Recovery Behaviors of Silica-Reinforced SBR Vulcanizates Using Circular Deformation Test

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Abstract: We introduced a new test method, the circular deformation method which changing a linear sample to a circular form by fixing the both ends with a pin, to investigate recovery behaviors and level of the permanent set of a rubber vulcanizate by thermal aging. The pin was removed after the thermal aging, and the gap distance between both ends of the sample was measured. The recovery increased as the measuring time elapsed. The instantaneous recovery less than 0.1 s could be obtained from the extrapolation method. Influence of the 1,2-unit content on the recovery behaviors of silica-filled SBR vulcanizates was also investigated. The SBR specimen with the higher 1,2-unit content had faster recovery behaviors than that with lower one. The silica-filled SBR vulcanizates containing the silane coupling agent had higher recoveries than those without the coupling agent irrespective of the 1,2-unit contents. The experimental results were explained with the crosslink density and the filler-polymer interactions. The instantaneous recovery at 0.09 s became larger as the crosslink density of the sample increased.

Keywords: circular deformation, recovery, thermal aging, crosslink density, SBR vulcanizate

Introduction

Rubber vulcanizates can be permanently deformed when they are deformed for a long time, especially in high temperatures. One of principal reasons about permanent deformation is change of crosslink density [1]. Crosslink density of a rubber vulcanizate is changed by thermal aging [2-6]. Sulfur linkages, especially polysulfides, are dissociated by heating [1,8,9] and this brings about reduction of the crosslink density. Curatives remained in a rubber vulcanizate make new crosslinks [1,9] and it results in increase of the crosslink density. In general, crosslink density of a sulfur-cured rubber vulcanizate increases with increase of the aging temperature [2-4]. However, for a rubber vulcanizate with an elemental sulfur-free cure system, the crosslink density decreased after thermal aging at high temperatures [5]. A rubber material has a recovery property to return to its original shape from deformation [10]. If states of a rubber vulcanizate such as crosslink density and type and arrangement of polymer chains are not changed by aging, the rubber specimen can be fully returned to its original shape. If not, a rubber specimen cannot be absolutely returned to the original shape.

Compression set test according to the ISO 3384 (Rubber, vulcanized or thermoplastic-Determination of stress relaxation in compression at ambient and at elevated temperatures) is a common method to measure the degree of deformation of a rubber vulcanizate. However, since specimens for the compression set are relatively thick (28.7 mm diameter and 12.7 mm height) differences in the initial states of the samples such as dimensions and crosslink densities are cannot be negligible. We introduced a new and simple method with low experimental errors to investigate recovery behaviors from deformation of a rubber vulcanizate. The circular deformation test is the simplest method to measure degree of the deformation of a rubber article since thin specimens of 2 mm thickness with uniform states are used.

Carbon black and silica are the most popular reinforcing fillers in rubber compounds. Silica has a number of hydroxyl groups (silanol, Si-OH), which results in strong
filler-filler interactions and adsorption of polar materials by hydrogen bonds [11]. Since intermolecular hydrogen bonds between silanol groups on the silica surface are very strong, it can aggregate tightly [12,13]. Its property can cause a poor dispersion of silica in a less polar rubber compound. In general, a silane coupling agent such as bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) is used to improve the filler dispersion and to prevent adsorption of curatives on the silica surface [14].

Styrene-butadiene rubber (SBR) is a copolymer of styrene and butadiene. The butadiene sequence has three different microstructures of cis-1,4-, trans-1,4-, and 1,2-units. Grades of SBR are determined by ratios of the four components. For a rubber compound having an accelerated sulfur cure system, crosslinking sites of a rubber compound are allylic carbons [8]. The 1,2-unit has one allylic carbon which is hindered by the vinyl group whereas the cis-1,4- and trans-1,4-units have two allylic carbons. One can expect that deformation and recovery behaviors of SBR vulcanizates will be varied with the SBR types. In the present work, we studied the recovery behaviors of the silica-reinforced SBR vulcanizates with different 1,2-unit contents using the circular deformation method. Three types of SBRs with different 1,2-unit contents of 18, 25, and 60 wt% were used. The instantaneous recoveries were calculated by extrapolation method and compared.

