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Thermal scanning rheometer analysis of curing kinetic of an epoxy resin: 2. An amine as curing agent

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Abstract

The curing reaction of the system diglycidyl ether of bisphenol A (DGEBA) with different amine concentrations (TETA) has been studied by means of thermal scanning rheometer (TSR) and dynamic mechanical thermal analyser (DMTA). The aim of this work was focused on studying the effect of the amine concentration on the kinetic, the rheologic characteristics during the crosslinking process, and the dynamic-mechanical properties of the system. Through TSR measurements, the gel time was observed to vary with amine concentration and cure temperature when measurements were carried out under isothermal conditions. The gel time also was found to depend on the heating rate when the measurements were done varying the temperature. The apparent activation energy (*Ea*) of each system was calculated from two different methods; the gel time (*tg*) and the complex viscosity (η^*) measurements, respectively. The study of the dynamic-mechanical properties of the resins such as epoxy by means of the three-point bending mode in DMTA, gives information of their viscoelastic properties allowing the calculation of the glass transition temperature (*Tg*) and the apparent activation energy of the relaxation process (*Ea**).

Keywords: Epoxy resins; Curing reaction; Dynamic-mechanical properties

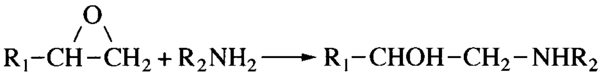
1. Introduction

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 resins which are studied in this work.

Nowadays, many of the matrices used in composites are polyfunctional epoxy resins cured by aromatic diamine to produce a strong crosslinked network. The high number of chemical reactions, the change in the physical state as the polymerisation takes place and the crosslinking process give rise to a complex kinetic behaviour [1]. The kinetic study involves a deep knowledge of the chemical reactions which take part in the curing process allowing development of quantitative models in order to predict the thermal curing cycles.

The methods used to study the epoxy curing process can be classified as chemical and physical methods. Classical analysis, liquid chromatography (h.p.l.c., g.p.c.), *FT* i.r., n.m.r., infrared spectroscopy and radiochemical methods are considered as chemical methods. Differential scanning calorimetry (d.s.c.), dynamic viscosimetry and dynamic-mechanical methods such as thermal scanning rheometry (TSR) and dynamical mechanical thermal analysis (DMTA) can be considered as physical methods.

The curing reaction of epoxy resins usually involves the reaction of oxirane group of the epoxy resin with the amine group of the amine. The major reaction mechanism with the amine has been proposed by Do Hyun Kim and Sung Chul Kim [2] as follows:



$$R_1\text{-}\overset{\overset{\displaystyle O}{/\quad\backslash}}{CH\text{-}CH_2} + R_2NH_2 \longrightarrow R_1\text{-}CHOH\text{-}CH_2\text{-}NHR_2$$

$$R_1 - CH - CH_2 + R_1 - CHOH - CH_2 - NHR_2 \rightarrow$$
$$[R_1 - CHOH - CH_2]_2 - NR_2$$

Both gelation and vitrification take place during the curing reaction. In other words, the gelation occurs when the reaction products form a three-dimensional network and the vitrification occurs when the liquid or rubbery reacting mixture is transformed into the glassy state as the molecular weight increases.

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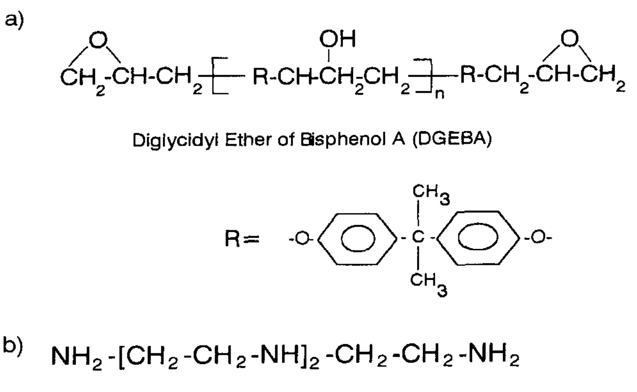

Fig. 1. (a) DGEBA epoxy resin (Rütapox LB64); (b) triethylentetramine (TETA).

The processability of the thermosetting resins requires a rheologic knowledge to determine the properties of the final product and the kinetic of the crosslinked reaction in order to calculate the apparent kinetic constant and activation energy [3]. The gel time is an important factor to take into account at the industrial level because from that time onwards the thermosetting system decreases its processability. In the literature, it is difficult to find measurements of rheological properties of the thermosetting systems due to the increase in the reaction rate caused by the heat generated during the crosslinking process. For this reason, it is better to study the rheological properties under isothermal conditions.

Nowadays, rheometric techniques have been found to be the most suitable methods for this kind of work [4], and for that reason, the thermal scanning rheometry technique (TSR) has been chosen for the epoxy/TETA system studies. A similar technique has been utilized and proved suitable in the study of plastisols by Hayward and co-workers [5–7].

Another factor to consider during the curing process is the effect that the degree of the resin crosslinking has on the glass transition temperature (*Tg*). This parameter is also relevant for the industrial applications in the thermosetting composite field.

