

Influence of the Filler CaCO_3 on the Cure Kinetic of the Epoxy Network Diglycidyl Ether of Bisphenol a (BADGE $n = 0$) With Isophorone Diamine

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ABSTRACT: The influence of the presence of CaCO_3 on the cure reaction of the epoxy network diglycidyl ether of bisphenol A with isophorone diamine has been studied. The total enthalpy of reaction, the glass transition temperature and the partial enthalpies at different isothermal temperatures have been determined using differential scanning calorimetry (DSC) in dynamic and isothermal mode. A kinetic model accounting the influence of the dif-

fusion of the reactive groups at high conversions was used. All the kinetic parameters have been compared with those of the system without filler (CaCO_3). © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3338–3342, 2009

Key words: resins; epoxy network; differential scanning calorimetry; curing reaction; kinetics polymerization; CaCO_3 ; filler

INTRODUCTION

Epoxy resins are used in different industrial sectors, one of the major problems is its fragile structure that can be improved by the introduction of a second component such as fillers. Several commercial fillers are suitable for the use with epoxy resins for the viscosity control, lower shrinking, lower thermal expansion and mainly for the lower cost of manufacture. The fillers can be inorganic or organic elements, though normally are used inert inorganic fillers with a particle size of 0.015 microns or higher. Besides it should be neutral or slightly basic and non reagents with the resin or the agent of cured. This requirement avoids the use of some fillers with some classes of hardening. In this project is used an inorganic filler: calcium carbonate (CaCO_3).

We have studied the curing kinetic for this epoxy network diglycidyl ether of bisphenol A (BADGE $n = 0$)/isophorone diamine (IPD)/calcium carbonate (CaCO_3) using calorimetric measurements.

An objective of this study has been to obtain calorimetric parameters (glass transition temperature, constant rates, reaction orders, diffusion parameters...) to allow the knowledge of curing kinetic. Ki-

netic data are compared with those obtained without filled in a previous study.¹

EXPERIMENTAL

Materials

The epoxy resin was a commercial diglycidyl ether of bisphenol A (BADGE $n = 0$) (Resin 332, Sigma Chemical Co. San Louis) with an equivalent molecular weight of 173.6 g/equiv., as determined by wet analysis.^{2,3} The curing agent was isophorone diamine (IPD) (IPD, Aldrich Chemical Co., Milwaukee, WI) with an equivalent molecular weight of 170.3 g/equiv. The filled agent was a white powder named Calcium Carbonate (Panreac Chemistry Laboratories S.A). The average particle size was 1 μm .

Sample preparation

These three reagents are commercial products and they have been used without previous purification. The resin solidifies easily and this hinders its handling when making it react with other products, hence, you must introduce in a stove at 40°C to maintain it in liquid state. The hardening one stays in a desiccator to avoid the hydrate, oxidation or carbonation. To the calcium carbonate it is not necessary to give it any specific treatment. The samples get ready using stoichiometric quantities of BADGE

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TABLE I
Values of Partial Enthalpies and Degree of Conversion at Different Cured Temperatures for the System With and Without Filler

T (°C)	Filler		Without Filler ¹	
	ΔH^T (J/g)	α	ΔH^T (J/g)	α
80			-520	0.95
70	-344 ± 10	0.84	-501	0.92
60	-324 ± 13	0.79	-484	0.89
50	-303 ± 15	0.74	-463	0.85
40	-276 ± 12	0.67	-445	0.81

$n = 0$ and IPD. By means of agitation the intimate and homogeneous contact is favoured among the two compounds, avoiding areas as much as possible with different degree of conversion. The good proportion has been determined in a previous study⁴ and it corresponds to (100 : 98). For the realization of this study 25 grams of BADGE $n = 0$ and 4.5 grams of curing agent were weighed. They become agitated during at least 5 min and then a 20% of the total weight of both components of calcium carbonate must be added. In previous dynamic calorimetric experiments,⁵ it was demonstrated that this percentage was the good one. The election approach was based in that this filler percentage was the only one that the measures of the variation of enthalpy on the dynamic scanning were reproducible. It seems reasonable since for very low (10–15%) proportions of filler the homogenization of the mixture is very difficult, with what is impossible to assure that the filler always notices to the same positions and, consequently, the system reacts since in a different way regions they would appear with densities of different crosslinking. For high (25–30%) proportions, the quantity of filler is so high that in certain areas of the structure can appear barriers that prevent that the system reacts freely. This fact has been proved in a previous paper using a scanning electronic microscopy (SEM)⁵. After 5 minutes of agitation of the three reagents, the mixture was encapsulated in aluminium pans for the differential scanning calorimeter (DSC) analysis.

