Recovery Prediction of Thermally Aged Chloroprene Rubber Composite Using Deformation Test

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ABSTRACT: The recovery prediction of chloroprene rubber (CR) composite from deformation was studied using the conventional compression set test and the circular deformation method to change a linear specimen into a circular shape. The CR composite was thermally aged at 60, 70, 80, 90, and 100°C for 1, 6, 15, and 30 days. The recovery was measured as a function of the measuring time (or releasing time) from the compressed or circular deformation. For the compression set test, because the recovery decreased and then increased as the measuring time elapsed, it was not reasonable to calculate the instantaneous recovery from the curve fitting equation. For the circular deformation method, the recovery was continuously increased by increasing the measuring time. The linear correlation for curve fitting was very high and the instantaneous recovery was obtained from the linear curve fitting equation. The half instantaneous recovery time at room temperature could be predicted from the experimental results of the accelerated thermal aging test. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3560–3565, 2008

Key words: recovery; prediction; circular deformation; compression; CR 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. If states of a rubber vulcanizate such as crosslink density, crosslink type, and arrangement of polymer chains are not changed by aging, the rubber specimen can fully return to its original shape. If not, a rubber specimen cannot return to the original shape. Rubber composites can be permanently deformed when deformed for a long time, especially at high temperatures. One of principal reasons for permanent deformation is change of crosslink density.[2] Crosslink density of a rubber vulcanizate is changed by thermal aging.[3–7] Sulfur linkages, especially polysulfides, are dissociated by heating[2,8,9] and this brings about a reduction of the crosslink density. Curatives remaining in a rubber vulcanizate make new crosslinks[2,9] and this results in an increase in crosslink density. In general, crosslink density of a sulfur-cured rubber vulcanizate increases with an increase in aging temperature.[3–5]

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 error. The ISO 815 says that the thickness of the aged specimen is measured 30 min after thermal aging. Gillen et al.[10] measured the variation of the compression set of rubber vulcanizate with the measuring time after the 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.

In this work, we studied the prediction method with regard to the recovery of chloroprene rubber (CR) composite from deformation using the conventional compression set test and circular deformation method.[2,11] The circular deformation method is a novel test method; a linear sample is deformed into a circular one by fixing both ends with a pin, 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 and fast recovery from deformation as well as sealing capability. It is very hard to directly measure the instantaneous recovery at less than 0.1 s, but the instantaneous recovery can be obtained from the linear

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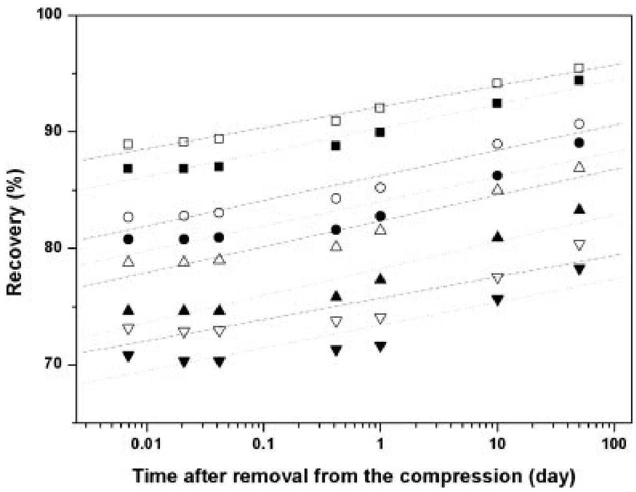

Figure 1 Variation of the recovery of the thermally aged CR composite after removal from the compression jig with the measurement time. The aging temperature was 60°C. The squares, circles, up-triangles, and down-triangles indicate the aging times of 1, 6, 15, and 30 days, respectively. The solid and open symbols stand for the compression ratios of 15 and 25%, respectively.

