

# Study on Kinetic of Natural Rubber Vulcanization by Using Vulcameter

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**ABSTRACT:** The velocity of vulcameter torque change during the vulcanization of natural rubber consists of two increasing and decreasing stages. The vulcanization process in the stage of velocity increasing is not a simple reaction, and can be expressed in an equation of  $\ln(M_H - M_t) = \ln A - K_1(t - t_0)^\alpha$ , which is different from the famous equation of  $V_{ut} = -(aK_3/K_4)\ln[(K_2e^{K_1t} - K_1e^{K_2t})/(K_2 - K_1)]$  deduced by Coran, the value of  $K_1^{1/\alpha}$  in the former can be used as a rate constant to calculate the value of activation energy ( $E_1$ )

according to the Arrhenius equation. The vulcanization process in the stage of velocity decreasing consists of two first-order reactions, and can be expressed in a kinetic equation of  $\ln(M_H - M_t) = \ln B - K(t - t_{dis})$ . The time ( $t_p$ ) at which the torque change reaches to the maximum velocity ( $V_m$ ) is corresponding to the time ( $t_{dis}$ ) suggested by Coran. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 680–684, 2003

**Keywords:** kinetic; rubber; vulcanization; vulcameter

## INTRODUCTION

The kinetic parameters of the vulcanization of rubber can be determined by the analyses of vulcanization curves. The kinetic parameters, in general, are calculated through an assumed reaction order. Coran<sup>1,2</sup> proposed that there exists an induction stage in the vulcanization of natural rubber, which is a process of the formation of crosslink precursors (a reaction product from rubber molecular chains and intermediates of sulfurs, accelerators, and activators). Coran<sup>1,2</sup> also suggested that the vulcanization process after the induction period ( $t_i$ ) be a first-order reaction and can be expressed in a kinetic equation of  $V_{ut} = V_{u\infty} [1 - e^{-k_2(t-t_i)}]$ , but the induction stage can be expressed in an equation of  $V_{ut} = -(aK_3/K_4)\ln[(K_2e^{K_1t} - K_1e^{K_2t})/(K_2 - K_1)]$ . The equations above deduced by Coran have been widely used not only in the kinetic analysis of rubber vulcanization but also in the kinetic analysis of rubber reversion.<sup>3</sup> The works of other authors<sup>4–7</sup> indicated that the vulcanization of natural rubber should consist of two first-order reactions. Through analyzing the vulcameter curves with the theory of molecular rheology, Furukawa<sup>8</sup> proposed that the vulcanization process consists of three stages, which can be expressed in three equations respectively. The S-shaped vulcanization curve of the torque changing with vul-

canization time is an actual reflection of the rubber vulcanization process. In the studies of the vulcanization kinetics of rubbers, as a matter of fact, there exists a considerable discrepancy in the conclusions resulting from the varieties of rubbers and the different vulcanization systems and test methods.<sup>9–11</sup> In this article, the characterization of vulcameter torque change during the vulcanization of natural rubber was studied and the kinetic of vulcanization was analyzed.

## EXPERIMENTAL

### Materials

The natural rubber was commercial Standard Chinese Rubber #5. Other materials were of industrial grade and were not purified.

### Sample preparation and test

The test samples were prepared according to the following formulation and tested by using a LHY-II Vulcameter at 140, 150, 160, and 170°C, respectively. The vulcameter curves were recorded. The procedures were performed in the light of the specifications of the relevant ISO standards.

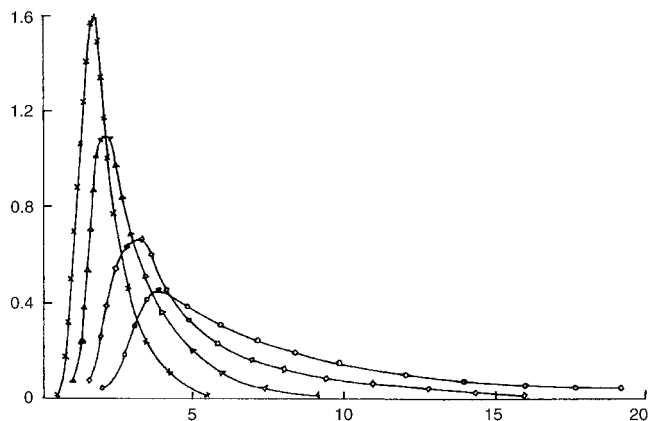
Formulation in per hundred of rubber: natural rubber 100, zinc oxide 5.0, stearic acid 0.5, 2-mercaptobenzothiazole 1.0, sulfur 3.0.

