Elastomers and Composites
Vol. 48, No. 3, pp. 181~189 (September 2013)
doi: http://dx.doi.org/10.7473/EC.2013.48.3.181

Recovery Behaviors of Natural Rubber Composites Thermally Aged in Altering Medium Systems of Air and Water

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(Received April 18, 2013, Revised May 16, 2013, Accepted May 10, 2013)

공기와 물의 교매질 시스템에서 열노화된 천연고무 복합체의 회복 거동

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접수일(2013년 4월 18일), 수정일(2013년 5월 6일), 게재확정일(2013년 5월 10일)

ABSTRACT : Unfilled, carbon black-filled, and silica-filled natural rubber (NR) composites were aged with a circular deformation at 60 - 90℃ and the recovery behaviors were investigated. The samples were aged under the altering aging medium systems of air and distilled water every day for 10 days. The order of the recoveries according to the filler systems was unfilled > silica > carbon black. The recoveries of the samples aged in the air to water altering system were greater than those of the samples aged in the water to air altering system. The initial aging medium dominantly influenced the deformation level.

요 약 : 비충전, 카본블랙 충전, 그리고 실리카 충전 천연고무(NR) 복합체를 원형 변형 상태로 60 − 90℃에서 노화시켜 회복 거동을 조사하였다. 시험편은 공기와 물을 매일 교대로 교체하는 교매질 시스템 하에서 노화시켰다. 충전 시스템에 따른 회복률의 순서는 비보강 > 실리카 보강 > 카본블랙 보강 순이었다. 공기에서 물로 교체하는 교매질 시스템에서 노화된 시험편의 회복률이 물에서 공기로 교체하는 교매질 시스템에서 노화된 시험편의 회복률보다 더 컸다. 최초 노화 매질은 변형 정도에 지배적으로 영향을 끼쳤다.

Keywords : *recovery, thermal aging, NR composite, filler system, aging medium*

Ⅰ. Introduction

Rubber components have been used for sealants and isolators because rubber material has a recovery property to return to its original shape from deformation.[1] Testing methods to examine the recovery behaviors of a rubber composite are compression set test[2], compression stress relaxation (CSR)[3,4], and circular deformation test[5-11]. Compression set test according to the ISO 815 (Rubber, vulcanized or thermoplastic—Determination of compression set at ambient, elevated or low temperatures) is a common method to measure the degree of deformation of a rubber composite under compression state. However, specimens for the compression set are relatively thick (28.7 mm diameter and 12.7 mm height) and many samples are required for aging experiments so that differences in the initial states of the samples such as dimensions and crosslink densities cannot be negligible. In sealing applications, stress relaxation of a polymeric seal after assembly directly reduces the sealing force. Stress relaxation tests are gaining greater relevance for the determination of rubber properties. However, CSR also needs a special equipment for the test and it is not convenient.

The circular deformation test method is a simple and reliable method to investigate the recovery behaviors of a rubber article such as the degree of permanent deformation, instantaneous recovery, and recovery rate, because thin specimens with 2 mm thickness in uniform states are used.[5-11] And it is also a suitable testing method for an aging experiment under various aging media such as water and organic solvents, because the specimen is small and a special equipment is not needed for aging experiment. This method just 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. When a linear sample of a vulcanized rubber is circularly deformed, the stress and strain vary uniformly across the thickness of the sample.[9]

If states of a rubber composite such as crosslink density,

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crosslink type, and arrangement of polymer chains are not at all changed by aging, the rubber specimen can wholly return to its original shape. Otherwise, the sample cannot fully return to its original shape. Rubber composites are permanently deformed when they are deformed for a long time, especially at high temperatures. One of the principal reasons regarding permanent deformation of a rubber composite is the crosslink density change.[12] Thermal aging causes the crosslink density of a rubber vulcanizate to change.[13-17]

