

## MODELLING THE CURING OF EPOXY-RESIN COATING AT LOW TEMPERATURE (50 °C)

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### ABSTRACT

The state of cure of a coating made of epoxy resin has been calculated using a kinetic equation expressed in terms of temperature and time. The kinetic equation follows an Arrhenius form with a single energy of activation which has been determined from calorimetry measurements in scanning mode. This equation has been used to follow the cure of coatings at temperatures as low as 50 °C. The hardness has also been used to follow the change in mechanical properties of the coating during the cure, and it has been related to the state of cure. Relationships between time and temperature have been determined in order to obtain coatings of good quality.

### INTRODUCTION

Epoxy resins have been widely studied, especially with respect to their use as polymeric matrices for composites and also for high performance coatings. Many studies deal with the mechanical properties of composites, but only a few papers are concerned with the prediction by calculation of the operational conditions necessary for the complete chemical reaction in the resin.

This paper is concerned with the general problem of determining the best conditions of temperature and time for preparing epoxy-resin coatings with good mechanical properties. Very often, when dealing with bulk materials, it is not easy to heat the resin in order to reduce the curing time. The problem is how to cure the resin coating at room temperature, or at least at a temperature around 50 °C, and to know the time required for obtaining a proper coating under these conditions.

Mathematical simulations of the curing process have been obtained using models for epoxy resin [1–3] and for epoxy resin containing various fillers and loads [4,5]. These models, based on numerical methods with finite differences, take into account not only the heat transferred by conduction through the material, but also the kinetics of the cure. The kinetics of the

heat evolved from the cure reaction has been determined using calorimetric techniques, either under isothermal conditions or in scanning mode [6–9]. Various equations have been proposed to describe the heat of reaction, some of them having two activation energies [9–11], others based on an Arrhenius form with a single activation energy [6–9].

The main purpose of this paper is to show that coatings made using epoxy resin can be cured at low temperatures, and that the state of cure (SOC) of the resin in terms of temperature and time can be predicted by calculation with the help of a kinetic equation using data obtained by calorimetry. In addition, a mechanical property, in this case hardness, was chosen to follow the cure, because this test is non-destructive for the coating.

## EXPERIMENTAL

### *Material*

The resin was obtained by mixing the epoxy resin (Lopox 200, CDF-Chimie) and the hardener containing an anhydride of MeTHP (D 2605, CDF-Chimie), with an accelerator containing 0.75% of an aromatic amine (type A, 105, CDF-Chimie). The binary mixture was prepared at room temperature with continuous stirring.

The best composition, according to ref. 12, is epoxy resin, 56 wt.%; hardener, 44 wt.% [13].

### *State of cure (SOC) of the resin*

After mixing the two components, the mixture was applied onto iron-steel sheets, with an average thickness of 1 mm.

The same mixture was encapsulated in a cylindrical steel holder, 5 mm in diameter. The holder was then dropped in the calorimeter and heated at a constant rate of  $5^{\circ}\text{C min}^{-1}$  to completion of the reaction. The heat flux was constantly recorded as a function of time and temperature, using a computer connected to the calorimeter. The order of reaction and the activation energy  $E$  was calculated from the heat-flux temperature values using Freeman and Carroll's technique.

## THEORETICAL CALCULATIONS

### *Assumptions*

In order to simplify the problem, the following assumptions were made.

(i) The rate of heating through the sample is very low when using the calorimeter in scanning mode because the heating rate of the calorimeter is low.

(ii) Following this first assumption, the temperature within the sample is uniform and is the same as the temperature of the calorimeter.

(iii) The sample, deposited in thin layers, is heated at rather low temperatures (50 °C) so that the curing time is longer than the heating time. If the heating time is neglected, the reaction can be considered as taking place at the constant applied temperature.

(iv) The rate of heat evolved from the overall reaction follows an Arrhenius form with a constant energy of activation.

(v) The SOC in the resin at time  $t$  is given by the heat evolved from the reaction up to time  $t$  as a fraction of the total heat evolved.

### *Mathematical treatment*

The rate of heat transferred through the thickness of the resin layer is

$$\rho c \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left[ \lambda \frac{\partial T}{\partial x} \right] + \rho \frac{dQ}{dt} \quad (1)$$

where the contribution by the heat conduction and by the heat evolved from the reaction can be seen in the second term.

