Vulcanization Kinetics of Low-Protein Natural Rubber with Use of a Vulcameter

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ABSTRACT: Kinetics of vulcanization of low-protein natural rubber (LPNR) was studied with the use of a vulcameter. In the induction period of vulcanization, the time t_0 of LPNR is longer than that of natural rubber (NR), and the temperature dependences of the time t_{dis} and the rate constant $k_1^{1/\alpha}$ of LPNR are greater than that of NR. Both the curing periods of LPNR and NR (except 170°C for LPNR) consist of two stages. The first stage follows first-order reaction. The rate constant k_2 of LPNR in the first stage is substantially the same as that of NR at the same temperature, and so is the activation energy E_2. The second stage (end stage of the curing period) does not follow first-order reaction, and the calculated reaction order n is in the range of 0.67–0.73. Both rate constants of LPNR (except 170°C) and NR at the same temperature are approximately the same, and so is the activation energy E_3. The whole process of curing period for LPNR at 170°C follows $n = 0.7$ order reaction. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 3255–3259, 2007

Key words: kinetics; protein; stage; rubber; vulcanization

INTRODUCTION

The process of rubber vulcanization consists of induction period, curing period, and overcure period, and the kinetics of rubber vulcanization has been studied extensively. Coran[1,2] deduced a famous scorch model to describe induction period, and treated curing period in one first-order kinetic equation. Pal and coworkers[3,4] proposed that curing period could be treated as two stages expressed in two first-order kinetic equations with different rate constants, respectively. Furukawa et al.,[5] through analyzing the vulcanization curve with the theory of molecular rheology, assumed that curing period could be expressed in two different equations, respectively. On consideration of the existence[6–8] of crosslink and aging (crosslink shortening, crosslink destruction, and S—S bond interchange) during the vulcanization, Russell et al.,[9] Duchacek,[10] Li,[11–13] and Gong et al.[14] suggested individually their kinetic equations to describe the vulcanization process, including curing period and overcure period. On the basis of Coran's model, Ding and coworkers[15,16] deduced two modified models to describe the curing and overcure period, one suits for styrene butadiene rubber with a change of equilibrium modulus and another for NR with reversion in overcure.

Wang et al.[17,18] suggested an empirical equation to express induction period, and proposed[19] that the curing period consists of two stages, the first stage following the first-order reaction and the reaction order of the second stage (end stage of the curing period) being $n < 1$. The change in the reaction order from $n = 1$ to $n < 1$ is probably a result from the effect of aging on crosslink.

Low-protein natural rubber (LPNR) is obtained from the preparation of separating the protein absorbed on the particles of natural rubber (NR) latex, with very low content of protein. The curing system used for NR is also suited for LPNR. The end products of LPNR can be especially used in the field of medical treatment.

There is a great difference between the protein contents of LPNR and NR. It is known that the protein in NR will affect the curing rate considerably. Since the curing system used for NR is also suited for LPNR, what we pay close attention to is how the protein would affect the kinetics of LPNR vulcanization.

This article is related to a research on vulcanization kinetics of LPNR with the use of a vulcameter. Our work was limited in the range of induction period and curing period. The test results were compared with that of NR to understand the effect of protein on kinetics of rubber vulcanization.

EXPERIMENTAL

Materials

LPNR was a product from South China Tropical Agricultural Product Processing Research Institute. NR is

Rubber	Nitrogen[a] (%)	Dirt (%)	Volatile matter (%)	Ash (%)
LPNR	0.1	0.03	0.4	0.4
NR	0.4	0.04	0.4	0.4

[a] As an estimation of content of protein in rubber.

a commercial standard Chinese rubber 5#. Other materials were of industrial grade.

The contents of protein and other compositions in LPNR and NR are listed in Table I.

Formulation is as follows (in parts per hundred of rubber): rubber 100.0 phr, sulfur 3.0 phr, stearic acid 0.5 phr, zinc oxide 5.0, phr 2-mercaptobenzothiazole 0.7 phr.

Sample preparation and test

The stocks were compounded according to Chinese standard GB6038-93(equivalent to ISO/DIS 2393-1989).

The vulcanization curves were obtained with the use of a 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

Calculation of kinetic parameters

The induction periods of LPNR and NR are expressed in an empirical equation as[17,18]

$$\ln(M_H - M_t) = A - k_1(t - t_0)^\alpha \qquad (1)$$

where M_H is the maximum torque; M_t is the torque at vulcanization time t, t_0 is the time when minimum torque M_L just begins to increase; A and k_1 are constants, α is a modified coefficient, and $k_1^{1/\alpha}$ is used as the rate constant of induction period.

