Effect of a Variation in Kinetic Parameters (Rate Constant, Activation Energy) on the Vulcanization of Rubber Sheets in Injection Molding Process

C. FERRADOU, B. ROCHETTE, and J. M. VERGNAUD, *Laboratory of Materials and Chemical Engineering, UER of Sciences, 23 Dr/P. Michelon, Saint-Etienne 42100, France*

Synopsis

As shown previously, a slight variation in the kinetic parameters (rate constant, activation energy) of the cure reaction has a pronounced effect on the vulcanization of rubber. The purpose of this work is to show that this effect is more important when the injection molding process is used and the temperature of injected rubber is higher. Experiments were performed using microcalorimetry for determining the kinetic parameters, and a heated mold pressing a 2 cm thick rubber sheet. The resulting variations in the temperature and state of cure at the midplane of sheets were calculated and compared for different temperatures of injected rubber ranging from 40 to 140°C, while the temperature of the mold was kept constant at 180°C.

INTRODUCTION

Since the tendency in the rubber industry is to look for processes able to reduce the cure time cycle, a great interest has been shown in the development of injection molding process. Accordingly, higher temperatures for the mold and also the storage bulb are being used for this purpose.[1,2] A good knowledge of vulcanization will be required for the development of high temperature injection molding processes. With this knowledge, shorter cure cycles could be developed without adversely affecting product quality.[3,4]

It has been shown recently[4-7] that the gradients of temperature developed in the rubber mass could be predicted by considering the balance of internal heat generation from the cure reaction, conduction through the rubber mass, and the mold–rubber interface. The profile of the extent of cure reaction can be also calculated. This problem is complicated by two factors: (i) The vulcanization is a complex chemical process involving simultaneous and successive reactions,[8,9] sulfur being converted into a great variety of sulfidic products; (ii) the thermal properties of rubber were found to vary with the temperature. This problem was solved by using an explicit numerical method with finite differences.[5-7] A simplification was found of interest by considering the heat evolved by the overall cure reaction described by a single reaction.[5-7,9]

Factors affecting both temperature development within the rubber and the resulting state of cure have been shown to include: the enthalpy of cure reaction which was already studied and found of interest,[10,11] and the kinetics of the overall reaction.

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The purpose of this work is to study two of these factors, the rate constant and activity energy, and to show the effect of a variation in the value of these factors on the time of vulcanization. This variation can be due to either a change in quality of vulcanizing agents or the lack of accuracy obtained for the kinetics parameters determined from calorimetric measurements. Two different results were considered: the one concerned with the effect of variation in the above-mentioned cure parameters on the rate of the reaction taking place in the storage bulb; the other by determining the temperature and extent of reaction obtained at the midplane of 2 cm thick rubber sheet inside the mold. As our paper was concerned with the mold injection process, different values were chosen for the temperature of the injected rubber, while the mold temperature was kept constant at 180°C. As shown in previous papers[5,13] the induction time of the reaction can be neglected for the rubber compound employed in this work, but usually it must be considered in the cure kinetics.

THEORETICAL

Mathematical Treatment

The rubber sheet is heated by the mold which faces are maintained at constant temperature T_m. Because of sample dimensions, the heat flow can be considered as unidirectional through the sheet, and defined by the general differential equation for transient conduction of heat by taking into account the heat generation from the cure reaction:

$$\frac{\partial T}{\partial t} = \frac{\lambda}{\rho \cdot C} \cdot \frac{\partial^2 T}{\partial X^2} + \frac{1}{\rho \cdot C} \cdot \frac{dQ}{dt} \qquad (1)$$
$$\text{conduction heat} \quad \text{reaction heat}$$

Initial and boundary conditions were as follows:

$$t = 0, \ 0 \leqslant X \leqslant L, \ T = T_0, \ \text{rubber space} \qquad (2)$$

$$t \geqslant 0, \ X < 0 \text{ and } X > L, \ T = T_m, \ \text{mold space} \qquad (3)$$
$$t > 0 \ \ 0 < X < L \qquad T = T_{x,t}, \ \text{rubber space}$$

