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CURE KINETIC OF THE EPOXY NETWORK DIGLYCIDYL ETHER OF BISPHENOL A (BADGE *n*=0)/AMANTIDINE

F. Fraga[1]*, *V. H. Soto*[2], *E. Rodríguez-Núñez*[1], *J. M. Martínez-Ageitos*[3] *and V. Rodríguez*[1]

[1]Departamento de Física Aplicada, Facultade de Ciencias, Universidade de Santiago de Compostela, Campus Universitario 27002 Lugo, Spain
[2]Departamento de Química Física, Facultade de Ciencias, Universidade de Santiago de Compostela, Campus Universitario 27002 Lugo, Spain
[3]Departamento de Enxeñería Química, Facultade de Ciencias, Universidade de Santiago de Compostela, Campus Universitario 27002 Lugo, Spain

The study of the cure reaction of the epoxy network diglycidyl ether of bisphenol A with amantidine is a useful tool to characterize the industrial behaviour of this material. The total enthalpy of reaction, the glass transition temperature and the partial enthalpies at different cured temperatures have been determined using differential scanning calorimetry in dynamic and isothermal mode. Two models, one based on chemical kinetics and the other accounting for diffusion were used and compared with experimental data. It can be seen that the inclusion of a diffusion factor in the kinetic model is negligible.

Keywords: *curing kinetics, DSC, epoxy network, resins*

Introduction

The use of materials derived from epoxy resins has grown considerably since they were first commercialized in the late 1940s. Epoxy resins find thousands of practical applications because they offer great versatility, low shrinkage, good chemical resistance, and outstanding adhesion. From the economic point of view, the use of these resins provides low manufacturing cost materials. Epoxy resins are of great commercial importance for elastic, abrasion-resistant and chemical-resistant paints and coatings, and for casting and impregnation resins. On account of their excellent adhesion to most types of surfaces they are also employed as adhesives and sealing agents.

There are a lot of polymers derived from epoxy resin BADGE (dyglycidyl ether of bisphenol A) and various diamines used as curing agents. Curing reactions of the thermosetting polymers originate a three dimensional network after chemical reaction of the epoxy resin and the chosen hardener. In the curing process of a polymer the glass transition temperature (T_g) of the material increases as a consequence of the increases in the cross-linking density.

A kinetic model used for explain the reaction processes was proposed by Sourour and Kamal [1] and is more general case of the model proposed by Horie [2]. This model assumes equal reactivity for all amine hydrogen. Hydroxyl groups generated during the reaction and the presence of initial impurities like water, markedly accelerated the course of the epoxy amine reaction.

For this study we chose a system consisting of epoxy resin, diglycidyl ether of bisphenol A (BADGE, *n*=0) and amantidine (1-adamantanamine) as the curing agent. Adamantane was used for both temperature and heat calibrations because of the fast and reversible transition in the presence of Zn [3, 4]. The adamantane polymers are characterized by the increased T_g and the thermal stability attributed to the unique ‘diamond-like’ cage structure of the adamantane which inhibits degradations reactions such as eliminations.

In the last years several articles have been reported above adamantane. For example some polyether imides were prepared using an adamantane based bis (ether anhydride) and several aromatic amines in two stages. Glass transition temperatures were in the range of 242–317ºC by DSC and 270–322ºC by dynamic mechanical analysis. They exhibited high resistance to thermal degradation, with 10 mass% loss temperatures been recorded between 514–538ºC in nitrogen and 511–527ºC in air [5].

De-Jang *et al*. [6] prepared adamantane-type cardo polyamides by using adamantane-type cardo dicarboxylic acid containing ether group, 2,2-*bis*[4-(carboxyphenoxy)phenyl]-adamantane (BCAPA). The polymers were amorphous and the polyamide films had a tensile strength and tensile modulus above 86 MPa and 2 GPa. These polyamides had glass transition temperatures be-

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* Author for correspondence: franfrag@lugo.usc.es

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

tween 254–292ºC and 10% mass loss temperatures in the range of 450–507 and 481–516ºC in nitrogen and air atmosphere, respectively. In other work [7], they synthesized a new diamine 2,2-*bis*-[4-(4-aminophenoxy)phenyl]-adamantane (BAPA). containing a pendant adamantane group and a flexible aryl ether unit. The glass transition temperature of these polyamides range from 254–294ºC. The polyamides remain fairly stable up to a temperature around 450ºC and lose 10 mass% between 490 and 524ºC in nitrogen atmosphere.

