

Effect of Hydrazine Dihydrochloride on Vulcanisation Kinetics of Natural Rubber by Using a Rheometer MDR2000

Y.Z. WANG^{#*}, B.L. ZHANG^{*}, H.H. HUANG^{*} AND X. ZHANG^{**}

Mooney viscosity is a technical parameter to control the processing performance of natural rubber (NR) compound. By treating NR with viscosity stabilisers, the NR of a relatively constant viscosity can be manufactured. In this paper, the vulcanisation kinetics of constant viscosity natural rubber (CVNR) prepared with hydrazine dihydrochloride and NR was studied by using a moving die rheometer (Rheometer MDR2000). The results show that the rate constants of induction and curing period of NR are slightly greater than that of CVNR and the activation energies of induction and curing period of NR are lower than that of CVNR. The activation energy of induction period of NR is reduced by 6.28% and the activation energy of curing period of NR is reduced by 3.09% compared to the activation energies of CVNR. The time t_{dis} of NR and CVNR reduce with increasing curing temperature while the time t_{dis} of NR is shorter than that of CVNR at the same temperature.

Keywords: Natural rubber; viscosity stabiliser; hydrazine dihydrochloride; vulcanisation kinetics; rate constant; activation energy

Mooney viscosity of NR will increase during storage while that of CVNR is relatively stable. The Mooney viscosity of CVNR increases from 50.6 to 51.7, 90 days after storage at room temperature where the Mooney viscosity of NR increases from 76.4 to 81.6¹. Wang, Y.Z., Zhang, B.L. and Huang H.H. (unpublished) show that the tensile strength and the elongation at break of vulcanisate of CVNR prepared with hydrazine dihydrochloride are higher than that of NR, after hot oxygen ageing. The thermal oxidation activation

energy of CVNR obtained with differential scanning calorimeter (DSC-220, Seiko Instruments Inc.) is also higher than that of NR. CVNR is prepared by adding viscosity stabiliser into fresh natural rubber latex (NRL). The CVNR with different Mooney viscosity can be obtained through adding various viscosity stabilisers¹. For example, CVNR with low Mooney viscosity can be obtained through adding hydroxylamine hydrochloride or hydroxylammonium sulphate, medium Mooney viscosity through adding aniline

* Agricultural Product Processing Research Institute, CATAS, Zhanjiang Guangdong, China.

** Rubber Research Institute, CATAS, Danzhou, Hainan, China.

Corresponding author (e-mail: wyz011120@163.com)

or semicarbazide hydrochloride, and high Mooney viscosity by adding aniline or hydrazine hydrate.

The process of rubber vulcanisation consists of induction, curing and over cure period. If the induction period and the curing period of NR are treated with first order kinetics equation of $\ln(M_H - M_t) = \ln B - k(t - t_0)$, the induction period does not follow first order kinetics equation as shown in *Figure 1*. The curing period consists of two stages; the first stage follows first order kinetics equation while the second stage (end stage of curing period) does not. Since Coran^{2,3} deduced the famous scorch model well describing the induction and curing period, the kinetics of rubber vulcanisation has been studied extensively. Pal *et al.*^{4,5} and Furukawa *et al.*⁶ treated the curing period as two stages that are expressed in two different equations. It is known that curing and ageing (crosslink shortening, crosslink destruction and S-S bond interchange) exist during vulcanisation⁷⁻⁹. Several researchers¹⁰⁻¹⁷ deduced the effect of ageing to describe the vulcanisation process after induction period. Wang *et al.*^{18,19} suggested an empirical equation to express induction period and proposed that the curing period consists of two stages; the first stage follows the first-order reaction and the reaction order of the second stage (end stage of the curing period) being $n < 1$ ²⁰. The change in the reaction order from $n = 1$ to $n < 1$ is probably a result from the effect of ageing on crosslink.

