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# Testing the kinetic and thermal parameters for the cure of an unsaturated polyester

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**Abstract**

The cure of an unsaturated polyester was studied by using experiments and a model of the process. Two kinds of experiment were conducted, one with the calorimetry in scanning mode for determining the kinetics of curve, the other with a rather large cylinder. The numerical model was constructed by taking into account the heat transferred by conduction through the resin, and convection at the surface, as well as the kinetics of heat generated by the cure reactions. The temperature–time histories in the middle of the cylinder obtained either from experiments or by calculation were compared, and found in good agreement, providing the accuracy of the values of the kinetic and thermal parameters.

*Keywords:* Calorimetry; Cure kinetics; Heat transfer; Modelling; Polyester

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## List of symbols

| | |
|---|---|
| C | heat capacity of the resin |
| $\rho$ | density of the resin |
| $\lambda$ | heat conductivity of the resin |
| $h$ | coefficient of convective heat transfer next to the surface of the resin |
| $k_0$ | pre-exponential term in Eq. (2) |
| $E$ | apparent energy of activation for the cure reaction |
| $p$ | apparent order of the cure reaction |
| $Q_t, Q_\infty$ | heat evolved from the cure reaction after time $t$, after infinite time, respectively |

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| | |
|---|---|
| $r, z$ | coordinates for the cylinder: radial, longitudinal |
| $t$ | time |
| $\Delta r, \Delta h$ | increments of space |
| $\Delta t$ | increment of time |
| $n, h$ | integers characterizing the position along the radius, the longitudinal axis |
| $i$ | integer characterizing the time: $t = i\Delta t$ |
| $M_r$, $M_h$ | dimensionless numbers |
| $N_r$, $N_h$ | number of intervals shown in Eqs. (4) and (4′) |
| $S$ | function described in Eq. (8) |
| $T_{n,h}$ | temperature at position $n$, $h$, at time $t$ |
| $TN_{n,h}$ | new temperature at position $n$, $h$, at time $t + \Delta t$ |

## 1. Introduction

Thermosets are widely used in various applications [1]; these materials generally consist of a composite made of a thermoset reinforced by fillers and fibres, covered with a gelcoat made of the pure thermoset. This gelcoat is very often spread over the composite surface with a spray gun which is able to dispense the mixture of resin and catalyst at the same time.

The problem of curing the resin is rather difficult, as the process is driven by the exothermic cure reaction leading to heat transfer by conduction through the resin and support and by convection into the surrounding air. Various studies have been made on the process of cure, and a few of them have been summarized [1]. The effect of temperature [2–8] is of great importance, as the rate of cure generally follows an Arrhenius relationship, as well as the composition of the resin and the percent catalyst or initiator [2,9]. The effect of the thickness is also of great concern, because the heat generated by the reaction is transferred by conduction and convection at a rather low rate, and an increase in temperature, and steep gradients of temperature are observed inside thick materials [7,10,11].

The kinetics of the cure reaction are generally determined by calorimetry experiments run either under isothermal conditions [12–14] or in scanning mode [4,15,16]. A fundamental study has defined precisely the advantages and drawbacks of these two calorimetry techniques [1]. High accuracy is needed for the determination of the kinetic parameters, as they strongly influence the process [17].

Simulation of the process of cure is of great importance, from a theoretical point of view in order to gain a fuller insight into the nature of the process, and from a practical point of view to optimize the operational conditions, as especially shown with epoxy resins [1, 11, 15, 16, 18–20].

The first objective in this paper was to describe a numerical model which takes into account all the known facts, e.g., heat transfer by convection on the external surface in contact with air, heat transfer by conduction through the resin, and heat evolved from the cure reaction. In order to test the accuracy of the parameters influencing the model, e.g., the thermal and kinetic parameters, measurements were made to evaluate the temperature–time history in the middle of a cylinder full of resin [1]. As this cylinder was rather flat, heat transfer by conduction was considered in both the radial and longitudinal directions.

