

Vulcanization of Rubber. Kinetic Parameters for SBR and Simulations of Vulcanization in a Mold

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SYNOPSIS

Differential scanning calorimetry (DSC) was used to characterize the vulcanization of styrene-butadiene rubber (SBR). The effect of three different fillers on the vulcanization process was also investigated. The fillers used were carbon black HAF and SRF and silica. The calculated reaction orders, activation energy, reaction energy, and preexponential factor, completed with physical properties, were used to calculate the temperature and extent of reaction inside a mold with time. The mathematical model used yields results that are in fair agreement with experimental temperature measurements inside the mold.

INTRODUCTION

Crosslinking, generally called cure or vulcanization, is the standard method for converting an elastomer into a commercially usable product having considerable mechanical strength.

Chemically, vulcanization is the tying together of two or more single chains along the already entangled morphology of an elastomer to yield a complex network. These chains are tied together at crosslinks. The theory of rubber elasticity defines that the characteristic properties appear if the elastomer consists of long chains with high flexibility, the chains are crosslinked sparsely to a three-dimensional network, and the attractions between molecules are as weak as in a liquid. The degree of conversion and number of fix points present in the elastomeric compound govern the nature of the physical properties that will exist after the vulcanization cycle is complete.

Numerous techniques, for example, rheology,¹⁻³ have been developed to characterize the cure process. These methods are often time-consuming and can only be used for quality control and comparison between different batches since generally absolute values of the kinetic parameters are not obtained. A few authors have used differential scanning cal-

orimetry (DSC) to monitor vulcanization reactions. Some descriptions of vulcanization kinetics of rubber compounds have been based on n th-order kinetics.⁴⁻¹⁰ More complicated models have been proposed and used in the literature dealing with thermosets.¹¹⁻²⁰ Nonisothermal curing kinetic data have also been fitted using the n th-order kinetics.^{21,22}

As indicated, it is possible to determine the exothermal heat of vulcanization and the overall kinetics for the elastomer by DSC measurements. In this work we have used these parameters together with physical properties such as density, thermal diffusivity, and specific heat to enable simulation of the profiles of temperature and state of cure developed in rubber sheets during vulcanization. The purpose of this work was to determine the kinetic parameters from DSC and test them in a mathematical model where profiles of temperature and degrees of cure were calculated. The results were then compared to experimentally found temperature profiles inside a mold. The effects of different fillers were also studied.

EXPERIMENTAL

Materials

The SBR types used were cold polymerized, the 1500 one without and the 1712 one with oil extension (37.5 phr). Six different blends were made, see Table

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Table I Recipes for the Six SBR Blends (in phr)

phr	SBR-0	SBR-1	SBR-2	SBR-3	SBR-4	SBR-5
SBR 1500	70.91	—	—	—	—	—
SBR 1712	40.00	—	—	—	—	—
Zinc oxide	2.50	—	—	—	—	—
Paraffine	1.00	—	—	—	—	—
TMQ ^a	1.00	—	—	—	—	—
Aromatic oil	10.00	—	5.00	10.00	—	0
Carbon black HAF	54.00	0	0	0	0	0
Carbon black SRF	0	54.00	25.00	0	0	0
Silica	0	0	0	54.00	54.00	0
Sulfur	1.90	—	—	—	—	—
CBS ^b	1.07	—	—	—	1.50	1.07
TMTD ^c	0.31	—	—	—	0.50	0.31
Diethylene glycol	0	0	0	0	2.00	0
Total	183.69	—	149.69	183.69	183.31	119.69

^a Dihydrotrimethylquinoline.

^b Cyclohexylbenzothiazylsulfenamide.

^c Tetramethylthiuramdisulfide.

I for recipes. The effects of three different fillers, carbon black HAF, carbon black SRF, and silica, were investigated. HAF has a typical particle size of 26–30 nm and SRF 61–100 nm. The specific surface area of the silica was 170 m²/g. Samples from five batches of each blend were used to test the reproducibility. The blends were made at Trelleborg AB.

Procedure

DSC

The instrument used was a Perkin-Elmer DSC-7. Indium was used for temperature and calorimetric calibrations, according to the procedure described in the operating manual of the instrument. All runs were performed in high-pressure capsulants to eliminate volatile losses during heating of the sample in the DSC cell. The samples weighed around 20 mg.

The heat of reaction was determined by following the reaction to completion at two different isothermal temperatures (140 and 160°C) and at three different scanning rates (5, 10, and 20°C/min). The area under the exothermal curve was proportional to the heat generated during the reaction.

Dynamic analyses were run at 5, 10, and 20°C/min in order to calculate the reaction orders, preexponential factor, and activation energy.

Specific heat, C_p , was determined from DSC measurements following the procedure in the operating manual. Al₂O₃ was used as a standard substance.

The rate of reaction, $d\alpha/dt$, can be calculated from the DSC measurements:

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_{\text{tot}}} \quad (\text{s}^{-1})$$

Thermal Diffusivity Measurement

The thermal diffusivity was measured by a quenching method, i.e., the solid sample at a uniform temperature was immersed in a temperature-controlled bath at a different temperature. The rate of change of temperature at the center was then monitored with an embedded thermocouple.²³ The sample geometry chosen was “infinite” flat slabs.

