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EFFECT OF A VARIATION IN THE ORDER OF THE OVERALL REACTION OF CURE ON THE PROFILES OF TEMPERATURE AND STATE OF CURE DEVELOPED AT THE MIDPLANE OF RUBBER SHEETS

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ABSTRACT

As an extension of previous works dealing with the effect of kinetic parameters on the extent of cure at the midplane of rubber sheets, this paper shows the great importance of the value chosen for the order of the overall reaction of cure. Although it has no importance at the beginning of the cure reaction, this effect becomes decisive when the state of cure is higher than 50%. Several values, ranging from 1 to 1.4, were tested for the order. The effect of this variation in the order on the profiles of temperature and extent of reaction were calculated and discussed: it was found to be of great importance, especially for the determination of the time necessary for the state of cure to reach the standard value of 90%.

INTRODUCTION

As the rubber industry is seeking the development of processes for faster vulcanization, several methods have been developed to reduce the cure time cycle using a higher temperature for the mold [1,2] or accelerators with ultra-strong activity [3,4]. However, we believe that the best method of reducing the time, without detriment to the quality of vulcanizates, is to ensure that the process is properly carried out and stopped at the correct time [5,6]. The achievement of this project, however, requires a sufficient knowledge of the time–temperature relation of the rubber at any point, and the kinetics of the cure reaction.

Some early works [7,8] indicated that the temperature gradients developed in rubber during the cure cycle could be calculated using the data of heat transfer and the kinetics of reaction. The extent of the cure reaction could also be determined by the balance of internal heat from the cure reaction, and conduction through the rubber mass and the mold–rubber interfaces. Although the vulcanization of rubber consists of a complex series of reactions, including successive and simultaneous ones [9,10], the overall reaction

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can be described as a first-order reaction with a single activation energy [11], when taking into account the reaction heat [8,12,15]. These measurements are obtained using differential microcalorimetry working either in scanning mode [12], or under isothermal conditions [7,8].

Several parameters were found to be important for the determination of the extent of the cure reaction: one concerned with operational conditions (temperature of the mold and rubber), and the thickness of rubber sheets; the others are dependent on the thermal properties of rubber, the parameters of the reaction kinetics, and the enthalpy of the cure reaction. Some of these parameters have been studied in particular. Although the cure reaction is not highly exothermic, the heat generated has an important effect on the temperature and state of cure obtained within the cure mass, since the rubber has a low thermal conductivity [13]. A slight variation in the kinetic parameters of vulcanization (rate constant and activation energy) has a pronounced effect on the vulcanization of a rubber sheet [14]. Up to now, a study has not been attempted considering the effect of a variation in the value of the order chosen for the overall cure reaction.

The purpose of this work is to determine the effect of a variation in the value of the order of the overall cure reaction on the profiles of temperature and extent of cure developed within rubber sheets. This variation in the value of the order is essentially due to the fact that these complex cure reactions are not easily accommodated on a single reaction; therefore, different values for the order could be chosen according to the part of the experimental kinetic curve under consideration. This work was achieved by using 2 cm thick sheets of rubber with 3% sulfur as vulcanizing agent involving a cure enthalpy of 15 cal g^{-1} of mixture, by choosing different values for the order (ranging from 1 to 1.4) and keeping the rate of reaction and activation energy constant. Calculations of temperature and state of cure were made with the help of a previously reported model [6,8] and an explicit method with finite differences.

THEORETICAL

Governing equations

The differential equation governing transient one-dimensional heat conduction with application to rubber technology has been discussed previously [11]

$$\underset{\text{(conduction heat)}}{\frac{\partial}{\partial x}\left(\frac{\partial T}{\partial x}\right)} + \underset{\text{(reaction heat)}}{\frac{\mathrm{d}Q}{\mathrm{d}t}} = \underset{\text{(total heat)}}{\rho C\frac{\partial T}{\partial t}} \tag{1}$$

where Q is a heat source term due to the cure reaction. The thermal conductivity, λ, of rubber is well represented as a linear function of temperature. The density decreases and the heat capacity increases with increasing temperature; therefore, the product ρC increases slightly with increasing temperature.

The heat of the overall reaction of cure is expressed by

$$\frac{I}{Q_\infty}\frac{\mathrm{d}Q}{\mathrm{d}t} = K_0\left(\frac{Q_\infty - Q_t}{Q_\infty}\right)^n \exp - \frac{E}{RT} \tag{2}$$

where K_0 is a constant (min^{-1}); E is the activation energy, n is the order of the overall reaction; Q_t is the heat evolved up to time t; and Q_∞ is the total heat of the cure reaction.