Another purpose of this study was not only to compare the temperature–time histories in the middle obtained either by experiments or calculation, but also to evaluate the profiles of temperature and of state of cure developed through the radius at the mid-height of the cylinder. This information is generally of interest in order to obtain better knowledge of the process.

## 2. Theoretical

### 2.1. Assumptions

Before deriving a numerical model the following assumptions are made in order to define the process precisely.

(1) The cure reaction takes place within a cylinder of resin of constant dimensions.

(2) Heat is transferred to and from the surface of the cylinder by free convection.

(3) Heat is transferred within the cylinder by radial and longitudinal conduction with constant parameters.

(4) The rate constants for the cure reactions follow an Arrhenius dependence. The state of cure at time $t$ is expressed by the heat evolved up to time $t$ as a function of heat evolved after infinite time.

(5) The model takes into account the heat generated by the cure reaction, as well as the heat transferred by conduction and convection.

(6) The temperature is initially uniform throughout the resin. It is lower than the temperature of the surrounding, in order that the components can be mixed without any cure taking place.

### 2.2. Mathematical treatment

The basic equation of heat conduction in two dimensions, through the cylinder with integral heat generated by the cure reaction is [1]:

$$\rho C \frac{\partial T}{\partial t} = \frac{\lambda}{r} \frac{\partial}{\partial r}\left( r \frac{\partial T}{\partial r} \right) + \lambda \frac{\partial^2 T}{\partial z^2} + \rho \frac{\partial Q}{\partial t} \tag{1}$$

where the parameters are described in the list of symbols.

The contributions from heat conduction, through either the radial or longitudinal directions, and of heat of reaction for the process appear on the right-hand side.

The rate of heat evolution from the exothermic cure reaction is expressed by the classical equation:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left( \frac{Q_t}{Q_\infty} \right) = k_0 \left( 1 - \frac{Q_t}{Q_\infty} \right)^p \exp\left( -\frac{E}{RT} \right) \tag{2}$$

with the usual kinetic parameters, as given in the list of symbols.

On the surface, the boundary condition is that the rate of heat transferred by convection is constantly equal to the rate of heat transfer by conduction,

$$-\lambda\frac{\partial T}{\partial r} = h(T_s - T_{ext}) \tag{3}$$

$$-\lambda\frac{\partial T}{\partial z} = h(T_s - T_{ext}) \tag{3'}$$

with the parameters as shown in the list of symbols.

### 2.3. Numerical analysis

No mathematical treatment is feasible, and the problem is resolved with a numerical model based on finite differences. As the principle of the method is described in detail elsewhere [1], only the main equations are given.

The radius of the cylinder $R$ is divided into $N_r$ intervals of equal thickness $\Delta r$, and the height $2H$ into $2N_h$ intervals of equal length $\Delta z$. Various positions in the cylinder are considered by using the notation:

$$r = n\Delta r \quad 0 \leq n \leq N_r \quad R = N_r\Delta r \tag{4}$$

$$z = h\Delta z \quad 0 \leq h \leq N_h \quad 2H = 2N_h\Delta z \tag{4'}$$

The temperature can thus be evaluated at various places defined by the integers $n$ and $h$ by using the following equations:

#### 2.3.1. Within the cylinder, at position n, h

The new temperature $TN_{n,h}$ after the lapse of time $\Delta t$ is expressed in terms of the previous temperatures at the same and adjacent places:

$$TN_{n,h} = T_{n,h} + \frac{1}{M_r}[T_{n-1,h} - 2T_{n,h} + T_{n+1,h}] + \frac{1}{2nM_r}[T_{n+1,h} - T_{n-1,h}] + \frac{1}{M_h}[T_{n,h-1} - 2T_{n,h} + T_{n,h+1}] + \frac{\Delta Q_{n,h}}{C} \tag{5}$$

