

Effect of Non-Rubber Substances on Vulcanization Kinetics of Natural Rubber

Wang Ping-Yue, Wang Yong-Zhou, Zhang Bei-Long, Huang Hong-Hai

Ministry of Agriculture Key Laboratory of Tropical Crops Processing, Agricultural Product Processing Research Institute, Chinese Academy of Tropical Agricultural Sciences, Zhanjiang 524001, People's Republic of China

Received 15 September 2011; accepted 19 January 2012

DOI 10.1002/app.36851

Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Effect of non-rubber components on vulcanization kinetics of natural rubber was studied with the use of a Rheometer MDR-2000. The results show that the rate constants of induction period and curing period of natural rubber (NR) are greater than that of natural rubber extracted with acetone (NR_E), and the activation energies of induction period and curing period of NR are lower than that of NR_E. The activation energy of induction pe-

riod of NR is reduced by 16.9% and the activation energy of curing period of NR is reduced by 3.2% compared to the activation energies of NR_E. The time t_{dis} of NR is shorter than that of NR_E at the same temperature. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: natural rubber; kinetics; non-rubber substances; rate constant; activation energy

INTRODUCTION

The kinetics of rubber vulcanization has been studied extensively during the past years. The process of rubber vulcanization consists of induction period, curing period, and overcure period. If the induction period and the curing period of natural rubber (NR) are treated with first-order kinetic equation of $\ln(M_H - M_t) = \ln A - k(t - t_0)$, it can be seen from Figure 1 that the curing period (except the end stage of curing period) follows first-order kinetic equation, but the induction period and the end stage of curing period do not follow first-order kinetic equation. Coran¹ deduced a famous scorch model well describing the induction period and treated² the curing period with one first-order kinetic equation. Pal et al.^{3,4} proposed that the curing period could be treated as two stages expressed in two first-order kinetic equations with different rate constants. Furukawa et al.,⁵ by analyzing the curve with the theory of molecular rheology suggested that curing period could be expressed in two different equations separately. In kinetic 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 interchange.^{6–8} On the basis of this consideration, numerous research workers, including Russell et al.,⁹ Duchacek,¹⁰ Li,^{11–13} Ding et al.,^{14,15} and Gong et al.¹⁶ individually deduced their equations to describe the vulcanization process after induction period. Wang et al.^{17,18} suggested an empirical equation to express induction period, and proposed¹⁹ 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. NR is made from fresh NR latex through coagulation and processing. In the production of NR, the coagulation of fresh NR latex is an important process step. The microbial coagulation and acid coagulation are commonly used two main methods to coagulate fresh NR latex. Wang et al.²⁰ studied the effects of the two coagulation methods on vulcanization kinetics of NR and came to a conclusion that the rate constants of induction period and curing period of NR coagulated by microorganisms are greater than that of NR coagulated by acid.

NR is a polymer containing about 95% *cis*-1,4-polyisoprene and 5% non-rubber substances such as organic acids, lipids, carbohydrates, proteins, and so on. It is known that non-rubber substances have significant effects on the properties of NR.^{21–23} However, no report is available on the effects of non-rubber substances on vulcanization kinetics of NR.

In our work, NR was extracted with acetone, and the effect of non-rubber components on vulcanization kinetics of NR was studied by a Rheometer

Correspondence to: W. Yong-Zhou (wyz011120@yahoo.com.cn).

Contract grant sponsor: National Natural Science Foundation of P. R. China; contract grant number: 50963006.

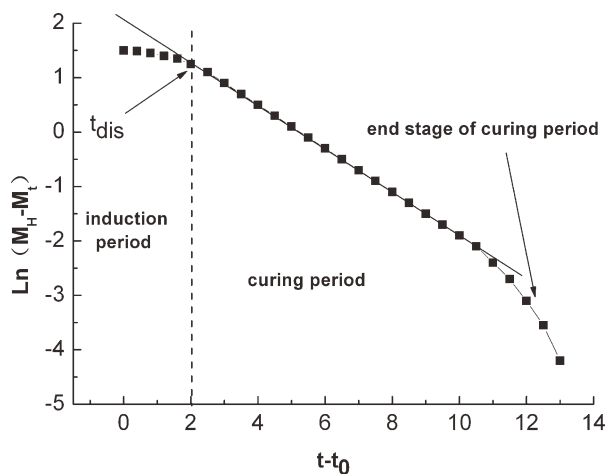


Figure 1 Illustration for induction period, curing period, end stage of curing period, and t_{dis} .

