

VULCANIZATION PROGRESS IN RUBBER SHEETS DURING COOLING IN MOTIONLESS AIR AFTER EXTRACTION FROM THE MOLD

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ABSTRACT

In order to reduce the time of cure cycles in the vulcanization of rubber, several complementary attempts are useful. This work is devoted to the study of the profiles of temperatures developed through 1.2-cm thick rubber sheets after extraction from the mold and cooling in motionless air at room temperature. As the heat transfer obtained by free convection in laminar range is very low, the high temperature inside the rubber mass was found to be responsible for another increase in the value of the state of cure, notably at the midplane. Calculations were achieved by using an explicit method with finite differences, heat transfer data on conduction and convection and kinetics results on the overall cure reaction being obtained by microcalorimetry. This reaction, appearing as a complementary step of the vulcanization, was of interest, especially at the midplane of sheets when the state of cure is lower than on the surface. Thus, it allows the rubber to have a more constant value for the state of cure throughout the mass.

INTRODUCTION

Understanding and predicting cure kinetics of elastomeric materials is of practical interest in the material manufacturing process. Conventionally, rules of thumb have been widely used in the industry for curing rubbers. In general, these rules do not apply to polymeric systems because the phenomena of heat transfer and cure kinetics have been oversimplified. Sulfur vulcanization of unsaturated elastomers is a very complex chemical process involving numerous consecutive and simultaneous reactions [1,2]. However, heat is the most important processing agent [3]. The curing reaction of rubber is not very exothermic, but since vulcanizates exhibit low thermal conductivity, the temperature and rate of reaction can vary considerably within the curing mass, particularly for thick castings [4]. Therefore, the extent of reaction (another expression for the state of cure) is a function of time and position.

An effective method of calculating the time-dependent temperature distribution in a vulcanizing article is actively being sought in the rubber industry [5–7]. Given the temperature history, one can readily optimize the cure cycle and thus reduce energy requirements. The purpose of some previous papers was to show that the temperature gradients developed in the polymer mass could be predicted if the kinetics of reaction and the physical properties of the polymer were known. Also, it was intended to show the effects of these temperature gradients on the gradients of cure for thin [8] and thick castings [9,10]. The temperature and state of cure were determined by the balance of internal heat generation from the cure reaction, conduction through the mold–rubber interface and the rubber mass, and heat exchange with the surroundings. A method of computation of the temperature and state of cure was given as a function of several parameters with time and position. The problem was solved using a method with finite differences based on the Dusiberre generalization of an incremental explicit method. Our model of vulcanization of rubber was used with success for sheets pressed into the slabs of heated molds [8–10] and for the injection molding process [11,12].

The present communication is concerned with the study of the profiles of temperature and state of cure developed through the rubber mass after it has been extracted from the mold and left in motionless air at room temperature. Some questions are of interest for this particular case, the problem being quite new for the rubber industry:

- (1) the rate at which heat can get out of rubber, being responsible for a new development of the profile of temperature throughout the mass;
- (2) the preceding profiles of temperature would be expected to lead to another development of the profiles of the state of cure, because of the high temperature inside the rubber and the cure reaction.

In this case, heat transfer is obtained by convection through the rubber–air interface, and it is described by dimensionless number as Grashof and Nusselt's numbers [13]. Therefore, present problem is more complicated than classical vulcanization because there is a two-step vulcanization process, the first step naturally being a classical vulcanization and the second step taking place at the moment at which the rubber is extracted from the mold and comes into contact with the air. This second step of the vulcanization is due to the low heat transfer from rubber to air, therefore, the following parameters could be of importance: the air temperature, and the overall air velocity. These parameters must be added to the parameters known to have an influence on this first step: the first three are concerned with the rubber, sheet thickness; cure enthalpy; and kinetics of vulcanization; and the two final characterizing operational conditions, the temperature of the mold and initial rubber; and the time of the cure cycle.

The decrease in the temperature at the midplane of 1.2-cm thick rubber sheets is particularly described, and a large part of this work focuses on the increase in the state of cure taking place after extraction of the rubber from

the mold. It is carried out for different values of the state of cure obtained at the moment at which the rubber sheet is extracted from the mold. As the air is kept motionless, heat transfer at the air–rubber interface is obtained by free convection in laminar range.

THEORETICAL

Vulcanization of rubber sheets is obtained by a two-step process: first, the classical vulcanization of rubber within the slabs of the heated mold; and second, starting from the moment at which the rubber is extracted from the mold and cooled in motionless air at room temperature.

Vulcanization of rubber sheets in the mold

Mathematical treatment

This classical problem has been studied in several different ways previously [6–12].

