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STUDY OF THE INFLUENCE OF ISOMERISM ON THE CURING PROPERTIES OF THE EPOXY SYSTEM DGEBA (n=0)/1,2 DCH BY DEA AND MDSC

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Modulated differential scanning calorimetry (MDSC) and dielectric analysis (DEA) have been used to characterize the cure process of the system diglycidyl ether of bisphenol A (DGEBA(*n*=0)/1,2 diaminocyclohexane (1,2 DCH). The trans isomer and a mixture cis/trans (30–70% respectively) of 1,2 DCH were used to find their different behaviour. The study allowed to check the influence of the cis isomer on the thermoset curing process. Gelation times were obtained through the equation proposed by Johari and vitrification times from the point of inflection of the complex calorific capacity modulus.

Keywords: *DEA, epoxy, isomer, MDSC*

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. Dielectric analysis is a technique very suitable for determination of gel times [1–5], while modulated differential scanning calorimetry (MDSC) measures accurately the vitrification times [6–8].

Knowledge of gelation and vitrification times allows the construction of a TTT diagram for the curing process [9–14].

The final properties of the product depend mainly on the curing agent, and on its geometry [18, 19]. Some of this hardeners show spatial isomery. López-Quintela *et al*. [15] have studied the differences in the cure of DGEBA(*n*=0) using trans-1,2 DCH and cis-1,2 DCH as curing agents by DSC and FTIR. This study shows a big difference between rate constants of the two systems and also between their activation energies.

In the present study, the thermoset DGEBA(*n*=0) was cured using, in one case, the trans isomer of 1,2-diaminocyclohexane and, in the other case, a mixture (30–70%) of cis and trans isomers, respectively. The main objective was to observe the influence of the isomery on properties such as: gel time, vitrification time, conductivity and heat capacity.

Experimental

Materials and sample preparation.

The epoxy resin was diglycidyl ether of bisphenol A (DGEBA *n*=0) (Resin 332, Sigma Chemical Co., St. Louis, MO) with an epoxy equivalent between 172 and 176. The curing agent was 1,2-diaminoyclohexane (DCH) (Fluka, Switzerland) 98% pure with an amine hydrogen equivalent weight of 28.5 and viscosity around 900 mPa s at room temperature. This diamine presents spatial cis-trans isomery. The study was made using the trans isomer in one case and a mixture containing 30% of cis isomer in the second case.

Resin and diamine were carefully and homogeneously mixed at stoichiometric ratio of 100:16.42. Finally, the samples were placed in aluminium pans or spread on ceramic cells for calorimetric and dielectric analysis, respectively.

Calorimetric measurements

The temperature modulated DSC measurements were performed with a TA Instruments Q100. The temperature, heatflow and heat capacity calibrations were performed by standards of indium and sapphire. The modulation conditions used in the quasi-isothermal curing reaction were an amplitude of 0.5 K and a period of 1 min. The DSC experiments were performed at the heating rate of 10 K min^{-1}. The sample mass was approximately 10–14 mg. The calorimetric scans were performed with a nitrogen gas flow of 50 mL min^{-1}. All the calibrations necessary were car-

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ried out according to the manual provided by TA Instruments [16,17].

In MDSC, a sinusoidal modulation was superimposed on a conventional linear cooling or heating ramp to provide a profile in which the average temperature of the sample changes continuously with time but not in a linear way. From a mathematic point of view, this can be written as:

$$T=T_0+\beta t+A_\mathrm{T}\sin(\omega t) \qquad (1)$$

where T_0 is the initial temperature, β is the heating rate, t is the curing time, A_T is the amplitude of the temperature sine wave and ω is the oscillation frequency.

From Eq. (1), the heating rate can be written as:

$$\frac{\partial T}{\partial t}=\beta+A_\mathrm{T}\omega\cos(\omega t) \qquad (2)$$

where $A_T\,\omega$ is the amplitude of the heating rate.

Modulation of temperature originates a modulated heat flow response with an amplitude A_HF.

