Thermochimica Acta 490 (2009) 8–12

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Comparison of recovery behaviors of thermally aged SBR composite from compressed and circular deformations

Sung-Seen Choi*, Dong-Hun Han

Department of Chemistry, Sejong University, 98 Gunja-dong, Gwangjin-gu, Seoul 143-747, Republic of Korea

ARTICLE INFO

Article history:
Received 18 August 2008
Received in revised form
20 November 2008
Accepted 29 January 2009
Available online 7 February 2009

Keywords:
Compression test
Circular deformation
Recovery
Thermal aging
SBR composite

ABSTRACT

Recovery behaviors of the SBR composite from the compressed and circular deformations after thermal aging were compared. Instantaneous recovery and target recovery time to describe the sealing properties of a sealant were obtained from the recovery variation with the measuring time. For the compressed deformation, the recovery decreased at the initial measurement time and then increased. Since the recovery from the compressed deformation showed a local minimum and the minimum point varied in accordance to the thermal aging conditions, the linearity of the recovery variation was very low. For the circular deformation, the recovery continuously increased as the measurement time elapsed, the linearity was very high, and the instantaneous recovery of less than 0.1 s could be obtained from the extrapolation method. The circular deformation method was found to be suitable for study of recovery behaviors of a rubber article. The recovery behaviors varied with the thermal aging conditions and the difference was explained with the crosslink density change by the thermal aging.

1. Introduction

Rubber vulcanizates can be permanently deformed when they are deformed for a long time, especially in high temperatures. One of the principal reasons for permanent deformation of a rubber article by thermal aging is change of the crosslink density [1]. Crosslink density of a rubber vulcanizate is changed by thermal aging [2–6]. Sulfur linkages, especially polysulfides, are easily dissociated by heating [1,7,8], and this brings about the reduction of the crosslink density. Curatives remaining in a rubber vulcanizate make new crosslinks [1,8], and this results in the enhancement of the crosslink density. Accelerated thermal aging at high temperatures of rubber articles reduces the test time and is used to predict the service lifetime [9,10].

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 investigate the degree of rubber vulcanizate deformation. However, specimens for the compression set are relatively thick (28.7 mm diameter and 12.7 mm height) and a great many samples are required for aging experiments so that differences in the initial states of the samples such as dimensions and crosslink densities are cannot be negligible. In this work, we introduced a novel test method of the circular deformation; a linear sample is deformed to a circular form by fixing the both ends with a pin, the pin is removed after the thermal aging, and the gap distance between the both ends of the sample is measured [1,11]. This method is the simplest and most efficient method with uniform states of the samples since thin specimens of 2–3 mm thickness are used.

Gillen et al. [12] measured the variation of the compression set of a rubber vulcanizate with the measuring time after the removal of the sample from the jig and reported that the compression set decreased in accordance with the measuring time. In the present work, we investigated the recovery behaviors of styrene-butadiene rubber (SBR) composite from the circular deformation with the measuring time after thermal aging at 70–100 °C, and they were compared to the recovery behaviors from the compressed deformation. Instantaneous recovery was also obtained from the good linear relationship between the recovery and the measurement time. A rubber material has a recovery property such that it returns to its original shape from deformation [13], and is used as a sealant material. The required property of a sealant is that it has high and fast recovery from deformation as well as sealing capability. It is of course hard to directly measure the instantaneous recovery at less than 0.1 s, but the instantaneous recovery can be obtained from the linear curve fitting equation of the recovery variation with the measurement time when its correlation coefficient is high enough.

2. Experimental

The SBR compound was made of SBR (SBR 1502 of Kumho Petrochemical Co., 100.0 phr), carbon black (55.0 phr), antidegradants

* Corresponding author. Fax: +82 2 462 9954.
E-mail address: sschoi@sejong.ac.kr (S.-S. Choi).

0040-6031/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2009.01.030

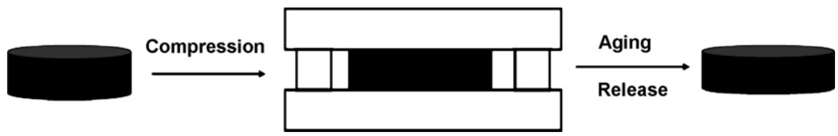

Fig. 1. Process of the compression set and recovery experiment.