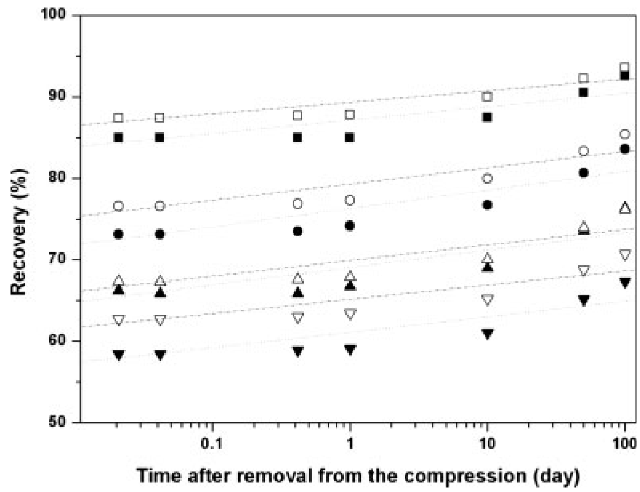

Figure 3 Variation of the recovery of the thermally aged CR composite after removal from the compression jig with the measurement time. The aging temperature was 80°C. The squares, circles, up-triangles, and down-triangles indicate the aging times of 1, 6, 15, and 30 days, respectively. The solid and open symbols stand for the compression ratios of 15 and 25%, respectively.

curve fitting equation of recovery variation with the measurement time when its correlation coefficient is enough high.

EXPERIMENTAL

The CR compound was made of CR (Neoprene WRT of Dupont, 100.0 phr), carbon black (42.0 phr), curatives (10.7 phr), and antidegradants and processing aids (16.0 phr). The vulcanizates were prepared by curing at 160°C for the t_{max} in a compression mold. The compression set test was performed according to the ISO 815 and the compression ratio was 15 and 25%. The compressed samples were thermally aged at 60, 70, 80, 90, and 100°C for 1, 6, 15, and 30 days in a convection oven. After the thermal aging, the samples were released from the compression jig and their thicknesses were measured 6.9×10^{-3}, 2.1×10^{-2}, 4.2×10^{-2}, 0.42, 1, 10, and 50 days after the thermal aging.

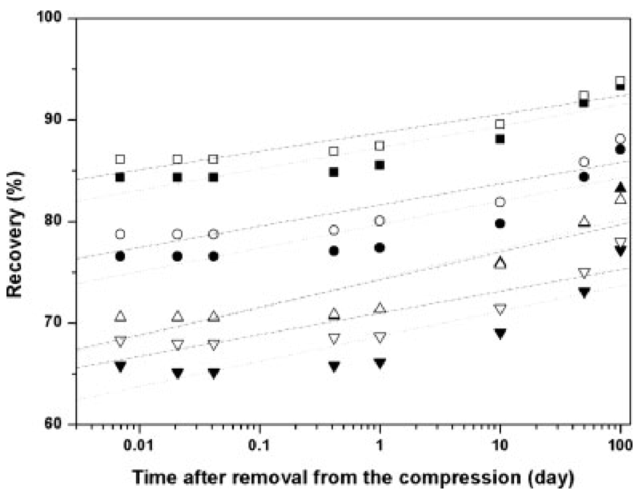

Figure 2 Variation of the recovery of the thermally aged CR composite after removal from the compression jig with the measurement time. The aging temperature was 70°C. The squares, circles, up-triangles, and down-triangles indicate the aging times of 1, 6, 15, and 30 days, respectively. The solid and open symbols stand for the compression ratios of 15 and 25%, respectively.

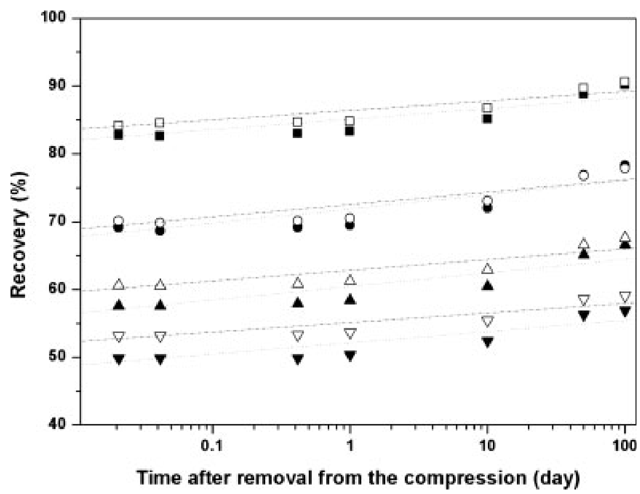

Figure 4 Variation of the recovery of the thermally aged CR composite after removal from the compression jig with the measurement time. The aging temperature was 90°C. The squares, circles, up-triangles, and down-triangles indicate the aging times of 1, 6, 15, and 30 days, respectively. The solid and open symbols stand for the compression ratios of 15 and 25%, respectively.