The complex heat capacity modulus is defined as:

$$\left|C_\mathrm{p}^*\right|=Kc_\mathrm{p}\frac{A_\mathrm{HF}}{A_\mathrm{T}\omega} \qquad (3)$$

where Kc_p is a calibration constant.

The study of the progress of the reaction is based on the measurements of the total heat flow which allows the calculation of the degree of conversion α the same that conventional DSC. The study of the vitrification phenomenon is based on the evolution of $\left|C_p^*\right|$ [9].

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 based on a coplanar interdigitated-comb-like electrode design. The sensors must be calibrated for every experiment. All the experiments were carried out under a dry nitrogen atmosphere at a gas flow rate of 500 mL $\mathrm{min^{-1}}$. The experiments were carried out at 12 different frequencies in the range from 10^{-1} to 10^5 Hz. The total time taken to scan all the different frequencies was 1.2 min.

The principle of this technique consists in placing the sample in a field of alternative voltage and measuring the resulting current and the phase-angle shift induced. The measured current was separated into 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′′. The permittivity, ε′, is proportional to capacitance and measures the alignment of dipoles, and ε′′ is proportional to the conductance and represents the energy required to align dipoles and move ions. Ionic conductivity is calculated as follows:

$$\sigma=\varepsilon_0\varepsilon''w \qquad (4)$$

where ε_0 is the absolute permittivity of free space ($8.85\mathrm{x}10^{-12}$ F/m) and w the pulsation of the applied voltage. When ε′′ is controlled by conductivity, Eq. (4) can be used to calculated σ. This happens in the first steps of curing.

Results and discussion

The glass transition of the fully cured epoxy system DGEBA(n=0)/cis-trans 1,2 DCH was determined from the point of inflection corresponding to the second temperature scan of heat flow using a heating rate of 10 K $\mathrm{min^{-1}}$, obtaining a value $T_{\mathrm{g}\infty}$=154ºC. For the system DGEBA(n=0)/trans-1,2 DCH this temperature was 164ºC [15] This means that the addition of 30% of the cis isomer diminishes by 10ºC the value of $T_{\mathrm{g}\infty}$. The different isothermal experiments were conducted at 50, 60, 70, 80, 90 and 100ºC both in dielectric and calorimetric tests.

Figure 1 shows a plot ε′-t corresponding to an isothermal dielectric analysis of the system DGEBA(n=0)/trans-1,2 DCH at 70ºC. The first zone shows no frequency dependence. This zone corresponds to the relaxed permittivity (ε_r).

Next, ε′ decreases as a consequence of vitrification and finally reaches a new horizontal zone of linear dependency that corresponds to the unrelaxed permittivity (ε_u).

Figure 2 shows a first zone in which ε′′ dramatically decreases. This is due to an ionic contribution that decreases with the cure degree. At larger times, a vitrification peak can be observed.

Figure 3 shows that σ does not depend on frequency at low times. This indicates that the conductivity is the most important contribution to ε′′. Because of this, ionic conductivity can be calculated.

Mangion and Johari [1–4] proposed an equation that relates the ionic conductivity (σ), the curing time (t) and the time to reach gelation (t_gel):

$$\sigma=\sigma_0\left(\frac{t_\mathrm{gel}-t}{t_\mathrm{gel}}\right)^\mathrm{x} \qquad (5)$$

where σ_0 is the conductivity at t=0 and x is a critical exponent that depends on the isothermal cure. See that for $t=t_\mathrm{gel}$, σ=0. In this way, the time necessary for gelation can be easily obtained.

Figures 4 and 5 are plots of σ *vs.* t together with fit to Eq. (5).

Values of the different parameters are listed in Table 1.

