

## EFFECT OF VARIATION IN THE KINETIC PARAMETERS ON THE VULCANIZATION OF RUBBER SHEET

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### ABSTRACT

The purpose of this work is to show that a slight variation in the kinetic parameters of vulcanization (rate constant, activation energy) has a very pronounced effect on the vulcanization of rubber sheet. Experiments were performed using microcalorimetry and a heated mold pressing a 2 cm thick rubber sheet. The resulting variations in the temperature profile through the rubber and the profile of the state of cure were considered. The variations in the kinetic parameters were due either to a slight change in the rubber composition or to experimental errors in calorimetry.

### INTRODUCTION

The rubber industry has shown great interest in the development of several processes for faster vulcanization. We have followed a few methods which were found to reduce the cure time cycle: higher temperature [1,2], and the use of accelerators with ultra-strong activity [3,4] have been reported as methods of achieving faster vulcanization. However, we believe that the best method of reducing the time is to ensure that the process is properly carried out and stopped at the right time [5,6]. Obviously, to achieve this object, a sufficient knowledge is required on the time–temperature relation at any point on the rubber.

Although vulcanization of rubber consists of a complex series of reactions [7,8], the overall reaction, when taking into account reaction heat, could be described by a first-order reaction with a single activation energy [9,10].

Some early works [11,12] have shown that the temperature gradients developed in the rubber mass during vulcanization could be predicted by using the data of the kinetics of reaction and heat transfer. The extent of the cure reaction could be determined by the balance of internal heat generation from the cure reaction, conduction through the rubber mass and the mold–rubber interfaces. This problem was solved by applying a numerical method based mainly on the incremental explicit method [13].

Several parameters were important on the profiles of temperature and the extent of cure reaction: some were concerned with the thermal properties of rubber and the exothermic nature of the cure reaction and the other with the parameters of the reaction kinetics as the constant rate of reaction and the activation energy.

The purpose of this work is to describe the effect of variation of the values of the parameters characterizing the reaction kinetics (rate constant of the reaction, activation energy) on the profiles of temperature and extent of cure developed through the rubber. This variation in the reaction constant and the activation energy could be due to two different facts: one resulting from a variation in the properties of rubber or vulcanizing agents and the other due to a lack of accuracy in the kinetic measurements. Of course, another reason and a very interesting one of this variation in kinetic parameters is the presence of accelerators or catalysts in the rubber compound.

## EXPERIMENTAL

### *Thermal properties of rubber and cure kinetics data*

A 150–250  $\mu\text{m}$  grain size of rubber powder having the following composition was used: 55% rubber hydrocarbon being a mixture of NR and SBR in the ratio of about 2/3, 14% acetone extractables, 25% carbon black and 6% ash.

The kinetic study of vulcanization was conducted with a differential scanning calorimeter (Setaram DSC 111) working under isothermal conditions at 160, 170 and 180°C, as reported previously [11].

The enthalpy of reaction,  $Q_{\infty}$ , was measured by DC, and the heat capacity by calorimetry. The thermal conductivity,  $\lambda$ , of rubber and vulcanizates were determined under steady conditions.

### *Temperature profiles at the midplane of rubber sheets*

Rubber powder and 2% sulfur as vulcanizing agent were mixed and pressed into the slabs with a  $10 \times 10 \times 2$  cm stainless steel mold. The temperature at the midplane of the 2 cm thick rubber sheet was also kept constant.

