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TTT CURE DIAGRAM
Epoxy system diglycidyl ether of bisphenol A and *m*-xylylenediamine

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Abstract

Curing reactions of the epoxy system consisting of a diglycidyl ether of bisphenol A (BADGE n=0) and *m*-xylylenediamine (*m*-XDA) were studied to calculate time-temperature-transformation (TTT) isothermal cure diagram for this system. Gel times were measured as a function of temperature using solubility test. Differential scanning calorimetry (DSC) was used to calculate the vitrification times. DSC data show a one-to-one relationship between T_g and fractional conversion, α independent of cure temperature. As a consequence, T_g can be used as a measure of conversion. The activation energy for the polymerization overall reaction was calculated from the gel times obtained using the solubility test (41.5 kJ mol^{-1}). This value is similar to the results obtained for other similar epoxy systems. Isoconversion contours were calculated by numerical integration of the best fitting kinetic model.

Keywords: DSC, epoxy-amine reactions, TTT diagram

Introduction

Curing reactions of thermoset materials originate a tridimensional network after chemical reaction of the epoxy resin and the appropriate hardener. During the cure process of a thermoset, the glass transition temperature (T_g) of the material increases as a consequence of the increase in the crosslinking density, and an increase on the molecular weight [1]. Because of this there is a decrease in the free volume of both epoxy groups and primary amine not reacted due to the fact that some chains become hindered in an infinite molecular weight network. The transformation from a viscous liquid to an elastic gel is sudden and irreversible and marks the first appearance of the infinite network; it is called the gel point. Gelation is characteristic of thermosets and it occurs at a well-defined and calculable stage in the course of the reaction that is at specific values of conversion and T_g. Another phenomenon that may occur at any stage during cure is vitrification. This transformation from a viscous liquid or elastic gel to a glass begins to occur as the glass transition temperature of the system be-

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comes coincidental with the cure temperature. The vitrification point marks a change in the reaction mechanism passing from chemically kinetically controlled to become diffusion-controlled. Samples vitrified during an isothermal curing (T_g>T_c) show an endothermic physical aging peak in the vicinity of T_g [2].

The isothermal time-temperature-transformation (TTT) cure diagram, which was developed to study epoxy systems, is a very useful tool in order to study cure processes of epoxy systems [3, 4]. This diagram is calculated by plotting the experimental times to reach various events during isothermal cure *vs*. cure temperature.

The TTT isothermal cure diagram records the phenomenological changes that occur during the cure reaction of the epoxy, such as vitrification and macroscopic gelation. Other different contours can be included in this diagram, such as carbonization (char) or thermal degradation curve and isoconversion or iso-T_g curves, in which full cure or maximum experimental isoconversion is included.

Experimental

Materials

The thermosetting system studied is a stoichiometric mixture of epoxy resin-diamine. The epoxy resin is a liquid diglycidyl ether of bisphenol A (BADGE n=0) (Resin 332, Sigma Chemical Co. St. Louis, USA) with an equivalent epoxy molecular mass of 173.6 g eq^{-1}, as determinated by wet analysis [5, 6]. The curing agent was metaxylendiamine 99% (m-XDA) (Aldrich). It was used as received.

Techniques

Experimental data reported in this work were obtained from DSC studies using a Perkin Elmer DSC-7 unit under a control of a 1020 system controller. The calorimeter was used to measure glass transition temperatures, and it was operated in both dynamic and isothermal modes.

Dynamic experiments were carried out in a temperature range from –50 to 250°C. Owing to the low temperature necessary for the performance of measurements, a cooling device (Intercooler II supplied by Perkin Elmer) was adapted to the DSC-7 equipment. The calorimeter was calibrated following the procedure given in the Perkin Elmer DSC-7 Manual [7]. Two standards (indium and bidistilled water obtained by the Milipore method) were used.

Five to seven milligram samples of uncured resin were sealed in aluminium pans and cured in the preheated DSC unit at isothermal cure temperatures from 60 to 110°C for various cure times.

These samples were then quenched to –50°C in order to keep them at their polymerization state [8, 9]. The samples were then scanned to 250°C at 5°C min^{-1}. This heating rate value was found to be the optimum in order that further relaxation of the glass to its equilibrium rate would not proceed during the heating period, and T_g would be independent of the heating rate.

It was mentioned that as thermosetting cures, its glass transition temperature increases from a minimum, initial value, T_{g0}, to a maximum value, $T_{g\infty}$, which corresponds to the fully cured material. For the epoxy system reported in this article, both values were measured in our laboratory, resulting in $T_{g0}=-35.76$°C and $T_{g\infty}=126.10$°C.