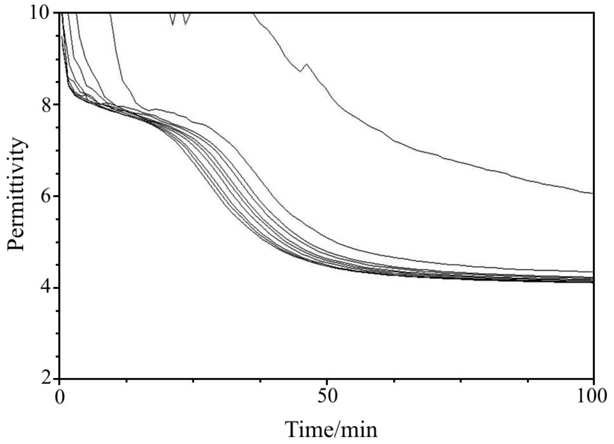

Fig. 1 Plot of ε′ *vs*. *t* corresponding to the isothermal cure at 70ºC, of the system DGEBA(n=0)/trans-1,2 DCH. The frequency decreases in the direction of increasing times

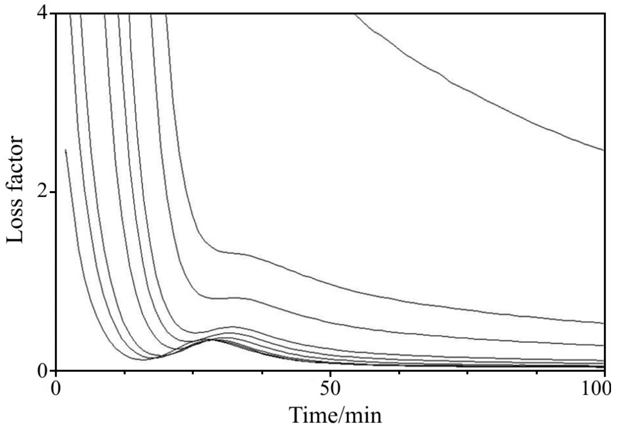

Fig. 2 Plot of ε′′ *vs*. *t* corresponding to the isothermal cure at 70ºC, of the system DGEBA(n=0)/trans-1,2 DCH. The frequency decreases in the direction of increasing loss factor

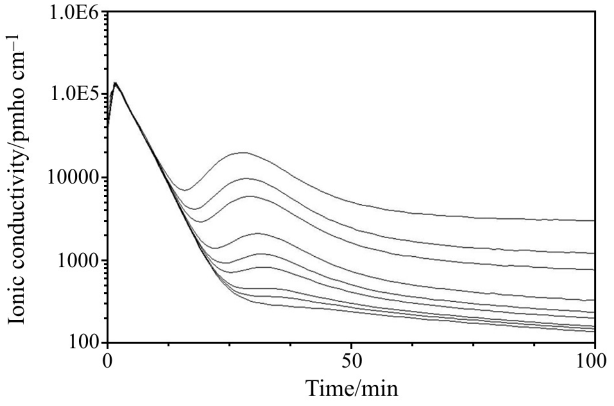

Fig. 3 Plot of δ (ε′′ε$_0$*w*) *vs*. *t* for the isothermal cure, at 70ºC of the epoxy system DGEBA(n=0)/trans-1,2 DCH. The fequency decreases in the direction of decreasing conductivity

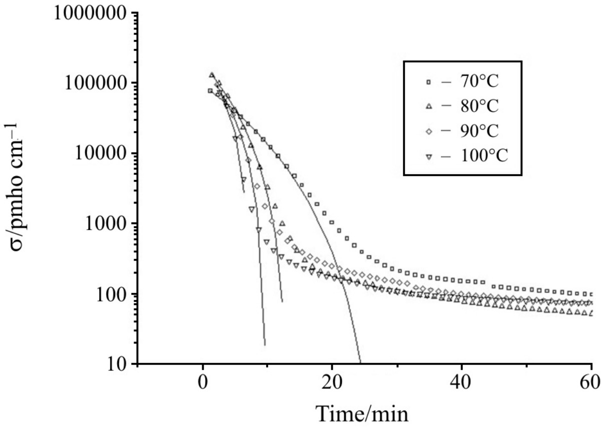

Fig. 4 σ *vs*. *t* corresponding to the cure of the system DGEBA(n=0)/trans-1,2 DCH at 70, 80, 90 and 100ºC

