

Calculation of Profiles of Temperature and State of Cure Developed within the Rubber Mass in Injection Molding Process

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Synopsis

Higher and higher temperatures for vulcanization and storage bulb are being used in order to reduce the time of cure cycle in processes of rubber injection molding. The purpose of this work was to show that the temperature gradients as well as the profiles of the state of cure developed in the rubber mass could be predicted by using the kinetics of reaction, the physical properties of the rubber, and a convenient model. Although vulcanization is a complex series of reactions, the overall result by considering the heat of reaction could be described by a single first-order reaction. The calculation was solved applying an explicit method with finite differences, by taking into account the internal generation of heat due to the cure reaction and the heat transfer by conduction with a temperature dependence of the physical properties of the rubber. The effect of the values of the temperature of the mold and storage bulb on the profiles of temperature and state of cure developed within rubber was studied by considering rubber sheets of different thicknesses.

INTRODUCTION

Up to now the tendency in the rubber industry was to look for processes in order to manufacture finished products more quickly. Accordingly, higher and higher temperatures for the mold and also the storage bulb are being used to reduce the time cycle of cure in injection molding processes for rubber. But in our opinion the best way of shortening the cure cycle without detriment to quality is to get a sufficient knowledge on the time-temperature history of the rubber and to be able to make sure that the process of vulcanization is properly conducted and stopped at the right time when the state of cure is acceptable.

The purpose of this work was to show that the profiles of temperatures and state of cure developed in rubber sheets could be calculated during vulcanization for injection molding processes, if the kinetics of reaction and the physical properties of the rubber were known. The effect of the values chosen for the mold and storage bulb was especially studied, because they are very important parameters in injection molding process of rubber. The study was performed by using several thicknesses for rubber sheets.

The problem concerned with temperature and state of cure determinations was solved by applying an explicit numerical method with finite differences.¹ This method was found to be as accurate as implicit methods, and more simple than the other, allowing the use of small inexpensive computers.² Vulcanization of rubber consists of a complex series of reactions,³ but the overall result could be described by a first-order reaction with a single activation energy, by con-

sidering the heat of cure reaction measured by calorimetry.⁴⁻⁶ The calculation of the temperature and extent of reaction, considered in this work as the state of cure, was performed from the heat balance by taking into account the internal generation of heat due to the cure reaction and the heat transfer by conduction through the rubber and the mold-rubber interface.

THEORETICAL

Mathematical Treatment

The unidirectional heat flow through the rubber sheet of thickness l was 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 as follows:

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

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

$$x > 1$$

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

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

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

the constant k having an Arrhenius form with a single activation energy,^{1,6}

$$k = k_0 \cdot \exp(-E/RT) \quad (5)$$

where Q_t is the heat of cure reaction evolved up to time t and Q_∞ 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. For the numerical analysis concerned with a cross section of the rubber sheet, the sheet was divided into n equal finite slices of thickness Δx . The heat balance was written on the plane n as follows:

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

where the dimensionless ratio M was

$$M = \frac{(\Delta x)^2}{\Delta t} \cdot \frac{\rho \cdot C}{\lambda} \quad (7)$$

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

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

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

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

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 Δt for both materials, and 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 α_{mold} and α_{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- μm 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 on a differential scanning calorimeter (DC) operated in isothermal mode. About 100–150 mg of the compound 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 the time.

The data concerned with kinetics parameters and heat transfer are shown in Table I.

Temperature Measurement at the Midplane of Rubber Sheet. Three series of temperature measurements were of interest in this work: the temper-

TABLE I
Thermal Properties of Rubber

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

ature of the mold; the difference between the temperature of the mold and that measured at the midplane of rubber sheets; the temperature of the rubber just before its introduction into the mold.

RESULTS

Before studying the effects of the temperature of injected rubber on the profiles of temperature and state of cure developed through rubber sheets within the mold, it was necessary to examine the rate of the reaction of vulcanization taking place within the rubber located in the storage bulb.

