

## Study on Vulcanization Kinetics of Constant Viscosity Natural Rubber by Using a Rheometer MDR2000

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**ABSTRACT:** Vulcanization kinetics of constant viscosity natural rubber (CVNR) prepared with hydroxylamine hydrochloride was studied by using a Rheometer MDR2000. The results show that the first stage of curing period follows first-order reaction, but the induction period and the end stage of curing period does not. The calculated reaction order  $n$  of the end stage of curing period of CVNR is in the range of 0.01–0.52, and that of natural rubber (NR) is in the range of 0.38–0.66. The reaction orders of the end stages of curing periods of CVNR and NR increase with increasing curing temperature, and the reaction order of the end stage of curing period of CVNR is smaller than that of NR at the same temperature. The rate constants of the induction period, the first stage of curing period and the end stage of curing period of CVNR are smaller than that of NR at the same temperature. The activation energies of the induction period, the first stage of curing period and the end stage of curing period of CVNR are greater than that of NR. The activation energy of the induction period of CVNR is increased by 13.52%, the activation energy of the first stage curing period of CVNR is increased by 3.95%, and the activation energy of the end stage of curing period of CVNR is increased by 1.60% compared with the activation energies of NR. The time  $t_{dis}$  of CVNR is longer than that of NR at the same temperature. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 47–53, 2013

**KEYWORDS:** rubber; kinetics; crosslinking; ageing

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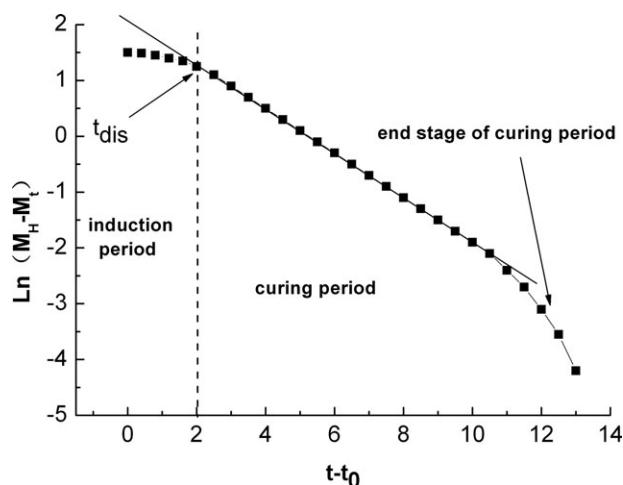
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### INTRODUCTION

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 kinetics equation of  $\ln(M_H - M_t) = \ln B - k(t - t_0)$ , it can be seen from Figure 1 that the induction period does not follow first order kinetics equation. The curing period consists of two stages, the first stage of curing period follows first order kinetics equation, but the second stage (end stage of curing period) does not follow first order kinetics equation. Since Coran<sup>1</sup> deduced a famous scorch model well describing the induction period and treated<sup>2</sup> the curing period with one first order kinetics equation, the kinetics of rubber vulcanization has been studied extensively. Pal et al.<sup>3,4</sup> and Furukawa et al.<sup>5</sup> treated the curing period as two stages, which is expressed in two different equations separately. It is known<sup>6–8</sup> that curing and “aging” (crosslink shortening, crosslink destruction and S–S bond interchange) exist during vulcanization. On the basis of the consideration of the effect of “aging” on vulcanization kinetics, Russell et al.,<sup>9</sup> Duchacek,<sup>10</sup> Li,<sup>11–13</sup> Ding et al.,<sup>14,15</sup> and Gong et al.<sup>16</sup>

individually deduced their equations to describe the vulcanization process after induction period. Wang et al.<sup>17,18</sup> suggested an empirical equation to express induction period, and proposed<sup>19</sup> 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 coagulating and processing. The coagulation of fresh NR latex is an important process step in the production of NR. The microbial-coagulation and acid-coagulation are commonly used two main methods to coagulate fresh NR latex. Wang et al.<sup>20</sup> 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% nonrubber substances. It is known that nonrubber substances have significant effects on the properties of NR.<sup>21–23</sup> Wang et al.<sup>24</sup> found



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

recently that the nonrubber substances play a significant role in promoting the reaction rate of NR vulcanization, particularly in promoting the reaction rate of induction period.

