Analysis of the Crosslinking Process of Epoxy–Phenolic Mixtures by Thermal Scanning Rheometry

J. M. Laza, J. L. Vilas, F. Mijangos, M. Rodríguez, L. M. León

Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV/EHU), Apartado 644, 48080 Bilbao, Spain

ABSTRACT: The curing reaction of different mixtures of an epoxy resin (diglycidyl ether of bisphenol A type) and a phenolic resin (resole type) cured with different amine concentrations (triethylene tetramine) was studied with thermal scanning rheometry under isothermal conditions from 30 to 95°C. The gel time, defined by several criteria, was used to determine the apparent activation energy of the process. Moreover, with an empirical model used to predict the change in the complex viscosity versus time until the gel time was reached, and under the assumption of first-order kinetics, the apparent rate constant and the apparent activation energy for the curing process were calculated. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 818–824, 2005

Key words: crosslinking; curing of polymers; resins; thermosets

INTRODUCTION

In recent years, there has been growing interest in the use of composite materials for the manufacture of structural components in industry. This is the result of the number of properties that make composites attractive alternatives to more traditional structural materials.[1] These properties include high specific strength and modulus, corrosion resistance, good fatigue and fracture properties, relative ease of fabrication into complex shapes, and ease of repair offered by composite materials.

Thermosetting resins exhibit crosslinked chains by chemical bonds forming a three-dimensional network; different kinds of resins belong to this group, such as the epoxy and phenolic resins studied in this work. Phenolic and epoxy resins are the most common thermosets used by the plastic-processing industry. In the cured state, they are infusible, insoluble, covalently crosslinked, thermally stable network polymer structures. The formation of these network structures is responsible for the desirable physical properties that are typical of thermosetting resins over a broad range of temperatures.

Phenolic resins have been widely applied as composite matrices to take advantage of their flame resistance, which is directly related to the aromatic-ring content in the molecular structure.[2–5] The thermal degradation of phenolic resins leads to the production of a structural char, which results in a low flame-spreading rate in comparison with other polymers.[6,7] Phenolics also exhibit excellent dimensional stability and chemical resistance as a result of the high crosslinking density. This characteristic, however, also results in a brittle material. Moreover, the evolution of water and formaldehyde during curing can promote microcracking and molded-in stresses in the final products. Therefore, the processing of phenolic materials requires temperature control to reduce the number of defects in the final components. The mechanical properties of phenolic resins may be improved by the addition of a rubbery phase or by blending with other polymers.[8–14]

On the other hand, epoxy resins exhibit good thermal properties, chemical resistance, and electric insulation through a crosslinking reaction with a curing agent that makes the two-dimensional epoxy structure change into the three-dimensional network structure.[15–17] These properties of cured epoxies are dependent on the structures of the curing agent and epoxy resin.

In previous work,[18,19] we have studied the curing processes of different epoxy and phenolic systems under isothermal conditions. Now, our purpose is to study the rheological behavior and kinetics of the curing process of epoxy–phenolic mixtures to prepare materials as strong as epoxy networks and retaining the flame retardancy properties of phenolics.

EXPERIMENTAL

Materials

The epoxy resin, diglycidyl ether of bisphenol A, with the commercial name Rütapox LB64, was supplied by

Bakelite (Guipuzcoa, Spain). This is a liquid epoxy resin suitable for the production of high-quality plastics or fiber-reinforced composites. Besides, an excellent wetting of different fibers can be obtained because of the very low surface tension exhibited by the resin.

The phenolic resin was a commercial liquid resole (pH 8.7) supplied as TH-215 by Fers Resins (Barcelona, Spain). It was kept sealed at 4°C under nitrogen to avoid any possible water condensation. Moreover, the viscosity of resoles is time-dependent, and an order of magnitude increase in the viscosity is possible even at room temperature over a period of a few months. Resoles are, therefore, stored at subambient temperatures at which the reaction is relatively slow.

The curing agent was triethylene tetramine (TETA) supplied by Merck (Darmstadt, Germany).

All the materials employed in this study were used as supplied by the manufacturer. The composition of the resins was evaluated by NMR and Fourier transform infrared spectroscopy.

Sample preparation

Both resins (epoxy Rütapox LB64 and phenolic TH-21S) were blended and cured simultaneously under the following conditions: 90/10, 80/20, 70/30, and 60/40 (wt %/wt %) epoxy/phenolic and 80, 100, 120, and 140 wt % TETA.