The heat flow is unidirectional through the plane sheet of rubber of thickness L , and is expressed by the differential equation of transient heat conduction

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

(conduction heat) (reaction heat)

It may be seen that the sum of conduction heat and reaction heat in the right-hand side of eqn. (1) makes a contribution to the rate of the temperature.

Initial and boundary conditions are as follows:

$$t = 0 \quad 0 < x < L \quad T = T_0 \quad (\text{rubber space}) \quad (2)$$

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

$$0 < x < L \quad T = T_{xt} \quad (\text{rubber space})$$

Because of the presence of the internal reaction heat, eqn. (1) cannot be solved in the mathematical way.

Although vulcanization is made up of complex series of reactions, the rate of the overall reaction can be expressed by a single first-order reaction with a single activation energy [8]

$$\frac{dQ_t}{dt} = k_0 (Q_\infty - Q_t) \exp - \frac{E}{RT} \quad (4)$$

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

This problem was solved by using a numerical method [8–12] based mainly on the Dunsiberre method [13].

The rubber sheet is divided into n equal finite slices of thickness Δx . By taking into account the heat balance on the plane n within the rubber sheet, we find that

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

where $T_{i,n}$ is the temperature at the plane n and the time $i\Delta t$, and the dimensionless number M is a function of the increments of time Δt and space Δx .

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

The internal heat generated by the cure reaction during the time Δt is calculated at the time $i\Delta t$ using the following three equations

$$Q_i = Q_\infty [1 - \exp(-S_i)] \quad \text{where } S_i = \int_0^{i\Delta t} k dt \quad (7)$$

$$\frac{dQ}{dt} \Delta t = Q_\infty [\exp(-S_i) - \exp(-S_{i+1})] \quad (8)$$

where S_i is obtained by the recursive relation

$$S_{i+1} = S_i + k_{T_{i\Delta t}} \Delta t \quad (9)$$

Heat transfer by free convection in motionless air

Mathematical treatment

As the air is kept motionless, heat transfer is obtained by natural convection, and calculated using dimensionless numbers as Prandtl–Grashof–Nusselt moduli.

Because of the low value of the Grashof's number, the free convection is conducted in laminar range

$$GrPr = 1.3 \times 10^7 \quad (10)$$

and the Nusselt's number is given as follows

$$Nu = a(GrPr)^{0.25} \quad (11)$$

The value of the coefficient a depends largely on the position of the rubber sheet.

For a vertical plane	$a = 0.56$
For an horizontal plane, for the face over the sheet	$a = 0.54$
for the face under the sheet	$a = 0.25$

Numerical calculation

For the air-rubber interface, the following equation is used

$$T_{i+1,0} = \frac{1}{M} [2T_{i,1} + (M - 2 - 2N)T_{i,0} + 2NT_a] \quad (12)$$

where $T_{i,0}$ is the temperature at the rubber face at time $i\Delta t$; T_a is the temperature of air; $T_{i,1}$ is the temperature at the first slice of the rubber.

The modulus N is as follows

$$N = \frac{h\Delta x}{\lambda} \quad (13)$$

where λ is the thermal conductivity of the rubber, and h is the coefficient of heat transfer at the interface.

EXPERIMENTAL

In our experiments, rubber powder and sulfur as vulcanizing agent were mixed and pressed into the mold slabs (SCAMIA 10t), at the cure temperature of 170°C. The dimensions of rubber sheets were 10 × 10 cm, with a thickness of 1.2 cm. The temperature was continuously measured and recorded at the rubber midplane as previously described [8,11]. A 150–250- μm grain size rubber powder containing about 55% rubber hydrocarbon, 14% acetone extractable, 25% carbon black, and 6% ash, was used; it was a mixture of NR and SBR at a ratio of about 2/3 [14].

The kinetic parameters of the cure reaction, as well as the enthalpy of reaction, were determined under isothermal conditions by differential microcalorimetry (SETARAM-DSC 111). The increase in heat was found to follow a first-order law with respect to time, and the activation energy was found to be constant [6, 8, 15] within the range of temperature studied. The thermal conductivity of rubber and vulcanizates were measured under steady state conditions and calculated by using previous data [16]. The thermal properties of the rubber are given in Table 1.