### Calculation of kinetic parameters

The velocity of the torque change was calculated with the cubic spline fitting. All the test data were treated with the SAS program.

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**Figure 1** Relation between the velocity ( $V$ ) of torque change and vulcanization time ( $t$ ).  $V$  is expressed on the vertical axis in  $N \cdot m/min$ .  $t$  is expressed on the horizontal axis in min.  $\circ$ : 140°C;  $\square$ : 150°C;  $\triangle$ : 160°C;  $\times$ : 170°C.

## RESULTS AND DISCUSSION

### Velocity of the vulcameter torque change

In our testes the value of the vulcameter torque change keeps in increasing from the minimum torque ( $M_L$ ) to the maximum torque ( $M_H$ ). The velocity ( $V$ ) of torque change consists of two stages (see Fig. 1). In the first stage the velocity increases and reaches a maximum velocity ( $V_m$ ) within a short time. In the second stage the velocity decreases and trends slowly to zero. The maximum velocity ( $V_m$ ) increases and the time ( $t_p$ ) at which the torque change reaches the maximum velocity ( $V_m$ ) decreases with the increase of the vulcanization temperature (see Table I).

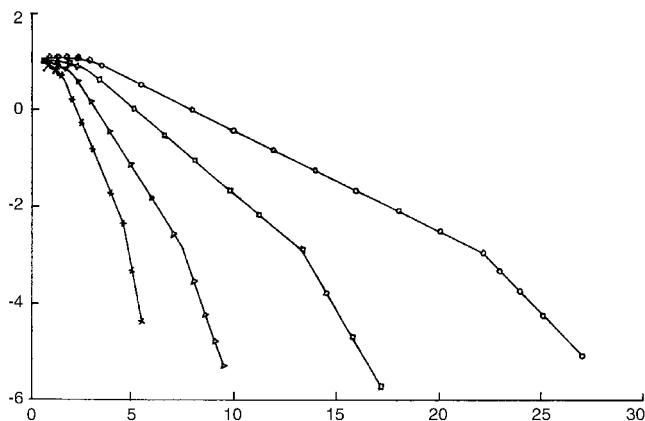
### Kinetic of vulcanization

Because the torque change is proportional to the crosslink density, the rate equation of vulcanization can be expressed in the velocity ( $V$ ) of the torque change.

$$V = -d(M_H - M_t)/dt = K(M_H - M_t)^n \quad (1)$$

where  $M_H$  is the the maximum torque;  $M_t$  is the torque at vulcanization time  $t$ ;  $K$  is the rate constant; and  $n$  is he reaction order.

For a first-order reaction eq. (1) can be written as



**Figure 2** Plots of eq. (2) for the vulcanization of natural rubber at various temperatures.  $\ln(M_H - M_t)$  is expressed on the vertical axis in  $N \cdot m$ .  $t$  is expressed on the horizontal axis in min.  $\circ$ : 140°C;  $\square$ : 150°C;  $\triangle$ : 160°C;  $\times$ : 170°C.

$$\ln(M_H - M_t) = \ln B - Kt \quad (2)$$

A curve and two straight lines are obtained by plotting  $\ln(M_H - M_t)$  against  $t$  (see Fig. 2). By comparing Figure 1 with Figure 2, the time at the cross-point of the curve and straight line is quite the same as  $t_p$ , indicating that the vulcanization stage of velocity increasing is not a first-order reaction. The feature of two straight lines in Figure 2 means that the vulcanization stage of velocity decreasing consists of two first-order reactions with the rate constants of  $K_2$  and  $K_3$ .

