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Use of rheology, dielectric analysis and differential scanning calorimetry for gel time determination of a thermoset

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Abstract

Measurements of gel time of the epoxy system DGEBA($n=0$)/*m*-XDA were carried out using rheometry and dielectric analysis with the objective of checking the validity of Mangion–Johari equation (DEA) and Harran–Laudouard criterium (rheometry) for gel time determination. In this work, gel times obtained by rheometry and dielectric analysis are compared and conversions at gel time calculated. From the experimental results obtained for gel times it was found a reasonable agreement between the two techniques that lead to gel conversion values very close to those obtained using Flory equation.

Keywords: Epoxy; Gelation; Thermal analysis

1. Introduction

The cure of a thermoset is a complex process as different chemical reactions are involved in it. In general, both gelation and vitrification are the most significant phenomena during this process that begins by formation and expansion of linear chains that soon start to branch, and subsequently to cross-link, originating in most cases three-dimensional networks [1]. As the cure advances, an increase in molecular weight proceeds and in the end various chains develop into an infinite molecular weight network. This sudden and irreversible transformation from a viscous liquid to an elastic gel is named 'gel point', that can be defined [2] as the instant at which the average molecular weight tends to infinity.

Molecular gelation takes place at a well-defined and generally calculable step in the course of a chemical reaction whose mechanism is temperature independent and free of non-crosslinking side reactions [3–5]. However, gelation depends on stoichiometry, reactivity and functionality of the reactants.

From the macroscopic point of view, gelation gives rise a considerable increase in viscosity that approaches to infinity (null ionic conductivity) and development of elastic properties not existing in the pre-gel resin.

Relationships developed by Flory [3] allow calculation of the gel point, provided the knowledge of the chemical reaction. At the same time, molecular gelation may be detected as the point at which the reacting system becomes insoluble (for example, by the solubility test using tetrahydrofuran as solvent) or as the point, where two linear zones of the log G'' curve intersect [6].

The estimation of the degree of conversion at the gel point (α_{gel}) can be done from the combination of the gel time measurements by DSC or any other available technique. In general, gelation does not restrain the curing reaction as the reaction rate stays unchanged, and it cannot be detected directly using techniques receptive only to the chemical reaction (TGA, DSC). However, these techniques can be used to determine the time-temperature behaviour of gelation if α_{gel} is known. Some authors proposed dynamic mechanical analysis (DMA) and dielectric analysis (DEA) [7–11] as techniques suitable for these kind of measurements.

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At the same time, this article reports on gel time measurements by DEA.

2. Experimental

2.1. Materials and sample preparation

Epoxy resin was diglycidyl ether of bisphenol A (DGEBA $n=0$) (Resin 332, Sigma Chemical Co., St Louis, MO, USA) with an epoxy equivalent between 172 and 176. The curing agent was metaxylylenediamine (*m*-XDA) (Aldrich, Switzerland) 99%. Both were used as received. Resin and diamine were carefully and homogeneously mixed at ratio 100:19.5. Finally, the samples were enclosed in aluminium pans, spread on ceramic cells or situated between a plate–plate geometry assembly for calorimetric, dielectric and rheometric analysis, respectively.

2.2. Calorimetric measurements

The calorimetric measurements were performed using a Q100 DSC from TA instruments. The temperature heat flow and heat capacity calibrations were performed by standards of indium and sapphire. DSC experiments were carried out in two steps. The first one was at constant temperature up to the moment at which a constant heat flow was observed. In a second step, the sample was cooled down to room temperature, and then immediately heated at 10 K/min to obtain the residual reaction heat. Weight of the sample was 10–14 mg. The calorimetric scans were performed under a nitrogen gas flow of 50 ml min^{-1}. All the calibrations necessary for the correct determination of experimental calorimetric data were carried out according to the manual books provided by TA instruments [12,13].

The study of the progress of reaction was based on the measurements of the total heat flow which allows calculating the degree of conversion α.

$$\alpha(t) = \frac{\Delta H(t)}{\Delta H_{\max}} \quad (1)$$

2.3. Dielectric measurements

Dielectric measurements were carried out using a dielectric analyser (DEA) 2970 from TA instruments using a ceramic single surface cell of 20×25 mm^2 based on a coplanar interdigitated-comb-like electrode design. The sensors were calibrated for every experiment. All the experiments were performed under a dry nitrogen atmosphere at a gas flow rate of 500 ml min^{-1}. The experiments were carried out at 12 different frequencies in the range from 10^{-1} to 10^5Hz. The total time taken to scan all the different frequencies was 1.2 min.

