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Influence of Aging Media and Filler System on Recovery Behaviors of Natural Rubber Composites

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노화 매질과 충진 시스템이 천연고무 복합체의 회복 거동에 미치는 영향

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ABSTRACT : Difference in recovery behaviors from the circular deformation of natural rubber (NR) composites aged in air and distilled water, respectively were investigated. Recoveries of the samples aged in air were larger than those of the samples aged in distilled water. Recovery rates of the samples reinforced with filler were faster than those of the unreinforced ones. Recovery rates of the carbon black-filled samples were faster than those of the silica-filled ones. Difference in the recovery behaviors according to the aging media can be explained by the crosslinking density changes and the annealing effect.

요 약 : 공기와 증류수에서 노화시킨 천연고무 복합체의 원형 변형으로부터의 회복 거동의 차이를 연구하였다. 공기에서 노화시킨 시험편의 회복률이 증류수에서 노화시킨 것보다 더 컸다. 충진제로 보강한 시험편의 회복속도가 비충진 시험편보다 더 빨랐다. 카본블랙으로 보강한 시험편의 회복속도가 실리카로 보강한 시험편보다 더 빨랐다. 노화 매질에 따른 회복 거동의 차이는 가교밀도 변화와 아닐링 효과로 설명하였다.

Keywords : recovery, circular deformation, thermal aging, NR, aging medium, filler system

Ⅰ. Introduction

A rubber material has a recovery property to return to its original shape from deformation.[1] If states of a rubber composite such as crosslink density, crosslink type, and arrangement of polymer chains are not changed by aging, the specimen can fully return to its original shape. If states of a rubber article are to some extent changed under deformation, the sample cannot absolutely return to its original shape. Rubber vulcanizates can be permanently deformed when they are deformed for a long time, especially at high temperatures. One of the principal reasons regarding permanent deformation is change of crosslink density.[2] Thermal aging causes the crosslink density of a rubber vulcanizate to change.[3-7]

When a rubber article is used for a long period of time, it becomes aged, usually becomes hardened, and often loses its damping capability. If a rubber component is to some extent permanently deformed, its physical properties deteriorate. Especially, recovery properties of a permanently deformed rubber component deteriorate, which lead to severe aggravation of the sealing properties. In the present work, recovery behaviors of natural rubber (NR) composites with different reinforcing systems of unfilled, carbon black-filled, and silica-filled systems were investigated. The specimens were aged and degree of the permanent deformation (limited recovery), instantaneous recovery, and recovery rate of the aged sample were examined. The circular deformation test method[8-14] was employed as the deformation and recovery test. It requires changing a linear sample to a circular form by fixing both ends with a pin to investigate the recovery behaviors of a rubber article. This method is the simple and reliable method to measure the degree of deformation of a rubber article since thin specimens with 2 mm thickness in uniform states are used. When a linear sample of vulcanized rubber is circularly deformed, the stress and strain vary uniformly across the thickness of the sample.[12]

Carbon black and silica are polular reinforcing fillers for a rubber composite.[15-17] Silane coupling agent[16,17] is used along

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with silica to improve the silica dispersion and to prevent adsorption of curatives on the silica surface. The linear NR samples were deformed to circular shape and aged. Degree of recovery of the aged sample was measured. Rubber articles contact to moisture and water as well as air. The samples were aged in distilled water as well as in air to examine the aging medium effect. Influence of the aging temperature on the recovery behaviors was also investigated.

Ⅱ. Experimental

Unfilled, carbon black-filled, and silica-filled NR compounds were made of rubber (SMR20 100.0 phr), filler (N330 50.0 phr for carbon black system, Z175 50.0 phr and Si69 3.0 phr for silica system), antidegradants (*N*-phenyl-*N*'-(1,3-dimethylbutyl)-*p*-phenylenediamine (HPPD) 2.0 phr and wax 2.0 phr), cure activators (stearic acid 2.0 phr and ZnO 2.0 phr), *N-tert-butyl*-2-benzothiazole sulfenamide (TBBS, 1.6 phr), and sulfur (1.4 phr). Mixing was performed in a Banbury type mixer and the vulcanizate was prepared using a compression mold (140 mm×140 mm×2 mm).

