Thermochimica Acta, 102 (1986) 83–92
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

EFFECT OF CURE ENTHALPY ON CURE PROGRESS DURING THE COOLING PERIOD IN MOTIONLESS AIR

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(Received 30 October 1985)

ABSTRACT

After extraction from the heated mold, rubber sheets are usually placed in motionless air. During this cooling period, a progress in cure reaction takes place especially in the middle of the sheet. Various parameters are shown to be of interest in this paper. To gain more insight into this complicated process, the effect of the cure enthalpy on the progression in the state of cure during the cooling period is studied. In various cases, for various thicknesses, and values of state of cure of rubber at the time of extraction from the mold, the increase in the state of cure obtained at the midplane of the sheet was found to vary linearly with the value of the cure enthalpy.

INTRODUCTION

A previous paper [1] was concerned with the determination of the profiles of temperature and state of cure developed through rubber sheets during the cooling period after they were extracted from the mold and left in motionless air at room temperature. The problem was resolved by modeling the whole process. This model, based on an explicit numerical analysis, takes into account not only the heat transfer through the rubber itself by conduction and the heat evolved from the cure reaction [2,3], but also heat transfer through the rubber–air interface [1,4]. It was found [1] that the decrease in temperature during the cooling period is rather slow within the rubber sheet and especially at the midplane, so that a vulcanization progress may be significant within the rubber. This increase in state of cure during the cooling period was found to depend largely on the initial value of the state of cure obtained for the rubber sheet when it was extracted from the heated mold.

As the vulcanization progress in the rubber mass during the cooling period may be significant and as this process costs nothing, it is important to study it thoroughly. Various parameters are of importance: (i) the temperature of the mold and air; (ii) the thickness of the rubber sheet or the shape of rubber mass; (iii) the velocity of air surrounding the rubber as shown previously when heat is transferred by convection; (iv) parameters concerned with the rubber compound itself, i.e. the enthalpy of cure reaction and heat conductivity.

This paper reports the study of the effect of the value of cure reaction on the vulcanization progress during the cooling period. The kinetic parameters of the cure reaction have been determined from calorimetric measurements [2]. The profiles of temperature through rubber sheets of 1 cm and 2 cm for the thickness, and especially the temperature at the midplane, obtained by calculation and by experiments, have been compared, in order to ensure that the model is correct. Mathematical simulations allowed the profiles of the state of cure developed through the rubber sheet during the heating period in the mold and after the extraction of the rubber from the mold to be obtained. A sufficient knowledge of the effect of cure enthalpy is necessary to afford a further insight into the nature of the process, and allow the study to progress further by considering the effect of the other parameters.

THEORETICAL CONSIDERATIONS

Although this study considers the cure progress during the cooling period, it is necessary to have adequate knowledge of the state of cure of the sample when it is extracted from the mold. In fact, as shown in this paper, the value of the state of cure of vulcanizate at the beginning of the cooling period is of importance. It is necessary to consider the process as following two steps: (i) classical vulcanization of rubber in the mold; (ii) extraction of the rubber from the mold and cooling in motionless air at room temperature [1].

(i) Vulcanization of rubber sheet in the mold

This is now a classical problem, and it has been studied previously by various methods [1–3,5–7].

As heat flow is unidirectional through the rubber sheet of thickness L, the equation of transient heat conduction is expressed by

$$\partial T/\partial t = \frac{1}{\rho c}(\partial/\partial x)(\lambda \partial T/\partial x) + (1/c)(\mathrm{d}Q/\mathrm{d}t) \qquad (1)$$

where the contribution of conduction heat and reaction heat to the rate of temperature change can be seen.