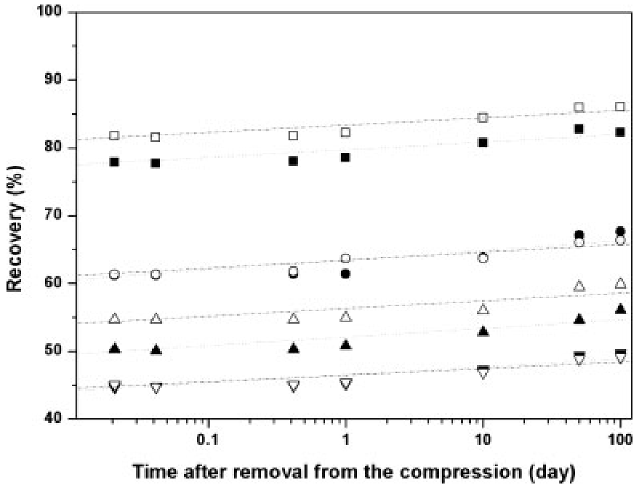

Figure 5 Variation of the recovery of the thermally aged CR composite after removal from the compression jig with the measurement time. The aging temperature was 100°C. The squares, circles, up-triangles, and down-triangles indicate the aging times of 1, 6, 15, and 30 days, respectively. The solid and open symbols stand for the compression ratios of 15 and 25%, respectively.

The experimental details for the circular deformation test have also been described in our previous reports.[2,11] The circular deformation experiments were carried out as follow: First, the sample was cut in dimensions of 5×120 mm^2 with 2 mm thickness. Second, the linear sample was changed into a circular form by fixing both the ends with a pin. Third, the circular forms were aged at 60, 70, 80, 90, and 100°C for 1, 6, 15, and 30 days in a convection oven.

TABLE I
The Linear Curve Fitting Equations for the Recovery from the 15% Compressed Deformation after the Thermal Aging

Aging temperature/ aging time	Curve fitting equation (correlation coefficient, *r*)
60°C/1 day	$y = 2.06 \log x + 90.3$ ($r = 0.98$)
60°C/6 days	$y = 2.15 \log x + 85.0$ ($r = 0.93$)
60°C/15 days	$y = 2.16 \log x + 72.8$ ($r = 0.95$)
60°C/30 days	$y = 1.97 \log x + 73.4$ ($r = 0.91$)
70°C/1 day	$y = 2.11 \log x + 87.3$ ($r = 0.92$)
70°C/6 days	$y = 2.31 \log x + 79.7$ ($r = 0.88$)
70°C/15 days	$y = 2.88 \log x + 74.4$ ($r = 0.90$)
70°C/30 days	$y = 2.48 \log x + 68.7$ ($r = 0.87$)
80°C/1 day	$y = 1.21 \log x + 86.7$ ($r = 0.81$)
80°C/6 days	$y = 1.70 \log x + 75.7$ ($r = 0.87$)
80°C/15 days	$y = 1.54 \log x + 68.4$ ($r = 0.79$)
80°C/30 days	$y = 1.40 \log x + 60.6$ ($r = 0.83$)
90°C/1 day	$y = 1.55 \log x + 85.1$ ($r = 0.84$)
90°C/6 days	$y = 2.09 \log x + 71.9$ ($r = 0.86$)
90°C/15 days	$y = 1.99 \log x + 60.4$ ($r = 0.87$)
90°C°C/30 days	$y = 1.66 \log x + 52.1$ ($r = 0.87$)
100°C/1 day	$y = 1.14 \log x + 79.7$ ($r = 0.87$)
100°C/6 days	$y = 1.43 \log x + 63.4$ ($r = 0.84$)
100°C/15 days	$y = 1.28 \log x + 52.1$ ($r = 0.88$)
100°C/30 days	$y = 1.17 \log x + 46.5$ ($r = 0.88$)