2. Experimental

2.1. Materials

A liquid epoxy resin, diglycidyl ether of bisphenol A (DGEBA), commercial name Rütapox LB64, and triethylentetramine (TETA), as curing agent, were used in this work. Fig. 1 shows the chemical structure of the epoxy resin and the amine. Table 1 shows the materials data which implies that the resin is suitable for the production of high quality plastics or fibre-reinforced composites. Besides, an excellent wetting of different fibres is obtained due to the very low surface tension exhibited by the resin.

2.2. Thermal scanning rheometer (TSR)

All the rheological measurements were carried out by means of the TSR supplied by Rheometric Scientific. The TSR is designed for monitoring the viscoelastic state of a wide range of materials and particularly the changes in the rheological properties with temperature or time. Since the TSR uses a probe and sample container which can be thrown away at the end of each experiment, the equipment may be used to track the change in viscoelastic properties of a thermoset up to full cure or solidification. The disposable probe is connected via a spring of known force constant to a linear vibrator which is driven at constant amplitude and frequency (2 Hz). As it reciprocates in the sample, the position of the probe is continuosly monitored by an accurate transducer. As the viscosity of the sample increases, so the motion of the probe is progressively damped by viscous drag. This change in amplitude and phase of the probe with respect to the drive motion is a function of the viscoelasticity of the material.

The force generated on the probe due to viscous drag is given by:

$$F = \omega\eta^* CP^* \qquad (1)$$

where η^* is the complex viscosity of the sample, P^* represents the complex motion of the probe when immersed in the sample, C represents a geometric factor related to the probe/material contact area (which is determined by

Table 1
Materials data

Properties	Unit	Rütapox LB64	TETA
Density at 20°C	g/cm^3	1.17 ± 0.01	0.98
Viscosity at 25°C	mPa·s	11 000 ± 2000	—
Equivalent	g/equiv.	188 ± 2	24.3 ± 0.1
Hydrol. chlorine content	%	< 0.4	—
Supplied form	—	liquid	liquid
Molecular weight	g/mol	—	146
No. of active hydrogen	—	—	6
Shelf life at 20–25°C in sealed containers	months	12	12

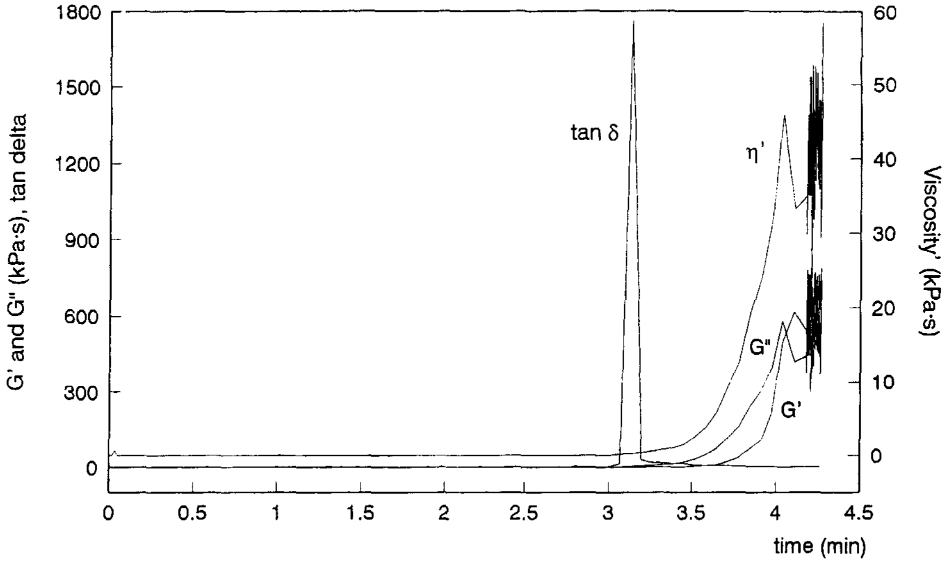

Fig. 2. Storage modulus (G'), loss modulus (G''), dynamic viscosity (η') and tanδ *versus* cure time for the epoxy/TETA system (100% TETA and 80°C).

calibration) and ω is the angular frequency:

$$\omega = 2\pi f$$

where f is the oscillation frequency.

This force acts on the spring which causes it to compress according to:

$$F = k(P_o - P^*) \qquad (2)$$

where P_o is the maximum amplitude of the probe in air and k is the force constant of the spring. The complex motion is made up from the in-phase component P' and the quadrature component P'':

$$P^* = P' - iP'' \qquad (3)$$

By combining these equations, the real dynamic viscosity η' and the imaginary viscosity η'' can be calculated from:

$$\eta' = \frac{P''P_o}{(P'^2 + P''^2)} \times \frac{k}{\omega C}$$

$$\eta'' = \left(1 - \frac{P'P_o}{(P'^2 + P''^2)}\right) \times \frac{k}{\omega C}$$

The shear storage modulus G' and the shear loss modulus G'' are then given by:

$$G' = 2\pi f \eta''$$

$$G'' = 2\pi f \eta'$$

The stoichiometric relation between the resin and the amine (which has been considered as 100% TETA) has been calculated following Eqs. (4) and (5):

$$\text{Amine H eq. wt.} = \frac{\text{MW of amine}}{\text{No. of active hydrogen}} \qquad (4)$$

$$\text{phr of amine} = \frac{\text{Amine H eq. wt.}\cdot 100}{\text{Epoxide eq. wt. of resin}} \qquad (5)$$

where phr is the parts by weight per 100 parts of resin.

