

## **CURE KINETICS OF A TETRAFUNCTIONAL RUBBER MODIFIED EPOXY-AMINE SYSTEM**

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### **Abstract**

In this work the curing kinetics behaviour of a rubber modified epoxy amine system is investigated through calorimetric analysis. This study is part of a wider investigation on new epoxy formulations to be used as matrices of composite materials. The aim is to enhance both the processing behaviour and the mechanical properties of the matrix in order to obtain higher performance composites for more demanding applications. The epoxy system is blended with a high molecular mass rubber containing functional groups reactive towards the epoxies. The formation of a rubber/epoxy network can be achieved by means of a 'pre-reaction' between the epoxy monomers and the rubber functional groups, carried out in the presence of a suitable catalyst and before the resin is cured with the amino hardener. In this work the influence of both the rubber and the catalyst on the resin cure kinetics is analysed.

**Keywords:** cure kinetics, DSC, modified epoxy-amine, epoxy rubber system

### **Introduction**

Epoxy resins are commonly used as polymeric matrices for high performance composites. Difficulties during the composites making processes and the epoxies inherent brittleness and moisture sensitivity can limit their application potential. Elastomers are often incorporated in epoxy matrix systems when modifications in the viscosity vs. temperature/pressure profiles or enhancements in their fracture toughness and/or thermal cycle resistance are sought [1, 2]. In the view of choosing the proper set of processing parameters for each specific thermoset-rubber system, the knowledge of cure kinetics is essential information.

The system object of kinetic study in this paper is essentially composed by a tetrafunctional epoxy monomer and a sulfonic amino curing agent, modified by an acrylonitrile-butadiene-methacrylic acid solid rubber.

Recently high Mw solid elastomers, carrying functional groups reactive towards the epoxy groups have been considered as an alternative to the well established reactive liquid butadiene-acrylonitrile copolymers technology [3, 4] in order to mini-

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mise deterioration in the inherent stiffness and strength of the epoxy matrix and reduction in glass transition temperature. Rubber's reactive moieties are reacted with certain amounts of one of the resin precursors in the presence of a proper catalyst, prior to cure. This 'pre-reaction' process allows to obtain 'in situ' cross-linked and chemically stable rubber-resin networks, which would, in turn, ensure generation of controlled morphologies and better toughening of the cured systems. All the other resin precursors and cross-linking agents are added after 'pre-reaction' to give the final formulation, ready to cure.

The aim of the present work is to investigate the influence of the presence of both the rubber phase in the epoxy matrix and the catalyst used for the 'pre-reaction' on the cure kinetics of the resin.

## Experimental

The epoxy components were a nominally tetrafunctional epoxy resin, MY9663 supplied by Ciba Geigy, and a nominally difunctional epoxy resin, Epon 828 supplied by Shell Chemicals. MY9663 was shown by HPLC analysis to be a mixture of monomeric tetraglycidyl-4,4'-diaminodiphenyl methane with various oligomeric species, starting materials and trifunctional epoxy derivatives. The batch used had an epoxide equivalent mass of 125.5. Epon 828 is, basically, the diglycidyl ether of bisphenol A (DGEBA) with an epoxide equivalent mass of 344. The curing agent used was 4,4'-diaminodiphenyl sulphone (DDS) supplied by Ciba Geigy as HT 976.

The rubber was a butadiene-acrylonitrile-methacrylic acid copolymer, 26/68.8/3.2% w/w, (trade name Nipol 1472) supplied by Nippon Zenon.

Three different formulations have been investigated:

1. the Nipol 1472/epoxy resin system, at 5% w/w of rubber content, where the rubber has been 'pre-reacted' with a large excess of TGDDM epoxy monomer in the presence of 0.5% w/w of ethyl triphenyl phosphonium iodide (ETPI), (PWE system);
2. the epoxy system with 0.5% w/w of ETPI, (SC system);
3. the base epoxy system (SCN system).

In the 'pre-reaction' procedure Nipol 1472 is previously dissolved in acetone and then charged into a flask containing the TGDDM monomer and the catalyst. The reactor is fitted with stirrer, nitrogen inlet and condenser. The contents are heated to gently reflux for 2 h and then allowed to cool to room temperature when the other epoxy oligomers and the curing agent are also charged and stirred until a homogeneous mixture is obtained.