TABLE II
The Linear Curve Fitting Equations for the Recovery from the 25% Compressed Deformation after the Thermal Aging

Aging temperature/ aging time	Curve fitting equation (correlation coefficient, *r*)
60°C/1 day	$y = 1.79 \log x + 92.2$ ($r = 0.99$)
60°C/6 days	$y = 2.16 \log x + 86.3$ ($r = 0.96$)
60°C/15 days	$y = 1.93 \log x + 72.2$ ($r = 0.96$)
60°C/30 days	$y = 1.83 \log x + 75.7$ ($r = 0.91$)
70°C/1 day	$y = 1.82 \log x + 88.7$ ($r = 0.93$)
70°C/6 days	$y = 2.09 \log x + 81.6$ ($r = 0.90$)
70°C/15 days	$y = 2.72 \log x + 74.3$ ($r = 0.91$)
70°C/30 days	$y = 2.14 \log x + 71.0$ ($r = 0.88$)
80°C/1 day	$y = 1.14 \log x + 89.0$ ($r = 0.88$)
80°C/6 days	$y = 1.58 \log x + 78.8$ ($r = 0.88$)
80°C/15 days	$y = 1.44 \log x + 69.4$ ($r = 0.84$)
80°C/30 days	$y = 1.32 \log x + 64.7$ (r = 0.84)
90°C/1 day	$y = 1.39 \log x + 86.4$ ($r = 0.87$)
90°C/6 days	$y = 1.82 \log x + 72.5$ (r = 0.88)
90°C/15 days	$y = 1.58 \log x + 62.8$ ($r = 0.88$)
90°C/30 days	$y = 1.41 \log x + 55.1$ ($r = 0.89$)
100°C/1 day	$y = 1.08 \log x + 83.4$ ($r = 0.89$)
100°C°C/6 days	$y = 1.16 \log x + 63.4$ ($r = 0.90$)
100°C/15 days	$y = 1.14 \log x + 56.3$ ($r = 0.82$)
100°C/30 days	$y = 0.97 \log x + 46.5$ ($r = 0.87$)

Finally, the pin was removed and the gap distance between both ends of the sample was measured after 6.9×10^{-3}, 2.1×10^{-2}, 4.2×10^{-2}, 0.42, 1, 10, and 50 days.

Crosslink densities of the samples were measured by the swelling method. Initially, crosslink density was measured by removing organic additives in the samples by extracting with THF and *n*-hexane for 2 days each. Then, they were dried for 2 days at room temperature. The weights of the organic materials-extracted samples were measured. They were soaked

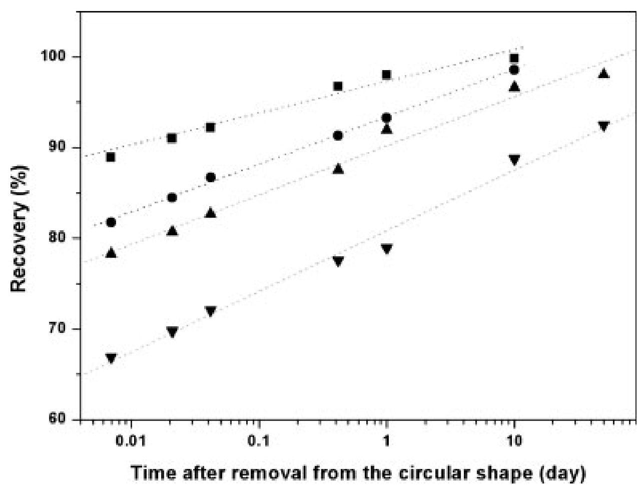

Figure 6 Variation of the recovery of the thermally aged CR composite after removal from the circular shape with the measurement time. The aging temperature was 60°C. The squares, circles, up-triangles, and down-triangles indicate the aging times of 1, 6, 15, and 30 days, respectively.