## THEORETICAL

### *Kinetic study*

The overall rate of cure was found to follow a first-order reaction [11] with a constant activation energy,  $E$ . However, our results on the rate

TABLE 1

Thermal properties and kinetics results

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$\alpha = \lambda / \rho C = 3.1 \times 10^{-3} (1 - 10^{-3} T) \text{ cm}^2 \text{ s}^{-1}$		
$\rho C = 0.41 [1 + 2.5 \times 10^{-3} (T - 293)] \text{ cal cm}^{-2} \text{ K}^{-1}$		
$E_3 = 25.4 \text{ kcal mole}^{-1}$	$E_2 = 25.2 \text{ kcal mole}^{-1}$	$E_4 = 25.6 \text{ kcal mole}^{-1}$
	$E_1 = 25.0 \text{ kcal mole}^{-1}$	$E_5 = 25.8 \text{ kcal mole}^{-1}$
$k_3 = 3.0 \times 10^9 \text{ s}^{-1}$	$k_4 = 2.7 \times 10^9 \text{ s}^{-1}$	$k_2 = 3.3 \times 10^9 \text{ s}^{-1}$
	$k_5 = 2.4 \times 10^9 \text{ s}^{-1}$	$k_1 = 3.6 \times 10^9 \text{ s}^{-1}$

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constant of reaction,  $k_0$ , and the activation energy,  $E$ , were liable to some experimental errors. We are attempting in our current work to determine the effect of these errors on the temperature profile developed through the rubber as well as its state of cure. Five possible values of the activation energy and the rate constant are given in Table 1 which indicates higher and lower values together with the average of these values.

#### *Transient heating of the 2 cm thick rubber slab*

As the heat flow is unidirectional, the transient conduction was defined by

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

i.e. total heat = conduction heat + reaction heat

The total reaction heat was expressed by

$$\frac{dq}{dt} = k_0 (q_\infty - qt) \exp\left(-\frac{E}{RT}\right) \quad (2)$$

The initial and boundary conditions were

$$t = 0 \quad 0 \leq x \leq l \quad T = T_0 \quad \text{rubber space} \quad (3)$$

$$t \geq 0 \quad x < 0, x > l \quad T = T_c \quad \text{mold space}$$

$$t > 0 \quad 0 \leq x \leq l \quad T = T_{x,t} \quad \text{rubber space} \quad (4)$$

The problem could only be solved by a numerical explicit method [11–13] with finite elements. If we let the solid be divided into equal slices of thickness  $\Delta x$ , the heat balance on the plane  $n$  taken within the rubber sheet was expressed by

$$T_{i+1,n} = \frac{1}{M} [T_{i,n-1} + (M-2)T_{i,n} + T_{i,n+1}] + \frac{1}{\rho C} \frac{dq}{dt} \Delta t \quad (5)$$

where the dimensionless modulus  $M$  is given by

$$M = \frac{(\Delta x)^2}{\Delta t} \frac{1}{\alpha} \quad (6)$$

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

As the mold and rubber slabs were assumed to be in perfect contact at the interface, the heat balance at this interface was followed by eqn. (4) by having two different values for the slices taken into the rubber and mold. This is shown in

$$\frac{\Delta x_{\text{mold}}}{\Delta x_{\text{rubber}}} = \left\{ \frac{\alpha_{\text{mold}}}{\alpha_{\text{rubber}}} \right\}^{1/2} \quad (7)$$

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

$$Q_i = Q_\infty [1 - \exp(-S_i)] \quad \text{where } S_i = \int_0^{i\Delta t} k dt \quad (8)$$

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

These equations were obtained by using the approximate recurrent relation

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

## RESULTS

The effects of variation in the value of the rate constant, the activation energy on the midplane temperature and the reaction heat extent are reported here.

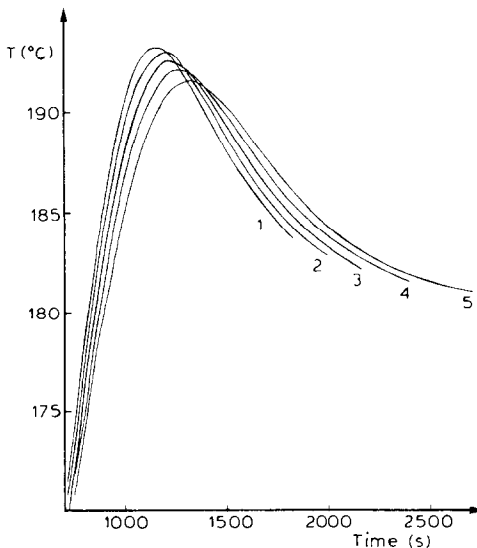


Fig. 1. Effect of variation in  $k_0$  on the midplane temperature (2 cm thick sheet,  $T_m = 180^\circ\text{C}$ ).  $k_0/10^9(\text{s}^{-1})$ : 1, 3.6; 2, 3.3; 3, 3.0; 4, 2.7; 5, 2.4.