Techniques

A differential scanning calorimeter Q100 of TA Instruments was used to obtain all the experimental data reported in this work. To determine the total heat of reaction ΔH_t a first scan was carried out in dynamic mode from -30°C to 250°C at constant heating rate of 10°C/min. A second scan from 15°C to 250°C at constant heating rate of 10°C/min was carried out to determine the glass transition temperature T_g of epoxy system. In the second phase of the

experimental investigation, the partial enthalpies ΔH^T have been determined using DSC in isothermal mode at different cured temperatures close to T_g : 40, 50, 60, and 70°C.

RESULTS AND DISCUSSION

The average experimental values obtained from the DSC dynamic experiments for the total heat of reaction and the glass transition temperature of the epoxy system are -411 ± 3 J/g and 71 ± 2 °C, respectively. These values were 25% and 16% lower than those obtained in a previous paper¹ for the system without filled. Both reductions are due to the impediments that it causes the filler in the reticulation process, increasing the hardness of the material but weakening the structural network. This data are in good agreement with those obtained by Núñez et al.^{5–7} for a similar epoxy system.

From the isothermal experiments performed around T_g , at the cured temperatures of 40, 50, 60, and 70°C, the values of partial enthalpies ΔH^T were determined. From these values the total degree of conversion α of this epoxy system for different cured temperatures can be calculated.

$$\alpha = \frac{\Delta H^T}{\Delta H_t} \quad (1)$$

Table I shows the partial enthalpies (ΔH^T) and the degree of conversion (α) at different cured temperatures for the system with and without filler. As can be seen value for the system with filler at 70°C is 157 J/g lower than the system without filler. This fact shows that the kinetic mechanism of the system with calcium carbonate filler is less exothermic. Besides the degree of conversion at this same

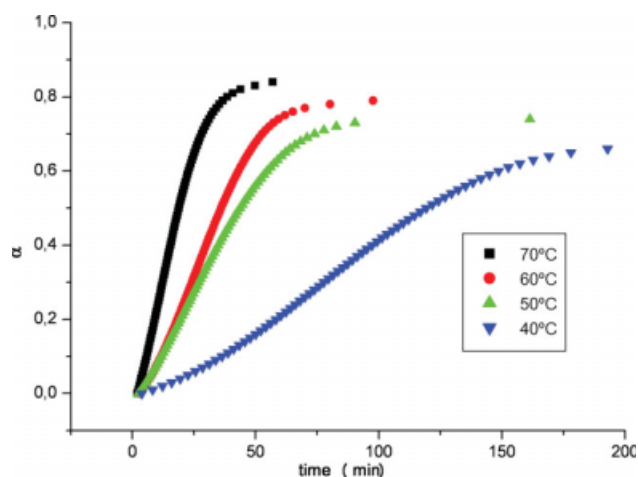


Figure 1 Conversion versus time at different isothermal temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

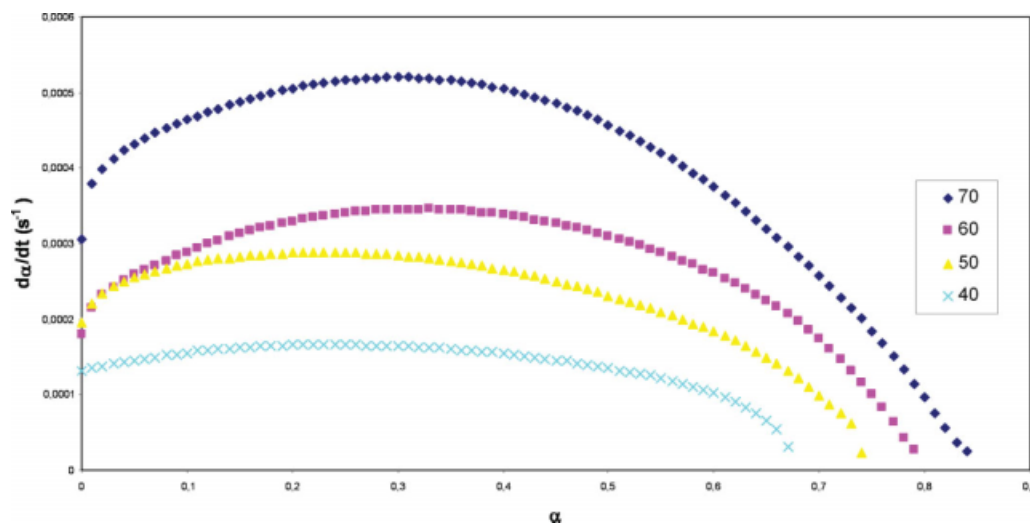


Figure 2 Reaction rates versus conversion at different isothermal temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

temperatures were 8% lower than for the system without filler. This reduction is due to the impediments that it causes the filler in the reticulation process. Figure 1 shows the degree of conversion versus time at different cured temperatures. It can be observed that conversion speedily increases with time reaching a practically constant value due to the molecular weight increases with time and higher times hindering mobility and consequently crosslinking steps.