#### 2.3.2. On the longitudinal axis, with n = 0, h:

$$TN_{0,h} = T_{0,h} + \frac{4}{M_r}[T_{1,h} - T_{0,h}] + \frac{1}{M_h}[T_{0,h-1} - 2T_{0,h} + T_{0,h+1}] + \frac{\Delta Q_{0,h}}{C} \tag{6}$$

where the dimensionless numbers $M_r$ and $M_h$ are given by:

$$M_r = \frac{(\Delta r)^2}{\Delta t}\frac{\rho c}{\lambda} \tag{7}$$

$$M_h = \frac{(\Delta h)^2}{\Delta t}\frac{\rho c}{\lambda} \tag{7'}$$

More complex equations are obtained on the surfaces, either circular or plane, and at the corner, as shown precisely elsewhere [1] but not given here.

Various conditions of stability are necessary for calculation, as shown previously [1].

### 2.3.3. *State of cure in the resin*

The heat evolved by the exothermic cure reaction up to time $i\Delta t$, and hence the state of cure, is calculated by using the integral function:

$$S_i = k_0 \int_0^{i\Delta t} \exp\left(-\frac{E}{RT_{\mathrm{i}}}\right) \mathrm{d}t \tag{8}$$

During a short time $\Delta t$, Eq. (7) can be approximated by

$$S_{i+1} = S_{\mathrm{i}} + k_0 \Delta t \exp\left(-\frac{E}{RT_{\mathrm{i}}}\right) \tag{9}$$

with

$$S_0 = 0 \tag{10}$$

Integration of Eq. (12) gives:

$$\frac{Q_\infty - Q_i}{Q_\infty} = [1 + (n+1)S_i]^{1/1-p} \quad \text{with } p \neq 1 \tag{11}$$

The state of cure is expressed as:

$$SOC_{n,h,i} = 100\frac{Q_{n,h,i}}{Q_\infty} \tag{12}$$

## 3. Experimental

### 3.1. *Materials*

The gelcoat was Bleu SI 2000 with 30% styrene (Neste, France). The catalyst was the peroxide of methyl ethyl ketone.

The catalyst (0.2%) was mixed with well stirred gelcoat kept at a temperature of − 20°C. The mixture was then either dropped into the sample holder of the calorimeter or into a larger cylinder 6 cm in height and 1.8 cm in diameter. A thermocouple was placed in the middle of the large cylinder, and the temperature was recorded during the process.

The larger cylinder with the resin was left in motionless air at room temperature (24.5°C).

The characteristics of the cylinder are shown in Fig. 1.

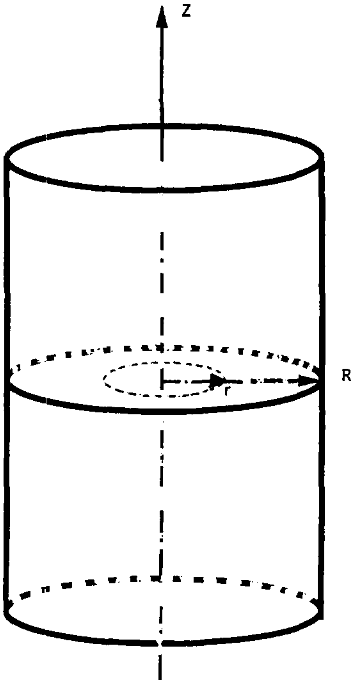

Fig. 1. Cylinder characteristics.

### 3.2. Kinetic and thermal parameters

The rate characteristics are listed in Table 1. The kinetic parameters were calculated from the heat flux–temperature curves obtained by differential scanning calorimetry (DSC 111, Setaram, France) at a low heating rate (1°C min$^{-1}$) using a rather large sample (about 150 mg) [1,15,16].

The coefficient of heat transfer under free convection $h$ was determined from the experimental and calculated curves of the temperature–time histories at the centre of the cylindrical resin obtained with the pre-cured resin.

