

## EFFECT OF MOLD TEMPERATURE AND CURE ENTHALPY ON THE STATE OF CURE AT THE MIDPLANE OF THIN RUBBER SHEETS

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(Received 9 June 1983)

### ABSTRACT

This work is concerned with the application of calorimetry in isothermal conditions for the study of the vulcanization in rubber. The effect of the mold temperature and cure enthalpy on the temperature and the state of cure is examined by considering the midplane which is an interesting location within the rubber sheet. A variation of 20% in the cure enthalpy is proved to be of slight importance, while a variation in the mold temperature of  $\sim 10^{\circ}\text{C}$  is shown to be decisive.

### INTRODUCTION

It was shown in earlier works [1,2] that the temperature gradients developed through the rubber mass could be predicted if the kinetics of the reaction and the physical properties of the rubber are known. Although vulcanization consists of a complex series of reactions [3], the overall result, by considering reaction heat, can be described by a first-order reaction and a single activation energy [4,5]. The cure reaction is not very exothermic, but since rubber exhibits a low thermal conductivity, the temperature and rate of cure reaction can vary considerably within the curing mass, particularly for a large bulk.

The extent of the cure reaction is a function of time and position, and has been determined by the balance of internal heat generation from the curing reaction, conduction through the rubber mass and the mold-rubber interface [6]. A method of computation of the temperature and extent of cure through the rubber mass is given as a function of time and abscissa, by using an explicit method with finite differences.

Some work has to be done concerning the important effect of the enthalpy of cure reaction on rubber vulcanization. On the one hand, this problem is an industrial one, because it is difficult to keep a constant value for the

percent vulcanizing agent in small samples taken from a large amount of blended rubber compound because of the non-ideal distribution of vulcanizing agent in this compound. On the other hand, it is sometimes difficult to have a perfect knowledge of the value of the enthalpy of the cure reaction. Our purpose in an earlier work was to show that the effect of a variation in the reaction enthalpy on the profiles of temperature and extent of cure developed through rubber sheets could be studied for a value of the mold temperature of 180°C [7]. The effect of this temperature chosen for the mold is very important. Though a high mold temperature allows a reduction of the cure process, it is also responsible for the development of problematic gradients of temperature and pyrolysis of the rubber [8].

From the consideration of these facts, this paper is devoted to the simultaneous study of the effects of mold temperature and cure enthalpy on the profiles of temperature and extent of cure developed through rubber sheets of constant thickness. The rubber sheets (1 cm thick) were heated by the two faces of a mold according to a mono-dimensional heat transfer in transient conditions.

## THEORETICAL

### *Mathematical treatment*

Unidirectional heat flow through rubber sheet of thickness 1 cm is expressed by the general equation of transient heat conduction

$$\frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left( \frac{\lambda}{\rho C} \cdot \frac{\partial T}{\partial x} \right) + \frac{1}{\rho C} \cdot \frac{dq}{dt} \quad (1)$$

conduction heat          reaction heat

by taking into account the internal heat generation from the cure reaction.

Initial and boundary conditions were

$$t = 0 \quad 0 \leq x \leq 1 \quad T = T_0 \quad \text{rubber space} \quad (2)$$

$$t \geq 0 \quad x < 0 \quad T = T_c \quad \text{mold space} \quad (3)$$

$$t > 0 \quad x > 1$$

$$t > 0 \quad 0 < x < 1 \quad T = T_{x,t} \quad \text{rubber space}$$

Although the sulfur vulcanization of the rubber is a complex chemical process [3], we found that the overall rate of cure is given by a single first-order reaction

$$\frac{dQ_{(x,t)}}{dt} = k(Q_\infty - Q_t) \quad (4)$$

the constant  $k$  having an Arrhenius form with a single activation energy

[1,6].

$$k = k_0 \cdot \exp - \frac{E}{RT} \quad (5)$$

where  $Q_t$  is the heat of cure reaction evolved up to time  $t$ , and  $Q_\infty$  the total enthalpy of this reaction in the rubber volume unit.

### Numerical calculation

The problem was solved by using an explicit numerical method with finite differences.