Because of the presence of internal heat due to cure reaction and variation in thermal properties of rubber with temperature, eqn. (1) cannot be solved mathematically. The mold can be heated in various ways, and the rubber can either be placed or injected into the mold. In any case, initial and boundary conditions are:

$$t = 0,\ 0 < x < L,\ T = T_0 \text{ initial rubber} \qquad (2)$$

$$t > 0,\ x < 0 \text{ and } x > L,\ T = T_m \text{ mold space} \tag{3}$$
$$\text{or, } 0 < x < L,\ T = T_{x,t} \text{ rubber space}$$

Vulcanization of rubber is made up by a complex series of reactions [8,9]. However, it has been proved [2] that the amount of heat evolved from the overall cure reaction can be expressed by a single reaction with a single activation energy

$$\mathrm{d}Y/\mathrm{d}t = \left(k_0(1 - Y)^n\right) \exp(-E/RT) \quad \text{with } Y = Q_t/Q_\infty \tag{4}$$

where Q_t is the heat of the cure reaction evolved up to time t, and Q_∞ the total enthalpy of reaction, in the rubber volume unit. The state of cure (SOC) in this paper is defined by the relation

$$\mathrm{SOC} = 100\ Y \tag{5}$$

The problem must be solved by using a numerical method with finite differences [2,3]. Consider the sheet to be divided into equal finite slices of thickness Δx by temperature-reference planes. By writing the heat balance on the plane n in the rubber sheet, we find that

$$T_{i+1,n} = (1/M)\left[T_{i,n-1} + (M-2)T_{i,n} + T_{i,n+1}\right] + (1/c)(\mathrm{d}Q/\mathrm{d}t)\Delta t \tag{6}$$

where the dimensionless number M is as follows

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

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

The heat generated by the cure reaction during the incremental time Δt is obtained at the time $i\Delta t$ by the following recurrent equations

$$Y = 1 - \exp(-S_i) \text{ if order } n = 1 \tag{8}$$

where

$$S_i = \int_0^{i\Delta t} k_T\, \mathrm{d}t \text{ where } KT = k_0 \exp(-E/RT) \tag{9}$$

and

$$(\mathrm{d}Y/\mathrm{d}t)\Delta t = \exp(-S_i) - \exp(-S_{i+1}) \tag{10}$$

S_i is obtained by the relation

$$S_{i+1} = S_i + k_T\ \Delta t \tag{11}$$

(ii) Heat transfer and cure progress during the cooling period

As the rubber sheet is placed in motionless air, heat is transferred by natural convection through the air–rubber interface, and conduction through the rubber, provoking a decrease in temperature for the rubber. Heat transfer by natural convection is calculated by using dimensionless numbers such as Prandtl–Grashof–Nusselt moduli. As the free convection is in laminar range, because of the low value of the Prandtl–Grashof product

$$(\mathrm{Gr})(\mathrm{Pr}) = 1.3 \times 10^7 \tag{12}$$

the Nusselt's number is obtained by the relation

$$\mathrm{Nu} = a((\mathrm{Gr})(\mathrm{Pr}))^{0.25} \tag{13}$$

The coefficient a is constant during the cooling period, and depends largely on the position of the rubber sheet. For instance, for the vertical plane used in this study, $a = 0.56$.

The decrease in temperature within the rubber sheet follows eqn. (6). On rubber faces, it is necessary to use another equation taking into account free convection in air and conduction in rubber.

$$T_{i+1,0} = 2/M\left[T_{i,1} + (M/2 - 1 - N)T_{i,0} + NT_{\mathrm{air}}\right] \tag{14}$$

where $T_{i,0}$ is the temperature on the rubber faces at time $i\Delta t$; T_{air} is the constant temperature of air; $T_{\mathrm{i,1}}$ is the temperature in the slice next to the face. The modulus N is dimensionless

$$N = h\Delta x/\lambda \tag{15}$$

where h is the coefficient of heat transfer at the interface, and λ the thermal conductivity of rubber. The coefficient h is obtained from Nusselt's number

$$\mathrm{Nu} = hL/\lambda_{\mathrm{air}} \tag{16}$$

where L is the dimension of the rubber in contact with air, and λ_{air} the thermal conductivity of air.