The vulcanization kinetics is great significance not only for theory study on rubber curing but also for production in rubber industry. The detailed understanding of curing mechanism and the vulcanization kinetics parameters can be obtained through study of vulcanization kinetics. The mechanical properties of rubber end product are closely relative to curing condition including curing temperature and curing time, and the choice of curing temperature and curing time will directly influence the mechanical properties and the cost of final end product. The curing mechanism and the vulcanization kinetics parameters contribute to the correct choice of curing temperature and curing time. Liu et al.<sup>25</sup> studied the curing kinetics of epoxy-cyclohexyl POSS/HXNBR with use of DSC method by the multiple-heating-rate model and the single-heating-rate model. They found that the activation energy obtained by the multiple-heating-rate models was dependence on the POSS content and the heating rate, and the activation energy obtained by the single-heating-rate model was also dependence on the heating rate. Sapkota et al.<sup>26</sup> studied the influence of nanoclay-carbon black hybrid fillers on cure of natural rubber compounds by using an Advanced Polymer Analyzer 2000 with autocatalytic model. They found that the activation energy of the networking process was decreased significantly with the addition of clay. They took the lower activation energy as an indicator of the ease of the crosslinking process. Roj et al.<sup>27</sup> studied the curing kinetics of NR/EMMT nanocomposites by using a rubber processing analyzer Scarabaeus SIS-V50 with autocatalytic model. They found that the activation energy of the curing reaction of NR was decreased in the presence of both OMMT and EMMT. They took the activation energy as an indicator for the energy required for the curing process. The lower energy required for the curing process means the less cost of the end product.

Mooney viscosity of NR will increase during storage, and that of CVNR is stability relatively. The Mooney viscosity of CVNR

containing hydroxylamine hydrochloride increases from 50.6 to 51.7 90days later storage at room temperature, but the Mooney viscosity of NR increases from 76.4 to 81.6.<sup>28</sup> The unpublished test results of authors show that the tensile strength and the elongation at break of vulcanizate of CVNR prepared with hydroxylamine hydrochloride after hot oxygen aging are higher than that of natural rubber after hot oxygen aging, and the thermal oxidation activation energy of the raw CVNR obtained with Differential Scanning Calorimeter DSC-220 (Seiko Instruments Inc) is also higher than that of raw NR.

CVNR is prepared by the method of adding viscosity stabilizer into fresh NR latex. The CVNR with difference Mooney viscosity can be obtained through adding various viscosity stabilizers. For example<sup>28</sup> CVNR with low Mooney viscosity can be obtained through adding hydroxylamine hydrochloride or hydroxylammonium sulfate, CVNR with medium Mooney viscosity can be obtained through adding aniline or semicarbazide hydrochloride, CVNR with high Mooney viscosity can be obtained through adding aniline or hydrazine hydrate.

CVNR is prepared with the same natural rubber latex and the same production method of coagulating and processing as that of NR, so the molecular structures of CVNR and NR are similar. The main difference between NR and CVNR is that CVNR contains hydroxylamine hydrochloride and NR does not. Plenty of paper has reported the vulcanization kinetics of NR, and the properties<sup>28–30</sup> of CVNR, such as Mooney viscosity, molecular weight, molecular weight distribution and dynamic mechanical behaviors have been studied, but no paper is available about the effect of hydroxylamine hydrochloride on the vulcanization kinetics of NR in the range of knowledge of authors. In this work CVNR was prepared with 0.05% of hydroxylamine hydrochloride. The vulcanization kinetics of CVNR was studied by a Rheometer MDR-2000 through comparing the vulcanization kinetic parameters of NR, for some understanding how hydroxylamine hydrochloride will affect the vulcanization kinetics of natural rubber.