The principle of this technique consists in placing the sample under an alternative voltage and measuring the resulting current and the phase angle shift induced. The measured current was separated into its capacitive and conductive components. An equivalent capacitance and conductance were then calculated and used to determine the dielectric permittivity ε' and the dielectric loss factor ε''. ε' is proportional to capacitance and measures the alignment of dipoles. ε'' is proportional to conductance and represents the energy required to align dipoles and move ions. Ionic conductivity was calculated as follows:

$$\sigma = \varepsilon_0 \varepsilon'' w \quad (2)$$

where ε_0 is the absolute permittivity of the free space (8.85×10^{-12} F/m) and w is the pulsation of the applied potential difference. When ε'' is controlled by conductivity, Eq. (2) can be used to calculate σ. This happens in the first steps of curing.

2.4. Rheological measurements

The rheological measurements were carried out with a TA instruments AR2000 stress control. Plate–plate geometry was used with disposable plates. The experiments were carried out in the dynamic mode at a frequency of 1 Hz. Because the viscosity of the system changes significantly during the curing process, a control program was used in which the oscillation amplitude diminishes with the applied stress increase. This allows cure characterization in the whole conversion range. To be more specific, the experimental procedure consisted of four stages. Each of them, with an amplitude 10 times lower than that of the previous stage. In a first stage, the oscillation amplitude was 1, with the condition that if the torque is over 200 μN m, the new oscillation amplitude changes to 0.1. Next condition is an amplitude of 0.01 when the torque is over 2000 μN m. Finally, when the torque is over 5000 μN m, the amplitude were chosen after a thorough study to get the optimum values to monitor the cure of the two systems under research.

In these kind of experiments, the sample was subjected to a sinusoid stress and the response was a strain of storage modulus G', loss modulus G'' and complex viscosity modulus $|\eta^*|$.

The gel time was taken as that corresponding to the change in slope of the two linear parts of the log G'' curve [6]. The gel times so defined are independent of experimental parameters such as amplitude and frequency. One of the physical reasons for the choice of this criterion is that this time coincides with that in which the phase angle fall reaches its maximum value, going from 90° (liquid) to 0° (solid).

3. Results and discussion

One of the aims of this study was to determine the

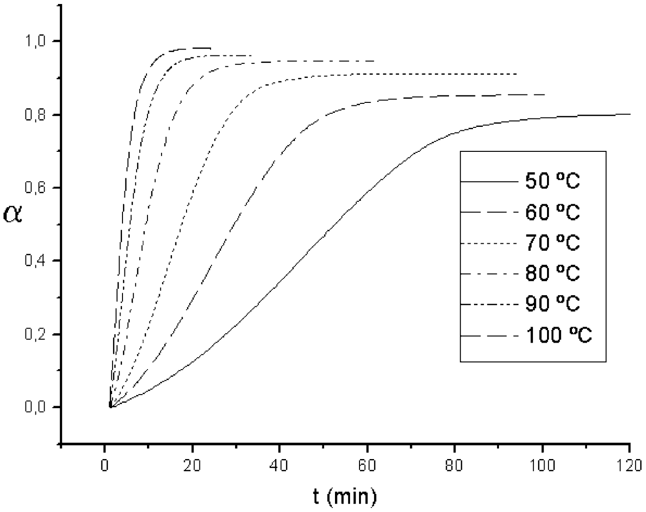

Fig. 1. α;–t curves corresponding to the different isothermal cure reactions of the system DGEBA($n=0$)/m-XDA.

conversion value corresponding to the gel times obtained by the use of the different techniques. Values of α were determined from the isothermal experiments carried out. These isothermal experiments were performed at temperatures of 50, 60, 70, 80, 90 and 100 °C. These temperatures were chosen because of the values of $_{\mathrm{gel}}T_{\mathrm{g}}$ (about 39 °C) [14] and $T_{\mathrm{g}\infty}$ (approximately 114 °C) [15]. In this way, and for all the isothermal experiments, gelation takes place before and markedly separate of vitrification.