Rubber articles contact with moisture and water as well as air. In the previous work,[18] recovery behaviors of a rubber composite aged in air and water were compared. In the present work, the circular deformation test method was employed to investigate the recovery behaviors of natural rubber (NR) composites alternately aged in air and water. The aging media of air and water changed every day for 10 days. Two altering aging medium systems of the altering air to water (A→W) and the altering water to air (W→A) were employed. The circular deformation test method is suitable for an aging test using an altering aging medium system, because it does not require any specific equipment or jig, and just a small specimen is used. The unfilled, carbon black-filled, and silica-filled NR composites were used to examine the influence of the reinforcing systems on the recovery behaviors. Carbon black and silica are polular reinforcing fillers for rubber articles.[19-21] Silane coupling agent is used along with silica to improve the silica dispersion and to prevent adsorption of curatives on the silica surface.[20,21] Influence of the aging temperature on the recovery behaviors was also examined.

II. Experimental

1. Sample preparation

Unfilled, carbon black-filled, and silica-filled NR compounds were made of rubber (SMR20 100.0 phr), filler (N330 50.0 phr for the carbon black system, Z175 50.0 phr and Si69 3.0 phr for the 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).

2. Aging process

Air and distilled water were used as the aging media. Two altering aging medium systems were employed: (1) the air to water altering system (A→W altering system, changing the aging medium every day, the initial medium was air) and (2) the water to air altering system (W→A altering system, changing the aging medium every day, the initial medium was distilled water). The altering aging medium systems are illustrated in Figure 1. The circular deformation experiments were carried out as follows. First, the NR composites were cut with the dimension of 5 mm × 100 mm (thickness 2 mm). Second, the linear sample was changed into a circular form by fixing both ends of the sample with a pin. Third, the circularly deformed samples were aged at 60, 70, 80, and 90°C for 10 days under the altering medium systems in a convection oven. Finally, the pin was removed after the 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.

3. Measurement of apparent crosslink density

Apparent crosslink densities of the samples before and after the thermal aging were measured by the 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)

$$\mathbf{Q} = (\mathbf{W_s} - \mathbf{W_u})/\mathbf{W_u} \quad (1)$$

where $\mathbf{W_s}$ and $\mathbf{W_u}$ are weights of the swollen and unswollen samples, respectively. 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

The recovery (R) was calculated by the equation (2)

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

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 2, 3, 4, and 5 show the recovery variations of the thermally aged samples at 60, 70, 80, and 90°C, respectively. The recovery increased as the measurement time elapsed irrespective of the aging temperatures and aging medium systems. The linear curve fitting equations for the recovery variations were sum-

