Finite element analysis of cure in a rubber cylinder

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The variation of temperature inside a rubber cylinder was recorded during vulcanization in a mould. The results were compared with those obtained by solving the transient heat equation by a finite element technique. Heat generation during cure was considered by means of first-order curing kinetics with the introduction of an induction time. The state of cure at any point of the object was obtained by using the equivalent time concept and was represented by a map of isocure curves.

(Keywords: rubber; state of cure; finite element simulation; heat transfer)

INTRODUCTION

The determination of the state of cure reached in a rubber compound for a given thermal history is of basic importance in the rubber industry. In fact, knowledge of the degree of cure of the processed material leads to optimization of the vulcanization cycles with improvement of the mechanical properties of the material and cost reduction.

In recent years, several investigators have studied the problem of simulating the temperature gradients within an elastomeric object subjected to different vulcanization conditions[1-10]. With this information, the vulcanization level can be calculated by using isothermal curves from rheometer tests[11] and the equivalent time law[1,11-13].

The variation of temperature, T, during vulcanization is governed by the general differential equation for transient conduction of heat defined by

$$\rho c \frac{\partial T}{\partial t} = \nabla \cdot (\lambda \nabla T) + \frac{\mathrm{d}Q}{\mathrm{d}t} \tag{1}$$

where c is the specific heat at constant pressure, λ the thermal conductivity, ρ the density of the material and Q the heat of reaction up to time t. The solution of equation (1), in problems related to heat transmission of elastomeric compounds, is generally obtained by means of the finite difference method in one or two dimensions[1-10].

This paper considers experimental results on the vulcanization of a cylinder of natural rubber filled with carbon black. These experimental results are compared with numerical results obtained from equation (1) by using the two-dimensional finite element method (FEM).

To obtain the state of cure at any time, equation (1) must be simultaneously solved with the kinetic equation of the reaction and the expression for heat generation, for given initial and boundary conditions. Kinetic characterization of the material is usually effected by using a differential calorimeter, but in the present investigation it was done, in part, through rheometer data. Finally, the cure level of the material, at every point of the body, is evaluated by means of time–temperature information obtained through the numerical analysis of a fixed cycle.

MODEL DESCRIPTION

The transient heat conduction equation (equation (1)) is solved by the finite element technique studied by Wilson and Nickell[14]. In this work, due to the cylindrical symmetry of the problem, ring elements with quadrilateral cross section were used to represent the symmetry of the solid. The model was modified by introducing thermal conductivity and reaction heat which changed with temperature. The option of treating the problem with an induction time, in which chemical reaction did not take place, was also considered.

The thermal conductivity of natural rubber filled with carbon black changes with temperature[1,15]. Generally, a linear relation such as

$$\lambda = a - b(T - 273.15\ \mathrm{K}) \tag{2}$$

was used, where a and b are experimental parameters depending on compound formulation[1,3-6,8]. In this paper, the temperature variation of ρ and c was not considered.

The kinetics of the vulcanization reaction was taken to be given by

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = k(Q_0 - Q)^n \tag{3}$$

where n is the reaction order, k the reaction rate and Q_0 the overall heat of reaction. The reaction rate is usually assumed to have an Arrhenius expression

$$k = k_0 \exp(-E/RT) \tag{4}$$

with k_0 the pre-exponential parameter, E the activation energy of the process and R the ideal gas constant.

Several investigators have shown that vulcanization is a first-order reaction[3-9,11], but Craig[16] suggests that it

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is second order. In a recent paper, Isayev and Deng[10], based on the work of Kamal and Sourour[17], propose more complicated kinetic models and consider an empirical expression for the kinetics of the vulcanization reaction.[18,19]

A rubber compound is generally vulcanized under non-isothermal conditions, where the material in many processes begins at ambient temperature. In this situation, if we work with a first-order kinetic reaction, equation (3) can be integrated to obtain

$$Q = Q_0\left[1 - \exp\left(-\int k\,\mathrm{d}t\right)\right] \tag{5}$$

Based on the analysis of Ferradou and Vergnaud[6], equation (3) can be expressed as