TABLE 1

Thermal properties of rubber

$Q = 18.1 \text{ cal g}^{-1}$ of total rubber mixture		
$\alpha = \lambda / \rho C = 3.1 \times 10^{-3} (1 - 10^{-3} T) \text{ (cm}^2 \text{ s}^{-1}\text{)}$		
$\rho C = 0.41 [1 + 2.5 \times 10^{-3} (T - 293)] \text{ (cal cm}^{-3} \text{ K)}$		
$E = 25.4 \text{ kcal mol}^{-1}$	$k_0 = 3 \times 10^9 \text{ (s}^{-1}\text{)}$	(eqn. 5)
λ : thermal conductivity	ρ : density	C : heat capacity
E : energy of activation	T : (K)	k_0 : reaction constant

RESULTS

Preparation of vulcanizates in the mold

Several 1.2-cm thick rubber sheets were vulcanized in the mold at 170°C, and extracted at different times, in order to obtain samples having different values of the state of cure (SOC). The operational conditions are described in Table 2.

For the small thickness chosen for rubber sheets (1.2-cm thick), the evidence available from calculations shown in Table 2 shows that the profiles of the state of cure are quite different according to the SOC value required at the midplane. To a significant extent of cure reaction, these profiles are about flat around the mean value. Slightly after the reaction, the profiles are steep with a higher value near the rubber faces (Table 3).

Study of the vulcanization progress after the extraction of rubber sheets from the mold

At the time necessary for the samples to obtain the value desired for the state of cure, the sheet is extracted from the mold and kept vertical in

TABLE 2

Operational conditions for vulcanization

Time (s)	330	570	875	1340	2360	$T_{\text{mold}} = 170^{\circ}\text{C}$
SOC	10	30	50	70	90	$T_{\text{ir}} = 20^{\circ}\text{C}$

TABLE 3

Profiles of state of cure of vulcanizate samples

SOC (%)	Position			
	Face	1st	2nd	Midplane
10	29.3	14.7	11.2	10.3
30	45.3	33.9	31	30.2
50	60.8	52.5	50.7	50.2
70	75.7	71.3	70.2	70.2
90	91.7	90.6	90.1	90.1

TABLE 4

Values of parameters for the cooling of samples

$a = 0.56$	$Gr = 1.3 \times 10^7$	$Pr = 0.7$	$h = 2 \times 10^{-4} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ K}^{-1}$
$M = 4$	$N = 0.055$	$\Delta x = 0.2 \text{ cm}$	$\Delta t = 5 \text{ s}$

motionless air at room temperature (20°C). In this case, the values of the parameters described above are given in Table 4.

Profiles of temperature

The profiles of temperature developed through the rubber mass were calculated during the cooling period of rubber sheets in motionless air. The temperature of the samples at which they were extracted from the mold, or as we say, the initial temperature of the rubber, was equal to the mold temperature (170°C). These profiles are shown in Fig. 1 for two different values of the state of cure calculated at the initial time: 60 and 90% at the midplane. The curves are similar.

Several facts of interest can be observed:

(1) the temperature decreased very quickly on the rubber faces, while the temperature at the midplane decreased very slowly. So, a time of 12 min is necessary for the midplane temperature to reach only 95°C , while the rubber faces are cooled to 90°C . After 22 min the temperature was already decreased to 67°C on the face while it was 71°C at the midplane;

(2) the profiles of temperature are about the same for the two values of the initial state of cure.

Increase in the state of cure at the midplane during the cooling

The profiles of the state of cure obtained through the rubber sheets at the

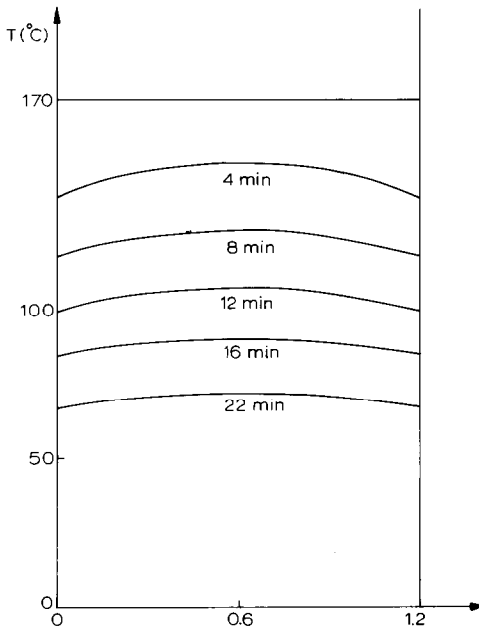


Fig. 1. Profiles of temperature developed through 1.2-cm thick rubber sheets during the cooling period. $T_{\text{mold}} = 170^{\circ}\text{C}$; $T_{\text{air}} = 20^{\circ}\text{C}$. These curves are similar for initial SOC = 60 and 90%.