EXPERIMENTAL

The rubber compound was pressed into the mold slabs at the cure temperature of 180°C (SCAMIA 10 t). The dimensions of the rubber sheets were 10 × 10 cm with a thickness of 1 and 2 cm. Kinetics of the cure reaction and the enthalpy were determined by calorimetry (DSC 111–SETARAM) working in scanning mode. The treatment by microcom-

TABLE 1

Kinetic parameters and thermal properties of rubber

$Q_\infty = 2-5-7.5-10$ cal g^{-1}
$n = 1$, $E = 25\,400$ cal mol^{-1}, $K_0 = 3 \times 10^9$ s^{-1}, $\rho = 1, 1$ g cm^{-3}
$\alpha = 1.85 \times 10^{-3}$ cm^2 s^{-1}, $C = 0.49$ cal cm^{-3} K^{-1}
$h = 5 \times 10^{-4}$ cal cm^{-1} s^{-1} K^{-1}
$\Delta x = 0.05$ cm, $N = 0.025$, $\Delta t = 0.2$ s

flux–time curves enabled the kinetic parameters of the heat evolved from the cure reaction to be obtained. The thermal conductivity of vulcanizates was determined under steady state conditions [1]. The values are given in Table 1.

During the cooling period after the extraction of the vulcanizate from the mold, the temperature was continuously measured at the midplane of the rubber sheet and recorded.

RESULTS

Decrease in temperature of vulcanizates during the cooling period

After the extraction of the vulcanizate from the mold, the rubber sheet was placed in contact with motionless air at 25°C, so that the large parallel faces were vertical. The decrease in temperature at the midplane of the sheet was determined experimentally and compared with that obtained by calculation using the model described. As shown in Fig. 1 a good agreement between these values was obtained, proving the validity of the model.

The model allowed the determination of the profile of temperature developed through the rubber sheet during the cure period in the mold [11,12]. The same model allowed calculation of the profile of temperature

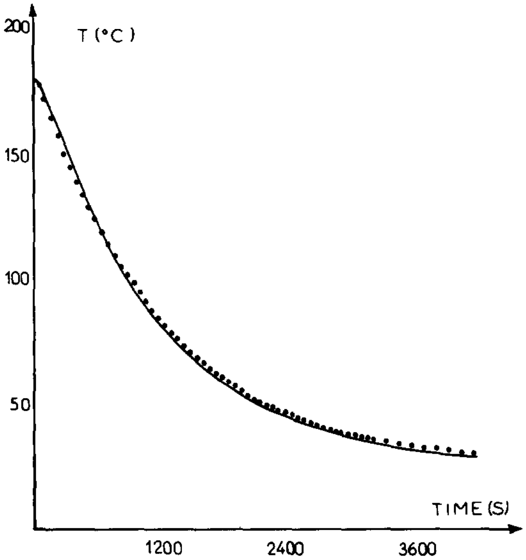

Fig. 1. Decrease in temperature at the midplane of a 2 cm thick rubber sheet. ——— Calculated; ······ experimental. $T_m = 180°C$. $T_{air} = 25°C$.

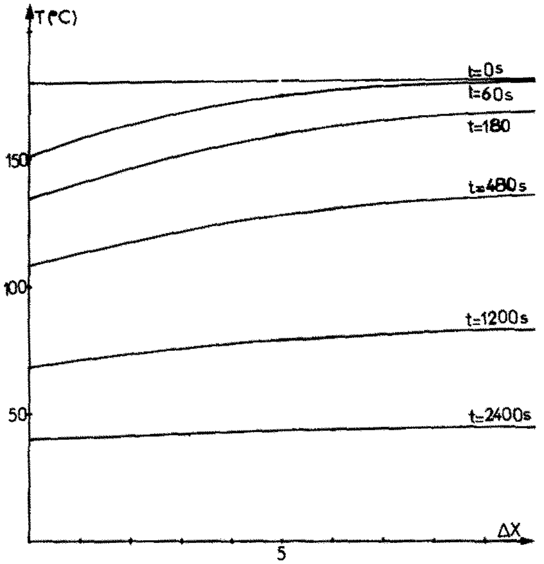

Fig. 2. Profiles of temperature developed through a 2 cm thick rubber sheet, for various times during the cooling period. Cure enthalpy, 5 cal g^{-1}, $SOC_i = 80\%$.

during the cooling period after extraction from the mold (Fig. 2). The temperature is lower on sheet faces, but remains high within the sheet especially at the midplane for a long time.

