Thermal Aging Behaviors of Elemental Sulfur-Free Polyisoprene Vulcanizates

Sung-Seen Choi,[*] **Dong-Hun Han, Seung-Won Ko,**[†] **and Hyung Sik Lee**[†]

Department of Applied Chemistry, Sejong University, Seoul 143-747, Korea. [*]E-mail: sschoi@sejong.ac.kr
[†]Agency for Defense Development, P.O. Box 35-5, Yuseong, Daejeon 305-600, Korea
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Rubber materials have good physical properties by crosslinking. Crosslink density of a rubber vulcanizate determines the physical properties.[1] By increasing the crosslink density, the modulus, hardness, resilience, and abrasion resistance increase, whereas the elongation at break, heat build-up, and stress relaxation decrease. Rubber compounds are crosslinked by a sulfur,[2-4] peroxide,[5] or resole cure system.[6] The sulfur vulcanization is the most popular method. In general, a rubber compound with an accelerated sulfur cure system contains elemental sulfur (S_8) and cure accelerators.
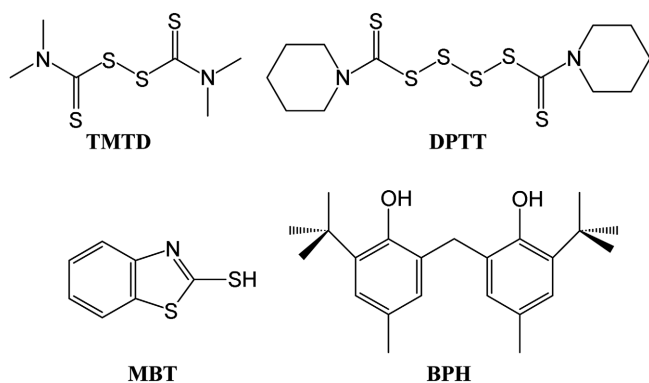
Sulfur linkages, especially polysulfides, are dissociated by heating[7-9] and this brings about decrease of the crosslink density. Curatives, especially sulfur, remained in a rubber vulcanizate make new crosslinks[3,9] and this results in increase of the crosslink density. Sulfur linkages are composed of monosulfide, disulfide, and polysulfides. Polysulfides of the total sulfur crosslinks increase by increasing the elemental sulfur content in a rubber compound. Cure accelerators such as *N-tert*-butylbezothiazole sulfenamide (TBBS), 2-mercaptobenzothiazole (MBT), and tetramethyl thiuramdisulfide (TMTD) make the cure rate of a rubber compound fast. TMTD and dipentamethylene thiuramdisulfide (DPTT) used in this study are sulfur donors (Scheme 1). Vulcanization with sulfur donors, in principle, entails a splitting of S_x (x = predominantly 1 or 2) from the sulfur donors and make sulfur crosslinks of shorter average length x than classical sulfur vulcanizations. This leads to better resistance to reversion and thermal aging. We investigated the thermal aging properties of polyisoprene (IR) vulcanizate with the sulfur donors and without elemental sulfur, and

Scheme 1. Chemical formulas of the cure accelerators and antidegradant.

its thermal aging behaviors were found to be different with the rubber vulcanizates with an accelerated sulfur cure system containing elemental sulfur.

Figure 1 shows the variations of the crosslink density changes by the thermal aging. Change of the crosslink density by the thermal aging was calculated by dividing the difference in the crosslink densities of the vulcanizates after and before the thermal aging by the crosslink density of the initial sample; ΔX_c (%) = $100 \times (X_c^{aged} - X_c^{ini})/X_c^{ini}$, where the X_c^{aged} and X_c^{ini} indicate the crosslink densities of the vulcanizates after and before the thermal aging, respectively.

The variations show different trends depending on the aging temperatures. For the thermal aging at 60 °C, the crosslink density change increases steeply until 20 days and then very slightly increases. Since the IR vulcanizate did not have elemental sulfur, the increased crosslink density is due to mainly the formation of new sulfur crosslinks through the combination reactions between sulfur pendent groups terminated by the curative residues. One of major sources to increase the crosslink density of a rubber vulcanizate by thermal aging is combination of pendent groups bonded to the rubber chains.[9,10] For example, TBBS is dissociated into MBT and *t*-butylamine radicals by heating at the beginning of vulcanization.[11] The radicals become the neutral molecules by abstracting a hydrogen atom from a rubber chain, a zinc complex formed by bonding with zinc ion,[12,13] or a pendent group.[14-16] The pendent sulfide groups terminated by an accelerator residue reacts with another pendent group of the neighboring rubber chains so a new crosslink is formed.

