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KINETIC PARAMETERS OF THE OVERALL REACTION OF SCRAP RUBBER VULCANIZATION BY 2% SULFUR

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ABSTRACT

The purpose of this work was to show that the temperature gradients developed in the rubber mass during vulcanization could be predicted if the kinetics of reaction and the physical properties of the rubber were known. Experiments were performed using differential calorimetry, and a mold pressing a 1 cm thick rubber sheet. The overall reaction was found to be first order with an activation energy of about 25 kcal mole^{-1}, when the sulfur percentage was 2.

INTRODUCTION

Sulfur vulcanization of unsaturated elastomers is a very complex chemical process involving numerous simultaneous and consecutive reactions [1–3]. Elemental sulfur is converted to a variety of sulfide products (crosslinked, non-crosslinked extra chain material, and extra network material), and the distribution among these products is dependent on the temperature and time for which the sample is vulcanized. Numerous techniques have been developed to characterize the cure process and the nature of the product. Most are time-consuming and tedious [4,5]. In recent publications [6,7], differential scanning calorimetry (DSC) was used to monitor vulcanization reactions, but interpretation of DSC thermograms is very difficult because of the complexity of the reactions involved, and the use of a dynamic heating program further complicated interpretation because of the unknown temperature dependence of each unknown reaction.

In the present study, scanning calorimetry was used as a differential calorimeter (DC) at constant temperature, and the rate of enthalpy change was registered as a function of time. Of course, determination of meaningful kinetic parameters for the complex reactions present was not feasible. A

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kinetic analysis of the enthalpy profile was only possible in the case of the overall reaction considered as a simple reaction.

On the other hand, transient heat transfer calculations were used to predict cure development in thick sections of rubber molding [8]. More recently, it was shown that the temperature gradients developed in the polymer could be predicted if the kinetics of reaction and the physical properties of the polymer were known [9,10].

The purpose of this work was to compare the experimental temperature gradients developed in the rubber mass with the calculated ones using the kinetic parameters determined by differential calorimetry under approximately the same conditions of temperature.

EXPERIMENTAL

Description of rubber powder

A 150–250 μm grain size was used for a rubber powder recovered from old tires by liquid nitrogen cooling and subsequent crushing (Air Liquide machine). The mean % composition of our material was: carbon, 83; hydrogen, 7; ash, 6; oxygen, 2; sulfur, 1.8. Another approximate analysis found that the worn tire contained about 55% rubber hydrocarbon, 14% acetone extractables, 25% carbon black, and 6% ash. These commercial rubbers were a mixture of normal rubber and SBR in a ratio of about 4/6 [11]. These values were confirmed by our experiments [12] using thermogravimetric analysis, derivative thermogravimetric analysis [13] and pyrolysis coupled with gas chromatography.

Temperature profiles with a slab mold

In our experiments, rubber powder and sulfur (2 wt.%) as vulcanizing agent were mixed and pressed into the slabs of a mold, using a constant temperature for the mold. The inner dimensions of the stainless steel mold pattern were $10 \times 10 \times 1$ cm.

The temperature-sensing assemblies were prepared from two iron/constantan thermocouple wires. The wires were fastened firmly at the mold edges to hold the position of the junction against the contraction and expansion forces during casting. The positions of the measuring junctions were checked after curing operations to make sure they had not been disturbed during the measurements. Two series of temperature measurements were of interest: the temperature of the mold; the difference between the temperature of the mold and that measured at the midplane of the rubber block. Both these temperatures were registered continuously on a recorder (Servotrace PED 2).

Differential calorimeter

A differential scanning calorimeter (DSC 111 — SETARAM, France) was used as a constant temperature calorimeter (DC), and the recording time-based instead of temperature-based. The calorimeter was temperature-stabilized at the desired value, the encapsulated sample introduced, and time base and recording started. About 50 mg of the compound was encapsulated in a hermetically-sealed aluminum holder; the ingredients in the sample were well dispersed. Repetitive experiments were undertaken on each compound to make sure that sulfur was well dispersed.

The differential calorimeter response is directly related to the rate of enthalpy change with time. Areas of exotherms were calculated using a computer, being set up to allow the fractional area at any point in time to be calculated.

THEORETICAL

Kinetic study

The assumption in the calorimeter calculation is that the partial enthalpy evolved up to time t, as a fraction of the totally enthalpy evolved, represents the conversion up to time t. The overall rate of cure is given by

$$\frac{\mathrm{d}q}{\mathrm{d}t} = k(q_\infty - q_t)^n \qquad (1)$$

where q_∞ is the overall heat of reaction, and q_t is the heat of reaction up to time t. The rate constant k is assumed to have the usual Arrhenius form, with the activation energy E.