As shown in previous papers,[5,13] the rate of the overall cure reaction is given by a single first-order reaction for this kind of rubber:

$$\frac{dQ}{dt} = K_0 \cdot (Q_\infty - Q_t) \cdot \exp\left(-\frac{E}{RT}\right) \qquad (4)$$

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

Numerical Calculation

The problem could be only solved by a numerical method with finite differences.[5-7] Let the rubber sheet be divided into a number of equal finite

slices of thickness ΔX by temperature–reference planes. The heat balance written on the plane n enables us to find the equation

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

where the dimensionless ratio M is

$$M = \frac{(\Delta X)^2}{\Delta t} \cdot \frac{\rho \cdot C}{\lambda} \qquad (6)$$

and $T_{i,n}$ is the temperature at time $i \cdot \Delta t$ and plane n.

The heat generated by the cure reaction on plane n during the time Δt was calculated at the time i $\cdot \Delta t$ by using the following equations:

$$\frac{dQ}{dt} \cdot \Delta t = Q_\infty \cdot [\exp(-S_i) - \exp(-S_{i+1})] \qquad (7)$$

where $S_i = \int_0^{i \cdot \Delta t} K \cdot dt$ and S_{i+1} is given by the approximative recurrent relation

$$S_{i+1} = S_i + K_{T_{i \cdot \Delta t}} \cdot \Delta t \qquad (8)$$

EXPERIMENTAL

Properties of the Rubber

A 150–200 μm 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 extractable, 25% carbon black, and 6% ash.

The enthalpy of reaction Q_∞ and the heat capacity were measured by calorimetry.[5] The thermal conductivity λ of rubber and vulcanizates were determined under steady conditions.[5,6]

The kinetics study of vulcanization was conducted under isothermal conditions at different temperatures ranging from 150 to 180°C [5,6] by using differential calorimetry (SETARAM DSC III). The overall rate of cure was found to follow a first-order reaction with a constant activation energy. Our results on the rate constant of reaction, K_0, and the activation energy E were liable to some experimental errors; so, three possible values of these parameters are given in Table I, which indicate higher and lower values together with the average of these values.

Temperature Profiles at the Midplane of Rubber Sheets

Rubber powder and 3% sulfur as vulcanizing agent were mixed and pressed into the slabs of a $10 \times 10 \times 2$ cm stainless steel mold at the cure temperature of 180°C. Three series of temperature measurements are of

TABLE I
Kinetics Data and Thermal Properties of Rubber

$\rho \cdot C = 0.41 \times [1 + 2.5 \times 10^{-3} (T - 293)]$		cal/cm^3 K
$\alpha = \lambda/\rho \cdot C = 3.1 \times 10^{-3} \times (1 - 10^{-3} \times T)$		cm^2/s
$E_1 = 25.2$ kcal/mol	$E_2 = 25.4$ kcal/mol	$E_3 = 25.6$ kcal/mol
$K_{0_1} = 2.4 \times 10^9$/s	$K_{0_2} = 3 \times 10^9$/s	$K_{0_3} = 3.6 \times 10^9$/s

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.[10,11]

These experiments were conducted by using the rubber compound described above, which the kinetics parameters correspond to the case 2 shown in Table I ($E = 25.4$ kcal/mol, $K_0 = 3 \times 10^9$/s).

RESULTS AND DISCUSSION

Isothermal Extent of Cure-Time Curves for the Rubber in the Storage Bulb

The effect of variation in the value of the rate constant and activation energy on the extent of cure–time curves obtained under isothermal conditions are reported here. These curves can give useful information for the time at which the rubber may be kept within the storage bulb without detriment to the injection.