The sample dimension for the thermal aging experiment was 5 mm×100 mm (thickness 2 mm). The circular deformation experiments were carried out as follows. First, the linear sample was changed into a circular form by fixing both ends of the sample with a pin. Second, the circularly deformed samples were aged at 60, 70, 80, and 90 ℃ for 10 days in a convection oven. The aging media were air and distilled water. Finally, the pin was removed after thermal aging and the gap distance between both ends of the aged sample was measured from 1 hour to 10 days. Previous studies provide a detailed description of the circular deformation test.[8-14] Experiments were performed three times and averaged.

Apparent 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. Then, 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 (1)

$$Q = (W_s - W_u) / W_u, \quad (1)$$

where W_s and W_u 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 averaged.

Ⅲ. Results and discussion

When the linear sample with 100 mm length and 2 mm thickness is changed to a circular form, the applied strain in the outer part and compression in the inner part were about 6%. The recovery (*R*) was calculated by the equation (2)

$$R(\%) = 100 \times (d / l) \quad (2)$$

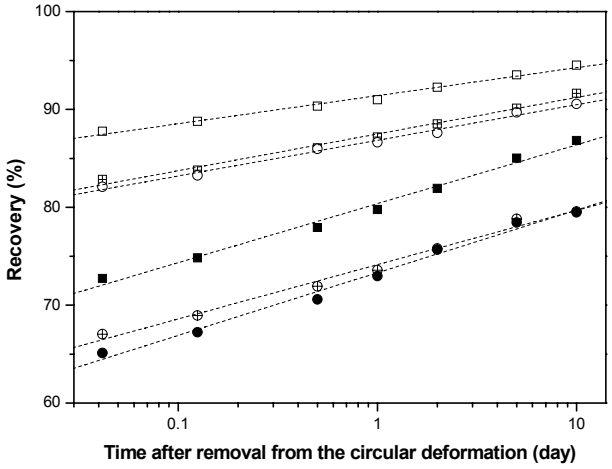

Figure 1. Recovery variations from the circularly deformed sample after thermal aging at 60℃ with the measurement time. The squares and circles indicate the aging media of air and distilled water, respectively. The open, solid, and crossed symbols denote the filler systems of unfilled, carbon black-filled, and silica-filled systems, respectively.

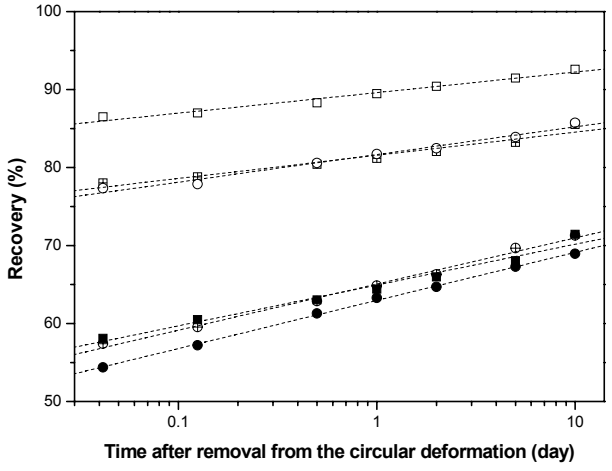

Figure 2. Recovery variations from the circularly deformed sample after thermal aging at 70℃ with the measurement time. The squares and circles indicate the aging media of air and distilled water, respectively. The open, solid, and crossed symbols denote the filler systems of unfilled, carbon-filled, and silica-filled systems, respectively.