Fig. 1 is a plot of conversion versus time for the different isothermal curing processes showing a typical behaviour for thermoset systems [15–17] with conversion increasing both with an increase in curing time and with an increase in temperature.

3.1. Study of gelation by rheometry

To begin this study, gel times were determined from rheological measurements. Fig. 2 shows storage modulus and loss modulus.

As it can be seen in this figure, both G' and G'' diminish as time increases. The origin of this behaviour is the need for time of the equipment to reach the necessary temperature. During this time, the temperature increases, originating a decrease in viscosity, loss modulus and storage modulus. Because of this, when comparing gel and vitrification times obtained by rheometry with those obtained by other techniques, it must be taken into account the time necessary for the rheometer to reach the isothermal cure temperature. At the temperature of the Fig. 2 (80 °C), this time is around 5 min. One other experimental problem is the imperfect control of the furnace temperature that makes this temperature not to be constant but varying 0.2 °C. This fact has an influence on G' and G'', mainly at low times.

From 7 min on, it can be observed an increase in G'', which corresponds to an increase in the real part of the complex dynamic viscosity η' ($G''\omega$) as a consequence of an increase in the molecular weight of the polymer. At low frequencies, G' is very low and approaches zero. In this zone named as pre-gel, G'' is greater than G' and because of this, $\tan\delta > 1$. In Fig. 2, this zone goes to around 13 min.

The critical region (approximately at 18 min in Fig. 2) begins with a sudden increase in G' of various decades. When G' and G'' intercept, $\tan\delta = 1$. After intercept, G' becomes greater than G'' and $\tan\delta$ becomes smaller than 1. This was one of the reasons why, the intercept ($\tan\delta = 1$) was at first considered as the gel point [18]. However, when

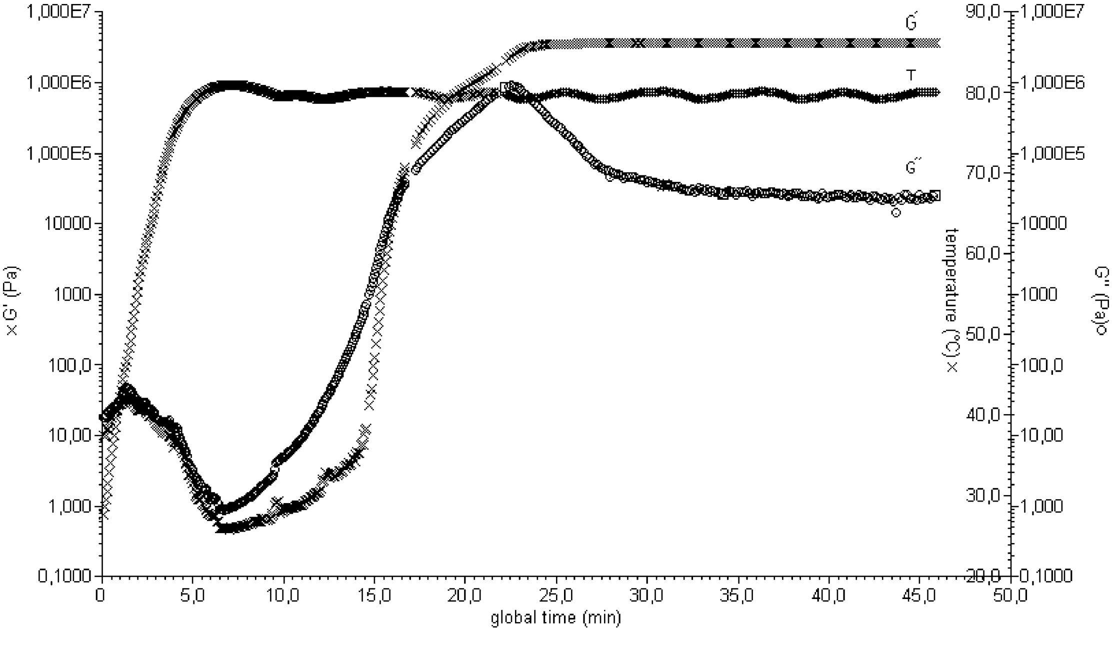

Fig. 2. Plots of log G', log G'' and T against time for the isothermal cure at 80 °C of the system DGEBA($n=0$)/m-XDA.

a reaction such as the one here studied is carried out at different frequencies, it was found that the time to reach tan $\delta = 1$ depends on frequency. As the gel time is a constant of the material, gel time should not depend on frequency and, because of this, the intercept of G' and G'' cannot be considered as the gel point.