## EXPERIMENTAL

### Materials

Fresh NR latex was used to prepare CVNR and NR, and was obtained from Mengpeng Farm in Yunnan province of P.R. China.

Viscosity stabilizer hydroxylamine hydrochloride was of chemical grade. Sulfur, zinc oxide, stearic acid, and 2-mercaptobenzothiazole were of industrial grade and were not purified.

### Samples Preparation and Test

CVNR with 0.05% of hydroxylamine hydrochloride and NR were prepared<sup>28</sup> with microbial-coagulation technology by authors of this article.

The formulation is as follows (in parts per hundred of rubber): rubber 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 Natural Rubber (NR) — Evaluation Procedure.

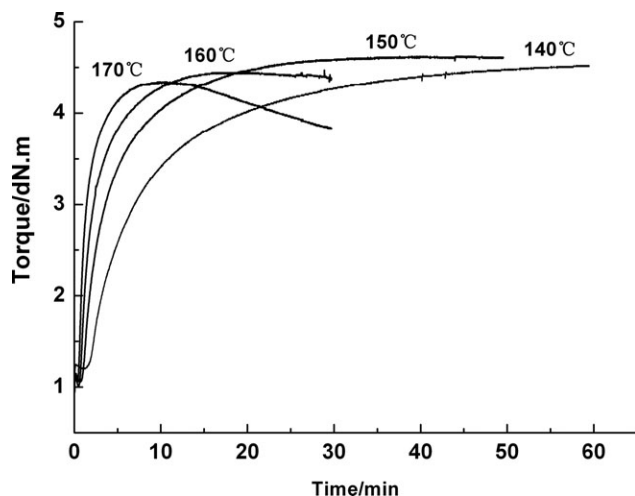


Figure 2. Original rheometer curves of NR.

The curves of vulcanization were obtained by using a Rheometer MDR2000 at 140, 150, 160, and 170°C, respectively.

## RESULTS AND DISCUSSION

### Calculations of Kinetic Parameters

The original rheometer curves of NR and CVNR are showed in Figures 2 and 3, respectively. The original rheometer curves before maximum torque are treated as three periods including induction period, first stage of curing period and end stage of curing period.

The induction period is treated with an empirical equation<sup>17,18,20</sup> of

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

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,  $\alpha$  is a modified coefficient, and  $k_1^{1/\alpha}$  is used as the rate constant of induction period.

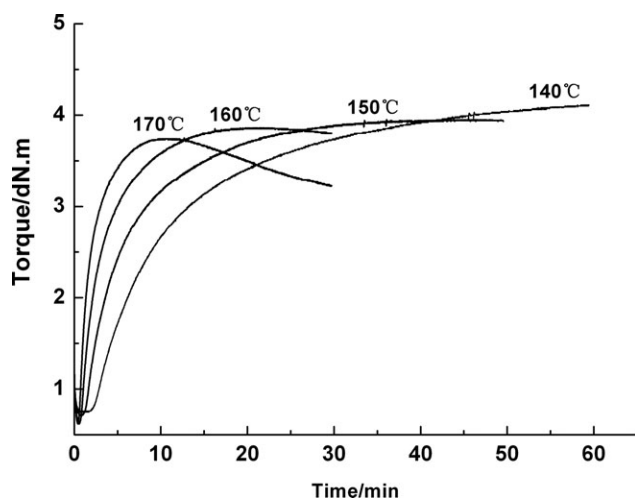


Figure 3. Original rheometer curves of CVNR.