The stoichiometric relation between the resins and the amine (which was considered 100% TETA) was calculated as follows:

$$\text{Amine H equivalent weight} = \frac{M_w \text{ of amine}}{\text{Active H's}}$$

Amine (phr)

$$= \frac{\text{Amine H equivalent weight}}{\text{Epoxide equivalent weight of resin}} \times 100$$

where phr is parts by weight per 100 parts of resin and M_w is the weight-average molecular weight.

The reactions were carried out from 30 to 95°C according to the reactivity of the system.

The mixture was stirred for a few minutes for homogenization, and then it was ready to be measured.

Rheological measurements

All the rheological measurements were carried out with a thermal scanning rheometer supplied by Rheometric Scientific (Surrey, UK). This technique, already described,[18] was designed and developed for monitoring the viscoelastic state of a wide range of materials and particularly the changes in the rheological properties with temperature or time. The complex viscosity (η^*) of a liquid is measured by the vertical oscillation
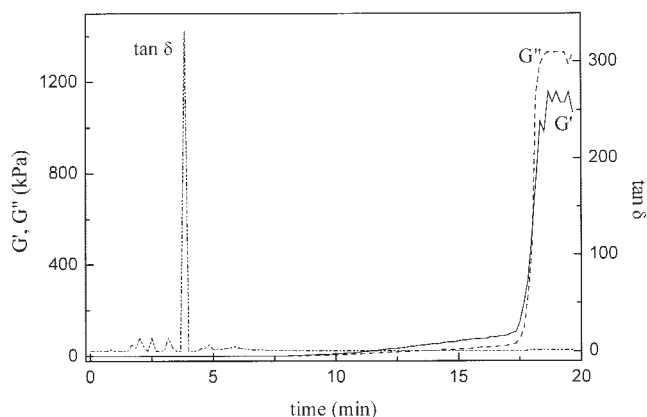
Figure 1 G', G'', and tan δ versus the cure time for an epoxy–phenolic system.

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 the viscosity, and its components, the storage modulus (G'), the loss modulus (G''), and the loss tangent (tan δ), during the curing process.

Figure 1 shows an example of the dynamic mechanical behavior of the studied systems.

RESULTS AND DISCUSSION

The isothermal curing of a thermosetting resin is usually characterized by gelation and vitrification. Gelation corresponds to the incipient formation of an infinite network of crosslinked polymer molecules, which occurs at a fixed extent of conversion as long as the reaction mechanism is not a function of temperature; it is responsible for the transformation from a liquid state to rubbery state. Vitrification involves a transformation from a liquid or rubbery state to a glassy state as a result of an increase in the molecular weight.

The cure of a thermosetting reactive prepolymer usually involves the transformation of low-molecular-weight monomers or oligomers from the liquid state to the solid state as a result of the formation of a polymer network by a chemical reaction of the reactive groups of the system.[20] Two stages, which are divided by the gel point, are distinguished in the process. It is accepted that growth and branching of the polymer chains occur in the liquid state, in which the reactive system is soluble and fusible. An infinite network of polymer chains appears and develops only after the gel time (t_g). The reactive system then loses its solubility and fusibility, and this leads to the final reactions, which take place in the solid state.

The change in the dynamic mechanical properties of a curing system is directly related to the extent of the reaction. From the study of these dynamic mechanical

TABLE I
t_g (min) Values for the 80% Epoxy/20% Phenolic/100% TETA Systems

T (°C)	t_{g1}	t_{g2}	t_{g3}	t_{g4}	t_{g5}	t_{g6}
40	33.0	350	140	81.2	97.6	142
45	21.4	—	100	64.4	80.6	130
50	19.0	83.7	50.0	42.5	50.4	75.8
55	11.2	32.3	26.0	23.6	27.4	41.1
60	9.01	25.5	20.2	20.9	26.1	47.4
65	8.67	19.9	18.0	16.6	19.5	31.5
70	4.83	7.81	8.60	8.53	9.84	16.4
75	4.17	4.85	5.51	5.50	6.69	—
80	3.08	3.10	3.75	4.86	5.37	6.09

