Determination of the optimum epoxy/curing agent ratio: A study of different kinetic parameters

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Abstract: Variation of the epoxy/curing agent ratio for a system containing a diglycidyl ether of a bisphenol A derivative epoxy resin and the isophorone diamine (3-aminomethyl-3,5,5-trimethylcyclohexylamine) was found to have a significant effect on the cure kinetic parameters. Determination of the optimum value of the epoxy/curing agent ratio was studied by means of differential scanning calorimetry. The method is based on the search for the maximum enthalpy change[1]. It was found that this maximum corresponds to a 100/34 value. The glass transition temperature (T_g) has been calculated using dynamic methods. Our values are in good agreement with those in the literature[2,3] for similar systems. At the same time other kinetic parameters were obtained using an isothermal method and the ratio values previously calculated. This kind of epoxy/curing agent systems are mainly used in civil engineering.

INTRODUCTION

Epoxy resins must posses certain properties such as high reactivity, high conversion at low temperatures, low viscosity and small toxicity in order to obtain a product with properties similar to those of commercial resins.

In this paper we report a study, based on the kinetics of an industrial epoxy resin made by GAIRESA (Valdoviño, Spain). With this aim, reaction enthalpies both in isothermal and dynamic modes were measured. It is known that both of these methods may be applied independently, but a combination consisting of the use of the isothermal method to determine the reaction degree and the dynamic method to evaluate the maximum enthalpy involved in the process can be very valuable.

EXPERIMENTAL

Materials

The resin was an epoxide derived from the diglycidyl ether of biphenol A labeled by GAIRESA as RESINA 41-13 SOLUBLE with an equivalent weight 140. The cure agent was the isophorone diameine (IPD) with equivalent weight 452.6. This system was chosen because its physical properties agree with those above mentioned.
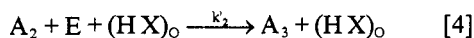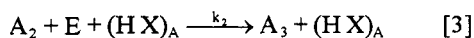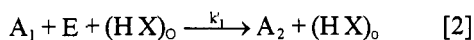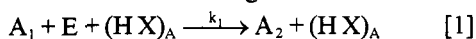
Techniques

Calorimetric measurements were made by differential scanning calorimetry (DSC). The calorimeter was calibrated using indium and bidistilled water a standards. The use of two standards was necessary because of the wide temperature range used (-30 to 230°C). The heating rate was 10°C/min. All the samples were about 5-6 mg in weight. The purge gas was 99.99999% pure nitrogen from Carburos Metálicos (La Coruña, Spain).

Kinetics

Kinetic treatment is based on that given by Horie et al[4] assuming equal reactivity for all amine hydrogen. Hydroxyl groups generated during the reaction and the presence of initial impurities such as water,

glycol, solvent, etc., markedly accelerate the course of the epoxy-amine reaction. The possibility that the catalytic effect could originate either from the impurities or from the OH groups generated in the course of the reaction led to the following reaction scheme.

$$A_1 + E + (HX)_A \xrightarrow{k_1} A_2 + (HX)_A \qquad [1]$$

$$A_1 + E + (HX)_0 \xrightarrow{k'_1} A_2 + (HX)_0 \qquad [2]$$

$$A_2 + E + (HX)_A \xrightarrow{k_2} A_3 + (HX)_A \qquad [3]$$

$$A_2 + E + (HX)_0 \xrightarrow{k'_2} A_3 + (HX)_0 \qquad [4]$$

Where $(HX)_A$ and $(HX)_0$ represent the hydroxyl groups and initial impurities, respectively. E, A_1, A_2 and A_3 represent epoxide, primary amine, secondary amine produced by addition of epoxide to primary amine, and tertiary amine as a final product, respectively.

From these equations assuming that any autocatalytic [eqs(1) and (3)] or externally catalysed mechanism, n-order path, [eqs(2) and (4)] could be produced, and also assuming equal reactivity for all amine hydrogens, as was mentioned, the following expression in terms of basic concentrations[5] can be derived

$$\frac{d\alpha}{dt} = (K'_1 + K_1 \alpha^m)(1-\alpha)^a(B-\alpha)^b \qquad [5]$$

Where $K_1 = 1/2\, k_1 e_0^2$ and $K'_1 = 1/2\, k'_1 e_0 c_0$ (e_0 and c_0 are the initial concentrations of epoxy and $(HX)_0$ respectively, B the epoxy amine molar ratio). When the resin and the amine are in stoichiometric relations (B = 1). Moreover if m = a = b = 1:

$$\frac{d\alpha}{dt} = (K'_1 + K_1 \alpha)(1-\alpha)^2 \qquad [6]$$

In general

$$\frac{d\alpha}{dt} = (K'_1 + K_1 \alpha^m)(1-\alpha)^n \qquad [7]$$

where n = a + b

The reduced reaction rate α^o is defined as :

$$\alpha^o = \frac{d\alpha/dt}{(1-\alpha)^a (B-\alpha)^b} = K'_1 + K_1 \alpha^m \qquad [8]$$

Following Horie et al[4], equation [5] may be derived from the rate of consumption of epoxide given by

$$\frac{dx}{dt} = k_1 a_1 e x + k_1 a_1 e c_0 + k_2 a_2 e x + k_2 a_2 e c_0 \qquad [9]$$

where a_1, a_2, e and c_0 are the concentrations of primary amine, secondary amine, epoxide and external catalyzer, respectively.

