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DETERMINATION OF THE KINETIC DATA OF RUBBER CURE AND INDUSTRIAL APPLICATION

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ABSTRACT

Although vulcanization of rubber consists of a complex series of reactions, the overall reaction when taking into account reaction heat could be described by a single equation. The enthalpy of reaction and kinetic data were determined by DCS working under isothermal conditions. Our model takes into account the enthalpy of the cure reaction and heat transfer by conduction through the rubber. The calculation of profiles of temperature and extent of cure developed through the rubber was made by applying an explicit numerical method with finite differences. Some problems of interest due to the lack of accuracy in calorimetric measurements or bad distribution of sulfur in samples were examined. So, the effect of a variation in the parameters of the kinetic equation of cure heat was particularly studied. Use of these studies were made for industrial applications : vulcanization of rubber in mold, in injection molding, and progress of vulcanization during the cooling period after the extraction from the mold.

INTRODUCTION

Numerous techniques have been developed to characterize the cure process but most of them are time-consuming and tedious. In the early days of the rubber industry various rules of thumb techniques for estimating cure time evolved. They worked well for many purposes although they were problems in some areas such as the curing of large articles. Measurements are often made on Monsanto Rheomater or Wallace-Shawbury Curometer as well as on the isothermal apparatus (ref. 1). But the Rheometer gives longer times than the Curometer and both give longer cure times than the isothermal apparatus. There are several reasons for this increase in the cure time : on the one hand with the Rheometer, heat is lost continuously by conduction from the rotor during the measurement, so that the centre is always cooler than the platens and the average temperature is less than the set temperature. On the other hand the Curometer samples take longer to heat up because they are thicker than the samples used in the isothermal apparatus. Unfortunately it takes a few weeks to determine a complete family of cure-time curves using the isothermal apparatus because each point has to be obtained separately by correlating the temperature-time history with the swelling of each sample in toluene. Another method of evaluation of the state of cure in a vulcanizing rubber article (ref. 2) was studied by considering the

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temperature history obtained from the heat transfer through the rubber. But in this method the rate of vulcanization was referred to the rate of the reference temperature of 149°C and a temperature coefficient of vulcanization of 1.85 was arbitrarily chosen (the reaction rate increases by a factor of 1.85 per 10°C). A first-order expression was also assumed to describe the reaction rate over the range of interest (ref. 3).

The purpose of this work is to show that the gradients of temperature and extent of cure developed in the rubber mass could be predicted during vulcanization if the kinetic of reaction and the thermal properties of the rubber were known (ref. 4, 5). These gradients are determined by the balance of internal heat generation due to the cure reaction, heat conduction through mold and rubber and heat exchange with the surroundings by convection. The sulfur vulcanization is a complex series of reactions (ref. 6) but kinetic analysis of the overall reaction was possible by studying the enthalpy profiles obtained by differential calorimetry (DC) at constant temperatures (ref. 4, 7, 8). The problem was solved by applying an explicit numerical method with finite differences.

The effect of several parameters concerned with the enthalpy of reaction (ref. 9) and kinetic of reaction (ref. 10) are examined and compared either in classical molding or injection molding process. The variation in these parameters can be due to a lack of accuracy in DC measurements or in the heterogeneity of samples. Another application of interest is given with the vulcanization progress during the cooling period after the extraction of the rubber from the mold.

THEORETICAL

Mathematical treatment

The overall rate of cure can be expressed by reaction with a single activation energy E as shown :

$$dQ/dt = k_0 \cdot (Q_\infty - Q_t)^n \cdot \exp{-E/RT} \qquad (1)$$

where Q_t is the heat of cure evolved up to time t , and Q_∞ the total heat for the rubber mass unit.

If a rubber sheet of thickness L is considered, the unidirectional heat flow is expressed by the general equation of transient heat conduction

$$\rho C \frac{dT}{dt} = \underbrace{\frac{d}{dx}\left(\lambda \cdot \frac{dT}{dx}\right)}_{\text{conduction heat}} + \underbrace{\frac{dQ}{dt}}_{\text{reaction heat}} \qquad (2)$$

by taking into account the heat of cure reaction.

Numerical calculation

The problem was solved by using an explicit numerical method with finite differences. The rubber sheet is divided into equal finite slices of thickness Δx. The temperature at the plane n and the time (i + 1). Δt is given as a function of the temperatures at the preceeding time i . Δt by the equation :

$$T_{i+1,n} = \frac{1}{M}\left[T_{i,n-1} + (M-2) \cdot T_{i,n} + T_{i,n+1}\right] + \frac{dQ}{dt} \Delta t \qquad (3)$$

where the dimensionless number M is a function of the increments of time t and space x.

$$M = \frac{(\Delta x)^2}{\Delta t} \cdot \frac{1}{\alpha} \qquad (4)$$

where α is the diffusivity of the rubber.

Eq. 3 is used for calculating the temperature and SOC into the rubber. It must be modified for rubber faces contacting the mold during the heating period (Eq. 5).

$$T_{i+1,\text{rubber face}} = \frac{1}{R+1}\left[R \cdot T_{i,\text{mold face}} + T_{i,1}\right] + \frac{dQ}{dt} \cdot \Delta t \qquad (5)$$

For rubber faces contacting air during the cooling period after the extraction from the mold, we have the following equations :

$$T_{i+1,\text{rubber face}} = \frac{1}{M}\left[2.N.T_a + (M-2-2N) \cdot T_{i,\text{rface}} + T_{i,1}\right] + \frac{dQ}{dt} \cdot \Delta t \qquad (6)$$

where the modulus N is a function of the thermal conductivity of the rubber λ and h is the coefficient of heat transfer at the air-rubber interface. This coefficient is obtained bu using the laws of chemical engineering.

$$N = \frac{h \cdot \Delta x}{\lambda} \qquad (7)$$

RESULTS

Our method of calculation is useful for predicting different kinds of information about the state of cure.

