Effect of Temperature of Motionless Air on the Cure of Vulcanizates after Removal from the Mold

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Synopsis

This paper determines the increase in the state of cure through the rubber mass during the cooling period after the vulcanizate is removed from the mold. The problem is complicated because of the great number of parameters. Some of them, such as the dimension of sample, the state of cure through the rubber at the time of its removal from the mold, the nature of the fluid, its agitation and temperature, are of interest. This work is concerned with the study of the effect of the temperature of motionless air in which the vulcanizate is cooled. This parameter is important in increasing the state of cure. Although the problem is complicated, it has been resolved by using a model based on a numerical method of calculation with finite differences. This model takes into account not only heat transfer by conduction through the rubber and by convection through rubber-air interface, but also the kinetics for heat evolved in the cure reaction.

INTRODUCTION

The rubber industry has been seeking rapid processes for the manufacture of vulcanizates as finished products. Higher and higher temperature have been used for the mold to reduce the cure time,[1] higher temperature being a common method of achieving faster vulcanization. Higher curing temperatures have also been used in molding processes such as injection molding[2-4] and microwave curing. The discovery and evaluation of new faster accelerators is also of continuous interest to the rubber industry.[5]

But it is our opinion that a sufficient knowledge of the time–temperature history of the rubber may lead to another way to shorten the vulcanization cycle without detriment to quality. After this history has been determined at any point in rubber, it is possible to find the extent of the cure by integrating the kinetic equation with respect to time. The temperature gradients developed in the polymer mass can be predicted if the kinetics of the cure reaction and the thermal properties of the polymer are known. By this approach, it has been possible to determine the profiles of temperature and state of cure developed through the rubber mass after the rubber has been removed from the mold and left in motionless air at room temperature.[6] It has been shown that vulcanization progress in rubber sheets could be followed during this cooling period in motionless air at room temperature.[6]

This paper reports an increase in state of cure during the cooling period by calculation and experiment, and determines especially the effect of the tem-

perature of motionless air. Among all the various parameters, such as the cure enthalpy,[7] thickness of sample, state of cure at the time of extraction of vulcanizate from the mold, and velocity of air, the temperature of motionless air is certainly one of the most important. A model previously described[8,9] has been applied to the problem at hand following a two-step process: cure in the mold and progress in cure during the cooling period. This model takes into account not only heat transfer through the rubber mass by conduction during the heating period in the mold, but also heat transferred through the rubber–air interface by free convection and the rubber mass by conduction during the cooling period. The model takes also into account heat evolved from the cure reaction which kinetics has been determined by calorimetry.[9,10] The calculation of the profiles of temperature and state of cure is generally complicated by two facts: the internal generation of heat due to vulcanization is a function of position and temperature, and the thermal properties of rubber such as heat capacity, thermal conductivity, and diffusivity vary usually with the temperature. These problems have been solved by applying a numerical method with finite differences, and using various temperatures for motionless air ranging from 25 to 100°C and two different thicknesses for the rubber.

THEORETICAL

This paper is concerned with a two-step process: first, when the rubber is vulcanized within the slabs of the mold; second, when the sample is extracted from the mold and cooled in motionless air at constant temperature. Since the progress in cure during the cooling period follows vulcanization in the mold, we must have well-defined information on the state of cure in vulcanizates at the time of removal from the mold.

Although this problem is complicated, our model can be used for studying the two steps of the process.

MATHEMATICAL TREATMENT

Several assumptions are made:

i. Plane sheets of rubber are used, and the heat flow is unidirectional through the thickness.

ii. The rubber is in good contact with the slabs of the mold.

iii. Heat is transferred through the rubber only by conduction.

iv. During the cooling period, air is motionless and heat is transferred through the rubber–air interface by free convection. The temperature of air is not modified by the presence of the sample.

v. The kinetics of heat evolved from the cure reaction follows a first-order reaction.

We may point out that some of these assumptions are not imposed by the use of the model, our model being able to work with different other assumptions.