Effect of a Variation in the Rate Constant K_0

Figure 1 illustrates the effect of a slight variation in the rate constant of the overall cure reaction on the extent of cure–time curves for the rubber
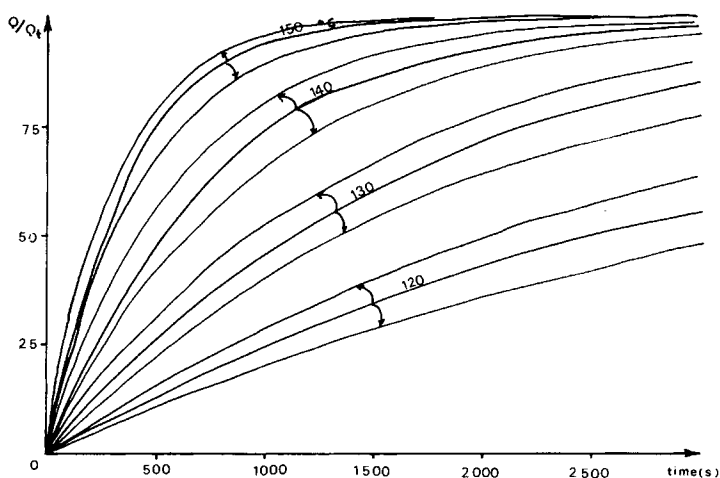

Fig. 1. Extent of cure reaction vs. time in bulb storage for different temperatures. Effect of variation in the rate constant K_0. Calculated data: $K_0 \times 10^9$/s = 2.4–3–3.6, $E = 25.4$ kcal/mol.

in the storage bulb. The relative error is generally less than 20% of the average value for the rate constant. So a variation in 20% around the mean value can be considered as very important for the rate constant. These isothermal curves are directly obtained from microcalorimetry measurements. Any value for the extent of cure resulting from a slight variation in the rate constant can be obtained with the help of the following equation derived from eq. (4) by differentiation when the order of the overall reaction is 1

$$\frac{\partial}{\partial K_0}\left(\frac{Q_t}{Q_\infty}\right) = t \cdot \left(1 + \frac{K_0 \cdot t}{2}\right)^{-3} \cdot \exp\left(-\frac{E}{RT}\right) \tag{9}$$

Effect of a Variation in the Activation Energy

Figure 2 shows the variation in the extent of cure vs. the time for the three different values of the activation energy of the overall reaction (E = 25,000–25,400–25,800 cal/mol). These values for the activation energy are beyond the probable experimental error. The variation in the extent of cure can be determined at any time by using eq. (10) which is the partial derivative from eq. (4):

$$\frac{d}{dE}\left(\frac{Q_t}{Q_\infty}\right) = t \cdot \left(I + \frac{K \cdot t}{2}\right)^{-3} \cdot \frac{-K_0}{RT} \cdot \exp\left(-\frac{E}{RT}\right) \tag{10}$$

These curves show the importance of the effect of an error in the activation energy on the time at which the rubber can be kept within the storage bulb without detrimental reaction.
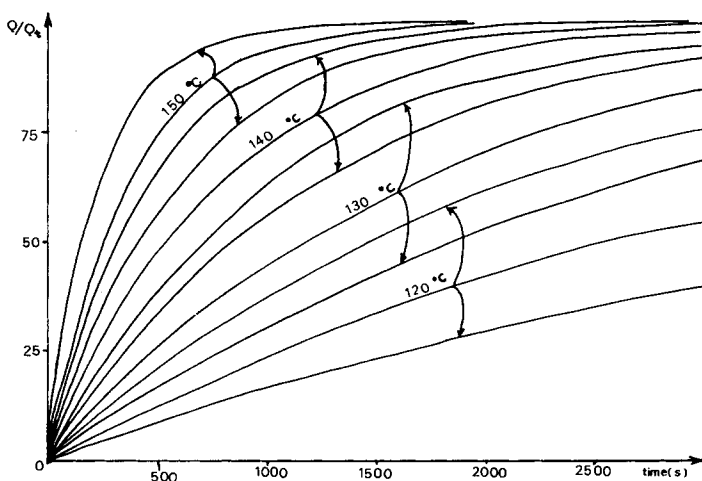

Fig. 2.   Extent of cure reaction vs. time in bulb storage for different temperatures. Effect of variation in the activation energy. Calculated data: E = 25–25.4–25.8 kcal/mol, $K_0 \times 10^9$ = 3/s.