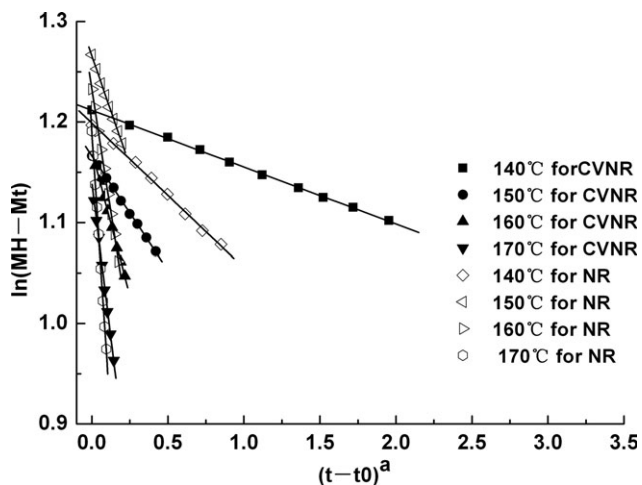


Figure 4. Relation between  $\ln(M_H - M_t)$  and  $(t - t_0)^{\alpha}$  for induction period.

The first stage of curing period is 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,  $B$  is constant.

The end stage of curing period is treated with an equation<sup>19,20</sup>

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

where  $k_3$  is a rate constant,  $C$  is constant.

The activation energy is calculated according to the Arrhenius equation

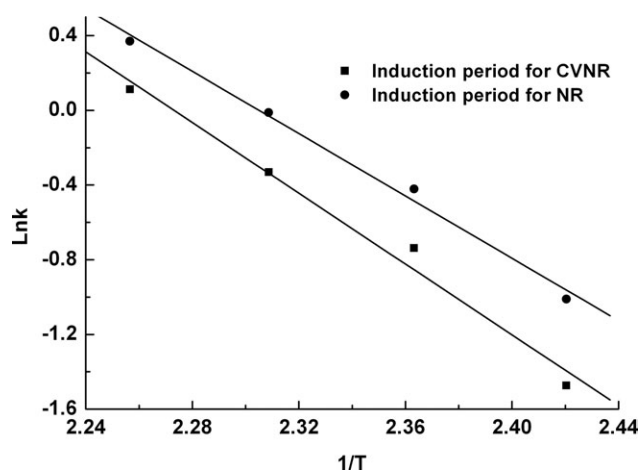
$$\ln k = \ln Z - E/RT \quad (4)$$

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<sup>17,18</sup>,

$$\begin{aligned} \ln(M_H - M_t) &= \ln A - k_1(t - t_0)^{\alpha} \\ \ln(M_H - M_t) &= \ln B - k_2(t - t_0) \end{aligned}$$

### INDUCTION PERIOD

The induction periods of CVNR and NR are treated with eq. (1), and a plot of  $\ln(M_H - M_t)$  against  $(t - t_0)^{\alpha}$  according to eq. (1) for induction periods of CVNR and NR is shown in Figure 4. The feature of the straight lines in Figure 4 indicates that both induction periods of CVNR and NR can be described well by eq. (1). Figure 5 shows that the relations between the rate constants and the temperatures of induction periods of CVNR and NR can be described well by Arrhenius equation. It is seen from the data in Table I that the rate constant  $k_1^{1/\alpha}$  of induction period of CVNR is smaller than that of NR at the same temperature, and the activation energy 78.75 kJ/mol of induction period of CVNR is obviously greater than the activation energy 69.37 kJ/mol of induction period of NR.