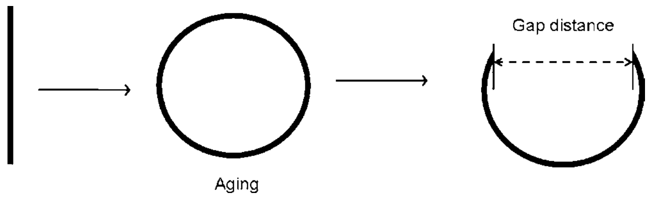

Fig. 2. Process of the circular deformation and recovery experiment.

(2.0 phr), cure activators (4.0 phr), cure accelerator (5.0 phr), and sulfur (0.8 phr). The compression set test was performed according to the ISO 815 and the compression ratio was 25%. The compressed samples were thermally aged at 70, 80, 90, and 100 °C for 6, 15, and 30 days in a convection oven. After the thermal aging, the samples were released from the compression jig and the thickness was measured 6.9×10^{-3}, 2.1×10^{-2}, 4.2×10^{-2}, 0.42, 1, 10, 50, and 100 days after the thermal aging (Fig. 1). The circular deformation experiments were carried out as follows (Fig. 2): First, the sample was cut to the dimensions of 5 mm × 120 mm with 2 mm thickness. Second, the linear sample was changed to a circular form by fixing both the ends with a pin. Third, the deformed samples with a circular form were also aged at 70, 80, 90, and 100 °C for 6, 15, and 30 days in a convection oven. Finally, removing the pin and the gap distance between both ends of the sample was measured 6.9×10^{-3}, 2.1×10^{-2}, 4.2×10^{-2}, 0.42, 1, 10, 50, and 100 days after the thermal aging with digital vernier calipers. Experiments were carried out three times and they were averaged.

Crosslink densities of the samples were measured by the swelling method. The procedure to measure the crosslink density was as follows: initially organic additives in the samples were removed by extraction with THF and *n*-hexane for 2 days each and 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 $Q = (W_s - W_u)/W_u$, where the W_s and W_u are the weights of the swollen and unswollen samples. The reciprocal swelling ratio ($1/Q$) was used as the apparent crosslink density.

3. Results and discussion

The recovery from the compressed deformation is calculated by the equation of $R(\%) = 100 \times (h_a - h_c)/(h_i - h_c)$, where the h_a is the height of the recovered sample after the thermal aging, the h_c is the height of the 25% compressed sample, and the h_i is the initial height of the sample. The compressed specimens are not fully recovered even 100 days after the thermal aging at 70 °C for 6 days. The recoveries are less than 90% irrespective of the thermal aging conditions as shown in Figs. 3–5. This implies that the SBR composite was permanently deformed by the thermal aging. Figs. 3–5 show the recovery variations from the compressed deformation with the measurement times of 6, 15, and 30 days, respectively, after the thermal aging. The recovery decreases as the aging temperature becomes higher and the aging time becomes longer. The recovery of the specimen aged for 6 days increases or decreases as the measuring time elapses and the linear relationship is very low (Fig. 3). The correlation coefficients (r) for the linear curve fitting equations

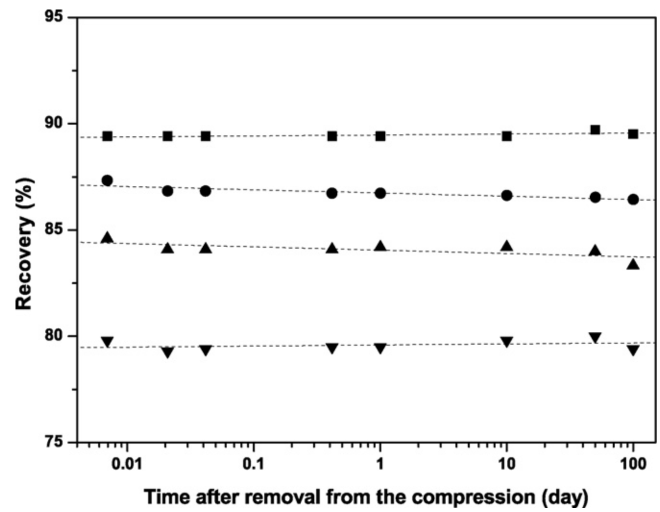

Fig. 3. Variation of the recovery of the SBR composite after removal from the compression jig with the measurement time. The sample was thermally aged for 6 days. The squares, circles, up-triangles, and down-triangles indicate the aging temperatures of 70, 80, 90, and 100 °C, respectively.