NR is made from NRL through coagulating and processing. The coagulation of NRL is an important step in the production of NR. The microbial and acid coagulation are two commonly used methods to coagulate NRL. The effects of the two coagulation methods on vulcanisation kinetics of NR showed that the rate constants of induction and curing period of NR coagulated by microorganisms are greater than that of NR coagulated by acid²⁰.

NR is a polymer containing about 95% *cis*-1,4-polyisoprene and 5% non-rubber substances. It is known that non-rubber substances have significant effects on the properties of NR²²⁻²⁴. Wang *et al.*²⁵ found recently that non-rubber substances play a significant role in promoting the reaction rate of NR vulcanisation particularly in promoting the reaction rate of induction period.

The vulcanisation kinetics is of great importance not only for study on rubber curing but also for production in rubber industry. The mechanical properties of rubber end products are closely related to curing condition including curing temperature and time. The curing mechanism and vulcanisation kinetics parameters contribute to the correct choice of curing temperature and time. Liu *et al.*²⁶ studied the curing kinetics of epoxycyclohexyl polyhedral oligomeric silsesquioxane/hydrogenated carboxylated nitrile rubber (POSS/HXNBR) with the use of DSC method by multiple and single heating rate model.

The activation energy obtained by the multiple heating rate model was dependent on the POSS content and the heating rate while the activation energy obtained by the single heating rate model was also dependent on the heating rate. Sapkota *et al.*²⁷ studied the influence of nanoclay-carbon black hybrid fillers on cure of NR compounds by using an Advanced Polymer Analyzer 2000 with autocatalytic model. The activation energy of the networking process decreased significantly with the addition of clay. The lower activation energy is an indicator of the ease of the crosslinking process. Roj *et al.*²⁸ studied the curing kinetics of NR/EMMT modified montmorillonite (NR/EMMT) nanocomposites by using a rubber processing analyser Scarabaeus SIS-V50 with autocatalytic model. The activation energy of the curing reaction of NR decreased in the presence of both organic

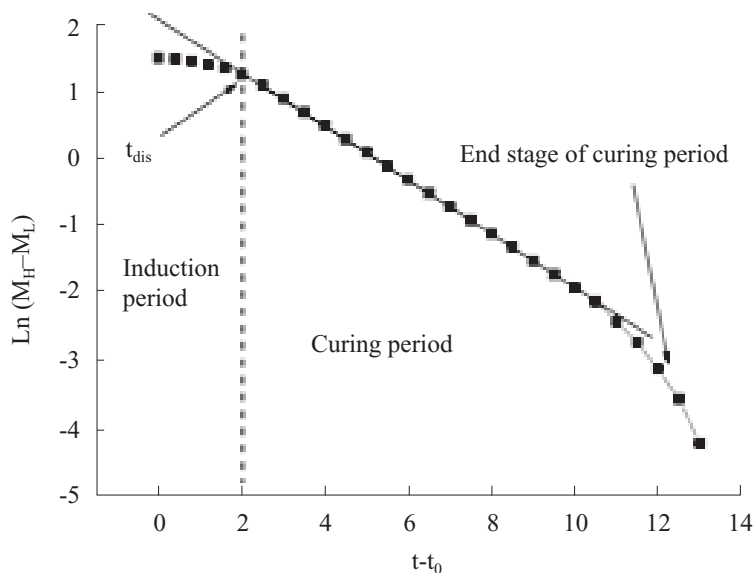


Figure 1. Illustration for induction and curing period, end stage of curing period and t_{dis} .

montmorillonite (OMMT) and EMMT. The activation energy is used as an indicator for energy required for curing process. The lower energy required for curing process means less cost of end products.

CVNR is prepared with the same NRL using the same production method. Hence, the molecular structures of CVNR and NR are similar. The main difference between NR and CVNR is that CVNR contains hydrazine dihydrochloride and NR does not. Many research reported the vulcanisation kinetics of NR and the properties^{29–30} of CVNR, such as Mooney viscosity, molecular weight, molecular weight distribution and dynamic mechanical behaviours but none on the effect of hydrazine dihydrochloride on the vulcanisation kinetics of NR.

