

## **STUDY OF KINETICS OF A THERMOSTABLE MATERIAL WITH GOLD NANOPARTICLES REINFORCED WITH NANOCLAY**

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### **Abstract**

The purpose of this paper was to study the curing kinetics of an epoxy system composed of Diglicidil Ether of Bisphenol A (BADGE  $n = 0$ ) epoxy resin and the meta-xylylenediamine (m-XDA) hardener with nanoparticles of gold and nanoclay type montmorillonite. It is intended to be able to arrive at a kinetic equation that could describe reaction rates as a function of curing degree for all the conversion range, using the model proposed by Kamal et al.

### **Keywords**

epoxy resin, gold nanoparticles, nanoclay, kinetic study

### **INTRODUCTION**

The epoxy system BADGE  $n=0$ /m-XDA/gold nanoparticles have been studied in a previous paper<sup>1</sup>.

Nanoclays are used as reinforcement not only with thermosetting polymers such as epoxy resins, but also with thermoplastics such as polyethylene, especially in the manufacture of films and covers for food and packaging use.

The use of nanoclays as reinforcement of epoxy matrices has been extensively studied during the last years, demonstrating its functionality in increasing properties such as reduction of water absorption, thermal stability, corrosion resistance and mechanical properties. The nanoclays employed are montmorillonite type, which are the most used for the manufacture of nanocomposites.

The reactions of these materials are exothermic due to the crosslinking of the polymer molecules. To study these reactions we use differential scanning calorimetry (DSC).

### **EXPERIMENTAL**

#### **Materials**

The epoxy resin was a commercial DGEBA ( $n = 0$ ) (Resin 332, Sigma Chemical Co., St. Louis, USA) with an equivalent molecular mass of 173.6 g eq<sup>-1</sup>. Gold(III) chloride trihydrate with molecular weight 393.83 g eq<sup>-1</sup> with 99.9+% purity, 3- mercaptopropionic acid, with molecular weight 106.14 g eq<sup>-1</sup> with 99+% purity, methyl alcohol with 99.8% purity and the curing agent meta-xylylenediamine (m-XDA), with an equivalent molecular mass of 151.25 g eq<sup>-1</sup> with 97% purity, were purchased from Sigma-Aldrich Chemie, GmbH, Germany. Sodium borohydride for synthesis with molecular weight

37.83 g eq-1 with 96% purity. Montmorillonite nanoclay were purchased from Sigma-Aldrich Chemie, GmbH, Germany

### Samples preparations

7 g of epoxy resin (BADGE n=0) in a beaker was placed in a glycerin bath at 70 °C. We add 1.4 ml of Au<sup>3+</sup> dissolved in methanol and 0.07 g of nanoclay (montmorillonite nanoclay). At this point, we will evaporate the methanol at 70°C during 2 hours. We add 2.63ml of borohydride at 40°C. The borohydride reduces the Au<sup>3+</sup> to Au<sup>0</sup>. Once added the borohydride would raise the temperature at 70°C. The mixture begins to take on a rosy pink color. We need about 2 hours to evaporate the methanol in which the borohydride is dissolved. 1 g of sample is mixed with m-XDA in stoichiometric ratio.

A heat flow calorimeter from the company TA, model DSC Q100, was used. We perform a dynamic calorimetric scan from -30 °C to 250 °C at heating rate of 10°C/minute to determine the total heat of curing reaction ( $\Delta H_0$ ). A second scan from 10°C to 200°C at the same heating rate was performed to determine the glass transition temperature ( $T_g$ ). Finally the samples were cured at different isothermal temperatures (from 50 °C to 110 °C). The isothermal reaction heats ( $\Delta H^T$ ) were used to obtain kinetic, diffusion and thermodynamic parameters.

### RESULTS AND DISCUSSION

The reaction rate of an epoxy system can be expressed by the contribution of two mechanisms: nth order and autocatalytic. Assuming stoichiometric proportions and equal reactivity for all amine hydrogen, the reaction rate using the Sourour and Kamal<sup>2</sup> kinetic model can be expressed

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

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 critical conversion ( $\alpha_c$ ), conversion at the beginning of the diffusion, 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<sup>3</sup> are used to study the diffusion controlled reaction rate. This equation can be expressed as

$$F(\alpha) = \frac{1}{1 + e^{[A_1 \cdot (\alpha - \alpha_c)]}} \quad (2)$$

where  $A_1$  is an adjustable parameter.

The total heat of reaction ( $\Delta H_0$ ) and the glass transition temperature ( $T_g$ ) for the curing process are shown in Table 1.

**Table 1.** Values of enthalpy changes and glass transition temperatures

Scans	$\Delta H$ (J/g)	$T_g$ (°C)
1	473.7	116.5
2	464.9	118.2
3	485.5	114.6
4	469.8	109.1
Average values	473.5	114.6
Standard deviation	8.8	4.0

The value of the total heat of reaction without filler is 482.5 J/g<sup>1</sup> and that of the  $T_g$  of 105.6 °C. As we can be seen the enthalpy with filler is smaller due to the crosslinking is more difficult because of steric hindrance.