Finally, in the post-gel region, G' increases very gently. When the isothermal cure temperature is below $T_{g\infty}$ (Fig. 2), G'' presents a peak that corresponds to vitrification of the system.

As it was previously mentioned, gel times will be taken as those corresponding to the change in slope of the two linear parts of log G''.

3.2. Study of gelation by DEA

Ionic conductivity originated by free ions motion diminishes with an increase in viscosity as a consequence of an increase in conversion. Ideally, as gelation takes place when viscosity approaches infinity, conductivity tends to zero. Mangion and Johari [7–10] proposed an equation that relates ionic conductivity (σ), curing time (t) and time to reach gelation (t_{gel}) in the form:

$$\sigma = \sigma_0 \left(\frac{t_{gel} - t}{t_{gel}} \right)^x \qquad (3)$$

where σ_0 is the conductivity at $t = 0$ and x is a critical exponent that depends on the isothermal curing temperature. From the above equation results $\sigma = 0$ for $t = t_{gel}$. In this way, t_{gel} can be roughly calculated. It must be pointed out the existence of a identical equation that uses viscosity data at zero shear rate to estimate gel times [19]. It is obvious that neither, conductivity reaches a zero value nor viscosity reaches infinity. For this reason, the validity of Eq. (3) for obtention of t_{gel} must be checked against values obtained by rheometry and/or the tetrahydrofuran test.

Figs. 3–5 are plots of permittivity, loss factor and ionic conductivity versus time, respectively, corresponding to the isothermal cure, at 90 °C, of the system DGEBA($n = 0$)/m-XDA in a frequency range from 10^{-1} to 10^5 Hz.

Even the experiments were carried out in the frequency range from 10^{-1} to 10^5 Hz, only curves corresponding to frequencies from 10 Hz onwards are shown in Fig. 4. The reason is that below this frequency, the electrode polarization [20] is so high that ε' undergoes a dramatic increase. In fact, the curve showing the highest permittivity values was carried out at 10 Hz. Values of ε' at frequencies below 10 Hz are not shown because they are so high that would increase excessively the scale. Electrode polarization at times near to zero does not contribute significantly to ε' at frequencies above 10 Hz. This kind of polarization diminishes also with increasing cure time owing to the increase in conversion that diminishes the effect of charge units on the electrodes. After this zone, it can be seen that permittivity decreases gently with time with coinciding values for all frequencies. This value corresponds to the relaxed permittivity (ε_r).

As time goes on, ε' suffers a significant decrease owing to the vitrification of the system that prevents molecular dipoles alignment with electric field. In this case, dipoles do not contribute to permittivity. Once the isothermal cure reaction is achieved, permittivity approaches a constant value (ε_u, unrelaxed permittivity) with the only contribution of atomic and electronic polarization that, at first, does not depend on conversion.

Fig. 4 is a plot of the loss factor as a function of time. Values of ε'' at frequencies below 100 Hz were not considered because they are very high, thus, increasing