MDR-2000 by comparing the vulcanization kinetic parameters of extracted natural rubber (NR_E) and NR without extract. The discussions in this article are limited to the range of induction period and curing period following first-order kinetics, for some understanding of the effect of the non-rubber components on the vulcanization kinetics of NR.

EXPERIMENTALS

Materials

The NR was commercial Standard Chinese Rubber no. 5 produced by China Hainan Rubber Industry Group (Haikou City, Hainan Province, P.R. China).

Acetone was of chemical grade. Sulfur, zinc oxide, stearic acid, and 2-mercaptobenzothiazole were of industrial grade and were not purified.

Samples preparation and test

Raw NR was cut into about 1-mm thick slices, then the slices were extracted with acetone at 60°C for 24 h. The extracted slices were dried in convulsions cabinet to constant weight.

The formulation is as follows (in parts per hundred of rubber): NR 100.0, sulfur 3.5, zinc oxide 6.0, stearic acid 0.5, and 2-mercaptobenzothiazole 0.5.

The stocks were compounded according to ISO1658:2009 NR-evaluation procedure.

The curves of vulcanization were obtained by using a Rheometer MDR-2000 at 140, 150, 160, and 170°C, respectively.

RESULTS AND DISCUSSION

Calculations of kinetic parameters

The induction periods of NR and NR_E are treated with an empirical equation^{17,18,20} of

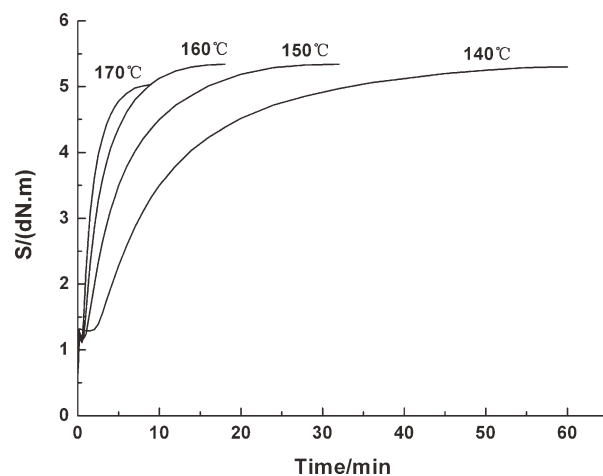


Figure 2 Original rheometer curves of NR

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

where M_H is the maximum torque; M_t is the torque at vulcanization time t , t_0 is the time for minimum torque M_L , which 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.

The curing periods of NR_E and NR are treated with first-order equation of

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

where k_2 is a rate constant and B is constant.

The activation energy is calculated according to the Arrhenius equation

$$\ln k = \ln Z - E/RT \quad (3)$$

The time t_{dis} corresponding to the tangent point of the curve and the straight line in Figure 1 can be obtained from the solution of the equation group^{17,18}

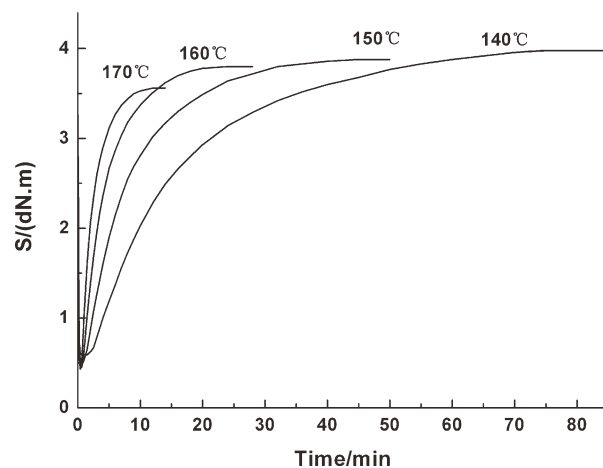


Figure 3 Original rheometer curves of NR_E.