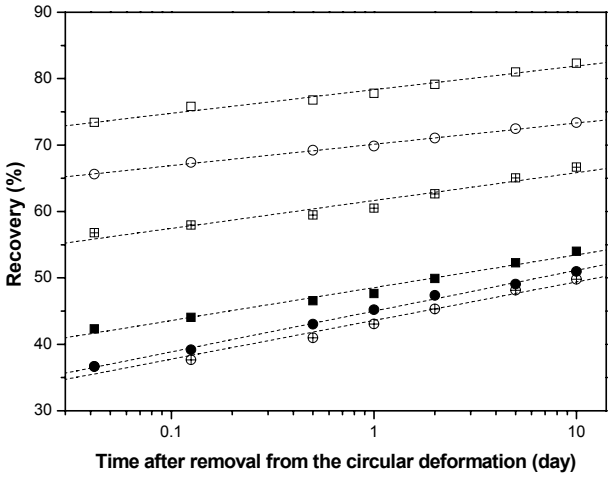

Figure 3. Recovery variations from the circularly deformed sample after thermal aging at 80℃ with the measurement time. The squares and circles indicate the aging media of air and distilled water, respectively. The open, solid, and crossed symbols denote the filler systems of unfilled, carbon-filled, and silica-filled systems, respectively.

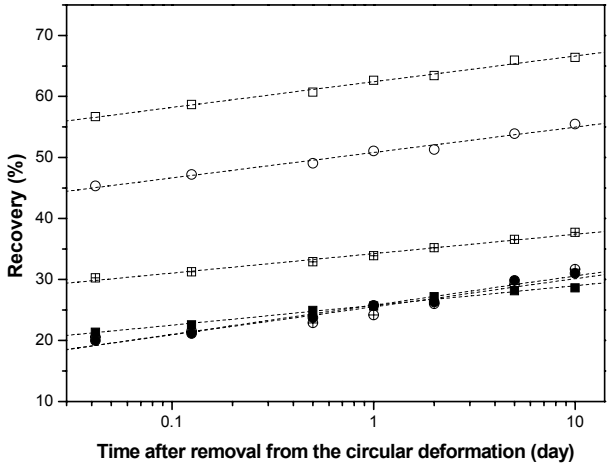

Figure 4. Recovery variations from the circularly deformed sample after thermal aging at 90℃ with the measurement time. The squares and circles indicate the aging media of air and distilled water, respectively. The open, solid, and crossed symbols denote the filler systems of unfilled, carbon-filled, and silica-filled systems, respectively.

where d is the gap distance between both ends of the deformed sample after thermal aging and l is the length of the linear sample. The gap distance between both ends of the thermally aged sample was measured and the recovery variation with the measurement time was investigated. Figures 1, 2, 3, and 4 show the recovery variations of the thermally aged samples at 60, 70, 80, and 90 ℃, respectively. The recovery linearly increased as the measurement time elapsed irrespective of the aging temperatures and aging media. The curve fitting equations for the recovery variations were summarized in Tables 1 - 4. The correlation coefficients were relatively high. The recovery decreased as the aging temperature increased. This indicates that degree of the permanent deformation became severe as the aging temperature increased.

Recoveries of the unfilled samples were larger than those of the filled ones irrespective of the aging temperatures and the aging media as shown in Figures 1 - 4. This may be due to rearrangement of deformed rubber chains and filler particles besides the crosslink density changes. Parameters affecting to permanently deform a rubber vulcanizate are the rearrangements of rubber chains and fillers and the change of crosslink density by aging.[2,8-14,18] When a rubber article is deformed, the rubber chains are strained and their microstructures are changed. If the strained polymer chains are settled in the deformed state by rearrangement and stabilization, degree of the permanent deformation of the rubber article will increase and the recovery behaviors will also be influenced. Positions of filler particles in a rubber sample will be also moved by deformation and they will be rearranged to settle down in new space. Newly fixed arrangement of filler particles in the deformed specimen may disrupt the recovery to its original linear shape by filler-filler interactions and interruption of movement of rubber chains. Furthermore, increment of the crosslink density of the unfilled sample was lower than those of the filled samples. The crosslink densities were increased by thermal aging. Apparent crosslink densities (1/Q) of the samples before and after the thermal aging at 90 ℃ were measured and the crosslink density changes (ΔX_c) were obtained by the equation (3)

$$\Delta X_c(\%) = 100 \times [(1 / Q_a) - (1 / Q_i)] / (1 / Q_i) \quad (3)$$

where $1/Q_i$ is the apparent crosslink density of the unaged sample, and $1/Q_a$ is the apparent crosslink density of the aged sample. The ΔX_cs of the NR composites aged in air were 5.1, 9.6, and 5.2% for the unfilled, carbon black-filled, and silica-filled samples, respectively. The ΔX_cs of the NR composites aged in distilled water were 6.9, 17.3, and 8.0%, respectively. Large increment of the crosslink density of a rubber composite leads to high degree of the permanent deformation.[10]