If the reaction order is $n = 1$, the curing period is expressed with the following equation[17,18]

$$\ln(M_H - M_t) = B - k_2(t - t_0) \qquad (2)$$

where B is a constant; k_2 is the rate constant.

If the reaction order $n \neq 1$, the curing period is expressed in an equation as[19]

$$1/(1 - n)(M_H - M_t)^{1-n} = C - k_3(t - t_0) \qquad (3)$$

where C is a constant; k_3 is the rate constant.

Parameter t_{dis} is the time when accelerators and/or intermediates react to depletion defined by Coran[1,2]. If the curing period after t_{dis} follows first-order reaction, the value of t_{dis} is calculated from the solution of eqs. (1) and (2). If the curing period after t_{dis} does not follow first-order reaction, the value of t_{dis} is calculated from the solution of eqs. (1) and (3).

Activation energy is calculated according to Arrhenius equation.

The calculated kinetic parameters of NR and LPNR are listed in Tables II and III.

Induction period

The induction periods of NR and LPNR are treated in eq. (1). The features of straight lines in Figures 1 and 2 show that both induction periods of NR and LPNR can be described by eq. (1). The values of t_0 in Table II are obtained from vulcanization curves. The longer t_0 of LPNR than that of NR indicates that the deficient protein in rubber gives rise to a delay of the formation of crosslink precursors. In other words, more level of protein in rubber brings about a shorter time of the formation of crosslink precursors. The time t_{dis}, being the time when accelerators and/or intermediates react to depletion, marks the termination of induction period and the beginning of curing period. The time t_{dis} of LPNR is longer than that of NR at 140°C, but shorter than that of NR at 170°C. The effect of protein on the rate constant $k_1^{1/\alpha}$ is similar to its effect on t_{dis}. The rate constant $k_1^{1/\alpha}$ of LPNR at 140°C is lower than

TABLE II
Kinetic Parameters of LPNR and NR in Induction Period

Rubber	T (°C)	α	$k_1^{1/\alpha}$	r^a	E_1(kJ/mol)	r^b	t_0 (min)	t_{dis} (min)
LPNR	140	1.9	0.1471	0.9995			4.3	3.11
	150	1.9	0.2287	0.9999	67.750	0.9996	2.9	2.33
	160	2.3	0.3562	0.9998			1.9	1.72
	170	2.5	0.5606	0.9994			1.4	1.32
NR	140	2.2	0.1709	0.9999			2.3	2.54
	150	2.0	0.2506	0.9999	53.451	0.9998	1.5	1.85
	160	2.0	0.3557	0.9999			1.2	1.65
	170	2.1	0.4904	0.9999			0.8	1.45

[a] Correlated coefficient of a and $k_1^{1/\alpha}$.
[b] Correlated coefficient of E_1.

TABLE III
Kinetic Parameters of LPNR and NR in Curing Period

| Rubber	T (°C)	$n = 1$				$n < 1$				
		k_2	r^a	E_2 (kJ/mol)	r^b	n	k_3	r^a	E_3 (kJ/mol)	r^b
LPNR	140	0.1382	0.9995			0.70	0.1117	0.9997		
	150	0.2465	0.9999	85.061	0.9999	0.68	0.1714	0.9998	65.214	0.9997
	160	0.4343	0.9998			0.70	0.2688	0.9999		
	170					0.70	0.6502	0.9996		
NR	140	0.1380	0.9996			0.67	0.1180	0.9998		
	150	0.2322	0.9989	83.548	0.9995	0.73	0.1691	0.9994	67.875	0.9969
	160	0.4187	0.9996			0.70	0.2818	0.9998		
	170	0.7080	0.9997			0.68	0.4413	0.9998		

[a] Correlated coefficient of k_2 and k_3.
[b] Correlated coefficient of E_2 and E_3.

that of NR, but greater than that of NR at 170°C. The activation energy E_1 (67.750 kJ/mol for LPNR and 53.451 kJ/mol for NR) shows clearly that the deficiency of protein gives rise to an increase in the temperature dependence of reaction rates of LPNR in the induction period.
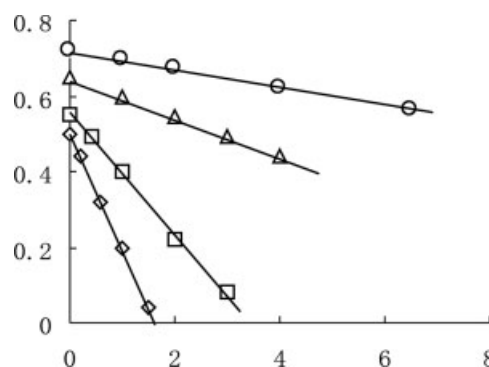
Curing period