The IR vulcanizate used in this study can have various pendent groups as shown in Scheme 2. Pendent groups in the IR vulcanizate can have terminal goups of piperidine, dimethylamine, and MBT generated from DPTT, TMTD, and MBT, respectively. Pendent groups terminated by piperidine can be more abundant than the others because the DPTT content is larger than the TMTD and MBT ones. When the combination reactions occur, some products of neutral molecules can be also formed as well as new sulfur crosslinks. There are free piperidines as well as the pendent groups in the vulcanizate since DPTT is dissociated during vulcanization. During the thermal aging, piperidine can be formed as a reaction product when the sulfide pendent group terminated by piperidine reacts with another one. Organic materials remained in the vulcanizate before and after the thermal aging were measured to investigate formations of

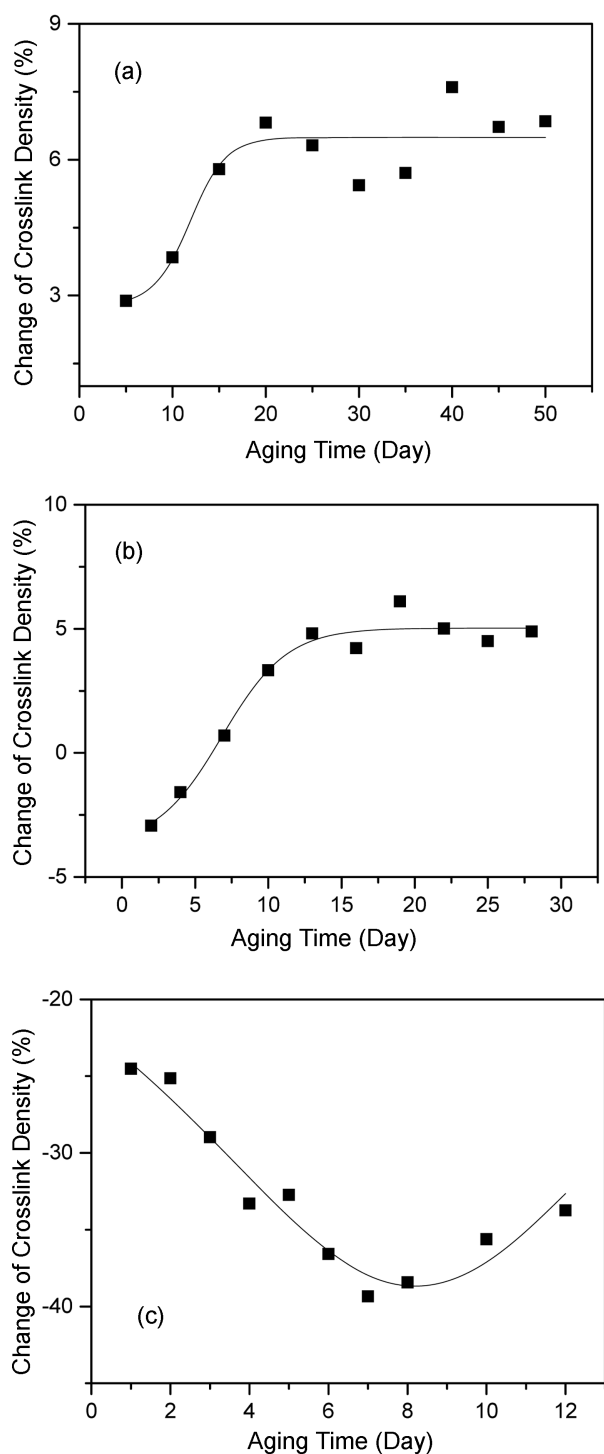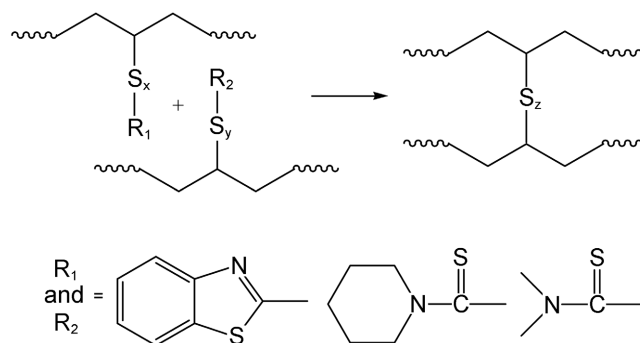1854   *Bull. Korean Chem. Soc.* **2005**, Vol. 26, No. 11

Notes

Figure 1. Variation of the crosslink density change of the IR vulcanizate by the thermal aging at 60 °C (a), 80 °C (b), and 100 °C (c) with the aging time.

Scheme 2. Pendent groups and their combination reaction.