The heat flow through the thickness of rubber sheet is expressed by the differential equation of transient heat conduction:

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

We can see the contribution of heat conduction and heat evolved from cure reaction, to the rate of the temperature.

Although rubber vulcanization is made up of a complex series of reactions,[11,12] the rate of the heat evolved from the overall reaction of cure can be expressed by a single reaction with a single activation energy.[13-16] The order or the reaction and the other parameters of kinetics of reaction depend largely on the composition of rubber compounds. In the case at hand, the kinetics follow a first-order reaction:

$$\frac{dQ}{dt} = k_0(Q_\infty - Q_t) \cdot \exp\left(-\frac{E}{RT}\right) \tag{2}$$

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

As the problem cannot be solved with mathematical methods, we have used an explicit numerical method with finite differences. The rubber sheet is divided into N equal slices of thickness Δx, by temperature-reference planes.

VULCANIZATION OF RUBBER SHEETS IN THE MOLD

Initial and boundary conditions are as follows:

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

$$t > 0: \quad 0 < x < L, \quad T = T_{x,i} \quad \text{rubber space}$$
$$\quad\quad\quad 0 > x > L, \quad T = T_m \quad \text{mold space} \tag{4}$$

By taking into account the heat balance on the plane n within the rubber sheet, we find

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

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

The dimensionless number M is a function of the increments of time Δt and space Δx

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

For the mold–rubber interface, the temperature $T_{t+1,0}$ is given as a function of the temperature of mold T_m and of the adjacent slice $T_{i,1}$ by the following equation[17]:

$$T_{i+1,0} = \frac{H}{1+H}T_{i,m} + \frac{1}{1+H}T_{i,1} \tag{7}$$

where H is defined by

$$H = \left(\frac{\alpha_m}{\alpha_r}\right)^{0.5} \cdot \frac{\lambda_r}{\lambda_m} \tag{8}$$

The heat generated by the cure reaction up to the time $i\Delta t$ is calculated by the following equations:

$$Q_i = Q_\infty \big[1 - \exp(-S_i) \big] \quad \text{with } S_i = \int_0^{i\Delta t} k \cdot dt \qquad (9)$$

and the extent of heat evolved during the increment of time at the time $i \cdot \Delta t$ may be obtained from

$$\frac{dQ}{dt} \Delta t = Q_\infty \big[\exp(-S_i) - \exp(-S_{i+1}) \big] \qquad (10)$$

and the recursive relation

$$S_{i+1} = S_i + k_i \cdot \Delta t \qquad (11)$$

VULCANIZATION DURING THE COOLING PERIOD

Heat is transferred by natural convection at the rubber–air interface, air being motionless.

The free convection is conducted in laminar range, because of the low value of the Grashof number:

$$\text{Gr} \cdot \text{Pr} < 10^9 \qquad (12)$$

and the Nusselt number is given as follows:

$$\text{Nu} = a(\text{Gr} \cdot \text{Pr})^{0.25} = \frac{h \cdot L}{\lambda_r} \qquad (13)$$

The value of coefficient a depends on the shape of the material, and for a sheet it depends on the position of the sample: For a vertical plane, $a = 0.56$; for an horizontal plane, for the face over the sheet, $a = 0.54$ and, for the face under the sheet, $a = 0.25$.

For the rubber–air interface, the following equation is used:

$$T_{i+1,0} = \frac{1}{M} \big[T_{i,1} + (M - 1 - N)T_{i,0} + N \cdot T_a \big] \qquad (14)$$

where $T_{i,0}$ is the temperature on the rubber face at time $i \cdot \Delta t$ and T_a is the temperature of air.

The modulus N is a function of the coefficient of heat transfer at the interface obtained from eq. (13), and the thermal conductivity of the rubber:

$$N = \frac{h \cdot \Delta x}{\lambda_r} \qquad (15)$$

During the cooling period, the temperature within the rubber sheet is calculated with eq. (7), and the extent of heat of cure with the help of eqs. (9) and (11).