The thermal parameters were taken from the literature [1]. The kinetics of cure were rather complex, but two teactions of the Arrhenius type were enough to describe the curves obtained by calorimetry.

## 4. Results

Three types of result were determined:

(1) the temperature–time histories obtained at various places in the cylinder and especially at the centre of the cylinder;

(2) the state of cure–time histories at various places in the cylinder;

Table 1
Kinetic and thermal parameters

| Activation energy/kJ mol$^{-1}$ | Order | Rate constant/s$^{-1}$ | Enthalpy/J kg$^{-1}$ |
|---|---|---|---|
| *1st reaction* | | | |
| $E_1 = 92$ | $p_1 = 1.4$ | $k_{01} = 1.4 \times 10^{-13}$ | $Q_{\infty 1} = 62.8$ |
| *2nd reaction* | | | |
| $E_2 = 100$ | $p_2 = 1.2$ | $k_{02} = 2.9 \times 10^{-13}$ | $Q_{\infty 2} = 184.2$ |
| $\rho = 1400$ kg m$^{-3}$ | | $\lambda = 0.45$W m$^{-1}$K$^{-1}$ | $C = 1.9$ kJ kg$^{-1}$ K$^{-1}$ |

The coefficents of heat transfer at the surface were also calculated using dimensionless numbers: Grashof, Prandtl and Nusselt, with the free convection in laminar range, as shown previously [1].

| | | |
|---|---|---|
| Lateral surface | $h_1 = 3.1\Delta T^{0.25}$ | W m$^{-2}$K$^{-1}$ |
| Lower plane surface | $h_2 = 3\Delta T^{0.25}$ | W m$^{-2}$K$^{-1}$ |
| Upper plane surface | $h_3 = 3.4\Delta T^{0.25}$ | W m$^{-2}$K$^{-1}$ |

(3) the temperature and state of cure profiles developed through the resin, and especially through the circular surface at mid-height.

### *4.1. Temperature–time histories in various places of the cylinder*

As shown in previous studies [1], comparison of the temperature–time histories obtained both by experiment and by calculation in various places is very useful in order to prove the validity of the model and to describe the progress of cure. The best place selected for this experiment was the centre of the cylinder for two reasons: at this place, the temperature varied to the greatest extent and there was a maximum in the temperature rise. Moreover, slight changes in position of the thermocouple had only a very slight effect on the measurements.

Fig. 2 shows the temperature–time histories at various places within the cylinder: the experimental curve at the cylinder centre (curve 1), the calculated curve at the cylinder centre (curve 2), and the calculated curve at the surface and mid-height (curve 3).

These curves lead to the following conclusions:

(1) Measurement started when the resin temperature was uniform at 5°C. Good agreement was obtained for the temperature–time histories at the centre of the cylinder, proving the validity of the model and the accuracy of the kinetic and thermal parameters.

(2) At the centre of the resin, the temperature–time history followed a typical pattern already shown [1,11,17]: the temperature increased rather slowly up to room temperature which was attained after about 1000 s. After this time, the temperature increased at a rate which became increasingly higher up to a maximum. This maximum temperature at the centre was approximately 139°C after 2200 s. After this maximum, the temperature decreased rather slowly to room temperature which was attained after more than 8000 s.