The thermal conductivity λ and the thermal diffusivity D , are used as quantitative measures of the heat transfer properties of a given material. They are related by

$$\lambda = D\rho C_p$$

where ρ is the density and C_p the specific heat.

The temperature bath had a temperature of 160°C, and the initial temperature of the samples was 26°C. The thickness of the slabs was 20 mm.

Vulcanization

The time-temperature curve was measured for the SBR materials in a brass mold. The brass mold was disk shaped with a diameter of 48 mm and a thick-

ness of 20 mm. The rubber was placed in the hot mold (160°C) and the mold was placed in a hot oil bath. The temperature rise in the center of the mold was followed by a thermocouple.

MATHEMATICAL TREATMENT

The assumptions made in the model of the curing process are: no flow, no mixing, and constant temperature in the walls during the reaction. The unidirectional heat flow through the rubber sheet of thickness 1 can be expressed by the general equation of transient heat conduction:

$$\rho C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(\frac{\partial T}{\partial x} \right) \lambda + G(x, y, z, t) \quad (1)$$

where ρ is the density, C_p is the specific heat, and λ is the thermal conductivity.

The volumetric internal heat generation rate $G(x, y, z, t)$ was assumed to be proportional to the curing reaction rate:

$$G(x, y, z, t) = \rho \Delta H_{\text{tot}} \frac{\partial \alpha}{\partial t} \quad (2)$$

where ΔH_{tot} is the total heat released per unit mass of resin and α the degree of cure.

Kamal et al.^{14,19} proposed a kinetic expression for the overall autocatalytic isothermal cure process.

$$\frac{\partial \alpha}{\partial t} = (k_0 + k_1 \alpha^m)(1 - \alpha)^n \quad (3)$$

where α is the relative degree of conversion and can be determined by DSC from the ratio of the total amount of heat evolved with time $H/\Delta H_{\text{tot}}$. ΔH_{tot} is the reaction energy of the system, which can be calculated from the area under the DSC curve; m and n are the reaction exponents and $m + n$ is the reaction order. The kinetic constants are

$$k_0 = A_0 \exp\left(\frac{-E_{a0}}{RT}\right) \quad (4)$$

$$k_1 = A_1 \exp\left(\frac{-E_{a1}}{RT}\right) \quad (5)$$

where A_0 and A_1 are the Arrhenius preexponential factors, E_{a0} and E_{a1} are the Arrhenius activation energies and R is the gas constant.

Han et al.²⁴ found that the rate of polymerization with k_0 was close to zero, and therefore the kinetic expression was assumed to be

$$\frac{\partial \alpha}{\partial t} = A \exp\left(\frac{-K_a}{R}\right) \alpha^m (1 - \alpha)^n \quad (6)$$

for the overall curing reaction. Although this expression does not correspond to a chemical reaction scheme, it has proven to work well in a mathematical model.^{20,25}

A FORTRAN program was written by Bergmark and Flodin²⁰ including a FORTRAN library routine document²⁶ as a subroutine for calculating the temperature and extent of cure as a function of time and distance from the wall. The subroutine integrates a system of linear or nonlinear parabolic partial differential equations in one space variable, using the method of lines and Gear's method.

The geometrical form of the mold was infinite plates at a distance of 20 mm. Boundary conditions were for space coordinate $x = 0$ at the wall. The extent of reaction was set to $\alpha = 0$ at the time $t = 0$. The wall temperature was set to 433 K (160°C) in the case studied. The temperature of the resin at $t = 0$ was $T_r = 293$ K.

KINETIC PARAMETERS

Activation Energy

It is possible to calculate the apparent activation energy by evaluating both dynamic and isothermal DSC thermograms.^{27,28} In this work the activation energy, E_a , was derived by Kissinger's²⁷ method involving the results from multiple dynamic DSC curves at various scan rates. This method assumes that the reaction rate reaches a maximum when dH/dt attains its maximum and the slope of the curve is equal to zero. With these assumptions Kissinger²⁷ obtained the following equation for the reaction, neglecting small differences:

$$\frac{d\left[\ln\left(\frac{dT/dt}{T_p^2}\right)\right]}{d(1/T)} = -\frac{E_a}{R} \quad (7)$$

where T_p is the peak temperature. Plotting $\ln[(dT/dt)/T_p^2]$ versus $1/T$ for several DSC curves obtained at various scan rates results in a straight line with the slope $-E_a/R$. In this case it was also assumed that the reaction order remains constant throughout the reaction.