TABLE I
Kinetic Parameters and Thermal Properties

Q_∞ = 5 cal/g of total rubber mixture
E = 25.4 kcal/mol; k_0 = 3 × 10⁹/s
α = 3.1 × 10⁻³(1–10⁻³ × T)   (cm²/s)
ρC = 0.41 × [1 + 2.5 × 10⁻³(T – 293)]   cal/cm³K

EXPERIMENTAL

Kinetic Treatment

Kinetic parameters of the cure reaction, as well as the enthalpy of reaction, were determined by differential microcalorimetry (SETARAM-DSC 111) working either under isothermal conditions[6] or in scanning mode.[14-17] For the rubber compound considered in this paper, the increase in heat of cure was found to follow a first-order law with respect to time, and the activation energy was constant within the range of temperature studied. Thermal conductivity of rubber and vulcanizates were measured under steady state conditions. The kinetic parameters and thermal properties are given in Table I.

EXPERIMENTS ON RUBBER SHEETS

Rubber compounds were pressed into sheets with the help of a heated mold (SCAMIA 10 t) at the cure temperature of 180°C for various times. The value of these curing times are of importance for the determination of the profiles of temperature and state of cure developed through the rubber sheet. The dimensions of rubber sheets were 10 × 10 cm with a thickness of 1 and 2 cm.

The temperature was continuously measured and recorded at the midplane of the rubber sheets. As shown in previous papers,[8-10] these measurements are considered as the most sensible and accurate for this problem.

After removal from the mold, the rubber sheets were cooled in motionless air kept at various temperatures, with the help of a large hot-air oven.

RESULTS

The process of vulcanization of rubber is very complicated, because several phenomena as heat transfer and cure reaction take place simultaneously, and also because of the large number of parameters characterizing the heat transfer by conduction[18] and the kinetic of cure reaction.[13-16] But the problem of the cooling of vulcanizates after removal from the mold is still more complex, because there is a two-step process. The first is concerned with the vulcanization in the mold and the second with the cooling period of vulcanizates and the increase in state of cure through the rubber mass. So studies on the cooling period of vulcanizates must take into account the preceeding step of the vulcanization in the mold. The increase in state of cure depends largely on operational conditions chosen for molding, especially the dimensions of the sample, the temperature of the mold, and the state of cure through the rubber mass resulting from the temperature–time history of the rubber in the mold.

Some of the parameters intervening in the process, such as the enthalpy of cure,[18] the kinetic of cure reaction, and thermal properties, have been previously studied. So in order to simplify the problem at hand, we have not considered them in this paper. We have described the effect of the following parameters: (i) the temperature of motionless air; (ii) the thickness of the sample; (iii) the value of the state of cure (SOC) in the rubber at the time of removal from the mold, on the progress in cure during the cooling period. We have estimated the effect of the temperature of motionless air on this cure progress, by coupling this important parameter with each of the other, in turn.

PREPARATION OF VULCANIZATE SAMPLES IN THE MOLD

Various rubber sheets of 1 and 2 cm thickness have been vulcanized in the mold at 180°C and removed at a definite time, in order to obtain vulcanizates having the following values for the state of cure at the midplane: 60 and 80%. The rubber at the initial temperature of 30°C was placed into the slabs of the mold kept at 180°C, and the time necessary for the state of cure to reach the right value has been calculated by using the above described model [eqs. (5)–(11)].

As shown in Table III, the values of the state of cure are quite different through the thickness of rubber sheets, especially for the thickness of 2 cm and the lower value of the state of cure (60%). The profiles of the state of cure through the thickness of rubber sheets are steep with a higher value of the state of cure near the rubber faces.

PROFILES OF TEMPERATURE DEVELOPED DURING THE COOLING PERIOD

When the rubber sheet is removed from the mold, the temperature on the faces is equal to the temperature of the mold (180°C).

TABLE II
Operational Conditions for Vulcanization[a]

Thicknesss (cm)	1		2	
Time (s)	645	990	1140	1470
SOC (%)	60	80	60	80

[a] T_{mold} = 180°C; $T_{i, rubber}$ = 30°C.