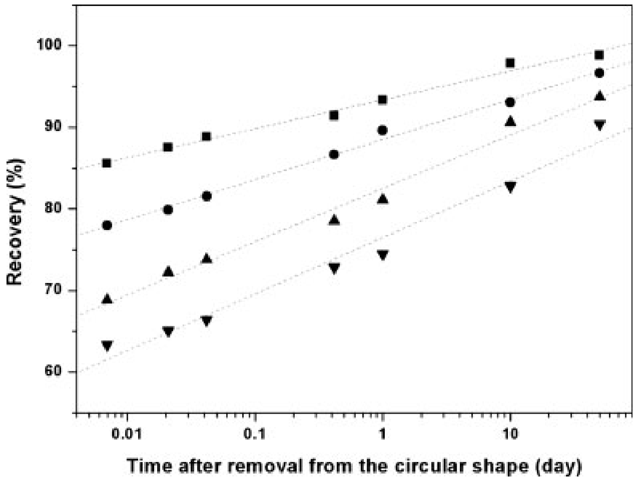

Figure 7 Variation of the recovery of the thermally aged CR composite after removal from the circular shape with the measurement time. The aging temperature was 70°C. The squares, circles, up-triangles, and down-triangles indicate the aging times of 1, 6, 15, and 30 days, respectively.

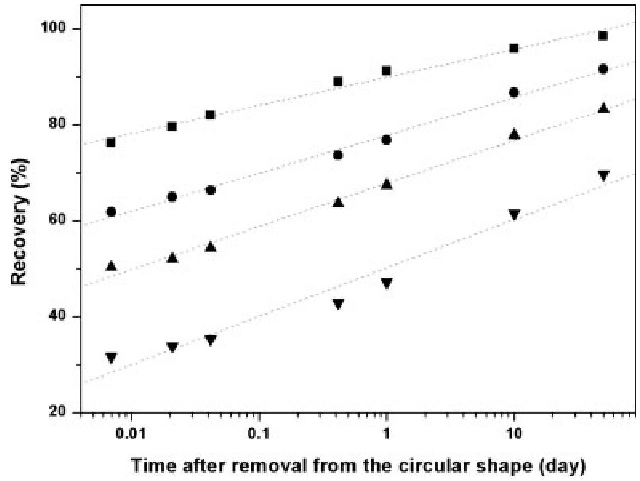

Figure 9 Variation of the recovery of the thermally aged CR composite after removal from the circular shape with the measurement time. The aging temperature was 90°C. The squares, circles, up-triangles, and down-triangles indicate the aging times of 1, 6, 15, and 30 days, respectively.

in toluene for 2 days and the weights of the swollen samples were measured. The swelling ratio (Q) was calculated by the equation of $Q = (W_s - W_u)/W_u$, where the W_s and W_u are weights of the swollen and unswollen samples. The reciprocal swelling ratio ($1/Q$) was used as the apparent crosslink density.

RESULTS AND DISCUSSION

The recovery from the compressed deformation was calculated by $R(\%) = 100 \times (h_a - h_c)/(h_i - h_c)$, where h_a is the height of the recovered sample, h_c is the height of the compressed sample, and h_i is the initial height of the sample. The recoveries of the 25% compressed samples after thermal aging were larger than those of the 15% ones irrespective of the aging conditions and the measurement times as shown in Figures 1–5. This may be because rebound resilience increases when the compression ratio increases. The recovery decreases with aging time and temperature. The compressed specimens did not fully recover within 50 days after the thermal aging. This implies that the specimens were permanently deformed by the thermal aging. Permanent deformation was due to the increased crosslink density which was caused by the thermal aging. For the 25% compressed samples, the crosslink densities of the

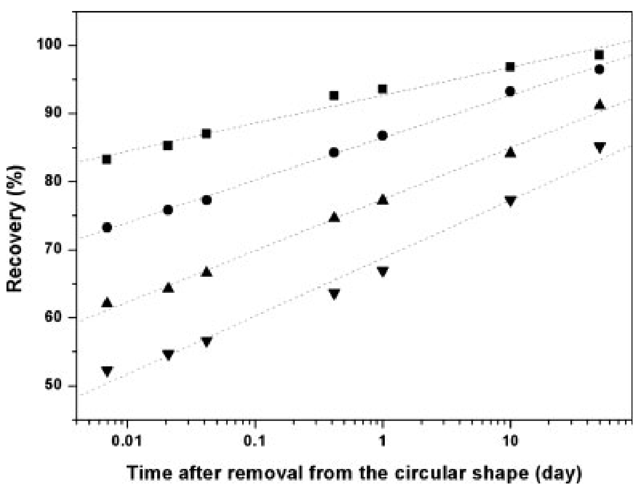

Figure 8 Variation of the recovery of the thermally aged CR composite after removal from the circular shape with the measurement time. The aging temperature was 80°C. The squares, circles, up-triangles, and down-triangles indicate the aging times of 1, 6, 15, and 30 days, respectively.