The isothermal runs were carried out at different curing temperatures 30, 40, 50, 60, 70 and 80°C and for different amine concentrations in the system: 60, 70, 80, 100, 120, 140 and 160% TETA. The non-isothermal runs were carried out by heating each epoxy/amine system with amine concentrations of 60, 100 and 160% TETA at heating rates of 1, 3 and 5°C/min.

Fig. 2 shows an example of the dynamic-mechanical behaviour of the system studied under isothermal conditions. A similar behaviour was observed when the system was heated.

2.3. *Dynamic mechanical thermal analyser (DMTA)*

The DMTA imposes a sinusoidal stress on a sample in the three-point bending mode and determines the sample modulus and tanδ as a function of temperature and/or frequency. In this mode, the sample is usually in the form of a rectangular bar clamped rigidly at both ends and with its central point vibrating sinusoidally by the drive clamp.

Rectangular bars of 36 × 11 × 2 mm were produced for all the epoxy/amine systems by compression moulding at a temperature of 60°C and pressure of 200 kg/cm^2 during 40 min. The compression moulding machine is a manual hydraulic press. Once the samples were moulded, they were postcured either at 80 or 110°C for 150 min. Afterwards, the postcured samples were stored in the freezer to stop and, therefore, control the level of the postcuring process. Mouldings were kept without postcuring treatment and stored in the freezer for comparison purposes.

These samples were tested under a three-point bending mode called ‘dual cantilever’. The runs were carried out at

Table 2
Gel times for the epoxy/TETA system cured at 50°C for all the criterions used

Isotherm 50°C					
% TETA	tg_1 (min)	tg_2 (min)	tg_3 (min)	tg_4 (min)	tg_5 (min)
60	45.3	65.5	50.9	55.0	61.8
70	37.2	49.1	40.9	43.6	47.9
80	33.7	44.6	37.0	39.3	42.7
100	31.2	38.3	33.1	34.6	37.1
120	29.4	36.2	31.4	32.9	34.7
140	22.7	27.6	24.5	25.6	27.0
160	22.2	26.4	23.5	24.4	25.6

tg_1: criterion of maximum peak in tanδ
tg_2: criterion of the tangent line to G' curve
tg_3, tg_4, tg_5: criterion of viscosity for $\eta' = 1000$, 2000 and 5000 Pa·s, respectively

an initial temperature of 30°C and a heating rate of 2°C/min. The oscillating frequencies were 2, 10 and 30 Hz.

From the DMTA measurements, the apparent activation energy (*Ea**) can be calculated by means of an Arrhenius relationship from the slope of the lineal plot, logarithm of the frequency *versus* the inverse of the temperature, at which the maximum peak of tanδ appears. The change from the glassy to the elastic state obtained when the temperature increases is directly related to the change in Young's modulus.

As the temperature increases, the deformation frequency reaches the frequency set, leading to a peak on the curve (tanδ). As the frequency increases, the tanδ peak is observed to be shifted to higher temperatures due to an increase in the chain mobility.

3. Results and discussion

3.1. Gel time and apparent activation energy (Ea) from the TSR measurements

The cure of a thermosetting reactive 'prepolymer' usually involves transformation of low molecular weight monomers or oligomers from the liquid to solid state as a result of the formation of a polymer network by chemical reaction of the reactive groups of the system [4]. Two stages, which are divided by a 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. The reactive system then loses its solubility and fusibility, leading to the final reactions which take place in the solid state.

In Fig. 2, three different regions are appreciated. At the first region, the G' modulus is parallel to the time axis. In the second region, this modulus increases exponentially *versus* time, where the gel time is. In the last region, the modulus increases more rapidly, where a great dispersion of the measurements are obtained indicating that the resin has been cured.

3.1.1. Gel time 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 dynamic-mechanical properties, a kinetic parameter can be determined allowing kinetic studies of the curing system; for example the gel time (*tg*). The gel time has been determined according to different criteria [8] (see Fig. 2) as:

1. Criterion of maximum peak in tanδ, based on the point where there is a maximum difference between the elastic and viscous behaviour of the system.
2. Criterion corresponding to the crossover between the G'

Table 3
Gel times (min) for the epoxy/TETA system by criterion of $\eta' = 1000$ Pas

% TETA	T (°C)					
	30	40	50	60	70	80
60	123	80.9	50.9	32.7	17.6	8.31
70	111	71.2	40.9	22.4	10.8	5.36
80	110	65.9	37.0	20.3	8.98	4.32
100	98.5	57.7	33.1	12.5	5.95	3.36
120	101	55.2	31.4	12.4	5.06	3.01
140	93.0	50.2	24.5	9.25	4.35	2.29
160	92.3	48.2	23.5	8.86	4.19	2.28

