) - 2.315]$$

$$*A = \ln[g(\alpha) / k_0]$$

$$\log a_T = 141.8 - \frac{1.6 \times 10^3}{T} \quad (8)$$

$$\log a_T = 71.8 - \frac{8.9 \times 10^3}{T} \quad (9)$$

Knowing the shift factor a_T any curing temperature, one can determine the iso- T_g curve. Thus, the resulting curve at $T_{ref} = 120^\circ\text{C}$ for lignin-phenolic and phenolic resol resins are displayed in Figure 4. An acceptable time-temperature superposition of both resins is obtained. However, the lignin-phenolic resin [Fig. 4(a)] master curve for curing times higher than t_v displays dispersion caused by vitrification phenomenon, which indicates the onset of diffusion. Therefore, the master curve is only valid for the kinetically-controlled segment.

The TTT cure diagrams of lignin-phenolic and phenolic resol resins studied include the iso- T_g curves and vitrification contours. Iso- T_g curves were calculated from the curing kinetics of the resins analyzed. In this work, Ozawa's method was applied to calculate the kinetic parameters of resins studied, as summarized in Table II. Experimental data fit [eq. (7)] presents, in most cases, correlation coefficients (R^2) that are between 0.98 and 1. Thus, the fit for each curing degree for both samples is exhibited in Figure 5. The values of the pre-exponential factor, A , and activation energy, E , previously obtained for different curing degrees can be fitted using an isoconversional expression such as:

$$\ln t = A + E/RT \quad (10)$$

which allows obtaining iso- T_g curves of resol resins (Fig. 6). In addition, the same expression was used to draw the gelation line of the LPF and PF resol

resins for a curing degree (α_{gel}) of 47% and 65%, respectively. Gelation was determined by TMA as the point at which the resin gels and there is an

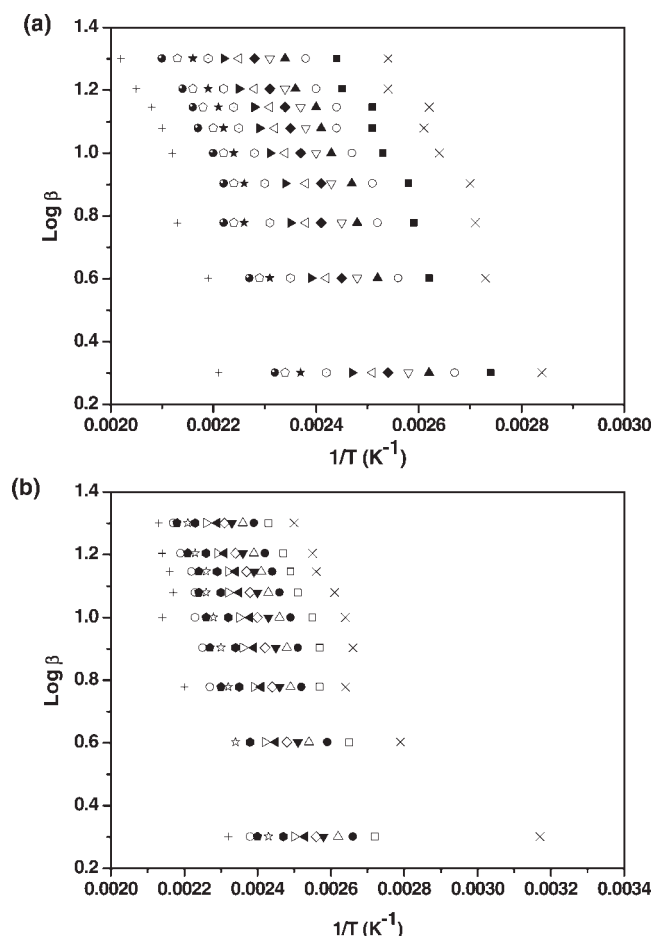


Figure 5 Log β vs. T^{-1} at different curing degrees applying Ozawa's method. (a) lignin-phenolic resin and (b) phenolic resin.