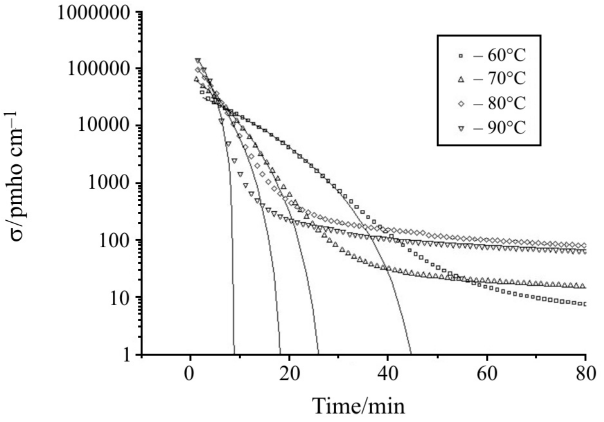

Fig. 5 σ *vs*. *t* corresponding to the cure of the system DGEBA(n=0)/cis/trans-1,2 DCH at 60, 70, 80 and 90ºC and fits through Eq. [5]

In this Table, values of the parameters corresponding to 50ºC are not reported neither for the system DGEBA(n=0)/trans-1,2 DCH nor for the system DGEBA(n=0)/cis/trans-1,2 DCH because of their bad fitting.

It can be observed that σ_0 increases with temperature [1–4]. Also, t_{gel} decreases with temperature being these times very similar for the two systems.

Figures 6 and 7 show plots of the complex heat capacity modulus as a function of the cure time for the two systems.

Figures 7 and 8 show that, at same cure temperature, the complex heat capacity modulus of the system DGEBA(n=0)trans-1,2 DCH is higher than that obtained the isomers mixture.

As it was previously mentioned, time to vitrification is a very important variable in our study. This time can be obtained from the point of inflection of the $|C_p^*|$ *vs*. *t* curve. Table 2 lists time to vitrification for the two systems under study at different tempera-

Table 1 Values of the parameters of the plot σ *vs*. *t*

T/ºC	trans-1,2 DCH			cis/trans-1,2 DCH		
	t_{gel} (s)	*x*	σ_0 (mho/cm)	t_{gel} (s)	*x*	σ_0 (mho/cm)
50	NA	NA	NA	NA	NA	NA
60	46.3	4.42	36732.6	48.5	4.21	38958.1
70	27.8	4.38	94866.1	28.0	4.40	73364.8
80	13.4	3.17	134716.6	19.5	4.32	133268.2
90	9.7	2.45	174548.3	8.7	2.20	207037.0
100	6.9	1.73	201612.2	6.48	1.97	235928.8

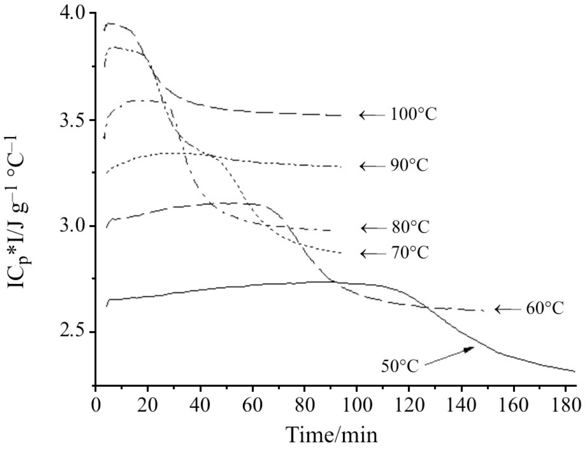

Fig. 6 Complex heat capacity modulus as a function of time, using MDSC for the system DGEBA(n=0)/trans-1,2 DCH