of the specimens thermally aged at 70, 80, 90, and 100 °C are 0.64, −0.88, −0.70, and 0.32, respectively, as listed in Table 1. The decreasing trends of the recoveries after the thermal aging at 80 and 90 °C are unexpected since rubber materials have recovery characteristics as described previously. The recoveries of the samples thermally aged for the long periods show increasing trends, but the correlation coefficients for the linear curve fittings are very low as shown in Figs. 4 and 5, and Table 1. If the recovery behaviors from the compressed deformation have good linear trends with the measuring time, instantaneous recoveries (less than 0.1 s) can be obtained from the extrapolation method. Degree of the instantaneous recovery is

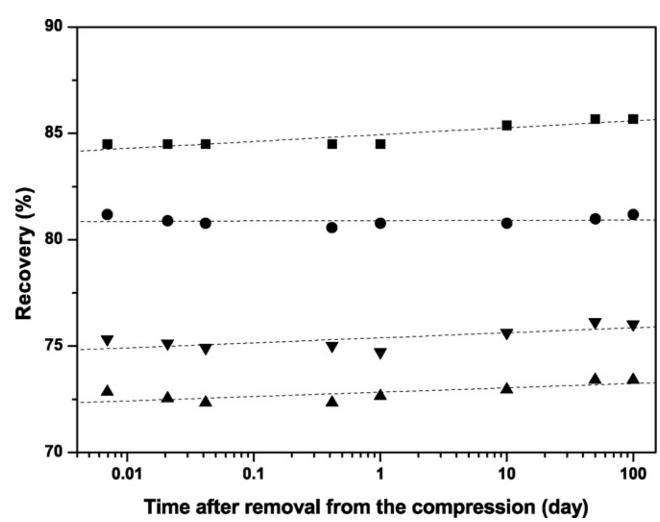

Fig. 4. Variation of the recovery of the SBR composite after removal from the compression jig with the measurement time. The sample was thermally aged for 15 days. The squares, circles, up-triangles, and down-triangles indicate the aging temperatures of 70, 80, 90, and 100 °C, respectively.

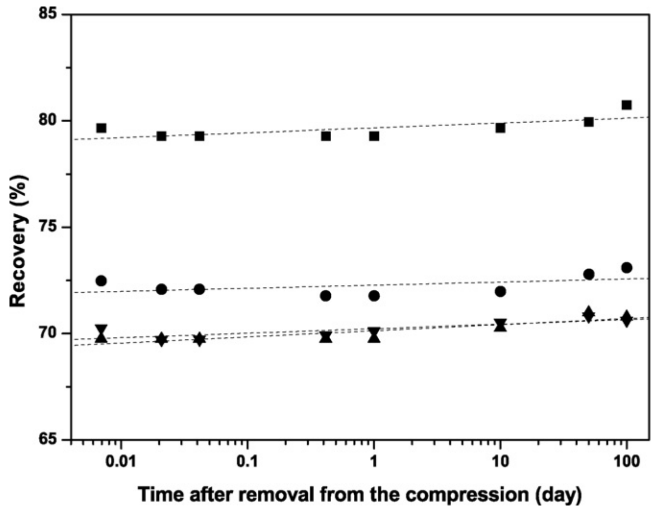

Fig. 5. Variation of the recovery of the SBR composite after removal from the compression jig with the measurement time. The sample was thermally aged for 30 days. The squares, circles, up-triangles, and down-triangles indicate the aging temperatures of 70, 80, 90, and 100 °C, respectively.