Effect of a Variation in the Rate Constant on the Extent of Cure within Rubber Sheets

The study was conducted by using 2 cm thick rubber sheets, and calculations were done with the three above-mentioned values of the rate constant ($K_0 \times 10^9$ = 2.4–3–3.6/s). Four different values were chosen for the temperature of the injected rubber (T_{ir} = 40–100–120–140°C), while the temperature of the mold was kept constant at 180°C. The effect of a variation in the rate constant on the temperature at the midplane can be appreciated in Figures 3(A) and 3(B). For each value of the four temperatures of injected rubber, the profiles of the temperature are about the same up to 160°C. Above this temperature, the increase in temperature is highest for the higher value of the rate constant. The temperature at the midplane reached maximum in a shorter time when the rate constant of the reaction is higher. The higher the constant rate, the higher the value of this maximum reached by the temperature at the midplane of sheets. After the maximum raised by this temperature, the three curves corresponding to the different values of the rate constant intersect, and that fact occured for every temperature of the injected rubber.
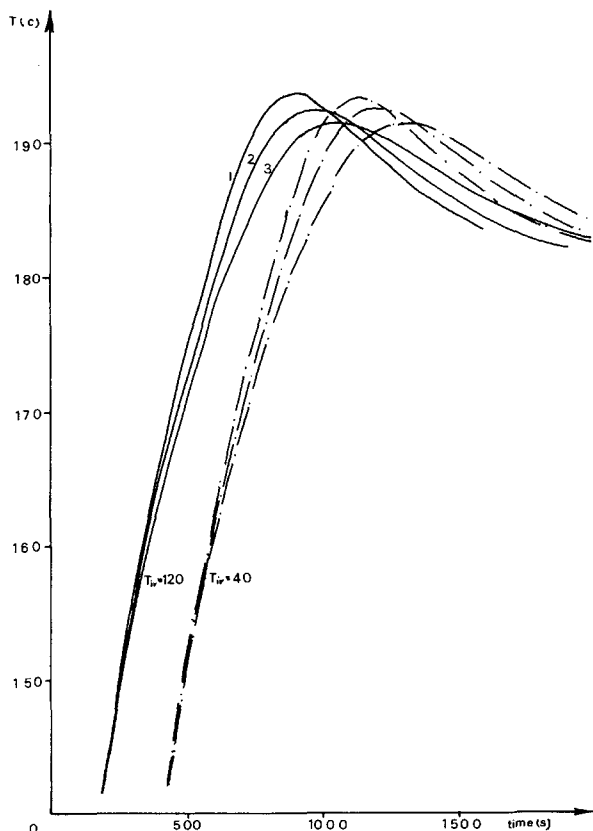

Fig. 3(A). Midplane temperature vs. time for different temperatures of injected rubber: T_{ir} = 40–120°C. Effect of variation in $K_0 \times 10^9$ = 2.4 (3)–3 (2)–3.6 (1). E = 25.4 kcal/mol, T_m = 180°C, 2 cm thick. Experimental and calculated data; (1 and 3) calculated data.

Extent of the Cure Reaction

Figures 4(A) and 4(B) show the increase in the extent of cure heat vs. the time for the three different values of the rate constant, by considering the four values chosen for the temperature of the injected rubber.

Of course, the higher the temperature of rubber when injected into the mold, the shorter the time necessary for the state of cure to reach selected values.[14] The curves obtained with the same values of the rate constant are displaced from each other by a translation along the time axis.

It is obvious that a higher value of the rate constant is responsible for an increase in the state of cure as measured by the extent of cure heat. Several points of interest on the time necessary to reach the particular value of 90% for the state of cure can be observed in Table II.