*Effect of variation in the rate constant of the overall cure reaction*

Figure 1 illustrates the effect of a slight variation in the rate constant of the overall cure reaction on the midplane temperature of the 2 cm thick rubber sheet. The curves were obtained for five different values of the rate constant,  $k_0$  ( $2.4 \times 10^9$ ,  $2.7 \times 10^9$ ,  $3 \times 10^9$ ,  $3.3 \times 10^9$  and  $3.6 \times 10^9 \text{ s}^{-1}$ ) keeping the mold temperature constant at  $180^\circ\text{C}$  and the activation energy  $25.4 \text{ kcal mole}^{-1}$ . The curve corresponding to the mean value ( $k_0 = 3 \times 10^9 \text{ s}^{-1}$ ) was in good agreement with the experimental values.

Two interesting facts from Fig. 1 are worth mentioning. First, the increase in temperature at the beginning of the operation was highest for the higher value of the rate constant,  $k_0$ . The other, that the temperature reached a maximum in a shorter time when the rate constant of the reaction was higher. The fall in temperature occurred faster in the case of the higher  $k_0$  value, and the midplane temperature raised the mold temperature in a shorter time.

It was also noticed that the maximum value of the midplane temperature was about  $1.5^\circ\text{C}$  higher for the higher  $k_0$  value than for the lower one.

Figure 2 shows the increase in the extent of cure heat vs. the time for the five different values of the rate constant,  $k_0$ . It was obvious that a higher value of the rate constant was responsible for an increase in the state of cure as measured by the extent of the cure heat. Several points of interest on the time necessary to reach a particular value of the state of cure were observed: a 20% variation in the constant rate  $k_0$  provoked a variation of about  $1/8$  in the time necessary for the state of cure to reach 75%. The variation in the time was more than  $1/6$  when the state of cure was of 95%. These two ratios showed the importance of the effect of an error in the rate constant,  $k_0$ , on the cure calculations.

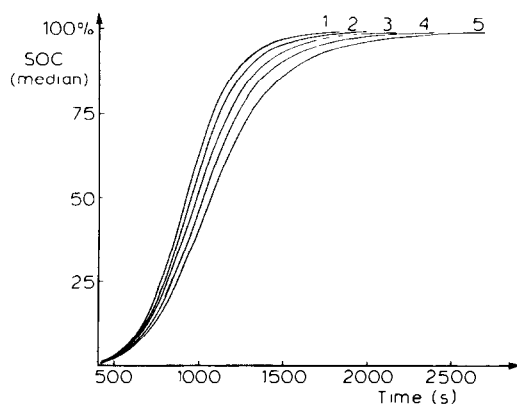


Fig. 2. Effect of variation in  $k_0$  on the extent of cure heat.  $k_0/10^9 \text{ (s}^{-1}\text{)}$ : 1, 3.6; 2, 3.3; 3, 3.0; 4, 2.7; 5, 2.4.

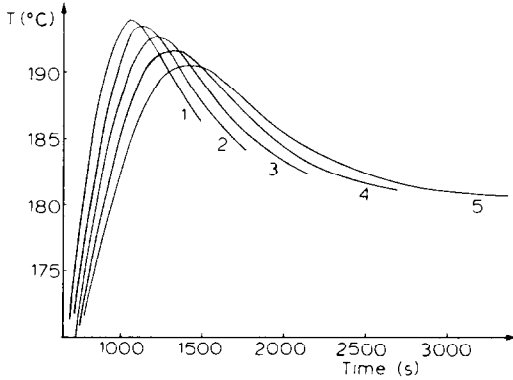


Fig. 3. Effect of variation in the activation energy on the midplane temperature (2 cm thick sheet,  $T_m = 180^\circ\text{C}$ ).  $E(\text{kcal mole}^{-1})$ : 1, 25.0; 2, 25.2; 3, 25.4; 4, 25.6; 5, 25.8.

