

Cure kinetics and shrinkage model for epoxy-amine systems

J.A. Ramos^a, N. Pagani^b, C.C. Riccardi^b, J. Borrajo^b, S.N. Goyanes^c, I. Mondragon^{a,*}

^a*Dpto. Ingeniería Química y M. Ambiente, Escuela Universitaria Politécnica, Universidad del País Vasco/Euskal Herriko Unibertsitatea. Pza. Europa 1, 20018 Donostia/San Sebastián, Spain*

^b*Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET). Av. Juan B. Justo 4302, 7600 Mar del Plata, Argentina*

^c*LPMPyMC, Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Buenos Aires, Ciudad Universitaria, Pabellón I, (1428) Buenos Aires, Argentina*

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Abstract

Manufacture of most of epoxy resins implies that cure needs to be carried out under pressure. Due to the significance of knowing the influence of the pressure factor in cure kinetics, cure shrinkage of a stoichiometric epoxy-amine system was measured using a pressure–volume–temperature (PVT) analyzer. Recording the specific volume change in the range of temperature from 100 to 180 °C and a pressure of 200 bar we could model the cure kinetics. The Runge-Kutta method was applied to obtain the kinetic constants of the cure reaction. In addition, using the differential scanning calorimeter (DSC) for measurements of 1 bar and the PVT analyzer for pressures of 200, 400, and 600 bar, we also model the kinetic constants as a function of pressure. The results obtained show that the effect of the temperature on the kinetic constants is higher than the effect of pressure. Therefore, both PVT and DSC are complementary techniques to describe the full range of cure kinetic process of epoxy mixtures.

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1. Introduction

Thermoset materials based on epoxy resins are widely used in many applications that require high thermal resistance, high tensile strength and modulus, and good chemical resistance. Pressure is an important factor to be controlled in molding processes for thermoset resins. The pressure applied in the molds varies from 800 bar for compression molding until 4 bar for reaction injection molding, taking intermediate values for resin transfer molding [1]. In these processes the thermoset resin starts as a liquid, more or less viscous, and ends as a solid due to the cure reaction [2–7]. It is well known that thermoset resins show volume changes through curing. During cure reaction in an unpressurized mold resin shrinkage leads to the generation of voids [5]. This problem can often be

solved by curing with a slight residual pressure. Therefore, the knowledge of how pressure influences over the kinetic reaction has an outstanding significance. However, few works that join volume changes monitored by pressure–volume–temperature analysis through the cure kinetics of epoxy resins have been published [6–10]. Some works, where dielectric measurements were carried out to follow cure kinetics, established a theoretical dependence between the kinetic constants and the pressure without giving experimental measured values [11,12]. High shrinkage can cause residual stress, warping, premature debonding of fibre from matrix, fibre buckling, and delamination in fibre-reinforced composites, as well as debonding from substrate in adhesives. Therefore, the evaluation of shrinkage through curing becomes of capital interest.

Since the density of thermoset materials depends on the degree of crosslinking, pressure–volume–temperature (PVT) experiments were performed to follow the cure shrinkage of a bifunctional epoxy resin cured with 4,4'-methylenebis(3-chloro-2,6-diethylaniline), MCDEA. PVT experiments allow to measure the specific volume at a defined temperature and pressure as a function of time. In

* Corresponding author. Tel.: +34 943 017271; fax: +34 943 017200.
E-mail address: iapmoegi@sc.ehu.es (I. Mondragon).

addition, differential scanning calorimetric measurements were carried out to model the kinetics of curing.

2. Experimental

2.1. Materials

The epoxy resin used was DER-332, a diglycidyl ether of bisphenol-A (DGEBA), kindly supplied by Dow Chemical, having an epoxy equivalent of around 175. The curing agent was an aromatic diamine with low reactivity, MCDEA, gifted by Lonza. The diamine was used at the stoichiometric ratio of epoxy to amino hydrogen groups. The chemical composition of these compounds is shown in Scheme 1.

