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CORRELATION BETWEEN THE STATE OF CURE OF A THERMOSET RESIN AND ITS HARDNESS

S. TADLAOUI, R. GRANGER and J. M. VERGNAUD*

Laboratory of Materials and Chemical Engineering, Faculty of Sciences, 23 Dr P. Michelon,
University of Saint-Etienne, Saint-Etienne 42023, France

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Abstract—It is of interest to determine the value of the state of cure of a thermoset and thus to correlate the state of cure with some properties of the material. In this study, the state of cure at time t is expressed by the extent of heat evolved from the overall cure reaction at time t as a fraction of the corresponding heat evolved after infinite time. Various sample sheets of Bulk moulding compound with polyester of given values of the state of cure are prepared. A numerical model enabled one to obtain the operational conditions necessary for preparing these samples. A correlation between the hardness of the sample and the state of cure is shown.

NOMENCLATURE

α: Thermal volumic dilation of air
Δt: Increment of time
Δx: Thickness of a slice
C: Heat capacity
E: Activation energy
h: Coefficient of heat transfer at the surface
g: Gravitation acceleration coefficient (m/s/s)
k_0: Pre-exponential factor
L: Mean dimension of the solid during cooling in air
λ: Thermal conductivity
MR, MM: Dimensionless number
n: Order of reaction
μ: Viscosity of the fluid
Q: Heat evolved from the cure reaction
ρ: Density
SOC: State of cure.

INTRODUCTION

In the same way as for rubbers [1], it is of interest to evaluate the value of the state of cure of a thermosetting resin. Various ways exist using either the advancement of the reaction or the mechanical properties of the material. Various techniques are able to follow the change in the mechanical properties of the material during the cure [2]. Moreover, the mechanical properties [2–6] as well as the resistance to liquids [7–10] of the final material are interesting information for the user. Nevertheless, the best way to follow the cure of the resin located in the mould consists of recording either the temperature in a given place within the resin such as the midplane of a sheet [2, 11] or the heat flux at the resin–mould interface [12] and using a numerical model taking into account all the facts. Of course, the second method with the heat flux is not a destructive test for the resin while the first method is destructive for the material and can be used only on laboratory scale.

The method for determining the state of cure of the resin during the cure has been developed [2, 11, 12]. It consists of coupling modelling and experiments. The numerical model takes into account all the known facts, namely, heat convection onto the external surface of the mould, heat conduction through the mould and resin, and internal heat generated by the cure reaction. The kinetics of the heat evolved from the overall cure reaction is determined by calorimetry in scanning mode with a rather large sample because of the heterogeneity of the small sample taken from a large batch of composite [13]. The model is tested by comparing the temperature–time histories obtained at the midplane of a sheet either by calculation or experiment. Moreover, the numerical model is capable of predicting the progress of reaction and the subsequent increase in cure within the sample after its extraction out of the mould when it has been cooled down either in air [14] or a liquid [15].

Correlation between the state of cure of the resin expressed on a thermodynamical basis and the hardness has been made for a coating of epoxy resin [16].

The main purpose in this paper is to prepare samples of a polyester composite with given values of the state of cure, all having a rather flat gradient of state of cure through the thickness of the sheet. The method coupling modelling and experiments is thus used [2, 15] for determining the operational conditions during the heating period when the resin is located in the heated mould and during the cooling period when the resin is cooled down in air or in a liquid.

The other objective of this study is to correlate the hardness of the surface of the sample with the value of the state of cure.

EXPERIMENTAL

Materials

The composite is a Bulk moulding compound (BMC) from Menzolit, with the main components: maleic polyester

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*To whom all correspondence should be addressed.

resin (16 wt%), vinyl acetate (10.7%), styrene (4.1%) and catalyst (0.5%), as well as additives such as hydrated alumina (66.7%), magnesia (0.1%). All these components are thoroughly mixed. Glass fibres (20 parts) are thus added and well dispersed in the viscous mixture (100 parts).