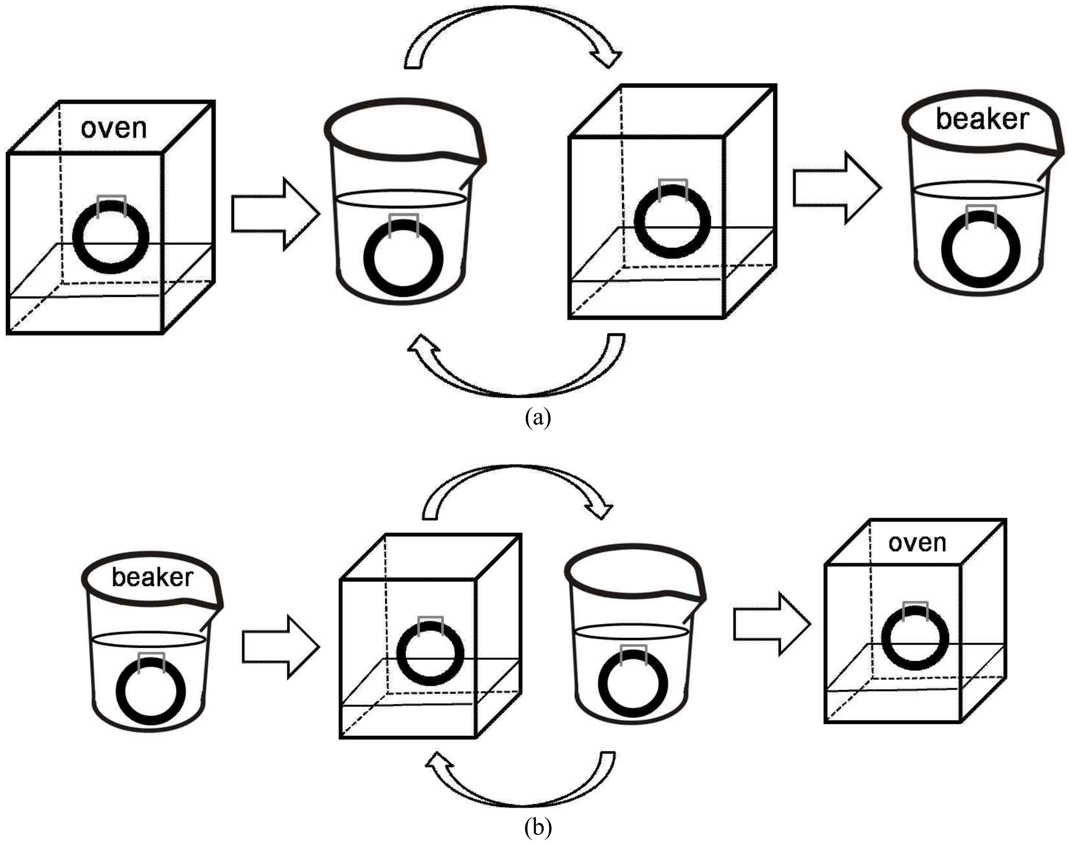

Figure 1. Altering aging medium systems of the circular deformation test. (a) the air to water altering system (A→W altering system, changing the medium each one day, the initial medium was air) and (b) the water to air altering system (W→A altering system, changing the medium each one day, the initial medium was distilled water).

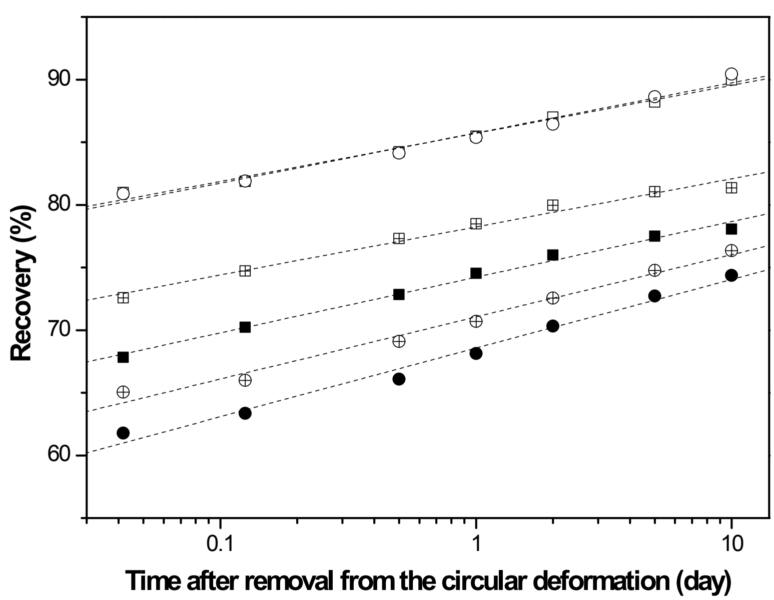

Figure 2. Recovery variations from the circularly deformed sample after thermal aging at 60°C with the measurement time. The squares and circles indicate the aging medium systems of the air to water (A→W) altering system and the water to air (W→A) altering system, respectively. The open, solid, and crossed symbols denote the filler systems of unfilled, carbon black-filled, and silica-filled systems, respectively.