According to Fig. 1, showing a cross-section of the rubber sheet, the sheet is divided into  $n$  equal finite slices of thickness  $\Delta x$ . The heat balance is written on the plane  $n$  as

$$T_{i+1,n} = \frac{1}{M} [T_{i,n-1} + (M-2)T_{i,n} + T_{i,n+1}] + \frac{1}{\rho C} \cdot \frac{dQ}{dt} \cdot \Delta t \quad (6)$$

where the dimensionless ratio  $M$  is

$$M = \frac{(\Delta x)^2}{\Delta t} \cdot \frac{\rho \cdot C}{\lambda}$$

and  $T_{i+1,n}$  is the temperature at plane  $n$  and at time  $(i+1)\Delta t$ .

The heat generated by the cure reaction during the incremental time  $\Delta t$  was calculated at the time  $i\Delta t$  by using the equations

$$Q_i = Q_\infty [1 - \exp(-S_i)] \quad (8)$$

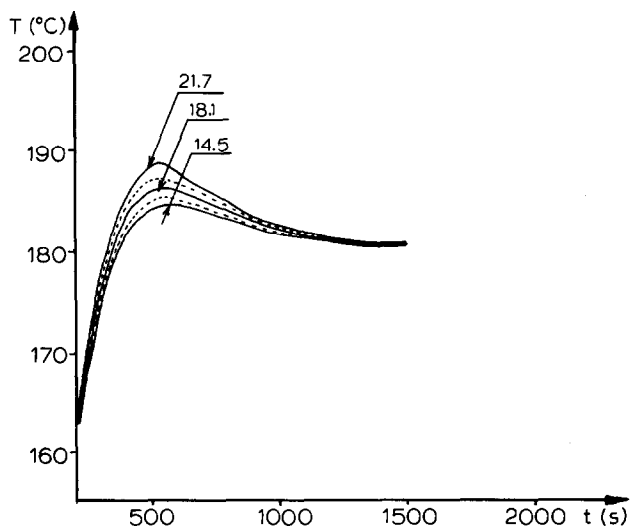


Fig. 1. Midplane temperature vs. time for different values of cure enthalpy: 21.7, 18.1 and 14.5 cal g<sup>-1</sup> ( $T_m = 180^\circ\text{C}$ ,  $T_{ir} = 40^\circ\text{C}$ , 1-cm thick rubber sheet).

where  $S_i = \int_0^{i\Delta t} k \cdot dt$

$$\frac{dQ}{dt} \cdot \Delta t = Q_\infty [\exp(-S_i) - \exp(-S_{i+1})] \quad (9)$$

and the approximative recurrent relation

$$S_{i+1} = S_i + k_{T_{i\Delta t}} \cdot \Delta t \quad (10)$$

The two slabs of materials, steel mold and rubber, were assumed to be in perfect contact at the interface. We desired to employ the same modulus and the same incremental time  $\Delta t$  for both materials, so the thickness of the slices had to be different for the mold and the rubber. The heat balance at the interface led to the conclusion that the ratio of the thicknesses of the slices had to be taken as equal to the square root of the thermal diffusivities  $\alpha_{\text{mold}}$  and  $\alpha_{\text{rubber}}$ .

$$\frac{\Delta x_{\text{mold}}}{\Delta x_{\text{rubber}}} = \left( \frac{\alpha_{\text{mold}}}{\alpha_{\text{rubber}}} \right)^{1/2} \quad (11)$$

## EXPERIMENTAL

### *Vulcanizate components*

A rubber powder (50–100  $\mu\text{m}$  grain size) recovered from old tires was used. The composition of this material was 55% rubber hydrocarbon, 14% acetone extractables and 25% carbon black. This commercial rubber powder was a mixture of NR and SBR in a ratio of about 2/3. Ultrafine powder of sulfur (2% of the total weight) was used as vulcanizing agent.