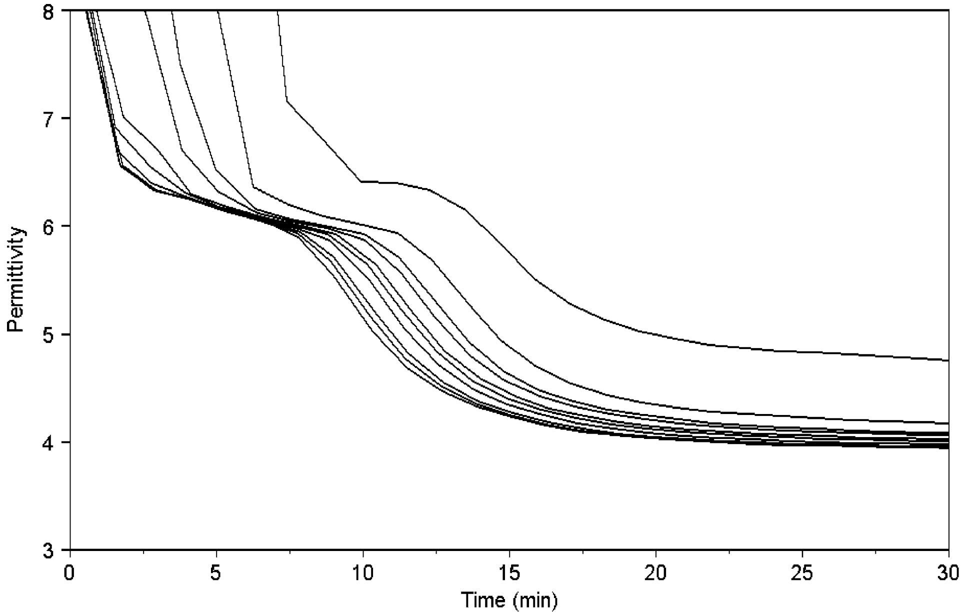

Fig. 3. Plot ε'–t corresponding to the isothermal cure (90 °C) of the system DGEBA($n = 0$)/m-XDA. Frequency decreases with increasing cure time.

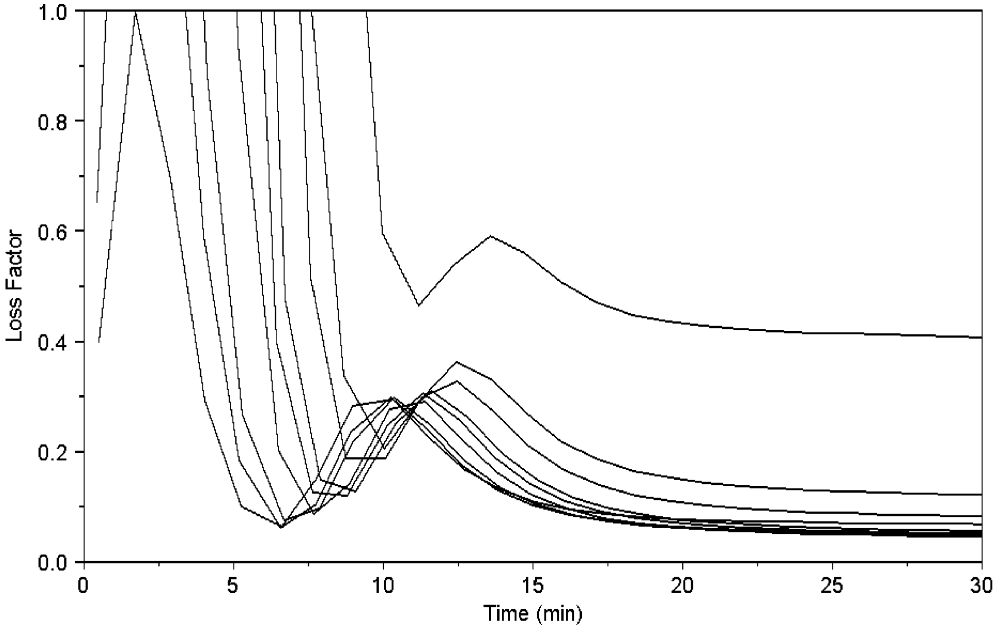

Fig. 4. Plot ε'–t corresponding to the isothermal cure (90 °C) of the system DGEBA($n=0$)/m-XDA. Frequency decreases with increasing cure time.

substantially the scale. As it was previously mentioned, there are two main phenomena contributing to ε'': ionic conductivity and dipole relaxations. Conductivity is the dominant factor, mainly at low cure times and low frequencies that can even mask the dipole maximum associated to vitrification. Fig. 4 also shows that loss factor decreases significantly with cure time because of a decrease in ionic conductivity. In the zone of low times, ionic conductivity shows an important contribution to ε''.

As cure time goes on, an increase in ε'' can be observed, that is originated by the beginning of the dipole relaxation associated to vitrification, which causes a maximum at a given time. Same that for ε', the time at which the maximum in ε'' takes place varies with frequency and is greater at low frequencies.

At the reaction progresses with time, ε'' approaches a constant value that depends greatly on the ionic conductivity of the cured system, σ_∞.

Because σ does not depend on frequency while dipole contribution does, a practical and quick way to check the dominant character of conductivity or dipole contribution to the loss factor, consists in plotting σ ($\varepsilon'' w \varepsilon_0$) against time at different frequencies (Fig. 5).