This paper reports the vulcanisation kinetics of CVNR with 0.05% of hydrazine

dihydrochloride. In understanding how hydrazine dihydrochloride will affect the vulcanisation kinetics of NR in induction and curing period, a Rheometer MDR–2000 was used to compare the vulcanisation kinetic parameters of NR.

EXPERIMENTAL

Materials

NRL used to prepare CVNR and NR was obtained from Mengpeng Farm (Yunnan, China). Viscosity stabiliser, hydrazine dihydrochloride of chemical grade was obtained from Shenzhen Huachang Chemical Co. Ltd. (Guangdong, China). Sulphur, zinc oxide, stearic acid and 2-mercaptobenzothiazole (MBT) were of industrial grade and obtained from Shenzhen Huachang Chemical Co. Ltd. (Guangdong, China).

Samples Preparation

CVNR with 0.05% of hydrazine dihydrochloride and NR were prepared²⁸ with microbial coagulation technology. The formulation is shown in *Table 1* (in parts per hundred of rubber). The curves of vulcanisation were obtained by using a Rheometer MDR-2000 at 140, 150, 160 and 170°C, respectively.

TABLE 1. FORMULATION OF CVNR

| Ingredients | p.p.h.r. |
|-------------------------|----------|
| Rubber | 100 |
| Sulphur | 3.5 |
| Zinc Oxide | 6.0 |
| Stearic acid | 0.5 |
| 2-mercaptobenzothiazole | 0.5 |

RESULTS AND DISCUSSION

Calculations of Kinetic Parameters

The rheometer curves of NR and CVNR are showed in *Figures 2* and *3*, respectively. The rheometer curves before maximum torque are treated in three periods: induction, first stage and end stage of curing period. The induction period is shown in the following equation^{18,19,21}:

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

where M_H is the maximum torque; M_t is the torque at vulcanisation 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 period is treated with first order equation of

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

where k_2 is a rate constant and B is constant.

The activation energy is calculated according to the Arrhenius Equation

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

where k and Z are constants; R is the molar gas constant; T is the thermodynamic temperature, E is for the activation energy.

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 *Equations 1* and *2*^{18,19}.

Induction Period

The straight lines in *Figure 4* indicate that both induction periods of CVNR and NR are well described by *Equation 1* while *Figure 5* shows the relations between the rate constants and the temperatures of induction periods of CVNR and NR by *Equation 3*. As shown in *Table 2* 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 77.46 kJ/mol of induction period of CVNR is slightly greater than the activation energy 72.88 kJ/mol of induction period of NR.

Curing Period

The first stage of curing periods of CVNR and NR are calculated and plotted according to *Equation 2*. The straight lines in *Figure 6* indicate that both first stages of curing periods of CVNR and NR are best calculated 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 are best calculated by *Equation 3*. From the data in *Table 3* the

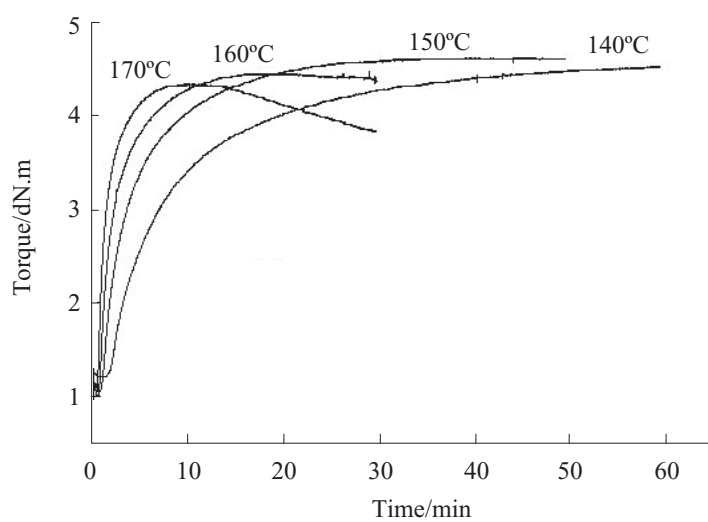


Figure 2. Rheometer curves of NR.