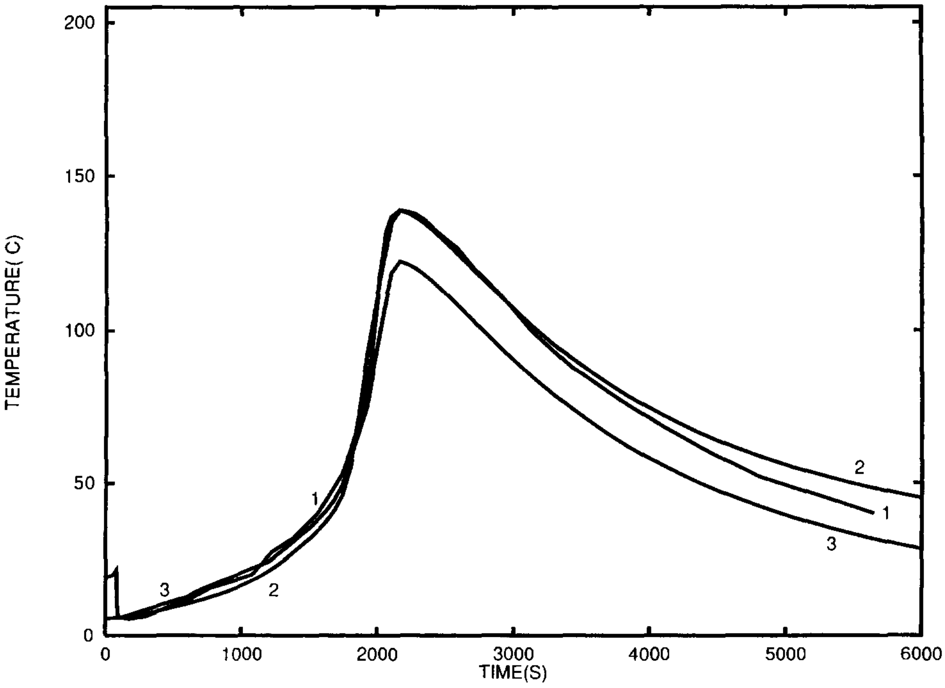

Fig. 2. Temperature-time history at various places in the cylinder: (1) experimental at the middle ($r = 0$) and mid-height; (2) calculated at the middle ($r = 0$) and mid-height; (3) calculated at the surface ($r = R$) and mid-height.

(3) Curve 3 was calculated on the surface at mid-height. Approximately the same pattern was obtained with only slight differences. The temperature was higher at the beginning of the process when the cylinder was also heated by the surrounding air by free convection. The rate of increase in temperature up to the maximum was lower than that obtained at the centre of the cylinder.

(4) The temperature increase up to about 139°C resulted from the internal heat generated by the exothermic cure reaction. This heat was transferred through the resin by conduction and out of the surface by free convection.

### *4.2. State of cure-time histories at various places*

The main interest in modelling is to provide the state of cure in various places of the resin. It is difficult to determine the value of the state of cure by experiments, especially for a non-transparent resin. The state of cure-time histories are drawn in Fig. 3 at various places: the centre of cylinder (1), half the radius at mid-height (2) and on the surface at mid-height (3).

A few observations can be drawn from these curves:

(1) The state of cure-time histories follows the same pattern, with slight differeces resulting from the position.