Table II Reaction Enthalpy and Apparent Activation Energies

	$-\Delta H_{\text{tot}}$ (J/g SBR)	E_a (kJ/mol)
SBR-0	38.4 ± 2.0	68.1 ± 3.4
SBR-1	40.1 ± 2.7	93.9 ± 5.6
SBR-2	33.7 ± 3.9	80.1 ± 0.9
SBR-3	28.9 ± 1.4	102.3 ± 1.4
SBR-4	34.1 ± 2.7	95.8 ± 1.0
SBR-5	27.2 ± 2.4	94.1 ± 15.3

Reaction Order Exponents

The kinetic expression was assumed to be [Eq. (6)]:

$$\frac{\partial \alpha}{\partial t} = A \exp\left(\frac{-E_a}{RT}\right) \alpha^m (1 - \alpha)^n$$

The change in conversion $\partial \alpha / \partial t$ can be calculated from a DSC analysis.

$$\frac{\partial \alpha}{\partial t} = \frac{dH/dt}{\Delta H_{\text{tot}}}$$

where dH/dt is the height of the curve at the scanned temperature and ΔH_{tot} is the area under the curve. Equation (6) can be rewritten:

$$\ln\left(\frac{(dH/dt)/\Delta H_{\text{tot}}}{\alpha^m (1 - \alpha)^n}\right) = \ln(A) - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) \quad (8)$$

The reaction exponents m and n can be calculated by an iterative computer program using the left-side expression versus $(1/T)$. Given an interval for each exponent, the program calculates the fit of a straight line for each combination of the m and n exponents. The program selects the combination that gives the best correlation coefficients, with the slope E_a/R as was found earlier according to Kissinger's method,²⁷ and this combination was taken to represent the overall reaction.

Table III Reaction Orders and Preexponential Factors

	m	n	$m + n$	A (s ⁻¹)
SBR-0	0.67 ± 0.03	1.09 ± 0.05	1.76 ± 0.08	7.8 ± 0.4 × 10 ⁵
SBR-1	0.52 ± 0.03	1.24 ± 0.07	1.76 ± 0.10	7.4 ± 0.4 × 10 ⁸
SBR-2	0.50 ± 0.01	0.90 ± 0.01	1.40 ± 0.02	1.1 ± 0.01 × 10 ⁷
SBR-3	0.44 ± 0.01	1.02 ± 0.01	1.46 ± 0.02	2.3 ± 0.02 × 10 ⁹
SBR-4	0.40 ± 0.01	0.92 ± 0.01	1.32 ± 0.02	6.4 ± 0.06 × 10 ⁸
SBR-5	0.90 ± 0.15	1.30 ± 0.21	2.20 ± 0.36	1.8 ± 0.30 × 10 ⁹

Table IV Physical Parameters

	Specific Heat (J/°C kg)	Density (vulc.) (kg/m ³)	Density (nonvulc.) (kg/m ³)	Thermal Conductivity (W/m °C)
SBR-0	1098	1130	1120	0.110
SBR-1	1113	1140	1100	0.116
SBR-2	1083	1070	1010	0.124
SBR-3	1195	1160	1140	0.112
SBR-4	1086	1160	1120	0.102
SBR-5	1262	990	910	0.114

Preexponential Factor

The preexponential factor A was calculated from the intercept in Eq. (8) for the optimal fitted line.

RESULTS AND DISCUSSION

Calculated Reaction Parameters

The kinetic parameters for the resins were calculated following the procedure described earlier. The values, shown in Tables II and III, are averages from two samples from five batches for each of the six blends.

The reaction order for the unfilled rubber was found to be 2.2, which is higher than what was found for the filled materials. SBR filled with carbon black, HAF, or SRF showed a reaction order of 1.8 while the silica-filled material presented an even lower order of reaction.

The apparent activation energy exhibited some dependence on the filler used, even though there were some uncertainties. Addition of carbon black HAF lowered the activation energy while silica-filled materials had a higher value than the unfilled rubber. Thus carbon black appeared to have an accelerating effect on the sulfur vulcanization of SBR.

The unfilled material had a lower heat of reaction

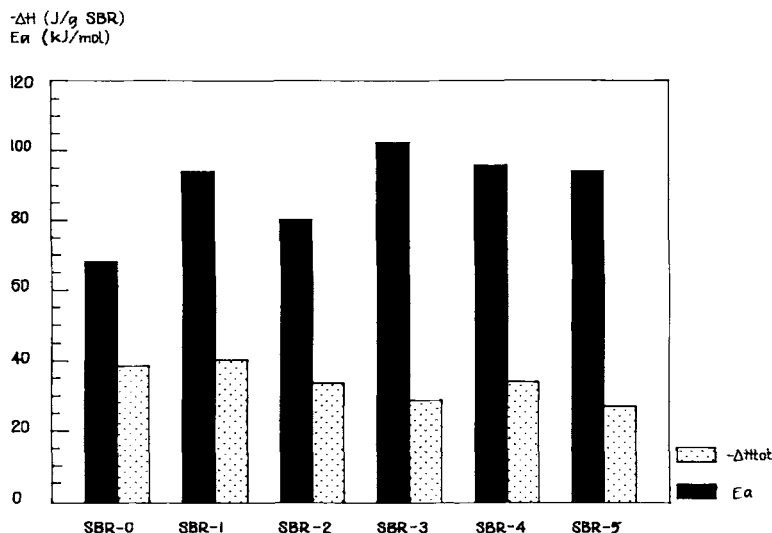


Figure 1 Activation energy and reaction enthalpy for the six blends.

than any of the filled materials. Carbon black fillers caused a greater increase in the heat of reaction than the silica filler, when compared at the same filler content. The explanation could be that an additional reaction took place or the vulcanization reactions were driven to higher conversion in the presence of carbon black. The silica filler used was inert in that respect, but addition of diethylene glycol modified this effect, possibly by wetting the surface of the filler particles.