2.2. Techniques

A differential scanning calorimeter (DSC 822e, equipped with an intracooler, Mettler Toledo) was used for both dynamic and isothermal cure experiments. The temperature calibration and the determination of the constant time of the instrument were performed by using standards of In and Zn, and the heat flow calibration with In.

DSC was also used for measuring the glass transition temperature, T_g . T_g of the fully cured network was measured by performing several dynamic scans at different heating rates after an isotherm scan at 200 °C for 2 h. The $T_{g\infty}$ was obtained from the extrapolation of the T_g values to 0 °C/min.

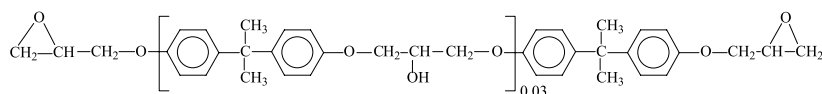
A pressure–volume–temperature analyzer (SWO/Haake PVT 100) was used to measure the volumetric shrinkage during cure reactions. The volume of polymer can be accurately determined in the 30–400 °C temperature range in a 1–2500 bar pressure range. Several isothermal and isobaric scans were carried out to measure specific volume variations along the time. The sample was put into the measurement cylinder in liquid state and removed in solid state.

3. Modelling approach

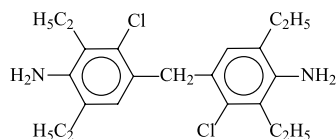
3.1. Determination of the chemical kinetic constants

The mechanism and kinetics of epoxy-amine curing reactions have been widely analyzed. As shown in Scheme 2, three main reactions can take place. Reaction 1 illustrates the reaction of the primary amine hydrogen with an epoxy group. This is followed by secondary amine hydrogen reacting with another epoxy group (reaction 2). Because of the low basicity of MCDEA, a good description of the whole previtrification stage requires consideration of etherification (reaction 3) in the kinetic model, as it has been proposed by Riccardi et al. for other diamines [13–16]. When the model used in those works is applied to a wider range of temperatures, it fails at low temperatures, as shown in Fig. 1. Therefore, other kinetic model was applied, where equilibrium between epoxy and hydroxyl groups as well as constant reactivity between primary and secondary amines were stated, to model the dynamic and isothermal DSC measurements [17]. This model failed, as well.

However, a simpler kinetic model was applied to our system, where etherification was not considered (Scheme 3). E, A₁, A₂, A₃ and OH are the epoxy, the primary, secondary and tertiary amine and hydroxyl groups, respectively; k_c and k_{ep} are the kinetic constants of the reaction to generate the complex epoxy–hydroxyl, EOH, out of equilibrium, so the complex concentration is different to the equilibrium; k_1 and k_2 express the rate constants of the noncatalytic mechanism; k'_1 is the rate constant for the mechanism catalyzed by hydroxyl groups initially present in the epoxy prepolymer and those generated during the reaction. In addition, contrary to what it was previously reported for this system [17–19], it was considered that the ratio of reactivities between the secondary and primary amino hydrogens, $r = k_2/k_1$, was not constant. Therefore, applying the Runge-Kutta method to the set of Eqs. (8) to (12) of Scheme 4, and defining $K_c = k_c [E]_0$, $K_{ep} = k_{ep}$, $K_1 = k_1 [E]_0$, $K'_1 = k'_1 [E]_0$ and $K_2 = k_2 [E]_0$, the reaction kinetics was determined.