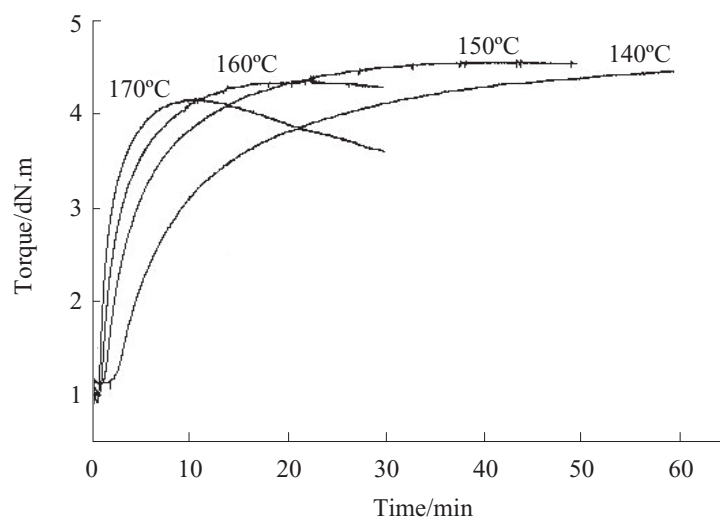


Figure 3. Rheometer curves of CVNR.

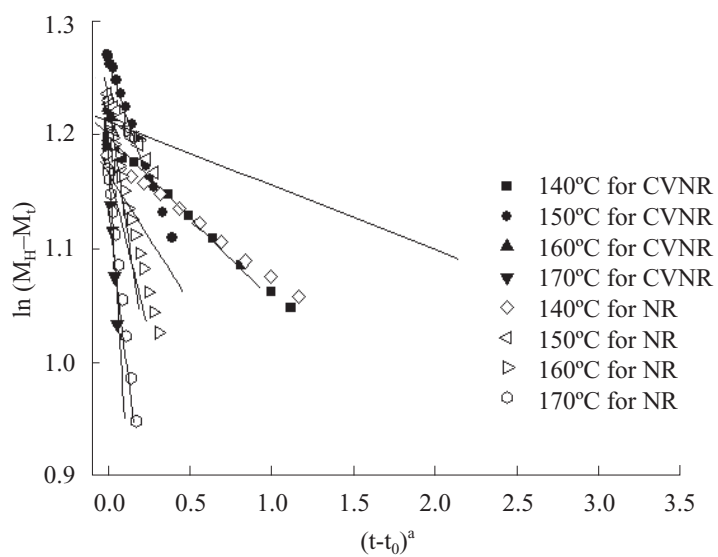


Figure 4. Relation between $\ln(M_H - M_i)$ and $(t - t_0)^a$ for induction period.