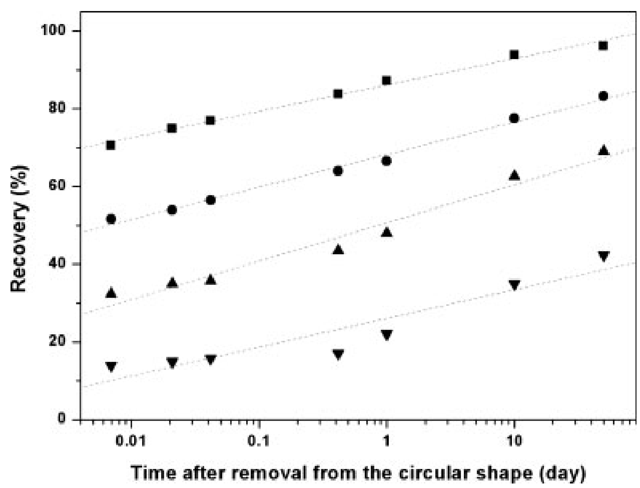

Figure 10 Variation of the recovery of the thermally aged CR composite after removal from the circular shape with the measurement time. The aging temperature was 100°C. The squares, circles, up-triangles, and down-triangles indicate the aging times of 1, 6, 15, and 30 days, respectively.

TABLE III
The Linear Curve Fitting Equations for the Recovery from the Circular Deformation after the Thermal Aging

Aging temperature/ aging time	Curve fitting equation (correlation coefficient, r)
60°C/1 day	$y = 3.61 \log x + 97.2$ ($r = 0.986$)
60°C/6 days	$y = 5.24 \log x + 93.3$ ($r = 0.999$)
60°C/15 days	$y = 5.42 \log x + 90.2$ ($r = 0.993$)
60°C/30 days	$y = 6.69 \log x + 80.8$ ($r = 0.994$)
70°C/1 day	$y = 3.54 \log x + 93.4$ ($r = 0.994$)
70°C/6 days	$y = 4.91 \log x + 88.5$ ($r = 0.997$)
70°C/15 days	$y = 6.53 \log x + 82.5$ ($r = 0.993$)
70°C/30 days	$y = 6.92 \log x + 76.5$ ($r = 0.989$)
80°C/1 day	$y = 4.10 \log x + 92.7$ ($r = 0.989$)
80°C/6 days	$y = 6.24 \log x + 86.5$ ($r = 0.999$)
80°C/15 days	$y = 7.55 \log x + 77.4$ ($r = 0.998$)
80°C/30 days	$y = 8.52 \log x + 68.7$ ($r = 0.992$)
90°C/1 day	$y = 5.85 \log x + 89.9$ ($r = 0.992$)
90°C/6 days	$y = 7.90 \log x + 77.8$ ($r = 0.997$)
90°C/15 days	$y = 9.00 \log x + 67.8$ ($r = 0.997$)
90°C/30 days	$y = 10.1 \log x + 50.2$ ($r = 0.985$)
100°C/1 day	$y = 6.78 \log x + 86.1$ ($r = 0.995$)
100°C/6 days	$y = 8.37 \log x + 68.2$ ($r = 0.995$)
100°C/15 days	$y = 9.86 \log x + 50.7$ ($r = 0.985$)
100°C/30 days	$y = 7.39 \log x + 26.1$ ($r = 0.941$)

specimens aged at 60, 70, 80, 90, and 100°C for 6 days increased by 4.8, 5.4, 6.7, 8.2, and 10.8%, respectively, and the specimens aged for 30 days were enhanced by 7.2, 8.5, 10.5, 11.5, and 15.6%, respectively. Degree of the recovery reduction became larger as the cross-link density increment became larger.