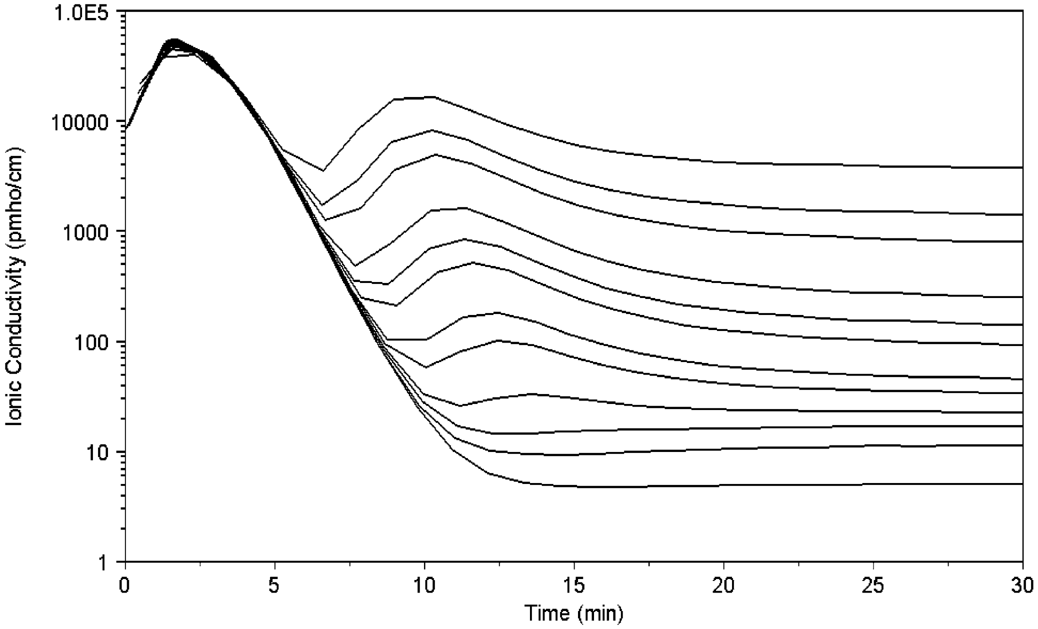

Fig. 5. Plot σ ($\varepsilon''\varepsilon_0 w$)–$t$ corresponding to the isothermal cure (90 °C) of the system DGEBA($n=0$)/m-XDA. Frequency decreases with increasing cure time.

In fact, Fig. 5 shows that, at first stages of cure, the conductivity is the dominant contribution to ε'', an that this contribution decreases with time increase. At high cure times, σ depends on frequency, thus, indicating that the epoxy system approaches vitrification, where dipole relaxation depends on frequency.

In this way, conductivity can be obtained from dielectric measurements as a function of the cure time carried out in an alternating electric field. It is important to remark that conductivity values were calculated from the loss factor at frequencies less than 1 Hz. Values of conductivity as a function of time and fittings through Eq. (3) are shown in Fig. 6, where only conductivity values corresponding to low times were recorded in order to show a reasonable fitting to Mangion and Johari equation.

Fig. 6 shows the typical behaviour of σ against time for an isothermal cure. It can also be observed that the time at which conductivity falls decreases with an increase in the curing isothermal temperature. This is a consequence of the increase in the reaction rate originated by an increase in temperature.

Finally, it can be seen that as times approaches zero, the conductivity increases with an increase in temperature. This behaviour is caused by an increase in kinetic energy, and thus, in ionic mobility, originated by an increase in temperature.

Table 1 lists values of the different parameters calculated by fitting σ versus time through Eq. (3).

As it was previously mentioned, a significant increase in σ_0 with increasing temperatures can be observed.

Table 1
Values of the fitting parameters of σ versus time

T °C	DGEBA($n=0$)/m-XDA		
	t_{gel}	x	σ_0
50	50.45	4.53	11234.3
60	33.03	3.25	23371.7
70	19.23	2.85	51319.4
80	11.15	2.2	61302.8
90	5.82	1.44	85295.0
100	4.06	0.55	113166.6

3.3. Comparison of gel times

Values of t_{gel} and the corresponding conversions at different isothermal temperatures, calculated through the different techniques used in this study are recorded in Table 2. These values were compared with those obtained using the tetrahydrofuran test [21,22].