Table 2 shows the enthalpies and the degree of conversion at different isothermal temperatures.

**Table2.** Values of enthalpy changes and conversion at different isothermal temperatures

Temperature (°C)	100	90	80	70	60	50
$\Delta H^T$ (J/g)	450.9	451.6	457.7	422.2	412.2	359.7
$\alpha$	0.93	0.94	0.95	0.88	0.85	0.75

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 nth order and autocatalytic paths at different isothermal temperatures.

**Table 3.** Values of  $k_1$  and  $k_2$  and reaction order for nth and autocatalyzed mechanism at different isothermal temperatures

T (°C)	50	60	70	80	90
$k_1(10^{-4} s^{-1})$	0.4	1.7	3.1	4.3	8.7
$k_2(10^{-4} s^{-1})$	6.1	11.6	22.8	33.7	54.9
m	0.8911	0.9930	1.0481	0.9761	0.9428
n	1.2849	1.2423	1.1240	1.1192	1.2436
$R^2$	0.9975	0.9992	0.9994	0.9999	0.9998

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

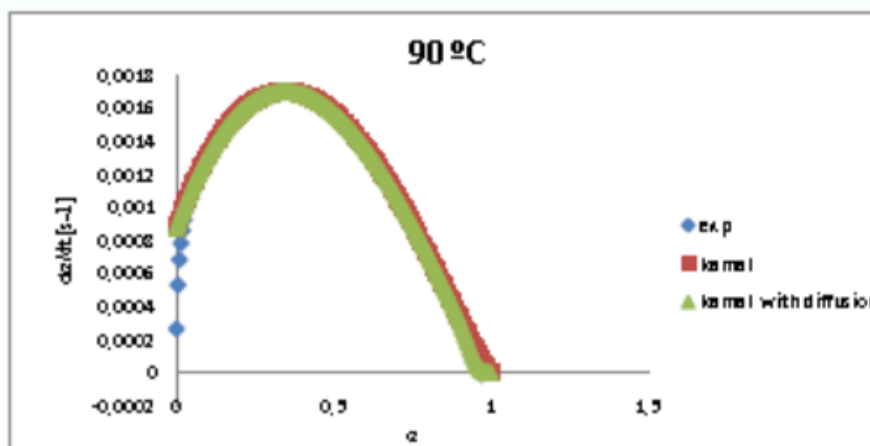
$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m) \cdot (1 - \alpha)^n \frac{1}{1 + e^{[A_1 \cdot (\alpha - \alpha_c)]}}$$

Table 4 shows the diffusion parameters at different isothermal temperatures.

**Table 4.** Diffusion parameters at different isothermal temperatures

T (°C)	50	60	70	80	90
A <sub>1</sub>	20.4067	31.4877	40.3929	52.0000	58.7204
α <sub>c</sub>	0.6357	0.7648	0.8767	0.9275	0.9499
R <sup>2</sup>	0.9096	0.9911	0.9941	0.9853	0.9943

Figure 1 shows the reaction rate versus the conversion at 90°C, and the experimental results are compared with those obtained with the chemical kinetic model and with the kinetic model accounting for diffusion. The agreement is extremely good between the experimental results and kinetic model accounting for diffusion.



**Figure 1.** Plot of the reaction rate versus α at 90°C

On the basis of Table 3, the activation energies corresponding to the n-order and autocatalytic paths have been obtained from an Arrhenius plot of ln k versus 1000/T (where k is the specific reaction rate and T is the absolute temperature), and they are shown in Table 5. Similar results for both activation energies were reported by Nuñez et al.<sup>4,5</sup> and Fraga et al.<sup>6</sup> The values suggest that the autocatalytic mechanism is predominant over the other one.

**Table 5.** Activation energies corresponding to the n-order and autocatalytic paths.

	nth-order mechanism	Autocatalyzed mechanism
Activation energies(kJ/mol)	69.6	53.4

## CONCLUSIONS

The total heat of curing reaction and the glass transition temperature of the system were determined by Differential Scanning Calorimetry, obtaining the values of 473.48 J

/g and 114.62 °C respectively. The values obtained without filler are 482.5 J/g and 105.6°C respectively. As we can see the enthalpy with filler is smaller due to the crosslinking is more difficult because of steric hindrance. A kinetic model that accounts for diffusion effects has been used. There is a good agreement between the experimental results and the kinetic model accounting for diffusion. The activation energies of the mechanisms involved in the curing reaction were estimated. These energies are lower than for the system without nanoclay. This is because a higher crosslinking temperature is required; therefore there is greater molecular kinetic energy which causes less energy to the formation of the activated complex. Because the total heat of curing reaction is relatively small, comparing the epoxy system with and without filler, and the variation of the glass transition temperature is also relatively small, we can consider interesting the use of nanoclay in this type of epoxy systems.

## REFERENCES

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