The recovery decreased at the initial measurement time and then increased. Thus, the minimum recovery point was observed at the measurement time of 30 min to 1 day. This type of recovery behavior from the compressed deformation makes the linear relationship of the recovery with the measurement time worse. The linear curve fitting equations of the recovery variations from the 15 and 25% compressed deformations and their correlation coefficients are listed in Tables I and II, respectively. The correlation coefficients of the samples aged at low temperature are relatively higher than those at high temperatures. The minimum recovery point varied with thermal aging conditions such as the aging time and temperature. The 25% compressed specimens aged at 60°C for 1 and 6 days did not show the minimum recovery point (Fig. 1), but the others clearly showed the minimum recovery points. The minimum recovery point was observed at the longer measurement time as the aging temperature became higher and the aging time longer. Thus, the measured values of the compression set should vary with the experimental conditions and have some experimental error.

The recovery from the circular deformation was obtained by the equation of $R(\%) = 100\times(l_{gap}/l_{lin})$, where l_{gap} is the gap distance between both ends of

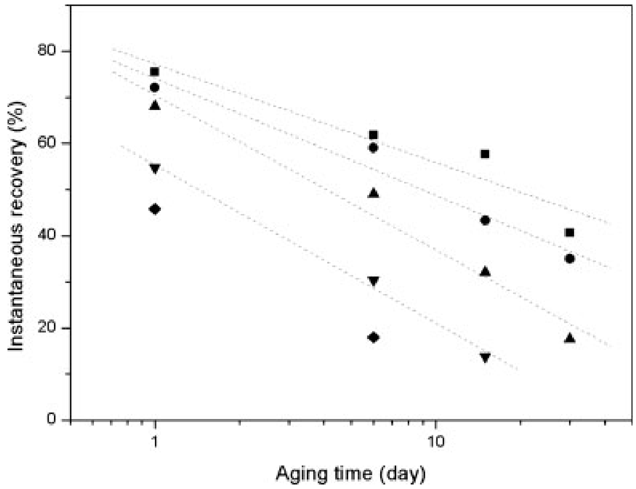

Figure 11 Variation of the instantaneous recovery at 10^{-6} day after removal from the circular shape of the CR composite with the aging time. The squares, circles, up-triangles, down-triangles, and diamonds indicate the aging temperatures of 60, 70, 80, 90, and 100°C, respectively.

the aged sample and l_{lin} is the length of the linear sample, 120 mm. Figures 6–10 show the recovery variations from the circular deformation with the measurement time of the specimens aged at 60, 70, 80, 90, and 100°C, respectively. The specimen aged at 60°C for 1 day fully recovered after 10 days of measurement time and the specimen aged at 60°C for 6 days also fully recovered before 50 days of measurement time. The recovery increases continuously as measurement time elapses. The linear curve fitting equations for the recovery variations from the circular deformation and their correlation coefficients are listed in Table III. As the experimental results show good linearity, it is possible to predict the recovery behaviors at lower temperatures using the accelerated thermal aging results.

The recovery is remarkably reduced by increasing the aging temperature. The recoveries obtained from the linear curve fitting equations at 1 day of the measurement time were 80.8, 76.5, 68.7, 50.2, and 26.1% for the specimens aged at 60, 70, 80, 90, and 100°C for 30 days, respectively. The recovery also declined by increasing the aging time. Recovery rate, which is the recovery difference per unit time at the

TABLE IV
The Linear Curve Fitting Equations for the Instantaneous Recovery at 10^{-6} Day from the Circular Deformation after the Thermal Aging

Aging temperature (°C)	Curve fitting equation (correlation coefficient, r)
60	$y = -21.37 \log x + 77.3$ ($r = -0.950$)
70	$y = -25.37 \log x + 74.1$ ($r = -0.982$)
80	$y = -33.58 \log x + 70.5$ ($r = -0.986$)
90	$y = -34.37 \log x + 55.40$ ($r = -0.997$)