Also a synthesis of star-shaped adamantane multipodes with rigid branches based on *p*-hydroxybenzoic acid have been reported [8]. These multipodes are able to crystallize but can also be obtained in the glassy state.

Because of the good properties of the material, recently have been obtained some polymers using BADGE and other epoxy derivatives with several adamantane derivatives to prepare dental filling materials [9].

Experimental

Materials and methods

The epoxy resin was a commercial BADGE (n=0) (resin 332, Sigma Chemical Co., St. Louis, MO) with an equivalent molecular mass of 173.6 g mol^{-1}. The curing agent was amantidine (1-aminoadamantane) (Sigma Aldrich, Germany), molecular mass 151.25 g mol^{-1} with a purity of 97%.

For calorimetric experiments, the epoxy resin and the curing agent were carefully weighed at a stoichiometric ratio avoiding the contact during this operation. Later, the products were homogeneously mixed as soon as possible (2–3 min). Then, samples between 7 to 8 mg in mass were sealed using a press in aluminium pans before introducing them into the calorimeter. The reference used was a sealed empty pan.

Differential scanning calorimetry

The calorimetric measurements were performed on a TA calorimeter model DSC-Q100 V6.19 Build 227 unit using nitrogen (caudal of 50 mL min^{-1}) as purge gas. The calorimeter was operated in both isothermal and dynamic modes. The evolved heat (ΔH_t) have been obtained using a temperature range from –30 to 250ºC with a heating rate of 10ºC min^{-1}. The glass transition temperature (T_g) were determined using a second scanning from 15 to 250ºC at the same heating rate.

Partial enthalpies corresponding to the following curing temperatures: 50, 60, 70 and 75ºC were measured in isothermal mode.

Results and discussion

The scans was carried out in dynamic mode to calculate the total heat of reaction (ΔH_t) and the glass transition temperature (T_g) for the curing process for the epoxy system BADGE n=0/amantidine. The experimental data are shown Table 1. Figure 1 shows a typical DSC curve used to determine ΔH_t and T_g. The average values were characterized by the low standard deviations generated. This data are in good agreement with those obtained by Núñez *et al*. [10, 11] and Fraga *et al*. [12] for a similar epoxy system. From the isothermal experiments performed around T_g at the temperatures of 50, 60, 70 and 75ºC, the values of partial enthalpies were measured. From these values the degree of conversion α of this epoxy system for different times can be calculated

$$\alpha=\frac{\Delta H^{T}}{\Delta H_{t}} \qquad (1)$$

where ΔH^T is the heat evolved up at a certain time and ΔH_t is the total heat of reaction.

From isothermal calorimetric scans (Figs 2a–d) can be determined the instantaneous heat flow dH/dt and the correspondence reaction rate dα/dt.

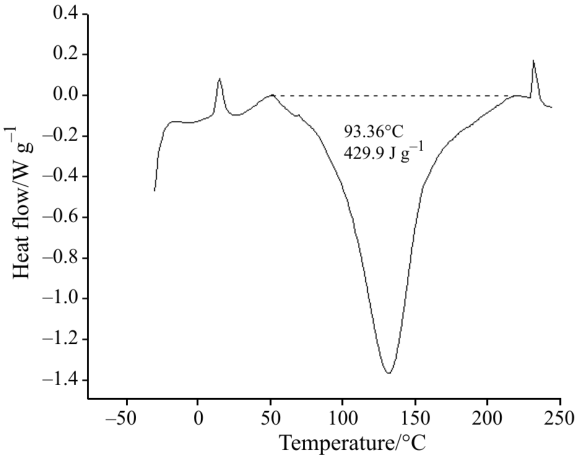

Fig. 1 DSC curve on dynamic mode at a heating rate of 10ºC min^{-1}

Table 1 Values of enthalpy changes and glass transition temperatures

Experiment number	ΔH/J g^{-1}	T_g/°C
1	425.56	75.12
2	428.70	73.78
3	424.40	73.60
4	432.00	71.89
5	429.90	72.49
Average values	428.11	73.38
Standard deviation	2.80	1.12