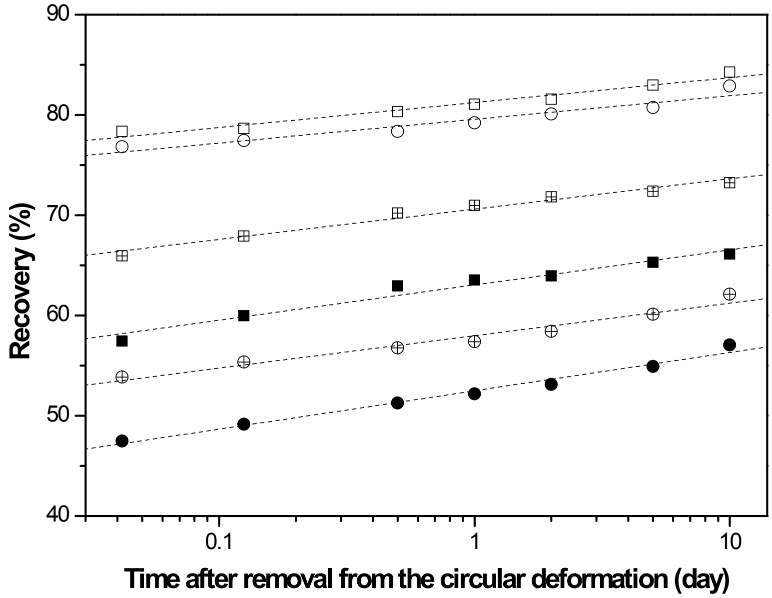

Figure 3. Recovery variations from the circularly deformed sample after thermal aging at 70°C with the measurement time. The squares and circles indicate the aging medium systems of the air to water (A→W) altering system and the water to air (W→A) altering system, respectively. The open, solid, and crossed symbols denote the filler systems of unfilled, carbon-filled, and silica-filled systems, respectively.

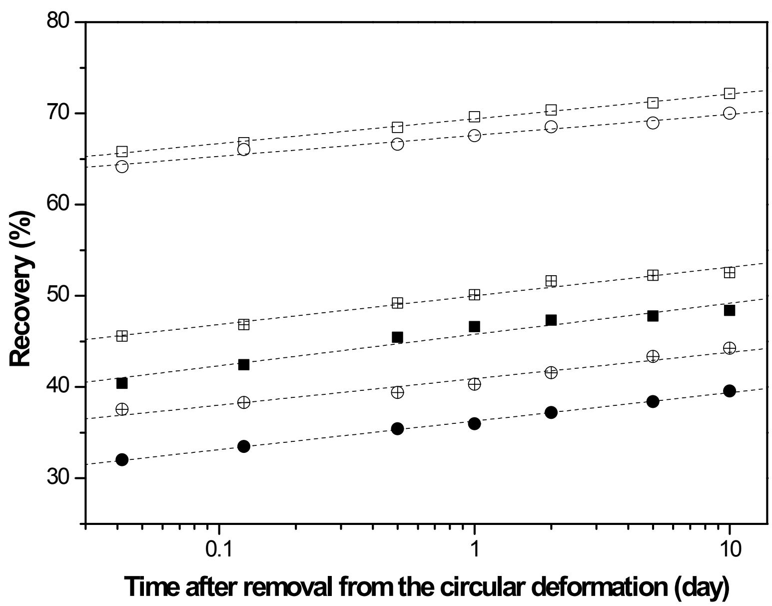

Figure 4. Recovery variations from the circularly deformed sample after thermal aging at 80°C with the measurement time. The squares and circles indicate the aging medium systems of the air to water (A→W) altering system and the water to air (W→A) altering system, respectively. The open, solid, and crossed symbols denote the filler systems of unfilled, carbon-filled, and silica-filled systems, respectively.