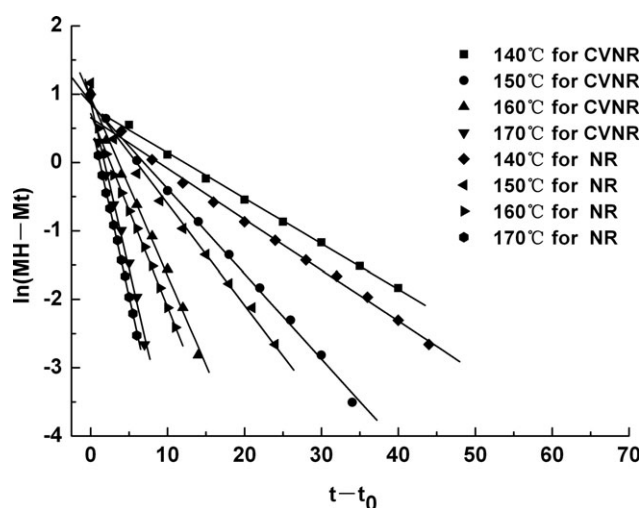
**Figure 5.** Relation between rate constant and temperature for induction period.

### First Stage of Curing Period

The first stage of curing periods of CVNR and NR are treated with eq. (2), and a plot of  $\ln(M_H - M_t)$  against  $(t - t_0)$  according to eq. (2) for the first stages of curing periods of CVNR and NR is shown in Figure 6. The feature of the straight lines in Figure 6 indicates that both first stages of curing periods of CVNR and NR can be described well by first order equation. Figure 7 shows that the relations between the rate constants and the temperatures of the first stages of curing periods of CVNR and NR can be described well by Arrhenius equation. It can be seen from the data in Table II that the rate constant  $k_2$  of the first stage of curing period of CVNR is smaller than that of NR at the same temperature, and the activation energy 102.15 kJ/mol of the first stage of curing period of CVNR is slightly greater than the activation energy 98.27 kJ/mol of the first stage of curing period of NR.

### End Stage of Curing Period

The end stages of curing periods of CVNR and NR are treated with eq. (3), and a plot of  $1/(1 - n)(M_H - M_t)^{1-n}$  against  $(t - t_0)$  according to eq. (3) for the end stages of curing periods of CVNR and NR is shown in Figure 8. The feature of the straight lines in Figure 8 indicates that both the end stages of curing periods of CVNR and NR can be described well by the equation of  $1/(1 - n)$



**Figure 6.** Relation between  $\ln(M_H - M_t)$  and  $(t - t_0)$  for the first stage of curing period.

$(M_H - M_t)^{1-n} = C - k_3(t - t_0)$ . Figure 9 shows that the relations between the rate constants and the temperatures of the end stages of curing periods of CVNR and NR can be described well by Arrhenius equation. The calculated rate constants  $k_3$  and the activation energy of the end stages of curing periods are presented in Table III. The data in Table III shows that the rate constant  $k_3$  of the end stage of curing period of CVNR is smaller than that of NR at the same temperature, and the activation energy 148.28 kJ/mol of the end stage of curing period of CVNR is slightly greater than the activation energy 145.94 kJ/mol of the first stage of curing period of NR as same as the first stage of curing period.

### Reaction Order $n$

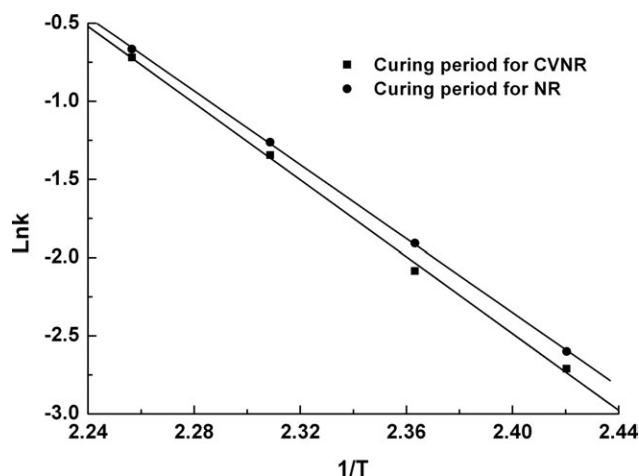
The calculated reaction order  $n$  in the end stage of curing period of CVNR is 0.01 at 140°C, 0.29 at 150°C, 0.42 at 160°C, and 0.52 at 170°C, and that of curing period of NR is 0.38 at 140°C, 0.52 at 150°C, 0.60 at 160°C, and 0.66 at 170°C. The reaction order  $n$  in the end stage of curing period of CVNR is smaller than that of NR at the same curing temperature. The reaction order  $n$  of the end stage of curing period of CVNR increases with increasing curing temperature, and so is that of NR.