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{Q_0}{\Delta t}\left[\exp(-S_i) - \exp(-S_{i+1})\right] \tag{6}$$

where Δt is the incremental time and S_i is calculated at time $i\Delta t$ as

$$S_i = \int_0^{i\Delta t} k\,\mathrm{d}t$$

S_{i+1} is given by the approximative recurrent relation

$$S_{i+1} = S_i + k(T_{i\Delta t})\,\Delta t \tag{7}$$

To include an induction time, t_i, in the numerical program, the fact that the vulcanization reaction does not occur at $t = 0$ was considered. This is because elastomeric compounds have in their formulations retardant chemicals which inhibit the initiation of the cure process. Then

$$\mathrm{d}Q/\mathrm{d}t = 0 \qquad t < t_i$$

Isayev and Deng[10] consider, for the isothermal problem, the exponential expression

$$t_i = B\exp(A/T) \tag{8}$$

where A and B are constants depending on the type of material. To consider a non-isothermal process, the equivalent time law[1,13] can be used to calculate the induction time. If we consider that the same degree of incubation can be reached at temperatures T_1 and T_2 during times t_1 and t_2 respectively, we can write

$$B = t_1\exp(-A/T_1) = t_2\exp(-A/T_2)$$

When a non-isothermal case is compared with an isothermal one, we have

$$B = \int_0^{t_f} \exp[-A/T(t)]\,\mathrm{d}t$$

where t_f is the time to reach the same degree of incubation. If t^* is defined as

$$t^* = \int_0^{t} \exp[-A/T(t)]\,\mathrm{d}t/B = \int_0^{t} \mathrm{d}t/t_i(T)$$

the reaction will begin when $t^* > 1$. This condition was verified in the program at each interval Δt.

EXPERIMENTAL

Material characterization

In this work natural rubber filled with carbon black was used. The following composition, in parts per hundred of rubber (pph rubber), was used: natural rubber, 100; carbon black HAF, 63; zinc oxide, 6; sulphur, 5; aromatic oil, 4; antioxidant, 3; stearic acid, 1; accelerator, 1.

Several laboratory tests were performed to obtain the kinetic parameters. The procedures used to obtain these parameters are given below.

Activation energy. The activation energy, E, was estimated from rheometer tests performed in a Monsanto 100 torque rheometer at different temperatures. A characteristic torque curve, on a normalized scale, is shown in *Figure 1*.

Using the rheometer curves at different temperatures, the time required to reach 90% ($t_{90\%}$) of the maximum torque was calculated[11]. Since the cure process is characterized by its activation energy, for each time and temperature we can write

$$C = kt = [k_0\exp(-E/RT)]t \tag{9}$$

where C is a constant corresponding to the cure level attained. From equation (9), E/R can be evaluated from the slope of a ln t *versus* $1/T$ plot for five temperatures (403, 415, 423, 433 and 463 K). Using the least squares method, with a good correlation ($r^2 = 0.997$), a mean value of $E = 95\ \mathrm{kJ\,mol^{-1}}$ was found with a standard deviation of $4\ \mathrm{kJ\,mol^{-1}}$. This value was similar to corresponding values reported for natural rubber[4].

Thermal parameters of compound and kinetic data. The thermal and kinetic parameters of the compound are shown in *Table 1*. The specific heat, at constant pressure, was measured with a differential calorimeter at temperatures between 298 and 423 K. The thermal conductivity was estimated by using the measured thermal diffusivity determined by classical methods[1,20,21].

Q_0 was estimated from the available literature, using the data of Brazier *et al.*[22,23], taking into consideration the sulphur content. The k_0 parameter was evaluated by comparing the experimental data with the data obtained by numerical fitting.

Induction time. The torque rheometer curves at different temperatures (403, 415, 423, 433 and 463 K) were used to evaluate the induction time of the com-

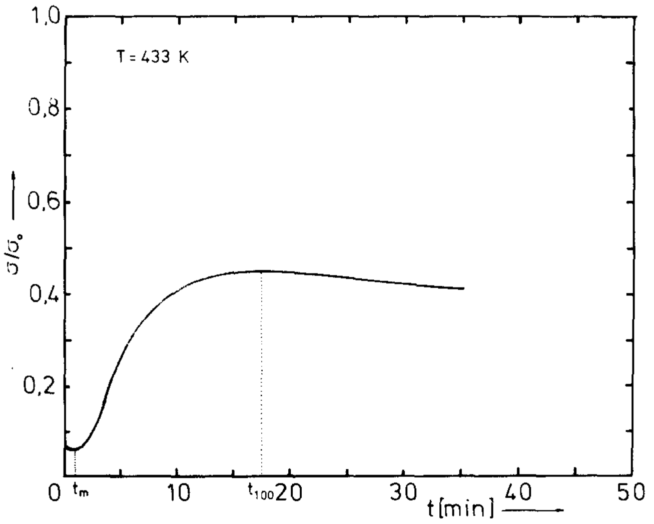

Figure 1 Rheometer curve at 433 K of the compound used. Times to minimum torque (t_m) and to maximum torque ($t_{100\%}$) are shown

