Available online at www.sciencedirect.com
ScienceDirect
JOURNAL OF RARE EARTHS 25 (2007) 396 - 400

JOURNAL OF
RARE EARTHS
www.elsevier.com/locate/jre

Study on Kinetics of Natural Rubber Vulcanization by S/La(DiPDP)$_3$

Lin Xinhua (林新花)[1,2], Liu Qingting (刘清亭)[1], Chen Zhaohui (陈朝晖)[1] *, Wang Dizhen (王迪珍)[1]
(1. College of Materials Science and Engineering, South China University of Technology, Guangzhou 510641, China; 2. Department of Chemical Engineering, Guangdong Industry Technical College, Guangzhou 510300, China)

Received 25 August 2006; revised 7 November 2006

Abstract: Kinetics of natural rubber (NR) vulcanization by lanthanum O, O′-diisopropyldithiophosphate [La(DiPDP)$_3$] was studied. La(DiPDP)$_3$ had remarkable accelerating effect on the vulcanization of NR. The rate constant k_6 of the reaction that turned polysulphidic cross-links into the modified main chain was higher than that of desulfuration reaction of polysulfidic cross-links (k_3). The activation energies (E_{a2}, E_{a3}, and E_{a6}) of the formation, desulfuration, and decomposition of polysulfidic cross-links were 87.57, 102.34, and 95.01 kJ · mol^{-1}, respectively. Activation energy (Ea_5) of the reaction that turned the cross-link precursors into the modified main chain was 82.67 kJ · mol^{-1}. It could be concluded that the proportion of polysulphidic cross-links was higher than mono- and di- sulphidic cross-links during induction and curing periods, mono- and di- sulphidic cross-links increased as curing temperature rose. In the temperature range of 140 ~ 160 ℃, the amounts of polysulphidic cross-links were similar. However, over 160 ℃, mono- and di- sulphidic cross-links increased rapidly. Moreover, cross-link density of the vulcanizates was determined from the equilibrium-swelling data. A chemical probe detected the concentration of polysulphidic cross-links of vulcanizates. The change trend of the results predicated from equation corresponded to that of the experimental results.

Key words: vulcanization kinetics; natural rubber; lanthanum O, O′-diisopropyldithiophosphate; rare earth accelerator
CLC number: TQ330.1; TQ332 **Document code:** A **Article ID:** 1002 - 0721(2007)04 - 0396 - 05

Currently, the application of rare earth compounds is getting abroad[1,2], and it has extended to rubber processing. For example, lanthanum O,O′-diisopropyldithiophosphate [La(DiPDP)$_3$] is rare earth dialkyldithiophosphate, which is an environmental-friendly accelerator, neither containing nitrogen nor producing nitrosamine during sulfur-curing process[3,4]. It is well known that rubber vulcanization is a complex chemical reaction and properties of vulcanizate strongly depend on the network structure of the vulcanizate. It is necessary to obtain the characteristic of energy and rheology during vulcanization for the analysis of rubber vulcanization and the structure of vulcanizate. The main goal of this study was to evaluate the effect of La(DiPDP)$_3$ on the vulcanization kinetics of natural rubber (NR). According to the current vulcanization kinetics model of Fan R L[5], the vulcanization of NR with S/La(DiPDP)$_3$ vulcanization system was simulated with Origin 6.0 (Microcal, USA). Cross-link density of vulcanizates was determined with the equilibrium-swelling data. A chemical probe detected the concentration of polysulphidic cross-links of vulcanizates. The results predicated from equation were compared with experimental results.

---

* **Corresponding author**(E-mail: pszhchen@scut.edu.cn)
Foundation item: Project supported by the Guangdong Natural Science Foundation (05006563)
Biography: Lin Xinhua (1965-), Female, Doctoral candidate; Associate professor

1 Experimental

1.1 Materials and equipments

Chemicals, acetone and piperidine, were of laboratory reagent grades and were supplied by Guangzhou Chemical Reagent Factory. N-decane and propane-2-thiol were of analytical grades from ACROS ORGANICS, USA. Lanthanum O,O′-diisopropyldithiophosphate was prepared as mentioned in previous studies[6,7]. NR was commercial SCR #5. The other materials were commercial and used without purification.