The initial and boundary conditions are as follows

$$t = 0 \quad 0 < x < L \quad T = T_0 \quad \text{rubber space} \tag{3}$$

$$t > 0 \quad x < 0 \text{ or } x > L \quad T = T_\mathrm{m} \quad \text{mold space}$$

$$0 < x < L \quad T = T_{x,t} \quad \text{rubber space} \tag{4}$$

Numerical method

As eqns. (1) and (2) cannot be solved by a mathematical treatment, eqn. (1) is set in finite difference form, using forward differences, to obtain the explicit equations [6–8].

A temperature at time $(i + 1)\,\Delta t$ can be calculated at any point, n, from a knowledge of the system properties and the temperature at node, n, and the surrounding $n - 1$ and $n + 1$ nodes at time $i\Delta t$. Let the solid be divided into equal slices of thickness Δx, the heat balance on plane n is expressed by

$$T_{i+1,n} = \frac{1}{M}\left[T_{i,n-1} + (M - 2)T_{i,n} + T_{i,n+1}\right] + \frac{1}{\rho C}\frac{\mathrm{d}Q}{\mathrm{d}t}\Delta t \tag{5}$$

where the dimensionless modulus, M, is given by

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

α being the thermal diffusivity of rubber. The stability of the explicit formulation is obtained when $M > 3$.

When hot, unvulcanized rubber is pressed against the clean metal surface of the mold, its thermoplastic nature assures intimate contact so that thermal resistance between metal and rubber can be neglected. This will also usually apply for vulcanized rubber because it is not too hard and is seated against metal with a reasonable pressure. Thus, the heat transfer at the interface follows eqn. (5) by having two different values for the slices taken from the rubber and mold. As the use of the same modulus, M, is desirable in both materials, since the increment of time, Δt, is the same for both, the ratio of the thicknesses of the slices must be taken as equal to the square root of the thermal diffusivities

$$\frac{\Delta X_{\text{mold}}}{\Delta X_{\text{rubber}}} = \left(\frac{\alpha_{\text{mold}}}{\alpha_{\text{rubber}}} \right)^{0.5} \tag{7}$$

The internal heat generated by the cure reaction during the incremental time, Δt, is calculated at the time $i\Delta t$ using eqn. (2).

EXPERIMENTAL

Cure kinetic data and thermal properties of rubber

Rubber, having the following composition, was used: 55% rubber hydrocarbon (being a mixture of NR and SBR in the ratio of 2/3); 14% extractable acetone; 25% carbon black; and ~ 6% ash.

The enthalpy of reaction Q_∞ was measured by differential scanning calorimetry (DSC III, Setaram, Lyon), and the heat capacity by calorimetry. The thermal diffusivity, α, of the rubber and vulcanizates was determined under transient conditions.

The kinetic study of vulcanization was conducted with DSC working at 150, 160 and 170 °C as reported previously [8] (Table 1).

Temperature profiles at the midplane of rubber sheets

Rubber and 3% sulfur were mixed and pressed into the slabs of a 10 × 10 × 2-cm stainless steel mold. The temperature at the midplane of the 2 cm thick rubber sheet was continuously registered, while the temperature of the mold was kept constant [8].

RESULTS

Kinetic study of vulcanization using differential calorimetry

Kinetic study of the cure was conducted using DC under isothermal conditions at 150–160–170 °C. These temperatures were chosen because the rate of vulcanization is high, giving cure times available for industrial applications.

TABLE 1

Thermal properties and kinetic results

$\alpha = 1.77 \times 10^{-3}$ cm^3 s^{-1}	$E = 17$ kcal mol^{-1}
$\rho C = 0.4$ cal cm^{-3} K^{-1}	$K_0 = 7 \times 10^5$ s^{-1}
$Q_\infty = 15$ cal g^{-1}	$n = 1, 1.2, 1.3, 1.4$