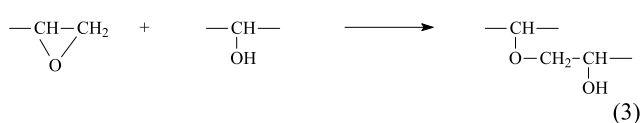
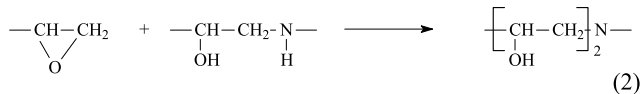


DGEBA (DER-332, Dow Chemical)

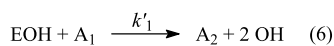
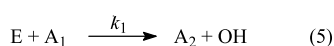
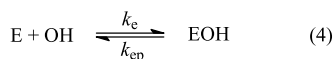


4,4'-methylenebis(3-chloro-2,6-diethylaniline) (MCDEA, Lonza)

Scheme 1. Chemical structures of DGEBA epoxy resin and MCDEA curing agent.



Scheme 2. Main reactions of epoxy-amine systems.



Scheme 3. Kinetic model used.

3.2. Modelling approach for PVT measurements

There are two different sources for the volume changes through curing of epoxy resins: (a) thermal expansion and contraction due to heating and cooling, and (b) cure shrinkage due to polymer chain crosslinking. The total volume change results from a superposition of these two effects. A likely hypothesis is to assume linear cure shrinkage with respect to the degree of cure [1,4]. Specific volume changes have been measured for several isothermal

and isobaric cure cycles. This means that all volume changes can be attributed to cure shrinkage, since no temperature changes occur. From this approach, conversion, just like for measurements of the crystalline fraction, could be approached by Ref. [20]:

$$x = \frac{v'_t - v'_0}{v_\infty - v_0} \quad (13)$$

where v'_t and v'_0 are the specific volume at t time and at $t=0$, respectively, for each cure temperature; and v_∞ and v_0 are the final and initial specific volume, respectively, at a reference temperature considered as the highest temperature used.

The influence of pressure on reaction rate can be attributed to a combination of two effects: acceleration of reactions according to thermodynamic laws; and slowing of reactions when it becomes diffusion controlled. According to thermodynamic laws, in the early stages of the reaction, pressure increases the reaction rate because of the product occupies less volume than the reactants [11]. In addition, densification of the liquid by pressure increases the density of reacting groups, so raising the probability of their mutual approach and hence it increases the reaction rate. In the final stages of the reaction, when the molecular diffusion rate is low, pressure lowers even more the molecular diffusion rate thus decreasing the rate of reaction [12].

According to the transition state theory, the reaction rate is itself related to pressure. The rate constant dependence upon pressure can be given by the following expression [21, 22]:

$$\left(\frac{\partial \ln k}{\partial P} \right)_T = -\frac{\Delta v^*}{RT} + \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (14)$$

where k is the reaction rate constant, P is pressure, T the cure temperature, R the gas constant, and Δv^* is the activation

$$\frac{d[E]}{dt} = -k_e [E][OH] + k_{ep} [EOH] - k_1 [E][A_1] - k_2 [E][A_2] \quad (8)$$

$$\frac{d[EOH]}{dt} = k_e [E][OH] - k_{ep} [EOH] - k'_1 [EOH][A_1] \quad (9)$$

$$\frac{d[A_1]}{dt} = -2[A_1](k_1 [E] - k'_1 [EOH]) \quad (10)$$

$$\frac{d[A_2]}{dt} = [A_1](k_1 [E] - k'_1 [EOH]) - k_2 [E][A_2] \quad (11)$$

$$\frac{d[OH]}{dt} = -k_e [E][OH] + k_{ep} [EOH] + [E](k_1 [A_1] + k_2 [A_2]) + k'_1 [EOH][A_1] \quad (12)$$

Scheme 4. Equations of the kinetic model used.

