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Diffusion control on the cure kinetics of DGEBA with ethylenediamines

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Abstract

The cure kinetics of DGEBA with aliphatic diamines was studied on the diffusion-controlled region. Two different diamines (ethylene-diamine (EDA) and N-(methyl)ethylenediamine (MEDA)) were selected, to achieve different cross-linked networks. Additionally, reaction of DGEBA with butylamine was followed to compare non-cross-linked systems with the above mentioned ones. Curing temperatures were between 20 and 60 °C. Concentrations of epoxy and primary amine functionality were both followed by near FTIR, and T_g was analyzed by DSC. An autocatalytic model was applied. Diffusion control kinetic in cross-linked polymers was analyzed in terms of free volume decrease. In that region, a model based on a WLF equation provides a good fi to the experimental data.

1. Introduction

Of all the thermosetting polymers, curing of DGEBA with amines has probably been the most extensively studied. Earlier work of Horie et al. [1] analyzed successfully the reaction by two different paths, one of them catalyzed by hydroxyl groups, which supplies a suitable mechanism for the polymerization reaction. This work was later modifie with no significan variations [2–4].

Nevertheless, epoxy curing leads to a highly cross-linked polymer with higher glass transition temperatures. At the last stage the reaction becomes diffusion-controlled and the classical kinetic scheme is not applicable. The proposed models for this region point to two directions. A classical approach [5] gives diffusion-controlled reaction rates in terms of $(T - T_g)$ from a semiempirical WLF relationship. T is the curing temperature and T_g is the glass transition temperature of the system, and it is taken as the reference temperature. Actually, T_g is dependent on conversion, increasing with time. The model loses it relation with the theoretical argument on which it is based, i.e., the free volume change in the system. What is more, the determination of glass transitions in highly cross-linked polymers is sometimes difficul The second approach is the application of semiempirical methods [6,7], which relate diffusion-controlled reaction rates with chemical reaction rate by exponential functions of $\alpha - \alpha_C$, where α_C is a critical conversion corresponding to the beginning of the diffusion control. α_C is difficul to evaluate with precision, so the diffusion control stage remains unsolved.

In this work we have studied the cure kinetics of the well-known system DGEBA/ethylenediamine (EDA), as well as other amines which lead to different cross-linked structures. Kinetics was followed at temperatures where vitrificatio occurs in the system and data were collected for a long time in that region.

2. Experimental

2.1. Materials

Bisphenol-A diglycidyl ether (DGEBA) (Aldrich, molecular weight 348 g/mol) was degasifie prior to use. EDA, N-(methyl)ethylenediamine (MEDA) and n-butylamine (n-BuA) were also Aldrich products. Both amines were boiled under reflu over potassium hydroxide and rectifie under nitrogen atmosphere.

2.2. Methods

2.2.1. Differential scanning calorimetry (DSC)

A Perkin Elmer DSC-7 differential scanning calorimeter equipped with a standard Perkin Elmer cooling unit was used for measurement. Samples of weight 10–15 mg were employed. The glass transition temperature of stochiometric

mixtures of DGEBA with the amines was measured for different curing degrees, with the computer software supplied by PE. Tests were performed from −50 to 150 °C at a heating rate of 10 °C min^{-1}.

2.2.2. Fourier transform infrared spectroscopy (FTIR)

A Perkin Elmer GX FTIR spectrometer was used to monitor the rate of disappearance of the epoxy ring and primary amino groups. All spectra were collected in the near IR (7000–4000 cm^{-1}). Each spectrum was obtained depending on the curing temperature, by averaging 4–20 scans at 4 cm^{-1} resolution with scanning rate (OPD) of 0.2 cm s^{-1}. Measurements at 40 and 60 °C were carried out using a temperature controller SPECAC. The epoxide formulations were cured in disposable cells made from microscope-glass slide plates, with an optical path of 1.0 mm determined by the thickness of a Teflo spacer. The values of absorbance and integrated absorbance corresponding to ultimate curing were obtained after curing at 180 °C (DGEBA/n-BuA) or 200 °C (DGEBA/EDA and DGEBA/MEDA) for at least 2 h.