Increase in the SOC during the cooling period.

As the temperature remains high within the rubber sheet during the cooling period, an increase in the state of cure could be expected. The profiles of the state of cure developed through the rubber thickness were determined at the time of the extraction from the mold (time = 0) and at various times after this extraction. As shown in Fig. 3, an increase in the state of cure is obtained, particularly at the midplane. As a result, the steeper state of cure–space curve shown at the time of extraction from the mold, is largely modified during the cooling period. At its end, the profile is rather flat, showing a more homogeneous material with respect to the state of cure. These results were obtained while the state of cure on rubber faces was 80% at the time of extraction from the mold.

Effect of the cure enthalpy

An interesting result is shown in Fig. 4 with the increase in the state of cure at the midplane of a 2 cm thick sheet as a function of time. These values were calculated with various values of the cure enthalpy ranging from 2 to 10 cal g^{-1} while the state of cure on rubber faces was 80% at the time of

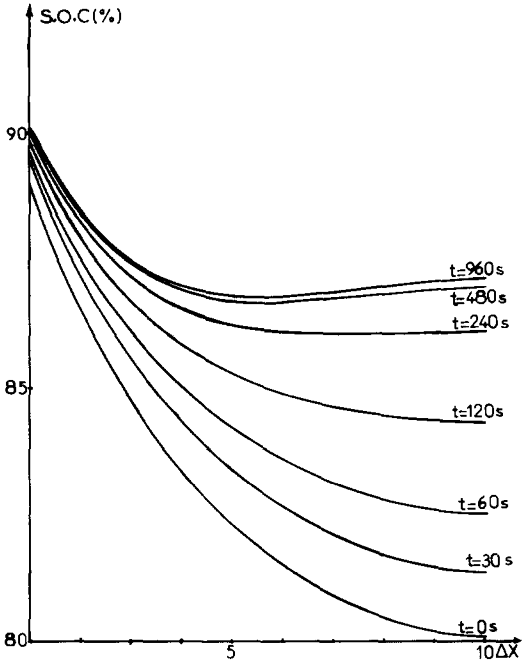

Fig. 3. Profiles of state of cure developed through 2 cm thick rubber during the cooling period. Cure enthalpy, 5 cal g^{-1}, $SOC_i = 80\%$.

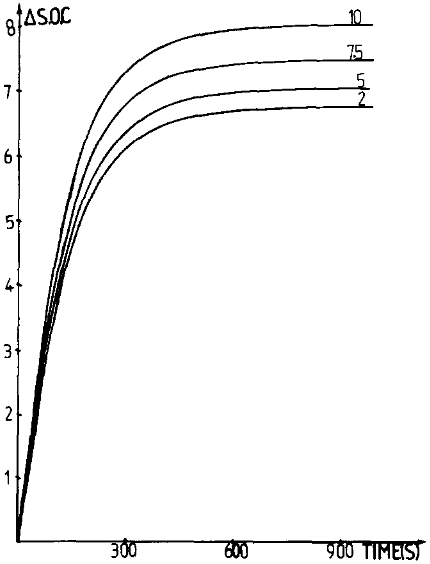

Fig. 4. Increase in state of cure at the midplane of 2 cm thick rubber as a function of time, for various values of cure enthalpy (2–10 cal g^{-1}). $SOC_i = 80\%$; SOC_t = SOC at the time of extraction.