Moulding and heating procedure

The composite with a thermocouple at the midplane is placed in a flat cylindrical mould. The dimensions of the composite are: thickness of 0.8 cm and diameter of 3.4 cm. The mould with the resin in it is immersed in silicone oil heated at a constant given temperature with a given rate of stirring. The mould with the sample in it is then extracted from the heated oil and allowed to cool either in motionless air or in motionless oil at constant temperature. Other experiments are made by extracting the resin from the mould and having it cooled in motionless air at constant temperature.

Kinetic and thermal parameters

The kinetic parameters are determined from the heat flux–temperature curves obtained by calorimetry run in scanning mode (DSC 111-SETARAM). Rather large samples (150–200 mg) are used, because of the question which arises on how a representative from the heterogeneity of the batch is too small a sample taken from a large batch. A low heating rate is selected because of the dimensions of the sample [13] and the sensitivity of reaction to temperature [2]. Kinetic parameters are determined by using various techniques, and their accuracy is assessed by comparing the heat flux–temperature curves obtained by experiment and calculation.

The values of the thermal parameters are drawn from the literature [2]. Their accuracy is tested by comparing the temperature–time histories at the midplane obtained by experiment and calculation with the precured sample during the heating period in oil and the cooling period in motionless air.

The values of thermal and kinetic parameters are shown in Table 1.

THEORETICAL

Assumptions

The following assumptions are made.

During the period of heating in the mould:

(i) a 1-dimensional heat transfer through the thickness of the sample is considered, as the sheet is thin enough [2]

(ii) the rate of heat evolved from the overall cure reaction is expressed in terms of temperature by an Arrhenius equation. The state of cure (SOC) at time t is the amount of heat evolved from the cure reaction up to time t as a fraction of the total heat evolved

(iii) the mould with the resin in it is immersed in stirred oil. Heat is transferred by forced convection at the external surface of the mould, and by conduction through the mould and resin

(iv) the thermal parameters slightly vary with temperature or the SOC, as shown in Table 1

(v) The kinetic parameters are constant

(vi) perfect contact between the resin and mould is achieved.

During the period of cooling of the sample:

(vii) the initial conditions for the temperature and SOC are the same as the final conditions for heating in heated oil

(viii) There is free convection on the surface of the mould when immersed in air or oil, and on the surface of the sample immersed in motionless air.

Table 1. Kinetic and thermal parameters

Composite		
$k_0 = 9 \times 10^{21}$/sec	$Q_\infty = 75.2$ kJ/kg	
$\rho = 1{,}770$ kg/m^3	$E = 181$ kJ/mol	order $n = 2.3$
$C = 1.13 + 4.18 \times 10^{-4} \times T(^\circ C)$ kJ/Kg $\cdot K$		
$\lambda = 0.794$ J/sec $\cdot$ m $\cdot$ K		when SOC < 80
$\lambda = 1.38$ J/sec $\cdot$ m $\cdot$ K		when SOC > 80
Mould (Duralumin)		
Thickness 0.38	$\rho = 2{,}700$ kg/m^3	
$\lambda = 123.7$ J/sec $\cdot$ m $\cdot$ K	$C = 0.92$ kJ/kg $\cdot$ K	
Coefficient of heat transfer at the surface h		
In stirred oil	$h = 344.4$	J/m^2 sec $\cdot$ K
In motionless air	$h = 10 \times (\Delta T)^{0.25}$	J/m^2 sec $\cdot$ K
Measurement of hardness		
Hardness of cured materials is measured using a Durometer Shore D (DIN 53 505 and ISO R 868).		

Mathematical treatment

The equation of 1-dimensional heat transfer by conduction with internal heat generated by the cure reaction is:

$$\rho \cdot C \cdot \frac{\partial T}{\partial t} = \frac{\delta}{\delta x}\left(\lambda \frac{\partial T}{\partial x}\right) + \rho \cdot \frac{\partial Q}{\partial t} \tag{1}$$

where the contributions due to conduction and internal heat from the cure reaction appear in the right member.

The rate of heat generated by the overall cure reaction at time t is expressed in terms of the partial heat evolved from the cure reaction up to time t, by the single equation [2, chapters 11–14].

$$\frac{1}{Q_\infty} \cdot \frac{dQ_t}{dt} = k_0\left(1 - \frac{Q_t}{Q_\infty}\right)^n \cdot \exp\left(-\frac{E}{R \cdot T}\right) \tag{2}$$

where n is the apparent order of the overall reaction, E the activation energy, and k_0 the pre-exponential factor.