Band assignation was done according to literature [8–10]. The main features in spectra are: (i) a decrease in the epoxi band at around 4530 cm^{-1}; (ii) a decrease in the primary amine group at 4938 cm^{-1}; (iii) an increase in the hydroxyl band in the region around 4800 cm^{-1}. An isosbestic point between the disappearance of the epoxy band and the appearance of the hydroxyl group indicates that both are directly related and Beer's law is obeyed over a wide range of conversion [8]. Integrated absorbance was done at two different wavelengths, one corresponding to the reacting group and the other to an invariant CH band. Band areas were referred to the invariant one.

3. Results and discussion

3.1. Curing of DGEBA with the amine systems

3.1.1. T_g vs. conversion

In Fig. 1 the variation on the glass transition temperature with epoxy conversion is represented for the three systems studied. The infinit T_g (i.e., the T_g for $\alpha = 1$) is about 115 °C for DGEBA/EDA, 63 °C for DGEBA/MEDA, and 0 °C for DGEBA/n-BuA. Good fi to the classical DiBenedetto equation [11] were achieved for the firs one. T_g on DGEBA/n-BuA is almost invariable because there is no cross-linking on the system. T_g of DGEBA/MEDA does not have a good fi and has an anomalous variation for thermosetting polymers. The T_g of this system increases faster at medium conversions compared to higher conversions. As will be stated later, for this system tertiary amine appears in the early stages of the reaction and it can be responsible for this behavior.

3.1.2. Reaction mechanism

A modificatio of the classical kinetic mechanism developed early by Horie et al. [1] was applied. This model takes into account two different reaction pathways, autocatalyzed and non-catalyzed. For stochiometric mixtures the following expression is achieved for a diepoxide/primary amine mixture:

$$\frac{d\alpha}{dt} = (1 - \alpha)(\lambda + R)(B - 2\lambda - \alpha)$$
$$\times \left[K_1' + K_1 \left(\frac{c_0}{e_0} + \alpha \right) \right] \qquad (1)$$

where α is the epoxy conversion, e_0 and c_0 are the initial concentrations of epoxide and catalyst, respectively. B is a
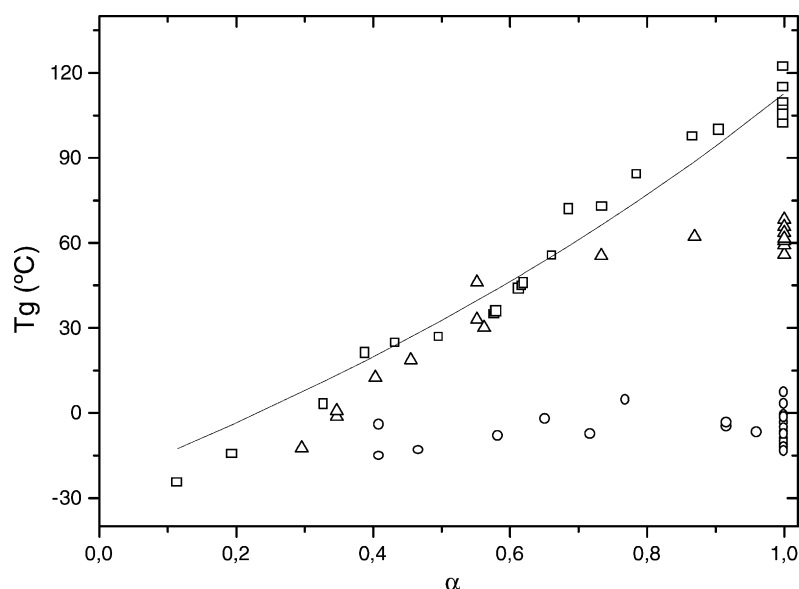