marized 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 greater than those of the filled ones irrespective of the aging temperatures and the aging medium systems as shown in Figures 2 – 5. This might be due to rearrangement of the deformed rubber chains and filler particles besides the crosslink density changes. Parameters leading to permanent deformation of a rubber com-

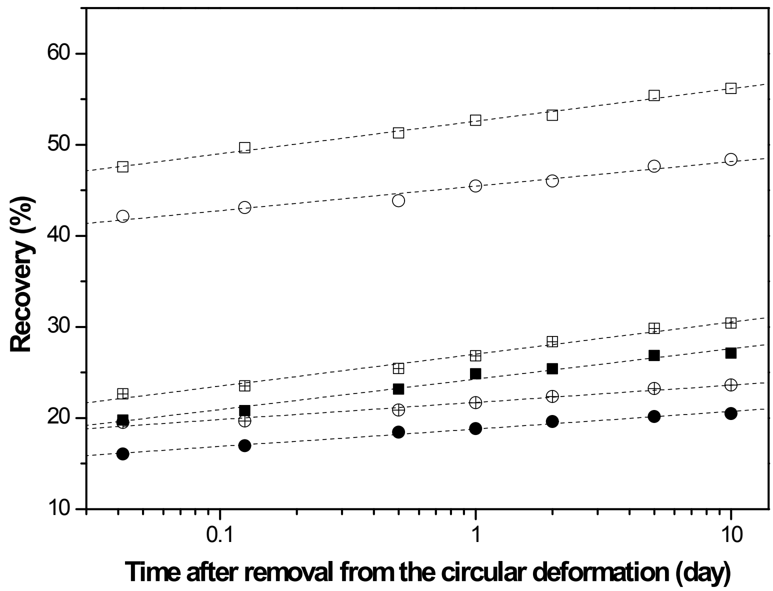

Figure 5. Recovery variations from the circularly deformed sample after thermal aging at 90°C with the measurement time. The squares and circles indicate the aging medium systems of the air to water (A→W) altering system and the water to air (W→A) altering system, respectively. The open, solid, and crossed symbols denote the filler systems of unfilled, carbon-filled, and silica-filled systems, respectively.

Table 1. Linear curve fitting equations of the recovery variations from the circularly deformed sample after thermal aging at 60°C with the measurement time (Figure 2)

Aging medium system	Filler system	Linear curve fitting equation (correlation coefficient, r)
Altering system from air to water (A→W)	Unfilled	y = 3.84x + 85.7 (r = 0.994)
	Carbon black	y = 4.44x + 74.2 (r = 0.996)
	Silica	y = 3.84x + 78.2 (r = 0.992)
Altering system from water to air (W→A)	Unfilled	y = 4.00x + 85.7 (r = 0.989)
	Carbon black	y = 5.48x + 68.6 (r = 0.993)
	Silica	y = 4.97x + 71.1 (r = 0.993)

Table 2. Linear curve fitting equations of the recovery variations from the circularly deformed sample after thermal aging at 70°C with the measurement time (Figure 3)

Aging medium system	Filler system	Linear curve fitting equation (correlation coefficient, r)
Altering system from air to water (A→W)	Unfilled	y = 2.49x + 81.2 (r = 0.982)
	Carbon black	y = 3.52x + 63.0 (r = 0.982)
	Silica	y = 3.02x + 70.6 (r = 0.987)
Altering system from water to air (W→A)	Unfilled	y = 2.36x + 79.6 (r = 0.964)
	Carbon black	y = 3.82x + 52.5 (r = 0.992)
	Silica	y = 3.24x + 58.0 (r = 0.981)

posite by aging are known to be the rearrangements of rubber chains and fillers and the change of crosslink density.[7,12,5-11] Thermal aging makes the crosslink density of a rubber vulcanizate to change.[13-17] But, the experimental results were not fully explained only by the crosslink density changes. Apparent crosslink densities (**1/Q**) of the samples before and after the

Table 3. Linear curve fitting equations of the recovery variations from the circularly deformed sample after thermal aging at 80°C with the measurement time (Figure 4)