Determination of the State of Cure of the Rubber in the Storage Bulb as a Function of Time and Temperature. Of course, the higher the temperature of the rubber when injected into the mold, the shorter the time necessary for the state of cure to reach the selected values. But too high a temperature in the storage bulb might be responsible for a reaction of vulcanization judged to be dangerous in this case. So it is necessary to have a sufficient knowledge on the rate of this cure reaction and to know exactly the time at which the rubber might be stored without vulcanization occurring.

Calorimetric results were used for calculations of the state of cure obtained in isothermal conditions. The results from this calculation gave a state of cure-time curve for every temperature. As shown in the typical Figure 1, heating for 0.5 h in the storage bulb produced a 20% state of cure of the rubber at a temperature of 140°C, and 35% state of cure at 150°C.

Effect of the Temperature of Injected Rubber on the Temperature at the Midplane Sheet. The temperature at the midplane of the rubber sheets rises from an initial value to a final value, T_m , the mold temperature, by reaching peak as shown in Figure 2 for a thickness of 1 cm and in Figure 3 for 2 cm. Different selected temperatures within the 40–140°C range were used for the rubber during injection. An excellent correlation was found between the calculated values and the experimental ones.

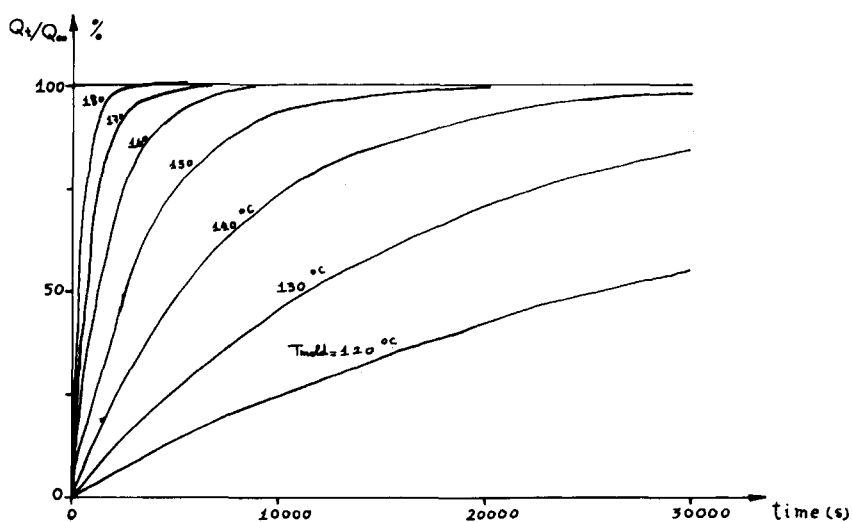


Fig. 1. Extent of reaction heat as a function of the time for different temperatures, in isothermal conditions.