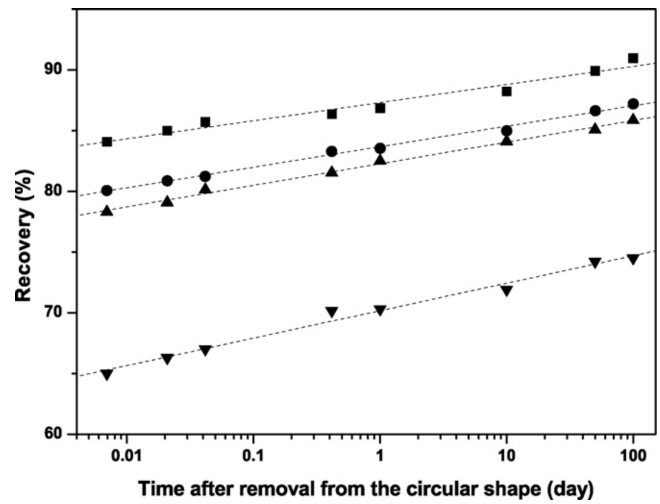

Fig. 6. Variation of the recovery of the SBR composite after removal from the circular shape with the measurement time. The sample was thermally aged for 6 days. The squares, circles, up-triangles, and down-triangles indicate the aging temperatures of 70, 80, 90, and 100 °C, respectively.

related to the sealing capability of a sealant such as O-ring. But the experimental results of the compression test do not show a good linearity. Moreover, some recoveries are even decreased and local minima are found in the some recovery curves. The local minima are observed in the recoveries of the samples thermally aged for 15 and 30 days as shown in Figs. 4 and 5.

The local minimum means that the recovery decreases in the initial releasing period and then increases. The local minimum is one of principal reasons for the low linear relationship of the recovery variation for the compression set test. For the samples thermally aged for 15 days, the local minimum is observed at the measuring time of 10 h to 1 day but the sample aged at 70 °C does not show the local minimum. All the samples thermally aged for 30 days show the local minima at the measuring time of 10 h to 1 day. These local minima worsen the linear correlation between the measuring time and the recovery.

Figs. 6–8 show the recovery variations of the SBR composite from the circular deformation with the measuring time after the thermal aging for 6, 15, and 30 days, respectively. The recovery from the circular deformation is calculated by the equation of $R(\%) = 100 \times (l_{gap}/l_{lin})$, where the l_{gap} is the gap distance between both ends of the aged sample as shown in Fig. 2 and the l_{lin} is the length of the linear sample, 120 mm. The recovery continuously increases as the measuring time elapses and the correlation coefficients for the linear curve fittings are very high as listed in Table 2. By increasing the aging time and temperature the recov-

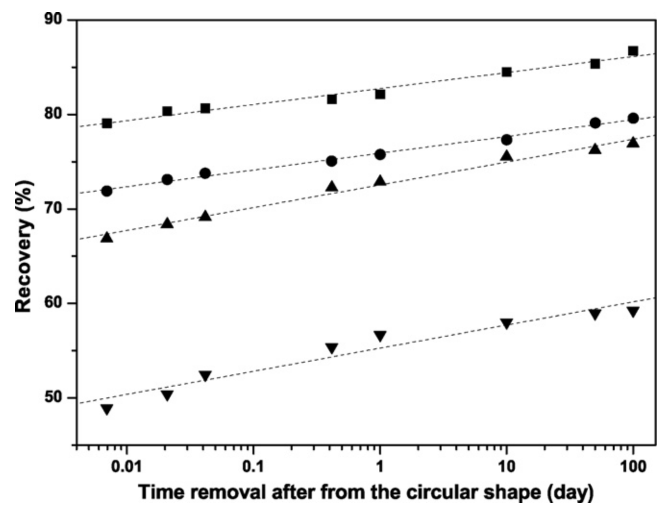

Fig. 7. Variation of the recovery of the SBR composite after removal from the circular shape with the measurement time. The sample was thermally aged for 15 days. The squares, circles, up-triangles, and down-triangles indicate the aging temperatures of 70, 80, 90, and 100 °C, respectively.

Table 1
The linear curve fitting equations for the recovery variations from the compressed deformation after the thermal aging (Figs. 3–5).

