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DETERMINATION OF THE STATE OF CURE OF EPOXY RESIN USED IN COMPOSITE WITH SAND

G. ROBERT, J.B. ROCHETTE, J. BOUZON and J.M. VERGNAUD

Laboratory of Materials and Chemical Engineering, U.E.R. of Sciences, 23, Dr. P. Michelon, University of St-Etienne, St-Etienne 42023 (France)

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ABSTRACT

A calculation model for predicting the time necessary for the cure reaction of an epoxy resin in a composite to reach a definite value has been described. The model takes into account the kinetics of the cure reaction and the heat transferred by conduction through the composite. The kinetics of cure were determined by differential scanning calorimetry using the composite itself. The kinetic parameters are about the same as those obtained with the pure resin. The enthalpy of cure is proportional to the amount of resin and hardener. The time calculated for curing the sample meant that the sample had good mechanical properties.

INTRODUCTION

Epoxy resins have been widely studied, especially for their use as a polymeric matrix for composites [1], and various reviews are particularly concerned with this topic. But if many studies deal with the mechanical properties of composites and the effect of fibres or loads on them, there is surely a lack of information on methods for predicting, by calculation, the operational conditions necessary for chemical reaction in the resin to be achieved properly.

The present paper is concerned with the general problem of determining the best conditions of temperature and time for preparing composites with a resin of good mechanical properties. Mathematical simulations are easily obtained with the help of models of the whole process. We have applied a general model [2–5] to the case at hand with small sheets, the composite being made of epoxy resin and sand. This model takes into account not only heat transferred by conduction through the material and the mold–material interface, but also the kinetics of the cure reaction.

The kinetics of the heat evolved from the cure reaction were determined by using the DSC technique with rather large samples (100–200 mg). As shown previously, the use of large samples in calorimetry is responsible for the development of large gradients of temperature through the sample

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because of low values of thermal properties and especially of the high value of the enthalpy of cure [2–5]. As a result, we preferred the scanning mode to work under isothermal conditions in order to reduce these high gradients of temperature, which are inappropriate for the determination of reaction kinetics [6–10]. In spite of these difficulties, the DSC technique with a large sample and a reaction of high enthalpy was found of interest in this study because of the high heterogeneity of these sand–epoxy resin mixtures.

After simulating the process by using the kinetics of the cure reaction and the values of thermal properties, the operational conditions obtained by calculation were used to prepare various samples of composites having good mechanical properties. Moreover, the simulation enables us to determine other information of interest, such as the profiles of temperature and state of cure developed through the sample during the process.

THEORETICAL

Assumptions

Several assumptions were made concerning the reaction of cure and heat transferred through the sample.

(i) Heat flow is unidirectional through the thinner dimension of the sample. Although the shape of the sample is rather complicated, we have made this assumption considering the sample as a sheet, because the thickness of this sheet is shorter than all other dimensions.

(ii) There is no flow and no molecular diffusion, so heat is transferred only by conduction.

(iii) Thermal parameters, such as thermal conductivity, λ, and heat diffusivity, α, are constant during heating and reaction. These parameters were calculated by using a linear contribution law from epoxy resin and sand.

(iv) Kinetic parameters are kept constant during the reaction, as has been found with the DSC technique [8–12].

(v) The temperature on slab faces remains the same as that in the mold when the sample is dropped into the slabs.

(vi) The slabs of the mold and sample are in perfect contact.

Mathematical treatment

The unidirectional heat flow through the thickness of the sample sheet is expressed by the equation of transient heat conduction:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} + \frac{1}{C_{(T)}} \frac{\mathrm{d}Q_t}{\mathrm{d}t} \tag{1}$$

where we can see the contribution of conduction heat and reaction heat.

Initial and boundary conditions are:

$$t = 0 \quad 0 \leqslant x \leqslant L \quad T = T_0 \qquad \text{sample space} \tag{2}$$

$$t > 0 \begin{cases} x < 0 \text{ and } x > L \quad T = T_m & \text{mold space} \\ 0 \leqslant x \leqslant L \quad T = T_{t,x} & \text{sample space} \end{cases} \tag{3}$$

Although the reaction of cure was a complex process, we found that the overall rate of heat evolved from the cure reaction was given by a single reaction with a constant activation energy.

$$\frac{dY}{dt} = k_T (1 - Y)^N \tag{4}$$

with

$$Y = \frac{Q_t}{Q_\infty} \text{ and } k_T = k_0 \exp(-E/RT) \tag{5}$$

Q_∞ being the total enthalpy, and Q_t the heat evolved from reaction (order N) up to time t. k_0 is a constant and E the activation energy.