The curing periods of NR and LPNR are treated in eq. (2). The features of straight lines and curves in Figure 3 show that the curing period of NR consists of two stages. The first stage follows first-order reaction and the second (the end stage of curing period) does not. The features of straight lines and curves in Figure 4 show that the curing period of LPNR in the range of 140–160°C consists two stages similar to NR. However, treatment of the curing period at 170°C with eq. (2) gives only a curve, indicating that the whole curing period of LPNR at 170°C does not follow first-order reaction completely. The rate constant k_2 of LPNR calculated from the slope of straight line is substantially the same as that of NR at the same tempera-

ture, and so is the activation energy E_2 (83.548 kJ/mol for NR and 85.061 kJ/mol for LPNR). These results show that the protein has no effect on the first-order reaction in the first stage of curing period. The vulcanization process (the curves in Figs. 3 and 4) that do not follow first-order reaction are treated in eq. (3). The features of straight lines in Figures 5 and 6 show that the processes that do not follow first-order reaction do follow $n \neq 1$ order reaction. The calculated reaction order n is in the range of 0.67–0.73. The rate constant k_3 of LPNR in this stage (except 170°C) is substantially the same as that of NR at the same temperature. The activation energy E_3 of NR calculated from k_3 of 140, 150, 160, and 170°C is 67.875 kJ/mol, and E_3 of LPNR from 140, 150, and 160°C is 65.214 kJ/mol. There is no significant difference between them. An interesting problem is why a change of reaction order occurs in the stage of curing period. The general accepted mechanism of NR vulcanization indicates that there exist crosslink and aging (crosslink shortening, crosslink destruction, and S—S bond interchange) during the vulcanization.[6–8] According to the earlier mechanism, the change of reaction order from $n = 1$ in the first stage of curing period to $n < 1$
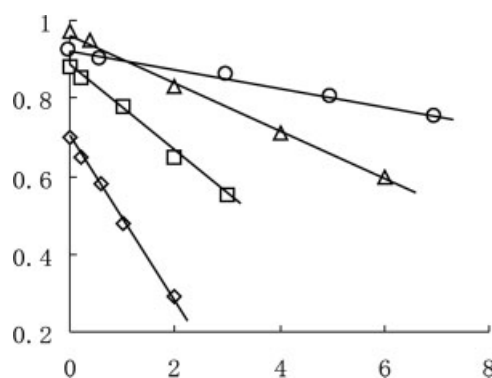
Figure 1 Plots of eq. (1) for induction period of NR. $\ln(M_H - M_t)$ is expressed on the vertical axis in N m. $(t-t_0)^\alpha$ is expressed on the horizontal axis in min. ○: 140°C; △: 150°C; □: 160°C; ◇: 170°C.

Figure 2 Plots of eq. (1) for induction period of LPNR. $\ln(M_H - M_t)$ is expressed on the vertical axis in N m. $(t-t_0)^\alpha$ is expressed on the horizontal axis in min. ○: 140°C; △: 150°C; □: 160°C: ◇: 170°C.
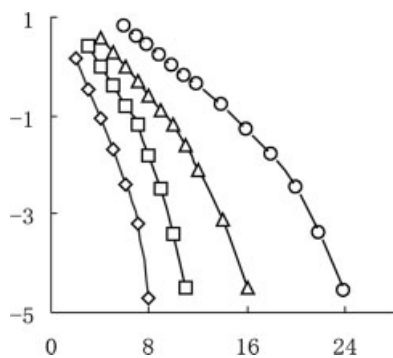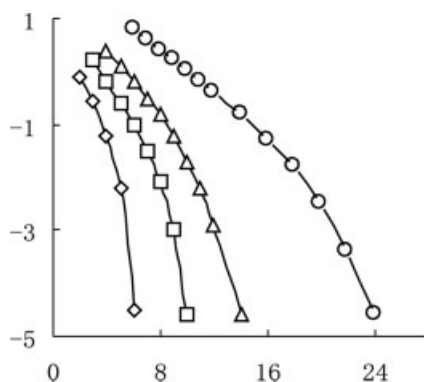
Figure 3 Plots of eq. (2) for curing period of NR. $\ln(M_H - M_t)$ is expressed on the vertical axis in N m. $(t - t_0)$ is expressed on the horizontal axis in min. $\bigcirc$: 140°C; $\triangle$: 150°C; $\square$: 160°C; $\diamond$: 170°C.
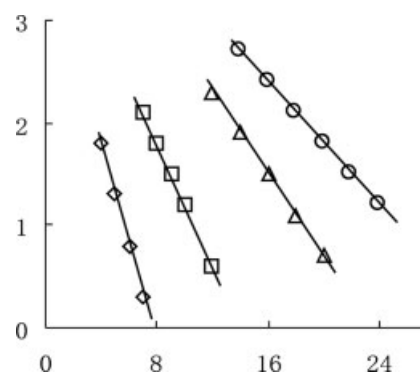
in the second stage (end stage) of curing period is probably a result from the effect of aging (crosslink shortening, crosslink destruction, and S—S bond interchange), although we have not yet determined which type of effect takes main responsibility for the change. As for that the reaction order is $n = 0.70$ in whole curing period of LPNR at 170°C, it may be also proposed that the deficient protein in NR will bring about an effect of aging on crosslink from the beginning of the crosslink reaction at high temperature.