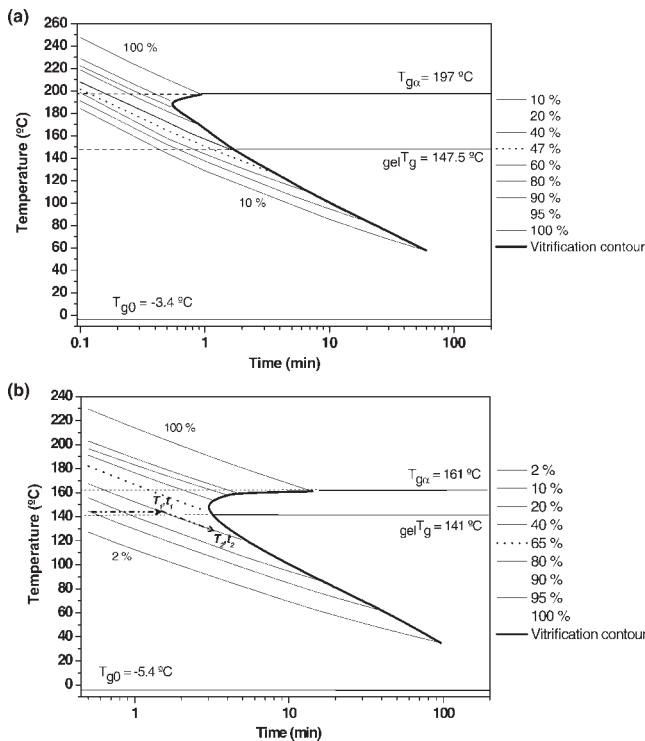


Figure 6 TTT cure diagram, for (a) lignin-phenolic resol resin and (b) phenolic resol resin.

abrupt change in shrinkage. Although the time taken by the resin to reach the gel point varies with the temperature, the α_{gel} value is independent of the curing temperature employed. This fact allows us to assume that the gelation, in both resins, obeys an isoconversional principle.^{15,25,31}

To construct the TTT cure diagrams of resins, it is also necessary to determine their glass-transition temperatures as the materials uncured (T_{g0}) and the ones fully cured ($T_{g\infty}$). T_{g0} values for lignin-phenolic and phenolic resol resins were -3.4°C and -5.4°C , respectively. From an industrial point of view, these temperatures indicate that uncured resins can be stored without reacting below T_{g0} , which is useful because it allows the useful life of the material to be prolonged. $_{gel}T_g$ is defined as the temperature at which the resin vitrifies and gels simultaneously. This value is obtained extrapolating the isoconversional line of α_{gel} . The lignin-phenolic and phenolic resins present $_{gel}T_g$ values of 147.5 and 141 °C, respectively. Vitrification points are calculated as the times needed for the polymer to reach the curing degree α_v at which $T_g = T_c$. The vitrification time values are obtained from the isoconversional expression [eq. (10)], as shown in Figure 6. The glass-transition temperature values, as a function of vitrification conversion and time, are shown in Figure 6(a, b) for lignin-phenolic and phenolic resins, respectively.

The vitrification lines of resols studied show similar tendencies; moreover, the vitrification contour of both resins displays a sigmoidal profile. However, polymers with T_g values very close to $T_{g\infty}$ display a partial vitrification line due to the effect of the decrease in reactive groups that will prevail over that effect of the increase in temperature.²⁵ Finally, the line corresponding to the vitrification contour is the border up to which no degradation takes place during the curing process of resins. If the cure reaction is above $T_{g\infty}$, then a great amount of resin is thermodegraded such that its properties are lost.

Note that TTT cure diagrams of lignin-phenolic and phenolic resol resins present differences. For instance, lignin-phenolic resin displays a higher T_{g0} value relative to commercial resin, which indicates that the polymer in the presence of lignosulfonate is more stable. In addition, a low $_{gel}T_g$ value of PF resin with respect to LPF resin indicates that the onset of diffusion occurs before during the curing process of commercial resin. However, commercial resol resin exhibits a $T_{g\infty}$ value lower than that of lignin-phenolic resin, which allows a fast cure of the material, whereas the lignin molecule makes it difficult to completely cure the polymer. In short, the data show that the molecular structure of lignosulfonate is more stable than that of a PF polymer.