Taking $e = e_0 - x$, assuming $k_2/k_1 = k'_2/k'_1 = 1/2$ (that is, assuming equal reactivity for all amine hydrogens) and considering that at time t the concentrations of a_1 and a_2 are equal to their initial values minus the amounts reacted, it follows $a_1 + a_2/2 = a_0 - x/2$ and :

$$\frac{dx}{dt} = (e_0 - x)(k_1 x + k_1 c_0)(a_0 - x/2) \qquad [9a]$$

using the reduced value a = x/e_0

$$\frac{d\alpha}{dt} = 1/2(k_1 e_o^2 \alpha + k_1 e_o c_o)(1 - \alpha)(2a_o/e_o - \alpha) \quad [11]$$

and finally

$$\frac{d\alpha}{dt} = (K_1' + K_1 \alpha)(1 - \alpha)(B - \alpha) \quad [12]$$

where $K_1 = \frac{1}{2} k_1 e_o{}^2$, $K_1' = \frac{1}{2} k' e_o c_o$, $B = 2a_o/e_o$

RESULTS AND DISCUSSION

Dynamic method

In order to evaluate the optimum resin/cure agent ratio, necessary for a posterior isothermal study, a dynamic study was carried out.
Table 1 reports enthalpy values for the different ratio values used.

From these data it can be concluded that the optimum ratio value is 100/34 which corresponds to the maximum value of ΔH.
The optimum value of the epoxy/curing agent ratio can also be evaluated from Tg values. It is expected that ΔH maximum value corresponds to the maximum value of Tg.
Table 2 shows Tg values corresponding to different epoxy/curing agent ratios.

TABLE 1. ΔH for different mixing ratios.

Ratio Epoxy/cure Agent	ΔH (J/g)
100/30.5	521.56
100/32	549.37
100/33	543.10
100/34	562.48
100/35	539.05
100/36	545.98
100/38	528.56

TABLE 2. Tg values for different mixing ratios.

Ratio Epoxy/cure Agent	Tg
100/30.2	72.85
100/32	75.76
100/33	76.83
100/34	77.37
100/35	73.37
100/36	75.36
100/38	76.82

From all this evidence it can be confirmed that 100/34 corresponds to the optimum ratio value.

Isothermal study

The curing reactions of diglycidyl ether of bisphenol A with isophorone diamine were studied using a differential scanning calorimeter (DSC) under isothermal conditions within the range 45-75°C. This range was chosen from the values given by the dynamic curves. Samples were introduced in aluminum pans hermetically closed and then introduced in the calorimeter at 5°C. Heating rate was 100°C/min.

From the curves produced, the reaction rate dα/dt is evaluated from dH/dt at different times as

$$da/dt = \frac{dH/dt}{\Delta H_o} \quad [13]$$

Reaction degree can be calculated from:

$$\alpha = \frac{\Delta H_t}{\Delta H_o} \quad [14]$$

TABLE 3.1. Values of reaction degree (α), reaction rate ($d\alpha/dt$) and reduced rate ($\alpha°$) as a function of the time at 45°C.

t	α	$d\alpha/dt$	$\alpha°$
2.10	0.0563	0.0422	0.0445
3.70	0.1079	0.0415	0.0467
6.30	0.1884	0.0397	0.0498
10.90	0.3174	0.0357	0.0556
14.90	0.4135	0.0319	0.0577
19.50	0.5060	0.0279	0.0602
24.50	0.5876	0.0242	0.0617
35.70	0.7110	0.0094	0.0618
42.90	0.7631	0.0071	0.0603
54.40	0.8192	0.0049	0.0569
66.70	0.8565	0.0036	0.0535
77.30	0.8783	0.0029	0.0420

TABLE 3.2. Values of reaction degree (α), reaction rate ($d\alpha/dt$) and reduced rate ($\alpha°$) as a function of the time at 55°C.

t	α	$d\alpha/dt$	$\alpha°$
3.74	0.0327	0.0249	0.02617
8.02	0.1122	0.0164	0.01961
15.52	0.2113	0.0127	0.01813
25.15	0.3060	0.0092	0.01591
50.31	0.4672	0.0052	0.01337
100.08	0.6526	0.0031	0.01514
150.40	0.7685	0.0017	0.01526
200.17	0.8481	0.0012	0.02027
250.49	0.9086	0.0008	0.02895
300.26	0.9548	0.0005	0.02203

Tables 3.1 and 3.2 show values of α, $d\alpha/dt$ and $\alpha°$ at different times t.

Finally, in order to check the validity of the kinetic model here used, a plot of the reduced reaction rate a° against a^m is made. According to eq [8], a straight line is expected. The problem consists of the search for the value of m best fitting this linearity. Different values of m were tried and it was found that m=1 is the best value (R>0.99). Once the value of m was found, eq [7] was used to find n, and so the overall reaction order. After different trials it was decided that n=1.5 is the value that best fits experimental and theoretical results (R > 0.99). There was excellent agreement between the experimental values and the theoretical curve with:

$$\alpha_o = 0.043447 + 0.033118\alpha \quad \text{(with R = 0.991)}$$

This gives 2.5 as the overall reaction order.

DISCUSSION

The value of the activation energy, 20.11 kcal/eq, here reported is lower than that of 22.29 kcal.eq found for a commercial resin EPIKOTE 828. This means that the resin now studied is a very good one to be used both in the building and automobile trades.
Two different ways were used in order to find the best mixing ratio value, that is, the search for the maximum enthalpy and for the maximum glass temperature seem to be very valuable.

Acknowledgments

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