Table 4
Gel times for the epoxy/TETA system cured under non-isothermal conditions

% TETA	Heating rate (°C/min)	tg_1 (min)	tg_2 (min)	tg_3 (min)	tg_4 (min)	tg_5 (min)
60	1	52.5	40.3	50.0	50.8	53.6
	3	22.5	19.9	21.2	23.5	24.2
	5	15.4	14.8	15.2	16.4	16.9
100	1	42.2	39.0	41.8	40.7	41.5
	3	18.4	17.8	18.8	18.2	18.3
	5	13.2	13.0	13.5	13.1	13.2
160	1	38.8	36.1	38.5	37.3	37.8
	3	15.9	16.0	16.5	16.1	16.2
	5	12.4	12.1	12.6	12.1	12.2

tg_1: criterion of the tangent line to G' curve
tg_2: criterion of maximum peak in tanδ
tg_3: criterion corresponding to the crossover between the G' and G'' curves
tg_4, tg_5: criterion of the viscosity for $\eta' = 1000$ and 2000 Pa·s, respectively

and G'' curves; at this point, the system presents not only an elastic but viscous behaviour as well, storing a similar amount of energy to the energy dissipated.

3. Criterion of the tangent line to the G' curve; this point corresponds to the crossing between the baseline ($G' = 0$) and the tangent drawn at G' curve when G' reaches a value close to 100 KPa·s.
4. Criterion of the viscosity; at this point the real dynamic viscosity η' reaches several determined values (1000, 2000 and 5000 Pa·s).

The gel time values obtained according to the above criteria for the cured epoxy/TETA system under isothermal and non-isothermal conditions show some interesting facts as:

1. The gel time decreases as the %TETA increases at a fixed cure temperature, due to the greater number of activated molecules that begin the reaction. Table 2 shows this dependency for systems cured at 50°C.
2. The gel time decreases when the cure temperature increases at a fixed %TETA. This means that when the temperature increases the molecular mobility increases and therefore, the curing reaction occurs more rapidly (see Table 3).
3. When the system has been cured under non-isothermal conditions, the gel time decreases with the heating rate due to a faster energetic contribution (see Table 4).
4. For all the systems studied the gel times vary depending on the criterion chosen. This fact can be explained taking into account that the gelification process occurs in a period of time and not in a punctual moment.

Table 3 shows the gel time results calculated from the criterion of the viscosity for a value of $\eta' = 1000$ Pa·s, as an example among the other criteria. This criterion is also used in all the figures shown in this paper. However, all the criteria have been considered for posteriori kinetic calculations.

3.1.2. Apparent activation energy (Ea)

The chemical conversion obtained at the gel time is considered constant for a given system [4]. Therefore, the gel

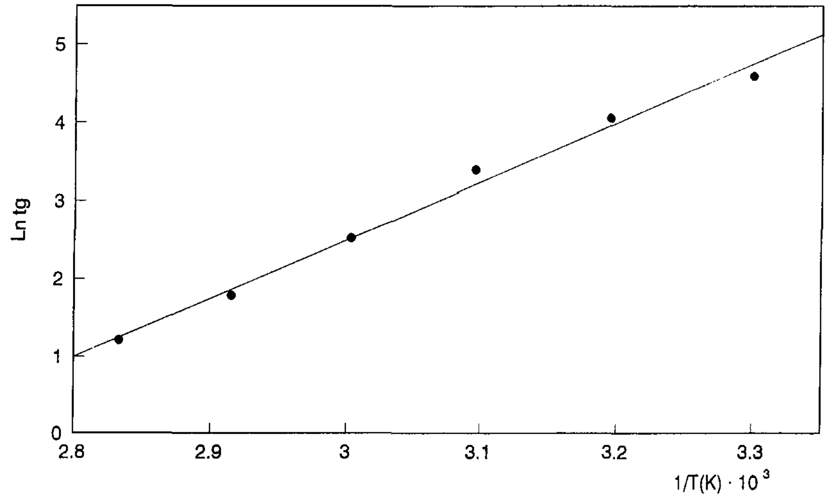

Fig. 3. Arrhenius plot based on gel time for the stoichiometric ratio of epoxy/TETA.