Experimental

The SBR compounds were made of SBR (100.0 phr), silica (Z175, 50.0 phr), silane coupling agent (Si69, bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT), 0.0 or 3.0 phr), stearic acid (2.0 phr), zinc oxide (2.0 phr), N-phenyl-N’-(1,3-dimethylbutyl)-p-phenylenediamine (HPPD, 2.0 phr), wax (2.0 phr), N-tert-butyl-2-benzothiazole sulfenamide (TBBS, 2.0 phr), and sulfur (2.0 phr). SBR 1502 of Kumho Petroleum Co., VSL 2525 of Lanxess Co., and NS 116 of Nippon Zeon Co. were employed as the SBRs. The 1,2-unit contents are 18, 25, and 60 wt%, respectively. The vulcanizates were prepared by curing at 160 °C for the tmax in a compression mold (140 × 140 × 2 mm²).

The circular deformation experiments were carried out as follow (Figure 1): First, the sample was cut with dimension of 5 × 120 mm² with 2 mm thickness. Second, the linear sample was changed to a circular form by fixing both the ends with a pin. Third, the samples with circular form were aged at room temperature for 30 days and at 80 °C for 7 days in a convection oven. Finally, removing the pin and the gap distance between both ends of the sample was measured after 6.9 × 10⁻³, 4.2 × 10⁻², 0.42, 1.0, 5.0, 10.0, and 30.0 days. 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 3 and 2 days, respectively, and they were dried for 2 days at room temperature. The weights of the organic materials-extracted samples were measured. They were soaked in toluene for 2 days and the weights of the swollen samples were measured. The swelling ratio (Q) was calculated by the equation of $Q = \frac{W_s-W_u}{W_u}$, where $W_i$ and $W_o$ are weights of the swollen and unswollen samples. In general, the reciprocal swelling ratio (1/Q) was used as the apparent crosslink density. Experiments were carried out three times and they were averaged.

Results and Discussion

In order to investigate the recovery behaviors from the circular form of the silica-reinforced SBR vulcanizates by the thermal aging, the gap distance between both ends of the sample was measured at 6.9 × 10⁻³, 4.2 × 10⁻², 0.42, 1.0, 5.0, 10.0, and 30.0 days after removing the pin. Gillen and coworkers [15] measured variation of the compression set of a rubber vulcanize with the measuring time after the removal of the sample from the jig to investigate the sealing properties and reported that the compression decreased the measuring time. We measured variation of the recovery behaviors from the circular shape with the measuring time and the instantaneous recoveries obtained from the extrapolation method. Degree of the instantaneous recovery is related with the sealing capability of sealant such as O-ring. Figure 2 is the photographs of the deformed specimens after the thermal aging at 80 °C. Level of the deformation is varied with the 1,2-unit contents of SBR and the existence or not of the silane coupling agent in the rubber compounds as well as the thermal aging conditions. Figure 2 shows partly deformed samples by thermal aging and this means that the rubber vulcanizates are permanently deformed by the thermal aging. The silicafilled SBR vulcanize containing Si69 is less deformed than that without the coupling agent.

Recovery (R) was calculated by the equation of $R(\%) = 100 \times \left(\frac{d_i}{d_o}\right)$, where $d_i$ and $d_o$ are the gap distance and the length of the linear sample, respectively. Figure 3
Figure 2. Photographs of the deformed silica-filled SBR vulcanizates with the 25 wt% 1,2-unit content by the thermal aging at 80 °C for 7 days. The measuring time is 17 days after removing the pin. (a) and (b) are the samples without and containing the silane coupling agent, respectively.

Figure 3. Variations of the recoveries of the SBR vulcanizates from the circular form after the thermal aging at room temperature for 30 days with the measuring time. The squares, circles, and triangles indicate the specimens with the 1,2-unit contents of 18, 25, and 60 wt%, respectively. The solid and open symbols stand for the SBR specimens without and containing the silane coupling agent, respectively.

shows variations of the recoveries with the measuring time after the aging at room temperature for 30 days. The recoveries enhance with increasing the measuring time. The linear curve fittings show good relations (the correlation coefficients are about 0.99). The SBR vulcanizates containing Si69 have better recoveries than those without the silane coupling agent. This can be explained with the crosslink densities. A rubber composite with higher crosslink density has higher modulus and is stiffer than that with lower one [16]. A rubber composite having the higher modulus property will be recovered faster from the deformed shape to the original linear form than that having the lower modulus. Crosslink densities of the SBR vulcanizates containing Si69 are higher than those without the coupling agent. The apparent crosslink densities (1/Q) of the SBR vulcanizates containing Si69 are 0.47, 0.48, and 0.54 for the specimens with the 1,2-unit contents of 18, 25, 60 wt%, respectively, whereas for the SBR vulcanizates without the coupling agent the apparent crosslink densities are 0.32, 0.37, and 0.41, respectively. Level of the enhanced recovery with the measuring time for the SBR specimen without Si69 is larger than for the SBR specimen containing Si69 as shown in Figure 3. The slopes obtained from the linear curve fittings for the SBR vulcanizates without Si69 are 6.99, 7.57, and 5.47 for the specimens with the 1,2-unit contents of 18, 25, and 60 wt%, respectively, whereas those for the SBR vulcanizates containing Si69 are 5.60, 5.06, and 4.57, respectively.