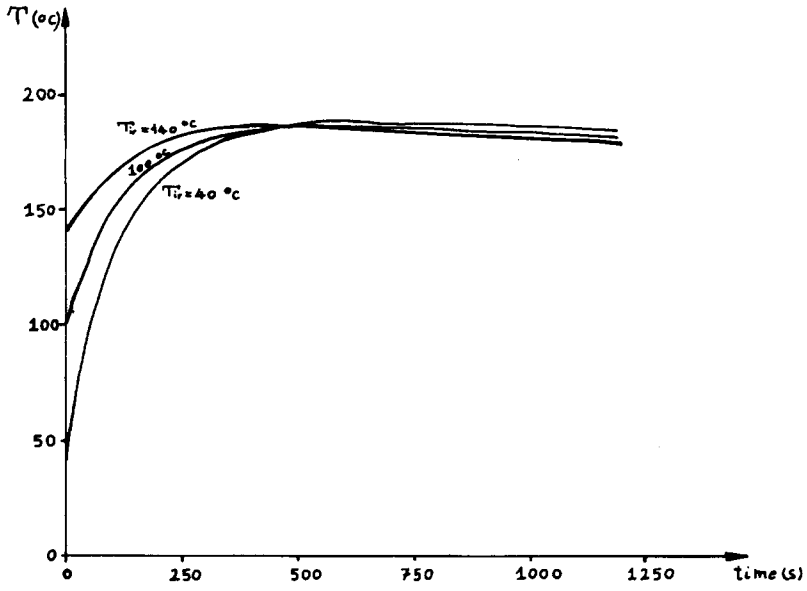


Fig. 2. Midplane temperature vs. time, for different rubber temperatures at the injection: $T_{ir} = 40^\circ\text{C}$, 100°C , 140°C ; $T_m = 180^\circ\text{C}$; 1 cm thick; $\Delta H = 18.1$ cal/g.

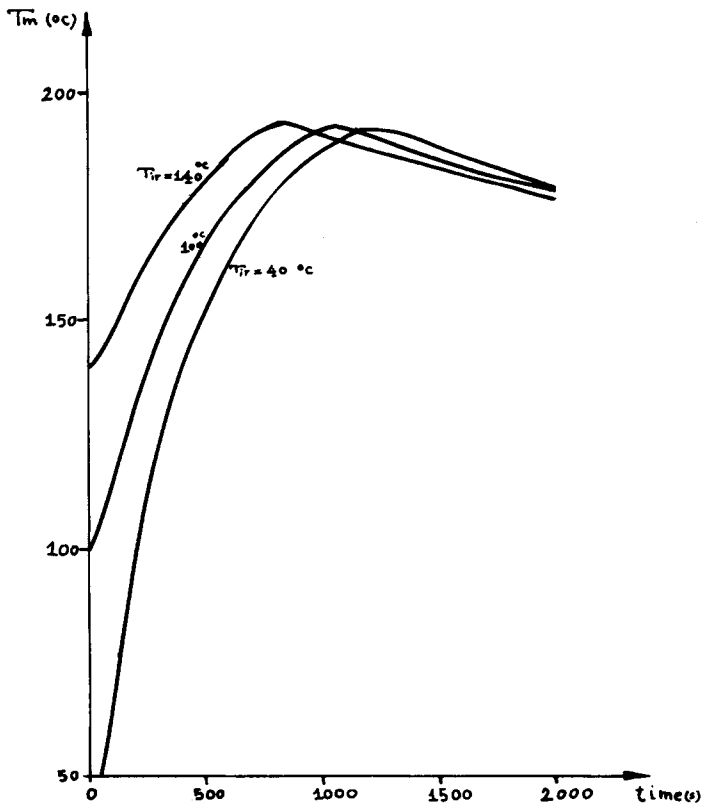


Fig. 3. Midplane temperature vs. time, for different rubber temperatures at the injection: $T_{ir} = 40^\circ\text{C}$, 100°C , 140°C ; $T_m = 180^\circ\text{C}$; 2 cm thick; $\Delta H = 18.1$ cal/g.

TABLE II
Maximum of the Midplane Temperature for a 2 cm Thick Sheet

T_{ir}	40	70	100	120	140
T_{max}	192.6	192.6	192.6	192.7	192.8
Time (s)	1200	1140	1050	960	840

As shown in these figures, an increase in the temperature of the injected rubber, T_{ir} , was responsible for two effects of interest: (1) the maximum value of the midplane temperature was reached at a shorter time; (2) the value of the maximum of the midplane temperature was increased.

These facts could be more precisely appreciated by examining the values listed in Table II.

Effect of the Temperature of Injected Rubber on the State of Cure at the Midplane Sheet. One of the most important applications of predicting temperatures during vulcanization is estimating the state of cure. The variation of the state of cure calculated at the midplane of rubber sheets could be expressed as a function of the time, for different values of the temperature of rubber at the beginning of the operation, T_{ir} . This variation is shown for a thickness of 1 cm in Figure 4 and 2 cm in Figure 5. The effect of the value given for T_{ir} on the state of cure-time curves was not very important for the thinner sheet. But the use of higher temperatures for rubber at the injection point was proved to be of great importance for the thicker sheet. On the whole, these curves were similar but displaced from each other by a translation along the time axis. The constance of this translation could be appreciated in Table III.