Numerical analysis

As the integration of eqn. (1) is not possible with mathematical treatment, the problem was solved by using an explicit numerical method with finite differences. The sample sheet is divided into equal finite slices of thickness Δx by considering temperature-reference planes [13]. The heat balance written on plane n during the time Δt, gives:

$$T_{i+1,n} = \frac{1}{M}\left[T_{i,n-1} + (M-2)T_{i,n} + T_{i,n+1}\right] + \frac{1}{C_{(T)}} \frac{dQ_t}{dt} \Delta t \tag{6}$$

where the dimensionless number M is

$$M = \frac{(\Delta x)^2}{\Delta t} \frac{1}{\alpha} \tag{7}$$

and $T_{i,n}$ is the temperature at plane n and time $i\Delta t$.

The heat generated by the cure reaction from the beginning to the time $i\Delta t$, was calculated by the following equations (if $N \neq 1$).

$$Q_t = Q_\infty \left[1 - (1 + (N-1)S_i)\frac{1}{1-N}\right] \quad Y = 1 - \left[1 + (N-1)S_i\right]^{\frac{1}{1-N}} \tag{8}$$

where

$$S_i = \int_0^{i\Delta t} k_{T_t} \, dt \tag{9}$$

$$\frac{dQ_t}{dt} \Delta t = Q_{i+1} - Q_t \tag{10}$$

and the approximate recurrent relation

$$S_{t+1} = S_t + k_{T,\Delta t}\Delta t \tag{11}$$

As the two faces of the mold were assumed to be in perfect contact with the sample, the heat balance at the interface enables us to find the following relation between the temperature of the mold, T_m and the temperature on sample faces, $T_{t,0}$.

$$T_{t+1,0} = \frac{H}{1+H}T_m + \frac{1}{1+H}T_{t,1} \tag{12}$$

by using the coefficient H evaluated by the relation

$$H = \left(\frac{\alpha_m}{\alpha_s}\right)^{0.5}\frac{\lambda_s}{\lambda_m} \tag{13}$$

EXPERIMENTAL

Materials

Epoxy resin with two components: epoxy DGEBA (Lopox 200 STO 1, CDF-Chimie) and hardener (cyclo-aliphatic, D2605, CDF-Chimie).

The formulation investigated contained 80 parts of curing agent per hundred parts of resin, by weight. The epoxy–hardener mixture was prepared at room temperature by adding the curing agent with continuous stirring until a clear mixture was obtained. Grains of sand were continuously added to the epoxy mixture at room temperature with appropriate stirring.

Determination of the kinetics of cure reaction

Heat flux–time curves were obtained using a calorimeter (DSC 111, Setaram, Lyon) working in scanning mode, with 100–150 mg samples. These samples are cylindrical in shape with a radius of 0.5 cm, and heating is radial. These rather large samples were very convenient when mixtures were studied, because of the heterogeneity of the materials. Heat flux–time curves were mathematically treated using various methods with finite differences [14], and the values of kinetic parameters were tested by comparing experimental heat flux–time curves with the calculated ones with the help of the above kinetic parameters. It was found previously that this comparison can be of interest of ensure that the kinetic parameters are correct, when a low value for the heating rate is chosen (2°C min^{-1} for this sample) [10,11].

Cure of samples in the mold

Various samples of thickness of 0.5 cm were prepared, while the temperature of the mold was kept constant at 150°C. The initial temperature of the material was 30°C.

RESULTS

Determination of the kinetics of cure reaction

The kinetic parameters were obtained from heat flux–time curves measured in scanning mode, by considering eqn. (4) to express the rate as a function of the reaction heat remaining to be evolved [10,11]. This type of equation is quite different from some found in the literature, rewritten several times in the same way, using two different rate constants and the activation energy [15–18].

The parameters for the kinetics of reaction are shown in Table 1, as well as the thermal parameters of the sand-resin mixture with 75% of sand by weight.

Determination of the profiles of SOC and temperature

The profiles of temperature developed through the thickness of the sample have been calculated using the model, along with the profiles of the state of cure (SOC). The parameters of interest for these calculations are: thickness, $L = 0.5$ cm; 10 slices; $\Delta x = 0.05$ cm; $\Delta t = 0.04$ s; $M = 5$.