### *Vulcanization kinetics studies*

These studies were performed using a differential scanning calorimeter (DC) working in isothermal conditions. About 100–150 mg of the compound

TABLE 1

Thermal properties of rubber

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Sample 1	: $Q_\infty = 18.1 \text{ cal g}^{-1}$ of total rubber mixture	
Samples 2 and 3	: $Q_\infty = 18.1 \pm 1.81 \text{ cal g}^{-1}$ of total mixture	
Samples 4 and 5	: $Q_\infty = 18.1 \pm 3.6 \text{ cal g}^{-1}$ of total mixture	
$\alpha = \lambda / \rho C$	$= 3.1 \times 10^{-3} (1 - 10^{-3} T) (\text{cm}^2 \text{ s}^{-1})$	
$\rho C$	$= 0.41 [1 + 2.5 \times 10^{-3} (T - 293)] (\text{cal cm}^{-3} \text{ K}^{-1})$	
$E$	$= 25.4 \text{ kcal mole}^{-1}$ $k_0 = 3 \times 10^9 (\text{s}^{-1})$ (eqn. (5))	
$\lambda$	: thermal conductivity	$\rho$ : density
$E$	: energy of activation	$T$ : temperature
		$C$ : heat capacity
		$k_0$ : reaction constant

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encapsulated in the holder was introduced into the sensitive zone [1,6]. The response of the DC is directly related to the rate of enthalpy change with time.

The data concerned with kinetic parameters and heat transfer are shown in Table 1.

#### *Temperature measurement at the midplane of rubber sheet*

Three series of temperature measurements are of interest in this work: the temperature of the mold; the difference between the temperature of the mold and that measured at the midplane of rubber sheets; and the temperature of the rubber just before its introduction into the mold.

## RESULTS

The effect of the cure enthalpy and the mold temperature on the values of the temperature and state of cure at the midplane sheet were studied using 1-cm thick rubber sheets.

#### *Variation in the cure enthalpy*

##### *Effect of cure enthalpy variation on the midplane temperature*

The temperature at the midplane of rubber sheets is of interest because it is easily measured, as shown in an earlier paper [1]. Moreover, this midplane

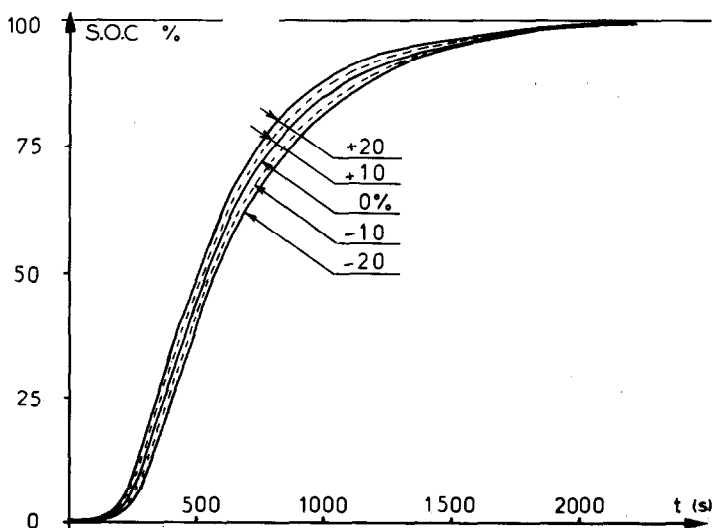


Fig. 2. State of cure at the midplane vs. time for different values of cure enthalpy ( $T_m = 180^\circ\text{C}$ ,  $T_{ir} = 40^\circ\text{C}$ , 1-cm thick rubber sheet).

temperature raised to a maximum value due to the internal reaction heat, which might have adverse consequences for the mechanical properties of the rubber. Figure 1 shows the variation of the midplane temperature against time for different values of the cure enthalpy within the range 14.5–21.7 cal  $\text{g}^{-1}$ . The temperature of the stainless-steel mold was kept constant at 180°C for the five experiments. The effect of the cure enthalpy on the midplane temperature is very important, not only for the maximum value reached, but also for the slope of these curves corresponding to the rate of heating.