The methodology employed with other materials can be applied for constructing the TTT cure diagrams of lignin-phenolic and phenolic resol resins,^{16,25,30-32} which are shown in Figure 6. In short, the TTT cure diagram of a polymeric material displays the characteristic thermal properties of the glass-transition temperatures: T_{g0} , $_{gel}T_g$, and $T_{g\infty}$. In the literature, the elaboration of TTT diagrams of different systems can be found, which present their respective characteristic values of T_{g0} , $_{gel}T_g$, and $T_{g\infty}$, as shown in Table III.^{25,32-36} Although each material presents a different TTT cure diagram, because there are remarkable differences between the materials, the

TABLE III
Glass Transition Temperatures Characteristic of TTT Cure Diagrams of Different Systems

Material polymeric	T_{g0} (°C)	$_{gel}T_g$ (°C)	$T_{g\infty}$ (°C)
Powder coating ²⁵	60	68.5	75
Anhydride-cured epoxy ³²	-40	4.5	150
Bisphenol A epoxy ³³	-	-	109
Bisphenol A epoxy ³⁴	-	-	212
DGEBA + epoxy diluent ³⁵	-46.8	45.7	163.7
Epoxy system ³⁶	-21.5	56.5	109
Phenol-formaldehyde ^a	-5.4	141	161
Lignin-phenolic ^b	-3.4	147.5	197

-: unknown value.

^a Commercial sample studied in the present work.

^b Sample studied in the present work.

information supplied allows optimization of the curing conditions for thermosetting polymers for their final applications. This issue would allow knowing the minimum time and temperature that the material needs to cure in the final application. For instance, to produce a structural material, you need to avoid dimensional changes and ensure that the glass-transition temperature of the resin is higher than cure temperature during its postcuring cycle. Thus, the material could be cured at curing temperature T_1 and time t_1 , while there are not structural variations (e.g., shrinkage). Next, it is possible to follow the iso- T_g curve with a modification of curing temperature T_2 and time t_2 based on the TTT cure diagram [Fig. 6(b)]. This cure diagram allows the optimization of multiple-steps cure or postcure cycles. On the other hand, TTT cure diagram is a useful tool to predict the material behavior during its postcuring.

CONCLUSIONS

During isothermal curing of resol resins, two stages are observed. In the first step, up to $T_g = T_c$, the overall curing process of the lignin-phenolic and phenolic resol resins display a kinetic control based on the chemical reaction step. At this point, the resol resins vitrify; moreover, both polymers continue their curing processes, but the curing is kinetically controlled by the diffusion of reactants. The time-temperature superposition principle was utilized to generate a master curve for the chemical curing of lignin-phenolic and phenolic resins.

Iso- T_g curves of both resol resins were determined from isoconversional fit of kinetic data to $\ln t = A + E/RT$. Previously, Ozawa's isoconversional method was applied to determine the kinetic parameters of the curing processes of both resol resins assayed. The vitrification contour of resins curing, which occurs when the kinetic control of overall process changes from chemical reaction to reactant diffusion, was calculated assuming a curing temperature equal to the glass-transition temperature. The methodology that was developed, based on DSC and TMA techniques, allowed the determination of TTT cure diagrams of LPF and PF resol resins.

NOMENCLATURE

a_T	shift factor
${}_{\text{gel}}T_g$	glass-transition temperature at gel point
t_{gel}	gel time
t_v	vitrification time
T_c	curing temperature

T_g	glass-transition temperature
T_{g0}	glass-transition temperature corresponding to uncured material
$T_{g\infty}$	glass-transition temperature corresponding to the fully cured material
T_{ref}	reference temperature

Greek

α	curing degree
α_{gel}	gel conversion
ΔH_0	total reaction heat
$(\Delta H_p)_t$	heat released up to time t
$(\Delta H)_{t, \text{res}}$	residual heat