A theory<sup>6-8</sup> of natural rubber vulcanization is the existence of crosslink and aging (crosslink shortening, crosslink destruction,

**Table I.** Kinetics Parameters of the Induction Period of Curing Period of NR and CVNR

Sample	$T$ (°C)	$\alpha$	$K_1^{1/\alpha}$	$r_K$	$E_1$ (kJ/mol)	$r_E$
CVNR	140	1.95	0.2293	0.9997	78.75	0.9921
	150	2.01	0.4784	0.9996		
	160	1.67	0.7184	0.9997		
	170	1.84	1.1188	0.9993		
NR	140	1.92	0.3642	0.9989	69.37	0.9962
	150	1.96	0.6565	0.9995		
	160	1.86	0.9876	0.9997		
	170	2.24	1.4481	0.9996		

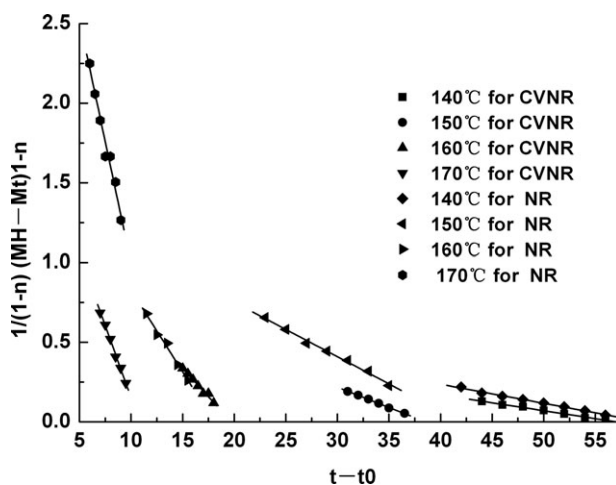
$r_K$  correlated coefficients of  $K_1^{1/\alpha}$ ;  $r_E$  correlated coefficients of  $E_1$ .



**Figure 7.** Relation between rate constant and temperature for the first stage of curing period.

and S—S bond interchange) during vulcanization. The earlier study<sup>19</sup> proposed that the change of reaction order from  $n = 1$  in the first stage of curing period to  $n < 1$  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) on crosslink, although which type of effect with main responsibility for the change has been not yet determined. NR is a polymer containing about 95% cis-1,4-polyisoprene and 5% nonrubber substances. It is known that the tocotrienol in nonrubber substances is a natural anti-ager for natural rubber.<sup>31</sup> A possible interpretation for that the reaction order  $n$  of the end stage of curing period of CVNR is smaller than that of NR may be the effect of viscosity stabilizer hydroxylamine hydrochloride on the effective of anti-aging of tocotrienol.

The data in Table III shows that the maximum torque  $M_H$  of CVNR and NR decreases with the increase in temperature except the maximum torque  $M_H$  of NR at 150°C and the reaction order  $n$  increases from a lower value close to  $n = 1$  with increasing temperature. The aging of natural rubber vulcanizate consists of the destructions of crosslink and molecular chain. It is known that the bond energy of crosslink C—S—C, C—S<sub>2</sub>—C and C—S<sub>x</sub>—C is 284.7 kJ/mol, 267.9 kJ/mol, and lower than 267.9 kJ/mol, respectively, and the rank of hot resistance of