Kinetic studies were performed using the differential scanning calorimeter Perkin Elmer DSC 7. Samples having a mass in the range of  $5-15 \cdot 10^{-3}$  g and sealed in aluminium pans were subjected to isothermal curing at different times and temperatures. At the end of each curing cycle the samples were quickly cooled in liquid nitrogen. The residual heat of reaction was evaluated through heating runs from 30 to 330°C at the heating rate of  $10^\circ\text{C min}^{-1}$ . The residual heat of reaction was evaluated from the area under the melting peak. In order to assign a characteristic heat of reac-

tion to the ring opening of the epoxide groups in different mixtures, the values determined by the DSC tests were referred to the mass of the epoxy monomers only.

## Results and discussion

In Table 1 the heats of reaction and the exothermic peak temperatures for SCN, SC and PWE systems are reported. Both SC and PWE have lower temperatures at the exothermic peak than SCN, while the heat of reaction is almost the same for all the systems. This is the first indication that the presence of the ETPI catalyst and/or the rubber can affect the curing rate of the epoxy system to some extent.

**Table 1** Heats of reaction and exothermic peak temperatures for SCN, SC and PWE systems

System	Peak (from-to)/°C	Peak temperature/°C	Heat of reaction/kJ mol <sup>-1</sup> *
SCN	176–246	275	840
SC	165–265	252	878
PWE	165–265	252	836

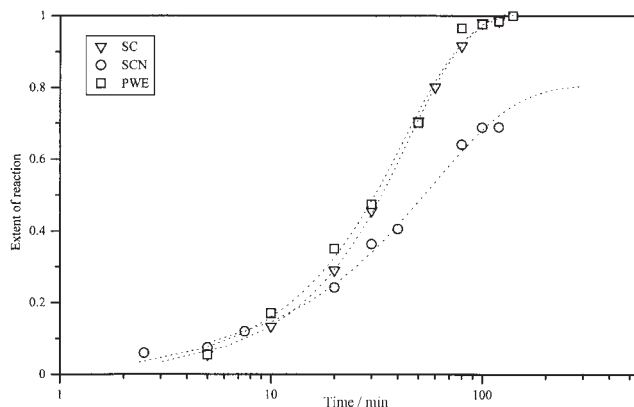
\*Grams of epoxy component

In order to obtain a more careful investigation about the influence of the rubber and the catalyst on the cure rate, the advancement of cure as a function of time was investigated measuring, by DSC technique, the heat evolved during isothermal cure at different temperatures. An assumption has been made that the heat evolved during cure reaction is proportional to the extent of cure process,  $x$ :

$$x = \frac{\Delta H_{\text{rxn}} - \Delta H_{\text{res}}}{\Delta H_{\text{rxn}}}$$

where  $\Delta H_{\text{rxn}}$  is the total heat liberated when the uncured mixture is taken to complete cure and  $\Delta H_{\text{res}}$  is the residual heat of reaction of partially cured samples. As already pointed out [5], this assumption is rigorously valid only when a single reaction dominates the cure process (large excess of primary amine), while leads to overestimate the epoxy conversion when more than one reaction is responsible for the advancement of the cure (i.e. epoxy-primary amine, epoxy-secondary amine, hydroxyl-amine, epoxy-epoxy reactions). Nevertheless previous results [5] demonstrate that the assumption of the heat evolved being proportional to the extent of the reaction, even if it is not conceptually correct, gives negligible deviation on the reaction rate of the system also in correspondence of low ratios of DDS primary amine and epoxy groups.

A comparison of the cure kinetics, at a fixed temperature, is shown in Fig. 1, where the extent of reaction vs. log(time) at 180°C for SCN, SC and PWE systems is reported. Always a sigmoidal form of the curves is observed, thus indicating an autocatalytic cure behaviour, SC and PWE systems present faster cure reactions.



**Fig. 1** Advancement of the reactions for isothermal cure at 180°C of the base epoxy system with ETPI (SC), the base epoxy system without ETPI (SCN) and the rubber/epoxy system 'pre-reacted' with ETPI (PWE)

In Figs 2–4 the extent of reaction *vs.*  $\log(\text{time})$  at different temperatures for SCN, SC and PWE systems respectively is reported. For each formulation all the curves have the same functional form, only shifted by a constant factor along the  $\log(\text{time})$  axis. It follows that all the *x vs. log(time)* curves at different temperatures should be superposable by simply shifting each curve along the  $\log(\text{time})$  axis relative to a curve at an arbitrary reference temperature by a shift factor,  $A(T) = \log(\text{time}_T - \log(tT))$ .