From isothermal calorimetric scans also can be determined the instantaneous heat flow dH/dt and the correspondence reaction rate $d\alpha/dt$

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_t} \quad (2)$$

Figure 2 shows plots of reaction rates versus degree of conversion at different cured temperatures. It can be seen that the reaction rate increases with temperature.

The conversions α and the reaction rates $d\alpha/dt$ for each cure temperature allowed to determine the kinetic coefficients and the global order of the cured reaction from the Sourour and Kamal kinetic model⁸

assuming stoichiometric proportions and equal reactivity for all amine hydrogens:

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

This model express the contribution of two mechanisms: n th order and autocatalytic. k_1 and k_2 are constant rates of two reactions, and n and m , parameters related to the two orders of reaction. The kinetic model was used to fit plots of reaction rates versus conversion at different cured temperatures. Table II shows constant rates and reaction orders for n th order and autocatalytic paths at different cured temperatures for the system with and without filler. The different isothermal experiments values for the filled system are lower than those obtained for the original epoxy system. Values listed in this table suggest a value of 2 for the overall reaction order ($m + n$), in good agreement with some of the values reported by Fraga et al.¹ for the system without filler, and Núñez et al.⁵⁻⁷ and Zvetkov⁹ for similar epoxy systems.

From the Table II, the activation energies corresponding to n th order and autocatalytic paths were

TABLE II
Values of k_1 , k_2 , m , and n at Different Cured Temperatures for the System With and Without Filler

T (°C)	Filler				Without Filler ¹			
	k_1 (10^{-4} s $^{-1}$)	k_2 (10^{-4} s $^{-1}$)	m	n	k_1 (10^{-4} s $^{-1}$)	k_2 (10^{-4} s $^{-1}$)	m	n
80					7.6	32.0	0.39	0.95
70	3.3	10.2	0.79	1.06	4.6	10.4	0.57	0.94
60	2.9	8.4	0.73	1.13	3.7	6.2	0.44	1.04
50	2.0	5.7	0.71	1.24	0.8	3.7	0.67	1.35
40	1.3	5.2	1	1.23				

TABLE III
Activation Energies for the System With and Without Filler

	Activation Energies (kJ/mol)	
	Filler	Without Filler ¹
n-th order mechanism	88.43 ± 5.26	78.96
Autocatalyzed mechanism	81.45 ± 8.40	56.34

obtained from the Arrhenius plot of lnk versus 1000/T and showing in Table III. Similar results for both activation energies were reported by Fraga et al.^{1,6,10} For the system with filler the values for nth order were slightly higher than autocatalytic mechanism that suggests to autocatalytic mechanism was not predominant over the other one. The vicinity of both values suggests that the cured reaction could be represented by means of an only energy of global activation among the obtained values. The values for the system with filler were higher as the presence of the filler hinders crosslinking between different zones of the material, thus increasing the energy necessary for a three-dimensional network.

It can be seen deviations between theoretical and experimental data from a critical conversion are due

TABLE IV
Critical Conversion (α_c) and A_1 for the System With and Without Filler

T (°C)	Filler		Without Filler ¹	
	α_c	A_1	α_c	A_1
80			0.85	17.98
70	0.78	20.23	0.83	18.01
60	0.75	31.05	0.77	19.62
50	0.72	32.78	0.74	18.19
40	0.66	54.09		

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 Pholein¹¹ and used by Cole et al.¹², Khanna and Chanda,¹³ Núñez and coworkers,^[4-7,10] and by Fraga et al.¹ was used to study the diffusion-controlled reaction rate. In this model a diffusion factor is defined as