**Figure 8.** Relation between  $1/(1 - n) (M_H - M_t)^{1-n}$  and  $(t - t_0)$  for the end stage of curing period.

crosslink is C—S—C > C—S<sub>2</sub>—C > C—S<sub>x</sub>—C. Natural rubber molecular chain has C—C and C=C molecular structures. The bond energy of C—C and C=C is 332 kJ/mol and 611 kJ/mol, respectively, which are higher than that of crosslink. During vulcanization of test sample, in the condition of hermetically sealed cavity of Rheometer MDR-2000 where no oxygen exists in, the destruction of crosslink will take place easier than that of natural rubber molecular chain because the bond energy of crosslink is obvious lower than that of molecular chain. The decrease in the maximum torque  $M_H$  means that the aging in the end stage of curing period at higher temperature is mainly crosslink destruction, although the destruction of natural rubber molecular chain could not be excluded. A possible explanation for the increase in the reaction order  $n$  of the end stage of curing period with increasing curing temperature may be the effect of crosslink destruction at higher temperature. Further investigation is necessary for an in-depth knowledge of the change of reaction order in the end stage of curing period with curing temperature.

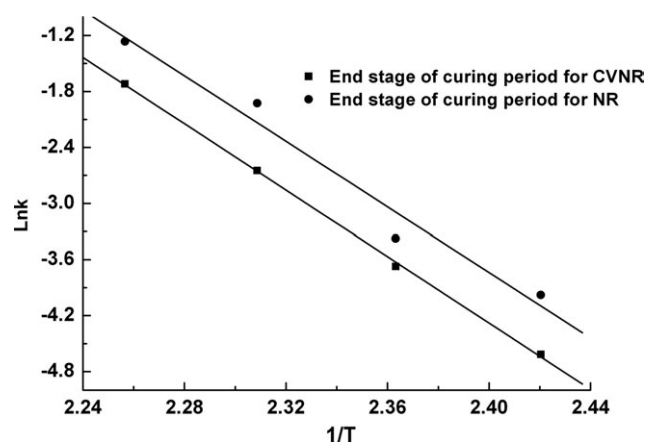
#### Comparison of the Activation Energy for CVNR and NR

The results have shown that all activation energies of induction period, the first stage of curing period and the end stage of curing period of CVNR are greater than that of NR. It is indicated

**Table II.** Kinetics Parameters of the First Stage of Curing Period of NR and CVNR

Sample	T (°C)	$K_2$	$r_K$	$t_{dis}$ (min)	$E_2$ (kJ/mol)	$r_E$
CVNR	140	0.0665	0.9989	3.09	102.15	0.9992
	150	0.1244	0.9986	1.71		
	160	0.2605	0.9976	1.08		
	170	0.4871	0.9970	0.71		
NR	140	0.0742	0.9986	2.65	98.27	0.9999
	150	0.1483	0.9941	1.24		
	160	0.2828	0.9993	0.93		
	170	0.5142	0.9994	0.70		

$r_K$  correlated coefficients of  $K_2$ ;  $r_E$  correlated coefficients of  $E_2$ .



**Figure 9.** Relation between rate constant and temperature for the end stage of curing period.

that the constant viscosity hydroxylamine hydrochloride gives rise to an increase in the temperature dependence of reaction rates of CVNR. The comparison of activation energies of CVNR and NR gives interesting information. The activation energy of induction period of CVNR is 13.52% greater than that of NR, the activation energy of the first stage of curing period of CVNR is 3.95% greater than that of NR, and the activation energy of the end stage of curing period of CVNR is 1.60% greater than that of NR. The obvious increment in activation energy of induction period of CVNR means that the effect of the viscosity stabilizer hydroxylamine hydrochloride on the induction period is obviously greater than that of the first stage of curing period and the end stage of curing period.