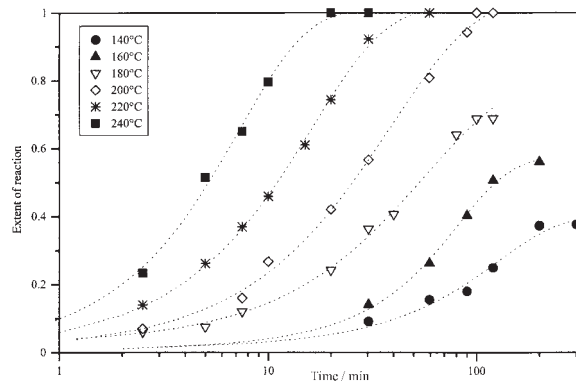
In Figs 5–7 the master curves of SCN, SC and PWE with  $T_c = 180^\circ\text{C}$  as reference temperature are reported. The master curve represents the progression of the cure reactions when a material is cured at a selected temperature, if the reaction is only kinetically controlled. During cure, it is possible, that the glass transition temperature increases over the curing temperature; this phenomenon is called vitrification. When the system vitrifies the cure reaction kinetics becomes diffusion controlled and the curve of conversion *vs.* time branches off from the master curve, rendering impossible the attainment of complete conversion. The master curves, reported in Figs 5–7, indicate that the SC system does not present vitrification phenomena at any of the cure temperatures considered, but, while for both the PWE and SCN systems vitrification occurs, it does for PWE in correspondence to lower temperatures and higher conversion values than for SCN. Therefore, the presence of the catalyst prevents from early occurrence of vitrification phenomena in both SC and PWE formulations.

In order to determine the cure activation energy we considered the phenomenological reaction rate expressions have general formula:

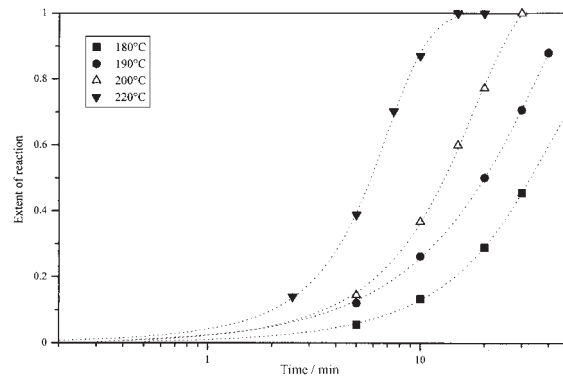
$$\frac{dx}{dt} = K f(x), \quad (1)$$

where commonly  $f(x)$  is considered depending only on  $x$  while  $k$  is considered depending on temperature in an Arrhenius form:

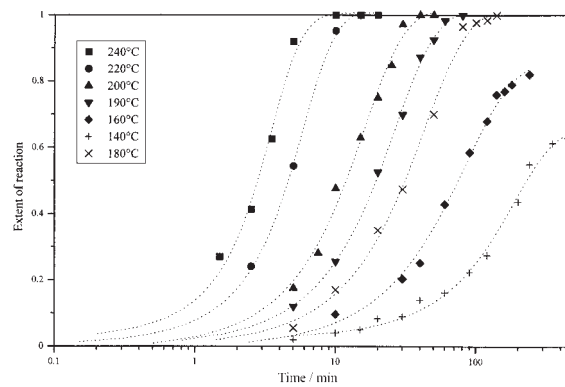
$$k(T) = A_0 \exp(-E/RT) \quad (2)$$



**Fig. 2** Advancement of the cure reactions for the base epoxy system without ETPI (SCN) at different cure temperatures



**Fig. 3** Advancement of the cure reactions for the base epoxy system with ETPI (SC) at different cure temperatures



**Fig. 4** Advancement of the cure reactions for the rubber/epoxy system 'pre-reacted' with ETPI (PWE) at different cure temperatures

where  $A_0$  is the frequency factor and  $E$  the apparent activation energy of the global reaction. The above discussed shift factors can be used to calculate the Arrhenius activation energy for the overall reaction:

$$A(T) = \ln(t_{\text{ref}}) - \ln(t_T) = [\ln k(T) - \ln k(T_{\text{ref}})] = -E/RT + E/RT_{\text{ref}} \quad (3)$$