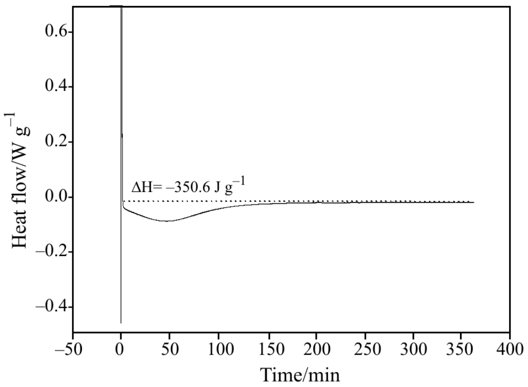

Fig. 2a DSC curve on isothermal mode at 75ºC

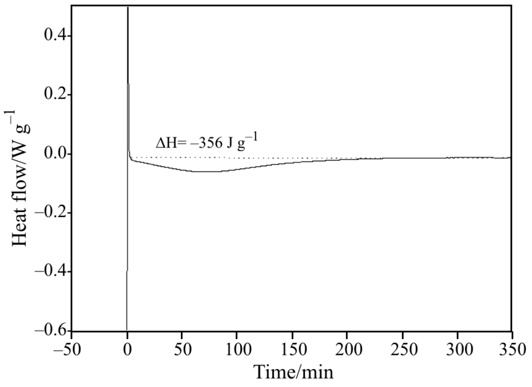

Fig. 2b DSC curve on isothermal mode at 70ºC

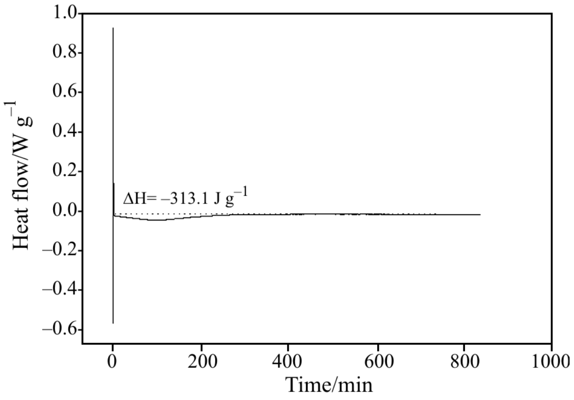

Fig. 2c DSC curve on isothermal mode at 60°C

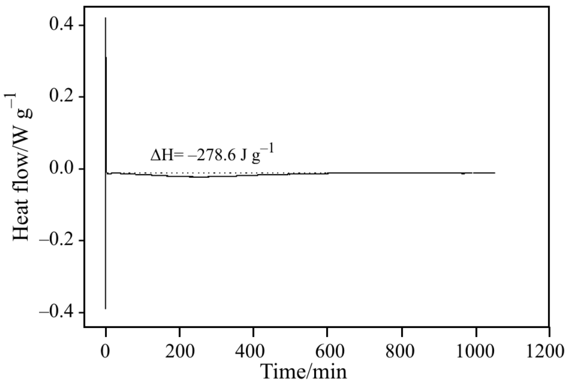

Fig. 2d DSC curve on isothermal mode at 75ºC

$$\frac{d\alpha}{dt}=\frac{dH/dt}{\Delta H_t} \tag{2}$$

assuming its proportionality to the rate of heat dH/dt. Table 2 shows the enthalpies and the degree of conversion at different isothermal temperatures. It can be observed that conversion speedily increases with time reaching a practically constant value due to the molecular mass increases with time and higher times hindering mobility and consequently cross-linking stops. For this system, maximum conversion is 83% at 70ºC and for higher temperatures (75ºC) the degree of conversion decreases, justifying the temperature range used in this paper to isothermal experiments. Figure 3 shows plots of reaction rates *vs*. conversion at different isothermal temperatures. It can be seen that the reaction rate increases with temperature.

Table 2 Values of enthalpy changes and conversion at different isothermal temperatures

Temperature/°C	50	60	70	75
ΔH_P/J g^{-1}	278.6	313.1	356	350.6
$\Delta H_P/\Delta H_T$	0.648	0.728	0.828	0.816

The reaction rate of an epoxy system can be expressed by the contribution of two mechanisms: *n* order and autocatalytic. Assuming stoichiometric proportions and equal reactivity for all amine hydrogen, the reaction rate using the Sourour and Kamal [1] kinetic model can be expressed

$$\frac{d\alpha}{dt}=(k_1+k_2\alpha^m)(1-\alpha)^n \tag{3}$$

where k_1 and k_2 are constants of two reactions, m and n are parameters related to the reaction orders for the autocatalytic reaction and n order paths, respectively.

