Strain Effect on Recovery Behaviors from Circular Deformation of Natural Rubber Vulcanizate

Sung-Seen Choi, Dong-Hun Han

Department of Chemistry, Sejong University, Gwangjin-gu, Seoul 143-747, Korea

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ABSTRACT: The recovery behaviors of vulcanized natural rubber from circular deformation were studied by varying sample length to investigate the influence of the degree of applied strain to the sample. The stress and strain varied uniformly across the thickness of the sample, and the degree of applied stress and strain to the sample decreased with increasing the sample length. The linear sample was made into a circular form and thermally aged in a convection oven. The recovery was measured after removing from the circular deformation. The recovery increased by decreasing the sample length. The difference in recoveries of the samples with different lengths reduced at high temperature. The short sample had higher heat-resisting property for recovery than the long sample. The experimental results were explained by the rearrangement and stabilization of the deformed rubber chains as well as the crosslink density change. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 935–939, 2009

Key words: recovery; circular deformation; stress and strain variation; sample length; NR composite

INTRODUCTION

Rubber materials have a recovery property that allows it to return to its original shape after deformation.[1] The recovery property of a rubber article is very important for sealing materials. 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 used to investigate the degree of deformation for rubber vulcanizate. However, specimens for the compression set are relatively thick (28.7 mm diameter and 12.7 mm height), and differences in the initial states of the samples such as dimensions and crosslink densities cause some experimental errors. Gillen et al.[2] measured the variation of the compression set of rubber vulcanizate with the measuring time after removal of the sample from the jig and reported that the compression set decreased with the measuring time. If the recovery behaviors do not show linearity with the measurement time, the obtained compression is flawed.

Circular deformation test[3–6] is a novel test method; a linear sample is made into a circular form by fixing both ends with a pin, the circularly deformed sample is aged, the pin is removed after thermal aging, and the gap distance between both ends of the sample is measured. Linear relationship of the recovery with the measurement time of the aged specimen was investigated. Required property of a sealant is high, fast recovery from deformation, and sealing capability. It is very hard to directly measure the instantaneous recovery at less than 1.0 sec. However, the instantaneous recovery can be obtained from the linear curve fitting equation of recovery variation with the measurement time when its correlation coefficient is high enough. This method is the simplest and reliable method to measure the degree of deformation of a rubber article since thin specimens of 2 mm thickness with uniform states are used. When a linear sample of vulcanized rubber is made into a circular form, the stress and strain applied to the circularly deformed sample vary uniformly across the thickness of the sample.

In this work, we studied the influence of the degree of applied strain to the deformed sample on the recovery behaviors from the circular deformation. The rubber samples with different lengths of 40–140 mm were used to vary the degree of applied strain. Recovery variations with the measurement time were investigated, and the variations of instantaneous recoveries calculated from the curve fitting equations were also compared.

EXPERIMENTAL

The carbon black-filled natural rubber (NR) vulcanizate was composed of NR (SMR20, 100.0 phr),

Correspondence to: S.-S. Choi (sschoi@sejong.ac.kr).

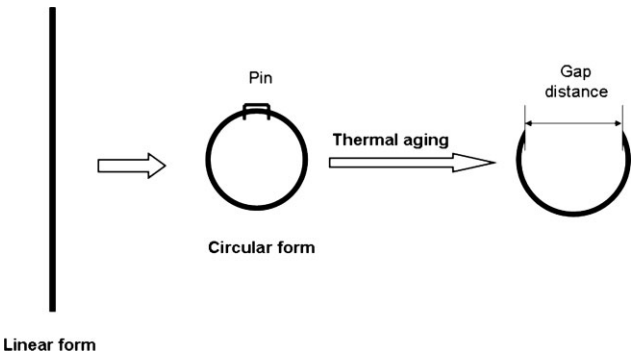

Figure 1 Process of the circular deformation and recovery experiment.

carbon black (N330, 40.0 phr), *N*-phenyl-*N*′-(1,3-dimethylbutyl)-*p*-phenylenediamine (HPPD, 1.0 phr), 2,2,4-trimethyl-1,2-dihydroquinoline (TMDQ, 2.0 phr), wax (2.0 phr), stearic acid (2.0 phr), ZnO (5.0 phr), *N*-*tert*-butyl-2-benzothiazole sulfenamide (TBBS, 1.2 phr), and sulfur (2.5 phr). Mixing of the compound was performed in a Banbury type mixer, and the vulcanization was performed at 160°C for 20 min.