Fig. 1. Plot of glass transition temperature (T_g) vs. epoxy conversion: DGEBA/EDA (squares), DGEBA/MEDA (triangles) and DGEBA/n-BuA (circles). Fit line was made with Dibenedetto equation.
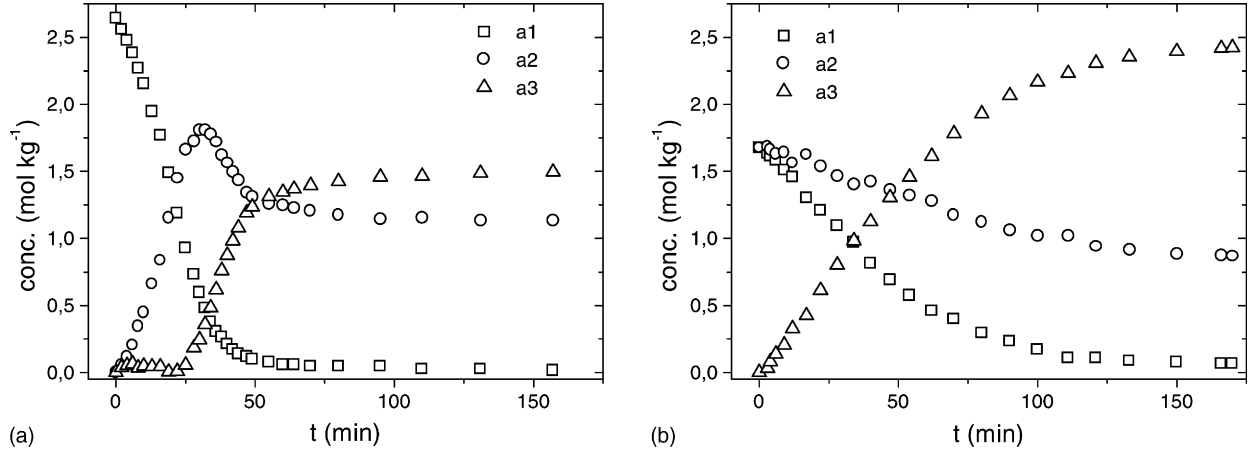
Fig. 2. (a) Time variation of the primary, secondary and tertiary amine for the DGEBA/EDA system at 60 °C. (b) Time variation of the primary, secondary and tertiary amine for the DGEBA/MEDA system at 40 °C.

constant, which means the initial ratio primary amine/epoxy ($B = 2a_{1.0}/e_0$) and λ the ratio primary amine/e_0 ($\lambda = a_1/e_0$). K_1 and K_1' are the global rate constants for the autocatalyzed and the non-catalyzed pathways, respectively. R represents the ratio of the rate constants k_2/k_1 (or k_2'/k_1') for the conversion of secondary amine into tertiary amine or from primary into secondary amine. Further details were published elsewhere [12]. In the case of the DGEBA/MEDA system, we found a very similar equation with only substitute B for $3/2B$ ($B = 2a_{1.0}/e_0 = 2a_{2.0}/e_0$).

The concentration of epoxy and primary amine was directly evaluated from the experimental data, and the concentration of secondary and tertiary amine were obtained by mass balances, which have the following expressions for n-BuA and EDA:

$$a_2 = e_0(\beta - \alpha) \tag{2a}$$

$$a_3 = e_0(\alpha - \beta/2) \tag{2b}$$

where β is the conversion of primary amino groups. In Fig. 2a the time dependence of concentration of primary, secondary and tertiary amine is shown for the DGEBA/EDA system at 60 °C. For the DGEBA/MEDA system there are two types of secondary amino groups, the ones formed by reaction of the primary amine with an epoxy group, and sec-

ondary amino groups already present in the MEDA at the beginning of the reaction. Mass balances can be modified leading to Eqs. (3a) and (3b):

$$a_2 = 2a_{1.0}\beta - e_0\alpha + a_2^N \tag{3a}$$

$$a_3 = e_0\alpha - a_{1.0}\beta \tag{3b}$$

where a_2^N and a_3^N are the concentration of secondary and tertiary amine attached to the methyl group, respectively. The time dependence of primary amine, overall secondary amine and tertiary amine concentration is shown in Fig. 2b for the DGEBA/MEDA system at 40 °C. Unlike the DGEBA/EDA system, the concentration of tertiary amine does not have an induction period, and begins to appear at very low conversions.