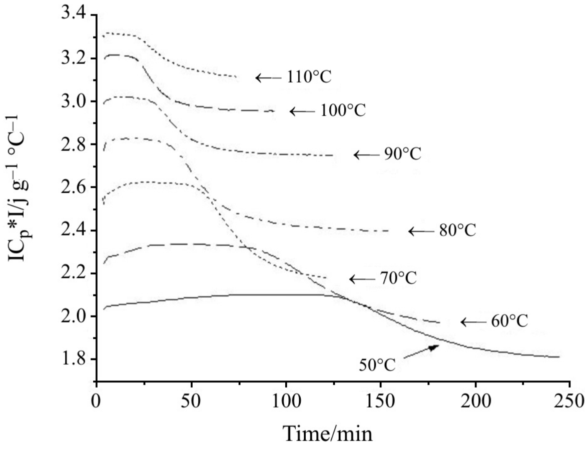

Fig. 7 Complex heat capacity modulus as a function of time using MDSC for the system DGEBA(n=0)/cis/trans-1,2 DCH

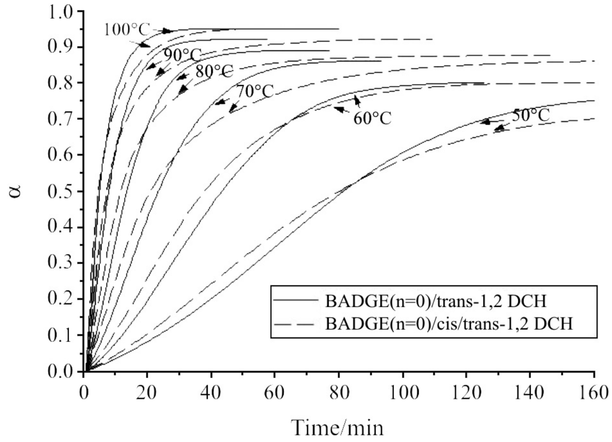

Fig 8. α *vs*. *t* at different isothermal cure temperatures for the two systems

Table 2 Vitrification times taken as those corresponding to the points of inflection of the curves shown in Figs 6 and 7 for the systems DGEBA(n=0)/trans-1,2 DCH and DGEBA(n=0)/cis/trans 1,2 DCH

T/ºC	*t*(min)1,2 DCH trans	*t*(min) 1,2 DCH cis/trans
50	135.6	149.7
60	76.2	108.3
70	53.7	67.5
80	31.8	47.0
90	23.6	31.9
100	17.8	26.2
110		26.1

tures in the range from 50 to 100ºC (and 110ºC for the mixture of isomers).

As it can be seen in Table 2, the times to vitrification for the system DGEBA(n=0)/cis/trans-1,2 DCH are always higher than those corresponding to the trans isomer. This can be due to the lower reactivity of the cis isomer. López-Quintela *et al.* [15] report on the different space configuration of both isomers. However, in the first stages of curing, that is at low α values, the cis isomer originates a catalytic effect and for this reason, gel times are very similar. Figure 8 is a diagram showing the behaviour of α as a function of time for the two systems. It can be seen that, as a consequence of the catalytic effect, the system with a mixture of isomers reaches, at a given time, higher conversions than the trans system. This happens up to times where α has values in the range 0.4–0.7 depending on the isothermal curing temperature. However, at times corresponding to conversions greater than 0.7, the system containing the trans isomer reaches higher α values than that containing the cis-trans mixture.

Conclusions

It was found that the use of a mixture containing 30 and 70% of the cis and trans isomers respectively of 1,2 DCH diminishes the maximum conversion at a given temperature and also decreases the $T_{g\infty}$ of the system in 10ºC.

Gel times for the systems DGEBA(n=0)/trans-1,2 DCH and DGEBA(n=0)/cis/trans-1,2 DCH as measured by dielectric analysis are very similar, while times to vitrification, as measured by modulated scanning calorimetry differ widely. This behaviour can be understood on the bases of a catalytic effect at first stages of curing in the case of the cis isomer that originates that conversions reach higher values for the mixture of isomers at low values while with the increase of conversion, because of its geometry, the reactivity of the cis isomer slows and, because of this, the reactivity of the isomers mixture.

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