TABLE 5

Maximum values of the increase in the state of cure obtained during the cooling operation

Initial SOC (%)	10	30	40	60	70	80	90
Increase in SOC (%)	14.3	12.4	10.6	7	5.2	3.4	1.7

time of extraction from the mold are very flat as shown in Table 3 for different times of vulcanization. During the cooling period, a cure reaction took place inside the rubber mass particularly where the temperature is kept to a high value. This fact of interest can be examined in Table 5 where the increase in the state of cure obtained during the cooling operation at the midplane are collated.

The increase in the state of cure at the midplane during the cooling operation is expressed as a function of time in Fig. 2 for the different values of the initial state of cure. Several results are worth noting:

(1) about 4 min is necessary for the state of cure to reach the maximum value because of the high value of the temperature during this time as shown in Fig. 1;

(2) the increase in the state of cure during the cooling operation is higher the lower the value of the initial state of cure. This fact was especially

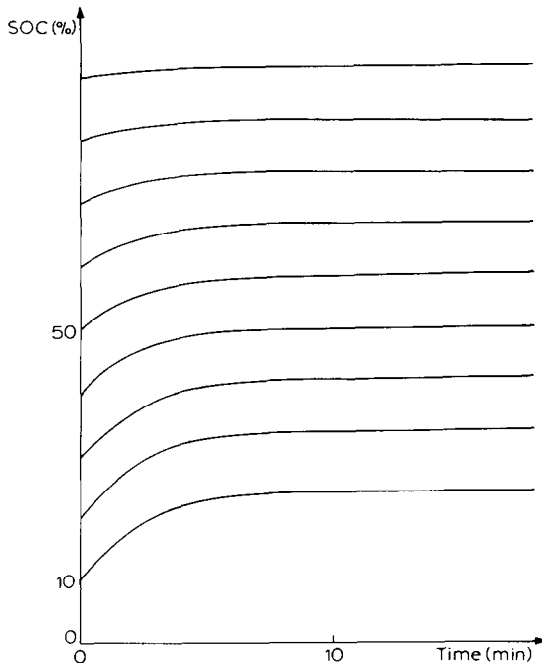


Fig. 2. Increase in the state of cure as a function of time for different values of the SOC obtained at the extraction of rubber from the mold.

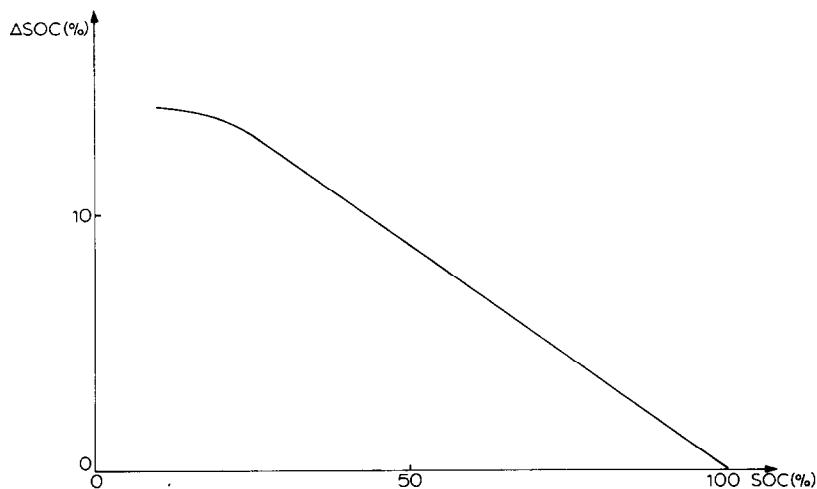


Fig. 3. Increase in the state of cure as a function of the value of SOC at the extraction of rubber from the mold.

pointed out in Fig. 3 where the increase in the state of cure obtained during the cooling is plotted against the value of the initial state of cure.

CONCLUSIONS

Within the framework of the general study of the vulcanization process using microcalorimetry data and computerization, we have laid some emphasis on the cooling period of rubber samples after their extraction from the heated mold. An increase in the state of cure during this cooling period was observed for thin rubber sheets, while the motionless air was kept at room temperature. This progress of the reaction takes place only at the beginning of the cooling period when the temperature is high enough. For the same reason, the progress of the state of cure is more important at the midplane of the rubber sheets. This increase in the state of cure depends largely on the value of the state of cure obtained at the time of the extraction of rubber from the mold. For instance this increase reaches about 140% of its initial value when this initial value is only 10, but it becomes very low (11%) when the initial state of cure was 60. Therefore, the increase in the state of cure is not very high for thin rubber sheets, but it is significant. This technique can be applied to thick rubber sheets with a greater interest and our work is progressing in this case.

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