A plot of  $\ln V$  against  $\ln(M_H - M_t)$  according to eq. (1) does not show the feature of straight lines (see Fig. 3), indicating that the vulcanization process in the stage of velocity increasing is not a simple reaction. By leading an exponent " $\alpha$ " to the term of time in eq. (2) as a modified coefficient, a suitable equation can be obtained.

$$\ln(M_H - M_t) = \ln A - K_1(t - t_0)^\alpha \quad (3)$$

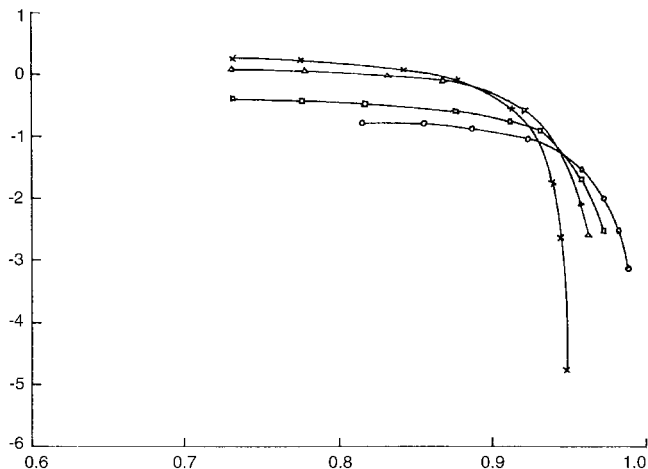
where  $t_0$  is the time for minimum torque  $M_L$ .

Determining the value of  $\alpha$  with the curve fitting, the straight lines are obtained by plotting  $\ln(M_H - M_t)$  against  $(t - t_0)^\alpha$  (see Fig. 4). By comparing eq. (3) with eq. (2), eq. (3) can be rewritten as

$$[\ln(M_H - M_t) - \ln A]^{1/\alpha} = -K_1^{1/\alpha}(t - t_0) \quad (4)$$

**TABLE I**  
Vulcanization Behavior of Natural Rubber at Various Temperatures

$T$ (°C)	$t_0$ (min)	$t_i$ (min)	$t_{dis}$ (min)	$t_p$ (min)	$V_m$ ( $N \cdot m/min$ )	P(%)
140	1.62	3.06	3.79	3.9	0.4465	14.03
150	1.16	2.39	2.98	3.2	0.6678	20.03
160	0.68	1.74	2.16	2.2	1.0978	25.59
170	0.46	1.29	1.56	1.7	1.5831	25.08

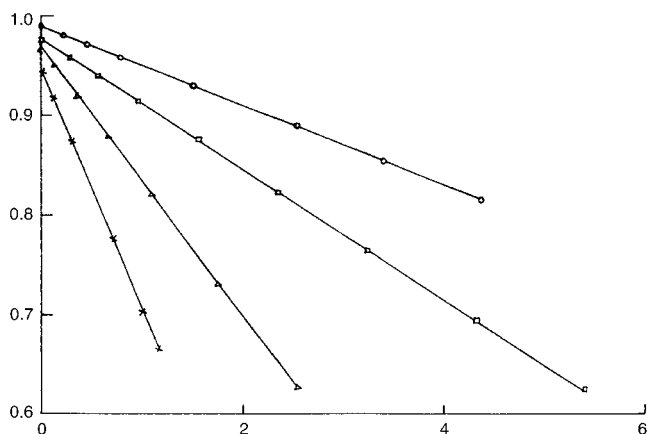


**Figure 3** Plots of  $\ln V$  vs.  $\ln(H_H - M_t)$  according to eq. (1).  $\ln V$  is expressed on the vertical axis in  $N \cdot m/min$ .  $\ln(H_H - M_t)$  is expressed on the horizontal axis in  $N \cdot m$ .  $\circ$ : 140°C;  $\square$ : 150°C;  $\triangle$ : 160°C;  $\times$ : 170°C.