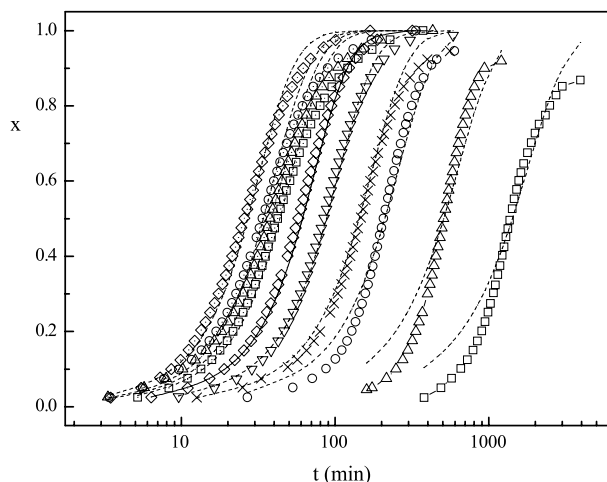


Fig. 1. Epoxy conversion vs. time at different temperatures: (□) 100 °C; (Δ) 120 °C; (○) 140 °C; (×) 150 °C; (∇) 160 °C; (◇) 170 °C; (◻) 180 °C; (△) 185 °C; (⊙) 190 °C; (◊) 195 °C; (...) kinetic model considering etherification reactions.

volume for the reaction. The compressibility factor, $(1/V)(\partial V/\partial P)$, can be defined as a linear function of pressure, as:

$$\frac{1}{V} \frac{\partial V}{\partial P} = \beta(P) = a + bP \quad (15)$$

where a and b are adjustable parameters.

The temperature and pressure dependence of the kinetic rate constants can be expressed by the Arrhenius and Eyring equations (integrated form of the Eq. (14)), respectively. Then, a combined expression of both dependences can be given by [23,24]:

$$k = k_0 e^{-\frac{E}{RT}} e^{\left(-\frac{\Delta V^\ddagger}{RT} + \frac{1}{V} \frac{\partial V}{\partial P}\right)(P-P_0)} \quad (16)$$

where k is the reaction rate constant at pressure P and k_0 the reaction rate constant at reference pressure P_0 . Therefore, for DSC measurements where $P=P_0=1$ bar the kinetic constants are independent of pressure.

4. Results and discussion

4.1. Kinetics modelling

Kinetic studies were isothermally performed with the DSC equipment working at several temperatures. Conversion was taken as the enthalpy recorded in the isothermal scan at each cure time divided by the total enthalpy, obtained from the 200 °C isotherm due to the difficulty to obtain it from a dynamic run as a consequence of the low reactivity of the amine used in this work. The used cure temperature was chosen as it is higher than $T_{g\infty}$ corresponding to the epoxy-amine system analyzed. A dynamic run after the isothermal one at 200 °C did not show any residual heat flow [25,26]. The kinetic rate parameters of Eqs. (15) and (16) are shown in Table 1. Experimental conversion vs. time data were fitted to the kinetic model for the Scheme 3 as shown in Fig. 2. Since the kinetic rate constants have an Arrhenius temperature dependence, an increase in temperature causes an increase in reaction rate. The simple kinetic model fits well experimental results for the whole previtrification stage, and thereafter typically deviates by overestimating measured conversions. Therefore, the reaction is chemically controlled at the early stage; diffusion control of the reaction becomes influential only in the vitrification region where the kinetic model fails. Some

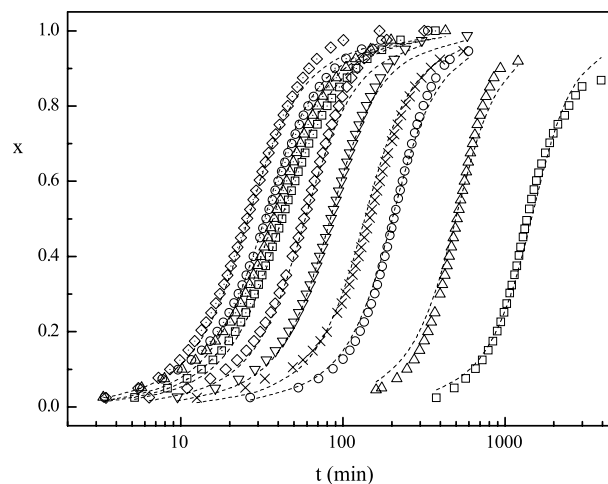


Fig. 2. Epoxy conversion vs. time at different temperatures: (□) 100 °C; (△) 120 °C; (○) 140 °C; (×) 150 °C; (▽) 160 °C; (◇) 170 °C; (◻) 180 °C; (△) 185 °C; (○) 190 °C; (◇) 195 °C; (...) simple kinetic model used.

