

Kinetics of Natural Rubber Vulcanization in the End Stage of Curing Period

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ABSTRACT: It was found that the change of vulcameter torque in the end stage of curing period of natural rubber does not follow first-order kinetics and can be expressed in

a kinetic equation of $\frac{1}{1-n}(M_H - M_t)^{1-n} = C - kt$ ($n \neq 1$).

The reaction order n calculated by the above equation is in the range of 0.68–0.74. The rate constant of the end stage increases with a rise in temperature and is well satisfied with Arrhenius equation, giving activation energy $E = 79.321$

kJ/mol. If whole curing period is treated by first-order kinetics without a change of reaction order from $n = 1$ to $n = 0.68$ – 0.74 , the values of torque in the end stage of curing period predicted with first-order kinetics equation will be lower than that obtained from vulcameter. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 580–583, 2006

Key words: kinetic; end stage; curing period; reaction order; natural rubber

INTRODUCTION

Vulcameter is commonly used in investigation of the kinetics of rubber vulcanization as it can continuously trace the whole process of rubber vulcanization with change in torque. A typical accelerated sulfur vulcanization curve of natural rubber is shown in Figure 1. The curve illustrates three periods of vulcanization process: scorch period or induction period, curing period, and overcure period. During the past years, by investigating the kinetics of rubber vulcanization, some mathematical equations have been deduced to express the vulcanization curve. Coran¹ deduced a famous scorch model well describing the induction period and treated² the curing period with one first-order kinetics equation. Pal and co-workers^{3,4} proposed that the curing period could be treated as two stages expressed in two first-order kinetics equations with different rate constants. Furukawa et al.,⁵ through analyzing the curve with the theory of molecular rheology, suggested that curing period could be expressed in two different equations separately. In kinetics analysis of rubber vulcanization, an important factor cannot be overlooked, which is the effect of "aging" on crosslink as the existence of crosslink shortening, crosslink destruction, and S—S bond in-

terchange.^{6–8} On the basis of this consideration, numerous research workers, including Russell et al.,⁹ Duchacek,¹⁰ Li,^{11–13} Ding and co-workers,^{14,15} and Gong et al.,¹⁶ individually deduced their equations to describe the vulcanization process after induction period.

The rate equation of rubber vulcanization by vulcameter 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 maximum torque, M_t is the torque at vulcanization time t , k is the rate constant and n is the reaction order. For a first-order reaction, eq. (1) can be written as

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

where B is a constant. For a reaction order $n \neq 1$, eq. (1) can be written as

$$\frac{1}{1-n}(M_H - M_t)^{1-n} = C - kt \quad (3)$$

where C is a constant.

The curing period of rubber vulcanization is generally treated with first-order kinetics, but it is always observed that the change of vulcameter torque nearing maximum torque does not follow the first-order kinetics. Although the vulcameter curves are well described by the above equations of researching work-

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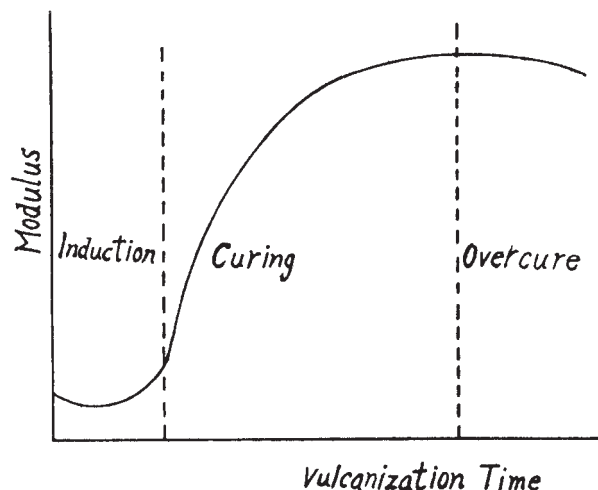


Figure 1 A typical accelerated sulfur vulcanization curve of natural rubber.

ers,⁹⁻¹⁶ our interest here is concentrated on the kinetics which the change of vulcameter torque with vulcanization time follows, especially the change in the end stage of curing period. In this article, the curing period of natural rubber vulcanization was treated as two stages with different reaction orders according to eqs. (2) and (3), for some understanding of the effect of aging on crosslink.

EXPERIMENTAL

Materials

The natural rubber was commercial standard Chinese Rubber no. 5. Other materials were of industrial grade and were not purified.