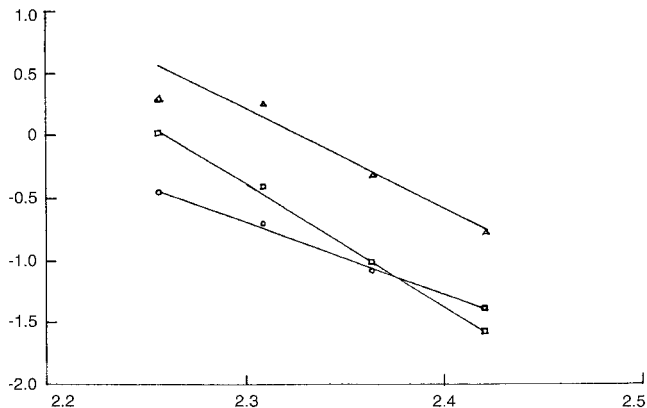
Thus, eq. (4) likes eq. (2) in the form of characterizing the dependence of torque change on vulcanization time and the value of  $K_1^{1/\alpha}$  can be used as a rate constant. A group of straight lines are obtained by plotting  $\ln K_1^{1/\alpha}$ ,  $\ln K_2$  and  $\ln K_3$  against  $1/T$ , respectively, according to the Arrhenius equation (Fig. 5), and the activation energies ( $E_1$ ,  $E_2$ , and  $E_3$ ) can be calculated from the slopes of the straight lines (see Table II).

As shown in Figure 6, Coran<sup>1,2</sup> proposed that the  $t_i$  is the induction time or delay time, and the  $t_{dis}$  is the time at which the accelerators or intermediates react to completion. The value of  $t_{dis}$  can be obtained by the solution of the equation group

$$\ln(M_H - M_t) = \ln A - K_1(t - t_0)^\alpha$$



**Figure 4** Plots of eq. (3) for the vulcanization stage of velocity increasing.  $\ln(H_H - M_t)$  is expressed on the vertical axis in  $N \cdot m/min$ .  $(t - t_0)^\alpha$  is expressed on the horizontal axis in min.  $\circ$ : 140°C;  $\square$ : 150°C;  $\triangle$ : 160°C;  $\times$ : 170°C.



**Figure 5** Relation between  $K$  and  $T$  according to Arrhenius equation.  $\ln K$  is expressed on the vertical axis.  $1/T \times 10^3$  is expressed on the horizontal axis.  $\circ$ : plot of  $\ln(K_1^{1/\alpha})$  vs.  $1/T$ ;  $\square$ : plot of  $\ln K_2$  vs.  $1/T$ ;  $\triangle$ : plot of  $\ln K_3$  vs.  $1/T$ .

$$\ln(M_H - M_t) = \ln B - K_2(t - t_0)$$

The calculated values of  $t_{dis}$  are shown in Table I. Coran<sup>1</sup> deduced an equation of  $V_t = V_\infty [1 - e^{-k(t - t_i)}]$  to express the first order reaction after  $t_i$ . The equation used to analyze the vulcameter curve can be written as follows:

$$\ln(M_H - M_t) = \ln B - K(t - t_i) \tag{5}$$

Although the value of  $t_i$  is very close to the value of  $t_{dis}$  (see Table I and Fig. 6), a curve is still seen from the test data between  $t_i$  and  $t_{dis}$ . By replacing  $t_i$  with the calculated  $t_{dis}$ , an equation that can more properly express the relation between the torque change and the vulcanization time is obtained.

$$\ln(M_H - M_t) = \ln B - K(t - t_{dis}) \tag{6}$$

The curve before  $t_{dis}$  in Figure 6 (or the vulcanization process before  $t_{dis}$ ) can be expressed by eq. (3). The vulcanization curves obtained from different vulcanization temperatures are treated according to eq. (3) and eq. (6), and the results are list as follow.

140°C

$$\ln(M_H - M_t) = 0.9910 - 0.0162(t - 1.62)^{2.9} \quad 3.79 \geq t \geq 1.62$$

$$\ln(M_H - M_t) = 0.8419 - 0.2045(t - 3.79) \quad 22.79 \geq t \geq 3.79$$

$$\ln(M_H - M_t) = 6.2407 - 0.4887(t - 3.79) \quad t \geq 22.79$$

150°C

$$\ln(M_H - M_t) = 0.9775 - 0.0477(t - 1.16)^{2.7} \quad 2.98 \geq t \geq 1.16$$

**TABLE II**  
Kinetic Parameters of the Vulcanization of Natural Rubber at Various Temperatures

T (°C)	$\alpha$ ( $r$ ) <sup>a</sup>	$K_1^{1/\alpha}$	$K_2$	$K_3$	$E_1$ (KJ/mol)	$E_2$ (KJ/mol)	$E_3$ (KJ/mol)
140	2.9 (0.9998)	0.2413	0.2045	0.4887			
150	2.7 (0.9992)	0.3240	0.3548	0.8007	50.356	81.153	56.035
160	3.0 (0.9979)	0.4632	0.6526	1.4184			
170	3.7 (0.9990)	0.6544	1.0064	1.3870			