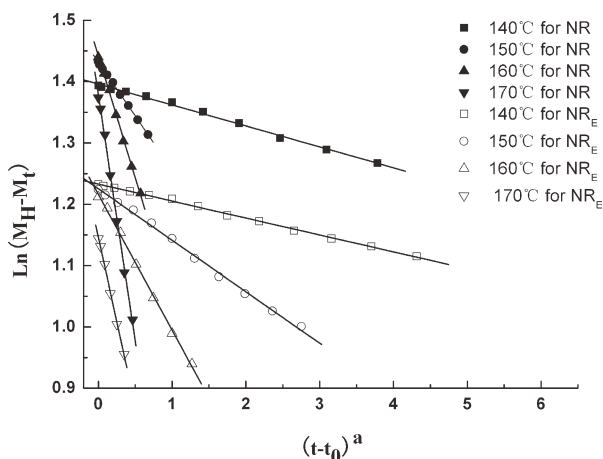


Figure 4 Relation between $\ln(M_H - M_t)$ and $(t - t_0)^\alpha$ for induction period.

$$\ln(M_H - M_t) = \ln A - k_1(t - t_0)^\alpha \quad (4)$$

$$\ln(M_H - M_t) = \ln A - k_2(t - t_0) \quad (5)$$

Effect on rate constant

Figures 2 and 3 are the original rheometer curves of NR and NR_E, respectively. It can be seen intuitively from Figures 2 and 3 that the curing rate of NR is faster than that of NR_E. The induction periods of NR_E and NR are treated with eq. (1), and the plots of $\ln(M_H - M_t)$ against $(t - t_0)^\alpha$ according to eq. (1) for induction periods of NR_E and NR are shown in Figure 4. The curing periods of NR_E and NR are treated with eq. (2), and the plots of $\ln(M_H - M_t)$ against $(t - t_0)$ according to eq. (2) for curing periods (except the end stage of curing period) of NR_E and NR are shown in Figure 5. The feature of the straight lines in Figures 4 and 5 indicates that both induction periods of NR_E and NR can be described well by eq. (1) and both curing periods (except the end stage of curing period) of NR_E and NR can be described well by first-order equation. The calculated rate constants $k_1^{1/\alpha}$ of induction periods and the calculated rate constants k_2 of curing periods

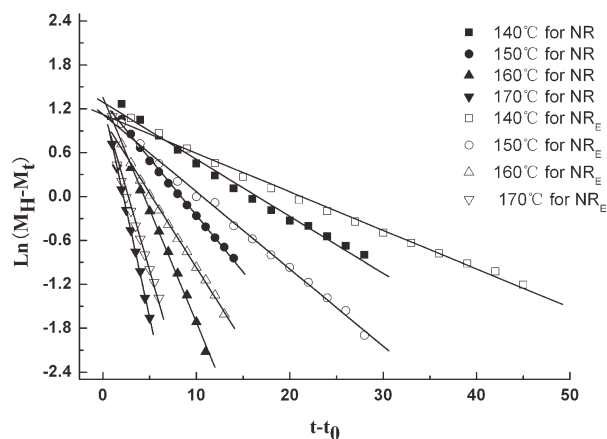


Figure 5 Relation between $\ln(M_H - M_t)$ and $(t - t_0)$ for curing period except the end stage of curing period.

(except the end stage of curing period) are presented in Table I. It can be seen from the data in Table I that the rate constant $k_1^{1/\alpha}$ of induction period of NR is greater than that of NR_E at the same temperature, and so is the rate constants k_2 of curing period (except the end stage of curing period). It means that non-rubber components can accelerate the reaction rate of NR.