If we consider the reaction rate for the primary amine, the following expression can be derived in all cases:

$$\frac{(da_1/dt)(1/a_1)}{1 - \alpha} = K_1' + K_1\left(\frac{c_0}{e_0} - \alpha\right) \tag{4}$$

By plotting the firs term of Eq. (4) against α we have obtained the values for the reaction rate constants that figur in Table 1. The ratio between constants $R = k_2/k_1 = k_2'/k_1'$ was obtained by the method described by Paz-Abuin et al. [13]. Its value is about 0.2–0.25 for all the systems.

Table 1
Reaction rate constants for the epoxy/amine systems studied[a]

System	Temperature (°C)	K_1' (min^{-1})	K_1 (min^{-1})	k_1' (kg mol^{-1} min^{-1})	k_1 (kg^2 mol^{-2} min^{-1})
DGEBA/EDA	20	$(1.15 \pm 0.2) \times 10^{-3}$	$(1.26 \pm 0.2) \times 10^{-2}$	$(2.2 \pm 0.4) \times 10^{-4}$	$(4.5 \pm 0.5) \times 10^{-4}$
	40	$(4.13 \pm 1.0) \times 10^{-3}$	$(5.80 \pm 1.2) \times 10^{-2}$	$(7.8 \pm 1.9) \times 10^{-4}$	$(20.7 \pm 4.3) \times 10^{-4}$
	60	$(14.8 \pm 1.3) \times 10^{-3}$	$(13.8 \pm 2.3) \times 10^{-2}$	$(28.0 \pm 2.5) \times 10^{-4}$	$(49.2 \pm 9.3) \times 10^{-4}$
		51.7 ± 1.9[b]	(48.7 ± 5.9)[b]		
DGEBA/MEDA	40	$(10.6 \pm 1.0) \times 10^{-3}$	$(5.70 \pm 0.9) \times 10^{-2}$	$(21.1 \pm 2.0) \times 10^{-4}$	$(22.5 \pm 3.6) \times 10^{-4}$
DGEBA/n-BuA	40	$(3.55 \pm 0.2) \times 10^{-3}$	$(5.50 \pm 0.2) \times 10^{-2}$	$(7.5 \pm 0.2) \times 10^{-4}$	$(24.3 \pm 2.2) \times 10^{-4}$

[a] For DGEBA/EDA system activation energy was calculated.
[b] E_a (kJ mol^{-1}).

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From the results presented in Table 1 we can conclude the following features. (i) The reaction rate constants for the catalyzed processes are two times higher than the ones for the non-catalyzed processes. (ii) Good agreement between constants at 40 °C with n-BuA and EDA as hardeners shows that the initial reaction mechanism is the same and, therefore, independent of amine functionality. (iii) The reaction rate constant for the system DGEBA/MEDA strongly disagrees with the above mentioned, being greater for the non-catalyzed process. The methyl substituent on the amino group seems to increase the reaction rate only for the non-catalyzed process. That means that a kinetic model based on similar reactivities for all the secondary amino groups is not accurate.

3.1.3. Autoacceleration

The theoretical curves obtained using the rate constants shown in Table 1 provide good fit till $\alpha < 0.3$, except for DGEBA/MEDA system, where α_{exp} is always above the predicted. An autoacceleration phenomenon was observed and was interpreted in terms of an excluded volume factor, f, define as $f = 1/(1 - V_{ex}/V_T)$ [12], where V_T is the total volume in the reaction mixture and V_{ex} the excluded volume to the surplus reactants. That is, V_{ex} is the volume occupied by branched high molecular weight species. We can now defin an effective concentration c^* of epoxy and amine define as $c^* = cf$ and the kinetic equation (1) is modifie by multiplying the reaction rate constants K'_1 and K_1 by the f factor squared and cubed, respectively.