The decrease in the cure time with the temperature of the rubber at the in-

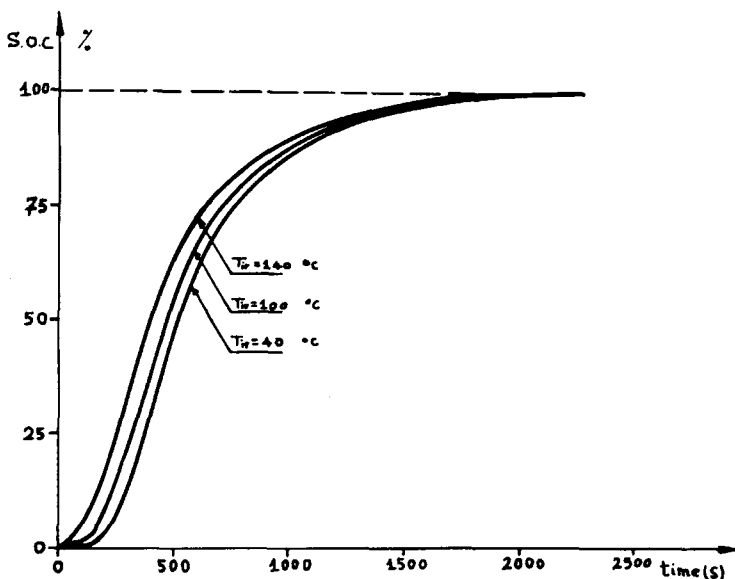


Fig. 4. State of cure at the midplane as a function of time, for different rubber temperatures at the injection: $T_{ir} = 40^{\circ}\text{C}$, 100°C , 140°C ; $T_m = 180^{\circ}\text{C}$; 1 cm thick.

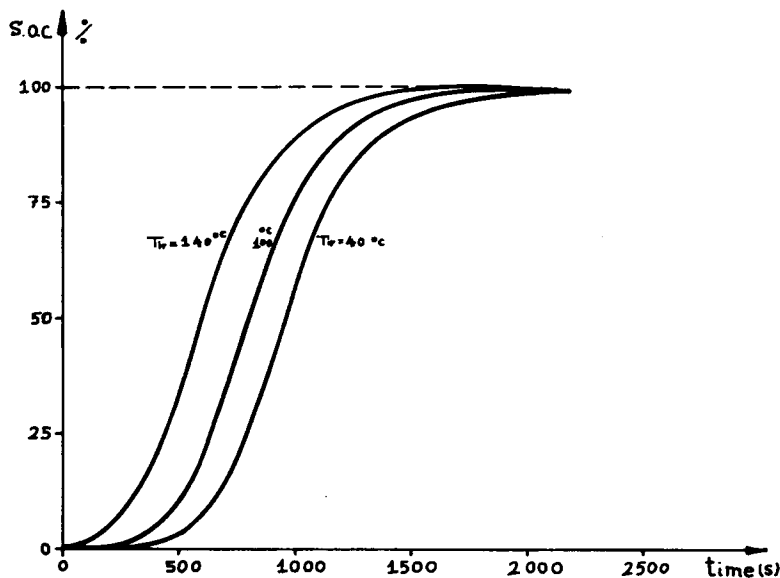


Fig. 5. State of cure at the midplane as a function of time, for different rubber temperatures at the injection: $T_{ir} = 40^\circ\text{C}$, 100°C , 140°C ; $T_m = 180^\circ\text{C}$; 2 cm thick.

jection point is shown in Figure 6, for a 2 cm thick rubber sheet. The importance of the use of a higher temperature for the storage bulb is clearly shown by examining the shape of the curve in Figure 6.

Effect of the Temperature of Injected Rubber on the Profiles of Temperature and State of Cure. The output from the simulation gave the temperature and extent of reaction at 20 locations in the curing mass, at different times. The predicted temperature rise in the curing mass is shown in Figure 7, for different values of the initial temperature of rubber.