The rate of the reaction is expressed in the Arrhenius form

$$\frac{d}{dt} \left[ \frac{Q_t}{Q_\infty} \right] = k_0 \left[ 1 - \frac{Q_t}{Q_\infty} \right]^n \exp - \frac{E}{RT} \quad (2)$$

## RESULTS

Two kinds of results are of interest in this paper: one is concerned with the determination of an equation expressing the value of the state of cure in terms of temperature and time, and with the use of this equation in the case of the coating; the other is concerned with the establishment of a relationship between the hardness and the state of cure.

### *Kinetic parameters for the curing of epoxy resin*

In this calorimetric technique, enthalpy changes accompanying chemical events in the sample are monitored as a function of temperatures (and time). The result is a profile of the rate of enthalpy change as a function of temperature, as the calorimeter is heated at a constant linear rate.

The positive part of the heat flux–temperature history, when the heat is emitted from the sample to the calorimeter detector, is due to the internal heat generated by the cure reaction.

The mathematical treatment of the experimental heat flux–temperature curve was achieved using Freeman and Carroll's technique. The main as-

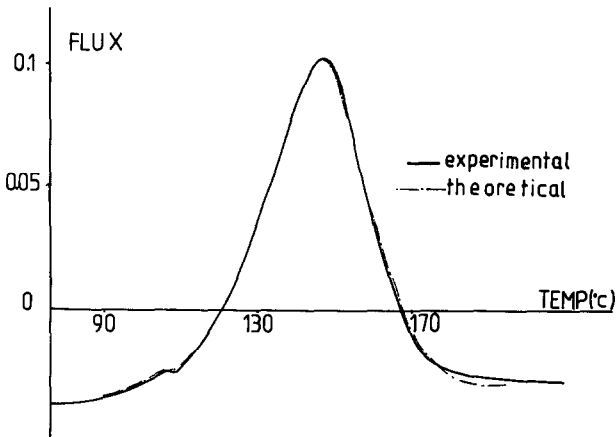


Fig. 1. Experimental and theoretical heat flux-temperature DSC curves for the curing of epoxy resin (heating rate,  $5^{\circ}\text{C min}^{-1}$ ).

assumptions for this determination are given in (i) and (ii) above. The kinetic parameters in eqn. (2) have thus been obtained. The accuracy of these kinetics parameters has been determined by comparing the calculated and experimental heat flux-temperature histories. As shown in Fig. 1, a good superimposition is observed between the curves, providing the validity of these kinetics parameters.

#### *Determination of the SOC of the epoxy-resin coating*

The value of the SOC of epoxy resin deposited in a coating of 0.9 mm thickness at  $50^{\circ}\text{C}$  has been calculated using the kinetic equation, eqn. (2), and the kinetic parameters in Table 1, assuming that the temperature is the same within the coating. The SOC-time history obtained is shown in Fig. 2, where the kinetic parameters (order  $n$ , constant  $k$  and activation energy  $E$ ) are constant.

#### *Sample in a calorimeter*

A large sample was chosen for the calorimetric determination (150 mg), because it must be representative of the homogeneity of the resin. The heating rate selected for the calorimeter is sufficiently low ( $5^{\circ}\text{C min}^{-1}$ ) so

TABLE 1

Kinetic parameters for the curing of epoxy resin

$$Q_{\infty} = 59 \text{ cal g}^{-1}$$

$$E = 29000 \text{ cal mol}^{-1}$$

$$n = 2$$

$$k_0 = 2 \times 10^{14} \text{ s}^{-1}$$

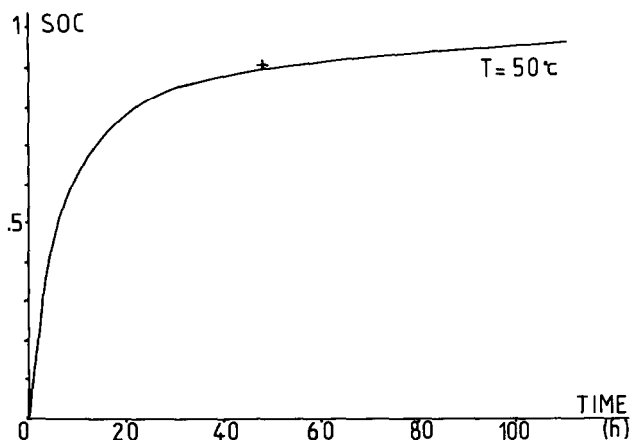


Fig. 2. SOC of epoxy resin coating as a function of time at 50°C: —, theoretical; +, experimental.