Table 1 Physical and chemical properties of materials used

	Compound	Mould and press
λ (W m^{-1} K^{-1})	0.27–0.0002(T − 273.15)	37.6
c (J g^{-1} K^{-1})	1.439	0.535
$10^6\rho$ (g m^{-3})	1.195	7.85
n	1	–
E (kJ mol^{-1})	95	–
Q_0 (J g^{-1})	36.8	–
k_0 (s^{-1})	3.6×10^8	–
t_i (s)	1.6×10^{-7} exp[8506.6/T (K)]	–

pound. The time at minimum torque, t_m, was considered the onset of the reaction.

To estimate the functional relation between induction time and temperature, equation (8) was considered. The parameters A and B of that relation were estimated by means of the least squares method with an acceptable correlation coefficient ($r^2 = 0.992$). Their values are shown in *Table 1* and their dispersions were ≈7.5%.

Temperature measurements

Compound vulcanization was performed in a cylindrical stainless steel mould of height 5 cm, internal radius 3.57 cm and external radius 4.47 cm. The mould had upper and bottom plate thicknesses of 1.6 cm. The mould was preheated at 451 K and pressed at 0.612 Pa.

To measure the temperature, three copper/constantan thermocouple wires were used. Two were placed in the middle of the upper and bottom plates. The other was situated in the centre of the rubber cylinder. It was fastened firmly to the mould to avoid movement of the junction during the first stage of vulcanization due to material flow. Once the experiment was finished, the final position of the wire was measured.

The measured temperatures were stored in an HP 3421A data acquisition connected to an HP85 desk computer. A BASIC program was used to obtain the data from the measurement system. The temperatures were measured over 100 min at intervals of 30 s. In *Figure 2* the temperature–time curves obtained are shown. The small initial temperature difference between the upper and the lower plates can be treated as a contribution to the experimental error.

RESULTS AND DISCUSSION

To evaluate the problem numerically, the finite element technique was used. Taking into account the symmetries of the mould and rubber block, the temperature profiles were calculated for the quadrant shown in the mesh of *Figure 3*. In this mesh three parts were considered: rubber, mould and press platen. The thermal and kinetic parameters of the materials used in the solution of the numerical problem are given in *Table 1*. To obtain better resolution near the thermocouple location, a higher node density was provided in that region.

Boundary conditions are specified in the caption to *Figure 3*. A temperature of 300 K was taken as the initial condition for the rubber block and 403 K for the mould. The value 403 K is a mean of the initial values measured for the upper and bottom plates in the experiment. The temperature of the platen (surface 3, *Figure 3*) was fixed at 451 K, simulating the experimental value.

Some heat is lost at surfaces 5, 6 and 7 of *Figure 3*, due to the natural convection to the air. The boundary condition is

$$-\nabla T = h(T_s - T_0) \qquad (10)$$

where T_s is the surface temperature and T_0 the ambient temperature. A value of 4.2 W m^{-2} K^{-1} was used for h. This is a typical value for natural convection in air.

In *Figure 4*, in the nodes corresponding to the position of the thermocouple wires, the variation of temperature obtained by the numerical method is compared with experimental data. The fit between experimental and numerical data is very good, with some differences in the onset of the heating. These differences are due to the difficulties of simulating the initial conditions of the mould exactly.

If no vulcanization is involved in the process ($Q_0 = 0$), the temperature–time curve shown in *Figure 4b* is obtained. It differs considerably from the curves with $Q_0 \neq 0$. This implies that there is a large influence of reaction heat in the problem simulation.

To evaluate the cure level of the compound at a given vulcanization time, the equivalent time concept was used.