Of course, the profiles of temperature and SOC can be calculated and notably the profiles of the SOC developed through a metal-rubber

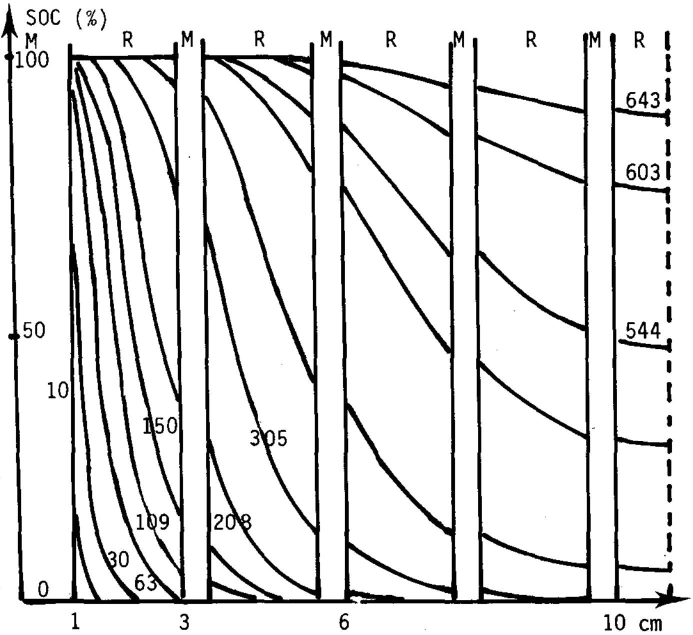

Fig. 1 : SOC through metal-rubber sandwich

sandwich initially at room temperature and submitted at a mold temperature of 170°C (Fig. 1).

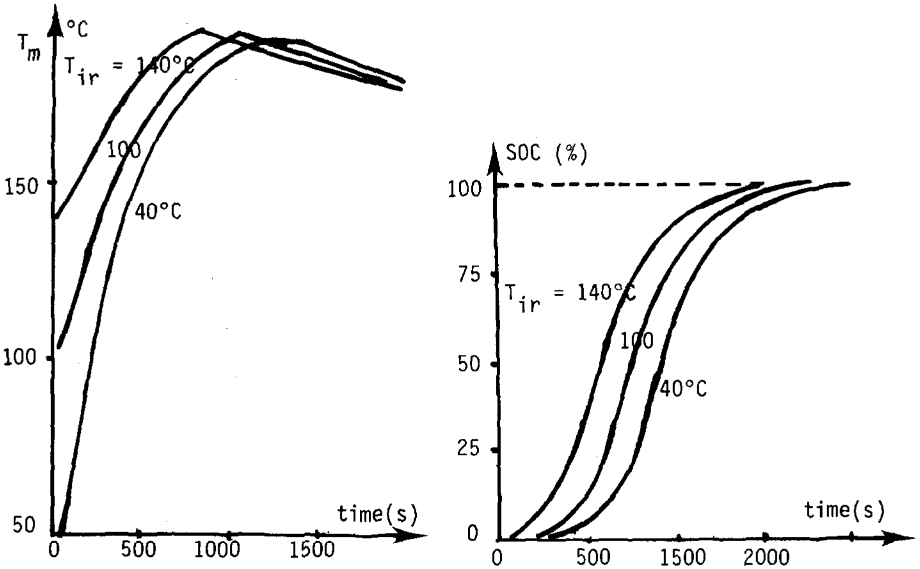

Fig. 2, 3 : Effect of T of injected rubber on T and SOC at the midplane

For injection molding process, the effect of the temperature of injected rubber T_{ir} can be appreciated : in Fig. 2 where the progression of the midplane is shown as a function of T_{ir} ; in Fig. 3 where the SOC at the midplane is shown.

REFERENCES

1 D. Hands and F. Horsfall, RAPRA Report.
2 G.A. Prentice and M.C. Williams, Rubber Chem. Technol., 53 (1980) 1023-1031.
3 S.D. Gehman, Rubber Chem. Technol., 40 (1967) 36.
4 A. Accetta, P. Le Parlouër and J.M. Vergnaud, Termochim. Acta, 59 (1982) 149-156.
5 A. Accetta, G. Gangnet, L. Vincent and J.M. Vergnaud, 3rd Internat. Conf. "Computers and Chemical Engineering", Paris, April 19-21, 1983.
6 A.Y. Coran, in Science and Technology of Rubber, F.R. Eirich ed., Academic Press, New-York, 1978, p. 7.
7 A. Accetta, J.C. David, P. Le Parlouër and J.M. Vergnaud, Internat. Conf. on Rubber, Paris, June 2, 1982.
8 A. Accetta and J.M. Vergnaud, Internat. Conf. on Rubber, Paris, June 2, 1982.
9 A. Accetta, B. Bouzon, A. Sadr and J.M. Vergnaud, J. Chim. Phys. 80 (1983) 691-95.
10 C. Ferradou and J.M. Vergnaud, Thermochim. Acta, 68 (1983) 283-290.
11 A. Sadr, M. Hivert and J.M. Vergnaud, Thermochim. Acta, 71 (1983) 237-245.