TABLE II
t_g (min) Values for the 90% Epoxy/10% Phenolic Systems Cured at 50°C

% TETA	t_{g1}	t_{g2}	t_{g3}	t_{g4}	t_{g5}	t_{g6}
80	26.7	—	42.2	34.6	38.7	46.9
100	20.3	36.0	29.0	23.9	25.9	29.1
120	13.1	23.0	17.5	15.3	16.2	17.7
140	12.1	20.0	15.5	13.6	14.3	15.2

properties, a kinetic parameter, such as t_g, can de determined, and from it, kinetic studies of the curing system can be made.

t_g is one of the most important kinetic characteristics of curing because it describes the attainment of a certain critical conversion responsible for the transition from the first stage to the second stage of the process. The gel point is characterized by the appearance in the reactive system of a macromolecule with an infinitely large molecular weight ($M_w \rightarrow \infty$). Therefore, t_g determines at which point the resin becomes physically unprocessable.

For this reason, the determination of the gel point is very important. There are a lot of experimental methods to determine it, such as dielectric measurements,[21] torsional braid analysis,[22,23] and chemiluminescence.[24] However, nowadays rheological techniques to determine t_g by means of extrapolation to infinite viscosity are the most suitable methods, and so thermal scanning rheometry (TSR) was chosen for this study.

t_g measurements and the determination of the apparent activation energy (E_a)

Figure 1 shows a typical result obtained in a TSR experiment; three different regions are apparent. In the first region, the G' modulus is low because of the low crosslinking. In the second region, in which t_g is reached, this modulus increases exponentially versus time. In the last region, the modulus increases more rapidly, and TSR is not able to measure it because of the high-medium-viscosity, highly disperse data being obtained, which indicate that the resin has been cured.

Several methods have been proposed to determine the gel point during isothermal cure,[25–33] and in this study, it has been determined according to the following criteria:

1. The maximum peak in tan δ (t_{g1}): This is based on the point at which there is a maximum dif-

ference between the elastic and viscous behaviors of the system.[32]

2. The crossover between the G' and G'' curves (t_{g2}): In this criterion, a correlation between the gel point and the intersection point of the curves of G' and G'' is proposed.[27] In the liquid state, the viscous properties are predominant ($G' < G''$ and tan δ > 1), whereas in the solid state, the elastic properties are predominant ($G' > G''$ and tan δ < 1). Therefore, at the gel point $G' = G''$, the loss energy is equal to the energy stored, and tan δ is 1.

3. Tangent line to the G' curve (t_{g3}): The gel point is taken at the point corresponding to the cross between the baseline ($G' = 0$) and the tangent drawn at the G' curve when G' reaches a value close to 100 kPa.[31]

4. Viscosity (t_{g4}, t_{g5}, and t_{g6}): At this point, the real dynamic viscosity (η') reaches several determined values (1000, 2000, and 5000 Pa s).[19,33]

Table I shows the t_g values obtained according to these criteria for the curing reactions of the 80% epoxy/20% phenolic/100% TETA systems, whereas Table II shows the values obtained for the 90% epoxy/10% phenolic systems cured at 50°C. Table III shows the t_g values for the 70% epoxy/30% phenolic systems according to the criterion of $\eta' = 1000$ Pa s; from these data, some facts could be observed:

- In some cases, it was not possible to determine a t_g value according to the criteria of $\eta' = 5000$ Pa s

TABLE III
t_g (min) Values for the 70% Epoxy/30% Phenolic System According to the $\eta' = 1000$ Pa s Criterion (t_{g4})