The SBR specimen with the higher 1,2-unit content shows better recovery behaviors than that with lower one. This can be explained with the crosslink density and silica dispersion. The SBR vulcanize with the higher 1,2-unit content has higher crosslink density than that with lower one as discussed above. The big difference in the recoveries (for example, the SBR vulcanizates with the 1,2-unit contents of 18 and 25 wt% which do not contain Si69) cannot be sufficiently explained only with the crosslink densities. The other principal reason may be the improved silica dispersion. The 1,2-unit is more interactive with silica than the other components of the cis-1,4- and trans-1,4-units and improves the silica dispersion, which leads to the enhanced modulus [17,18]. Major factors influenced on the modulus are the crosslink density, filler-filler interactions, and polymer-filler interactions [19-21]. For the vulcanizates without Si69, the moduli at 100 % strain are 17.5, 25.0, and 35.7 kg/cm² for the specimens with the 1,2-unit content of 18, 25, and 60 wt%, respectively. For the vulcanizates containing Si69, the 100 % moduli are 28.4, 32.5, and 42.2 kg/cm², respectively.

Figure 4 shows variations of the recovery after the thermal aging at 80 °C with the measuring time. The recovery behaviors after the thermal aging at 80 °C show similar trends to those after the aging at room temperature; the recoveries enhance with increasing the measuring time. Levels of the recoveries after the thermal aging at 80 °C are lower than those after the aging at room temperature. Degree of the increased recovery with the measuring time for the SBR specimen without Si69 is on the whole larger than for the SBR specimen containing the coupling agent. The slopes obtained from the linear curve fittings for the SBR vulcanizates without Si69 are 4.70, 4.94, and 4.98 for the specimens with the 1,2-unit contents of 18, 25, 60 wt%, respectively, whereas those for the SBR vulcanizates containing the coupling agent are 3.56, 5.01, and 4.80, respectively. The increased recovery rates for the thermal aging at 80 °C are on the whole lower than for the aging at room temperature. For the thermal aging at 80 °C, the difference in the in-
Increased recovery levels between the SBR vulcanizates without and containing Si69 is smaller than for the aging at room temperature.

Instantaneous recoveries were obtained from the linear curve fitting equations of Figures 3 and 4. Let the recovery at 1.0 × 10⁻⁶ day (0.09 sec) be the instantaneous recovery. For the aging at room temperature, the instantaneous recoveries of the SBR vulcanizates without Si69 are 30.9, 26.6, and 52.4 % for the specimens the 1,2-unit contents of 18, 25, and 60 wt%, respectively, while those of the SBR vulcanizates containing the coupling agent are 43.1, 58.0, and 62.5 %, respectively. For the thermal aging at 80 °C, the instantaneous recoveries of the SBR vulcanizates without Si69 are 7.03, 15.3, and 21.7 %, respectively, while those of the SBR vulcanizates containing the coupling agent are 18.5, 27.0, and 32.3 %, respectively. The instantaneous recoveries of the SBR vulcanizates containing Si69 are larger than those of the SBR vulcanizates without the coupling agent and the instantaneous recovery is enhanced by increasing the 1,2-unit content.

Crosslink density of a rubber composite determines the physical and chemical properties. Relations between the instantaneous recovery and the crosslink density were investigated. Figure 5 shows the variation of the instantaneous recoveries with the apparent crosslink density. The instantaneous recovery is almost linearly increased by increasing the apparent crosslink density. It can lead to a conclusion that the recovery becomes larger as the crosslink density and the polymer-filler interactions increase and the instantaneous recovery also becomes larger as the crosslink density increases.

**Conclusion**

The recovery from the circular shape after thermal aging was increased by elapsing the measuring time. The SBR vulcanizates containing the silane coupling agent had better recoveries than those without the coupling agent because crosslink densities of the formers were higher than those of the latter. The recovery after the thermal aging at room temperature was higher than that after the thermal aging at 80 °C. The increased recovery rates for the thermal aging at 80 °C were lower than for the aging at room temperature. The instantaneous recovery was obtained from the linear curve fitting equation and was linearly increased by increasing the apparent crosslink density.

**References**