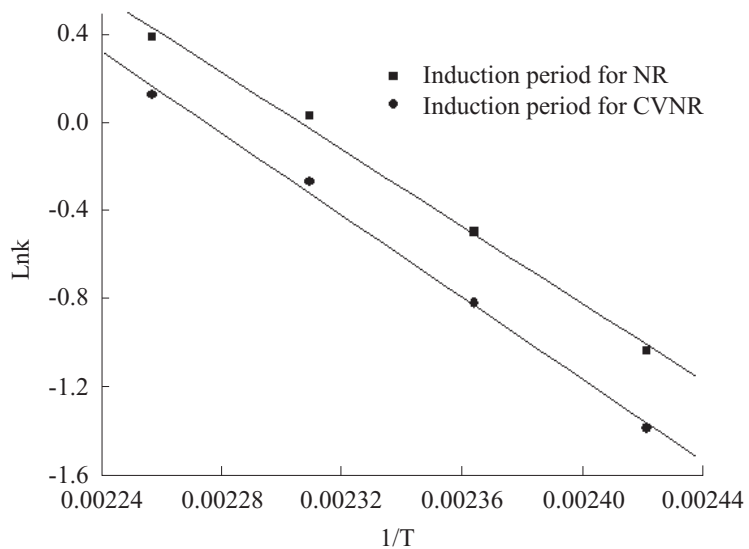


Figure 5. Relation between rate constant and temperature for induction period.

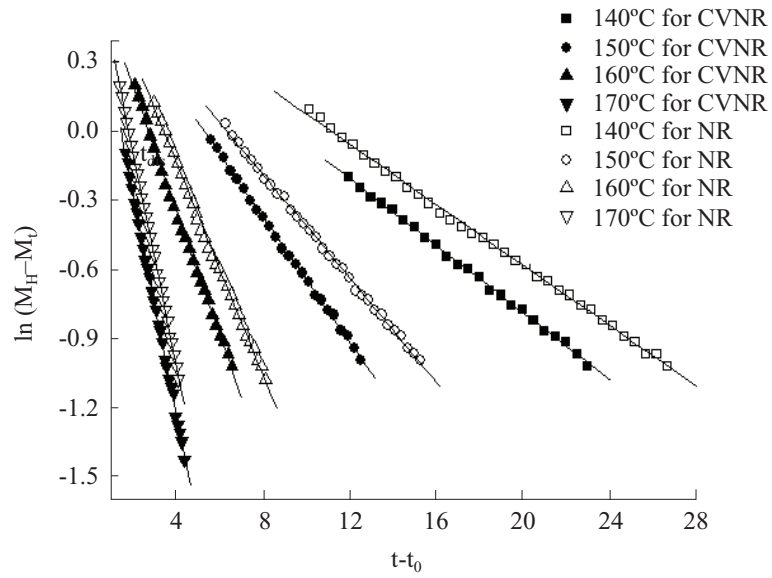


Figure 6. Relation between $\ln(M_H - M_t)$ and $(t - t_0)$ for the first stage of curing period.

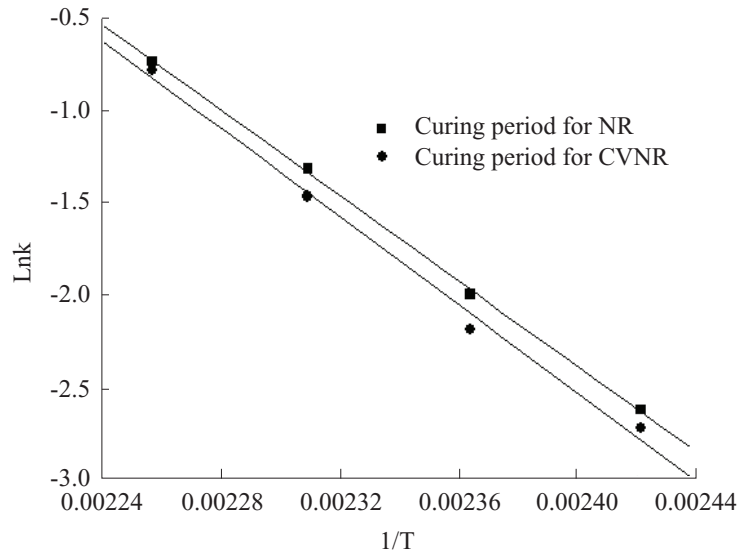


Figure 7. Relation between rate constant and temperature for curing period.