TABLE III
Profiles of State of Cure of Vulcanizates

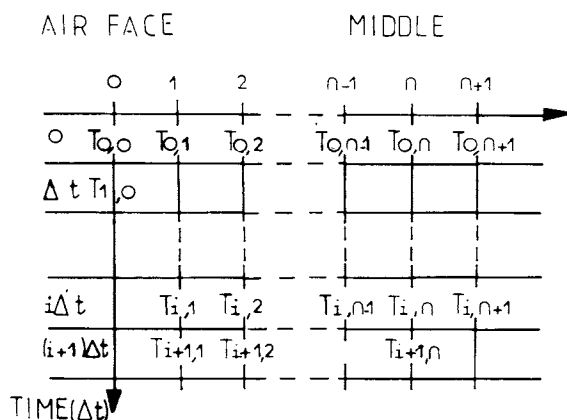| Thickness (cm)	Face	1st	2nd	Midplane
1	65.1	61.4	59.9	59.5
2	78.5	66.7	61.2	59.4
2	89	83.4	80.9	80.1

Fig. 1.   Diagram space–time.

The decrease in temperature at the midplane during the cooling period has been obtained from experiments and by calculation. As shown in Figure 2, for a rubber sheet 2 cm thick and the value of 60% for the state of cure at the time of removal from the mold, as good agreement has been found between experimental and calculated values. These curves have been obtained for the same temperature of the mold, and various temperatures of motionless air ranging from 25 to 125°C.
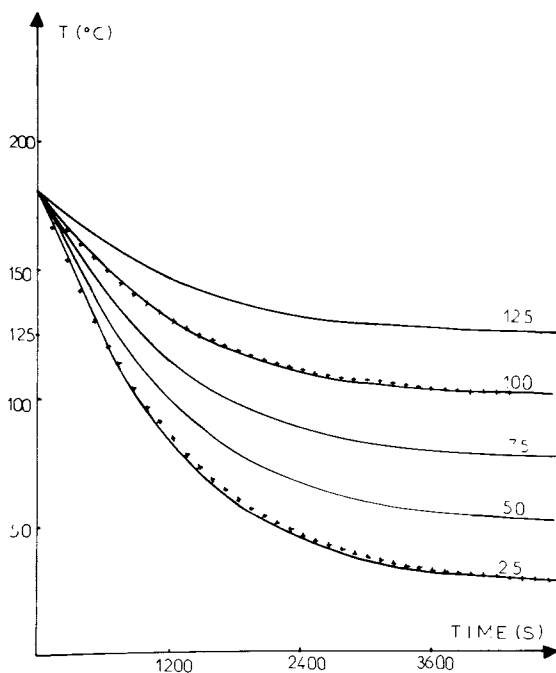

Fig. 2.   Decrease in temperature at the midplane of a 2 cm thick rubber sheet, for various values of the temperature of motionless air: Initial SOC = 60%; T_{mold} = 180°C; (+) experimental; (———) calculated.

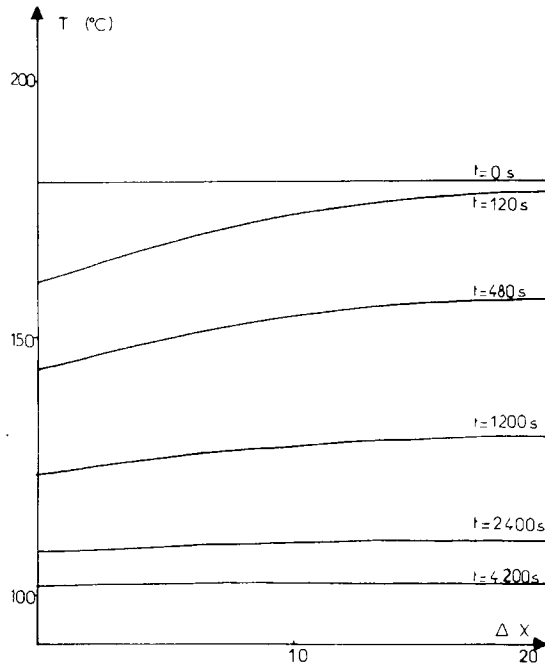Fig. 3. Profiles of temperature through a 2 cm thick rubber sheet: Initial SOC = 60%; T_{mold} = 180°C; T_{air} = 100°C; (0) face; (20) midplane.