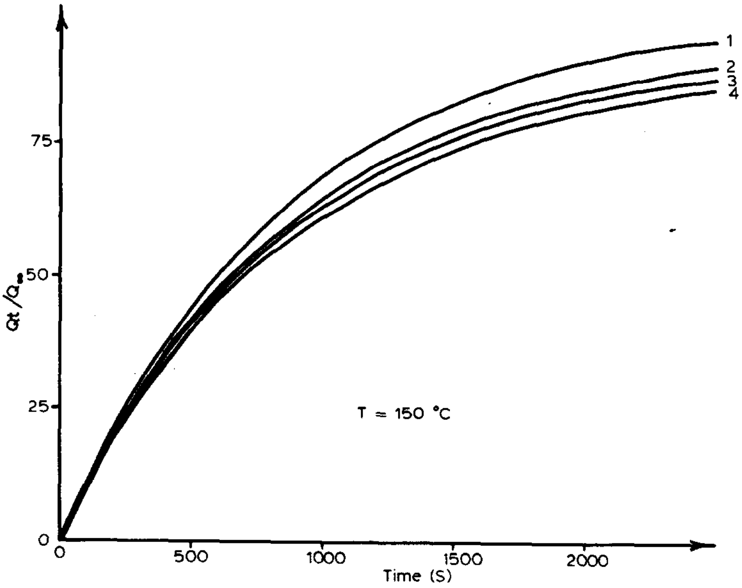

Fig. 1. Exotherms (SOC vs. time) obtained at 150 °C, for different values of the order of the overall reaction. $n=1$ (1), 1.2 (2), 1.3 (3), 1.4 (4); $K_0=7\times10^5$ s^{-1}; $E=17$ kcal mol^{-1}.

Figure 1 illustrates the DC exotherm at 150 °C for a compound with a sulfur/rubber ratio of 3%, and Figs. 2 and 3 are obtained at 160 and 170 °C. These exotherms, expressing the extent of cure as a function of time, were

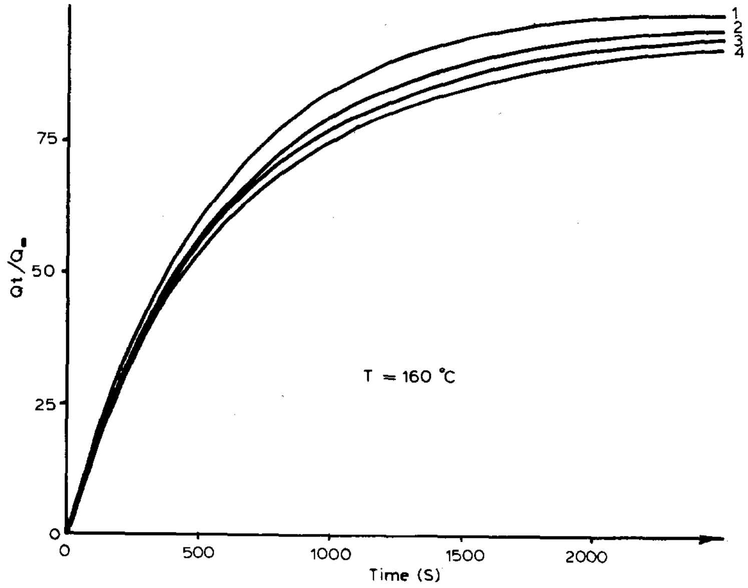

Fig. 2. Exotherm obtained at 160 °C for different values of the order of the overall reaction. $n=1$ (1), 1.2 (2), 1.3 (3), 1.4 (4); $K_0=7\times10^5$ s^{-1}; $E=17$ kcal mol^{-1}.