#### *Effect of variation in the activation energy*

The effect of variation in the value of the activation energy on the midplane temperature is shown in Fig. 3. The curves obtained were for five different values of the activation energy ( $E = 25.0, 25.2, 25.4, 25.6$  and  $25.8 \text{ kcal mole}^{-1}$ ) while the rate constant,  $k_0$ , was kept constant to  $3 \times 10^9 \text{ s}^{-1}$ . A slight variation of  $0.2 \text{ kcal mole}^{-1}$  for the activation energy was responsible for a relative variation of  $1/15$  in the time necessary for the temperature to reach the maximum value. The same variation on  $E$  produced a variation of more than  $0.5^\circ\text{C}$  in the maximum temperature.

The importance of the effect of variation of the chosen value for the activation energy is illustrated in Fig. 4. The lower the value of the activation energy, the higher was the rate of reaction,  $k$ . Consequently, the variation of  $0.2 \text{ kcal mole}^{-1}$  for the activation energy involved an absolute variation on

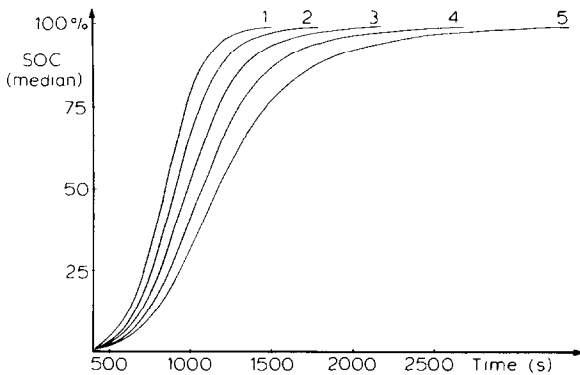


Fig. 4. Effect of variation in the activation energy on the extent of cure heat.  $E(\text{kcal mole}^{-1})$ : 1, 25.0; 2, 25.2; 3, 25.4; 4, 25.6; 5, 25.8.

TABLE 2

Values of  $k_0$ ,  $E$  and  $k$ 

$E$ (kcal mole <sup>-1</sup> )	$k_0/10^9$ (s <sup>-1</sup> )	$k \times 10^3$ (s <sup>-1</sup> ) (160°C)	$k \times 10^3$ (s <sup>-1</sup> ) (180°C)
25.0	3.0	0.88	3.14
25.2	3.0	0.70	2.52
25.4	3.0	0.55	2.00
25.6	3.0	0.44	1.62
25.8	3.0	0.35	1.30
25.4	2.4	0.44	1.62
25.4	2.7	0.50	1.82
25.4	3.0	0.55	2.00
25.4	3.6	0.66	2.43

the time of 150 s which corresponded to a relative variation of 12% in the cure time, when the state of cure was 75%. This relative variation in the time was 30% for a higher state of cure (around 95%).

## CONCLUSION

The effect of a slight variation in the value found by calorimetry for the kinetic parameters of the overall reaction of vulcanization on the cure time was found to be of great importance. The effect appeared to be higher for the activation energy than for the rate constant,  $k_0$ , of the cure reaction. However, if a comparison was drawn between these two parameters, it was necessary to consider the values of the rate constant,  $k$ , of the overall reaction given in Table 2, corresponding to the different values of  $E$  and  $k_0$ . The values in Table 2 show that the variation of the rate constant,  $k$ , corresponding to the variation in the activation energy around its mean value was larger than the one obtained with the variation of the rate constant,  $k_0$ . This fact had to be taken into consideration when a quantitative comparison was desired between the effect of variation in the activation energy and the rate constant,  $k_0$ .

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