Recoveries of the silica-filled samples were larger than those of the carbon black-filled ones irrespective of the aging temperatures and the aging media. This may be due to the difference in the crosslink density changes of the silica-filled and carbon black-filled samples. Increments of the crosslink densities of the carbon black-filled composites were larger than those of the silica-filled ones by about twice for the thermal

Table 1. Linear curve fitting equations of the recovery variations from the circularly deformed sample after thermal aging at 60℃ with the measurement time (Figure 1).

Aging medium	Filler	Linear curve fitting equation (correlation coefficient, r)
Air	Unfilled	y = 2.86x + 91.4 (r = 0.994)
	Carbon black	y = 6.02x + 80.6 (r = 0.995)
	Silica	y = 3.75x + 87.5 (r = 0.994)
Distilled water	Unfilled	y = 3.65x + 86.8 (r = 0.996)
	Carbon black	y = 6.40x + 73.3 (r = 0.995)
	Silica	y = 5.55x + 74.1 (r = 0.994)

Table 2. Linear curve fitting equations of the recovery variations from the circularly deformed sample after thermal aging at 70℃ with the measurement time (Figure 2).

Aging medium	Filler	Linear curve fitting equation (correlation coefficient, r)
Air	Unfilled	y = 2.64x + 89.6 (r = 0.988)
	Carbon black	y = 5.23x + 64.9 (r = 0.988)
	Silica	y = 2.97x + 81.6 (r = 0.976)
Distilled water	Unfilled	y = 3.55x + 81.7 (r = 0.990)
	Carbon black	y = 6.17x + 63.0 (r = 0.999)
	Silica	y = 5.93x + 65.1 (r = 0.996)

Table 3. Linear curve fitting equations of the recovery variations from the circularly deformed sample after thermal aging at 80℃ with the measurement time (Figure 3).

Aging medium	Filler	Linear curve fitting equation (correlation coefficient, r)
Air	Unfilled	y = 3.56x + 78.3 (r = 0.988)
	Carbon black	y = 4.94x + 48.5 (r = 0.992)
	Silica	y = 4.19x + 61.6 (r = 0.975)
Distilled water	Unfilled	y = 3.21x + 70.1 (r = 0.999)
	Carbon black	y = 6.13x + 45.0 (r = 0.998)
	Silica	y = 5.82x + 43.6 (r = 0.990)

Table 4. Linear curve fitting equations of the recovery variations from the circularly deformed sample after thermal aging at 90℃ with the measurement time (Figure 4).

Aging medium	Filler	Linear curve fitting equation (correlation coefficient, r)
Air	Unfilled	y = 4.22x + 62.4 (r = 0.995)
	Carbon black	y = 3.24x + 25.8 (r = 0.995)
	Silica	y = 3.18x + 34.2 (r = 0.994)
Distilled water	Unfilled	y = 4.17x + 50.8 (r = 0.992)
	Carbon black	y = 4.79x + 25.8 (r = 0.987)
	Silica	y = 4.60x + 25.5 (r = 0.956)

aging at 90 ℃ as discussed above. In general, degree of the permanent deformation of a rubber composite becomes more severe as the crosslink density is increased by thermal aging.[10,12]

Recoveries of the samples aged in air were on the whole larger than those of the samples aged in distilled water irrespective of the filler systems and the aging temperatures. This can be explained with the difference of crosslink density changes and annealing effect by water. Increments of the crosslink densities of the samples aged in air were smaller than those of the samples aged in distilled water as discussed above. In addition to this, the sample contacted with water can be annealed and the rubber chains can be more stabilized and settled compared to the samples aged in air. This contributes to permanent deformation.