Effect on activation energy

The calculated rate constants in Table I are treated with Arrhenius equation as shown in Figure 6. The feature of the straight lines in Figure 6 indicates that the relation between reaction rate and reaction temperature for the induction periods and curing periods (except the end stage of curing period) of NR_E and NR can be described well by Arrhenius equation. The calculated activation energies are also presented in Table I. It is shown that the activation energy 96.135 kJ/mol of induction period of NR_E is obviously greater than the activation energy 79.879 kJ/mol of induction period of NR, and that the activation energy 104.237 kJ/mol of curing period (except the end stage of curing period) of NR_E is a slightly greater than the activation energy 100.892

TABLE I
The Calculated Kinetics Parameters of NR and NR_E

Sample	T (°C)	a	$K_1^{1/a}$	r_1	K_2	r_2	t_{dis} (min)	E_1 (kJ/mol)	r_1	E_2 (kJ/mol)	r_2
NR	140	1.92	0.1722	0.998	0.0810	0.996	3.40	79.88	0.991	100.89	0.999
	150	1.76	0.3671	0.999	0.1506	0.999	1.71				
	160	1.56	0.5531	0.999	0.3014	0.999	1.04				
	170	1.50	0.8627	0.999	0.5884	0.999	0.77				
NR _E	140	1.51	0.1017	0.998	0.0509	0.999	6.39	96.14	0.993	104.24	0.999
	150	1.22	0.1629	0.998	0.0996	0.999	4.18				
	160	1.31	0.3165	0.999	0.1977	0.999	2.27				
	170	1.51	0.6746	0.999	0.3989	0.999	0.97				

(r_1 correlated coefficient of $K_1^{1/a}$ and E_1 ; r_2 correlated coefficient of K_2 and E_2).

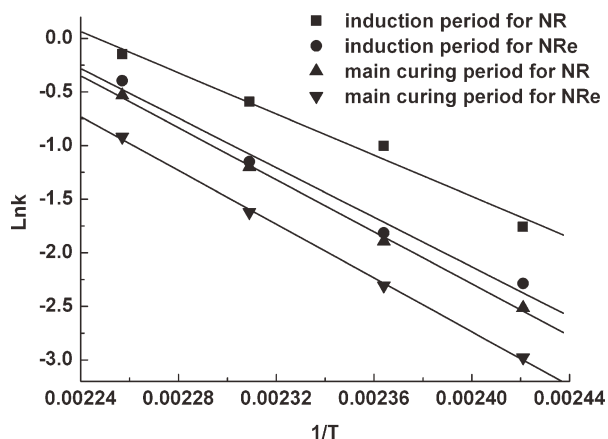


Figure 6 Relation between rate constant and temperature.

kJ/mol of curing period (except the end stage of curing period) of NR. It means that the existence of non-rubber components gives rise to a decrease in the temperature dependence of reaction rates of NR. The data in Table I also show that the activation energy of induction period of NR is reduced by 16.9% and the activation energy of curing period (except the end stage of curing period) of NR is reduced only by 3.2% compared to the activation energies of NR_E. It is indicated that the effect of non-rubber components on induction period is obviously greater than that of curing period.

Effect on the time t_{dis}

The concept of vulcanization intermediates or crosslink precursors formed in the initial stage of NR vulcanization is generally accepted and confirmed experimentally.^{24–27} The time t_{dis} , being the time when accelerators and/or intermediates react to depletion defined by Coran,^{1,2} marks the termination of induction period and the beginning of curing period. The values of t_{dis} are calculated with the solution of the equation group

$$\ln(M_H - M_t) = \ln A - k_1(t - t_0)^{\alpha}$$

$$\ln(M_H - M_t) = \ln A - k_2(t - t_0)$$

and are listed in Table I. It is clear that the time t_{dis} shorten with the increase in curing temperature and the time t_{dis} of NR is shorter than that of NR_E at the same temperature. The shorter time t_{dis} of NR means that the termination of induction period of NR is faster than that of NR_E. It may be assumed that the non-rubber components promote the reaction of accelerators and/or intermediates in induction period of NR vulcanization. It is known²⁸ that the content of non-rubber substances which is extracted by acetone is about 3% of dry NR and the non-rubber

substances extracted by acetone are tocotrienol, fatty acid, and phospholipids. The main compositions in the phospholipids which is extracted by acetone are cephalin and lipositol. The tocotrienol is a natural anti-ager for NR, the fatty acid is a natural plasticizer for NR processing, and the phospholipids is a natural accelerator for vulcanization. A possible interpretation for the effect of non-rubber substances on the vulcanization kinetics of NR may be the phospholipids promoting the formation of vulcanization intermediates or crosslink precursors in the initial stage of NR vulcanization.