Heating by transient conduction

Consider the case of heating through a plane sheet of rubber of thickness l and thermal conductivity λ, whose surfaces $x = 0$, $x = l$ are maintained at constant temperature T_0. The heat flow is unidirectional and the general differential equation for transient conduction of heat is defined by

$$\frac{\partial T}{\partial t} = \underbrace{\frac{\lambda}{\rho C} \cdot \frac{\partial^2 T}{\partial x^2}}_{\text{conduction heat}} + \underbrace{\frac{1}{\rho C} \cdot \frac{\mathrm{d}q_t}{\mathrm{d}t}}_{\text{reaction heat}} \qquad (2)$$

Initial and boundary conditions are

$$\begin{array}{llll} t = 0 & 0 \leqslant x \leqslant l & T = T_0 & \text{rubber space} \\ t \geqslant 0 & x < 0 & T = T_\mathrm{e} & \text{mold space} \qquad (3) \\ & x > l & & \qquad\qquad\qquad\quad (4) \\ t > 0 & 0 < x < l & T = T_{xt} & \text{rubber space} \end{array}$$

The problem was solved by using a numerical method, based mainly on the Dusinberre generalization of the increment method applied to one-dimensional transient conduction. Let the solid be divided into a number of equal finite slices of thickness Δx by temperature-reference planes. Upon replacing the dimensionless ratio $(\Delta x)^2\lambda/\rho C\Delta t$ by the modulus M, we have

$$T_1' = \frac{1}{M}\left[T_0 + (M-2)T_1 + T_2\right] + \frac{1}{\rho C}\cdot\frac{\mathrm{d}q_t}{\mathrm{d}t}\cdot\Delta t \tag{5}$$

where T_1' is the new temperature at plane 1, after the elapse of a finite time increment Δt, and T_0, T_1 and T_2 are the temperatures at planes 0, 1 and 2, respectively, before the elapse of Δt.

In fact the heat transfer coefficient at the steel–rubber surface was large, the surface temperature changed substantially instantaneously, and consequently the initial surface temperature was taken as the arithmetic mean of the original surface temperature and the temperature of the first rubber slice next to the surface. Another complication was introduced due to the fact that $\lambda/\rho C$ was found to vary with temperature. The problem was solved by keeping M constant and using a variable time increment Δt.

RESULTS

Kinetic study using DC

Figure 1 illustrates DC exotherms obtained on the same time scale for a compound with a sulfur/rubber ratio of 2. These temperatures (160, 165, 170°C) were chosen so that the vulcanization rate was sufficiently high to allow a short cure time for industrial applications.

The increase of heat follows the first order law with respect to time since plots of log(heat rate) against $\log(Q_\infty - Q_t)$ are linear for the three temperatures, with a slope equal to 1 (Fig. 2). Q_t and Q_∞ are the enthalpies associated with the overall reaction at time t and infinite time, respectively. They were determined by measuring the area under the exotherms shown in Fig. 1. In earlier studies, the decrease of free sulfur was found to follow a first order law with respect to time, for natural rubber and for SBR with sulfamide type accelerators [14].

The temperature coefficients k were determined by measuring the ordinate intercept in Fig. 3, for the three temperatures (160, 165, 170°C). The energy of activation E was found from the slope of log k vs. $1/T$ plots (Fig. 3); it was also obtained using the method of least squares with a good correlation factor ($r^2 = 0.99$) (Table 1). The value of the activation energy was of the order of magnitude with corresponding values reported for natural rubber [14].

The enthalpy of reaction Q_∞ was measured using DC at three tempera-

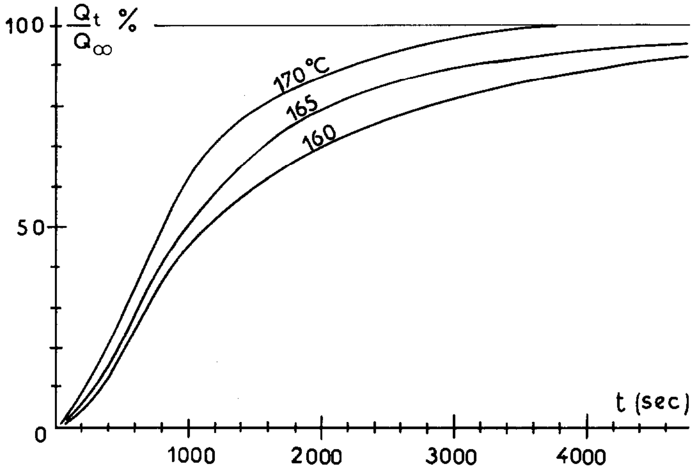

Fig. 1. DC experimental curves. Q_t against time at 160, 165 and 170°C.