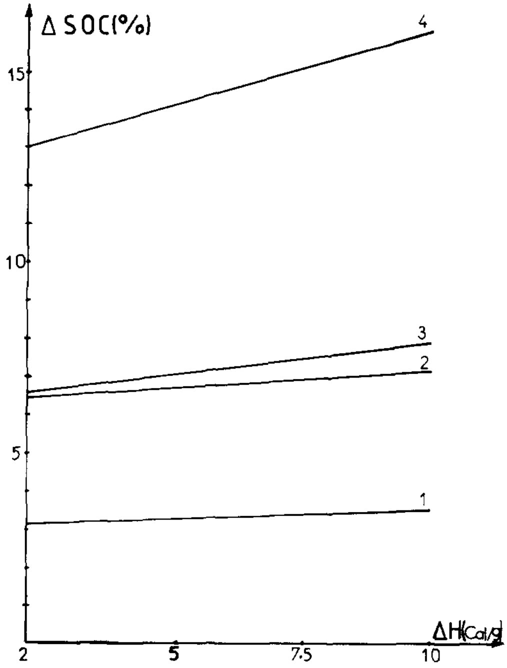

Fig. 5. Variation of the state of cure at the midplane of rubber sheets with the value of cure enthalpy, for various thicknesses of sheets (1–2 cm) and values of SOC at the time of extraction (SOC_t = 60%–SOC_t = 80%). (1) 1 cm, 80%; (2) 1 cm, 60%; (3) 2 cm, 80%; (4) 2 cm, 60%.

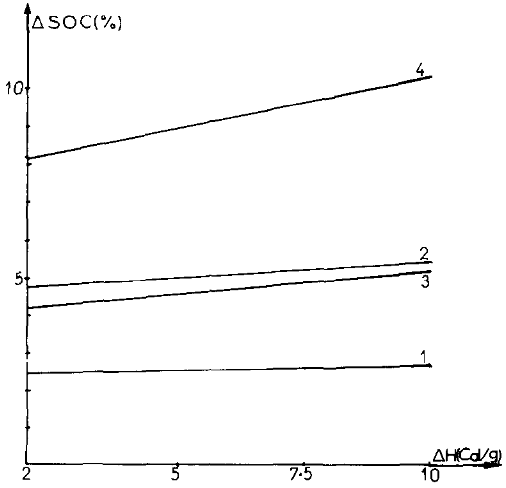

Fig. 6. Increase in SOC as a function of ΔH, at the plane located at the centre of midplane and faces. (1) 1 cm, 80%; (2) 1 cm, 60%; (3) 2 cm, 80%; (4) 2 cm, 60%.

extraction from the mold. Figure 4 shows that the higher the cure enthalpy, the higher the increase in the state of cure.

In order to obtain quantitative laws, the increase in the state of cure at the midplane obtained at the equilibrium was plotted as a function of various values of the cure enthalpy (Fig. 5) and a proportionality was found between the highest value of the increase in the state of cure and the cure enthalpy. The slope of these straight lines depends largely on two parameters; the thickness of the rubber sheet, and the state of cure in the rubber when it was extracted from the mold.

Similar results were obtained for the linearity of the variation in the state of cure with time during the cooling period, in the plane located at the middle of midplane and faces. As shown in Fig. 6, the increase in the state of cure at this position is not as large as that obtained at the midplane; this result can be predicted by the profiles of temperature calculated through the thickness of rubber sheets (Fig. 2) showing that the value obtained for the temperature is maximum at the midplane.

CONCLUSIONS

This study has emphasized the effect of the cure enthalpy on the increase in the state of cure of vulcanizates during the cooling period after extraction from the mold. Various other parameters of interest were observed, such as the thickness of sheet, and the state of cure of the rubber at the time of extraction from the mold. The maximum value for the increase in state of cure obtained at the midplane of the sheet was found to vary linearly with the value of the cure enthalpy.

It is necessary to consider this paper as the first part of a study of the complicated process taking place in rubber sheets during the cooling period in motionless air after their extraction from the mold. Various other parameters are shown to be of interest, and some further studies will be necessary in order to afford more insight into the nature of this process.

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