Aging time/Aging temperature	Curve fitting equation (Correlation coefficient, r)
6 days/70 °C	$y = 0.043 \log x + 89.5$ ($r = 0.640$)
6 days/80 °C	$y = -0.152 \log x + 86.7$ ($r = -0.877$)
6 days/90 °C	$y = -0.155 \log x + 84.1$ ($r = -0.700$)
6 days/100 °C	$y = 0.050 \log x + 79.6$ ($r = 0.317$)
15 days/70 °C	$y = 0.323 \log x + 84.9$ ($r = 0.899$)
15 days/80 °C	$y = 0.017 \log x + 80.9$ ($r = 0.124$)
15 days/90 °C	$y = 0.204 \log x + 72.8$ ($r = 0.753$)
15 days/100 °C	$y = 0.237 \log x + 75.4$ ($r = 0.721$)
30 days/70 °C	$y = 0.229 \log x + 79.7$ ($r = 0.704$)
30 days/80 °C	$y = 0.146 \log x + 72.3$ ($r = 0.475$)
30 days/90 °C	$y = 0.289 \log x + 70.1$ ($r = 0.872$)
30 days/100 °C	$y = 0.211 \log x + 70.2$ ($r = 0.797$)

Table 2
The linear curve fitting equations for the recovery variations from the circular deformation after the thermal aging (Figs. 6–8).

Aging time/Aging temperature	Curve fitting equation (Correlation coefficient, r)
6 days/70 °C	$y = 1.494 \log x + 87.3$ ($r = 0.982$)
6 days/80 °C	$y = 1.688 \log x + 83.7$ ($r = 0.997$)
6 days/90 °C	$y = 1.778 \log x + 82.3$ ($r = 0.998$)
6 days/100 °C	$y = 2.259 \log x + 70.2$ ($r = 0.993$)
15 days/70 °C	$y = 1.694 \log x + 82.7$ ($r = 0.987$)
15 days/80 °C	$y = 1.772 \log x + 75.9$ ($r = 0.996$)
15 days/90 °C	$y = 2.414 \log x + 72.5$ ($r = 0.993$)
15 days/100 °C	$y = 2.448 \log x + 55.3$ ($r = 0.971$)
30 days/70 °C	$y = 1.830 \log x + 77.2$ ($r = 0.989$)
30 days/80 °C	$y = 1.930 \log x + 69.8$ ($r = 0.994$)
30 days/90 °C	$y = 2.597 \log x + 61.8$ ($r = 0.989$)
30 days/100 °C	$y = 2.210 \log x + 33.8$ ($r = 0.984$)

Number of significant figures in the factor of $\log x$ is unrealistically high.

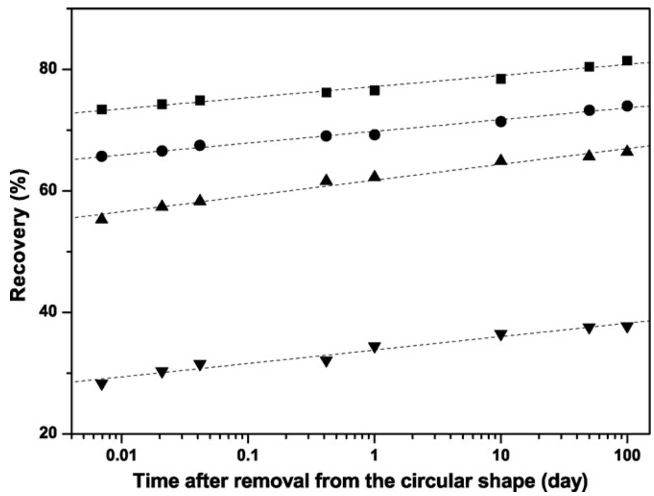

Fig. 8. Variation of the recovery of the SBR composite after removal from the circular shape with the measurement time. The sample was thermally aged for 30 days. The squares, circles, up-triangles, and down-triangles indicate the aging temperatures of 70, 80, 90, and 100 °C, respectively.