Table 5
Apparent activation energy (Ea) obtained for the epoxy/TETA system taking into account the different criteria

[Ea (kJ/mol)]					
% TETA	Ea_1	Ea_2	Ea_3	Ea_4	Ea_5
60	52.7	52.3	46.4	43.1	38.1
70	55.6	57.7	53.9	53.9	53.5
80	58.5	60.2	57.3	57.7	57.7
100	63.1	63.9	62.3	62.3	63.1
120	65.2	67.3	64.8	65.2	65.6
140	66.9	69.8	67.7	68.1	69.0
160	66.9	71.1	67.7	68.5	69.4

Ea_1: criterion of maximum peak in tanδ
Ea_2: criterion of the tangent line to G' curve
Ea_3: criterion $\eta' = 1000$ Pa·s
Ea_4: criterion $\eta' = 2000$ Pa·s
Ea_5: criterion $\eta' = 5000$ Pa·s

time (tg) can be related to the apparent kinetic constant (k') of the reaction through the equation:

$$tg = cte \cdot \frac{1}{k'} \qquad (6)$$

Assuming that the apparent kinetic constant of the reaction k' is related to the temperature by an Arrhenius relationship:

$$k' = k_0'' \cdot \exp\left(-\frac{Ea}{R \cdot T}\right) \qquad (7)$$

the following can be obtained:

$$\ln tg = cte' + \frac{Ea}{R} \cdot \frac{1}{T} \qquad (8)$$

There is a lineal relationship between ln tg and the inverse of temperature for isothermal curing reactions. From the slope of this relationship, the apparent activation energy (Ea) is obtained (see Fig. 3 and Table 5). An interesting %TETA–apparent activation energy dependency is observed, where the apparent activation energy increases as the %TETA increases. As the %TETA increases, a higher number of epoxy groups are activated leading to a greater chain entanglement and, therefore, to an increase in the system viscosity. Moreover, extra energy is necessary to increase the molecule mobility and favour in this way the curing reaction. The apparent activation energy values obtained are similarly independent of the criterion used for its calculation apart from the 60% TETA system.

3.1.3. Gel time–%TETA

Taking into account Eq. (6), the gel time can be related to the %TETA considering that the apparent kinetic constant k' is a function of the amine concentration at a given temperature:

$$k' = f(\%TETA) \qquad (9)$$

Fig. 4 shows the tg^{-1} *versus* %TETA plot for all the curing

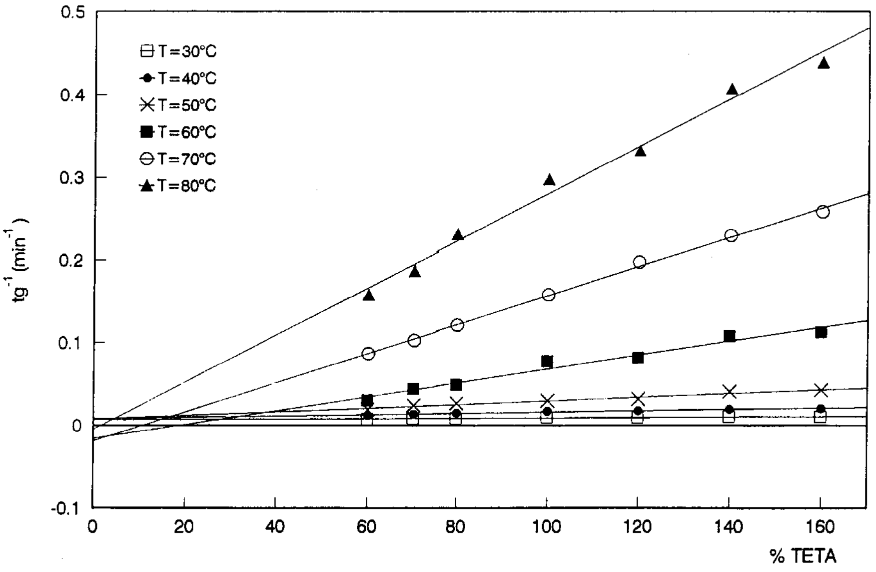

Fig. 4. Influence of the amine concentration (%TETA) in the gel time for isothermal experiments.

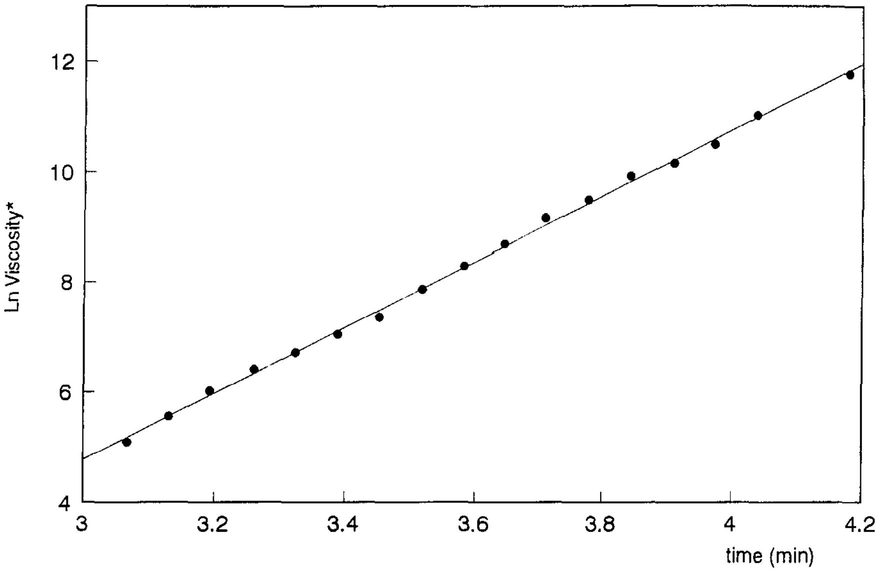

Fig. 5. Complex viscosity dependency with the time from the TSR measurements (100% TETA and 80°C).

temperatures used (isothermal conditions). Comparing the plots obtained for the systems cured at different temperatures, a more pronounced gel time–%TETA dependency is observed as the curing temperature increases. As it is expected when the %TETA decreases the Y-axis tends to zero as the tg tends to infinity ($1/tg = 0$). Similar dependency was also observed for the systems cured under non-isothermal conditions. Moreover, this dependency is more pronounced when the heating rate increases.