that this rate is lower than the rate of heat transfer through the sample. As a result, the temperature within the sample is constant and equal to the temperature of the calorimeter (assumptions 1 and 2). The rate of the reaction can then be determined at any time by eqn. (2).

#### *Sample in a thin sheet*

After application on the metal support, the resin was exposed to air kept at constant temperature. As this temperature is low and the thickness of the resin layer is small, thermal equilibrium is reached quickly, and the reaction can be considered as proceeding under isothermal conditions. Equation (2) is then also used for determining the value of the state of cure at any time for the selected constant temperature.

After curing for 44 h, a fragment of the coating was taken as a sample and placed in the calorimeter for determination of the value of the residual state of cure. The value obtained ( $6 \text{ cal g}^{-1}$ ), shown (+) in Fig. 2, is located on the theoretical SOC–time curve, thus supporting the validity of this result.

The time necessary for the state of cure to reach 90% is expressed as a function of the constant temperature applied to the coating in Fig. 3. It is easy to appreciate the great effect of temperature on the rate of the cure reaction.

#### *The hardness of the coating in relation to the SOC*

The coating hardness was monitored because it is easy to determine and it is non-destructive for the sample. A small “pocket-type” hardness meter was used for measuring the hardness (Shore Durometer D, ISO R 868). In spite

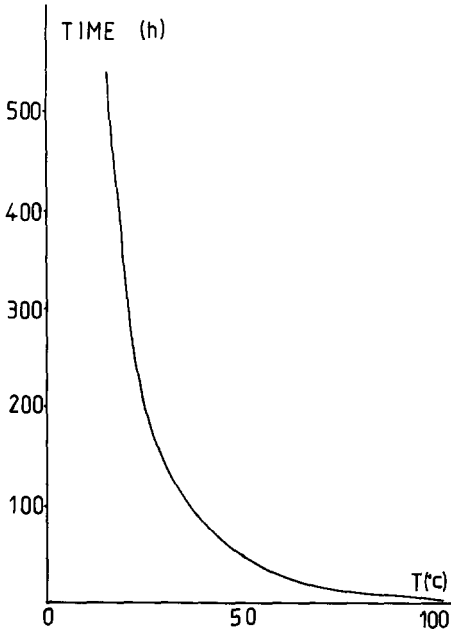


Fig. 3. Cure time as a function of the temperature for an SOC of 90%.

of the small thickness of the coating (1 mm), hardness measurements were made for coatings cured at various temperatures (50, 90 and 100 °C). The hardness was determined after the coating had been cooled down to room temperature.

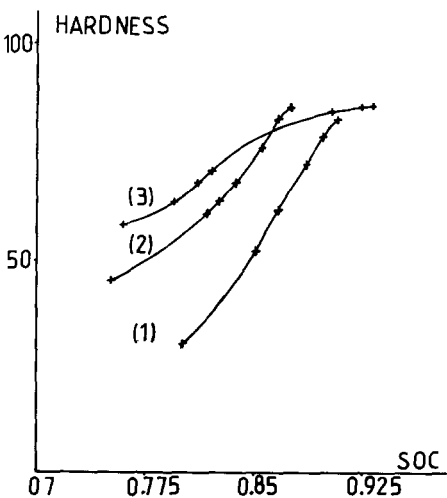


Fig. 4. Hardness of epoxy resin coatings as a function of SOC for cure obtained at various temperatures: (1), 100 °C; (2), 90 °C; (3), 50 °C.