The Physical Parameters

The physical parameters, thermal conductivity, specific heat, and density were determined as described earlier. The values are shown in Table IV and in Figure 1.

The Rate of Reaction

The rate of reaction was calculated from the DSC measurements. The results are shown in Figure 2.

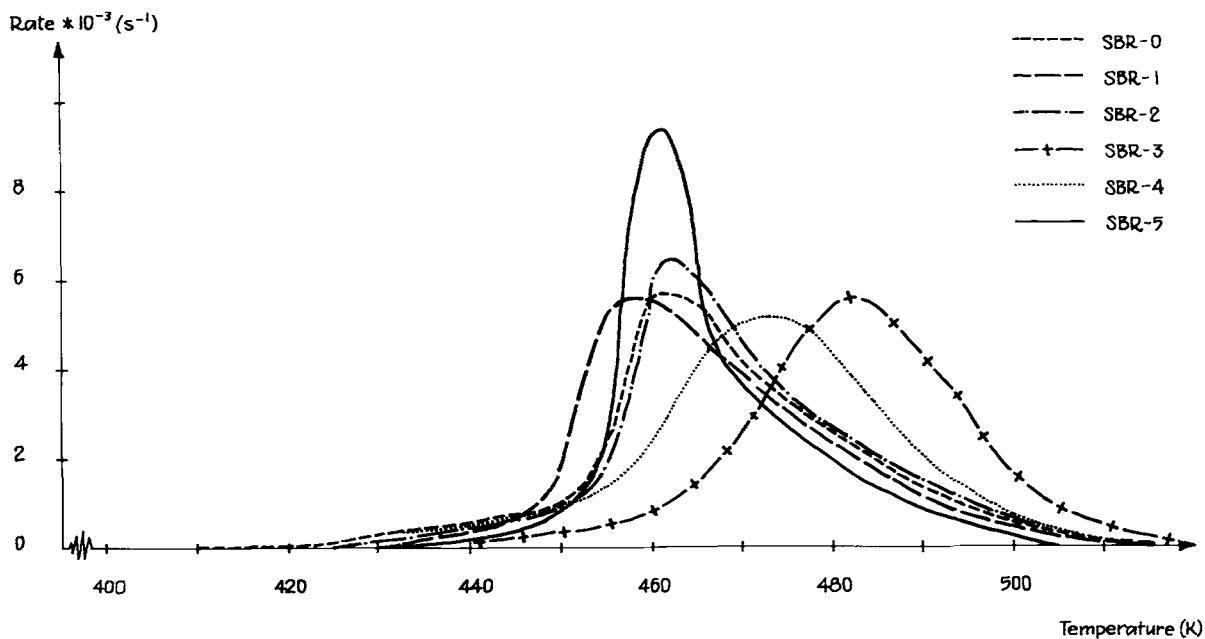


Figure 2 Rates of reaction calculated from DSC measurements.

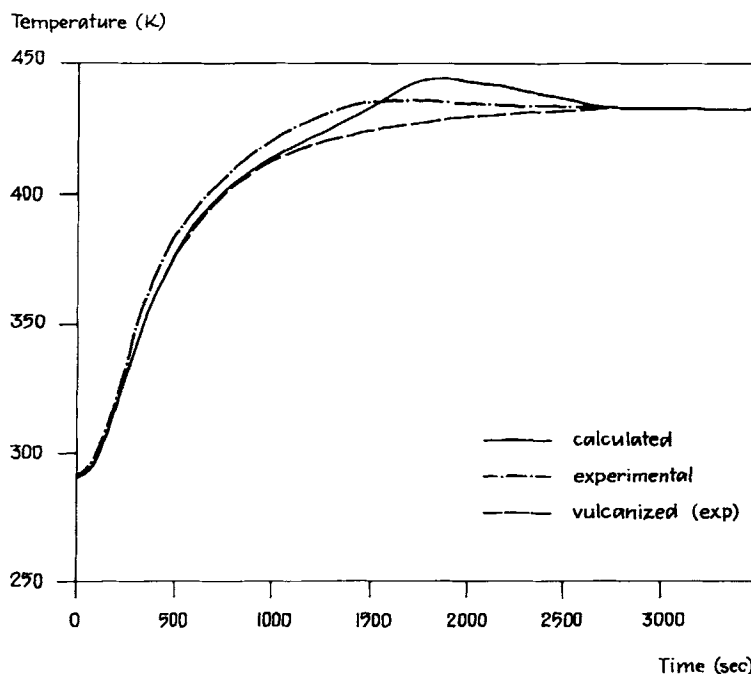


Figure 3 SBR-0 carbon black filler. Temperature profiles from the center of the mold, experimental (vulcanized and nonvulcanized) samples, and simulated nonvulcanized samples.