3.1.4. Kinetic analysis through the viscosity measurements

There are different methods for the quantitative viscosity data treatment obtained from thermosetting systems cured under isothermal conditions. Most of them are mainly based on the Williams–Landel–Ferry (WLF) equation [9,10]:

$$\log a_T = -C_1 \cdot \frac{T - Ts}{C_2 + (T - Ts)} \qquad (10)$$

where a_T is the shift factor, Ts is a temperature of reference, C_1 and C_2 are two universal constants with values 17.44 and 5.16, respectively, only if Ts is the Tg of the material. This equation was considered exclusively to observe the dynamic-mechanical relaxation times on the zone Tg to $Tg + 50$°C.

Other authors[9] reported that the increase in the Tg during the isothermal curing is a consequence of the increase in the crosslinking which is controlled by the chain mobility. Therefore, the WLF equation is not suitable for this process.

Tajima and Crozier [11,12], however, reported that at any stage of the reaction, the temperature dependency of the viscosity for an epoxy/amine system can be described as:

$$\log\eta(T) = \log\eta(Ts) - \frac{26.8 \cdot (T - Ts)}{13.4 + (T - Ts)} \qquad (11)$$

where the parameters Ts and $\eta(Ts)$ vary with the degree of reaction for an epoxy-amine system, which at the same time is determined by the amine concentration (%TETA).

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

$$\eta(T, \alpha) = \eta(T) \cdot \eta(\alpha) \qquad (12)$$

Table 6
k' (min^{-1}) values obtained for all the amine concentrations and curing temperatures used

%TETA	T (°C)					
	30	40	50	60	70	80
60	0.060	0.106	0.170	0.252	0.121	0.128
70	0.071	0.131	0.262	0.439	0.278	2.426
80	0.081	0.164	0.305	0.694	0.642	3.603
100	0.105	0.212	0.418	1.153	3.437	6.027
120	0.103	0.229	0.471	1.589	5.716	8.610
140	0.115	0.262	0.660	2.230	11.44	9.670
160	0.126	0.287	0.753	2.704	15.64	24.53

Table 7
Global kinetic constants (k)

T (°C)	$k/10^{-3}$ (min^{-1})
30	0.626
40	1.776
50	5.640
60	24.76
70	158.2
80	196.5

Assuming that the kinetic of the reaction in the liquid state is the order $n = 1$ until the gel time is reached, taking into account that $\eta(\alpha)$ is related to the degree of entanglement and that for a fixed temperature $\eta(T)$ can be considered as a constant, η_0:

$$\ln\eta = \ln\eta_0 + k'\cdot t \qquad (13)$$

where η is the viscosity as a function of the temperature and the conversion 'α'; η_0 is the viscosity at $t = 0$ and k' is the apparent kinetic constant.

The complex viscosity dependency with the time $\eta^*(t)$ is obtained from the TSR measurements. Plotting $\ln\eta^*$ *versus* time according to Eq. (13), a lineal plot (see Fig. 5) is observed only in the gelation stage which corresponds with the second region in Fig. 2. This fact was observed for all the TSR experiments.

Table 6 shows that k' increases as the curing temperature increases for a determined %TETA. As expected from Eq. (9), k' increases as the %TETA increases for a fixed curing temperature. Therefore, from the k' *versus* %TETA plot, a lineal relation is obtained whose slope indicates the global kinetic constant, k, independent of the amine concentration for all the curing temperatures studied (Table 7).

Considering that the temperature dependency of k is given by an Arrhenius relationship:

$$\ln k = \ln k_\infty - \frac{Ea}{R\cdot T} \qquad (14)$$

the global activation energy of the process was calculated:

$Ea = 101.48$ kJ/mol

This activation energy is greater than the values calculated from the gel time methods (53–71 kJ/mol). This difference could be due to the influence that the stages after the gel time exert on the reticulation process, as from that point the diffusion phenomenon begins to be important. This fact was also observed in our laboratory [13] for a DGEBA resin, using a methyl tetrahydrophthalic anhydride (HMTPA) as curing agent and a tri(dimethylaminoethyl) phenol (DMP 30) as initiator.