The kinetic model was made to fit plots of reaction rates *vs*. conversion at different isothermal temperatures. Table 3 shows constant rates and reaction orders for n^{th} order and autocatalytic paths at different isothermal temperatures. Values listed in this table

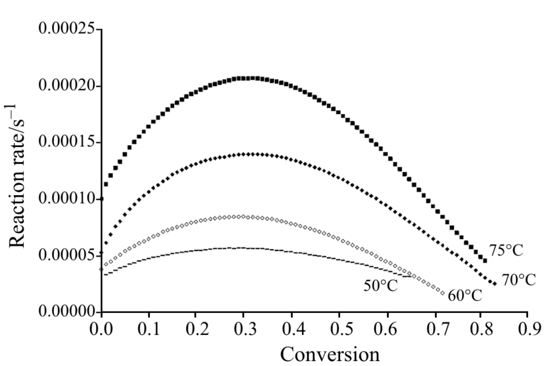

Fig. 3 Reaction rate *vs*. conversion at different isothermal temperatures

Table 3 Values of k_1 and k_2 and reaction order for n^{th} and autocatalyzed mechanism at different isothermal temperatures

Temperature/°C	50	60	70	75
$k_1/10^{-4}$ s^{-1}	0.3	0.4	0.6	1.1
$k_2/10^{-4}$ s^{-1}	2.4	5.5	6.6	10.6
m	1.02	1.12	0.97	1.09
n	1.71	2.18	1.73	1.80

suggest a value of 3 for the overall reaction order, in good agreement with values reported by Núñez *et al*. [13] for similar epoxy systems.

The cure reaction of an epoxy resin with an amine is controlled by the chemical kinetic. However, the deviations between theoretical and experimental data from a critical conversion (58% typically) are due to a gradual decrease in the reaction and a higher increase of the viscosity. The critical conversion for the formation of the network can be used to calculate the critical fraction free volume at which the curing reaction becomes diffusion controlled. A semiempirical model based on free volume considerations, proposed by Chern and Polheim [14] and used by Cole *et al*. [15], Khanna and Chanda [16] and by Núñez *et al*. [10, 11, 17] are used to study the diffusion controlled reaction rate.

Using the diffusion factor $F(\alpha)$ the reaction rate can be expressed in the following form to account for effects of diffusion:

$$\frac{d\alpha}{dt}=(k_1+k_2\alpha^m)(1-\alpha)^n F(\alpha) \qquad (4)$$

In our case identical results were observed for all conversion values and probably chemical kinetics controlled all the reaction process because of the large volume of amantidine diminishes the total free volume necessary for diffusion processes. Figure 4 shows the behaviour of $F(\alpha)$ *vs*. conversion at 70ºC. It can be seen that the value of $F(\alpha)$ is almost 1 in all the conversion range and that means that the system are controlled by chemical kinetics, therefore diffusion were not observed in the used temperature range. To corroborate this behaviour, we represented the reaction rate *vs*. the degree of conversion at 70ºC (Fig. 5). Similar results can be observed at all cured temperatures. It can be seen that the kinetic model are in a good agreement with the experimental results in all conversion range that means no diffusion control are present in the studied system.

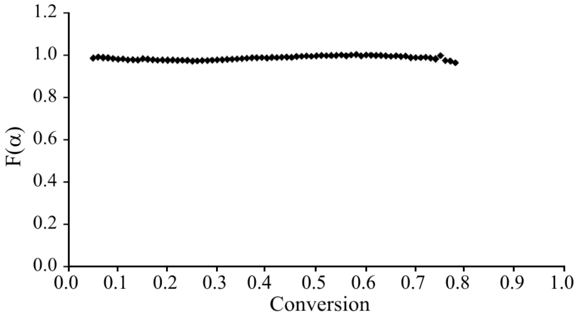

Fig. 4 $F(\alpha)$ *vs*. conversion at 70ºC

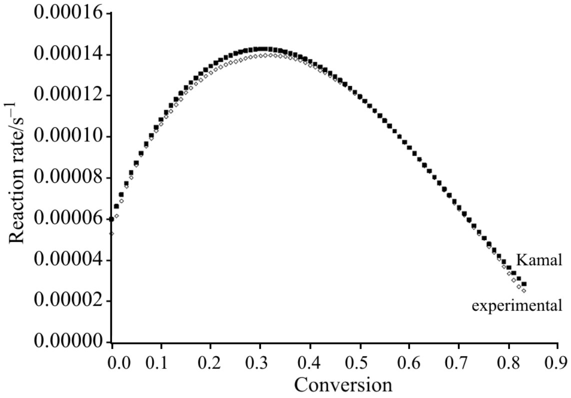

Fig. 5 Rlot of reaction rate *vs*. conversion at 70ºC

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