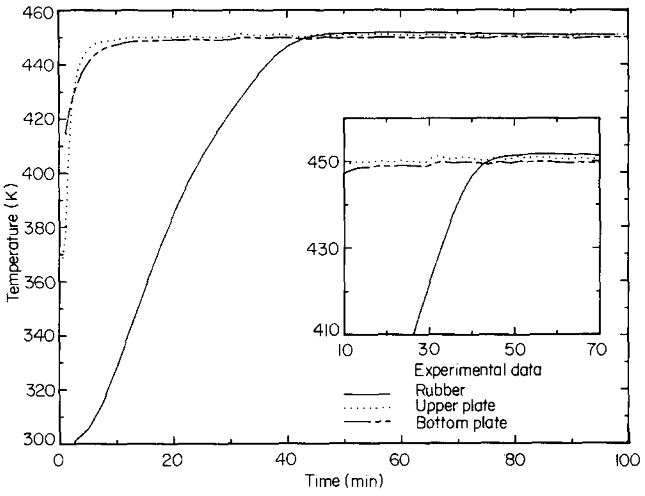

Figure 2 Temperature evolution of rubber block and mould during vulcanization

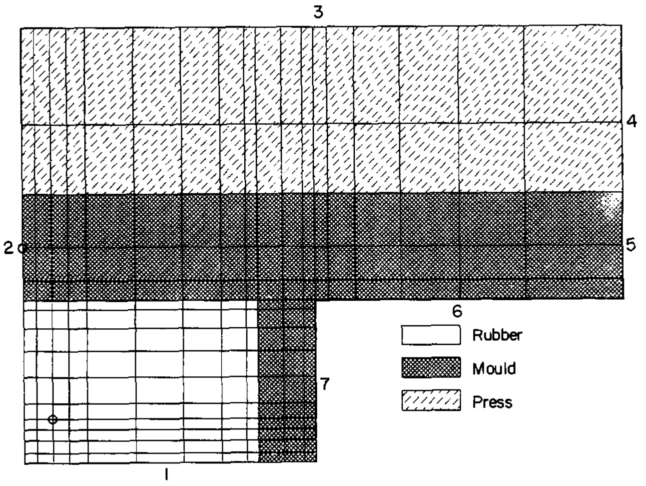

Figure 3 Mesh for finite element calculation. Different materials and boundary conditions are shown. Circles represent nodes where the thermocouple wires were placed in the experiment. Boundary conditions: surfaces 1, 2 and 4, $\nabla T = 0$; surfaces 5, 6 and 7, $-\nabla T = h(T_s - T_0)$; surface 3, $T = 451$ K

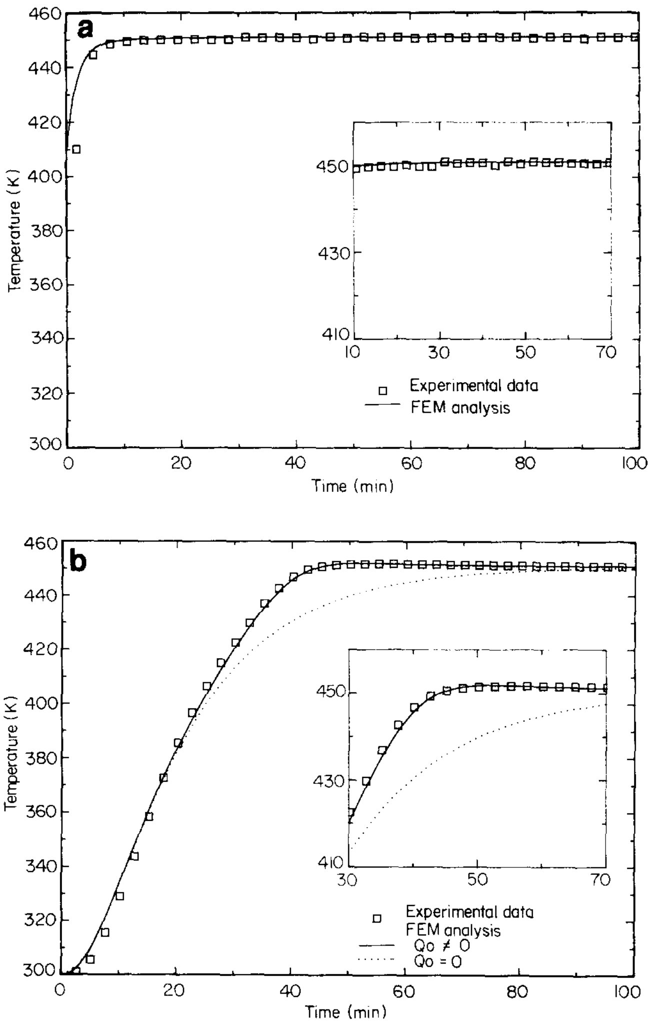

Figure 4 Comparison between experimental and numerical data for time–temperature curves: (a) inside the mould; (b) inside the rubber block