TABLE 1

Kinetic and thermal parameters

$Q_\infty = 15.3$ cal g^{-1}; $N = 1.5$; $E = 26.630$ cal mol^{-1}; $k_0 = 4 \times 10^{11}$ s^{-1}
$C = 0.2225 + 4 \times 10^{-4}$ T (°C)(cal g^{-1} deg^{-1}); $\alpha = 0.0125$ cm^2 s^{-1}; $H = 24.3$

TABLE 2

Mechanical properties of composites

		σ_R(MPa)	E(MPa)
Sand 75–Resin 25	Tension	23	6800
	Compression	93	2250
Sand 75–Concrete 25	Tension	2	2100
	Compression	15–50	10000

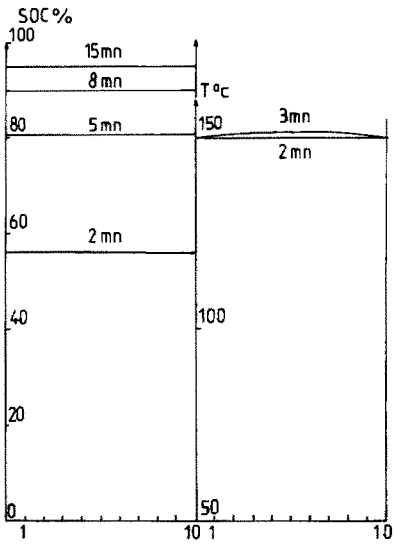

Fig. 1. Profiles of temperature (right) and state of cure (left) developed through the thickness of the composite, for various times.

Figure 1 illustrates the development of the profiles of SOC (on the left) and temperature (on the right) through the thickness of the sample, for various times. The thermal properties of the sand are higher than those for the resin, and this fact allows the profiles of temperature to be much flatter than those obtained with the pure resin. As a result of this interesting fact, the profiles of SOC are also flat, showing a good homogeneity for the state of cure through the sample.

A time of about 8 min is necessary for the state of cure to reach the value of 90%, and 15 min for 95%, when the temperature of the mold is 150°C.

Other results of interest can be seen in Figs. 2 and 3 where the tempera-

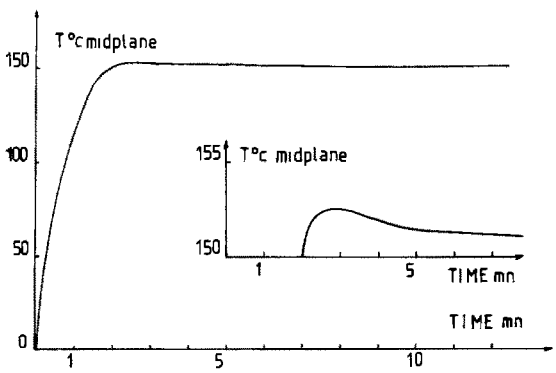

Fig. 2. Temperature at the midplane of a composite sheet as a function of time.

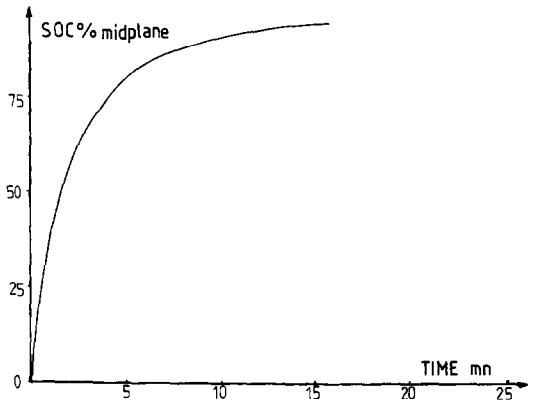

Fig. 3. Variation of the state of cure at the midplane of a composite sheet with time.

ture (Fig. 2) and the state of cure (Fig. 3) at the midplane of the sheet were drawn as a function of time. A maximum value for the temperature at the midplane can be seen at about 3 min, and the difference between this maximum value and the temperature of the mold does not exceed 3°C.

The state of cure–time curve in Fig. 3 allowed us to choose the right time necessary for the state of cure to reach the value of 95%.

Mechanical properties of sand–resin samples

Standard static tests were performed on samples, under tension and compression: ultimate tensile strength (ASTM D412) and modulus, by using stress–strain curves obtained with a Dynamometer (DY 14 Adamel Lhomargy).

The results shown in Table 2 can be compared with those obtained with a sand–concrete mixture with the same proportion of sand (75% by weight).

Mechanical properties of composites containing epoxy resin have higher values than those obtained with concrete under compression, and especially under tension, for which concrete is bad.

CONCLUSIONS

This paper is concerned with the preparation of composites made of sand and epoxy resin, in order to compare their mechanical properties to those obtained with concrete.

The cure reaction is especially studied for the purpose of finding a method for calculating the time necessary for the state of cure to reach a definite value. The kinetics of cure reaction have been determined by DSC using the composite itself. The kinetic parameters were about the same as

those obtained with pure epoxy resin. The heat of the cure reaction was proportional to the resin content in the mixture. The model described, taking into account the kinetics of the cure reaction and the thermal properties of the mixture, is able to provide some results of interest as the profiles of temperature and state of cure develop through the composite as a function of time.

Composites with good mechanical properties under tension and compression have been prepared by using the time of cure derived with the model.

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