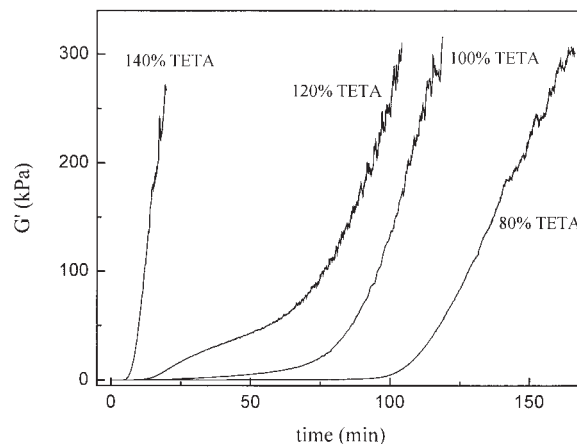| T (°C)	80% TETA	100% TETA	120% TETA	140% TETA
60	404	238	50.9	26.4
65	235	148	41.5	18.5
70	146	83.4	36.1	—
75	115	77.7	30.8	8.52
80	75.8	65.1	—	8.15
85	65.6	42.8	11.9	6.50
90	61.3	34.1	10.0	5.78
95	45.5	30.5	2.42	4.39
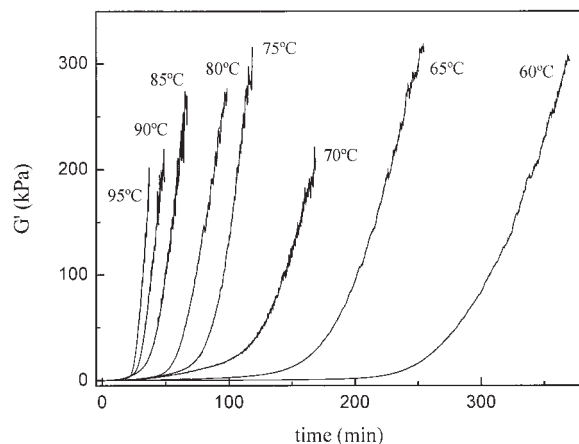
Figure 2 G' versus the cure time at different isothermal curing temperatures for the 70% epoxy/30% phenolic/100% TETA system.

Figure 3 G' versus the cure time with different percentages of TETA for the 70% epoxy/30% phenolic system cured at 75°C.

because the viscosity did not reach this value. Besides, in the 90% epoxy/10% phenolic/80% TETA system, the crossover between G' and G'' was not clear enough to allow the determination of the gel point.

- For all the systems studied, t_g depends on the criteria chosen. This fact can be explained if we take into account that the gelification process is not an instantaneous process but occurs during a period of time.
- t_g decreases when the cure temperature increases at a fixed percentage of TETA for all the epoxy–phenolic systems studied (see Fig. 2). This means that when the temperature increases, the molecular mobility increases, and, therefore, the curing reaction occurs more rapidly.
- t_g also decreases as the percentage of TETA increases at a fixed cure temperature for all systems (Fig. 3) because of the greater number of activated molecules that begin the reaction. The crosslinking of the resin occurs in the first stages; therefore, the curing reaction is faster, the system has a higher viscosity, and t_g decreases.
- t_g increases as the percentage of the phenolic resin in the system increases at a fixed cure temperature and percentage of TETA (Fig. 4). This behavior can be explained if we consider that the amine only acts as a curing agent for the epoxy resin and the phenolic resin can also cure thermally, it being determined[18,19] that the t_g values for phenolic resins are larger than those for epoxy resin.

From the t_g values, E_a can be obtained for the gelation process.

If the chemical conversion (α) at t_g is considered constant for a given system,[20] the integration of the kinetic equation gives

$$\int_0^{\alpha_g} \frac{d\alpha}{(1-\alpha)^n} = \text{cte} = k' \int_{t_0}^{t_g} dt \tag{1}$$
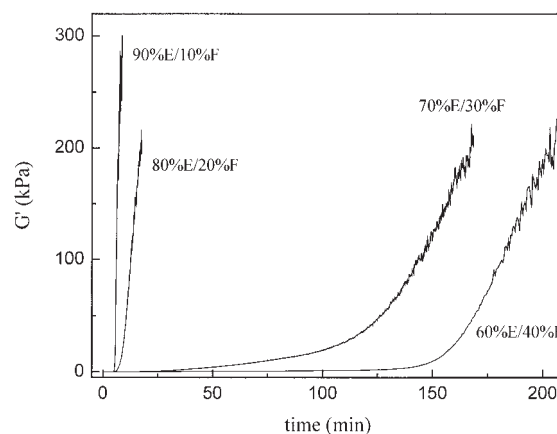
$$t_g \propto \frac{1}{k'} \tag{2}$$

where cte is the constant, k' is the apparent kinetic constant and n is the kinetic order.

Then, if an Arrhenius relationship is assumed for k'

$$k' = k_0 \exp\left(\frac{-E_a}{RT}\right) \tag{3}$$

where k_0 is the pre-exponential factor, T is the absolute temperature and R is the universal gas constant.

$$\ln t_g = C + \frac{E_a}{R} \times \frac{1}{T} \tag{4}$$

Figure 4 G' versus the cure time for all systems cured at 70°C with 100% TETA (E = epoxy, F = phenolic).