TABLE 2. KINETICS PARAMETERS OF INDUCTION PERIOD OF NR AND CVNR

| Sample | T (°C) | a | $K_1^{1/\alpha}$ | r_1 | E_1 (kJ/mol) | r_1 |
|--------|--------|------|------------------|--------|----------------|--------|
| NR | 140 | 1.96 | 0.3563 | 0.9993 | 72.88 | 0.9986 |
| | 150 | 1.82 | 0.6108 | 0.9998 | | |
| | 160 | 1.92 | 1.03328 | 0.9982 | | |
| | 170 | 2.46 | 1.4732 | 0.9995 | | |
| CVNR | 140 | 1.63 | 0.2506 | 0.9992 | 77.46 | 0.9982 |
| | 150 | 1.81 | 0.4421 | 0.9986 | | |
| | 160 | 1.90 | 0.7655 | 0.9996 | | |
| | 170 | 1.90 | 1.137 | 0.9999 | | |

TABLE 3. KINETICS PARAMETERS OF CURING PERIOD OF NR AND CVNR

| Sample | T (°C) | K_2 | r_2 | t_{dis} (min) | E_2 (kJ/mol) | r_2 |
|--------|--------|---------|--------|-----------------|----------------|--------|
| NR | 140 | 0.07271 | 0.9994 | 5.19 | 96.72 | 0.9996 |
| | 150 | 0.1360 | 0.9995 | 2.8 | | |
| | 160 | 0.2689 | 0.9990 | 1.34 | | |
| | 170 | 0.48236 | 0.9995 | 0.91 | | |
| CVNR | 140 | 0.06567 | 0.9992 | 7.46 | 99.71 | 0.9992 |
| | 150 | 0.1127 | 0.9995 | 4.25 | | |
| | 160 | 0.2314 | 0.9988 | 2.81 | | |
| | 170 | 0.4608 | 0.9997 | 1.32 | | |

rate constant k_2 of the first stage of curing period of CVNR is smaller than that of NR at the same temperature while the activation energy 99.71 kJ/mol is slightly greater than the activation energy 96.72 kJ/mol of NR.

(6.28% and 3.09%, respectively) are slightly greater than that of NR. This shows that the effect of the viscosity stabiliser hydrazine dihydrochloride on the induction period is slightly greater than that of the curing period.

Comparison of the Activation Energy for CVNR and NR

The results showed that all activation energies of induction and curing period of CVNR are slightly greater than that of NR. The constant viscosity hydrazine dihydrochloride gives slight increase in the reaction rates of CVNR that is temperature dependence of reaction rates of CVNR. The activation energy of induction and curing period of CVNR

Time t_{dis}

The time t_{dis} , being the time when accelerators and/or intermediates react to depletion as defined by Coran^{2,3}, marks the termination of induction period and the beginning of curing period. The values of t_{dis} are calculated with the solution of *Equations 1 and 2* as listed in *Table 3*. It is clear that time t_{dis} is shorter with the increase in curing temperature for NR and CVNR while the time t_{dis} of CVNR is longer

than that of NR at the same temperature. The concept of vulcanisation intermediates or crosslink precursors formed in the initial stage of natural rubber vulcanisation is generally accepted and confirmed experimentally^{32–35}.

CONCLUSION

Both the rate constants of induction and curing period of CVNR is smaller than that of NR at the same temperature and both the activation energies of induction and curing period of CVNR is slightly greater than that of NR. 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. From the results we can conclude that the hydrazine dihydrochloride has slight effect on rate constants and activation energies of NR, which means that the hydrazine dihydrochloride has little effect on vulcanisation processing of NR. It also increases t_{dis} of NR which is good for the safety of NR vulcanisation process.

ACKNOWLEDGEMENTS

This work was financially supported by the Fundamental Research Funds for Rubber Research Institute, CATAS (No.1630022015017) and the Earmarked Fund for China Agriculture Research System (No.CARS-34-GW9), respectively.

Date of receipt: April 2014

Date of acceptance: January 2015

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