Results and discussion

Gelation study

Gelation is a phenomenon that takes place during thermosetting polymer cure reactions. It corresponds to the incipient formation of a network with an infinite mass average molecular mass. Gelation occurs at a well-defined stage in the cure reaction and is dependent on the stoichiometry, functionality, and reactivity of the reactants. This phenomenon typically occurs to conversions between 55 and 80% (conversion degree = 0.55–0.80).

According to Flory [10], for epoxy-diamine reactions, gelation occurs when conversion degree reaches the following value:

$$\alpha_g = \sqrt{\frac{B}{3}} \tag{1}$$

where B is the ratio of amine hydrogen equivalents to epoxide equivalents initially. In our case $B=1$ as stoichiometric quantities are mixed. This leads to a value of $\alpha_g=0.58$, that is, 58% of conversion.

Prior to gelation, the polymers remain soluble in suitable solvents; after gelation, samples show a rubber viscoelastic behavior and become insoluble.

As a cure reaction proceeds, the molecular mass increases, and several chains link together into networks of infinite molecular mass. This sudden and irreversible transformation from a viscous liquid to an elastic gel is the gel point; and the time at which it occurs, at a given isothermal cure temperature, is the gel time. This gel time can be experimentally determined following different procedures. In the present study, we have followed the solubility test.

Solubility test

In this method, the time to reach a fibriform structure in tetrahydrofurane is measured [11]. The experimental method is as follows. An aluminium can containing the sample is introduced into a thermostated bath filled with polyethylene glycol. The sample was continuously shaken; and at different times, a part of it was taken out of the container and poured into a beaker containing tetrahydrofurane. This was done to determine the time necessary for the sample to become insoluble at which a fibriform structure is visualized. Table 1 shows the gel formation (gel times) and the corresponding conversions at the different temperatures used in this study.

Table 1 Times and conversions at gel point from the solubility test

T/°C	t_{gel}/min	α
110	3.44	0.60
100	4.41	0.50
90	5.00	0.30
80	8.00	0.29
70	14.20	0.24
60	25.10	0.25

The overall activation energy for the cure reaction process can be obtained from gel time data assuming that all reactions taking place during the curing process can be described through differential equations containing one unique apparent activation energy, E_a, according to the following equation [12, 13]:

$$\frac{d\alpha}{dt}=Ae^{-E_a/RT}f(\alpha) \tag{2}$$

where A is a constant, E_a is the apparent activation energy for the overall curing reaction, T is the isothermal curing temperature, and $f(\alpha)$ is a temperature independent function of conversion.

Integration of Eq. (2) from $\alpha=0$ to $\alpha=\alpha_g$ and taking natural logarithms gives

$$\ln\int_0^{\alpha_g}\frac{d\alpha}{f(\alpha)}=\ln A+\ln t_g-\frac{E}{RT} \tag{3}$$

The left hand side of this equation is temperature independent, so:

$$\ln t_g=\text{const}+\frac{E}{RT} \tag{4}$$

The activation energy can be calculated as the slope of a $\ln t_g$ *vs.* $1/T$ plot. Using the gel times reported in Table 1, an activation energy of 41.5 kJ mol^{-1} was obtained for the epoxy system under study. This value is similar to those obtained for other similar epoxy systems [14–23].

Vitrification study

DSC plots of dH/dT as a function of T show an endothermic step change in heat capacity at the glass transition. Glass transition temperature, T_g, is taken as the midpoint of this transition [8].

Figure 1 shows T_g values as a function of cure time t_c, for the different isothermal cure temperatures. As can be seen, T_g increases rapidly with cure time up to vitrification time, at which T_g=T_c [14]; then the increase in T_g becomes slower, owing to diffusion effects. In this sense, t_v denotes the time at which incipient vitrification takes place. For $t>t_v$, two different effects are associated with the further increase of T_g: on the one hand, con-

