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Effect of ZnO particle sizes on thermal aging behavior of natural rubber vulcanizates

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ABSTRACT

The effects of ZnO particle size on crosslinking and thermal aging behavior of natural rubber (NR) were investigated. NR vulcanizates filled with nano ZnO allowed higher crosslink density, lower polysulfide crosslink, and stronger mechanical properties than those filled with micro ZnO. After thermal aging, NR filled with nano ZnO exhibited much more stable chemical and mechanical properties. The high crosslink density as well as the formation of more stable mono- and di-sulfidic crosslinks was attributed to the good dispersion and high surface area of the nano ZnO.

1. Introduction

Natural rubber (NR) is widely used in various industries owing to its unique elasticity and excellent damping and mechanical properties [1–4]. The mechanical properties of rubber materials have been improved by the formation of crosslinks which are affected by the formulation of vulcanization [5,6]. In general, NR is crosslinked by sulfur vulcanization, in which the basic additives, such as sulfur, ZnO, strearic acid, and others are used.

ZnO is an activator and reacts with stearic acid, forming zinc stearate, which increases the efficiency of the crosslinking system [7]. Recently, the use of nano ZnO has been investigated in the NR vulcanization due to the size effect as well as environmental consideration [8–14]. Pryzybyszewska et al. [6] studied and discussed the effect of ZnO nanoparticle on the crosslinking density and mechanical properties of carboxylated nitrile rubber vulcanizates, in which the three-dimensional snowflake ZnO nanoparticles achieved higher crosslink density and better mechanical properties compared to the vulcanizates with micro ZnO. Panampilly et al. [9] reported that the NR vulcanizates filled with ZnO nanoparticles (20–90 nm) showed fast optimum cure time and high cure rate index compared to conventional micro ZnO. The rod-shaped ZnO nanoparticles (50 nm) were synthesized by Sahoo et al. [10] and used for carboxylated nitrile rubber, in which enhanced cure rate and crosslink density were reported. Kim and his coworkers [13] reported that the increase in the specific surface area of nano ZnO increased the degree of crosslinking in silica-filled NR and butadiene rubber vulcanizates.

As shown above, many researchers investigated the effects of ZnO particles size on crosslinking behavior and mechanical properties of NR vulcanizates, however, the effect of the ZnO particle size on the thermal aging properties related with the crosslink structures has not been reported elsewhere.

When sulfur-cured NR products are exposed to a thermal oxidative aging environment, the mechanical properties change significantly, which are directly related to the changes in the crosslinking density and structure [15,16]. Polysulfide linkages are dissociated by heating to form mono- and di-sulfide linkages and finally decomposed to gum state and often accompanied by the variations in the crosslink density and crosslink structure [17–20]. So, the crosslink structure directly affects the thermal stability and physical properties of NR vulcanizates [21,22].

Therefore, the focus of the study was to investigate the effect of ZnO particle size on curing behavior after thermal aging of NR vulcanizates. The variation of crosslink structure and mechanical properties of NR vulcanizates after thermal aging were carefully monitored and discussed in detail.

2. Experimental

2.1. Materials

61% Natural rubber latex (stabilized with 0.67% ammonia, pH 10.52) was supplied by Jungwoo Co., Ltd. (Republic of Korea). ZnO (1–1.2 μm, Kanto Chemical Co., Inc. and 150–200 nm, Alfa Aesar) was used as received, and the size distribution was analyzed as shown in Supporting Information. Sulfur powder, stearic acid, *N*-cyclohexyl-2-benzothiazole sulfonamide (CBS), and tetramethylthiuram disulfide (TMTD) were purchased from Pyunghwa Co., Ltd. (Republic of Korea).

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2.2. Vulcanization of NR according to size of ZnO

The aqueous suspension of ZnO (5 wt%) was prepared under stirring for 30 min and sonication for 2 h. The ZnO suspension was dropped into the NR latex and vigorously stirred for 1 h. The ZnO/NR suspension was dropped into 400 mL ethanol and the solid content of ZnO/NR was washed with deionized water several times, and dried in a vacuum oven at 50 °C for 48 h. The ZnO/NR were further mixed with other additives using a two-roll mill for 20 min at room temperature. The curing composition is as follows; NR 100 phr, sulfur 1 phr, stearic acid 1 phr, CBS 1 phr, TMTD 0.5 phr, and various amount of ZnO. The well-mixed rubber vulcanizates were cured in a hydraulic press at 160 °C for 10 min. The product was labeled as N_X or M_X, where x refers to the weight (phr) of nano ZnO or micro ZnO, respectively.

2.3. Instrumentation

Particle size and distribution of ZnO particles were analyzed using a Mastersizer χ (Malvern, UK). Scanning electron microscopy (SEM, JEOL JSM-7000F, and Japan) was used to examine the dispersion of ZnO particles in the fractured surface of NR vulcanizates. Curing characteristics of the vulcanized NR were monitored using a rheometer (MYUNG-JI Tech, model ODR 2020, Seoul, Republic of Korea) at 160 °C for 10 min under an oscillation angle of 1 arc. Tensile test was measured using an ISO 37 using dumbbell-shaped specimens (Type 1A, 2 mm in thickness) of the vulcanized NR using an automatic universal testing machine (Z010, Zwick Roell AG, Germany) at a speed of 500 mm/min. The tensile modulus, tensile strength and elongation at break were obtained by taking the average of four specimens. The hardness of the vulcanized NR was measured by ISO 7619-1 using a durometer (HD-1110, Ueshima Seisakusho Co., Japan) by taking the average of five different spots of the samples (40 × 40 × 8 mm^3).