models exist for analyzing the diffusion controlled regime but they have not been used in this study [11,12,19].

As shown above, in the approach used, a good description of the whole previtrification stage does not require the consideration of etherification reactions in the kinetic model.

4.2. Cure shrinkage modelling

Five isothermal cure temperatures at 200 bar have been investigated using the PVT analyzer: 100, 120, 140, 160, 180 °C. Measurements at temperatures lower than 140 °C could be carried out due to the high sensitivity of the PVT to record small changes in the specific volume. Fig. 3 shows the specific volume changes upon time at those temperatures. Due to thermal expansion of the material, higher the temperature higher the initial value of specific volume was. After an induction period, shorter as higher the temperature, cure reaction began and the volume decreased due to cure shrinkage. Eventually, the specific volume curves reached a plateau and the vitrification phenomena was assigned to the early stage of the plateau. Although in this stage the reaction could continue slowly, the volume change would be too small to be recorded.

Fig. 4 shows both initial and final data of specific volume. The thermal expansion coefficient (TEC), defined

Table 1

Kinetic constant parameters for temperature range from 100 to 200 °C at 1 and 200 bar, and pressure range from 1 to 600 bar at 160 °C

	k_0 (min ⁻¹)	E (kJ mol ⁻¹)	Δv^* (cm ³ mol ⁻¹)	A (bar ⁻¹)	b (bar ⁻²)
K_c	3.5869×10^7	73.186	155.00	0.00848	-1.8547×10^{-6}
K_{sp}	2.1252×10^7	67.025	-42.227	-0.01203	1.5410×10^{-5}
K_1	7.0851×10^4	66.608	-302.28	-0.00941	2.6387×10^{-6}
K'_1	1.1455×10^4	36.986	-108.15	-0.00216	5.0698×10^{-6}
K_2	6.3867×10^8	78.023	-66.019	-0.00403	8.0975×10^{-6}

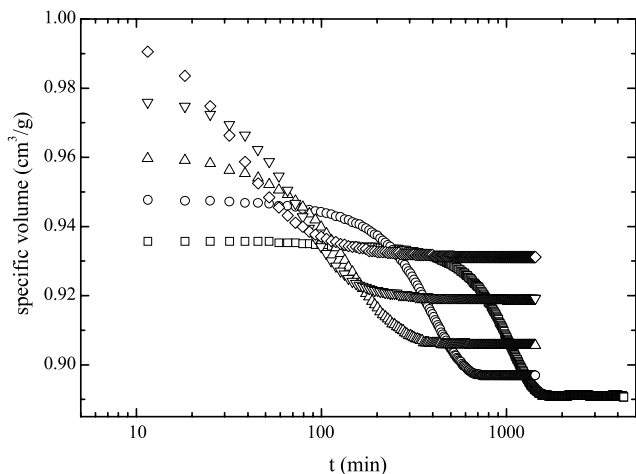


Fig. 3. Variation of specific volume vs. time at different cure temperatures and 200 bar: (□) 100 °C; (○) 120 °C; (△) 140 °C; (▽) 160 °C; (◇) 180 °C.

as the slope of the line shown in the figure, $\Delta v/\Delta T$, can be calculated from the initial values of specific volume, being its value $7.29 \times 10^{-4} \text{ cm}^3/\text{g}^\circ\text{C}$, similar to that for other unreacted epoxy resins [6]. However, TEC for the cured material can not be obtained from the final volume values because the epoxy resin has different final conversions at each isothermal scan.