When  $T_{\text{ref}}$  is fixed and all the other data are shifted relatively to the reference temperature, plotting the shift factor  $A(T)$  vs.  $1/T$  should yield a straight line with slope given by  $-E/R$  and intercept equal to  $E/(RT_{\text{ref}})$ . For the SCN system the activation energy of  $71.9 \text{ kJ mol}^{-1}$  and for the PWE and SC systems the same activation energy value of  $75.2 \text{ kJ mol}^{-1}$  were respectively determined. These values represent the overall activation energy for the curing process, when the curing rate is kinetically controlled.

The general rate equation can be more specified when it applies to a particular system. Therefore considering that vitrification stops the reaction before its completeness is achieved, to satisfy the condition of zero reaction rate at the vitrification conversion ( $x = x_{\text{max}}$ ), the above mentioned function  $f(x)$  may be transformed into:

$$f(x) = (x_{\text{max}} - x)^n g(x) \quad (4)$$

In particular,  $g(x)$  for the autocatalytic model can be expressed as  $(K_1 + K_2 x^m)$  [2]. The values of  $K_1$ ,  $K_2$ ,  $m$  and  $n$  must be determined from experimental data. When the reaction temperature is above the glass transition temperature of the completely cured resin  $x_{\text{max}} = 1$ , and the Eq (1) becomes:

$$dx/dt = (1-x)^n (K_1 + K_2 x^m) \quad (5)$$

The values of  $m$  and  $n$ , the sum of which represents the overall reaction order, are calculated by using a linear regression of the reduced reaction rate  $dx/dt/(1-x)^n$  over  $x^m$  in a range of conversion where there is no influence of the diffusion control on the rate of reaction. Plots of reduced reaction rate vs. extent of reaction were used to calculate  $K_1$  and  $K_2$  from the intercept and the slope of the linear part of the curve, respectively, using Eq. (5).

The values of the order of reaction and the rate constants, reported in Tables 2–4 have been calculated, while the activation energies associated to the two-rate constants  $K_1$  and  $K_2$  for SCN, SC and PWE are reported in Table 5.  $E_{a1}$  and  $E_{a2}$  are very close for the two systems with catalyst, the calculated ‘overall’ activation energy for each is equal to the average value of these two distinct contributions. Comparing these values with those for SCN system we notice a reduction of  $E_{a1s}$  together with a substantial constancy of the  $E_{a2}$  values, thus implying that ETPI, used to promote reaction between the rubber and the epoxy monomer, also catalyses the epoxy ring opening during the first part of the curing process.

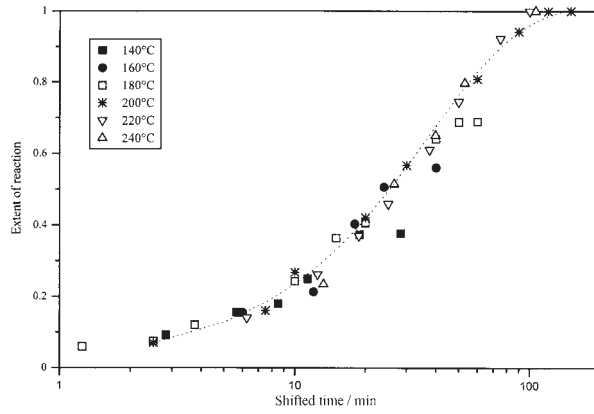


Fig. 5 Master curve for the base epoxy system without ETPI (SCN)

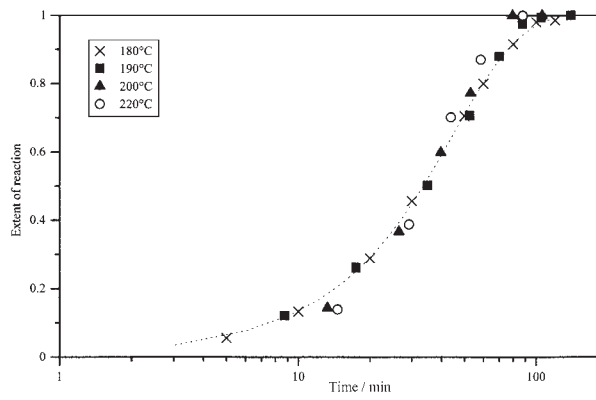


Fig. 6 Master curve for the base epoxy system with ETPI (SC)