3.2. Dynamic-mechanical analysis

The DMTA is a method with great sensitivity in detecting changes in internal molecular mobility. The structure and solid viscoelastic properties can be determined from the dynamic and damping moduli. Moreover, the apparent activation energy of the relaxation process (Ea^*) is calculated from the glass transition temperatures (Tg) measured at three different frequencies [14]. These Tg are shown at temperatures where the tanδ exhibits a maximum peak at each frequency. Secondary relaxations in the glassy state

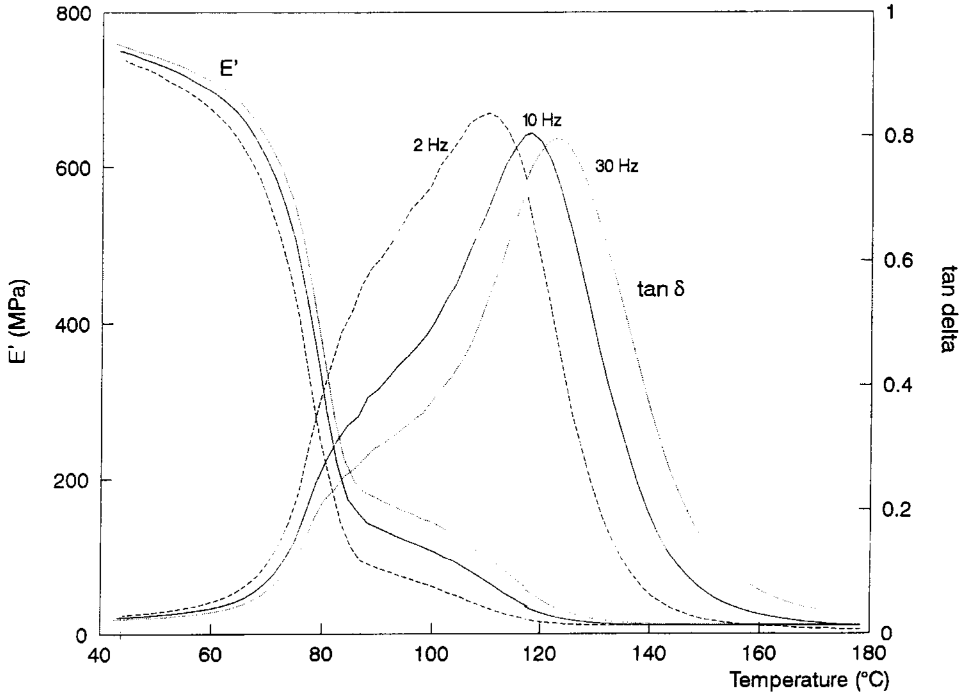

Fig. 6. Storage modulus (E') and tanδ *versus* temperature for the stoichiometric ratio of epoxy/TETA system unpostcured.

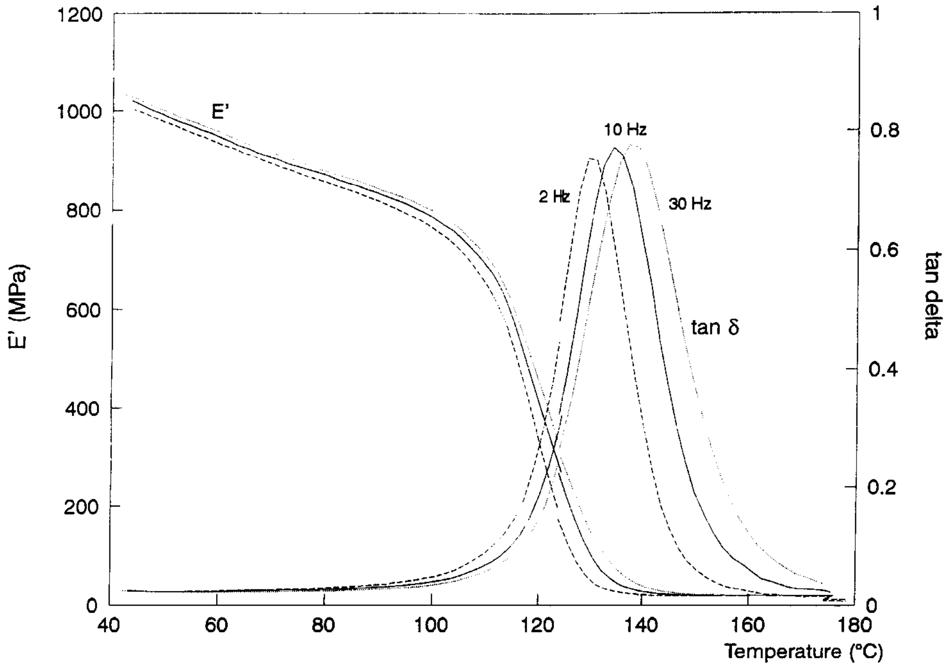

Fig. 7. Storage modulus (E') and tanδ *versus* temperature for the stoichiometric ratio of epoxy/TETA system postcured at 110°C.

can also be easily studied as well as the glass transition relaxation process.