Numerical analysis

The problem is resolved by using an explicit numerical method with finite differences, as the mathematical treatment is not feasible [2].

The plane sheet and mould are divided into 2 N_r and N_m slices of thicknesses Δx_r and Δx_m. The midplane of each slice is associated with an integer n, and time is divided in increments Δt (Fig. 1). The heat balance is evaluated during the increment of time Δt within various slices by considering heat transfer by conduction and heat generated by the cure reaction in the resin and only heat conduction in the mould. From these calculations, the new temperature after elapse of time Δt can be expressed in terms of the previous temperatures at the same and adjacent places. The values are given in various places as follows.

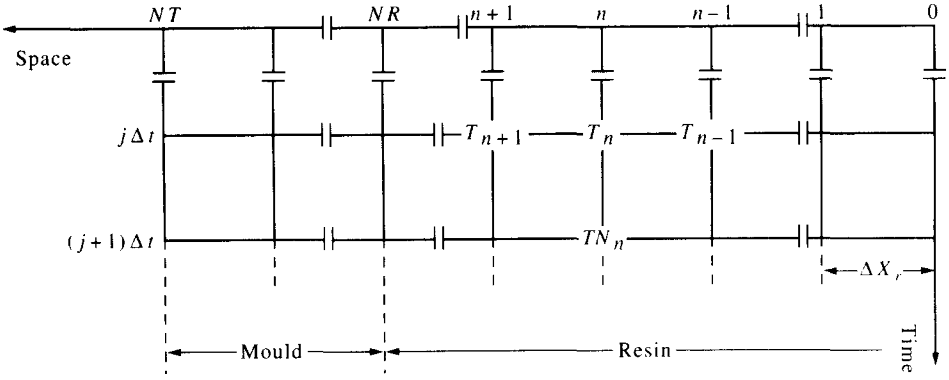

Fig. 1. Diagram for numerical analysis.

Within the resin, with $0 < n \leqslant N_r - 1$.

$$TN_n = \frac{1}{MR_n}[T_{n+1} + (MR_n - 2) \times T_n + T_{n-1}] + \frac{\Delta Q_n}{C_n} \quad (3)$$

where ΔQ_n is the amount of heat generated by the cure reaction at position n during the time Δt, per unit mass of the resin, with the dimensionless number MR_n

$$MR_n = \frac{(\Delta x_r)^2}{\Delta t} \cdot \left(\frac{\rho \cdot C_n}{\lambda}\right)_r \quad (4)$$

Within the mould $N_r + 1 \leqslant n \leqslant N_m + N_r - 1$.

$$TN_n = \frac{1}{MM_m}[T_{n+1} + (MM_n - 2)T_n + T_{n-1}] \quad (5)$$

with the dimensionless number MM_n

$$MM_n = \frac{(\Delta x_m)^2}{\Delta t} \cdot \left(\frac{\rho \cdot C_n}{\lambda}\right)_m \quad (6)$$

Resin–mould interface, with $n = Nr$.

$$TN_{Nr} = A \cdot T_{Nr+1} + (1 - A - B) \cdot T_{Nr} + B \cdot T_{Nr-1} + \tfrac{D}{4}(3\Delta Q_{Nr} + \Delta Q_{Nr-1}) \quad (7)$$

with the coefficients:

$$A = \frac{\Delta t}{F}\left(\frac{\lambda}{\Delta x}\right)_m \quad B = \frac{\Delta t}{F}\left(\frac{\lambda}{\Delta x}\right)_r$$

$$D = \frac{(\rho \cdot \Delta x)_r}{2F} \quad 2F = (\rho \cdot C \cdot \Delta x)_m + (\rho \cdot C \cdot \Delta x)_r \quad (8)$$

Mould–oil interface during the stage of heating.