The silica-filled materials showed a delayed reaction compared to the unfilled and carbon-black-filled materials. This behavior is well correlated to the measurements of activation energy and heat of reaction.

Experimentally Found and Simulated Data

The experimentally found temperatures in the center of a mold at a wall temperature 160°C (433 K) are displayed in Figures 3–5. The geometrical form

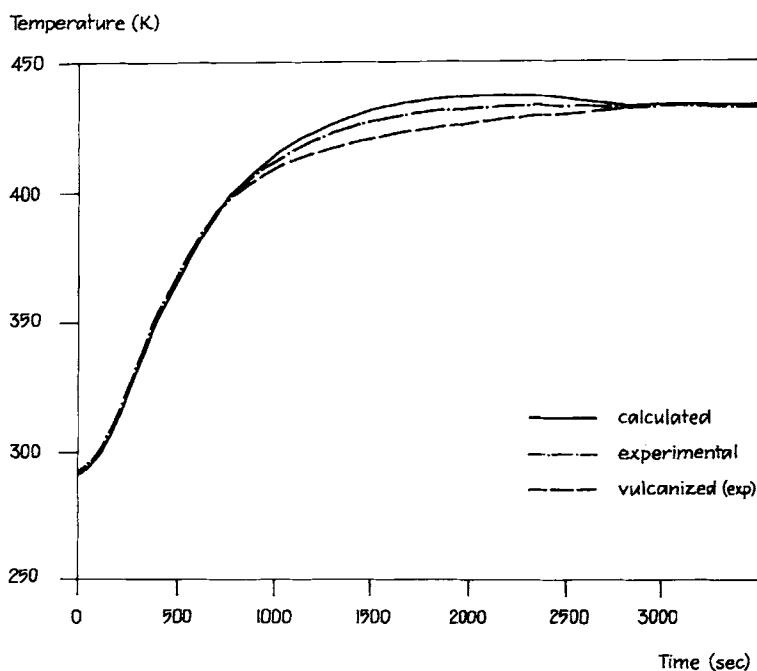


Figure 4 SBR-3 silica filler. Temperature profiles from the center of the mold, experimental (vulcanized and nonvulcanized) samples, and simulated nonvulcanized samples.

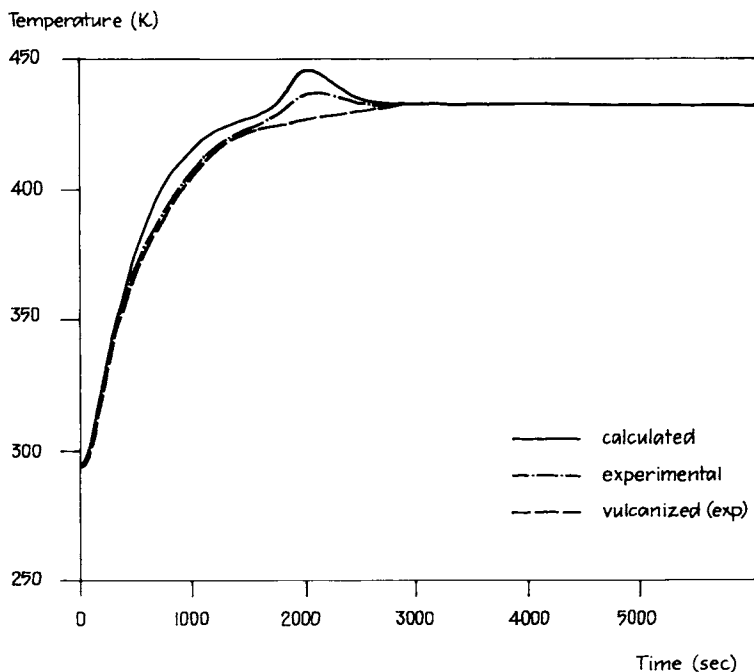


Figure 5 SBR-5 nonfilled. Temperature profiles from the center of the mold, experimental (vulcanized and nonvulcanized) samples, and simulated nonvulcanized samples.

of the mold was plates at a distance of 20 mm. The agreement between the experimental and the kinetic model presented in this article was fair. For carbon black the deviation between the model and experimental data was approximately 15°C at the peak

temperature (Fig. 3). The experimental results showed that the exotherm was stretched out during the heating period while the model described a thermal conductivity period and then an exothermal period. In the case of silica-filled SBR the model pre-