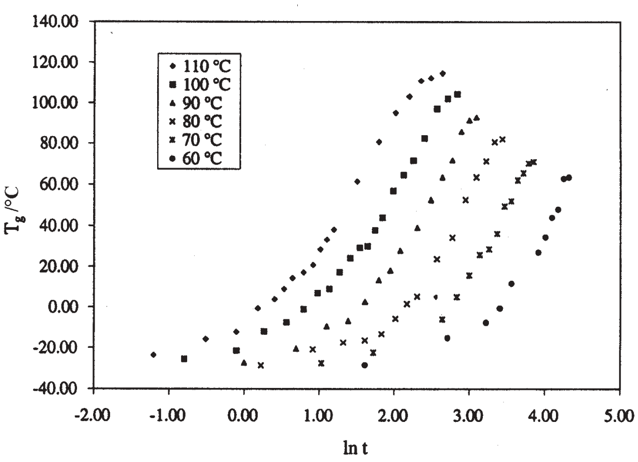

Fig. 1 T_g values *vs.* cure time

version continues to increase, although at a greatly diminished rate; on the other hand, physical aging of the sample with were in the glassy state leads to an increase in T_g. To remove all traces of physical aging, it is necessary to heat the samples, which were previously cooled, to a temperature just beyond the observed T_g followed by a rapid cool and a second heat to determine the correct T_g. This procedure can be employed when the curing rate during the first heating may be neglected. In order to get T_g *vs.* α relationship, it is recommended to use T_g *vs.* ln*t* plot only up to t_v [8].

The experimental T_g *vs.* α DSC data are shown in Fig. 2. It can be noted that the relationship between T_g and conversion is independent of cure temperature. This fact agrees with studies reported in the literature [8, 9]. The one-to-one relationship between T_g and conversion implies that either the molecular structure of the materials,

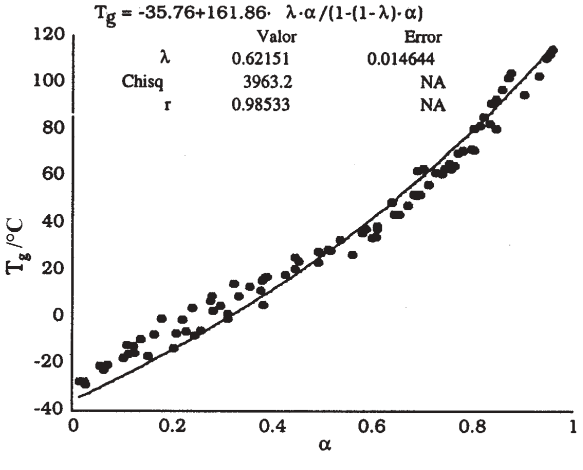

Fig. 2 T_g values *vs.* α DSC data

cured at different temperatures, does not present significant changes, if it does, the changes do not have a significant effect on the glass transition temperature (i.e., the differences in structure occur on a size scale smaller than that measured by T_g).

Nielsen reported a modified form of the empirical DiBenedetto equation [24]:

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda\alpha}{1-(1-\lambda)\alpha} \tag{5}$$

where T_{g0} is the T_g of uncured monomer, $T_{g\infty}$ is the maximum glass transition temperature obtained experimentally for the fully cured material, and λ is taken as an adjustable structure-dependent parameter between 0 and 1. Pascault and Williams [24] show that λ is theoretically equated to $\Delta C_{p\infty}/\Delta C_{p0}$, where $\Delta C_{p\infty}$ and ΔC_{p0} are the differences in heat capacity between the glassy and rubbery (or liquid, prior to gelation) states at T_g for the fully cured network and monomer, respectively.

The DiBenedetto equation will be used when it is necessary to convert T_g to conversion and viceversa. In order to calculate vitrification times, DSC data of experimental T_g *vs.* α were fitted to the DiBenedetto equation, as is shown in Fig. 2. In this equation, λ is treated as an adjustable parameter and was determined to be 0.6215. Application of this equation, using the value of α=0.58 given by the Flory theory, led to the calculation of ${}_{gel}T_g$=38.99°C.

Table 2 Vitrification time at various isothermal cure temperatures

T/°C	t_v/min
60	74.20
70	42.89
80	28.80
90	22.70
100	14.80
110	9.19

Vitrification times corresponding to the different isothermal cure temperatures are shown in Table 2.

TTT diagram

The TTT isothermal cure diagram was calculated from the contours of the time to gel and to vitrify as a function of the reaction temperature (Fig. 3). Data were fitted to curves, taking into account that the gelation curve and vitrification curve intersect at the curing time, corresponding to ${}_{gel}T_g$ calculated using the DiBenedetto equation and the value of α=0.58 (theoretical gelation). Isoconversion curves corresponding to α=0.33, 0.50, 0.58, 0.68, 0.8, 0.88, and 0.97 are plotted. These curves were calculated by numerical integration of the best fitting kinetic model [16, 21].