*Effect of cure enthalpy variation on the state of cure*

One of the most important applications of temperature calculation during rubber cure is for estimating the state of cure. The state of cure is expressed by the ratio  $Q_t/Q_\infty$ , and it corresponds to the extent of the internal reaction heat of cure. Figure 2 shows the variation of the state of cure against time at the midplane rubber sheet while the mold temperature is kept constant at 180°C. The effect of a slight variation in the cure enthalpy on the profiles of these curves is very important. On the whole, a higher value of the cure enthalpy and the state of cure were obtained. For instance, a relative variation of  $\pm 20\%$  in the cure enthalpy was responsible for a variation of  $\pm 4\%$  in the state of cure for a time of  $\sim 900$  s.

*Time required for the state of cure to reach selected values*

The times required for the state of cure (SOC) to reach selected values were calculated at the midplane rubber sheet and plotted in Fig. 3 for the

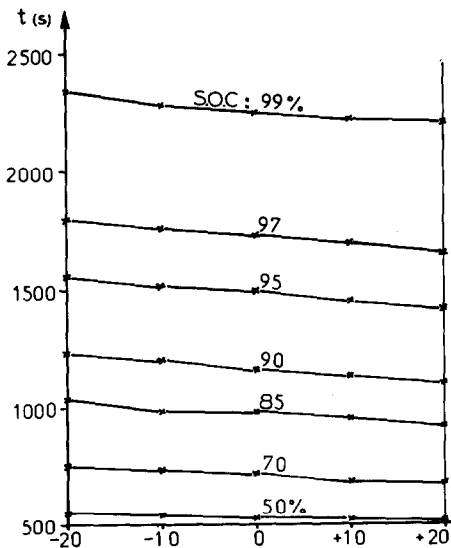


Fig. 3. Time necessary for the state of cure to reach selected values vs. cure enthalpy values ( $T_m = 180^\circ\text{C}$ ,  $T_{ir} = 40^\circ\text{C}$ , 1-cm thick rubber sheet).

five different rubber compounds. These curves do not deviate from linearity within the range studied for the cure enthalpy. Times needed were higher when cure enthalpy values were lower, i.e., when the percent sulfur added to the rubber compounds was decreased.

### *Effect of mold temperature*

#### *Effect of the mold temperature on the midplane temperature of rubber sheets*

Figure 4 shows the variation of the maximum value obtained by the midplane temperature against the cure enthalpy for different mold temperatures. Two conclusions are of interest: the mold temperature and the maximum value of the midplane temperature are both higher. The effect of an increase in the cure enthalpy on this maximum value is higher when the mold temperature is increased.

#### *Effect of the mold temperature on the SOC-time curve*

The increase in the state of cure with time at the midplane is shown in Fig. 5 for different mold temperatures and the three values chosen for the cure enthalpy ( $18.1 \pm 3.6 \text{ cal g}^{-1}$ ). The effect of both mold temperature and cure enthalpy on the state of cure appear to be interesting, but nevertheless the effect of mold temperature is the most important.

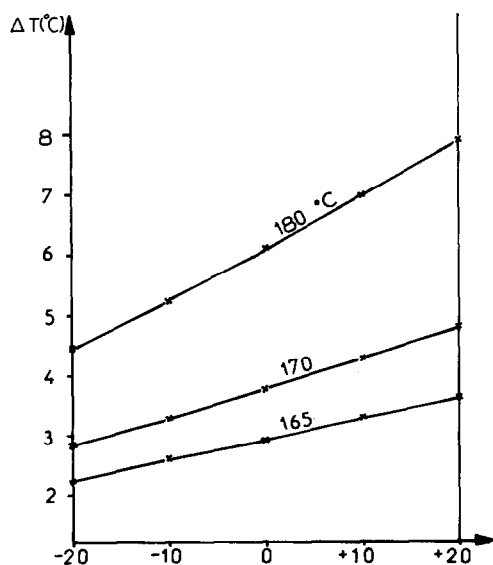


Fig. 4.  $T_{\max} - T_m$  ( $\Delta T$ ) vs. cure enthalpy values for different mold temperatures ( $T_m = 165, 170$  and  $180^\circ\text{C}$ ,  $T_{ir} = 40^\circ\text{C}$ , 1-cm thick rubber sheet).