Aging medium system	Filler system	Linear curve fitting equation (correlation coefficient, r)
Altering system from air to water (A→W)	Unfilled	y = 2.71x + 69.4 (r = 0.997)
	Carbon black	y = 3.43x + 45.8 (r = 0.974)
	Silica	y = 3.14x + 50.0 (r = 0.989)
Altering system from water to air (W→A)	Unfilled	y = 2.31x + 67.6 (r = 0.988)
	Carbon black	y = 3.12x + 36.3 (r = 0.999)
	Silica	y = 2.90x + 40.9 (r = 0.978)

Table 4. Linear curve fitting equations of the recovery variations from the circularly deformed sample after thermal aging at 90°C with the measurement time (Figure 5)

Aging medium system	Filler system	Linear curve fitting equation (correlation coefficient, r)
Altering system from air to water (A→W)	Unfilled	y = 3.58x + 52.6 (r = 0.996)
	Carbon black	y = 3.34x + 24.3 (r = 0.991)
	Silica	y = 3.51x + 27.0 (r = 0.992)
Altering system from water to air (W→A)	Unfilled	y = 2.69x + 45.4 (r = 0.985)
	Carbon black	y = 1.93x + 18.8 (r = 0.995)
	Silica	y = 1.89x + 21.7 (r = 0.988)

thermal aging at 60 and 80°C were measured and the crosslink density changes ($\Delta\mathbf{X_c}$s) were obtained by the equation (3)

$$\Delta\mathbf{X_c}(\%) = 100\times[(\mathbf{1/Q_a}) - (\mathbf{1/Q_b})]/(\mathbf{1/Q_b}) \quad (3)$$

where the $\mathbf{1/Q_b}$ and $\mathbf{1/Q_a}$ are the apparent crosslink densities before and after the thermal aging, respectively. The $\Delta\mathbf{X_c}$s of the NR composites aged in the A→W altering system at 60/80°C were 3.0/9.3, 1.7/9.5, and 1.9/9.0% for the unfilled, carbon black-filled, and silica-filled samples, respectively. The $\Delta\mathbf{X_c}$s of the NR composites aged in the W→A altering system at 60/80°C were 2.2/8.3, 0.2/11.0, and 1.6/4.6%, respectively. For the thermal aging at 60°C, the $\Delta\mathbf{X_c}$s of the unfilled composite were greater than those of the filled ones. For the thermal aging at 80°C, the $\Delta\mathbf{X_c}$s of the carbon black-filled composite were greater than those of the unfilled and silica-filled ones. Hence, it is believed that there are various parameters leading to the recovery of a rubber article besides the crosslink densities. When a rubber article is deformed, the rubber chains are strained and their conformations are changed. When the linear sample with 100 mm length and 2 mm thickness is changed to a circular form, the applied strain was about 6%. If the strained polymer chains are settled under the deformed state, the degree of permanent deformation of the rubber article will increase and the recovery behaviors will be also influenced. Positions of the filler particles in a rubber article will be also moved by deformation and they will be also re-arranged to settle down in a new space. Newly fixed arrangement of the filler particles in the deformed specimen could disrupt the full recovery to the original shape by the filler-filler interactions as well as the interruption of movement of rubber chains.

Recoveries of the silica-filled sample were greater than those of the carbon black-filled one (Figures 2 – 5). This might be due to the crosslink density change. The crosslink density changes of the silica-filled composite were smaller than those of the carbon black-filled one as discussed above. The recoveries of the samples aged in the A→W altering system were on the whole greater than those aged in the W→A one irrespective of the filler systems and the aging temperatures. This could not be explained by the crosslink density changes because the $\Delta\mathbf{X_c}$s of the samples aged in the A→W altering system were on the whole greater than those of the samples aged in the W→A one as discussed previously. In general, recovery of a rubber composite aged in air is greater than that aged in water due to the annealing effect by water.[18,22] At the first aging day of 10 days, recovery of the sample aged in the A→W altering system is greater than that aged in the W→A one. Both the altering aging medium systems have the same time periods of 5 days in air and 5 days in water. Hence, according to the experimental results, the initially more deformed condition can lead to the finally severe deformation.