References

- Sellers, T, Jr. *Plywood and Adhesive Technology*; Marcel Dekker: New York, 1985.
- Sellers, T, Jr.; Kim, M. G.; Miller, G. D.; Haupt, R. A.; Strickland, R. C. *Forest Prod J* 1994, 44, 63.
- Vázquez, G.; González-Álvarez, J.; López-Suevos, F.; Antorrena, G. *Bioresour Technol* 2003, 87, 349.
- Wooten, A. L.; Sellers, T, Jr.; Tahir, P. Md. *Forest Prod J* 1988, 38, 45.
- Turunen, M.; Alvila, L.; Pakkanen, T. T.; Rainio, J. *J Appl Polym Sci* 2003, 88, 582.
- Lee, S.-H. *J Appl Polym Sci* 2003, 87, 1365.
- Khan, M. A.; Ashraf, S. M.; Malhotra, V. P. *J Appl Polym Sci* 2004, 92, 3514.
- Piccolo, R. S. J.; Santos, F.; Frollini, E. *J Macromol Sci A* 1997, 34, 153.
- Alonso, M. V.; Oliet, M.; Rodríguez, F.; Astarloa, G.; Echeverría, J. *J Appl Polym Sci* 2004, 94, 643.
- Ysbrandy, R. E.; Sanderson, R. D.; Gerischer, G. F. R. *Holzfor-schung* 1992, 46, 249.
- Alonso, M. V.; Rodríguez, J. J.; Oliet, M.; Rodríguez, F.; García, J.; Gilarranz, M. A. *J Appl Polym Sci* 2001, 82, 2661.
- Alonso, M. V.; Oliet, M.; Rodríguez, F.; García, J.; Gilarranz, M. A.; Rodríguez, J. J. *Bioresour Technol* 2005, 90, 1013.
- Prime, R. B. In: *Thermal Characterization of Polymeric Materials*; Turi, E. A., Ed.; Academic Press: New York, 1997; Chapter 6.
- Gillham, J. K. *Soc Plast Eng Annu Tech Conf* 1980, 38, 268.
- Cadenato, A.; Salla, J. M.; Ramis, X.; Morancho, J. M.; Marroyo, L. M.; Martín, J. L. *J Therm Anal* 1997, 49, 269.
- Ramis, X.; Salla, J. M. *J Polym Sci, Part B: Polym phys* 1997, 35, 371.
- Vargha, V.; Körmendy, Z. *J Therm Anal Calorimetry* 2005, 79, 195.
- Yang, Y. S.; Lee, L. J. *Polym Proc Eng* 1987, 5, 327.
- Riesen, R.; Sommerauer, H. *Am Lab* 1983, 15(1), 30, 32, 34.
- Hofmann, H.; Glasser, W. G. *Thermochim Acta* 1990, 166, 169.
- Mijovic, J.; Kenny, J. M.; Nicolais, L. *Polymer* 1993, 34, 207.
- Enns, J. B.; Gillham, J. K. *J Appl Polym Sci* 1983, 28, 2567.
- Hsu, C. P.; Lee, L. J. *Polymer* 1993, 34, 4496.
- Verchére, D.; Sautereau, H.; Pascault, J. P. *Macromolecules* 1990, 23, 725.
- Ramis, X.; Cadenato, A.; Morancho, J. M.; Salla, J. M. *Polymer* 2003, 44, 2067.
- Alonso, M. V.; Oliet, M.; García, J.; Rodríguez, F.; Echeverría, J. *Chem Eng J* 2006, 122, 159.

27. Doyle, C. D. *Anal Chem* 1961, 33, 77.
28. Ozawa, T. *Bull Chem Soc Jpn* 1965, 38, 1881.
29. Flynn, J. H.; Wall, L. A. *J Res Natl Bur Stand Sect A Phys Chem* 1966, 70, 487.
30. Simon, S. L.; Gillham, J. K. *J Appl Polym Sci* 1992, 46, 1245.
31. Jiménez, R.; Fernández-Francos, X.; Salla, J. M.; Serra, A.; Mantecón, A.; Ramis, X. *Polymer* 2005, 46, 10637.
32. Teil, H.; Page, S. A.; Michaud, V.; Manson, J. A. E. *J Appl Polym Sci* 2004, 93, 1774.
33. Montserrat, S. *J Therm Anal* 1993, 40, 553.
34. Stutz, H. *J Appl Polym Sci* 2003, 89, 3894.
35. Núñez, L.; Villanueva, M.; Núñez, M. R.; Rial, B.; Fraga, L. *J Appl Polym Sci* 2004, 92, 1190.
36. Yu, H.; Mhaisalkar, S. G.; Wong, E. H.; Khoo, G. Y. *Thin Solid Films* 2006, 504, 331.