Effect of a Variation in the Activation Energy on Cure within Rubber Sheet

Temperature at the Midplane of the Sheet

The effect of a slight variation in the value of the activation energy of cure reaction on the midplane temperature of 2 cm thick rubber sheets is
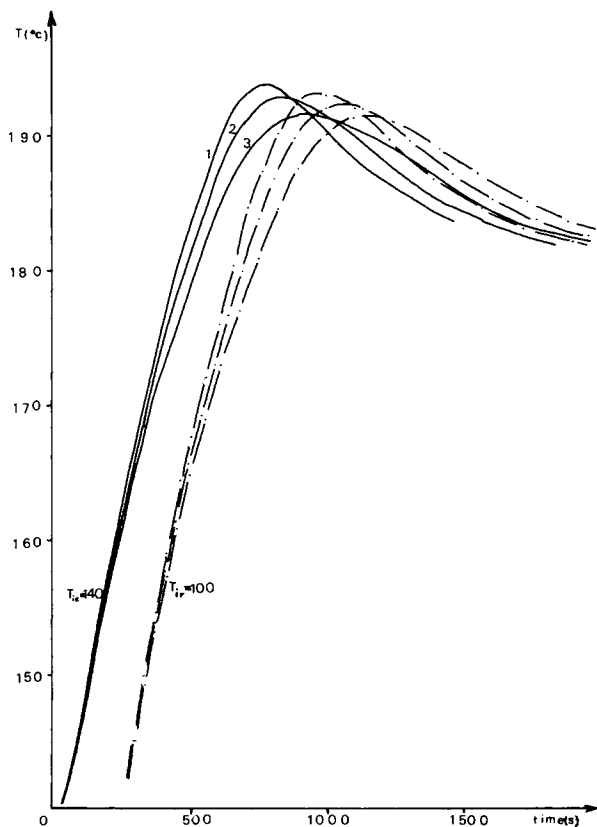

Fig. 3(B). Midplane temperature vs. time for different temperatures of injected rubber: T_{ir} = 100–140°C. Effect of variation in K_0: $K_0 \times 10^9$ = 2.4 (3)–3 (2)–3.6 (1). E = 25.4 kcal/mol, T_m = 180°C, 2 cm thick. (2) Experimental and calculated data; (1 and 3) calculated data.

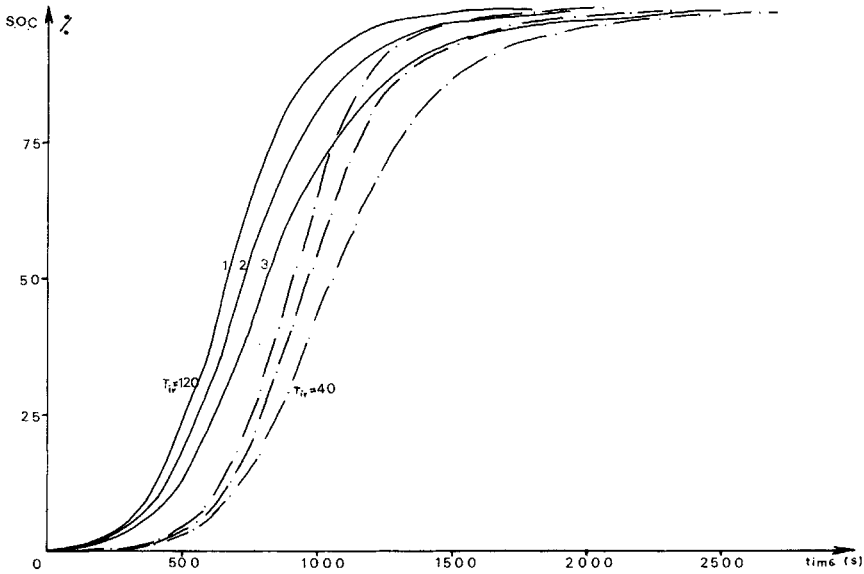Fig. 4(A). SOC at the midplane vs. time for different temperatures of injected rubber: T_{ir} = 40–120°C. Effect of variation in K_0: $K_0 \times 10^9$ = 2.4 (3)–3 (2)–3.6 (1). E = 25.4 kcal/mol, T_m = 180°C, 2 cm thick, calculated data.