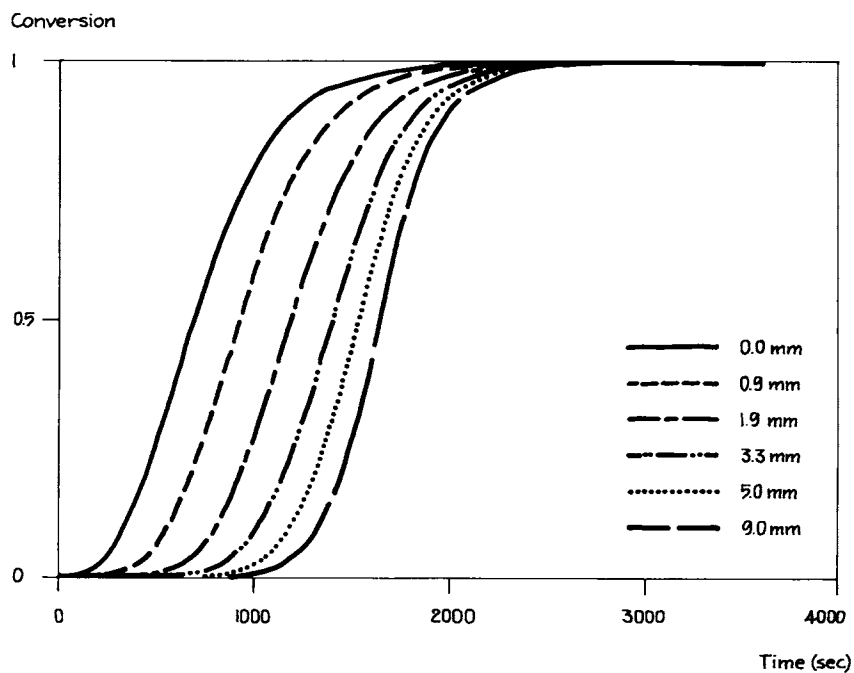


Figure 6 SBR-0. Calculated extent of reaction inside mold. The wall temperature was 160°C (433 K).

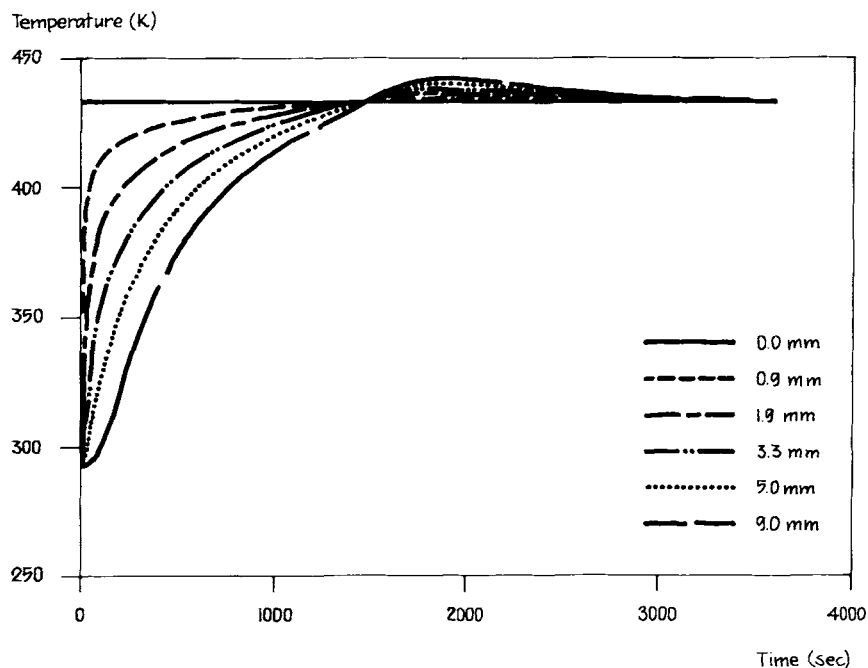


Figure 7 SBR-0. Calculated temperature profiles inside mold. The wall temperature was 160°C (433 K).

dicted a 10°C higher exotherm than the measured temperatures, (Fig. 4). The start of the exotherm was the same for both the calculated and experimental data. For nonfilled material (Fig. 5), the difference in peak temperature was approximately

15°C . The model indicated a more rapid heat conduction in the material than what could be measured experimentally.

The kinetic model used here, based on kinetic parameters from DSC experiments and calculated

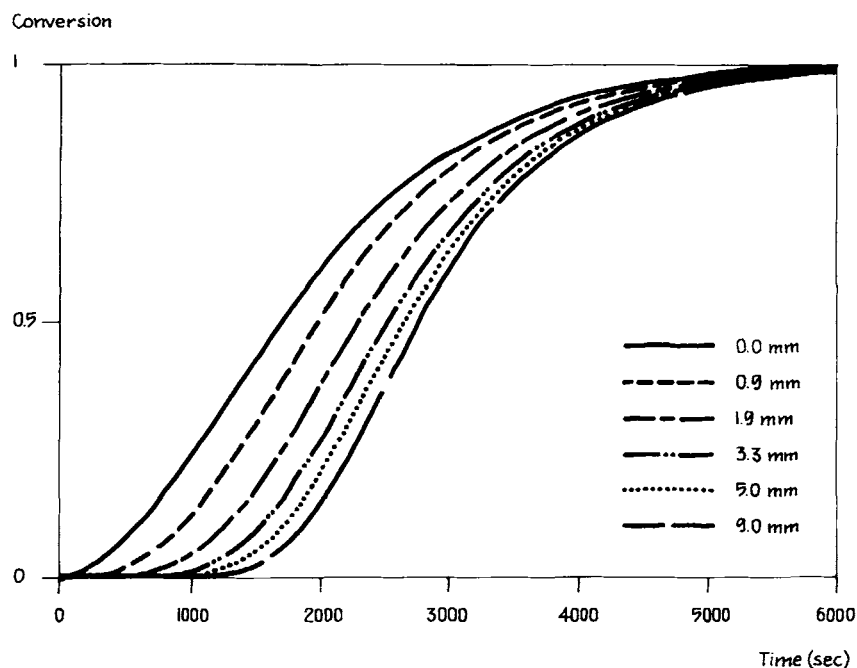


Figure 8 SBR-3. Calculated extent of reaction inside mold. The wall temperature was 160°C (433 K).