TABLE IV
E_a (kJ/mol) Values for All the Epoxy–Phenolic Systems

% TETA	E_{a1}	E_{a2}	E_{a3}	E_{a4}	E_{a5}	E_{a6}
60% epoxy/40% phenolic						
80	49.2	74.3	75.7	72.6	74.6	56.2
100	50.9	75.8	74.6	68.6	70.4	81.7
120	41.5	78.9	61.1	54.6	75.7	50.4
140	46.7	87.4	76.5	70.9	67.9	65.0
70% epoxy/30% phenolic						
80	49.8	68.5	66.4	60.6	62.3	60.2
100	58.0	73.9	71.1	58.2	61.4	62.3
120	47.2	78.1	105	64.	79.7	84.6
140	45.0	78.2	57.3	50.4	54.5	69.9
80% epoxy/20% phenolic						
80	81.6	74.4	80.8	65.1	74.2	75.9
100	53.3	90.1	82.9	68.0	69.4	70.8
120	58.2	101	81.2	73.4	75.0	77.8
140	56.3	85.1	77.5	73.3	74.7	76.3
90% epoxy/10% phenolic						
80	68.1	85.9	72.9	67.8	64.1	64.7
100	59.2	74.7	66.6	60.1	60.4	59.9
120	54.5	74.4	67.5	63.3	64.3	64.9
140	62.0	66.7	66.0	62.1	63.2	64.3

where C is a constant related to α at t_g.

A linear relationship was observed between $\ln t_g$ and the inverse of the absolute temperature for the isothermal curing reactions of all epoxy–phenolic systems; from the slope of this relationship, E_a of the gelation process can be obtained.

Table IV shows the E_a values for the gelification process of all the epoxy–phenolic systems according to the different t_g criteria. An increase in E_a was not observed as the percentage of TETA increased, as could be observed in other systems previously[18] studied. In these systems, moreover, the E_a values obtained according to the different t_g criteria were less concordant than those obtained for each resin; this could be due to the fact that E_a obtained for the epoxy–phenolic systems does not correspond to a unique process, but in these systems, there are several gelation processes taking place simultaneously.

Kinetic analysis from viscosity data

There are different treatments for the quantitative viscosity data obtained for thermosetting systems cured under isothermal conditions.[34–36] Most of them are mainly based on the Williams–Landel–Ferry (WLF) equation:[37]

$$\log a_T = -C_1 \times \frac{T - T_s}{C_2 + (T - T_s)} \quad (5)$$

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 of 17.44 and 51.6, respectively, only if T_s is the

glass-transition temperature (T_g) of the material. This equation is exclusively used to observe the dynamic mechanical behavior in the T_g to $T_g + 50°C$ zone.

However, the reaction rate is a function of $T - T_g$, and the increase in T_g during isothermal curing is a result of the increase in the crosslinking, which is controlled by the chain mobility. Therefore, the WLF equation is not suitable for this process.

These treatments usually are very complicated; therefore, viscosity data can also be treated through fitting to empirical equations in which the temperature and conversion dependence of the viscosity is separated into two independent terms:[38–40]

$$\eta(T,\alpha) = \eta(T) \times \eta(\alpha) \quad (6)$$

If it is assumed in eq. (1) that the reaction in the liquid state follows first-order ($n = 1$) kinetics until t_g

$$\int \frac{d\alpha}{1 - \alpha} = k' \int dt \quad (7)$$

$$\ln(1 - \alpha) = k't \quad (8)$$

For a fixed temperature, $\eta(T)$ can be considered a constant (η_0):

$$\ln \eta = \ln \eta_0 + k_\eta t \quad (9)$$

where η is the viscosity, which is a function of the temperature and conversion; η_0 is the viscosity at $t = 0$; and k_η is the apparent kinetic constant.

From TSR measurements, the complex viscosity dependence on time [$\eta^*(t)$] could be obtained. Plotting $\ln \eta^*$ versus time according to eq. (9), we can observe a linear plot only in the gelation stage, which corresponds to the second region in Figure 1. This fact was observed in all TSR experiments, and the obtained k_η values are shown in Table V for the 80% epoxy/20% phenolic/100% TETA system.

Table V shows that k_η increases as the curing temperature increases for a fixed percentage of TETA. A

TABLE V
k_η for the 80% Epoxy/20% Phenolic/100% TETA System

T (°C)	$k_\eta \times 10^3$ (min^{-1})
40	76.10
45	110.9
50	172.0
55	329.9
60	433.1
65	613.6
70	1541
75	3148
80	4108

linear relationship can be obtained by the plotting of k_η versus the percentage of TETA, and from the slope, the global kinetic constant (k) can be obtained, independently of the amine concentration, for all curing temperatures studied (Table VI).