As described above, several DSC scans were carried out at different heating rates to obtain the $T_{g\infty}$ value. The value obtained was 176 °C. This means that all isothermal scans carried out above this temperature will reach full conversion. Therefore, by considering 180 °C the reference temperature for the model previously proposed by Eq. (13), conversion vs. time curves can be obtained for each isothermal measurement (Fig. 5). As for DSC measurements at 1 bar, an increase in temperature involves an increase in kinetic rate. The kinetic rate parameters of Eqs. (15) and (16) for temperature range from 100 to 180 °C at 200 bar are shown in Table 1. The constant values for PVT measure-

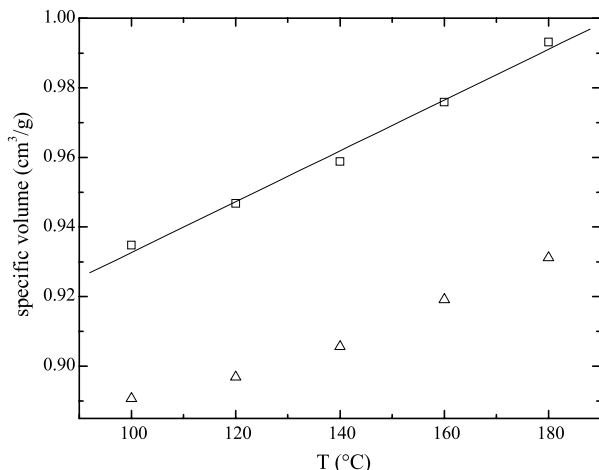


Fig. 4. Initial (□) and final (△) specific volume vs. temperature.

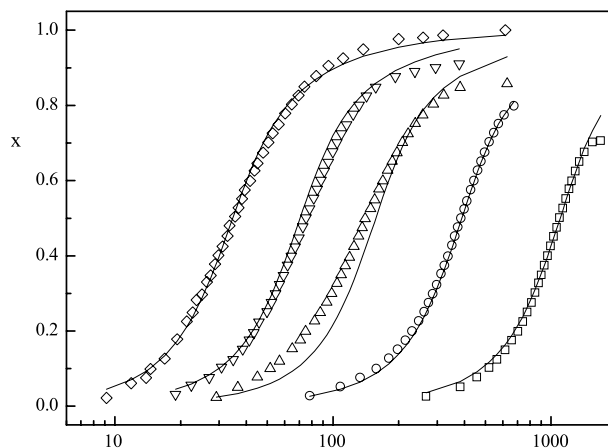


Fig. 5. Epoxy conversion vs. reaction time at different cure temperatures and 200 bar: (□) 100 °C; (○) 120 °C; (△) 140 °C; (▽) 160 °C; (◇) 180 °C; (—) simple kinetic model used.

ments are higher than the values for DSC, as it is discussed below.

4.3. Determination of kinetic constants as a function of pressure

Volumetric shrinkage at constant pressure and temperature was studied at 160 °C in the range of 200–600 bar. By assuming the same hypothesis of linearity between volumetric shrinkage and conversion, and by using the values of DSC at 160 °C for 1 bar as well, Fig. 6 was obtained.