<sup>a</sup>  $r$  is the correlated coefficient.

$$\ln(M_H - M_t) = 0.7671 - 0.3548(t - 2.98)$$

$$11.59 \geq t \geq 2.98$$

$$\ln(M_H - M_t) = 5.5380 - 0.8007(t - 2.98) \quad t \geq 11.59$$

160°C

$$\ln(M_H - M_t) = 0.9702 - 0.0994(t - 0.68)^{3.0}$$

$$2.16 \geq t \geq 0.68$$

$$\ln(M_H - M_t) = 0.6948 - 0.6526(t - 2.16)$$

$$7.51 \geq t \geq 2.16$$

$$\ln(M_H - M_t) = 4.7927 - 1.4184(t - 2.16) \quad t \geq 7.51$$

170°C

$$\ln(M_H - M_t) = 0.9439 - 0.2083(t - 0.46)^{3.7}$$

$$1.56 \geq t \geq 0.46$$

$$\ln(M_H - M_t) = 0.6720 - 1.0064(t - 1.56)$$

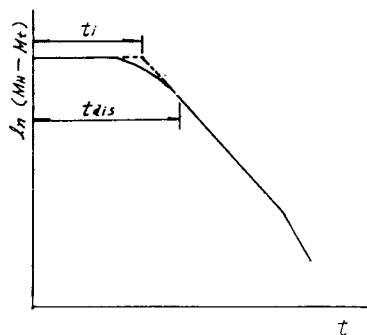
$$3.24 \geq t \geq 1.56$$

$$\ln(M_H - M_t) = 1.3121 - 1.387(t - 1.56) \quad t \geq 3.24$$

The vulcanization degree ( $P$ ) at  $t_{dis}$  can be calculated from the following equation.

$$P = [1 - (M_H - M_t)/(M_H - M_L)] \times 100\% \quad (7)$$

where  $M_L$  is the minimum torque.



**Figure 6** Illustration for  $t_i$  and  $t_{dis}$ .

The values of  $P$  calculated according to eq. (7) are shown in Table I. It depicts that the vulcanization degree ( $P$ ) increases with the increase of the vulcanization temperature in the low temperature range and does not increase but keeps a value of about 25% in the high temperature range.

By comparing  $t_p$  with  $t_{dis}$ , it can be seen that the vulcanization stage of velocity increasing is the stage of the formation of crosslink precursors and the completion of accelerator or intermediate. The increase of torque in the stage should, in fact, be ascribed to the formation of crosslink precursors, or the increase of viscoelasticity. This may be the partial reason why the vulcanization stage of velocity increasing is not of a simple reaction.

### CONCLUSION

The velocity of vulcameter torque change during the vulcanization of natural rubber consists of two stages of velocity increasing and decreasing. The maximum velocity ( $V_m$ ) increases and the time ( $t_p$ ) at which the torque change reaches to  $V_m$  decreases with the increase of vulcanization temperature. The vulcanization stage of velocity increase is not correlated to the rate equation of a simple reaction, and can be expressed in an equation of  $\ln(M_H - M_t) = \ln A - K_1(t - t_0)^\alpha$ . The value of  $K_1^{1/\alpha}$  can be used as a rate constant to calculate the activation energy ( $E_1$ ) according to Arrhenius equation. The time ( $t_p$ ) at which the torque change reaches the maximum velocity ( $V_m$ ) is corresponding to  $t_{dis}$  suggested by Coran. The vulcanization degree ( $P$ ) at  $t_{dis}$  increases with the increase of vulcanization temperature in the low temperature range, and does not increase but keeps at a value of about 25% in the high temperature range. The vulcanization stage of velocity decreasing consists of two first-order reactions with the rate constants ( $K_2$  and  $K_3$ ), and can be more properly expressed in an equation of  $\ln(M_H - M_t) = \ln B - K(t - t_{dis})$ . The value of activation energies ( $E_2$  and  $E_3$ ) are calculated from the rate constants ( $K_2$  and  $K_3$ ) according to Arrhenius equation.

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