The temperature dependence of k is given by an Arrhenius relationship:

$$\ln k = \ln k_\infty - \frac{E_a}{RT} \qquad (10)$$

Figure 5 shows the Arrhenius plot for the 90% epoxy/10% phenolic system, and in Table VI, the global activation energy values of the gelation process for all the systems are presented. These E_a values are of the same order of magnitude or are slightly lower than the
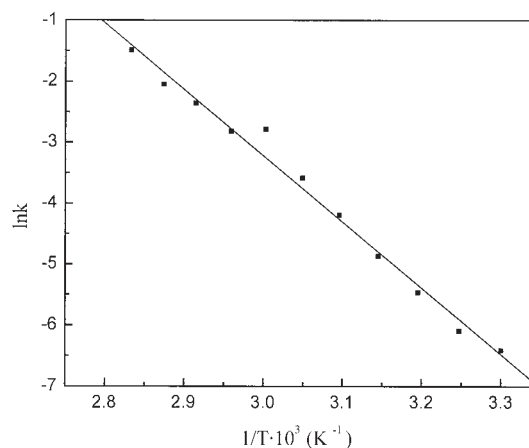

Figure 5   Arrhenius plot for the 90% epoxy/10% phenolic system.

ones previously calculated for the epoxy resin cured with TETA (101.5 kJ/mol),[18] whereas they are clearly lower than the E_a value calculated for phenolic resin cured thermally in the absence of an initiator (124.0 kJ/mol).[19]

This fact was already observed for the E_a values calculated from t_g measurements. This indicates that the epoxy system needs extra energy to allow the molecular mobility and the curing reaction in comparison with epoxy–phenolic systems, but phenolic resin needs even more extra energy to start the curing reaction thermally.

On the other hand, the E_a values calculated in this manner are greater than those calculated with the t_g method. This fact was already observed in our laboratory for different cure systems such as epoxy,[18] phenolic,[19] and even vinyl ester resins.[33] The difference could be due to the influence that the stages after the gel point exert on the reticulation process when diffusion phenomena begin to be important.

CONCLUSIONS

The t_g value depends on the criterion used; this means that gelation is not an instantaneous process but occurs over a period of time. t_g is a good parameter for studying the crosslinking process of this kind of thermosetting system.

t_g measurements have been employed to calculate the apparent activation energies of all the epoxy–phenolic systems. For these systems, the different criteria of t_g determination give different E_a values; this did not occur for epoxy and phenolic systems, and in our opinion, it could be due to the complexity of the system under study, in which several gelation processes can coexist simultaneously.

The apparent activation energies have also been determined from viscosity data. The obtained values

TABLE VI
k and Global E_q Values for the Gelation Process

System	T (°C)	$k \times 10^3$ (concentration^{-1} min^{-1})	E_a (kJ/mol)
60% epoxy/40% phenolic	65	1.620	96.0
	70	1.991	
	75	3.510	
	80	5.771	
	85	9.820	
	90	15.13	
	95	22.51	
70% epoxy/30% phenolic	60	1.570	74.2
	65	1.961	
	70	4.320	
	75	5.871	
	80	6.892	
	85	9.470	
	90	15.88	
	95	19.44	
80% epoxy/20% phenolic	40	2.161	104
	45	2.010	
	50	6.281	
	55	7.120	
	60	21.68	
	65	28.51	
	70	53.69	
	75	135.4	
	80	181.5	
90% epoxy/10% phenolic	30	1.640	90.3
	35	2.251	
	40	4.232	
	45	7.660	
	50	15.12	
	55	27.67	
	60	61.59	
	65	59.79	
	70	94.31	
	75	128.6	
	80	225.7	

are different from those calculated with the t_g method, and this could be due to the fact that in the viscosity method, the full process, not only a point of the gelation process, is considered; therefore, in our opinion this method could be more adequate.