Basically, as Chehebar and Galli[12] point out, for a cure cycle characterized by a temperature history $T(t)$, at a given point in the specimen, it is possible to find the equivalent time t_e, required to reach the same cure level, when the cure process is performed at a constant reference temperature, T_r. The equivalent time is obtained by using the Arrhenius equation

$$t_e = \int_{t_0}^{t_f} \exp\{-(E/R)[1/T(t) - 1/T_r]\}\, dt \qquad (11)$$

with t_0 and t_f the initial and final time of the cycle.

Using equation (11) and the results of the transient heat equation solution according to the FEM, an equivalent curing time can be calculated for each node.

A FORTRAN program based on the Chehebar and Galli paper[12] was developed to calculate the equivalent times. This information is used in another program to draw lines of equal cure level (isocure curves). The software is based on the GCONTR subroutine[24].

Taking 433 K as reference temperature, the rheometer curve of *Figure 1* can be used to calculate the state of cure of the rubber block during vulcanization. In the rheometer curve, the maximum torque is attained at 17.5 min and after this period of time there is reversion in the modulus value and, in the rubber industry, the compound is considered overvulcanized. The time at which a maximum torque is obtained is called $t_{100\%}$. With this reference, the other cure levels can be calculated[11].

In *Figure 5* different cure levels are shown in the rubber block for two vulcanization times. According to this information, a significant proportion of the rubber block is overcured after 40 min of the cycle.

SUMMARY

Finite elements analysis using the transient heat equation, taking into account the contribution due to internal heat generation, can be used to simulate the temperature profile of an elastomeric object. Rheometer data are needed to calculate some kinetic parameters (energy activation, induction time) needed to solve the equation. A map of cure levels at a given time of the cure cycle is obtained. This information gives us a rapid view of the state of cure of the object analysed and allows the evaluation of alternatives for the vulcanization cycle.

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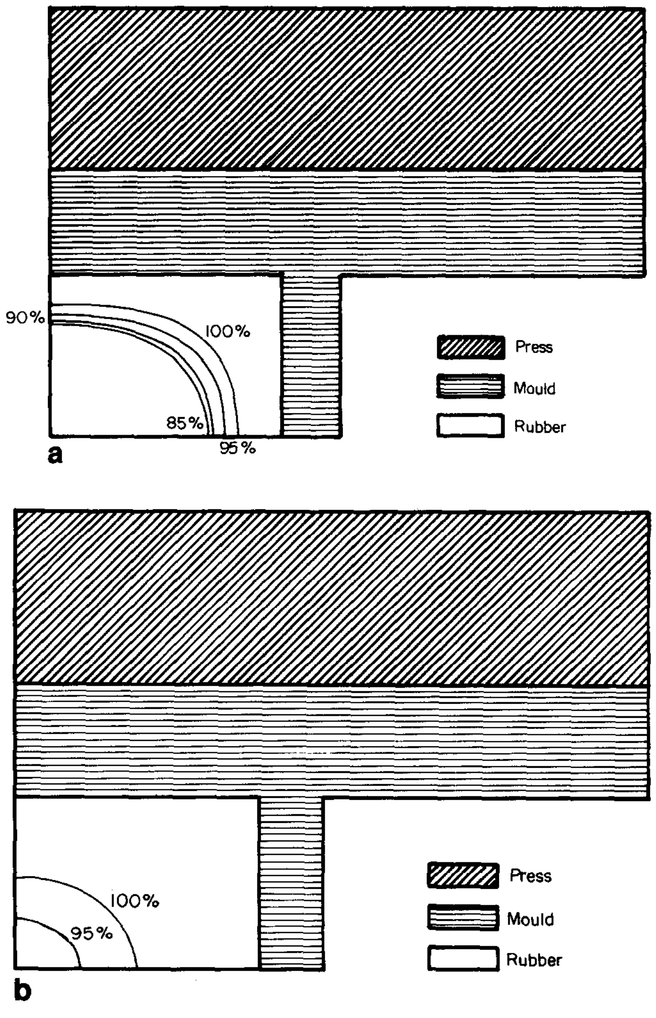

Figure 5 Simulated isocure curves at different cure levels in the rubber block: (a) cure time = 30 min; (b) cure time = 40 min

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