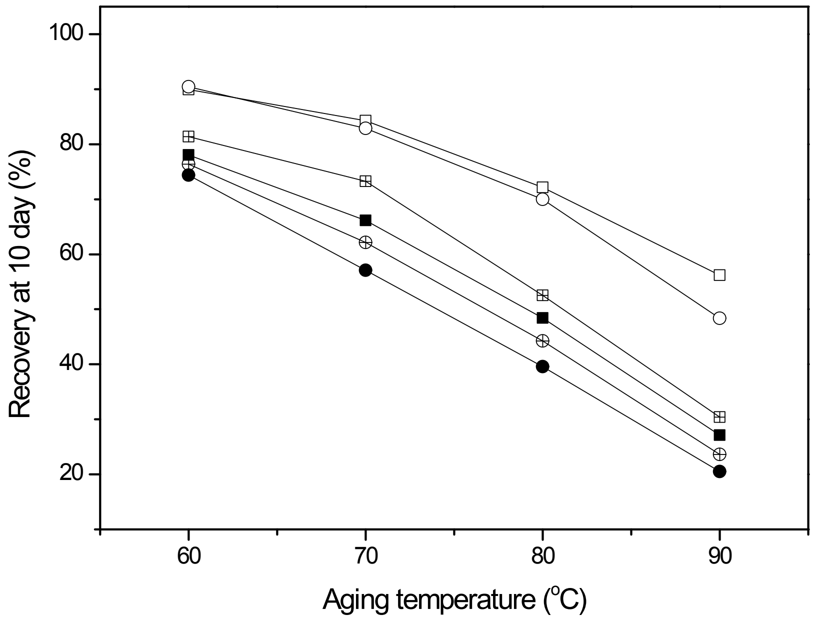

Figure 6. Variations of the limited recoveries (recoveries at the measurement time of 10 days) with the aging temperature. The squares and circles indicate the aging medium systems of the air to water (A→W) altering system and the water to air (W→A) altering system, respectively. The open, solid, and crossed symbols denote the filler systems of unfilled, carbon-filled, and silica-filled systems, respectively.

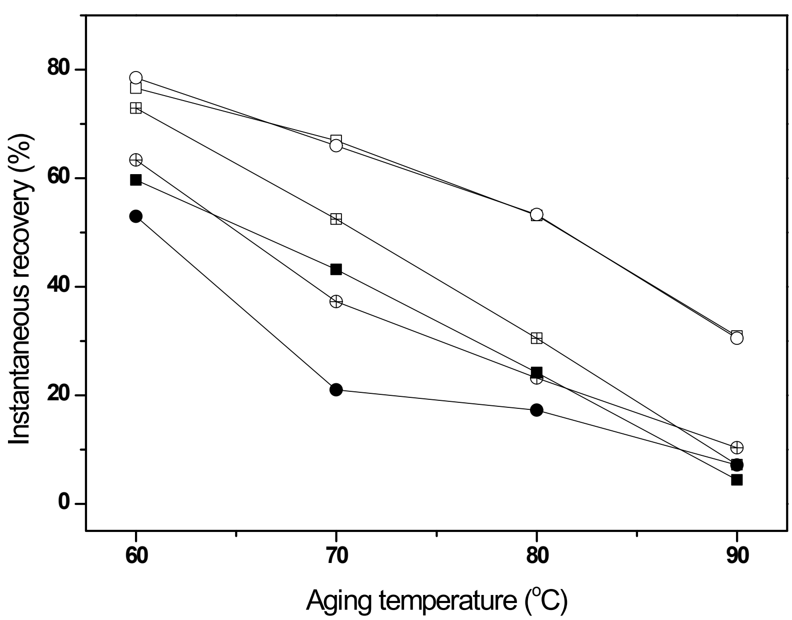

Figure 7. Variations of the instantaneous recoveries at 10^{-6} day with the aging temperature. The squares and circles indicate the aging medium systems of the air to water (A→W) altering system and the water to air (W→A) altering system, respectively. The open, solid, and crossed symbols denote the filler systems of unfilled, carbon-filled, and silica-filled systems, respectively.