The slopes of the linear curve fitting equations indicate the recovery rates depending on the measurement time. The recovery rates of the filled samples were on the whole faster than those of the unfilled ones as listed in Tables 1 - 4. The recovery rates of the carbon black-filled composite were faster than those of the silica-filled one. This is explained with the elascity due to the initial crosslink density. Initial apparent crosslink densities ($1/Q_i$) of the unfilled, carbon black-filled, and silica-filled samples were 0.266, 0.555, and 0.520, respectively. Since the carbon black-filled and silica-filled samples contained 50.0 phr filler, the rubber fraction was 0.667. Thus, the corrected apparent crosslink densities were calculated by multiplying the $1/Q_i$ by the rubber fraction. The corrected apparent crosslink densities of carbon black-filled and silica-filled samples were 0.370 and 0.347, respectively. If the crosslink density of a rubber composite increases, length between the crosslink points reduces and the elastic stress increases. The high elastic stress can lead to fast recovery (Figure 5).

The recovery rates of the filled samples aged in distilled water were faster than those aged in air as listed in Tables 1 - 4. This can be explained with evaporation of water swollen

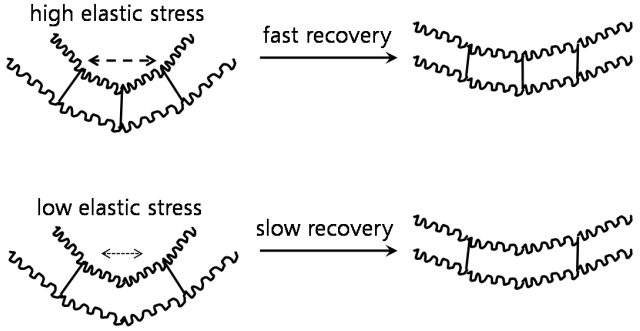

Figure 5. Recovery from the circularly deformed sample with high and low elastic stresses.

Figure 6. Recovery to void formed by water evaporation.

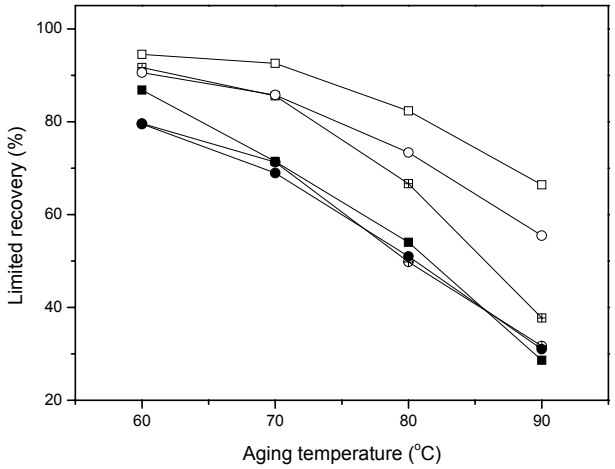

Figure 7. Variations of the limited recoveries (recoveries at the measurement time of 10 days) with the aging temperature. The squares and circles indicate the aging media of air and distilled water, respectively. The open, solid, and crossed symbols denote the filler systems of unfilled, carbon-filled, and silica-filled systems, respectively.

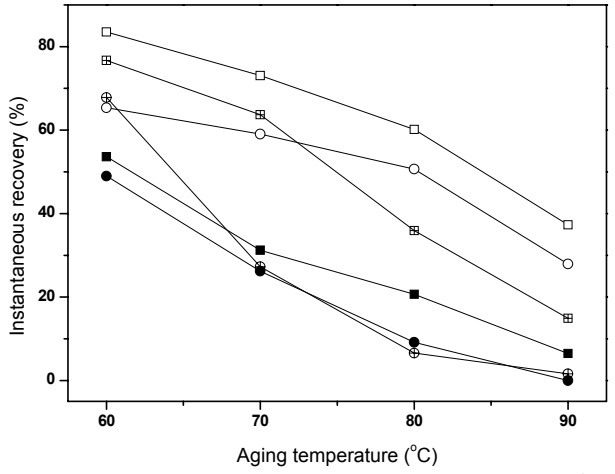

Figure 8. Variations of the instantaneous recoveries at 10^{-6} day with the aging temperature. The squares and circles indicate the aging media of air and distilled water, respectively. The open, solid, and crossed symbols denote the filler systems of unfilled, carbon-filled, and silica-filled systems, respectively.