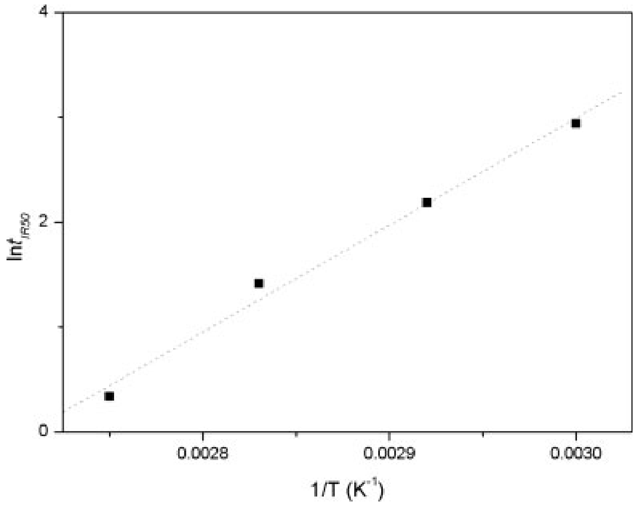

Figure 12 Variation of the half instantaneous recovery time (t_{IR50}) as a function of reciprocal temperature ($1/T$).

two measurement times, was calculated by $r_t = \Delta R/\Delta t_{aging}$, where ΔR is the recovery difference and Δt_{aging} is the aging time difference. This equation helped investigate the influence of aging time and temperature on the recovery behaviors in greater detail. For example, the recovery rate (r_t) of the specimens aged at 70°C for 1 and 6 days ($r_{1\text{–}6}$ at 70°C) was 0.98%/day { = (93.4–88.5)/(6–1)}. The recovery rate declined with increasing aging time. The $r_{1\text{–}6}$, $r_{6\text{–}15}$, and $r_{15\text{–}30}$ at 100°C were 3.58, 1.94, and 1.64%/day, respectively, and those at 80°C were 1.24, 1.01, and 0.58%/day, respectively. However, the recovery rate increased by increasing the aging temperature. The $r_{1\text{–}6}$s at 60, 70, 80, 90, and 100°C were 0.78, 0.98, 1.24, 2.42, and 3.58%/day, respectively, and the $r_{6\text{–}15}$s were 0.34, 0.67, 1.01, 1.11, and 1.94%/day, respectively. This may be due to the crosslink density changes brought about by the thermal aging. Crosslink densities of all the specimens after thermal aging were enhanced. Crosslink densities of the specimens aged at 60, 70, 80, 90, and 100°C for 6 days increased by 4.44, 7.12, 8.60, 11.11, and 16.41%, respectively. The degree of crosslink density change tends to increase by increasing the aging temperature and time.

Instantaneous recovery for describing sealing properties of a sealant can be obtained from the recovery variation with measuring time because the linearity is very good (Table III). The degree of instantaneous recovery is related to the sealing capability of a sealant such as O-ring. Instantaneous recoveries at 10^{-6} day (about 0.09 s) were calculated from linear curve fitting equations. The instantaneous recovery decreased with increasing the aging time and temperature as shown in Figure 11. Because values of the instantaneous recoveries of the specimens aged at 100°C for 15 and 30 days and the specimens aged at 90°C for 30 days were negative, they were not included in the plot. Variations of the instantaneous recoveries at 60, 70, 80, and 90°C show good linearity (Table IV). Half instantaneous recovery time (t_{IR50}, time to take 50% instantaneous recovery) was employed to predict instantaneous recovery at ambient temperature. The t_{IR50} at every aging temperature was obtained from the linear curve fitting equation for the instantaneous recovery variation. Plot of $\ln t_{IR50}$ versus $1/T$ shows good linearity (Fig. 12). The linear curve fitting equation for the plot was $\ln t_{IR50} = 10{,}205(1/T) - 27.62$ and its correlation coefficient was 0.995. Thus, the t_{IR50} at ambient temperature can be obtained from the curve fitting equation. For example, the t_{IR50} at 30°C is 428 days.

CONCLUSIONS

We tried to predict the recovery behavior of rubber composite using the conventional compression set test and the novel circular deformation method. The conventional compression set test was not suitable for the prediction method because the recovery variation with the measurement time showed local minimum and the linearity was relatively low. As the recovery variations from the circular deformation showed good linearity, the instantaneous recoveries were obtained from the linear curve fitting equations. We were also able to predict the instantaneous recovery at ambient temperature using the accelerated thermal aging results.

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