The variation in the profiles of the extent of reaction through the rubber thickness is shown in Figure 8 at different times during the reaction. It can be seen that the reaction is faster near the walls of the mold and slower at the center at the beginning of the cure cycle. But, because of the internal production of heat due to the cure reaction, the extent of cure became faster at the center and slower near the rubber surfaces at the end of the operation. At a particular time, the value of which depends on the initial temperature of rubber ($T_{ir} = 40^\circ\text{C}$, 20

TABLE III
Decrease in Cure Time as a Function of T_{ir}

State of cure	25	50	70	80	90	95
From $T_{ir} = 70$ to $T_{ir} = 40$	60	61	60	60	60	60
From $T_{ir} = 100$ to $T_{ir} = 40$	155	150	150	150	151	160
From $T_{ir} = 120$ to $T_{ir} = 40$	233	233	238	238	233	244
From $T_{ir} = 140$ to $T_{ir} = 40$	360	360	360	355	361	360

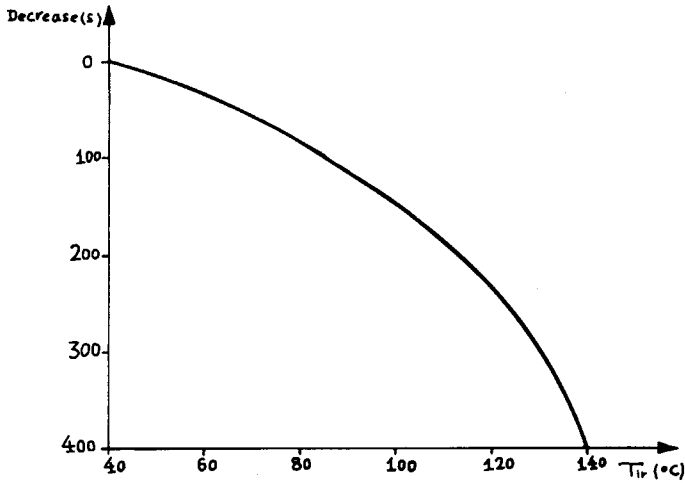


Fig. 6. Decrease in cure time as a function of rubber temperatures at the injection: $T_m = 180^\circ\text{C}$; 2 cm thick.

min; $T_{ir} = 100^\circ\text{C}$, 16 min; $T_{ir} = 140^\circ\text{C}$, 13.5 min), the extent of cure became the same through the rubber thickness.

CONCLUSIONS

Conventionally, rules of thumb have been widely used in the industry for curing rubbers. But in general these rules cannot be applied to all polymeric systems because the phenomena of heat transfer and cure kinetics have been oversimplified.

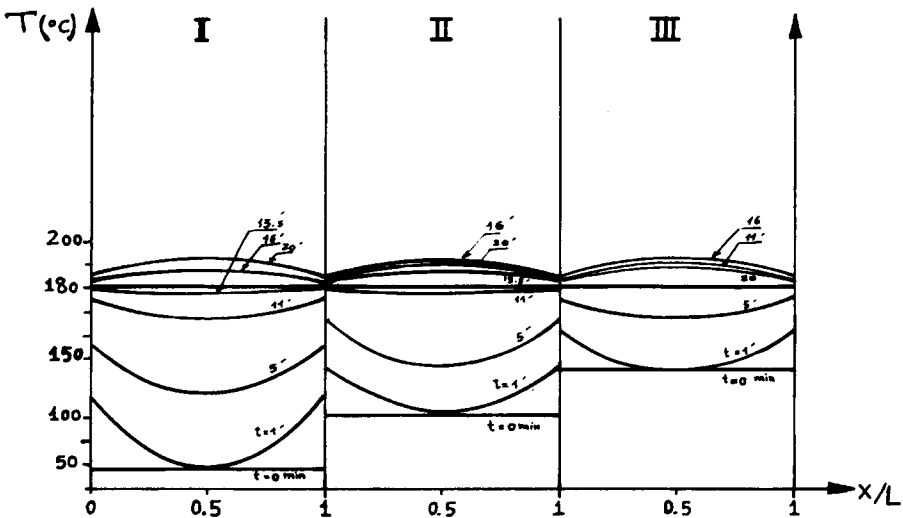


Fig. 7. Profiles of temperatures at different times, for three values of the rubber temperature at the injection: $T_m = 180^\circ\text{C}$; 2 cm thick; (I) $T_{ir} = 40^\circ\text{C}$; (II) $T_{ir} = 100^\circ\text{C}$; (III) $T_{ir} = 140^\circ\text{C}$.