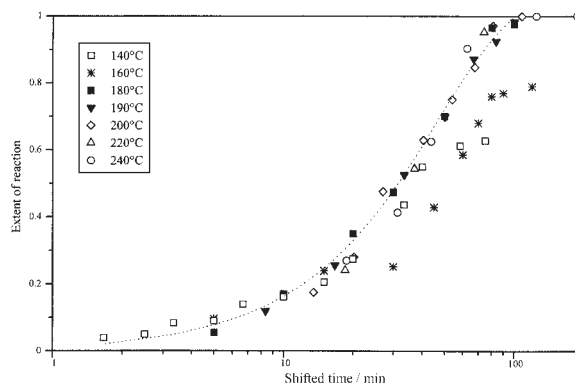


Fig. 7 Master curve for the rubber/epoxy system 'pre-reacted' with ETPI (PWE)

**Table 2** Order of reaction and kinetic parameters for SCN system

Cure temperature/ °C	Conversion range	<i>m</i>	<i>n</i>	<i>K</i> <sub>1</sub>	<i>K</i> <sub>2</sub>	Correlation coefficient
140	0–20	1	2	0.0021	0.006	0.9898
160	0–30	1	2	0.0033	0.0227	0.9970
180	0–60	1	2	0.0124	0.0203	0.9970
200	0–70	1	1	0.0247	0.0086	0.9826
220	0–70	1	1	0.051	0.0415	0.9987
240	0–80	1	1	0.0999	0.1347	0.9986

**Table 3** Order of reaction and kinetic parameters for PWE system

Cure temperature/ °C	Conversion range	<i>m</i>	<i>n</i>	<i>K</i> <sub>1</sub>	<i>K</i> <sub>2</sub>	Correlation coefficient
180	0–80	1	1	0.0151	0.029	0.9943
190	0–80	1	1	0.0227	0.0529	0.9987
200	0–80	1	1	0.0369	0.0935	0.9879
220	0–85	1	1	0.0563	0.4218	0.9776
240	0–90	1	1	0.0678	0.7823	0.9978

**Table 4** Order of reaction and kinetic parameters for SC system

Cure temperature/ °C	Conversion range	<i>m</i>	<i>n</i>	<i>K</i> <sub>1</sub>	<i>K</i> <sub>2</sub>	Correlation coefficient
180	0–60	1	1	0.0127	0.0348	0.9822
190	0–60	1	1	0.0252	0.0381	0.9884
200	0–70	1	1	0.0227	0.1408	0.9939
220	0–80	1	1	0.032	0.4342	0.9999

**Table 5** Cure reaction activation energies system

System	<i>E</i> <sub>a1</sub> /kJ mol <sup>-1</sup>	Correlation coefficient	<i>E</i> <sub>a2</sub> /kJ mol <sup>-1</sup>	Correlation coefficient
SCN	70	0.997	134	0.997
PWE	48	0.9352	111	0.9856
SC	37	0.7348	127	0.9397

## Conclusions

Extent of reaction *vs.* reaction time curves present for all the systems considered the same sigmoidal functional form, thus suggesting an autocatalytic cure behaviour.



The ETPI catalyst, used for the 'pre-reaction' between the functional groups of the rubber and one of the epoxy resin polymerisation precursors and present in both the epoxy base system (SC) and the rubber modified system (PWE) formulations, causes a substantial increase in the cure reaction rate with comparison to the cure kinetics of the resin system with no rubber and catalyst (SCN).

This effect is revealed by a comparison between the peak temperatures in the curves of cure reactions and it is also manifested in a reduction of the values of the activation energy relative to the initial stage of the cure for systems containing the catalyst when compared with the corresponding value for the base epoxy resin. As a consequence of faster cure reactions vitrification does not occur for SC and occurs in correspondence to higher temperatures for PWE than for SCN system. The almost identical response from SC and PWE would suggest that the rubber itself does not significantly influence the cure kinetics.

## References

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