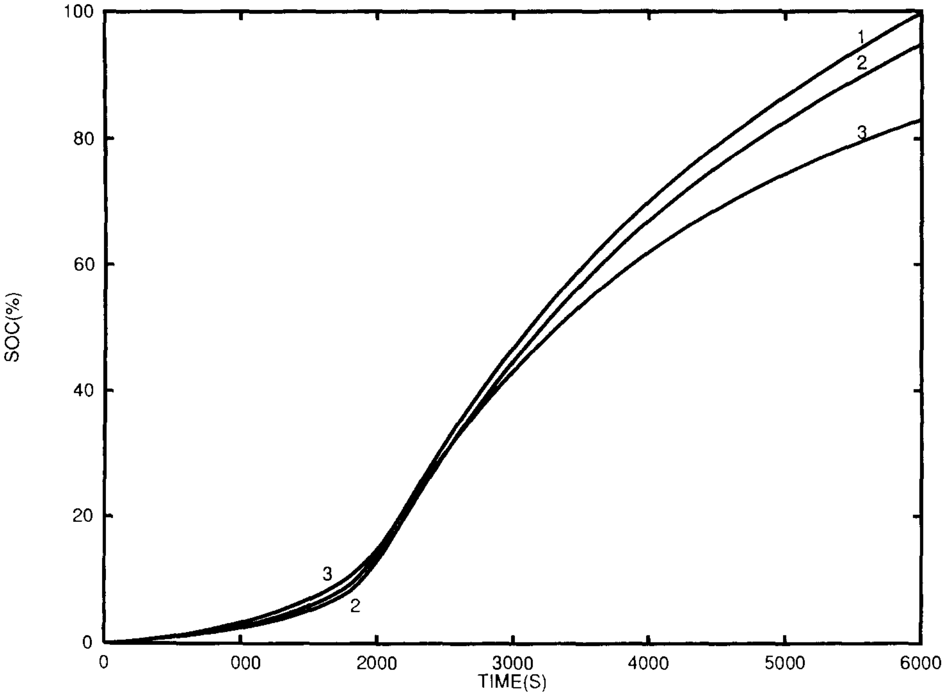

Fig. 3. State of cure (SOC)-time history at mid-height at various places: (1) $r = 0$; (2) $r = R/2$; (3) surface, $R$.

(2) The cure starts very slowly up to 2000 s at the various places when the temperature is rather low. After 2000 s, and especially when the maximum of temperature is reached, the rate of increase of the state of cure becomes greater.

(3) The rate of cure is about maximum when the temperature has reached the maximum value.

(4) For longer times, the cure progresses with a pattern which differs slightly depending on the position: it was higher at the centre of the circular midplane and lower on the surface.

### 4.3. Profiles of temperature and state of cure in the circular mid-plane at half height

The profiles of temperature (Fig. 4) and of state of cure (Fig. 5) developed through the circular mid-plane at the half-height of the cylinder, at various times, gave a fuller insight into the nature of the process.

The following facts were observed:

(1) From the beginning of the process up to 1200 s the temperature increased slowly with a higher value on the surface. Over this period of time, a very slight increase in the state of cure was observed with perhaps a higher value on the surface.

(2) As a result of the development of the cure reaction, the temperature increased in various places, and especially at the centre. Over the period of time between 1800 and

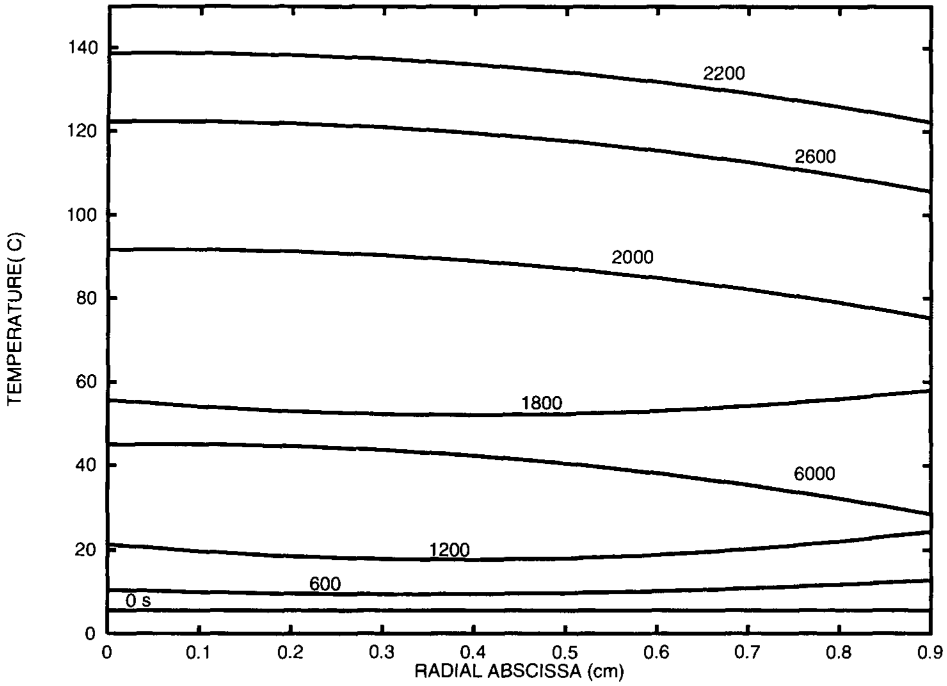

Fig. 4. Profiles of temperature at mid-height, at various times.