For the initial mixture $f = 1$, and it increases gradually with the conversion till a point where the reaction becomes diffusion-controlled. In Fig. 3 fit of the modifie Eq. (1) to the experimental data for DGEBA/EDA and DGEBA/n-BuA at 40 °C are represented.

The beginning of the diffusion-controlled region is clearly observed on the cross-linked system. For the non-cross-linked system, good fit are achieved during the entire interval. Nevertheless, for DGEBA/EDA, predictions clearly lead to higher conversions than the experimental ones for

$\alpha > 0.40$ at 20 °C, $\alpha > 0.55$ at 40 °C and $\alpha > 0.62$ at 60 °C, in other words, at conversions 20% below the ultimate conversion for each temperature.

3.2. Diffusion-controlled region

Diffusion-controlled kinetic rate constants were included applying the Rabinovitch model [14]:

$$\frac{1}{K_E} = \frac{1}{K} + \frac{1}{K_D} \tag{5}$$

where K_E is the overall rate constant, K the rate constant (chemical) and K_D the diffusion-controlled rate constant. We can now replace K_1 and K'_1 with K_E and K'_E in Eq. (1). One assumes bimolecular mechanism for the two processes. That can be done because the catalyzed process consists really of a fast activation stage followed by a slow reaction stage [15]. Here K_E and K'_E have the following expressions, where k_d and k_{dc} are the diffusion-controlled rate constant for the non-catalyzed and the autocatalyzed process, respectively

$$K'_E = e_0 \left(\frac{1}{k'_1 f^2} + \frac{1}{k_d} \right)^{-1} \tag{6a}$$

$$K_E = e_0^2 \left(\frac{1}{k_1 f^3} + \frac{e_0}{k_{dc}} \right)^{-1} \tag{6b}$$

Analytical solution for the above mentioned equations is not possible. A non-linear Newton algorithm was used to fin numerical solutions. Fig. 4 shows the values obtained for k_d and k_{dc} for the system DGEBA/EDA at 60 °C. One observes that initially only k_{dc} decreases with conversion whereas k_d remains unchanged and its value is near 1. According to this result, diffusion control in the early stage is of the vitrificatio region acts over the autocatalyzed path but, at a certain conversion (marked with a row in the figure) the non-catalyzed path begins to be diffusion-controlled too. This conversion is 0.76 for curing at 60 °C, 0.70 for curing at 40 °C and 0.57 for curing at 20 °C, which corresponds to
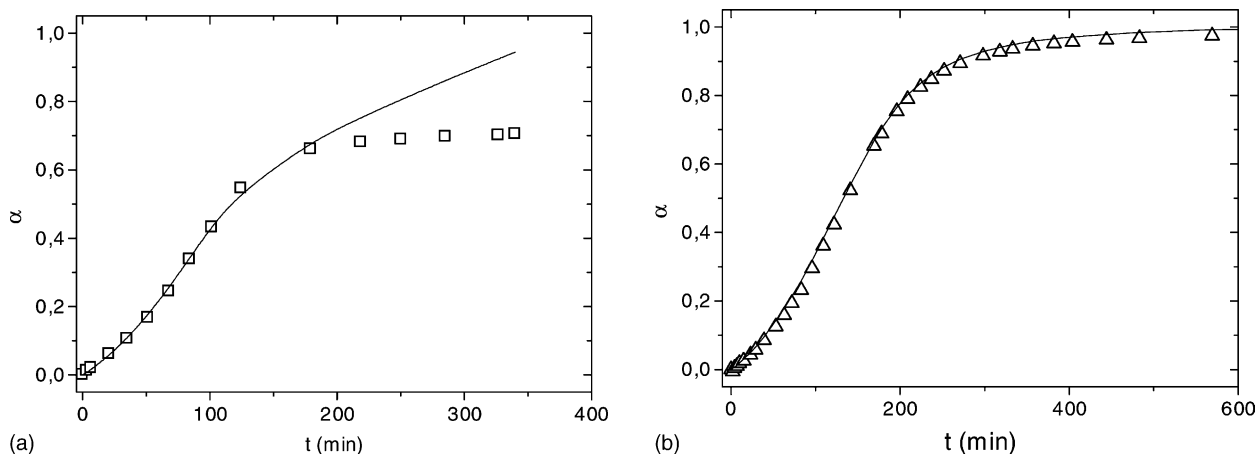