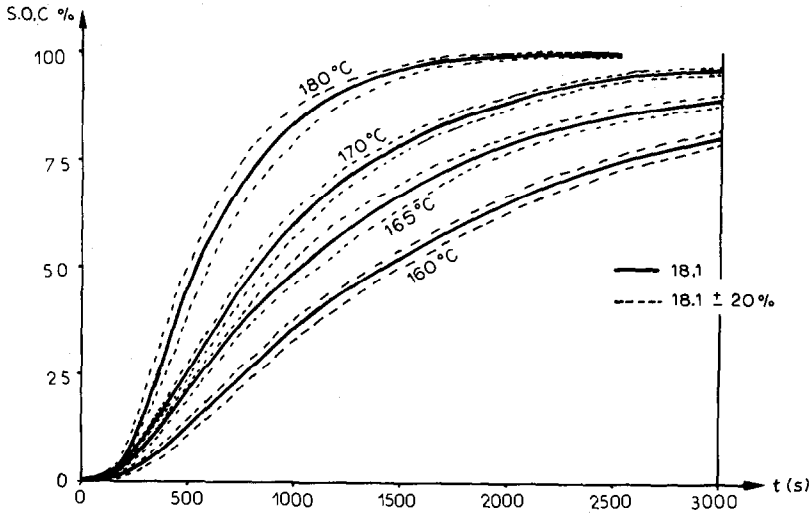


Fig. 5. State of cure at the midplane vs. time for different values of cure enthalpy and mold temperature ( $T_{ir} = 40^\circ\text{C}$ , 1-cm thick rubber sheet).

*Effect of mold temperature on the time necessary for the state of cure to reach selected values*

Figure 6 shows the variation of time necessary for the state of cure to reach selected values with the mold temperature for different values of the cure enthalpy ( $18.1 \pm 3.6 \text{ cal g}^{-1}$ ). This state of cure was calculated at the

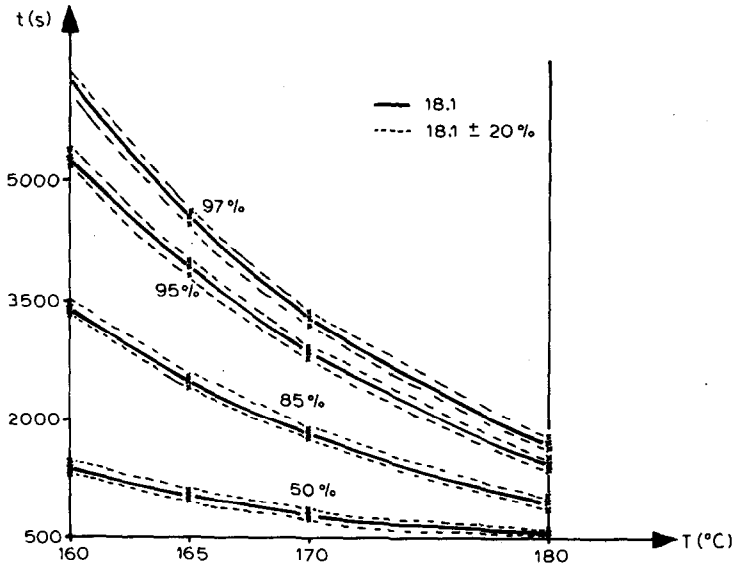


Fig. 6. Time necessary for the state of cure to reach selected values vs. mold temperature for different values of cure enthalpy ( $T_{ir} = 40^\circ\text{C}$ , 1-cm thick rubber sheet).



midplane of the rubber sheets. An increase in the mold temperature of 10°C, from 160 to 170°C, or from 170 to 180°C, is responsible for a decrease in these times, their ratio being ~ 0.57.

## CONCLUSIONS

Calorimetry has proved to be an interesting technique for studying the exothermic reaction of vulcanization taking place within a rubber mass heated by conduction. The kinetic parameters of the overall reaction of vulcanization determined by DC in isothermal conditions are very useful for calculating the values of the state of cure and the temperature at the midplane of rubber sheets. The effects of the mold temperature and the cure enthalpy on these values have been shown to be of interest.

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