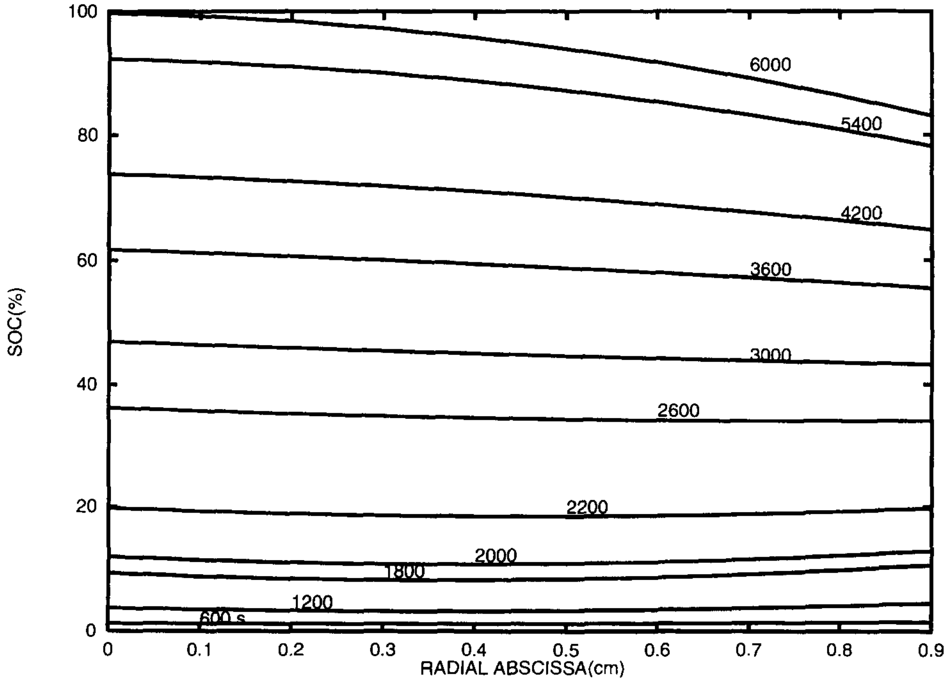

Fig. 5. Profiles of state of cure at mid-height, at various times.

2000s, a deep change in the temperature profile appeared, and at 2000s, the temperature was higher in the centre of the cylinder.

(3) After the maximum of the temperature at around 2200s, the temperature decreased in the various places, the gradient of temperature retaining the same shape and with a higher value in the centre.

(4) The profiles of state of cure also followed a typical pattern. The cure started on the surface at the very beginning of the process, when the temperature was higher in this region. After approximately 2600 s, the state of cure became higher in the centre of the cylinder. The gradient of the state of cure became increasingly steeper up to 6000 s.

## 5. Conclusions

The study of curing with a gelcoat gave results of interest by combining experiments and modelling. The cylinder was selected for the resin because of the symmetry, and its dimensions were responsible for a higher increase in temperature.

The numerical model taking into account all the known facts, e.g., the heat transferred by free convection and conduction and the internal heat generated by the cure reaction, was able to give various results of interest, such as the temperature–time histories at various places as well as the state of cure–time histories.

Experiments made with the temperature–time history at the centre of the resin, were of interest for testing the accuracy of the thermal parameters of convection and conduction of the kinetic parameters of the cure reaction.

It clearly appeared that the operation of spreading a gelcoat needs great care. Spraying the mixture of resin and catalyst is best way, while brushing or rolling may bring some drawbacks.

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