Fig. 3. Time variation for epoxy conversion at 40 °C: (a) DGEBA/EDA at 40 °C; (b) DGEBA/n-BuA at 40 °C. Fit lines were made by plotting Eq. (1) modifie with f factor (see text).
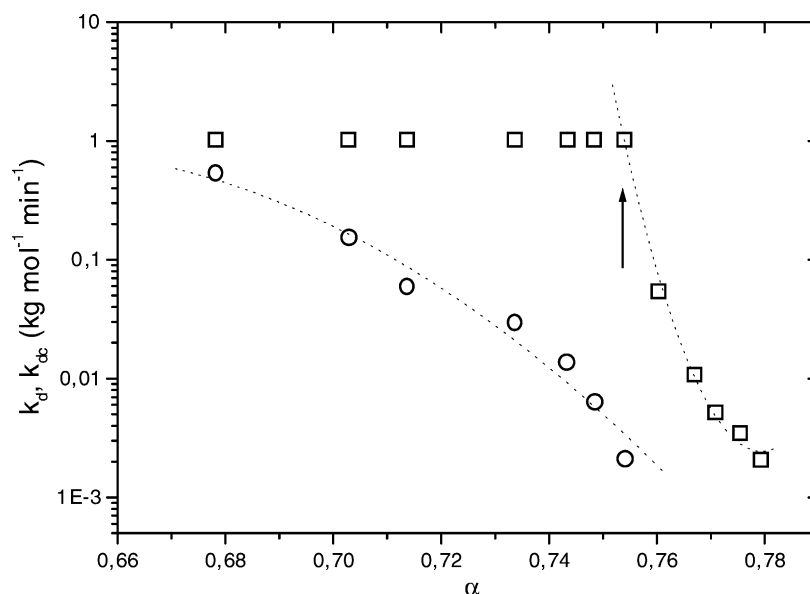
Fig. 4. Logarithmic plot of diffusion-controlled reaction rate constants with conversion for the non-catalyzed path (squares) and for the autocatalyzed path (circles). DGEBA/EDA system at 60 °C.

glass transition temperatures (Fig. 1) of 70, 61 and 42 °C, respectively.

This approach allows differentiating between the two different processes. The firs process to become diffusion-controlled is the autocatalyzed path. When the curing is only 5% far from the limit conversion, and the T_g of the thermoset is at least 10 °C higher than the curing temperature, the non-catalyzed process begin to become diffusion-controlled too, and it is responsible for the last advances in the reaction before complete vitrification

Assuming a linear relation between epoxy conversion and T_g of the thermoset (this is a good approach only for low conversion intervals, as can be seen in Fig. 1), a modifie WLF equation with the form $\log(k_d/k_{d,r}) = \mathrm{P1}(\alpha - \alpha_r)/[\mathrm{P2} + (\alpha - \alpha_r)]$ can be used to fi k_d values, with the reference state fi ed to from the point where $k_d < 1$ on. Values of P1 and P2 were interpreted according to the WLF equation. f_r (the free volume at the reference state) is about 0.1 and the free volume expansion coefficien is comparable in the literature. Adjust reveals that apparent free volume in the system is about 10% when reaction becomes diffusion-controlled.

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