3.2.1. Glass transition temperature (Tg)

In Figs 6 and 7 are plotted the tanδ and the storage modulus E' *versus* temperature. The postcured mouldings exhibit a very narrow tanδ peak in comparison to the non-postcured mouldings. Furthermore, a decrease in the area of the tanδ peak was observed. This decrease in the peak area implies a greater energy absorption by the material as the postcured temperature increases. The breadth of the peaks obtained for the non-postcured mouldings is due to the broader interval of temperature in which the glass transition occurs [15]. This interval is narrower as

Table 8
Glass transition temperature (*Tg*) *versus* %TETA

%TETA	Only cured	Postcured at 80°C	Postcured at 110°C
	Tg (°C) for frequency 2 Hz		
60	63.5	96.0	93.0
80	80.0	114	119
100	110	120	129
120	138	138	140
140	133	134	129
160	112	121	114
	Tg (°C) for frequency 10 Hz		
60	69.0	101	98.0
80	85.0	119	124
100	118	125	134
120	143	139	144
140	137	139	132
160	116	125	117
	Tg (°C) for frequency 30 Hz		
60	72.5	105	102
80	91.5	123	127
100	122	129	137
120	148	146	148
140	140	146	136
160	119	128	120

Table 9
Apparent activation energy (*Ea**) *versus* %TETA

%TETA	*Ea** (kJ/mol)		
	Only cured	Postcured at 80°C	Postcured at 110°C
60	289.8	331.9	344.3
80	249.0	362.5	463.4
100	281.3	396.3	481.1
120	409.3	459.1	490.5
140	503.3	507.0	529.1
160	508.0	509.1	571.0

the postcured temperature increases. These peaks are also influenced by the frequency used during the test where an increase in the frequency shifts the peaks to higher temperatures [16].

From Table 8 it can be concluded that for all the postcuring conditions and for all the frequencies used during the test, the *Tg* increases as the postcuring temperature and the amine concentration increase. However, when the amine concentration is higher than 120%, the *Tg* tends to decrease. Therefore, a higher increase in the amine concentration does not give rise to a greater degree of crosslinking (higher *Tg*). On the contrary, it has a plastificant effect over the polymer chains as the amine molecules are placed among them leading to an increase in the free volume. Another factor affecting the free volume, and therefore the *Tg*, is the pressure used while samples were processed or cured by compression moulding. During compression, the free volume tends to decrease giving rise an increase in the *Tg* values [17].

3.2.2. Apparent activation energy (Ea)*

The apparent activation energy *Ea** has been calculated taking into account the Arrhenius relationship[18]:

$$\ln w = \ln w_0 - \frac{Ea^*}{R \cdot T} \qquad (15)$$

where w is the frequency set and w_0 is the minimum deformation frequency of the material.

Table 9 shows the effect that the postcured temperature and amine concentration have on *Ea**. For a fixed composition, the highest values of the apparent activation energy correspond to the mouldings postcured at higher temperatures. For a fixed postcured temperature, *Ea** increases as the amine concentration increases; this fact is due to a greater crosslinking among the chains of the material as a result of the greater number of activated molecules responsible for the crosslinking reaction.

However, for mouldings which are only cured, the apparent activation energy does not increase as the amine concentration increases (see Table 9), the behaviour being inconsistent. This could be explained by the time spent from the curing process to when they were tested, as these samples could have gained a different degree of crosslinking. Besides, the non-postcured mouldings undergo a certain postcured treatment given by the test itself. Therefore, these mouldings are not comparable to those postcured mouldings.

4. Conclusions

This paper has shown that the TSR is a good technique to measure gel times and therefore to study the rheological properties during the crosslinking process in the thermosetting systems. The gel time is an important parameter to take into account at an industrial level to determine at what point the processability of the material is not desirable.

The gel time depends on the criterion used from the literature, meaning that the gelation process does not happen at a punctual time but in a period of time. Despite it all, the gel time is a good parameter to study the kinetic crosslinking process of the thermosetting systems.

From the results, it can be concluded that the gel times decrease with the temperature, amine concentration, and heating rate. The apparent activation energy (*Ea*) increases with the amine concentration because the viscosity of the epoxy/TETA system increases with the degree of crosslinking. Therefore, an extra energy is necessary to continue the curing reaction. However, the apparent activation energy calculated from the different gel time criteria shows similar values.

The apparent activation energy (*Ea*) has also been determined from viscosity data. The complex viscosity η^* *versus* time measured by the TSR indicates that the apparent activation energy has a value of 101.48 kJ/mol, this value is greater than those energies calculated from the gel time method.

On the other hand, dynamic-mechanical analysis shows that the maximum peak in tanδ (*Tg*) appears to be sharper when the material has been postcured. The *Tg* increases as %TETA increases, which implies a greater degree of crosslinking among the chains and therefore, better mechanical properties. However, for an amine concentration higher than 120% TETA the *Tg* decreases due to the plastificant effect produced by the remaining molecules of amine. These molecules do not take place in the crosslinking process. This fact has been observed for both postcured and non-postcured mouldings.

Moreover, for a fixed composition and frequency, the *Tg* increases when the postcured temperature is raised. For a given composition and postcured temperature, the *Tg* increases as the frequency set is greater.

Furthermore, in all DMTA tests, it is observed that when the degree of the epoxy/TETA crosslinking increases, the apparent activation energy of the relaxation process (*Ea**) tends to increase.

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