Table 1. Amounts of evaporated BPH, MBT, and piperidine after the thermal aging at 100 °C for 2 and 12 days (%)

Aging time (day)	BPH	MBT	piperidine
2	58.4	94.7	89.9
12	97.5	98.0	92.9

of an organic chemical in the initial and aged samples, respectively. The amount of evaporated BPH notably increases by increasing the aging time, but for piperidine and MBT the differences between the two aging times are relatively small. This means that MBT and piperidine are generated during the thermal aging, especially piperidine. Although piperidine is smaller than BPH and MBT, the amount of piperidine remained in the sample after the thermal aging at 100 °C for 12 days is larger than those of BPH and MBT. This is a concrete evidence that there are lots of pendent sulfide groups terminated by piperidine and new piperidines are formed by the combination reactions.

For the thermal aging at 80 °C, the crosslink density decreases at the initial aging period and then increases as shown in Figure 1(b). The crosslink density change increases steeply until 15 days and then very slightly increases. The initial decrease of the crosslink density at high temperature of 80 °C can not be observed in a conventional rubber vulcanizate with an accelerated sulfur cure system.[9,10] In general, crosslink density of a rubber vulcanizate with an accelerated sulfur cure system is increased by thermal aging and the increment becomes larger as the aging time elapses. The decreased crosslink density by the thermal aging was observed more seriously at 100 °C.

Variation of the crosslink density change at 100 °C shows abnormal behaviors as shown in Figure 1(c). The crosslink density after the thermal aging at 100 °C steeply decreases. The decrement increases until 8 days and then decreases. The serious decrease of the crosslink density at 100 °C may be due to the short sulfur crosslinks of S_x (x = 1 or 2). Short sulfur crosslinks are more stable than long ones. Bond strengths of mono- (~C-S~), di- (~S-S~), tri- (~S_2-S~), and tetrasulfides (~S_2-S_2~) are 295–340, 266–281, 218–232, 177–202 kJ/mol, respectively.[8] Thus, the dissociation reactions of the sulfide linkages will be more and more activated by increasing the temperature.

accelerator residues by the thermal aging. Table 1 shows the amounts of evaporated BPH, MBT, and piperidine after the thermal aging at 100 °C for 2 and 12 days. BPH, MBT, and piperidine were measured with GC/MS after extracting them with THF. The amounts of evaporated organic chemicals by the thermal aging were calculated by $M_{evap}(\%) = 100 \times (M_{ini} - M_{aged})/M_{ini}$, where the M_{ini} and M_{aged} indicate the amounts

Notes

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The experimental results say that the crosslink density change of the IR vulcanizate with sulfur donors and without elemental sulfur by thermal aging is varied with the aging temperature. The dissociation reactions of the existing sulfur crosslinks are more activated than the combination reactions as the aging temperature increases and the combination reactions between the pendent groups can occur even at low temperature. Thus, the crosslink density of the vulcanizate decreases for the thermal aging at high temperature but it increases for the thermal aging at low temperature.

Experimental Section

Elemental sulfur-free polyisoprene (IR) vulcanizate was composed of IR (100 phr), $CaCO_3$ (20.0 phr), TiO_2 (7.0 phr), oil (7.0 phr), 2-mercaptobenzothiazole (MBT, 0.3 phr), tetramethyl thiuramdisulfide (TMTD, 0.2 phr), dipentamethylene thiuramdisulfide (DPTT, 0.6 phr), 2,2'-methylene-bis(4-methyl-6-*tert*-butylphenol) (BPH, 1.0 phr). MBT, TMTD, and DPTT are cure accelerators and BPH is a non-staining antidegradant. TMTD and DPTT are sulfur donors. Scheme 1 shows their chemical formulas. Dimension of the test sample is 3.0×5.0 cm (2.0 mm thick). The thermal aging experiments were carried out at constant temperatures of 60, 80, and 100 $^{\circ}$C in a convection oven. Amounts of the cure accelerator residues and antidegradant remained in the rubber vulcanizates were measured by gas chromatography/mass spectrometry (GC/MS) of Agilent Technol. 5890N/5987 GC/MS after extracting the organic materials with THF.

Crosslink densities of the samples before and after the thermal aging were measured by swelling method. Organic additives in the samples were removed by extracting with THF and *n*-hexane for each 2 days and they were dried for 2 days at room temperature. The weights of the organic material-extracted samples were measured. They were soaked in *n*-decane for 2 days and the weights of the swollen samples were measured. The swelling ratio (**Q**) was calculated by the equation of $\mathbf{Q} = (\mathbf{W_s} - \mathbf{W_u})/\mathbf{W_u}$, where $\mathbf{W_s}$ and $\mathbf{W_u}$ are weights of the swollen and unswollen samples. The reciprocal swelling ratio, **1/Q**, was used as the apparent crosslink density.[17] Experiments were carried out three times and they were averaged.

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