The circular deformation experiments were carried out as follow (Fig. 1): First, samples were cut with dimensions of 40, 60, 80, 100, 120, and 140 mm length (5 mm width and 2 mm thickness). Second, the linear sample was made into a circular form by fixing both ends with a pin. Third, the samples with circular form were aged at 50, 70, and 90°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 eq. (1)

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

where W_s and W_u are the 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

When a linear rubber sample is made into a circular form, the interior component of the sample is compressed, whereas the exterior component is elongated. The degree of strain varies depending on the sample length. The strain ratio increases with decreasing the sample length as listed in Table I. The strain ratio (%) was calculated by the equation of compression ratio (%) = 100 × (center circumference − inner circumference)/center circumference or elongation ratio (%) = 100 × (outer circumference − center circumference)/center circumference. Values of the compression and elongation ratios are the same, and they are used as the strain ratios.

Figure 2 shows the degree of recovery from the circular deformation of the thermally aged NR composite at 70°C. The recoveries increase by increasing the measurement time after removal from the circular deformation. Figures 3, 4, and 5 show the recovery variations with the measurement time of the samples aged at 50, 70, and 90°C, respectively. The recovery from the circular deformation was obtained by the eq. (2)

$$R(\%) = 100 \times (l_{gap}/l_{lin}) \quad (2)$$

where l_{gap} is the gap distance between both ends of the aged sample, and l_{lin} is the linear sample length before deformation. The recoveries notably decrease with increase in the aging temperature. The deformed samples did not completely return to their initial linear shapes. The sample aged at high temperature is more permanently deformed than the sample aged at low temperature. This can be explained by the crosslink density change. As shown in Table II, the crosslink densities increased about 1, 10, and 30% after thermal aging at 50, 70, and 90°C, respectively. One of the principal reasons for permanent deformation of a rubber article by thermal aging is change of crosslink density.[3,5] Crosslink density of a rubber vulcanizate increases or decreases based on thermal aging conditions and the cure systems.[4–8] Formation of new crosslinks brings about an increase of the crosslink density, whereas dissociation of the existing crosslinks in a rubber article leads to a decrease of the crosslink density. Sulfur linkages, especially polysulfides, are dissociated by heating[3,9,10] and this brings about a reduction of the crosslink density. Curatives remaining in a rubber vulcanizate make new crosslinks.[3,10] During thermal aging of a rubber vulcanizate, formation of

TABLE I
Diameters and Maximum Strain of the Circularly Deformed Samples. The Sample Thickness is 2 mm

Length (mm)	40	60	80	100	120	140
Inner diameter (mm)	10.7	17.1	23.5	29.8	36.2	42.6
Center diameter (mm)	12.7	19.1	25.5	31.8	38.2	44.6
Outer diameter (mm)	14.7	21.1	27.5	33.8	40.2	46.6
Maximum strain (%)	15.7	10.5	7.8	6.3	5.2	4.3

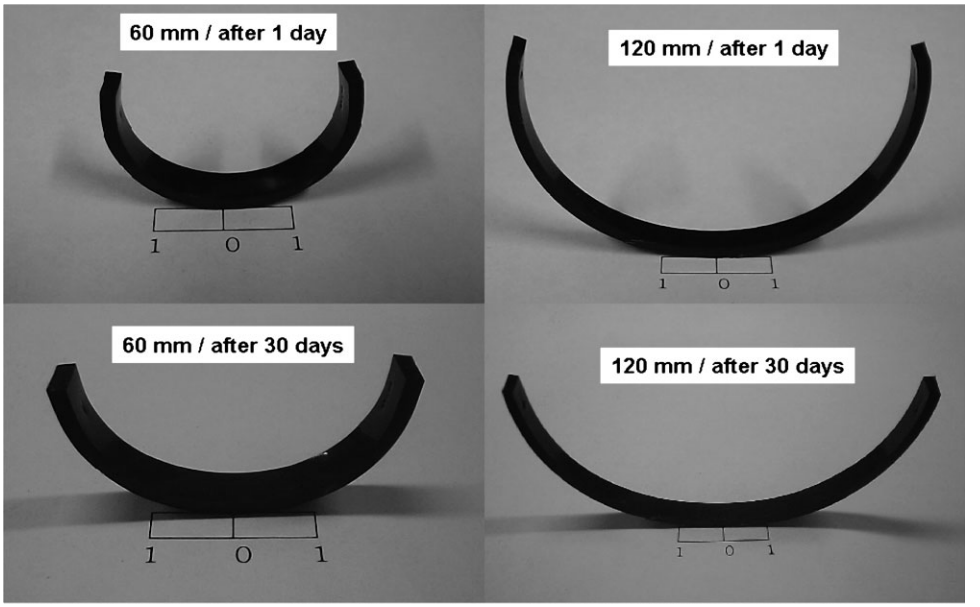

Figure 2 Photographs of the samples after the thermal aging at 70°C with the circular deformation. Unit of the scale bar in the photographs is cm.