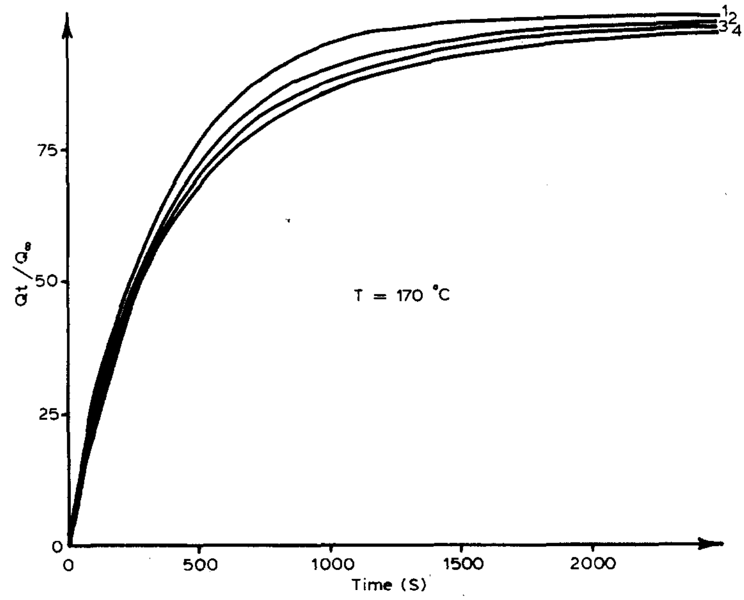

Fig. 3. Exotherms obtained at 170 °C for different values of the order of the overall reaction. $n = 1$ (1), 1.2 (2), 1.3 (3), 1.4 (4); $K_0 = 7 \times 10^5$ s^{-1}; $E = 17$ kcal mol^{-1}.

calculated for different values of the order of the overall reaction (eqn. 2), ranging from 1 to 1.4. It is often said, and perhaps taken for granted, that the order of the overall reaction of cure is described by a first-order reaction [8,11,15–17]. The assumption is that the partial enthalpy, Q_t, evolved up to time t, as a fraction of the total enthalpy evolved, represents the conversion to time t.

Our experimental exotherms follow the calculated curves corresponding to a first-order reaction exactly when the extent of reaction is below 50%, but differ from this calculated curve when the extent of reaction is higher than 50%. In fact, the plots of log (heat rate) vs. log (remaining sulfur) in eqn. (2) are not exactly linear as shown previously [8], and the slopes of this curve vary with the extent of reaction from 1 to ~ 1.4. In other words, the order of the overall reaction was found to vary with the value of the extent of cure.

As shown in Table 2, the effect of a variation in the value of the order is

TABLE 2

Effect of the value of the order on the extent of cure

Order	$Q_t/Q =$	0.9	0.5	0.25	0.1
1.1		0.9	0.5	0.25	0.1
1.1		0.89	0.47	0.22	0.08
1.2		0.88	0.44	0.19	0.06
1.3		0.87	0.41	0.16	0.05
1.4		0.86	0.38	0.14	0.04

negligible for the rate of cure when the extent of cure is below 50%, but becomes increasingly higher when the extent of cure is increased from 50 to 100%. Thus, the curves in Figs. 1 to 3 differ from one another according to the value of the order when the extent of cure is higher than 50%.

Temperature and state of cure obtained at the midplane of a 2 cm thick rubber sheet

Calculations were achieved using the present model and eqns. (5) and (6) for the temperature, and eqn. (2) for the heat of reaction with the different values chosen for the order of the overall reaction.

Figure 4 shows the variation of the temperature at the midplane of 2 cm thick rubber sheets when the temperature is 170 °C for the mold and 40 °C for the rubber injected into the mold. The maximum rise in the midplane temperature is obtained at about the same time for all the curves, but the maximum value for this temperature varies slightly with the value taken for the order: the lower the order, the higher is the maximum of this temperature. However, it is not so easy to appreciate this difference in the temperature at the maximum value because it is lower than 2 °C.

Another fact can be shown for the value of the time around 20 min: all these temperature–time curves intersect, and for a time greater than 20 min