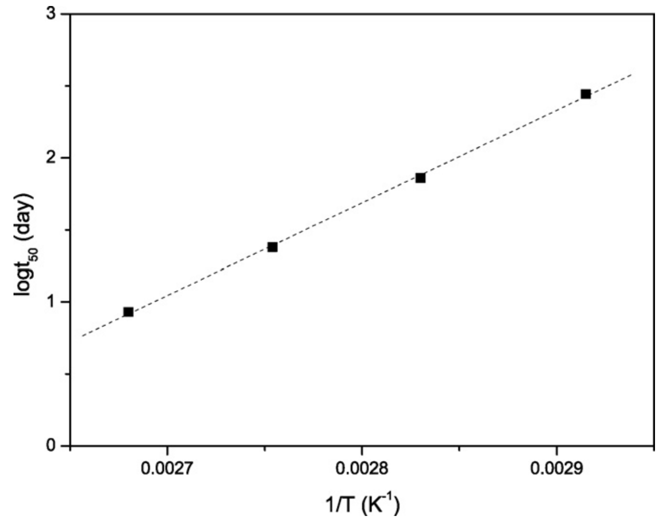

Fig. 10. Arrhenius plot of the 50% instantaneous recovery time at 0.09 s (1.0×10^{-6} days).

ery decreases. The recovery of the sample thermally aged at 100 °C is much lower than those of the samples aged at 70–90 °C, irrespective of the aging times. The difference in the recoveries of the samples aged at the different aging temperatures increases as the aging time increases. The recovery differences of the samples aged at 70 and 80 °C of the measurement time of 1 day are 3.6, 6.8, and 7.4% for the aging times of 6, 15, and 30 days, respectively, and those at 90 and 100 °C are 12.1, 17.2, and 28.0%, respectively. This may be due to the difference in the crosslink density change by the thermal aging. The crosslink density of the specimen is increased by thermal aging. The crosslink density increment is getting larger as the aging temperature and time increases as shown in Fig. 9. Therefore, the larger the difference in the crosslink density changes by the thermal aging is, the larger the difference in the recoveries is. The slope of the curve fitting equation is increased by increasing the aging temperature as listed in Table 2. Using the curve fitting equations as listed in Table 2, the time to reach to a certain recovery (for example 50% recovery, half recovery) can be obtained. The half recovery times of the specimens aged at 70, 80, 90, and 100 °C for 6/15/30 days are $9.3 \times 10^{-21}/4.3 \times 10^{-15}/1.2 \times 10^{-10}$, $9.4 \times 10^{-16}/2.1 \times 10^{-10}/4.8 \times 10^{-6}$, $5.9 \times 10^{-14}/4.1 \times 10^{-5}/2.5$, and $9.9 \times 10^{-5}/5.9 \times 10^{2}/6.3 \times 10^{5}$ s, respectively. The half recovery time strikingly increases as the aging time and temperature increase.

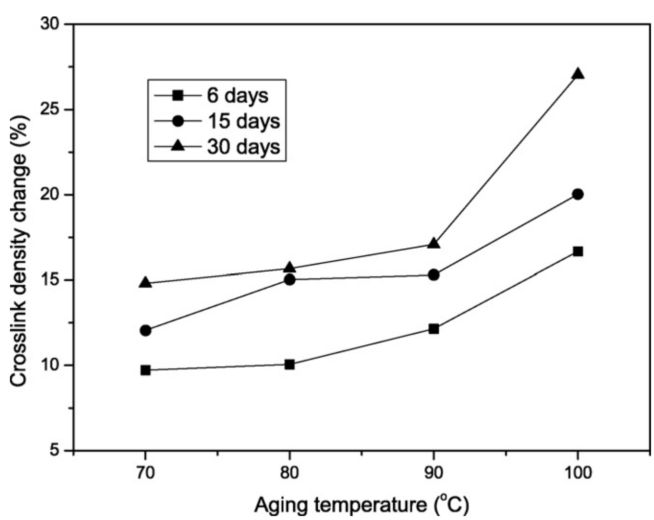

Fig. 9. Variation of the crosslink density change of the circularly deformed SBR composite after the thermal aging with the aging temperature. The squares, circles, and triangles indicate the aging times of 6, 15, and 30 days, respectively.