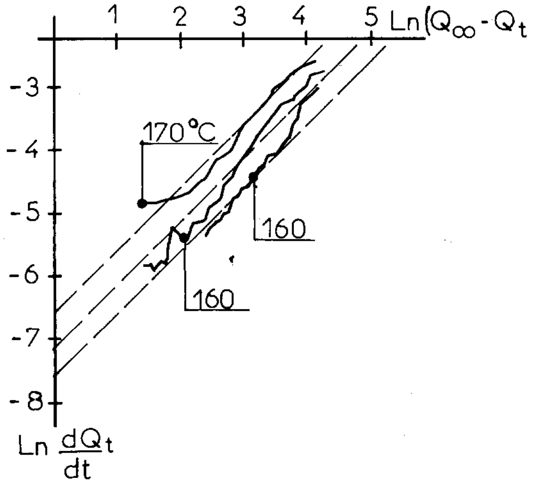

Fig. 2. n dQ_t/dt vs. $\ln(Q_\infty - Q_t)$ at 160, 165 and 170°C.

TABLE 1

Kinetic parameters

$k(s^{-1})$ at 160°C $= 5.5 \times 10^{-4}$
at 165°C $= 7.67 \times 10^{-4}$
at 170°C $= 10.6 \times 10^{-4}$
$n = 1$
$k_0(s^{-1}) = 3 \times 10^9$
E(kcal mole^{-1}) $= 25.4$

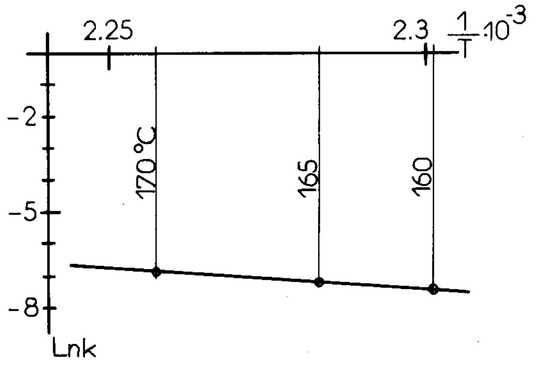

Fig. 3. ln$k$ vs. $(1/T)$ T K.

TABLE 2

Heat transfer values

$Q_{\infty} = 18.1$ cal g^{-1}
$\lambda/\rho C = 3.12 \times 10^{-3}(1 + 10^{-6}T)$ cm^2 s^{-1} (T in K)
$\rho C = 0.35[1 + 2.5 \times 10^{-3}(T - 293)]$ cal cm^{-3} K^{-1}

tures (160, 165, 170°C), and using DSC (SETARAM DSC 111) programmed with a heating rate of 10°C min^{-1} between 300 and 550 K. For DSC measurements, the sample was cooled and rescanned to give the baseline which would be observed in the absence of cure. The values found (Table 2) are about the same as the most recent data chosen among those which are in good agreement [4,6,15]. The heat capacity C was measured by calorimetry, and the product ρC being of interest in eqn. (2) was found to increase slowly with increasing temperature, as reported in the literature [6,15].

The thermal conductivity of rubber and vulcanizates was measured under steady-state conditions, using a parallel-faced slab with heat flow normal to the surfaces at different temperatures [17]. These values were well represented by a linear function of temperature as already reported [16,18].

Heat transfer through the rubber sheet

Figure 4 shows the variation of the midplane temperature of a rubber sheet against time. Two experiments were performed: one with the heat transfer only, the other with the heat transfer and vulcanization using 2% sulfur. The thickness of the rubber sheet was 1 cm; and the temperature of the stainless mold was kept constant at 180°C. Theoretical curves were obtained by using eqn. (3) and the experimental values shown in Tables 1 and 2. In both cases, experimental and theoretical curves were in agreement.

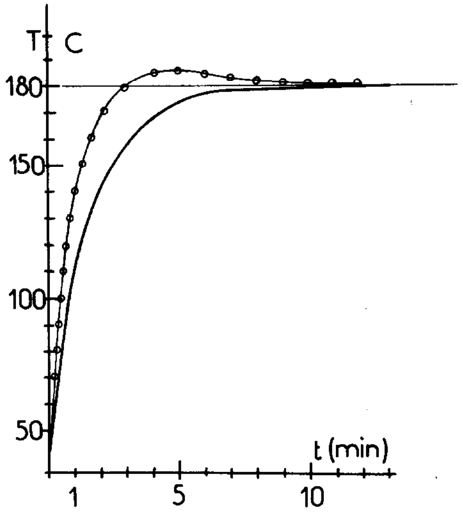

Fig. 4. Heat transfer. Temperature (taken at the midplane of a rubber sheet) vs. time: ——, without vulcanization; O——O, with 2% sulfur. One cm thick sheet experimental and theoretical curves.

CONCLUSIONS

Although vulcanization is a complex series of reactions, the overall result for practical purposes can be described by an Arrhenius equation and a single activation energy. The activation energy for the vulcanization of rubber powder recovered from tires is about 25 kcal mole^{-1}, and the overall reaction is first order. Kinetic parameters of the overall reaction were determined by differential calorimetry using a very small sample. The values of those parameters were in agreement with those obtained using the vulcanization of a rubber sheet in a large sample, and by comparing the experimental with the theoretical temperature at the midplane of the rubber sheet.

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