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CURE KINETICS OF AMINE CURED TETRAFUNCTIONAL EPOXY BLENDS WITH POLY(STYRENE-CO-ACRYLONITRILE)

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Abstract

Cure kinetics using a differential scanning calorimetry (DSC) technique were analyzed for a thermoplastic modified tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) epoxy resin cured with diaminodiphenylsulphone (DDS), an aromatic diamine. The neat resin and its blends with the poly(styrene-co-acrylonitrile) (SAN) of various compositions were studied by applying a phenomenological model proposed by Kamal. Kinetic parameters were determined by fitting experimental data. This model gives a good description of cure kinetics up to the onset of vitrification. Diffusion control was incorporated to describe the cure in the latter stages of cure. The results showed that the addition of SAN did not alter the nature of the reaction, but the reaction rates and final conversions decreased when SAN contents increase, due to reduction of mobility of the reacting species.

Keywords: cure kinetics, DSC, epoxy resin, SAN, thermoplastic blends

Introduction

Thermosetting epoxies possess many desirable properties such as high tensile strength and modulus, excellent chemical and solvent resistance, dimensional and thermal stability, and fatigue properties. These characteristics make them ideal candidates for many important applications including adhesives, electronic encapsulants, and as matrices for fiber-reinforced composites. However, the epoxy resins are generally brittle due high crosslink densities. Modification in order to achieve greater toughness has been an intense subject of studies for many researches [1, 2]. Toughening epoxy matrices using liquid reactive rubbers has been widely reported in the literature [3]. When reactive rubbers are used at levels high enough to noticeably enhance the fracture toughness, T_g (the glass transition temperature) depression of the modified epoxy became severe. Other studies [4] have demonstrated that polymeric thermoplastics, can enhance fracture toughness without sacrificing T_g, strength, stiffness, or other desirable properties of thermosetting resin systems.

In this work a tetrafunctional epoxy resin, tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM), and an aromatic diamine hardener diaminodiphenylsulphone

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(DDS) were blended with the thermoplastic poly(styrene-co-acrylonitrile) (SAN). Since a completely rigorous approach to reaction mechanisms is very difficult considering the complexity of the chemistry of the epoxies curing processes, different approaches were applied to cure kinetics [5–7].

This paper is concerned with a description of the kinetics of cure not only in the first stages of cure, controlled by chemical kinetics, but also in the later stages where gelation and vitrification effect is dominant and the reaction is controlled by diffusion instead of chemical kinetics [8].

Experimental

Materials

The epoxy resin used was tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) (Ciba-Geigy MY 720). The neat epoxy and its blends with poly(styrene-co-acrylonitrile) (Polidux SAN LNA-21 from Repsol Química) were cured with an aromatic amine hardener, diaminodiphenylsulphone (DDS), from Fluka Chemie.

All these components were commercial products, and were used as received without purification. The weight per epoxy equivalent for TGDDM was determined in our laboratory by hydrochlorination [9] and a value of 130 g eq^{-1} was obtained. The hardener has a molecular mass of 248.31 and purity >96% according to the supplier.

DDS-cured TGDDM/SAN blends with 10 and 30 parts of SAN per hundred parts of the TGDDM resin (phr) were prepared following the same procedure: first, SAN was weighted and dissolved in dichloromethane and the solution was mixed with the TGDDM. The solvent was removed in a vacuum oven for 12 h at 100°C. The solvent evaporation was controlled with a thermobalance. The mixture was placed in an oil bath at 120°C and a stoichiometric amount of DDS was slowly added, which continuous mechanical stirring until a homogeneous mixture was observed, which took about ten minutes. The negligible extent of the curing reaction during the mixture process was controlled by isothermal DSC analysis. Samples were then cooled and stored in a freezer until required.

Differential scanning calorimetry

A differential scanning calorimeter, Perkin Elmer DSC-7, equipped with an intracooler and a computer for data acquisition and analysis was used for isothermal and dynamic analysis. The DSC was calibrated using high purity indium standard, and dry nitrogen flow of 40 ml min^{-1} was used as purge gas. Samples of 5–10 mg were placed in aluminium pans. The average values of the heats of reaction determined by dynamic scans at 5, 7.5, 10, 15, 20 and 30°C min^{-1} were taken as the total heats of reaction, ΔH_T, of the neat epoxy and its blends. These values were 525 J g^{-1} for the neat epoxy, and 520 and 545 J g^{-1} for the blends with 10 and 30 phr of SAN respectively. It should be noted that the calculation of these reaction heats was based on per gram of TGDDM/DDS, being the masses of SAN in the blends discounted.

Isothermal cure reactions were realized at three temperatures 190, 200, and 210°C. Each reaction was considered complete when the isothermal DSC curve levelled off the baseline. The isothermal conversion at time t was defined as $\alpha(t)=\Delta H_t/\Delta H_T$, where ΔH_t is the heat under the exotherm curve at time t, calculated by the integration of the DSC isothermal signal.