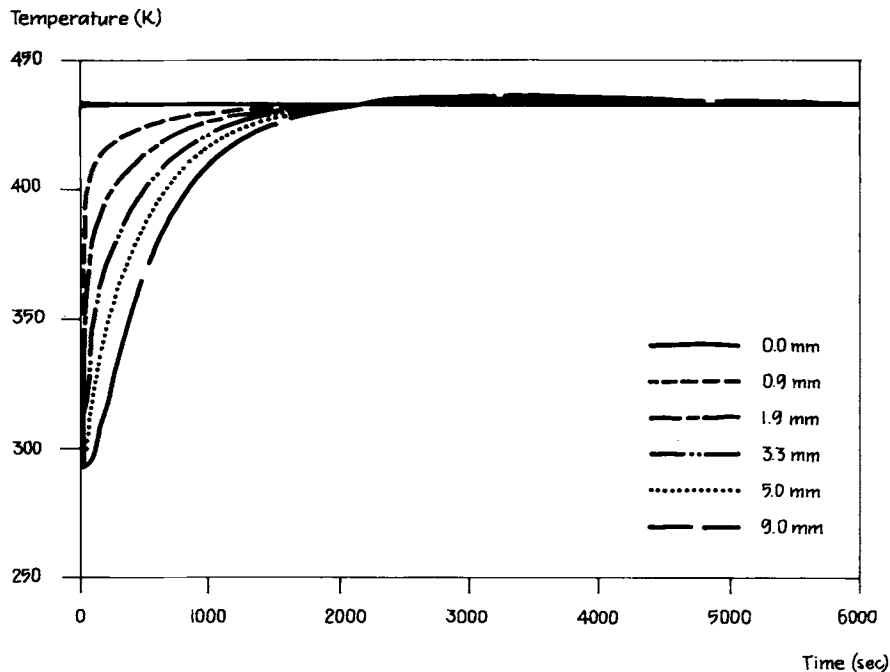


Figure 9 SBR-3. Calculated temperature profiles inside mold. The wall temperature was 160°C (433 K).

in the mathematical model, gives plots of temperatures with times at different distances from the mold wall (see Figs. 7, 9, and 11). The extent of reaction following from the temperature profiles

with time was also obtained by the computer program (Figs. 6, 8, and 10).

Carbon black did not change the vulcanization time compared to the time required by the unfilled

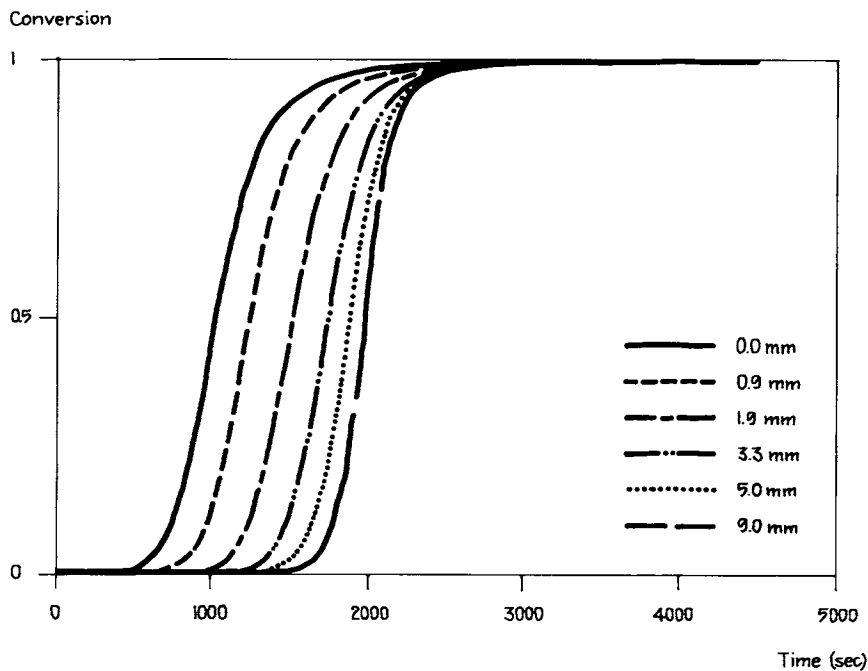


Figure 10 SBR-5. Calculated extent of reaction inside mold. The wall temperature was 160°C (433 K).