CONCLUSIONS

1. The induction periods of LPNR and NR can be expressed in an equation of $\ln(M_H - M_t) = A - k_1 (t - t_0)^\alpha$. The value t_0 of LPNR is longer than that of NR. The time t_{dis} of LPNR is longer than that of NR at lower temperature but shorter than that of NR at 170°C. The rate constant $k_1^{1/\alpha}$ of LPNR is slower than that of NR at lower temperature but faster than that of NR at 170°C. The activation energy of LPNR is greater than that of NR.
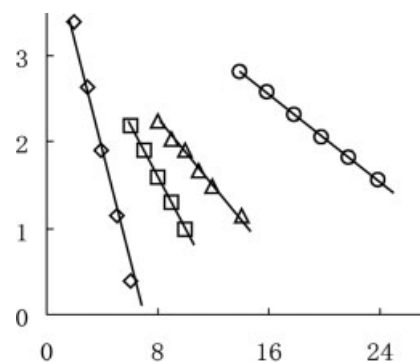

Figure 4 Plots of eq. (2) for curing period of LPNR. $\ln(M_H - M_t)$ is expressed on the vertical axis in N m. $(t - t_0)$ is expressed on the horizontal axis in min. $\bigcirc$: 140°C; $\triangle$: 150°C; $\square$: 160°C; $\diamond$: 170°C.

Figure 5 Plots of eq. (3) for end stage of curing NR. $1/(1 - n)(M_H - M_t)^{1-n}$ is expressed on the vertical axis in N m. $(t - t_0)$ is expressed on the horizontal axis in min. $\bigcirc$: 140°C; $\triangle$: 150°C; $\square$: 160°C; $\diamond$: 170°C.

2. The curing periods of LPNR (except 170°C) and NR consist of two stages. The first stage follows first-order reaction and can be expressed in an equation of $\ln(M_H - M_t) = B - k_2(t - t_0)$. The second stage (the end stage of curing period) does not follow first-order reaction and can be expressed in an equation of $1/(1 - n) (M_H - M_t)^{1-n} = C - k_3 (t - t_0)$, and the reaction order is in the range of 0.67–0.73. The rate constants k_2 of the first stage for LPNR and NR at the same temperature are proximately the same, and so are the rate constants k_3 of the second stages. The activation energy E_2 of LPNR (85.061 kJ/mol) in the first stage is substantially the same as that of NR (83.548 kJ/mol). The activation energy E_3 of LPNR (65.214 kJ/mol) in the second stage is also substantially the same as that of NR (67.875 kJ/mol).
3. The whole process of curing period for LPNR at 170°C does not follow first-order reaction and can be expressed in an equation of $1/(1 - n) (M_H - M_t)^{1-n} = C - k_3 (t - t_0)$. The calculated reaction order is $n = 0.7$.

Figure 6 Plots of eq. (3) for end stage of curing period of period of LPNR. $1/(1 - n)(M_H - M_t)^{1-n}$ is expressed on the vertical axis in N m. $(t - t_0)$ is expressed on the horizontal axis in min. $\bigcirc$: 140°C; $\triangle$: 150°C; $\square$: 160°C; $\diamond$: 170°C.

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