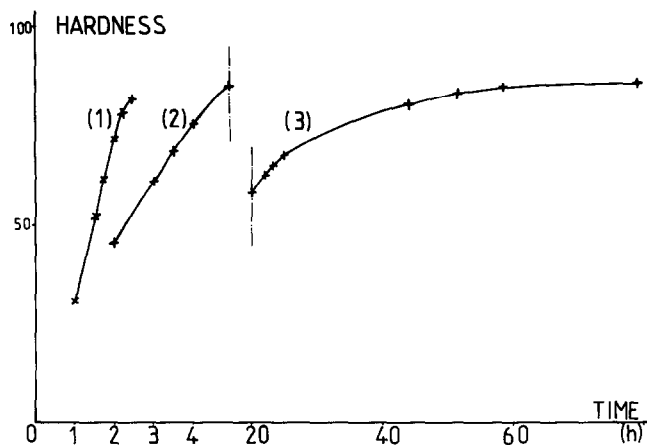


Fig. 5. Hardness of epoxy resin coatings as a function of cure time for cure obtained at various temperatures: (1), 100°C; (2), 90°C; (3), 50°C.

The hardness of the coating was expressed as a function of the state of cure, calculated using eqn. (2), for the three temperatures 50, 90 and 100°C. As shown in Fig. 4, there is some correlation between hardness and the state of cure although it is far from perfect. Hardness values ranging from 80 to 85 are obtained when the state of cure reaches 90%, for various temperature conditions.

The increase in hardness as a function of time for the temperatures 50, 90 and 100°C is illustrated in Fig. 5. As was shown in the case of the increase in the SOC, the effect of temperature on the hardness–time curves is very significant.

## CONCLUSIONS

The value of the state of cure of epoxy resin applied as a coating was determined in terms of temperature and time using a kinetic relationship. This expression follows an Arrhenius form with a simple constant energy of activation. The kinetic parameters were obtained from calorimetric measurements in scanning mode. Thus, it is possible to predict by calculation the time necessary for the coating to reach a known SOC when the coating is kept at constant temperature or when the coating follows a definite temperature–time history.

The hardness of the coating was also determined and related to the value of the SOC.

These results are of interest in the understanding of the low-temperature curing of resin coatings.

## LIST OF SYMBOLS

$C$	heat capacity of the resin
$E$	activation energy of the cure reaction
$k_0$	pre-exponential factor
$n$	order of the cure reaction
$Q_t, Q_\infty$	heat evolved up to time $t_i$ , total heat evolved from the cure reaction
$t$	time
$T$	temperature
$x$	abscissa

*Greek letters*

$\lambda$	thermal conductivity
$\rho$	density of the resin

## REFERENCES

- 1 M. Chater and J.M. Vergnaud, *Europ. Polym.*, 24 (1988) 245.
- 2 M. Chater, J. Bouzon and J.M. Vergnaud, *Plast. Rubber Proc. Applic.*, 7 (1987) 199.
- 3 M. Chater and J.M. Vergnaud, *J. Polym. Eng.*, 8 (1988) 1.
- 4 G. Robert, J.B. Rochette, J. Bouzon and J.M. Vergnaud, *Thermochim. Acta*, 102 (1986) 93.
- 5 A. El Brouzi, J. Bouzon and J.M. Vergnaud, *Plast. Rubber Applic.*, 12 (1989) 71.
- 6 J.M. Vergnaud, *Thermochim. Acta*, 114 (1987) 15.
- 7 J.Y. Armand, J. Bouzon and J.M. Vergnaud, *Thermochim. Acta*, 116 (1987) 301.
- 8 H. Liu, J.Y. Armand, J. Bourgois and J.M. Vergnaud, *Thermochim. Acta*, 126 (1988) 81.
- 9 K. Kretschmar and K.W. Hoffmann, *Thermochim. Acta*, 83 (1985) 139.
- 10 M.E. Ryan and A. Dutta, *Polymer*, 20 (1979) 203.
- 11 M.R. Kamal, *Polym. Eng. Sci.*, 14 (1974) 231.
- 12 M. Chater, K. Lalart, J. Michel-Dansac and J.M. Vergnaud, *Europ. Polym. J.*, 22 (1986) 805.
- 13 M. Chater and J.M. Vergnaud, *Europ. Polym. J.*, 23 (1987) 563.