The kinetic rate parameters of Eqs. (15) and (16) for pressure range from 1 to 200 bar at 160 °C are shown in Table 1. An increase in pressure leads to an exponential increase in kinetic rate constants due to the increase in the density of reacting groups and thermodynamic laws [12,21, 22]. Nevertheless, the dependence of the kinetic constants with temperature is greater than the dependence with

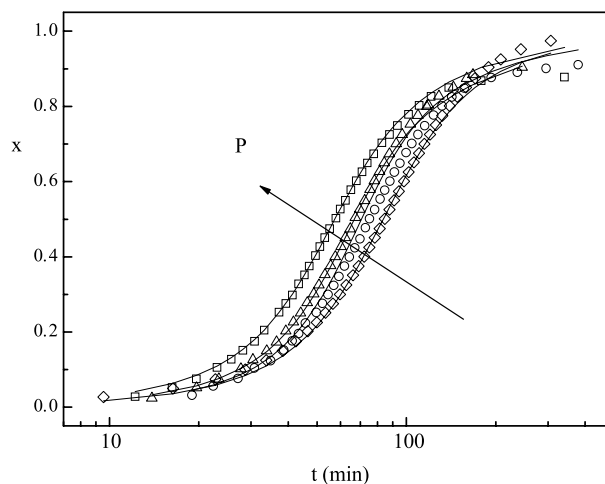


Fig. 6. Epoxy conversion vs. reaction time at different pressures and 160 °C: (◇) 1 bar; (○) 200 bar; (△) 400 bar; (□) 600 bar; (—) simple kinetic model used.

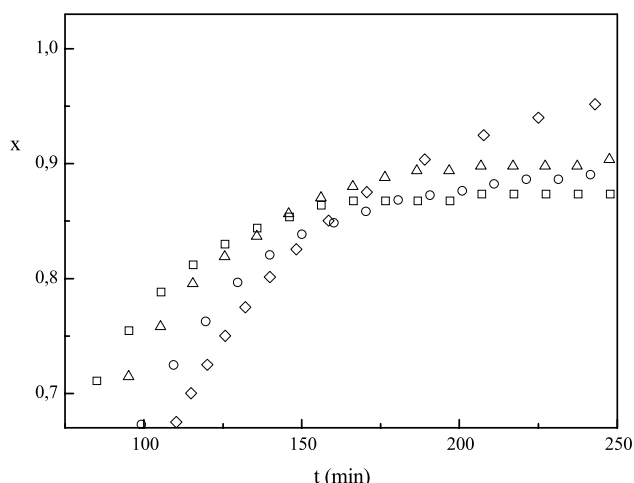


Fig. 7. Cure kinetics at different pressures and 160 °C in the high conversion region: (\diamond) 1 bar; (\circ) 200 bar; (\triangle) 400 bar; (\square) 600 bar.

pressure. In order to appreciate these dependences, the following comparison can be carried out: an increase in temperature of 40 °C, from 140 to 180 °C, at 1 bar of pressure, led to an 82% increase of K_1 , whilst for an increase in pressure of 400 bar, from 200 to 600 bar, at 160 °C, an 38% increase was obtained.

Fig. 7 shows in more detail the experimental final conversion at 600 bar, which was slightly lower than at 200 bar. This effect could be due to the fact that cure kinetics become diffusion-controlled after vitrification [12]. In this stage the viscosity of the system is too high as a result of cure reactions, and a further increase in pressure lowers even more the molecular diffusion, thus decreasing the possibility of reaction of reacting groups, and, therefore, decreasing the final conversion at high pressures.

5. Conclusions

Kinetic studies of a low reactivity epoxy-amine system were carried out by two different techniques: DSC and PVT.

Previous studies have been centred in the influence of temperature or pressure in the kinetic rate constants, while the present work centres its efforts in obtaining a kinetical expression which combine both effects.

PVT technique is a powerful tool for studying the cure kinetics of epoxy resins under pressure, following specific volume variation that takes place during cure reactions. The model proposed to obtain kinetic constants, based on volume shrinkage through curing, fits well in the previtrification stage. A better selection of the compressibility expression and the use of a diffusion rate constant might improve the fitting results. The clearest effect that can be noticed is that both temperature and pressure increase the reaction rate. However, the kinetic constant strongly depends on cure temperature, whereas the influence of pressure is lower.

Although curing is a rather slow process at low

temperatures, volumetric shrinkage can be followed along the whole process by using PVT measurements.

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