The instantaneous recovery can be obtained from the curve fitting equation. For example, the instantaneous recoveries at 10^{-6} day (about 0.09 s) of the specimens aged at 70, 80, 90, and 100 °C for 6 days are 78.3, 73.6, 71.6, and 56.6%, respectively. The instantaneous recovery decreases as the aging temperature increases. This implies that the sample aged at a high temperature is permanently deformed more than the sample aged at a low one and the sealing property or the response to the instantaneous deformation of a sealant is getting worse. The instantaneous recovery also decreases as the aging time increases. The instantaneous recoveries at 1.0×10^{-6} day of the specimens aged at 70, 80, 90, and 100 °C for 15/30 days are 72.5/66.2, 65.3/58.2, 58.0/46.2, and 40.6/20.5%, respectively. Using the variations of the instantaneous recoveries at 1.0×10^{-6} day with the aging time, the half instantaneous recovery times at 1.0×10^{-6} day can be obtained. The half instantaneous recovery times are 278, 72, 24, and 9 days for the aging temperatures 70, 80, 90, and 100 °C, respectively. Arrhenius plot of the half instantaneous recovery time and the aging temperature shows a good linearity as shown in Fig. 10, therefore the service lifetime at a certain temperature can be obtained. The curve fitting equation of Fig. 10 is $y = 6423x - 16.30$ ($r^2 = 0.999$).

The circular deformation method is a very simple and efficient test method and the recovery behaviors show good linear relationships. By changing the linear specimen to the circular shape, both compression and tension are simultaneously applied to the sample. The inner part is compressed and the outer one is elongated. Due to the good linearity of the recovery behaviors to the measurement time, the instantaneous recovery and the target recovery time to apply the sealing property of a sealant can be obtained from the curve fitting equation.

4. Conclusions

The SBR composite was thermally aged under compressed and circular deformations and the recovery behaviors were compared. It was difficult to obtain the instantaneous recovery using the conventional compression set test because the recovery behaviors were not linear. The circular deformation method that changes a linear specimen to a circular shape was found to be a good test method to obtain the instantaneous recovery and target recovery time because the recovery behaviors showed good linear relationships with the measurement time. The recovery was reduced by increasing the aging time and temperature. The instantaneous recoveries and target recovery times were obtained from the linear curve fitting equations. The instantaneous recovery decreased as the aging temperature and time increased. The half recovery time remarkably increased as the aging temperature and time increased. Since the recovery variations from the circular deformation at high temperatures showed good linear relationships, the service lifetime could be obtained using the accelerated thermal aging results.

References

[1] S.-S. Choi, Bull. Kor. Chem. Soc. 21 (2000) 628.
[2] S.-S. Choi, Kor. Polym. J. 7 (1999) 108.
[3] S.-S. Choi, J. Appl. Polym. Sci. 75 (2000) 1378.
[4] S.-S. Choi, Polym. Int. 50 (2001) 107.
[5] S.-S. Choi, D.-H. Han, S.-W. Ko, H.S. Lee, Bull. Kor. Chem. Soc. 26 (2005) 1853.
[6] S.-S. Choi, S.-H. Ha, C.-S. Woo, Bull. Kor. Chem. Soc. 27 (2006) 429.
[7] S.-S. Choi, Kor. Polym. J. 5 (1997) 43.
[8] R.W. Layer, Rubber Chem. Technol. 65 (1992) 211.
[9] R.P. Brown, T. Butler, Natural ageing of rubber, in: Changes in Physical Properties Over 40 Years, RAPRA Technology Ltd., 2000.
[10] R.P. Brown, T. Butler, S.W. Hawley, Ageing of Rubber. Accelerated Heat Ageing Test Results, RAPRA Technology Ltd., 2001.
[11] S.S. Choi, H.M. Lee, J.E. Ko, M.C. Kim, J. Ind. Eng. Chem. 13 (2007) 1169.
[12] K.T. Gillen, R. Bernstein, M.H. Wilson, Polym. Deg. Stab. 87 (2005) 257.
[13] B. Erman, J.E. Mark, Annu. Rev. Phys. Chem. 40 (1989) 351.