new crosslinks and dissociation of the existing crosslinks simultaneously happen. Increase of the crosslink density of the NR composite after the thermal aging indicates that formation of the new crosslinks overcame and dissociation of the existing crosslinks. Difference in the crosslink density increments depending on the sample length did not show any clear trends. However, the degree of the crosslink density increase of the long sample is on the whole slightly higher than that of the short one as shown in Table II.

The recovery linearly increases with increasing the measurement time. The recovery of the long sample is smaller than that of the short one. This can be explained by the rearrangement and stabilization of the deformed rubber chains not the crosslink density change because the difference in the crosslink density increments was not big enough. Privalko et al.[11] suggested the contribution of structural rearrangements at the rubber/filler interface by the mechanism of chain slippage operative in both stretching and contraction regimes. When a rubber article is deformed, the rubber chains are strained and their

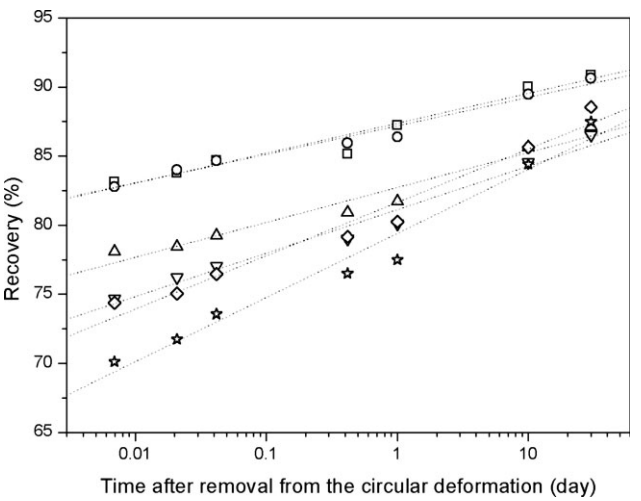

Figure 3 Variations of the recoveries of the NR vulcanizate by thermal aging at 50°C for 7 days with the measurement time after removal from the circular form. The squares, circles, up-triangles, down-triangles, diamonds, and stars indicate the sample lengths of 40, 60, 80, 100, 120, and 140 mm, respectively.

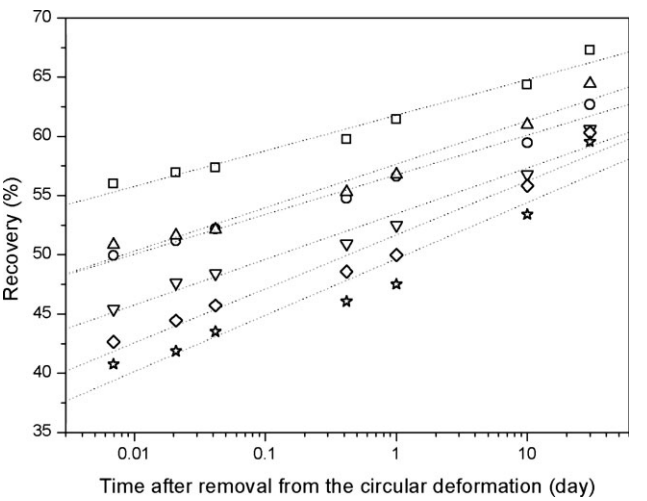

Figure 4 Variations of the recoveries of the NR vulcanizate by thermal aging at 70°C for 7 days with the measurement time after removal from the circular form. The squares, circles, up-triangles, down-triangles, diamonds, and stars indicate the sample lengths of 40, 60, 80, 100, 120, and 140 mm, respectively.

TABLE II
Changes of the Apparent Crosslink Densities after the Thermal Aging (%)

Length (mm)	50°C	70°C	90°C
40	0.1	8.0	30.4
60	0.3	9.8	30.4
80	1.1	8.7	32.4
100	1.4	10.5	33.5
120	1.0	10.1	31.4
140	0.8	11.4	33.7

microstructures are changed. If the strained polymer chains settle in the deformed state by rearrangement and stabilization, the degree of the permanent deformation of the rubber article will increase, and the recovery behaviors can be also influenced. The degree of deformation of the circularly deformed sample increases by decreasing the sample length. Thus, the short sample requires longer time to rearrange and stabilize the deformed rubber chains than the long sample.