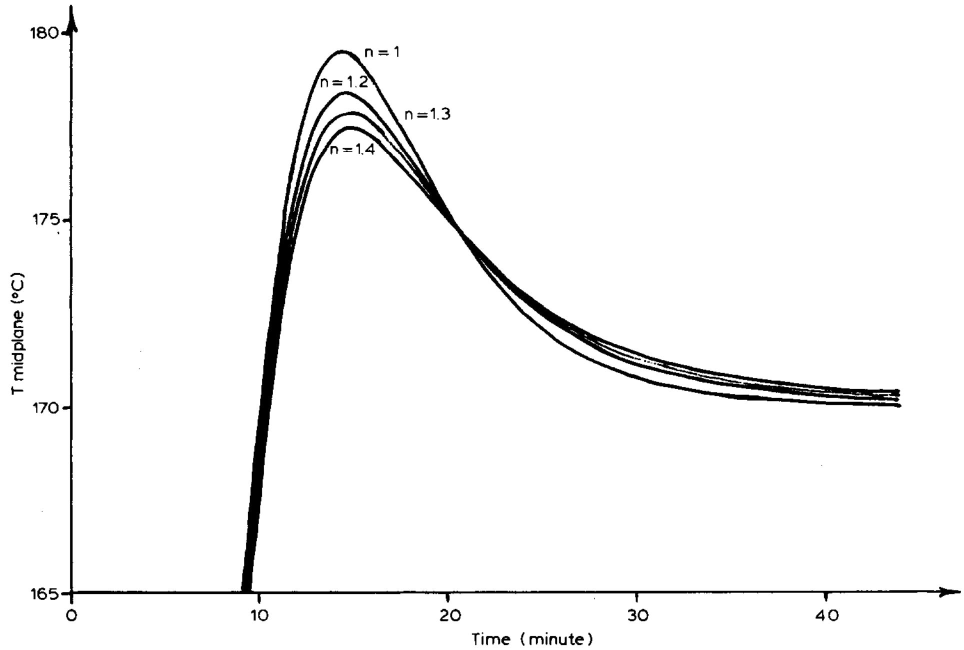

Fig. 4. Temperature at the midplane as a function of time, for different values of the order. $n=1$, 1.2, 1.3, 1.4; 2 cm thick sheet; $K_0 = 7.10^5$ s^{-1}; $E = 17$ kcal mol^{-1}; $T_m = 170$ °C; $T_{ir} = 40$ °C.

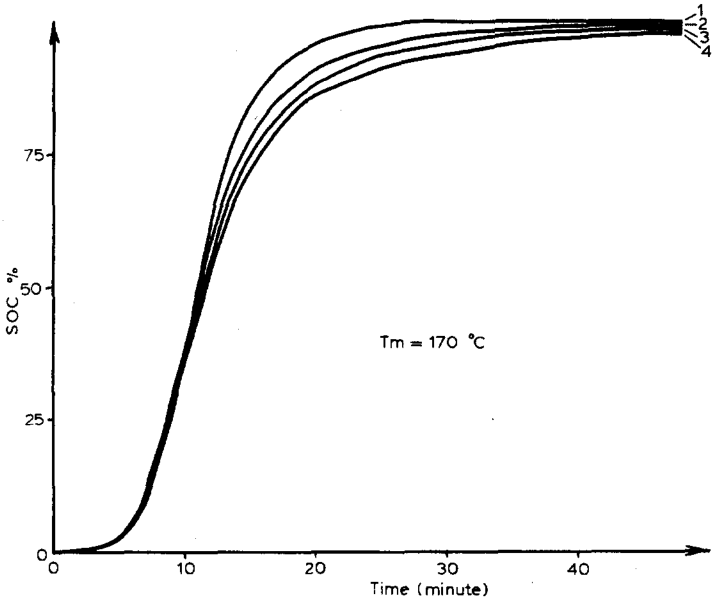

Fig. 5. State of cure at the midplane as a function of time, for different values of the order. $n = 1$ (1), 1.2 (2), 1.3 (3), 1.4 (4); 2 cm thick sheet; $K_0 = 7 \times 10^5$ s^{-1}; $E = 17$ kcal $mole^{-1}$; $T_m = 170\,°C$; $T_{ir} = 40\,°C$.

the midplane temperatures become higher when the order is higher. The difference between these values for the temperature cannot, however, be determined precisely experimentally because of their insignificance.

The variation of the state of cure with the time at the midplane of sheets can be appreciated from Fig. 5. The effect of the order on the extent of cure is insignificant when the extent of cure is lower than 50%. On the contrary, the effect of the order becomes important for values of the extent of cure higher than 50%: the lower the value of the order the higher the state of cure. The value of finding the correct value for the order of the overall reaction can be clearly seen from Table 3, in which the times necessary for the state of cure at the midplane to reach the standard 90% value are collected.

CONCLUSIONS

In this paper, the effect of the kinetic data, and especially the value for the order of the overall reaction of cure, is indicated by considering the profiles

TABLE 3

Time (S) necessary for the SOC to reach 90%, for different n

Order, n	1	1.2	1.3	1.4
Time, S	996	1167	1280	1395

of temperature and extent of cure developed at the midplane during the cure reaction. A variation in the value of the order is insignificant at the beginning of the cure reaction when the state of cure is below 50%. When the state of cure increases, however, the effect of the order chosen for the cure reaction becomes significant: the lower the order the higher the value calculated for the state of cure.

Two conclusions can be drawn from this information: (1) it is better to make the choice for the order within the 50–100% range of the state of cure; (2) apart from the complexity, it can be of interest to use a value of the order varying with the value of the extent of cure.

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