shown in Figures 5(A) and 5(B). The curves are obtained for three different values of the activation energy (25–25.4–25.8 kcal/mol) and for four different temperatures of the rubber at injection, whereas the rate constant is kept constant at 3×10^9/s. A slight variation of 400 cal/mol in the activation energy is responsible for an appreciable variation in the midplane temperature–time curves. Up to 160°C, the three curves are about the same, but
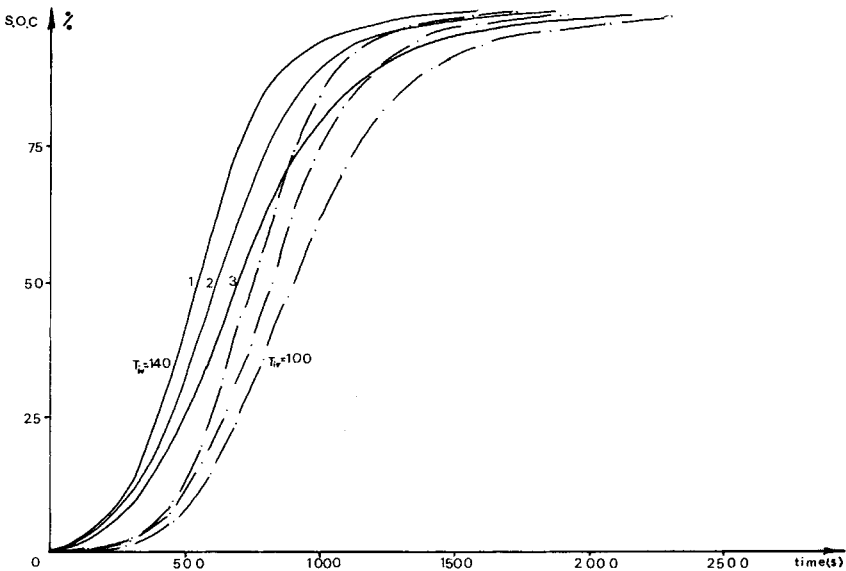

Fig. 4(B). SOC at the midplane vs. time for different temperatures of injected rubber: T_{ir} = 100–140°C. Effect of variation in K_0: $K_0 \times 10^9$ = 2.4 (3)–3 (2)–3.6 (1). E = 25.4 kcal/mol, T_m = 180°C, 2 cm thick, calculated data.

TABLE II
Time Necessary for SOC to Reach 90% for Different Values of K_0

Tir	40°			100°C			120°C			140°C	
$K_0 \times 10^3$	2.4	3	3.6	2.4	3	3.6	2.4	3	3.6	2.4	3
Time (s)	1580	1370	1220	1430	1220	1000	1350	1130	1000	1220	1000

above this temperature they largely diverged. The maximum values raised by the midplane temperature differed only a little according to the value given to the activation energy, but the time at which they are obtained is quite different.