Results and discussion

Kinetic analysis was performed by mean of an autocatalytic equation proposed by Kamal [10]

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

where α is the conversion of epoxide groups, k_1 and k_2 the rate constants, $d\alpha/dt$ the rate of reaction, and m and n the kinetic exponents of reaction. Constants k_1 and k_2 are temperature dependent according to an Arrhenius law.

Experimental data to model curing are obtained from DSC taking into account that heat evolved during cure is proportional to epoxide groups reacted, i.e.:

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

Figure 1 shows the reaction rates *vs.* time, t, measured directly by the analyzer, in isothermal mode at 200°C for the neat resin, and the blends with 10 and 30 phr of SAN. It can be observed the nature typically autocatalytic in all cases, with maximum rate of conversion at $t>0$. The rate of conversion is affected by the presence of SAN, decreasing when SAN contents increase. Kinetics parameters in Eq. (1) are computed in several ways [10, 11]. Here, the m, n, k_1, and k_2 parameters were esti-

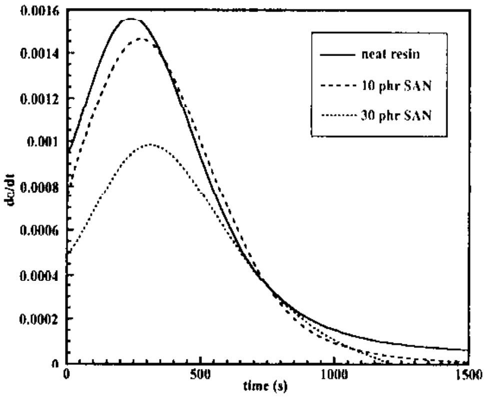

Fig. 1 Plots of the reaction rates *vs.* time at 200°C for the neat resin, and the blends with 10 and 30 phr of SAN

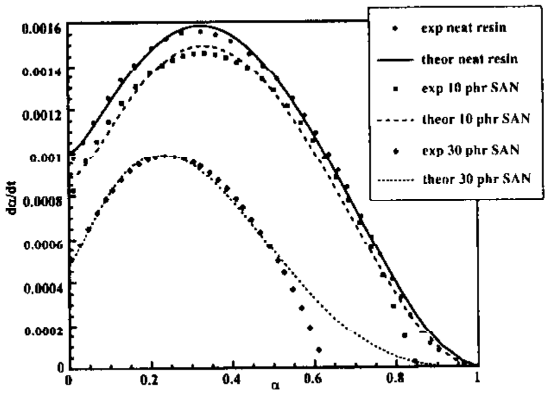

Fig. 2 Comparison between experimental data with the Kamal model predictions at 200°C for the neat resin, and the blends with 10 and 30 phr of SAN

mated without any constraints, using a least square method. Experimental data plotted as dα/d*t* *vs*. α and the model predicted by Kamal are shown in Fig. 2. Rate constants, reaction orders and the corresponding activation energies and preexponential factors obtained by plotting ln*k* *vs*. 1/*T*, for the neat resin, and the blends with 10 and 30 phr of SAN are presented in Table 1.

Table 1 Kamal model parameters for the SAN/epoxy blends

T/°C	m	n	k_1/min^{-1}	k_2/min^{-1}	E_{a1}/ KJ mol^{-1}	E_{a2}/ KJ mol^{-1}	lnA_1	lnA_2
neat epoxy								
190	1.1	1.8	0.000546	0.00488				
200	1.1	1.8	0.00088	0.00757	80.5	81.1	13.5	15.8
210	1.2	2.0	0.0013	0.0117				
SAN/epoxy 10 phr								
190	0.8	1.4	0.00050	0.0026				
200	0.9	1.3	0.00075	0.0047	83.9	75.8	14.2	13.9
210	1.1	1.5	0.0013	0.0077				
SAN/epoxy 30 phr								
190	1.2	3.2	0.00037	0.0110				
200	1.2	3.2	0.000488	0.0135	91.5	68.4	15.8	12.8
210	1.3	2.1	0.00149	0.0203				

To consider diffusion effect a semiempirical equation [12], was used. When the degree of cure reaches a critical value, α_c, diffusion becomes the dominant phenomenon in cure progress, and the rate constant k_d is given by

$$k_d = k_c\exp(-C(\alpha - \alpha_c) \tag{3}$$

where k_c is the rate constant for chemical kinetics and C is a parameter. Equation (3) corresponds to a rather abrupt onset of diffusion control at $\alpha=\alpha_c$, though the onset is somewhat more gradual and there is region where both chemical and diffusion factors are controlling the reaction. According to the expression for the overall effective rate constant, k_e, expressed in terms of k_d and k_c is

$$\frac{1}{k_e} = \frac{1}{k_d} + \frac{1}{k_c} \tag{4}$$

it can be combined with Eq. (3), and to obtain the diffusion factor $f(\alpha)$

$$f(\alpha) = \frac{k_e}{k_c} = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \tag{5}$$

For α much smaller than the critical value, $\alpha \ll \alpha_c$, then $f(\alpha)$ approximates unity, the reaction is kinetically controlled and the effect of diffusion is negligible. As α approaches α_c, $f(\alpha)$ begins to decrease and approaches zero as the reaction effectively stops. The effective reaction rate at any conversion is equal to the chemical reaction rate multiplied by $f(\alpha)$. The diffusion factor was obtained as ratio of experimental reaction rate to the reaction rate predicted by the Kamal model. Figure 3 shows the behaviour of $f(\alpha)$ with increasing conversion at 200°C for the blend with 30 phr of SAN.