Samples preparation and test

The formulation is as follows (in parts per hundred of rubber): natural rubber 100.0, sulfur 3.0, zinc oxide 5.0, stearic acid 0.5, and 2-mercaptobenzothiazole 1.0. The stocks were compounded according to Chinese standard GB6038-93 (equivalent to ISO/DIS 2393-1989). The curves of vulcanization were obtained by using LHY-II vulcameter at 140, 150, 160, and 170°C, respectively, according to Chinese standard GB9869-88 (equivalent to ISO 3417-1977).

RESULTS AND DISCUSSION

Reaction order

The vulcameter curves obtained at 140, 150, 160, and 170°C were treated according to eq. (2). The feature of the straight lines and the curves in Figure 2 indicates that the curing period of natural rubber vulcanization

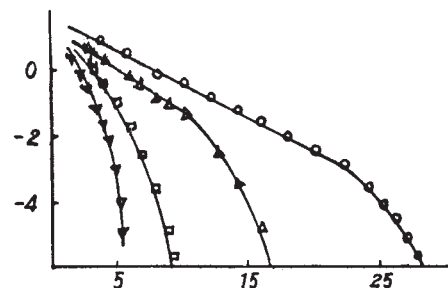


Figure 2 Relation between $\ln(M_H - M_t)$ and t for curing period. $\ln(M_H - M_t)$ is expressed on the vertical in N m, and t is expressed on the horizontal axis in minutes. (○), 140°C; (△), 150°C; ([multi]), 160°C; (□) 170°C.

consists of two stages: stage I follows first-order kinetics and stage II does not. The curves which do not follow first-order kinetics were treated according to eq. (3). The feature of the straight lines in Figure 3 indicates that stage II does follow $n \neq 1$ order kinetics. The values of reaction order n for stage II were calculated by curve fitting and listed in Table I together with the values of k , B , and C in eqs. (2) and (3). The reaction orders of stage II are in the range of 0.68–0.74.

A plot of torque against vulcanization time for the curing period at different vulcanization temperatures is shown in Figure 4, where the points ○ were calculated according to eq. (2), with the values of B and k in Table I, the points △ according to eq. (3), with values of C , k , and n in Table I, and the solid lines were obtained from vulcameter. A comparison of the points ○ and the points △ gives an interesting information that the values of torque in the end stage of curing period predicted with eq. (2) are lower than that predicted with eq. (3) and that the values predicted with eq. (3) are in the solid line obtained from vulcameter. It means that the values of torque in the end stage of curing period will be lower if the increase in torque value continuously follow first-order kinetics through-

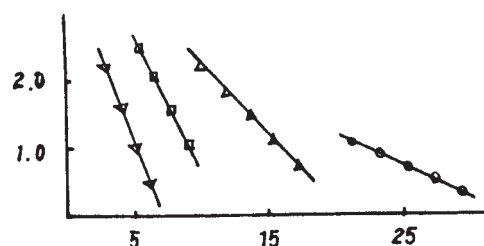


Figure 3 Relation between $\frac{1}{1-n}(M_H - M_t)^{1-n}$ and t for end stage of curing period. $\frac{1}{1-n}(M_H - M_t)^{1-n}$ is expressed on the vertical axis in N m, and t is expressed on the horizontal axis in minutes. (○), 140°C; (△), 150°C; ([multi]), 160°C; (□), 170°C.

TABLE I
Kinetic Parameters of Two Stages

Stage	140°C	150°C	160°C	170°C
$n = 1$				
n	1.00	1.00	1.00	1.00
k	0.2045	0.3546	0.6238	1.0215
B	1.6170	1.8222	1.9851	2.2779
E	81.938			
r_1^a	0.9998	0.9986	0.9999	0.9996
r_2^b	0.9999			
$n \neq 1$				
n	0.74	0.74	0.72	0.68
k	0.1469	0.2467	0.4143	0.7045
C	5.0209	5.0425	4.6541	4.6256
E	79.321			
r_1^a	0.9996	0.9995	0.9994	0.9989
r_2^b	0.9997			

^a r_1 : correlated coefficients of n and k calculated according to eqs. (2) and (3).

^b r_2 : correlated coefficients of E calculated according to Arrhenius equation.

out the curing period, without a change in reaction order in the end stage of curing period.

The theory⁶⁻⁸ generally accepted is that the initially formed networks undergo reaction of crosslink shortening, crosslink destruction, and S—S bond interchange. On the basis of this theory, possible explanation for Figure 4 is that the change of torque nearing maximum torque is controlled by the above reaction. Thus, the change of reaction order from $n = 1$ in stage I to $n \neq 1$ in stage II could be considered as a reflection of the effect of aging on crosslink.