The profiles of temperature developed through the rubber mass have been calculated during the cooling period. Of course, the initial time of this cooling period corresponds with the time the rubber was removed from the mold. The profiles of temperature (Fig. 3) have been obtained with a rubber sheet of 2 cm thickness having an initial state of cure of 60%, and cooled in motionless air kept at 100°C.

Three facts of interest are worth noticing:

i. The profiles of temperature are about the same for various values of the state of cure at the time of removal, as shown previously.[6]

ii. At the beginning of the cooling period, the temperature decreases more quickly on rubber faces than inside the rubber, and especially at the midplane. Of course, this fact is due to the low thermal conductivity of the rubber.

iii. The temperature on rubber faces decreases rather slowly, because of the low value of heat transfer by free convection through the rubber–air interface.

INCREASE IN STATE OF CURE DURING THE COOLING PERIOD

Following the low rate of decreasing temperature in the rubber mass during the cooling period, an increase in the state of cure can be expected.

The increase in the state of cure as a function of time is illustrated in Figures 4–6 as obtained by calculation for various temperatures of motionless air and different thicknesses of rubber sheets and the state of cure at the time of removal from the mold (initial state of cure).
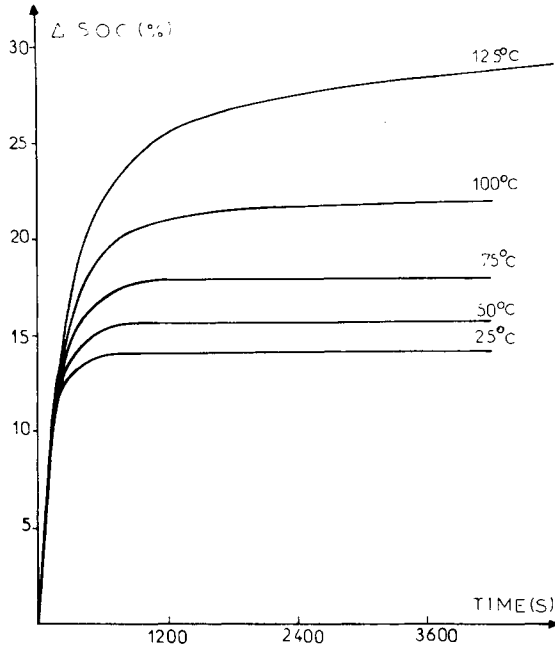
Fig. 4. Increase in the state of cure at the midplane of rubber sheet as a function of time, for various air temperatures: 2 cm thick; T_{mold} = 180°C; initial SOC = 60%.