Application of nonlinear regression to $f(\alpha)$ *vs.* α data to Eq. (5) gives values of α_c and C, listed in Table 2. A moderate increasing in α_c was observed for the neat system and the blends when increasing temperature. At the same temperatures, the

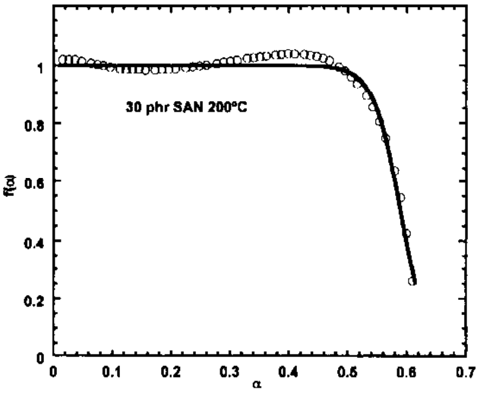

Fig. 3 Diffusion factor, $f(\alpha)$ *vs.* α for the blend with 30 phr of SAN at 200°C

Table 2 Values of critical conversion, α_c, and C parameter for the SAN/epoxy blends

T/°C	α_c	C
neat epoxy		
190	0.74	20.87
200	0.75	36.44
210	0.77	51.43
SAN/epoxy 10phr		
190	0.71	19.8
200	0.73	34.9
210	0.76	37.5
SAN/epoxy 30 phr		
190	0.57	47.9
200	0.59	42.9
210	0.74	30.6

values of α_c decreased when the SAN contents increased due to the difficulties imposed by the thermoplastic to the progress of the reaction. It may be noted that critical conversion is not an adjustable parameter because it reflects the onset of diffusional limitation that occurs only in the later stages of reaction. It is also not an observable quantity since the transition to the diffusion regime is gradual. As cure progress, the mobility of the reacting species is reduced and this leads to diffusional effects. Hence, α_c would reflect the state of cure of the system rather than the temperature of cure.

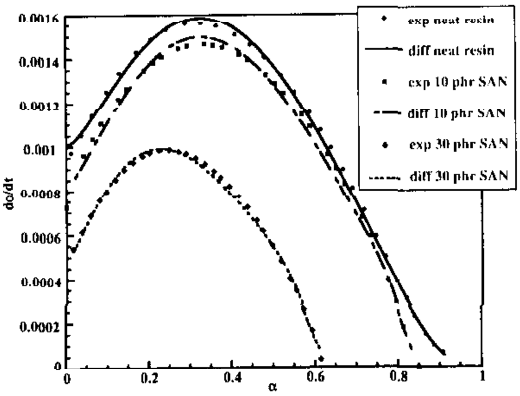

Fig. 4 Comparison of experimental data, dα/dt *vs.* α, with the model with diffusion predictions for the neat resin, and the blends with 10 and 30 phr of SAN

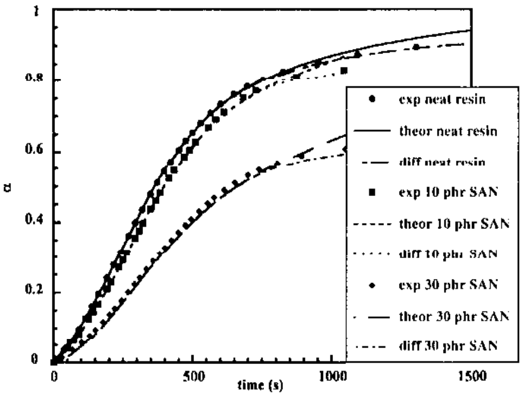

Fig. 5 Plots of α *vs.* t comparing the experimental data with the predictions of the model of Kamal, and the model with diffusion

Figure 4 shows the experimental data, $d\alpha/dt$ *vs.* α and the corrected data when is applied the model with diffusion, and Fig. 5 displays the curves α *vs.* t comparing the experimental data with the predictions of the Kamal model and the model with diffusion.

Conclusions

A phenomenological model proposed by Kamal was used to study the curing kinetics of a DDS-cured TGDDM/SAN system. Fitting experimental data to the model, a good agreement was reached between the predicted and the obtained values up to gelation and vitrification phenomena occurs. To characterize the fact of diffusion the model was modified by introducing a diffusion factor that corrects appreciably the experimental data. By combining the Kamal model and a diffusion factor, it was possible to predict the cure kinetics over the whole range of conversion.

The results showed that when the SAN contents increase there is a reduction of the rates of conversion and the final conversions obtained, due to reduction of mobility of the reacting species imposed by the SAN, however the thermoplastic did not change the autocatalytic nature of curing reaction.

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