in the sample and consequent rearrangement of the neighboring rubber chains to fill the void (Figure 6). The difference in the recovery rates of the silica-filled NR composite aged in distilled water and in air was on the whole larger than that of the carbon black-filled one. The differences for the silica-filled NR composite at 60, 70, 80, and 90 ℃ were 1.48, 2.00, 1.39, and 1.45, respectively. The differences for the carbon black-filled NR composite were 1.06, 1.18, 1.24, and 1.48, respectively. Since silica has lots of silanol groups on the surface, the silica-filled NR composite can absorb water molecules more than the carbon black-filled one. For the unfilled sample, the recovery rates showed different trends according to the aging temperatures. For the aging at 60 and 70 ℃, the recovery rates in distilled water were faster than those aged in air as similar to the filled samples (Tables 1 and 2). However, for the aging at 80 and 90 ℃, the recovery rates in distilled water were slower than those aged in air (Tables 3 and 4). The differences for the unfilled NR composite at 60, 70, 80, and 90 ℃ were 1.28, 1.34, 0.90, and 0.99, respectively.

The recoveries hardly changed longer than 10 days after the thermal aging. The recovery at the measurement time of 10 days is used as the limited recovery. Figure 7 shows the limited recovery variations with the aging temperature. Limited recoveries of the unfilled samples were larger than those of the filled ones, and those of the silica-filled samples were larger than those of the carbon black-filled ones irrespective of the aging media. This may be also due to the degree of the crosslink density changes and filler effects. Limited recoveries of the samples aged in air were larger than those of the samples aged in water irrespective of the filler systems. This may be also due to the degree of the crosslink density changes and annealing effect by water.

Instantaneous recoveries, defined as the degree of recovery observed immediately following release from deformation, can be obtained from the recovery versus measurement time curves by extrapolating the linear equation to very short measurement time. The instantaneous recovery can be used as a convenient criterion to ascertain the quality of a rubber sealant such as an O-ring since common requirements of rubber sealants include high elasticity and fast recovery following deformation. Figure 8 shows the variations of the instantaneous recoveries at 1.0×10^{-6} day (0.09 sec) with the aging temperature. Instantaneous recoveries of the unfilled samples were larger than those of the filled ones, and those of the silica-filled samples were larger than those of the carbon black-filled ones irrespective of the aging media. This may be also due to the degree of the crosslink density changes and filler effects. Instantaneous recoveries of the samples aged in air were larger than those of the samples aged in water irrespective of the filler systems. This may be also due to the degree of the crosslink density changes and annealing effect by water.

Ⅳ. Conclusions

The unfilled, carbon black-filled, and silica-filled NR composites were aged in air and distilled water. The recoveries increased as the measurement time increased. The limited recoveries of the unfilled samples were larger than those of the filled ones, and those of the silica-filled samples were larger than those of the carbon black-filled ones irrespective of the aging media. The limited recoveries of the samples aged in air were larger than those of the samples aged in water irrespective of the filler systems. Variations of the limited recoveries according to the filler systems and aging media can be explained with the degree of the crosslink density changes and annealing effect by water. The recovery rates of the filled samples aged in distilled water were faster than those aged in air. This can be explained with evaporation of water swollen in the sample and consequent rearrangement of the neighboring rubber chains to fill the void. The difference in the recovery rates of the silica-filled NR composite aged in distilled water and in air was on the whole larger than that of the carbon black-filled one. The instantaneous recoveries of the unfilled samples were larger than those of the filled ones, and those of the silica-filled samples were larger than those of the carbon black-filled ones. The instantaneous recoveries of the samples aged in air were larger than those of the samples aged in water irrespective of the filler systems. This may be also due to the degree of the crosslink density changes and annealing effect by water.

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