Instantaneous recovery for describing sealing properties can be obtained from the recovery variation with the measuring time because the linearity is very good. Instantaneous recoveries at 10^{-6} day (0.9 sec) were calculated and displayed as a function of the sample length as shown in Figure 6. The instantaneous recoveries notably decrease with increase of the aging temperature. This may be due to the permanent deformation caused by crosslink density change. Increments of the crosslink densities of the samples aged at high temperature are much larger than those of the samples aged at low temperature as listed in Table II. The instantaneous recovery linearly decreases with increase in the sample length. This can be explained by the degree of applied strain to the sample not the crosslink density change. Since the short samples are less strained than the long ones, the force needed to return to the linear shape of the short sample will be larger than that of the long one. Difference in the instantaneous recoveries according to the sample lengths reduces by increasing the aging temperature. The slopes of the linear fitting equations are −0.24, −0.22, and −0.05 for the aging temperatures of 50, 70, and 90°C, respectively. This may be due to the fast rearrangement and stabilization of the deformed rubber chains at high temperature. The strained polymer

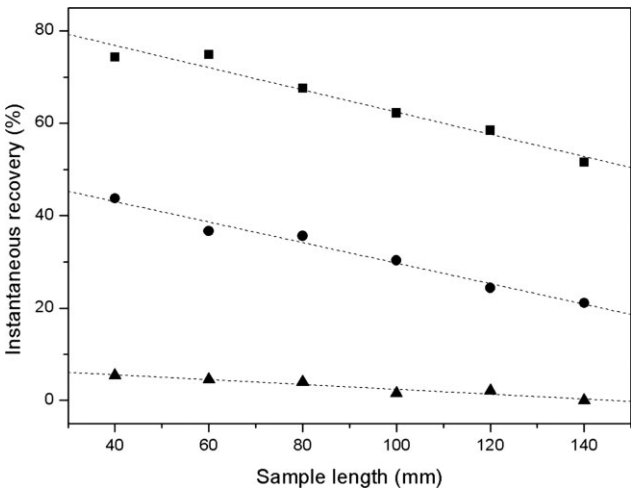

Figure 6 Variations of the instantaneous recoveries at 10^{-6} day of the NR vulcanizate as a function of the sample length. The squares, circles, and triangles indicate the thermal aging at 50, 70, and 90°C, respectively.

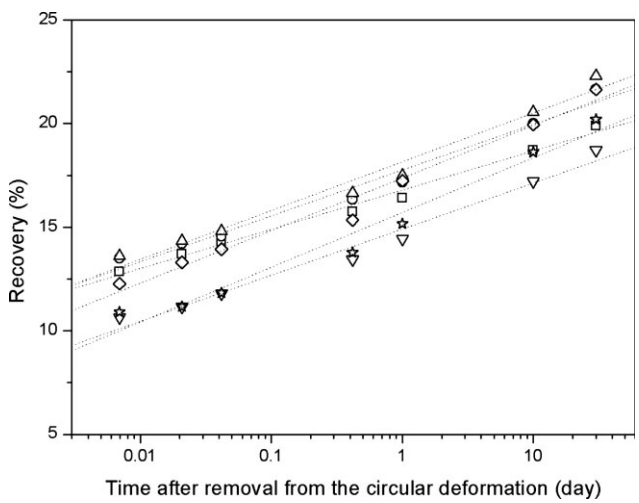

Figure 5 Variations of the recoveries of the NR vulcanizate by thermal aging at 90°C for 7 days with the measurement time after removal from the circular form. The squares, circles, up-triangles, down-triangles, diamonds, and stars indicate the sample lengths of 40, 60, 80, 100, 120, and 140 mm, respectively.