The slopes of the linear curve fitting equations indicate the recovery rates depending on the measurement time. For the thermal aging at 60 – 80°C, recovery rates of the filled samples were faster than those of the unfilled one as listed in Tables 1 – 3. The recovery rates of the carbon black-filled composite were faster than those of the silica-filled one. This is explained by the elasticity due to the initial crosslink density. Initial apparent crosslink densities (**$1/Q_b$**) of the unfilled, carbon black-filled, and silica-filled samples were 0.276, 0.549, and 0.528, respectively. If the crosslink density of a rubber composite increases, length between the crosslink points reduces and the elastic stress increases.[18] For the thermal aging at 90°C, the recovery rates of the filled samples were slower than those of the unfilled ones (Table 4). This might be due to the activation of filler rearrangement at high temperature. Movement of filler particles to rearrange in a new space will be more activated at high temperature. The recovery rates of the samples aged at 60°C in the W→A altering system were faster than those of the samples aged in the A→W one irrespective of the filler systems (Table 1). But, these trends were inversely changed as the aging temperature increased. For the unfilled NR composite at 70 – 90°C, the recovery rate of the sample aged in the W→A altering system was slower than that of the sample aged in the A→W one (Tables 2 – 4). For the filled NR composites at 80 and 90°C, the recovery rates of the samples aged in the W→A altering system were slower than those of the samples aged in the A→W one (Tables 3 and 4).

The recoveries hardly changed more than 10 days after the thermal aging. The recovery at 10 days of the measurement time was used as 'limited recovery'. Figure 6 shows the limited recovery variations with the aging temperature. The limited recoveries of the unfilled sample were greater than those of the filled ones, and those of the silica-filled sample were greater than those of the carbon black-filled one. The limited recoveries of the samples aged in the A→W altering system were on the whole greater than those of the samples aged in the W→A one. This can be also due to the crosslink density changes and the annealing effect by water, and also suggests that degree of the initial deformation affects the whole deformation.

Instantaneous recovery is defined as the recovery observed immediately following release from the deformation, and they were obtained from the recovery versus measurement time curves as shown in Figures 2 – 5 by extrapolating the linear curve fitting equation to a 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, because common requirements of rubber sealants include high elasticity and fast recovery following deformation. Figure 7 shows variations of the instantaneous recoveries at 1.0×10^{-6} day (0.09 sec) with the aging temperature. The order of the instantaneous recoveries according to the filler systems was the unfilled sample > the silica-filled sample > the carbon black-filled sample. This could be due to the crosslink density changes and the filler effects. The instantaneous recoveries of the samples aged in the A→W altering system were on the whole greater than those of the samples aged in the W→A one irrespective of the filler systems. This could be also due to the crosslink density changes and the annealing effect by water as discussed above.

IV. Conclusion

The unfilled, carbon black-filled, and silica-filled NR composites were aged in the altering aging medium systems of air and water. The order of the limited and instantaneous recoveries according to the filler systems was the unfilled sample > the silica-filled sample > the carbon black-filled sample. The limited and instantaneous recoveries of the samples aged in the A→W altering system were on the whole greater than those of the samples aged in the W→A one. Parameters leading to the permanent deformation by aging of a rubber composite are the rearrangements of rubber chains and fillers and the change of crosslink density. The experimental results suggest that the initial aging condition decisively affected the degree of the deformation.

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