#### Time $t_{dis}$

The time  $t_{dis}$ , being the time when accelerators and/or intermediates react to depletion defined by Coran,<sup>1,2</sup> 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

$$\ln(M_H - M_t) = \ln A - k_1(t - t_0)^a$$

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

and are listed in Table II. It is clear that the time  $t_{dis}$  shortens with the increase in curing temperature for NR and CVNR, and

the time  $t_{dis}$  of CVNR is longer than that of NR at the same temperature. The longer time  $t_{dis}$  of CVNR means that the termination of induction period of CVNR is slower than that of NR or the beginning of curing period of CVNR is slower than that of NR.

The concept of vulcanization intermediates or crosslink precursors formed in the initial stage of natural rubber vulcanization is generally accepted and confirmed experimentally.<sup>32–35</sup> It was found in very recent publication of authors<sup>24</sup> that rate constants of induction period and curing period of natural rubber (NR) are greater than that of natural rubber extracted with acetone (NR<sub>E</sub>), and the activation energies of induction period and curing period of NR are lower than that of NR<sub>E</sub>. The time  $t_{dis}$  of NR is shorter than that of NR<sub>E</sub> at the same temperature. It is known<sup>31</sup> that the content of nonrubber substances extracted by acetone is about 3% of dry NR and the nonrubber substances extracted by acetone are tocotrienol, fatty acid, and phospholipids. 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. On the basis of the consideration that the molecular structure of constant viscosity natural rubber is the same as that of natural rubber, the only difference between natural rubber and constant viscosity natural rubber is the constant viscosity natural rubber contains hydroxylamine hydrochloride but natural rubber does not, and the changes of rate constant and activation energy of constant viscosity natural rubber are near the same as that of natural rubber extracted with acetone, it is assumed that a possible explanation for the longer time  $t_{dis}$  of CVNR may be that the viscosity stabilizer hydroxylamine hydrochloride inhibits the accelerating effect of the phospholipids on the formation of vulcanization intermediates or crosslink precursors in the initial stage of natural rubber vulcanization.

## CONCLUSIONS

1. The calculated reaction order  $n$  of the end stage of curing period of CVNR is 0.01, 0.29, 0.42, and 0.52, and the reaction order  $n$  increases with increasing curing temperature. The calculated reaction order  $n$  of the end stage of curing period of NR is 0.38, 0.52, 0.60, and 0.66, and the reaction order  $n$  increases with increasing curing temperature as the same as CVNR. The reaction order  $n$  of the end stage

**Table III.** Kinetics Parameters of the End Stage of Curing Period of NR and CVNR

Sample	$T$ (°C)	$K_3$	$r_K$	$E_3$ (kJ/mol)	$r_E$	$n$	$M_H$ (dN/m)
CVNR	140	0.0099	0.9966	147.87	0.9996	0.05	4.11
	150	0.0254	0.9992	0.29	3.95		
	160	0.0708	0.9990	0.42	3.86		
	170	0.1794	0.9986	0.53	3.75		
NR	140	0.0187	0.9967	145.94	0.9851	0.38	4.52
	150	0.0342	0.9972	0.52	4.62		
	160	0.1459	0.9943	0.60	4.44		
	170	0.2823	0.9993	0.66	4.34		

$r_K$  correlated coefficients of  $K_3$ ;  $r_E$  correlated coefficients of  $E_3$ .

of curing period of CVNR is smaller than that of NR at the same curing temperature.

- All the rate constants of induction period, first stage of curing period and end stage of curing period of CVNR is smaller than that of NR at the same temperature, and all the activation energies of induction period, first stage of curing period, and end stage of curing period of CVNR is greater than that of NR.
- The activation energy of induction period of CVNR is increased by 13.52%, the activation energy of first stage of curing period of CVNR is increased by 3.95%, and the activation energy of end stage of curing period of CVNR is increased by 1.60% comparing to the activation energies of NR.
- The time  $t_{dis}$  shorten with the increase in curing temperature for NR and CVNR, and the time  $t_{dis}$  of CVNR is longer than that of NR at the same temperature.

#### ACKNOWLEDGMENTS

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