The crosslink density of the vulcanized NR was measured by the swelling method (see supporting information) [23]. The sheet of vulcanized NR (5 × 5 mm^2) was extracted in acetone for 24 h and then, immersed in toluene for 72 h. Finally, the swollen sheet was dried in a vacuum oven for 24 h. The degree of crosslink was calculated by the Flory-Rehner equation [23]. The structure of crosslink of the vulcanized NR was sorted by mono-, di-, and polysulfide according to the number of sulfur molecules incorporated in crosslinking of NR. [24,25]. To analyze thermal aging resistance of the vulcanized NR, the specimens were placed in convection oven at 80 °C for 2, 4, 6, and 8 days according to ASTM 572-99 and the specimens were cooled at room temperature for 16 h. The mechanical properties and crosslink structure of the thermal aged specimens were measured by the above-mentioned method.

3. Results and discussion

3.1. Cure characteristics of NR vulcanizates

The use of ZnO in combination with accelerator has a pronounced effect on the speed of vulcanization and on crosslinks structure. Fig. 1 shows the rheometric curves of the NR vulcanizates according to the amount of ZnO during the vulcanization. The curing characteristics are expressed in terms of torque value at initial ($torque_{min}$) and late stage ($torque_{max}$), ts_2 (scorch time), t_{90} (optimum cure time), and cure rate index (CRI) as listed in Table 1. The $torque_{max}$ value is increased by increasing ZnO content, indicating that degree of crosslinking NR increased gradually. The 5 phr nano ZnO-filled system (N5) exhibited the highest $torque_{max}$ value implying the system was fully cured. Comparing the effect of ZnO on the vulcanization, nano ZnO is more effective than micro ZnO due to the higher surface area. Considering the speed of curing, as the content of ZnO increased, ts_2 and t_{90} increased and the CRI decreased which is due to the longer time required for chelate complex formation with higher amount of Zn ion. [5,26]. Nano ZnO-filled system also exhibited much slower cure rate than micro ZnO-filled system due to the higher effective surface area [5,9,13].

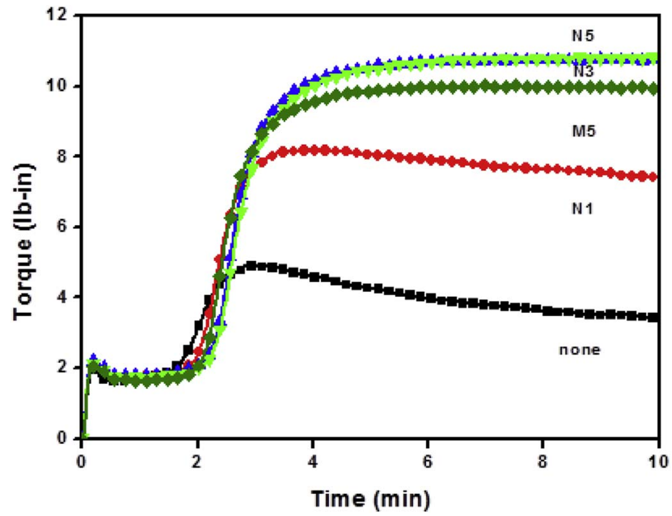

Fig. 1. Rheometer curves of NR vulcanizates as a function of ZnO content at 160 °C.

Table 1
Cure characteristics of NR vulcanizates as a function of ZnO content.

Sample	$Torque_{max}$ (lb-in)	ts_2 (min)	t_{90} (min)	CRI (min^{-1})
N 0	4.91	2.08	2.42	294.11
N 1	8.22	2.23	2.92	144.92
N 3	10.79	2.47	3.72	80.00
N 5	10.84	2.52	3.83	76.33
M 5	10.06	2.33	3.33	100.00

ts_2:scorch time; t_{90}:optimum cure time; cure rate index (CRI), 100/(t_{90}-ts_2).

Fig. 2 shows the SEM images of the fractured surface of the NR vulcanizates. Nano ZnO was uniformly dispersed in the NR vulcanizates, while micro ZnO was coagulated. These results can be in good accordance with the mechanical property data and aging behavior.

The crosslink density of the NR vulcanizates was further measured by the swelling method [21]. The crosslink structure was determined by the selective degradation of di- and polysulfide using reactive solvents [24,25]. The most unstable polysulfide was decomposed in 2-propanol and piperidine. The crosslinked disulfide was degraded in hexanethiol and piperidine (see supporting information). The most stable monosulfide remains in the NR vulcanizates. The crosslink density and structure of NR vulcanizates as a function of ZnO content and particle size are listed in Table 2 and Fig. 3. As the ZnO content increased, total crosslink density is increased. Considering the crosslink structure, increasing ZnO content yielded decreasing polysulfide and increasing monosulfide content while disulfide content is not influenced seriously. In general, it has been well accepted that the higher ratio of ZnO/sulfur produced higher proportion of mono- and di-sulfide than polysulfide due to the accelerating effect of ZnO on sulfurization. [5,26]. Considering the size of ZnO, nano ZnO-filled system (N5) also yielded much lower amount of polysufide and higher amount of monosulfide than that of micro ZnO-filled system (M5). It has been reported that mono- and di-sulfidic crosslinks have more stable structure compared with polysulfidic crosslinks. [16]. These results suggest that the nano ZnO is highly effective in achieving higher crosslink density and more stable crosslink structure than that of micro ZnO system.

3.2. Mechanical properties of NR vulcanizates

The mechanical properties of NR vulcanizates as a function of ZnO content are listed in Table 3. With increasing ZnO content, the