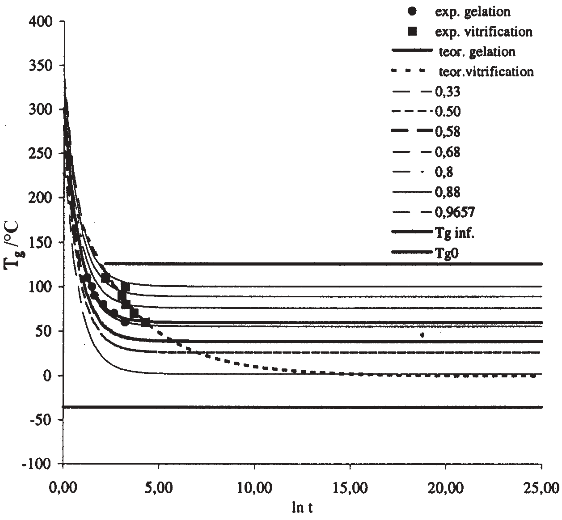

Fig. 3 TTT isothermal curve diagram

The isoconversion curve α=0.97 corresponds to the maximum achievable experimental extent of conversion.

To plot a TTT diagram, it is necessary to know three principal temperatures: T_{g0}, the initial T_g of the system; ${}_{gel}T_g$, the temperature at which vitrification and gelation occur simultaneously (i.e., the temperature at which the conversions for vitrification and gelation are the same); and $T_{g\infty}$, the maximum glass transition temperature of the fully cured system.

For the system studied here (BADGE-*m*XDA), T_{g0} and $T_{g\infty}$ were experimentally determined; and ${}_{gel}T_g$ was calculated using the DiBenedetto equation and the value α=0.58, which corresponds, according to Flory, to the theoretical gelation. Values of T_{g0} and $T_{g\infty}$ were measured by DSC. ${}_{gel}T_g$ was determined as the temperature corresponding to the intercept of gelation and vitrification curves in a T_c *vs.* ln*t* plot. The values of the three characteristic temperatures were T_{g0}= –35.76°C, ${}_{gel}T_g$=38.99°C, and $T_{g\infty}$=126.10°C.

According to the TTT cure diagram, as a thermosetting material cures, its glass transition temperature increases with the extent of conversion. When the T_g reaches the value of the isothermal cure temperature, T_c, the material vitrifies. In the vicinity of vitrification, the segmental mobility decreases, and the overall rate of the reaction may become controlled by the limiting diffusion of reacting species.

T_{g0} (–35.76°C) corresponds to the glass transition temperature of the material with the degree of conversion α=0. Below this temperature, the thermoset is a glassy solid soluble in suitable solvents. The system does not react below T_{g0}.

${}_{gel}T_g$ (38.99°C) is the temperature at which the system gels and vitrifies simultaneously.

Between T_{g0} and ${}_{gel}T_g$ (–35.76<T_c<38.99°C), the system will react until its continuously rising glass transition temperature becomes coincidental with the cure temperature. At this stage vitrification will begin and the reaction becomes diffusion controlled, so gelation may not be achieved. For vitrification below ${}_{\text{gel}}T_g$, the resulting material will have a low molecular mass and it will flow on heating. $T_{g\infty}$ (126.10°C) is the maximum temperature at which glass transition can be achieved. Between ${}_{\text{gel}}T_g$ and $T_{g\infty}$ ($38.99<T_c<126.10$°C), gelation precedes vitrification.

After gelation, the curing sample contains sol as well as gel fractions. The gel initially formed is weak and can be easily disrupted. To produce a structural material, cure has to continue until most of the sample is connected into the three-dimensional network, in which case, the sol fraction becomes small; and for many cured materials, it has to be essentially zero. If the material achieves the maximum extent of conversion, no soluble fraction is present.

If the cure reaction is above $T_{g\infty}$ (126.10°C), no vitrification occurs; thus the reaction is kinetically controlled, and total conversion may be theoretically achieved. However, as time increases, a great amount of material is thermodegraded so that its useful properties are lost.

From the TTT isothermal cure diagram, the cure conditions for the cure reaction of an epoxy system studied may be determined.

From the observation of the TTT diagram for the system BADGE (n=0)/mXDA, it can be deducted that a cure at 40°C for 20 min and then 28 min at 105°C will allow an optimum result with a final conversion coincidental with the maximum achievable extent of conversion at $\alpha=0.97$. These optimum properties were corroborated studying the dynamomechanical properties as well as the thermodegradation process and the lifetime of the system cured with the conditions indicated.

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