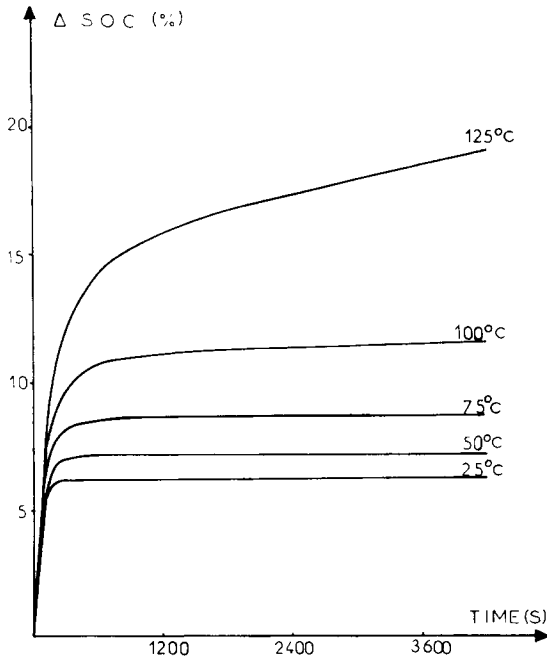Fig. 5. Increase in the state of cure at the midplane of rubber sheet as a function of time, for various air temperatures: 1 cm thick; T_m = 180°C; initial SOC = 60%.
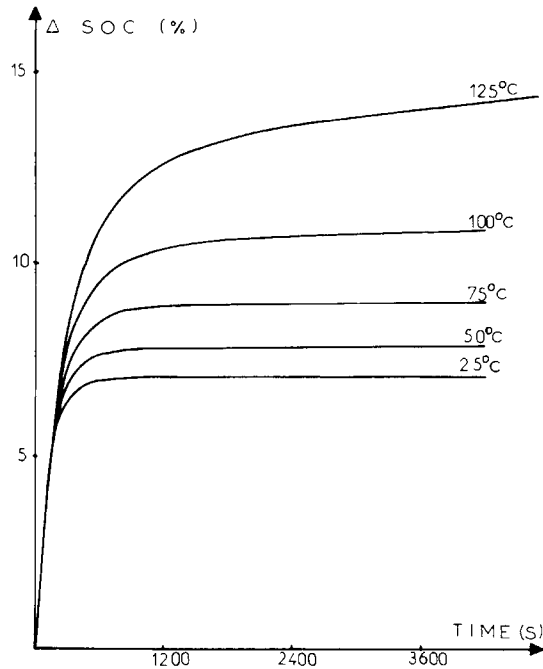
Fig. 6.   Increase in the state of curve at the midplane of rubber sheet as a function of time, for various air temperatures: 2 cm thick; $T_m = 180°C$; initial SOC = 80%.

In Figure 4 with a sample thickness of 2 cm and an initial state of cure of 60%, we observe an increase in the state of cure of about 30% when the air temperature is 125°C and of more than 21% when the temperature is 100°C.

In Figure 5 with a sample thickness of 1 cm and initial state of cure of 60%, the increase in the state of cure is not so large as in the preceeding case, about 20 and 12% when the air temperature is 125 and 100°C, respectively.

The additional effect of the initial value of the state of cure on the increase in the state of cure during the cooling period can also be noted by comparing the corresponding curves drawn in Figures 3 and 6. The curves in Figure 6 have been determined with a 2 cm thick rubber sheet having an initial state of cure of 80%. For instance, with a temperature of 125°C for motionless air, the increase in the state of cure is about 30 and 15% when the initial state of cure is 60 and 80%.

In Figure 7, profiles of the state of cure are drawn when the air temperature is 100°C and the 2 cm thick rubber sheet has an initial state of cure of 60%. A fact of interest, characterizing the heterogeneity of the rubber as far as the state of cure is concerned, must be shown: As the increase in the state of cure is higher at middle of the rubber than on its faces, improved homogeneity of the sample is obtained at the end of the cooling period.