Rubber test equipment was RPA2000 rubber process analyzer (Alpha, USA). Main equipments for chemical analysis were Soxhlet extract, vacuo oven, and nitrogen gas cylinder.

1.2 Preparation of the rubber blends

NR had been stored for 24 h after it was passed ten times on a two-roll mill. After this, zinc oxide, stearic acid, and accelerator lanthanum O,O′-diisopropyldithiophosphate were added and the mixing time for each chemical was controlled for 2 min, respectively. The compounds were then cooled prior to further mixing with sulfur for 3 min.

1.3 Method

1.3.1 Determination of curing curve and data treating

The curing curve of each compound was determined by using RPA2000 according to GB 9869-88. Points were chosen from these curing curves. In our tests, induction time was t_{10}(corresponding to torque T_{t10}), point (t_{10}, T_{t10}) was assumed to the origin of coordinate (0, 0). Fitting points (t-t_{10}, T_t-T_{t10}) contained starting point (t_{10}, T_{t10}) till end point. The curing process of NR with S/La(DiPDP)$_3$ vulcanization system was simulated with Origin 6.0.

1.3.2 Determination of cross-link density and concentration of polysulphidic cross-link of vulcanizates

Cross-link density of vulcanizates was determined with the equilibrium-swelling data and was calculated by methods reported by Mullins[8]. The concentration of polysulphidic cross-links of vulcanizates was estimated from the change in the cross-link density of the vulcanizates before and after treatment with propane-2-thiol and piperidine, which only cleaved the polysulphidic cross-links in the network[9].

1.3.3 Vulcanization kinetics model Coran described the induction period of NR kinetically[10]. Fan R L described the curing period and reversion period of NR kinetically[5]:

$$B \xrightarrow{k_2} S_x \xrightarrow{k_3} \alpha S_{12}$$

$$B \xrightarrow{k_5} D$$

$$S_x \xrightarrow{k_6} D$$

The corresponding vulcanization process could be expressed in a kinetic equation of

$$Vu = S_x + S_{12} = \frac{B_0 k_2}{k_{36} - k_{25}}(e^{-k_{25}t} - e^{-k_{36}t}) + \frac{B_0 k_2 k_3 \alpha}{k_{36} - k_{25}} \left(\frac{e^{-k_{36}t} - 1}{k_{36}} - \frac{e^{-k_{25}t} - 1}{k_{25}}\right)$$

where B was the cross-link precursor (a reaction product from rubber molecular chains and intermediates of sulfur, accelerator, and activators), B_0 was the initial reactant concentration of the cross-link precursors, S_{12} was the sum of the monosulphidic cross-links (S_1) and the disulphidic cross-links (S_2), S_x was the polysulphidic cross-links which not only desulfurated to S_1 and S_2 but also decomposed and decreased the cross-linking efficiency at high temperature, α was the adjustable stoichiometric parameter, and D was the modified main chain. It was reported that S_1 and S_2 did not decompose until 400 ~ 800 ℃[11]. It was thus considered that S_1 and S_2 did not decompose at the present experimental temperatures and during limited cure time. Vu was the total cross-link density, t was the cure time which deducted induction time, k_2 was the rate constant for formation of polysulfidic cross-links, k_3 was the rate constant for desulfuration of polysulfidic cross-links, k_5 was the rate constant of reaction which turned the cross-link precursors into the modified main chain, and k_6 was the rate constant for decomposition of the polysulfidic cross-links, $k_{25} = k_2 + k_5$, and $k_{36} = k_3 + k_6$.

2 Results and Discussion

2.1 Kinetics of natural rubber vulcanization by S/La(DiPDP)$_3$

2.1.1 Nonlinear fitting curing curves It is reported that the cross-linked rubber accelerated by the lanthanum complex with 2-mercaptobenthiazol had good accelerating vulcanization properties[12]. In this article, the formulation of mix is given as follows (parts by weight): NR, 100.0; zinc oxide, 5.0; stearic acid, 1.0; sulfur, 2.0; vulcanizing accelerator La(DiPDP)$_3$, 1.56. The ability of the model to describe the vulcanization kinetics of the mixes at 140, 150, 160, 170 and 180 ℃, respectively, are shown in Fig. 1, where the accordance between the experimental and fitting curves can be observed. La(DiPDP)$_3$ has remarkable accelerating effect on the vulcanization of NR. Moreo-