State of Cure at the Midplane of the Sheet

The importance of the effect of a variation in the activation energy on the profiles of the state of cure at the midplane is illustrated in Figures 6(A) and 6(B). Of course, the lower the value of the activation energy, the higher the rate of reaction and the lower the time necessary for the state of cure to reach a definite value. The variation in the time necessary for the SOC to reach 90% is clearly shown in Table III, for the four different
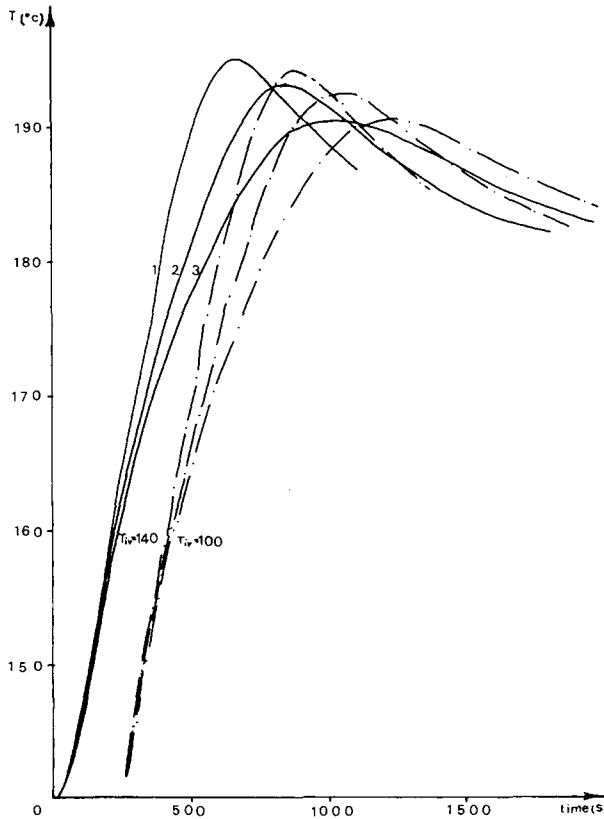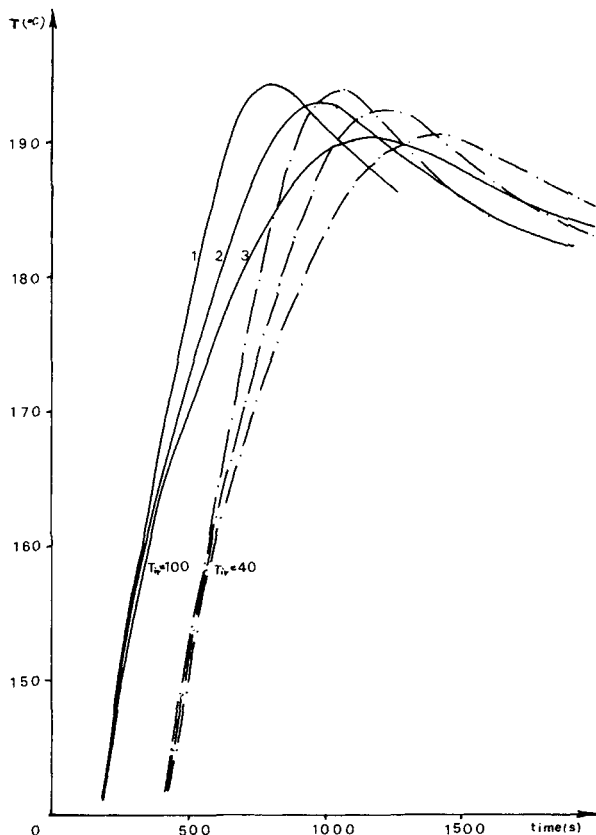

Fig. 5(A). Midplane temperature vs. time for different temperatures of injected rubber: T_{ir} = 40–120°C. Effect of variation in E: E = 25 (1)–25.4 (2)–25.8 (3). $K_0 \times 10^9$ = 3/s, T_m = 180°C, 2 cm thick. (2) Experimental and calculated data; (1 and 3) calculated data.

Fig. 5(B).   Midplane temperature vs. time for different temperatures of injected rubber: T_{ir} = 100–140°C. Effect of variation in E: E = 25 (1)–25.4 (2)–25.8 (3). $K_0 \times 10^9$ = 3/s, T_m = 180°C, 2 cm thick. (2) Experimental and calculated data; (1 and 3) calculated data.

values of the temperature of rubber at injection. Consequently, a variation of 400 cal/mol in the activation energy involved a relative variation of about 32% in the cure time, when the state of cure is 90% and the temperature of injected rubber is 40°C. This relative variation is increased when the temperature of injected rubber is higher than 40°C and reaches the value of 50% when T_{ir} is equal to 140°C.