CONCLUSIONS

The rate constants of induction period and curing period (except the end stage of curing period) of NR is greater than that of NR_E, and the activation energies of induction period and curing period (except the end stage of curing period) of NR is lower than that of NR_E. The activation energy of induction period of NR is reduced by 16.9% and the activation energy of curing period (except the end stage of curing period) of NR is reduced only by 3.2% compared to the activation energies of NR_E. The time t_{dis} of NR is shorter than that of NR_E at the same temperature. The changes of the kinetics parameters indicate that non-rubber components play a significant role in promoting the reaction rate of NR vulcanization, particularly in promoting the reaction rate of induction period.

References

1. Coran, A. Y. *Rubber Chem Technol* 1964, 37, 689.
2. Coran, A. Y. *Rubber Chem Technol* 1964, 37, 679.
3. Pal, D.; Basu, D. K. *Kautsch Gummi Kunstst* 1983, 36, 358.
4. Pal, D.; Adhikari, B.; Basu, D. K.; Chaudhuri, A. K. *Kautsch Gummi Kunstst* 1983, 36, 859.
5. Furukawa, J.; Onouchi, Y.; Inagaki, S.; Okamoto, H. *Plast Rubber Process Appl* 1981, 1, 173.
6. Bateman, L.; Moore, C. G.; Porter, M.; Saville B. In *The Chemistry and Physics of Rubber-Like Substances*; Bateman L., Ed.; Maclaren: London, 1963; Chapter 15.
7. Morrison, N. J.; Dorte, M. *Rubber Chem Technol* 1984, 57, 63.
8. Krejsa, M. R.; Koenig J. L. *Rubber Chem Technol* 1993, 66, 376.
9. Russell, R.; Smith, D. A.; Welding G. N. *Rubber Chem Technol* 1963, 36, 835.
10. Duchacek, V *J Appl Polym Sci* 1971, 15, 2079.
11. Li, Y. J. *China Synth Rubber Ind* 1995, 18, 28.
12. Li, Y. J. *China Synth Rubber Ind* 1995, 18, 168.
13. Li, Y. J. *China Synth Rubber Ind* 1997, 20, 108.
14. Ding, R.; Leonov, A. I.; Coran, A. Y. *Rubber Chem Technol* 1996, 69, 81.
15. Ding, R.; Leonov, A. I. *J Appl Polym Sci* 1996, 61, 455.
16. Gong, P.; Zhang, X. F.; Zhang, Y. X. *China Synth Rubber Ind* 1997, 4, 195.
17. Wang, P. Y.; Qian, H. L.; Yu, H. P.; Chen, J. *J Appl Polym Sci* 2003, 88, 680.
18. Wang, P. Y.; Qian, H. L.; Yu, H. P. *J Appl Polym Sci* 2004, 92, 3260.

19. Wang, P. Y.; Qian, H. L.; Yu, H. P. *J Appl Polym Sci* 2006, 101, 580.
20. Wang, Z. F.; Li, S. D.; She, X. D. *Adv Mater Res* 2011, 160–162, 1181 (Online available since 2010/Nov/11 at www.scientific.net).
21. Zeng, Y.; Wang D.; Ji, B. R.; Zhang, Zh. Q. *China Rubber Ind* 1999, 1, 26.
22. Li, P. W.; Chen, Y., Xu, K.; Yang, Ch. L.; Chen, X. G. *World Rubber Ind (China)* 2004, 8, 5.
23. Chen, Y.Y.; Zhao, T. J.; Fu, X. *China Elastomer* 2010, 2, 36.
24. Campbell, R. H.; Wise, R. W. *Rubber Chem Technol* 1964, 37, 635.
25. Campbell, R. H.; Wise, R. W. *Rubber Chem Technol* 1964, 37, 650.
26. Morrison, N. J. *Rubber Chem Technol* 1984, 57, 86.
27. Morrison, N. J. *Rubber Chem Technol* 1984, 57, 97.
28. Yuan, Z. C., Qian, H. A. *Properties of Natural Rubber Latex & Commercial Latex Technology*; Agriculture Press: Beijing, China, 1990; Chapter 1, p 23.