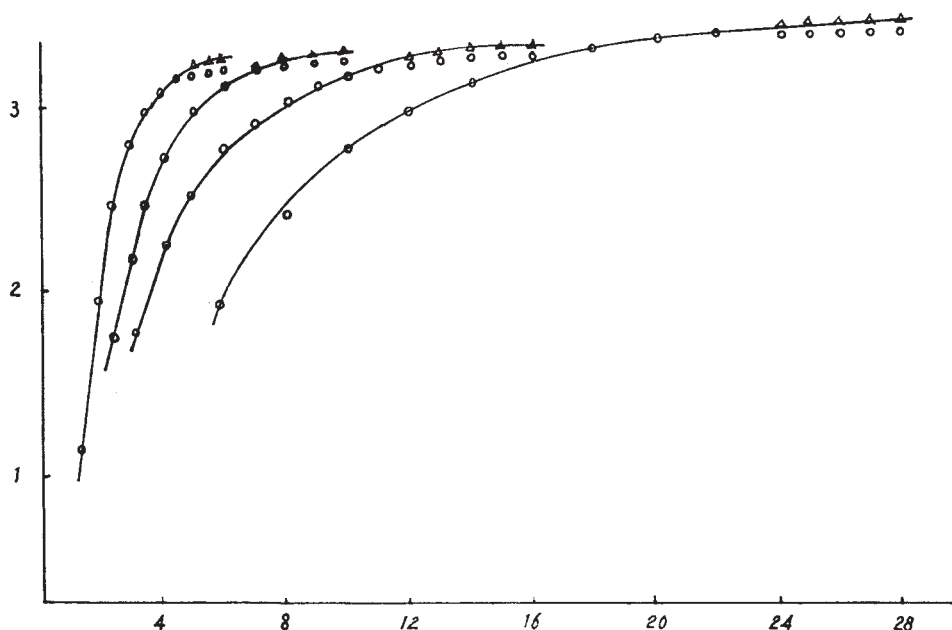


Figure 4 Relation between torque and vulcanization time for curing period. Torque is expressed on the vertical axis in N m, and t is expressed on the horizontal axis in minutes. (O): torque value calculated with eq. (2); (Δ): torque value calculated with eq. (3). Solid line was obtained from vulcameter.

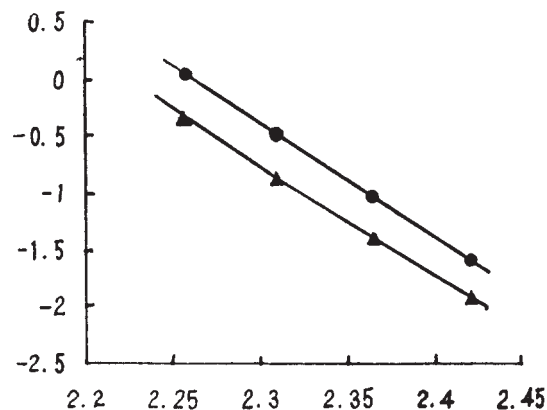


Figure 5 Relation between reaction rate and temperature. $\ln k$ is expressed on the vertical axis. $1/T \times 10^3$ is expressed on the horizontal axis. (O): $n = 1$ stage; (Δ): $n \neq 1$ stage.

Reaction rate and its temperature dependence

The rate constant of the stage following first-order kinetics is faster than that of the stage following $n \neq 1$ order kinetics at the same temperature (Table I). The rate constants increase with a rise of vulcanization temperature. Calculation of activation energy E (81.938 and 79.321 kJ/mol for stage I and stage II, respectively) and Figure 5 show that the rate constants of two stages are well satisfied with Arrhenius equation with very good correlated coefficients of 0.9999 and 0.9997.

CONCLUSIONS

1. The curing period of natural rubber vulcanization can be treated as two stages. Stage I follow

first-order kinetics and stage II follow $n \neq 1$ order kinetics. The value of reaction order for stage II can be calculated by a kinetic equation of $\frac{1}{1-n}(M_H - M_t)^{1-n} = C - kt(n \neq 1)$, resulting in values of reaction order in a range of 0.68–0.74.

2. If whole curing period is treated by first-order kinetics without a change of reaction order from $n = 1$ to $n = 0.68$ – 0.74 , the value of torque in the end stage of curing period predicted with first-order kinetics equation will be lower than that obtained from vulcameter.
3. The rate constant of the stage following first-order kinetics is faster than that of the stage following $n \neq 1$ order kinetics at the same temperature. The rate constants of two stages are well satisfied with Arrhenius equation, and the calculation of activation energy gives values of 81.938 and 79.321 kJ/mol for stage I and stage II, respectively.

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