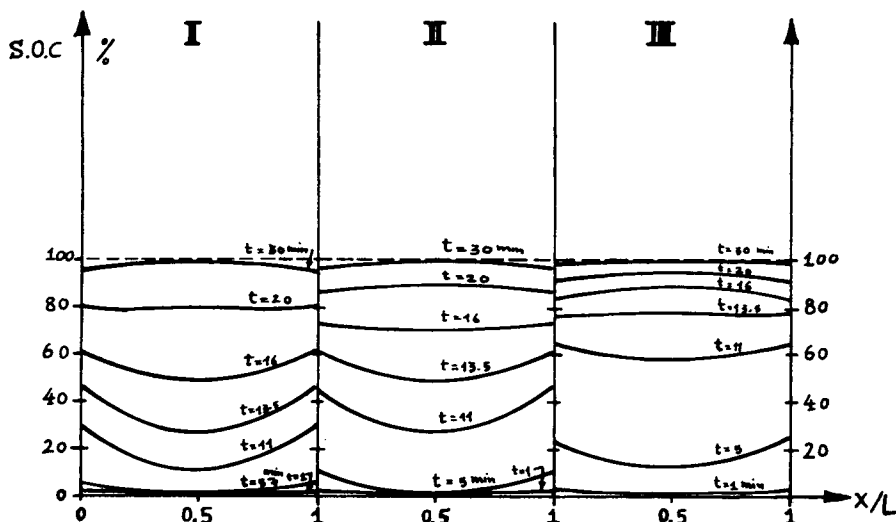


Fig. 8. Profiles of the state of cure at different times, for three values of the rubber temperature at the injection: $T_m = 180^\circ\text{C}$; 2 cm thick; (I) $T_{ir} = 40^\circ\text{C}$; (II) $T_{ir} = 100^\circ\text{C}$; (III) $T_{ir} = 140^\circ\text{C}$.

A model of cure kinetics has been developed in this paper, using calorimetric measurements and taking into account the effect of heat transfer. The model allowed us to predict the profiles of temperature and state of cure through the rubber mass at different times.

The effects of varying a parameter of importance, such as the temperature of the rubber when injected into the mold, was examined by considering (a) the profiles of temperature and state of cure and (b) the variation of the temperature and state of cure at the midplane of rubber sheets. Two different thicknesses were chosen for these sheets, and the effect of the temperature T_{ir} was found to be decisive for a rubber having a thickness greater than 1 cm. The shortening of the cure time was correlated with the initial temperature of the rubber.

References

1. A. Accetta, P. Le Parlouer and J. M. Vergnaud, *Thermochim. Acta*, **59**, 149 (1982).
2. A. Accetta, G. Gangnet, L. Vincent, and J. M. Vergnaud, Third International Conference on Computers and Chemical Engineering, Paris, April 20, 1983.
3. A. Y. Coran, in *Science and Technology of Rubber*, Eirich, Ed. Academic, New York, 1978, p. 7.
4. S. D. Gehman, *Rubber Chem. Technol.*, **40**, 36 (1967).
5. A. Accetta, J. C. David, P. Le Parlouer, and J. M. Vergnaud, Second International Rubber Conference, Paris, June 3, 1982.
6. A. Accetta and J. M. Vergnaud, Second International Rubber Conference, Paris, June 3, 1982.
7. A. Accetta and J. M. Vergnaud, *Rubber Chem. Technol.*, **54**, 302 (1981).

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