References

1. Hiltz, J. A.; Kuzak, S. G.; Waitkus, P. A. J Appl Polym Sci 2001, 79, 385.
2. Martin, R. W. The Chemistry of Phenolic Resins; Wiley: New York, 1956.
3. Megson, N. J. L. Phenolic Resin Chemistry; Buttherworth: London, 1958.
4. Ellis, C. The Chemistry of Synthetic Resins; Reinhold: New York, 1969.
5. Knop, A.; Pilato, L. A. Phenolic Resins; Springer-Verlag: Berlin, 1985.
6. Chiu, H. T.; Chiu, S. H.; Jeng, R. E.; Chung, J. S. Polym Degrad Stab 2000, 70, 505.
7. Brown, J. S.; Fawell, P. D.; Mathys, Z. Fire Mater 1994, 18, 167.
8. Puglia, D.; Manfredi, L. B.; Vazquez, A.; Kenny, J. M. Polym Degrad Stab 2001, 73, 521.
9. Manfredi, L. B.; De la Osa, B.; Galego, N.; Vazquez, A. Polymer 1999, 40, 3864.
10. Vazquez, A.; Rojas, A.; Borrajo, J.; Williams, R. J. Polymer 1978, 28, 1156.
11. Wu, H. D.; Ma, C. C. M.; Chu, P. P. Polymer 1997, 38, 5415.
12. Kuzak, S. G.; Hiltz, J. A.; Waitkus, P. A. J Appl Polym Sci 1998, 67, 349.
13. Smith, M. E.; Ishida, H. Macromolecules 1994, 27, 2701.
14. Manfredi, L. B.; Claro, J. A.; Kenny, J. M.; Mondragon, I.; Vazquez, A. Polym Compos 1999, 20(9), 37
15. Potter, W. G. Epoxy Resins; Springer: New York, 1970.
16. Kiujo, N.; Ogata, K.; Keneda, A. Adv Polym Sci 1989, 88, 1.
17. Lee, H.; Neville, K. Handbook of Epoxy Resins; McGraw-Hill: New York, 1982.
18. Laza, J. M.; Julian, C. A.; Larrauri, E.; Rodríguez, M.; León, L. M. Polymer 1998, 40, 35.
19. Laza, J. M.; Vilas, J. L.; Rodríguez, M.; Garay, M.; Mijangos, F.; León, L. M. J Appl Polym Sci 2002, 83, 57.
20. Babayezsky, P. G.; Gillham, J. K. J Appl Polym Sci 1973, 17, 2067.
21. Senturia, S. D.; Sheppard, N. F. Adv Polym Sci 1986, 80, 3.
22. Aronhime, M. T.; Gillham, J. K. Adv Polym Sci 1986, 78, 84.
23. Joundeau, A.; Binse, B.; Pouyet, B.; Fesquet, F. Composites 1988, 3, 180.
24. George, G. A.; Schweinsberg, D. P. J Appl Polym Sci 1987, 33, 2281.
25. Chambon, F.; Winter, H. Polym Bull 1985, 13, 499.
26. Chambon, F.; Winter, H. J Rheol 1987, 31, 683.
27. Tung, C.; Dynes, P. J. J Appl Polym Sci 1982, 27, 569.
28. Harran, D.; Landourd, A. Rheol Acta 1985, 24, 596.
29. White, R. P. Eng Sci 1974, 14, 50.
30. Gillham, J. K. Polym Eng Sci 1979, 19, 676.
31. Willard, P. E. Polym Eng Sci 1974, 14, 273.
32. Malkin, A. Y.; Kulichikin, S. G. Adv Polym Sci 1991, 111, 217.
33. Martin, J. S.; Laza, J. M.; Morras, M. L.; Rodríguez, M.; León, L. M. Polymer 2000, 41, 4203.
34. Barton, J. M.; Greenfield, D. C.; Hood, K. A. Polymer 1992, 6, 1177.
35. Tajima, Y. A.; Crozier, D. Polym Eng Sci 1986, 26, 427.
36. Tajima, Y. A.; Crozier, D. Polym Eng Sci 1983, 23, 186.
37. Ferry, J. D. Viscoelastic Properties of Polymer, 2nd ed.; Wiley: New York, 1970.
38. Hou, H. T. Soc Plast Eng Annu Tech Conf 1985, 85, 1253.
39. Hou, T. H. Aerosp Technol Div, PRC Kentron Inc.: Hampton, VA; NASA Contract. Rep., 1985.
40. Apicella, A.; Nicolais, L.; Nobile, M.; Castaglione Morelli, M. A. Compos Sci Technol 1985, 24, 101.