$$TN_{Nm} = \frac{1}{MM}[2T_{Nm-1} + (MM - 2N - 2)T_{Nm} + 2N \cdot T_{\text{oil}}] \quad (9)$$

where T_{Nm-1} is the temperatrue in the mould at position $Nm - 1$ and T_{oil} the temperature of oil, and MM and N are dimensionless numbers given by equations 6 and 10, respectively.

$$N = h\left(\frac{\Delta x}{\lambda}\right)_m. \quad (10)$$

The coefficient of heat transfer h is given by: in motionless oil in laminar state:

$$h = h_0 \cdot \Delta T^{0.25} \quad (11)$$

in stirred oil:

$$h = \text{constant}. \quad (12)$$

Resin: air during the stage of cooling. Equations 3 and 4 are used in the resin during the stage of cooling. At the resin surface with free convection, there is:

$$TN_{Nr} = \frac{1}{MR_n}[T_{Nr-1} + (MR_n - 2N' - 2) \times T_{Nr} + 2N' \cdot T_{\text{air}}] + \frac{\Delta Q_n}{C_n} \quad (13)$$

The dimensionless number N' *is given as follows.*

$$N' = h'\left(\frac{\Delta x}{\lambda}\right)_r \quad (14)$$

and the coefficient of heat transfer by free convection in air h' is obtained by using the dimensionless numbers Grashof: Prandtl and Nusselt.

$$G_r = \frac{\alpha \cdot g \cdot \rho^2 \cdot L^3}{\mu^2}\Delta T \quad (15)$$

$$P_r = \frac{\mu \cdot C}{\lambda} \quad N_u = \frac{h \cdot L}{\lambda} \quad (16)$$

where α, ρ, μ, C are characteristics of air, ΔT is the difference of temperatures between air and the surface, and L is the main dimension of the solide (the diameter in the present case).

RESULTS

As the numerical model has already been tested by comparing the temperature–time histories at the mid-plane of the resin [15], two kinds of results are presented in this paper:

(i) the profiles of state of cure developed through the tickness for various samples
(ii) the change in the hardness of the samples with their state of cure at the surface.

Profiles of state of cure developed within the sample

The profiles of state of cure are calculated with the help of the numerical model using the data shown in Table 1.

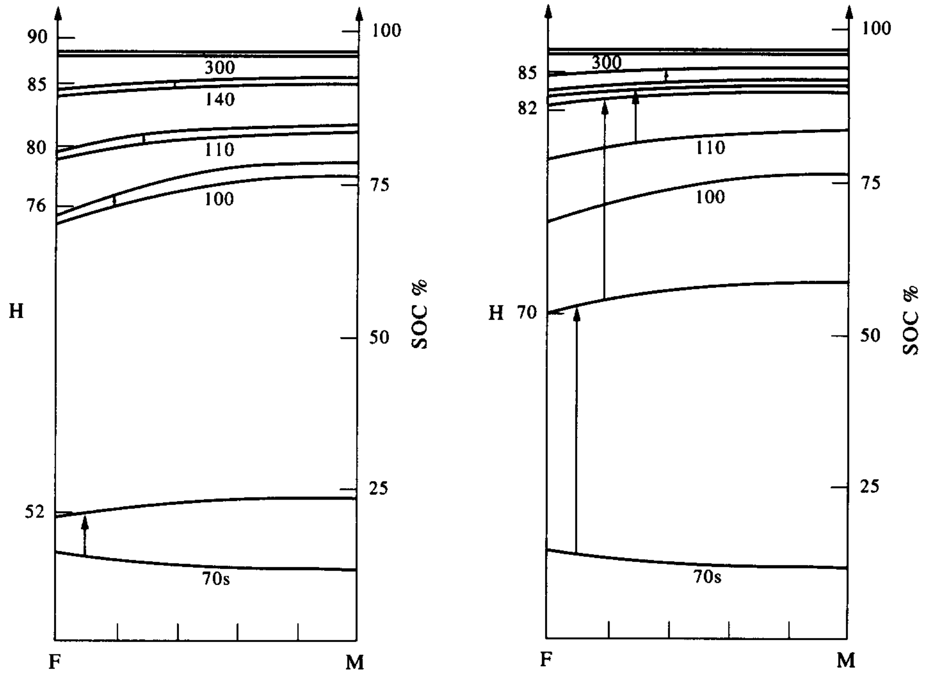

Fig. 2. Profiles of SOC developed through the thickness of the resin after heating in the mould at 146° for given times, and after cooling in oil at 25° (left) and after cooling in air at 25° (right). The arrow shows the increase in the SOC obtained during the cooling stage. F: face; M: middle.