$$F(\alpha) = \frac{1}{1 + e^{(A_1(\alpha - \alpha_c))}} \tag{4}$$

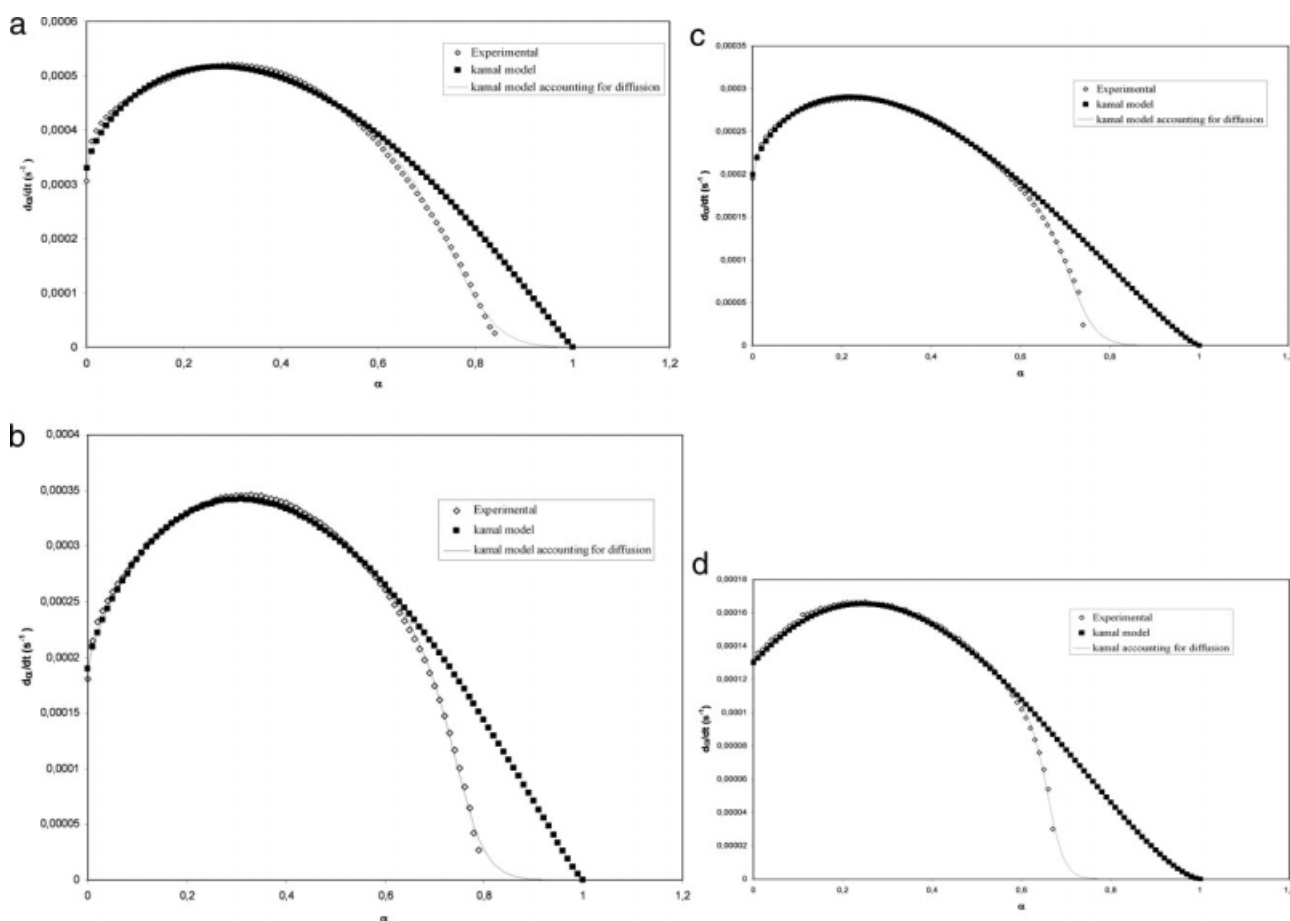


Figure 3 Plots of the reaction rates versus conversion at a) 70°C, b) 60°C, c) 50°C, and at 40°C.

where α_c is the critical conversion, yA_1 is an adjustable parameter.

Table IV shows values of A_1 and α_c at cured temperatures for the system with and without filler. A_1 parameter is around to a value of 18 for the system without filler,¹ while for the system with filler increases when the temperature decreases. This is an anomalous behaviour when it is compared with other similar systems,^{5,10} where A_1 increases with the temperature. The critical conversion increases with the temperature, indicating that the diffusion effects appear later. The filler also makes that the beginning of the diffusion was a little before.

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

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \cdot F(\alpha) \quad (5)$$

In the Figures 3 (a–d) are shown the reaction rate versus conversion at different temperatures where experimental results are compared with those obtained to a chemical kinetic model and to the kinetic model accounting for diffusion. It can be seen that the agreement is extremely good between exper-

imental results and kinetic model accounting for diffusion. It was expected that the filler only reduces the reticulation but it doesn't change the kinetic model that controls the reaction mechanism.

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