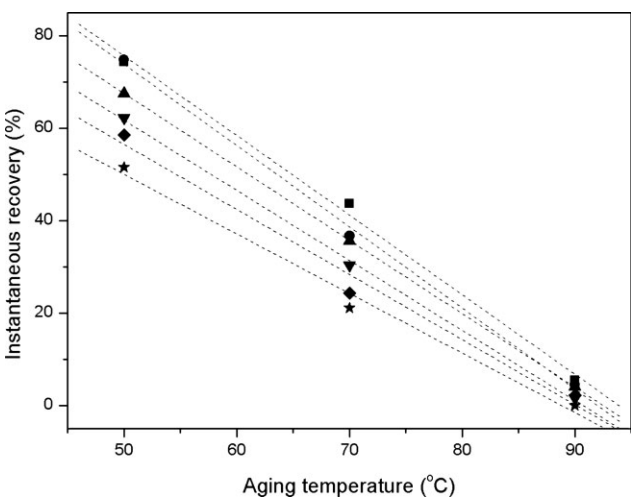

Figure 7 Variations of the instantaneous recoveries at 10^{-6} day of the NR vulcanizate as a function of the aging temperature. The squares, circles, up-triangles, down-triangles, diamonds, and stars indicate the sample lengths of 40, 60, 80, 100, 120, and 140 mm, respectively.

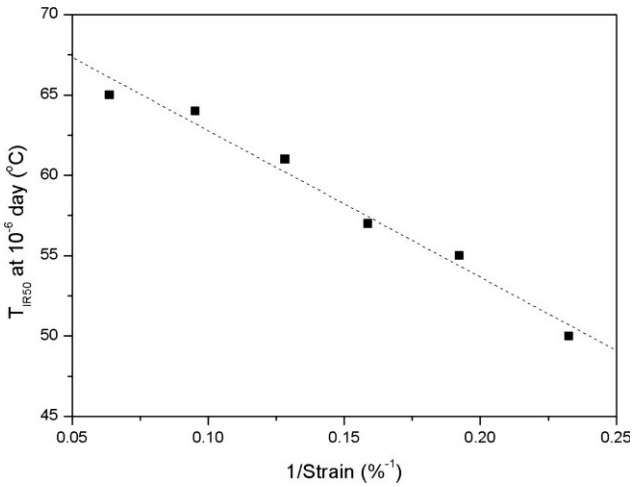

Figure 8 Variation of the T_{IR50} as a function of the reciprocal of the applied strain to the circularly deformed sample. T_{IR50} is the half instantaneous recovery temperature at 10^{-6} day (T_{IR50}, temperature to take 50% instantaneous recovery).

chains in the circularly deformed sample can settle in the deformed shape by rearrangement and stabilization. This process will be more activated at high temperature since mobility of polymer chains is getting faster at high temperature. The fast stabilization will reduce the differences in the instantaneous recoveries according to the sample lengths.

To investigate the influence of the aging temperature on the instantaneous recovery behaviors in detail, the instantaneous recovery variations were plotted as a function of the aging temperature as shown in Figure 7. Decreases in the instantaneous recoveries with the aging temperature clearly appear. The slope decreases with increasing the sample length. This means that the long sample is less affected by aging temperature than the short sample. This is because the long sample is less strained than the short one. Using the linear curve fitting equations of Figure 7, half instantaneous recovery temperatures at 10^{-6} day (T_{IR50}, temperature to take 50% instantaneous recovery) were calculated for every sample length. To investigate the relationship between T_{IR50} and the degree of applied strain to the sample, we tried various plots such as T_{IR50} vs strain, T_{IR50} vs log(strain), $1/T_{IR50}$ vs strain, $1/T_{IR50}$ vs log(strain), strain vs T_{IR50}, strain^{-1} vs T_{IR50}, and so on. Of the plots, variation of the T_{IR50} with the strain^{-1} shows a good linear relationship as shown in Figure 8. The linear curve fitting equation is $T_{IR50} = -91.2(\text{strain}^{-1}) + 71.9$ ($r = -0.97$). Thus, we can say that the half instantaneous recovery temperature (T_{IR50}) decreases in proportion to the strain^{-1}. This indicates that, for sealing force of a sealant, thermal resistance of a rubber article increases by increasing the degree of applied strain to the sample.

CONCLUSIONS

We introduced the circular deformation test method to investigate the influence of applied strain to the rubber sample by varying the sample length. The degree of applied strain increased with decreasing the sample length. The circularly deformed sample was thermally aged, and the recovery was measured after removing from the circular deformation. The recovery continuously increased as the measurement time elapsed. The recovery increased with increase in the applied strain. The strain effect appeared better for the sample aged at low temperature than for the sample aged at high temperature. Thermal resistance of the rubber article, in terms of the instantaneous recovery, was enhanced by increasing the degree of applied strain to the sample. Differences in the recovery behaviors of the samples with different lengths were explained by the rearrangement and stabilization of the deformed rubber chains not the crosslink density change.

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