Two types of profiles of state of cure are shown; the one when the resin and mould are heated in stirred oil kept at 146° (Fig. 2), and the other when the oil temperature is 135° (Fig. 3). In Fig. 2, the progress in the cure during the cooling period is shown when the mould and sample are immersed in oil at 25° (left) and in motionless air at 25° (right). In Fig. 3, the profiles of state of cure are drawn when the cooling period is achieved in oil at 25° (left) and in motionless air at 25° (right).

In each figure, the profiles of state of cure through the tickness of the resin are drawn at the end of the heating stage in heated oil and at the end of the cooling stage either in oil or in air at 25°. For instance, in Fig. 2, a sample is extracted at 70 sec out of heated oil and cooled in oil. The profile of stage

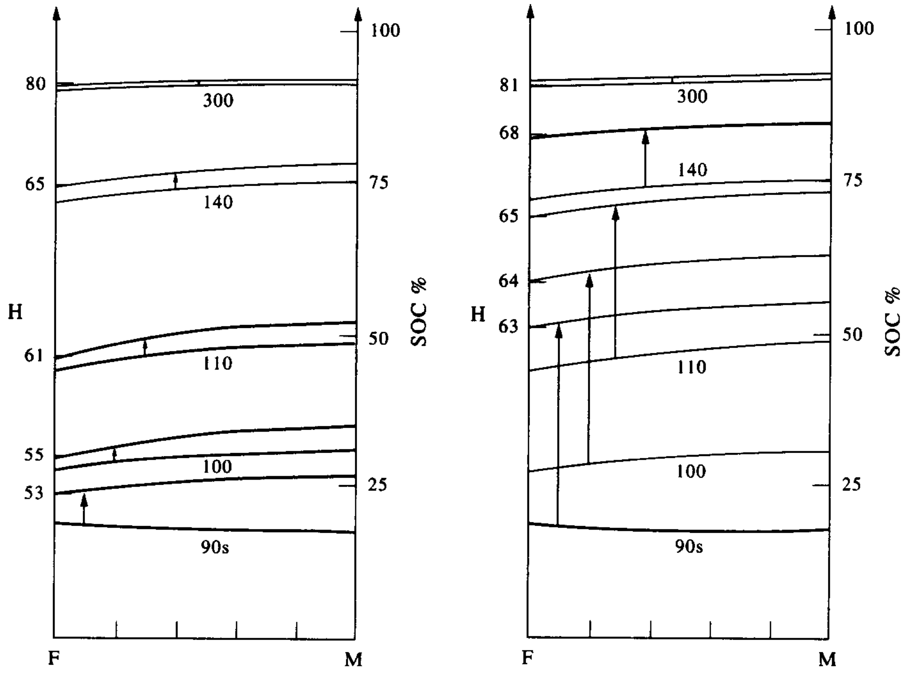

Fig. 3. Profiles of SOC developed through the thickness of the resin after heating in the mould at 135° for given times, and after cooling in oil at 25° (left) and cooling in air at 25° (right). The arrow shows the increase in the state of cure during the cooling stage. F: face; M: middle.