The effect of the air temperature on the increase in the state of cure has been especially pointed out, by plotting this increase in state of cure against the values of air temperature in Figure 8 for various thicknesses and initial values of the state of cure, not only in the middle of the sheet but also on the faces.
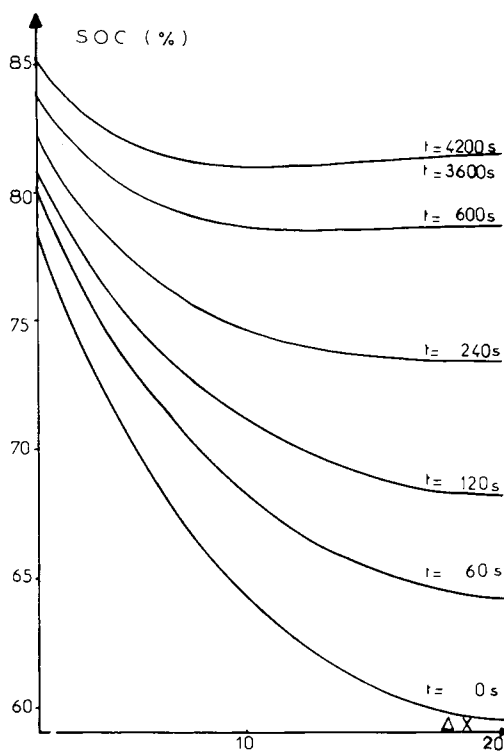
Fig. 7. Profiles of state of cure developed at various times: 2 cm thick; $T_{mold} = 180°C$; $T_{air} = 100°C$; initial SOC = 60%; (0) face; (20) midplane.
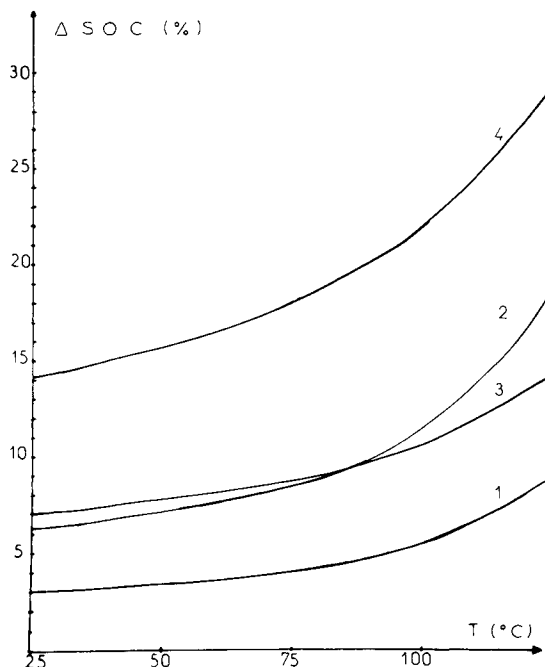

Fig. 8. Increase in the state of cure as a function of the temperature of motionless air, for various cases: (1) 1 cm, 80%; (2) 1 cm, 60%; (3) 2 cm, 80%; (4) 2 cm, $SOC_i = 60\%$.

CONCLUSIONS

Some emphasis has been laid on the vulcanization process of rubber and especially during the cooling period of rubber sheets taking place after removal from the mold. This work has been achieved within the framework of a study on vulcanization based on the use of heat transfer through the rubber and the kinetics of heat evolved from the cure reaction.

A significant increase in the state of cure during the cooling period has been calculated within the rubber, by considering temperature measurements and computerization for determining the value of the state of cure. The rate of the cure reaction is high, especially at the begining of the cooling period when the temperature in the rubber is high. As the temperature decreases more quickly on rubber faces than within the mass, the increase in the state of cure is more important in the mass than on the faces of the rubber. This is responsible for producing better homogeneity of the cure through the rubber mass.

Although various parameters are concerned with this problem, the temperature of motionless air plays a very important role. While the rubber industry could be tempted to use higher and higher temperatures for motionless air, a limitation for this temperature exists, due to the variation in properties of rubber samples with the temperature, for instance, the stickiness and stiffness.

APPENDIX: NOMENCLATURE

C	heat capacity of rubber
E	activation energy
Gr	Grashof number
h	coefficient of heat transfer through rubber–air interface
H	coefficient characterizing the quality of contact between the mold and rubber
k_0	frequency factor
M, N	dimensionless numbers
Nu	Nusselt number
Pr	Prandtl number
Q_t	extent of heat evolved up to time t
Q_∞	enthalphy of cure
t	time
$T_{i,n}$	temperature at time $i\Delta t$ and position r
α_m, α_r	thermal diffusivity of the mold and rubber, respectively
ΔX	increment of space X
Δt	increment of time t
λ_m, λ_r	thermal conductivity of the mold and rubber, respectively
ρ	density of rubber

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