Table 2 shows that σ_{gel} values obtained using both thermal analysis techniques are practically constant and independent of temperature. This fact is in agreement with the assumption that gelation does not depend on the isothermal process temperature but on conversion. It can be also seen that gel times obtained through the tetrahydrofuran test are lower than those obtained by the other two techniques. Conversions obtained by the tetrahydrofuran test are lower than that 0.58 proposed for gelation by Flory [3], at any temperature, taking into account epoxy and diamine functionalities.

However, conversion values obtained using rheometry

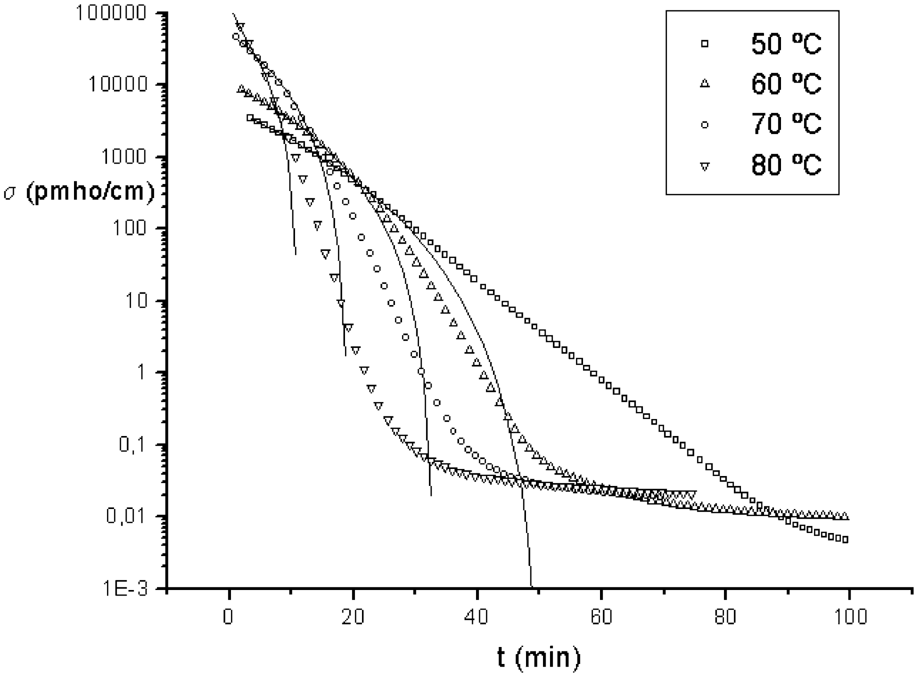

Fig. 6. Plot of σ versus t corresponding to the curing reaction of the system DGEBA($n=0$)/m-XDA at 50, 60, 70 and 80 °C and their, respectively, fittings to Eq. (3).

Table 2
Gel times and conversions calculated using DEA, rheology and the tetrahydrofuran test, respectively

	DEA		Rheometry		Tetrahydrofuran test	
	t_{gel} (min)	σ	t_{gel} (min)	σ	t_{gel} (min)	σ
50	50.45	0.47	63.0	0.63		
60	33.03	0.57	38.2	0.66	25.1	0.41
70	19.23	0.56	20.4	0.59	14.2	0.39
80	11.15	0.60	11.6	0.62	8.0	0.41
90	5.82	0.52	6.2	0.56	5.0	0.43
100	4.06	0.53	4.1	0.54	4.41	0.58

and dielectric analysis are in better agreement with Flory's proposal as mean values for σ_{gel} are 0.60 (rheological analysis) and 0.54 (DEA).

Comparison of gel times listed in Table 2 shows a reasonable agreement between values obtained using DEA and rheometry at all temperatures, thus, showing that DEA is a reliable technique that allows the obtention of isothermal curing gel times.

4. Conclusions

Dielectric analysis and rheometry were used for determination of gel times obtaining values that are in agreement with those obtained through Mangion and Johari equation and dielectric analysis data. Conversions at gel times were calculated through DSC measurements. It was found that σ_{gel} values at all the isothermal temperatures used in this study were in good agreement with those predicted by Flory for a two component system consisting of a functionality two resin and a functionality four diamine.

In our opinion, these results confirm the validity of DEA as an alternative method to obtain gel times, at least, for systems with a high crosslinking degree.

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