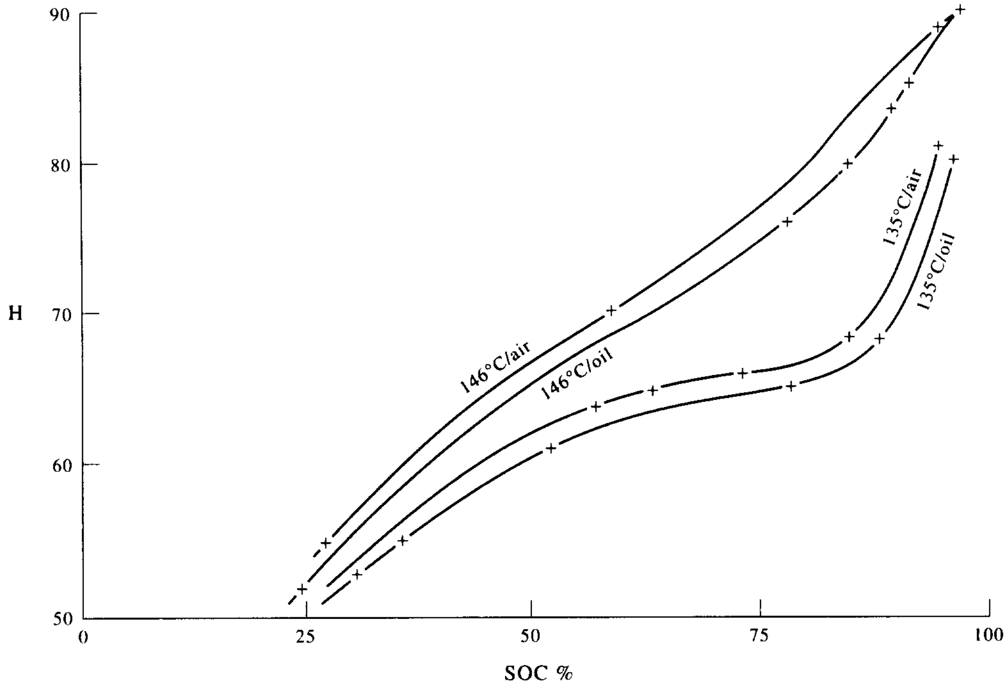

Fig. 4. Hardness of the final sample as a function of the state of cure on the surface, for various cure histories.

of cure at the end of the heating stage in oil exhibits a higher value on the surface, while it is reversed during the cooling stage in oil with a lower value on the surface. An arrow is located between these two profiles of state of cure, showing the increase in state of cure during the cooling period.

The following conclusions can be drawn:

(i) an increase in the state of cure is observed during the cooling period
(ii) the increase in the state of cure during the cooling period is higher when the sample is cooled in air
(iii) the increase in the state of cure depends largely on the value of the state of cure obtained at the end of the heating stage, with the obvious statement: the higher the SOC at the end of the heating stage, the lower the increase in the SOC during the cooling period
(iv) rather flat gradients of SOC are obtained with this method
(v) the hardness is noticed on the left and the SOC on the right on the coordinates.

Relationship between the hardness and SOC

The hardness is plotted as a function of the state of cure on the surface for the various samples in Fig. 4. These curves lead to some conclusions of interest:

(i) a correlation exists between the hardness of a resin with the value of the state of cure
(ii) this correlation is not simple. Two different curves are obtained, the one when the temperature of oil is 146° the other when it is 135°
(iii) Higher hardness is obtained when the temperature of oil is higher.
(iv) The curves obtained with the cooling stage either in oil or in air at 25° are about the same, with a slight translation
(v) it is thus possible to prepare composite samples with a higher hardness, by determining the operational conditions necessary to obtain a higher value of the state of cure, by using the numerical model. The time of cure can be determined after a simulation of the process.

CONCLUSIONS

The important problem of preparing composite samples with a given hardness may find a solution. A correlation exists between the hardness of the sample and its state of cure. However, the problem is not simple for at least two reasons.

A profile of state of cure is expanded through the thickness of the sample, and it is difficult to obtain a flat profile associated with an homogeneous material.

The hardness of the composite depends not only on the value of the state of cure on the surface but also on the way through which the composite has been heated. Higher temperature during the heating stage is responsible for higher hardness of the material. The effect of the nature of the fluid in which the material is cooled after its extraction out of the heated system, e.g. air or oil, is also of concern. The increase in the state of cure is obviously higher in air than in oil during the cooling period. Moreover, the increase in the state of cure during the cooling period depends notably on the value of the state of cure of the resin at the end of the heating period in oil. As shown in equation 2, the following statement holds: the higher the value of the state of cure at the end of the heating stage, the lower the progress of the state of cure during the cooling period.

This study paves the way to other studies concerned with the establishment of relationships between the state of cure of a composite and its mechanical properties and resistance to liquids.

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