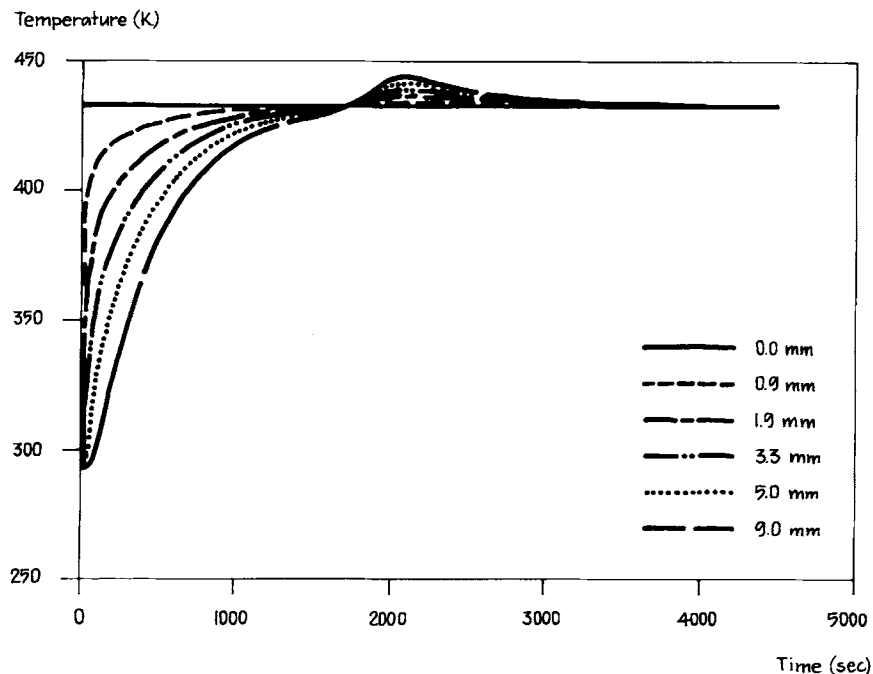


Figure 11 SBR-5. Calculated temperature profiles inside mold. The wall temperature was 160°C (433 K).

rubber. For SBR-0, which was filled with HAF, the vulcanization started earlier than in the case of the unfilled material possibly because of the higher thermal conductivity. Because of the larger exotherm in the unfilled material, SBR-5, the materials

reached high conversions after about the same time (Fig. 12).

The silica filler used slowed down the reaction considerably and according to the model needed more than double the processing time. This effect

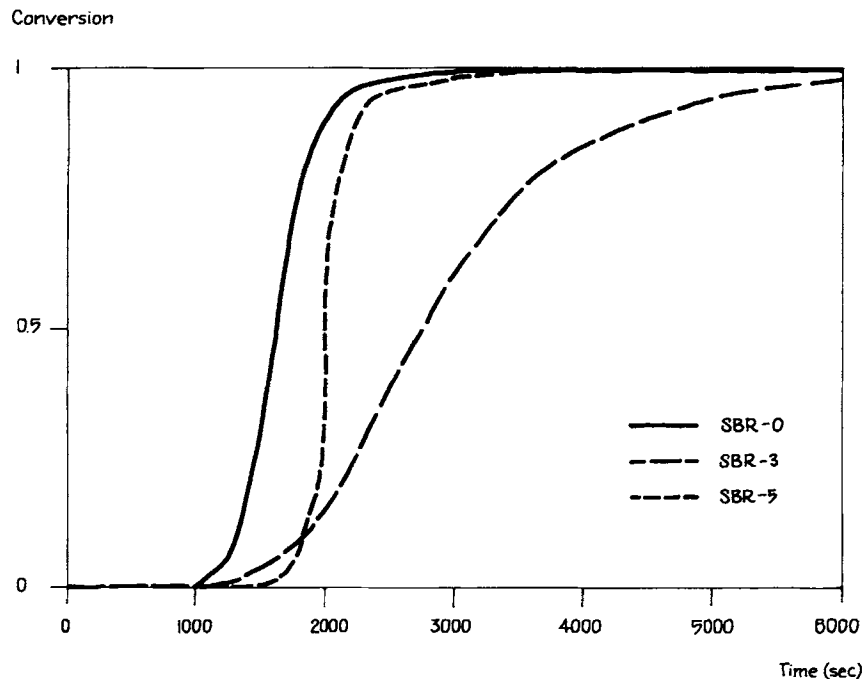


Figure 12 Comparison of the extent of reaction in the center of the mold for samples with different fillers; carbon black (SBR-0), silica (SBR-3), and non-filled (SBR-5).

could be somewhat modified by addition of diethyleneglycol (SBR-4).

CONCLUSION

The vulcanization reaction inside a mold can be simulated by use of the mathematical model presented in this article. The kinetic data necessary for calculations could be determined by DSC with analysis by Kissinger's method²⁷ and by finding the reaction exponents m and n in the model of Kamal et al.^{14,19} giving the best fit of a straight line with the slope E_a/R . The mathematical model was found to be representative for the reaction as there was fair agreement between calculated and experimental results.

The model makes it possible to determine the necessary reaction time at a specific mould temperature, and thereby improve the quality and optimize the process time.

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