CONCLUSIONS

The effect of a variation in the values found by microcalorimetry for the kinetic parameters of the overall cure reaction on the vulcanization within rubber sheets was found to be of great importance. This effect appeared to be especially important for the activation energy, for which a variation of 400 cal/mol around the mean value of 25,400 cal/mol cannot be accepted: The time necessary for the state of cure to reach 90% differed from the mean value by more than 30%. Moreover, the relative error in this particular time was found to increase largely with the temperature of rubber at injection. The effect of a variation in the rate constant is not so large than that of the activation energy.
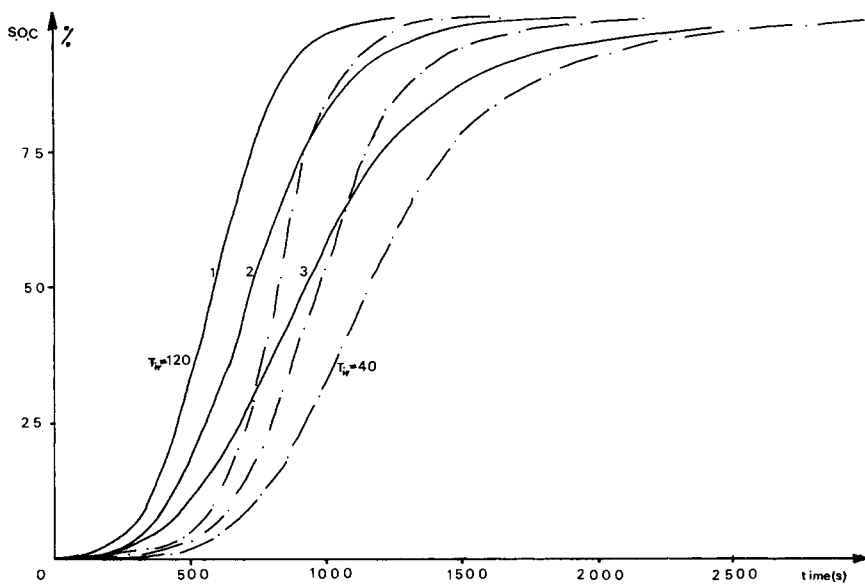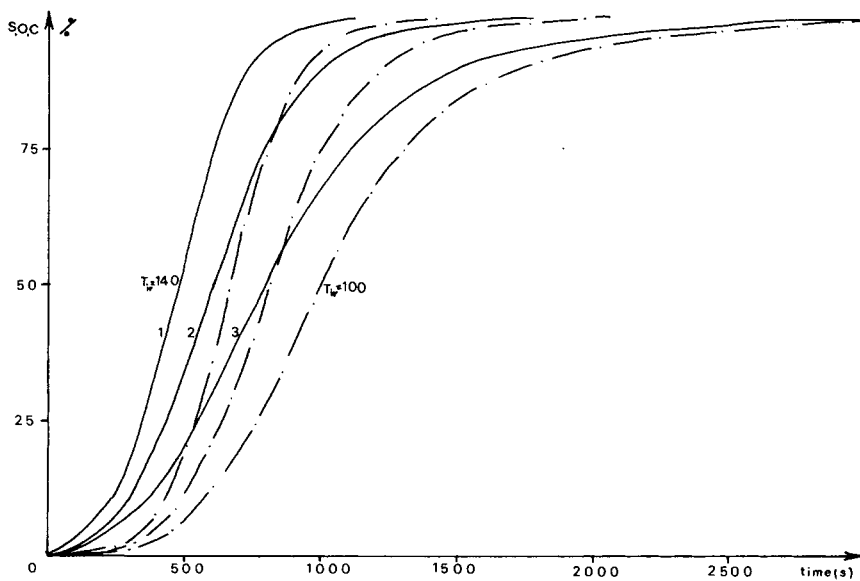
Fig. 6(A).

Fig. 6(B).

FERRADOU, ROCHETTE, AND VERGNAUD

TABLE III
Time Necessary for SOC = 90% for Different Values of E

Tir	40°C			100°C			120°C			140°C		
E	25.0	25.4	25.8	25	25.4	25.8	25	25.4	25.8	25	25.4	25.8
Time (s)	1080	1370	1860	940	1210	1720	850	1130	1620	730	1000	1500

All these facts have to be taken into consideration when the kinetic parameters of the overall reaction of cure are determined by microcalorimetry.

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