

Influence of Styrene Contents on Retraction Behaviors of SBR Vulcanizates

Sung-Seen Choi[†], Chang-Su Woo*, and Dong-Ho Chang**

Department of Applied Chemistry, Sejong University, 98 Koonja-dong,
Kwangjin-gu, Seoul 143-747, Korea

*Korea Institute of Machinery and Materials, P. O. Box 101, Yusong,
Daejeon 305-600, Korea

**Kumho Research and Development Center, 555 Sochon-dong, Kwangsan-gu
Kwangju 506-711, Korea

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SBR 가황물의 회복 거동에 미치는 스티렌 함량의 영향

최 성 신[†] · 우 창 수* · 장 동 호**

세종대학교, *기계연구원, **금호타이어

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ABSTRACT : Influence of the styrene content on the retraction behaviors of SBR vulcanizates was studied. SBRs with different styrene contents of 15 and 21 wt% were used. The vulcanizate with low styrene content started to recover at lower temperature than that with high one. The recovery rate of the vulcanizate with low styrene content was slower than that with high one. The recovery difference between the two vulcanizates with different styrene contents was larger for the carbon black-filled vulcanizates than for the silica-filled ones. The experimental results were explained with the glass transition temperature and modulus.

요약 : 스티렌 함량이 SBR 가황물의 회복 거동에 미치는 영향에 대해 연구하였다. 스티렌 함량이 15와 21 wt%인 SBR을 사용하였다. 스티렌 함량이 적은 가황물이 스티렌 함량이 많은 가황물에 비해 더 낮은 온도에서 회복하기 시작하였으며, 스티렌 함량이 적은 가황물의 회복 속도가 스티렌 함량이 많은 가황물보다 느렸다. 두 가황물 간의 회복 차이는 카본블랙으로 보강된 가황물이 실리카로 보강된 것보다 컸다. 실험 결과는 유리전이온도와 모듈러스로 설명하였다.

Keywords : retraction behaviors, SBR vulcanizate, styrene content, glass transition temperature, modulus

I. Introduction

Rubber materials have been widely used for vibration damping. The low glass transition temperature (T_g) property leads to use of vibration damping at low temperature. A rubber material has

a recovery property to return to its original shape from deformation.¹⁻³ Retraction behaviors of rubber vulcanizates are affected by type and content of filler, crosslink density, and processing aids.⁴⁻⁶

Styrene-butadiene rubber (SBR) is a copolymer of styrene and butadiene. Chemical and physical properties of SBR depend on the styrene content. In this work, we studied influence of the styrene

[†] 대표저자(e-mail : sschoi@sejong.ac.kr)

contents on the retraction behaviors of SBR vulcanizates. Variation of the retraction behaviors of SBR vulcanizates with the filler types was also investigated. SBR compounds reinforced with carbon black and silica (with and without a coupling agent) were prepared.

II. Experimental

The SBR compounds were made of SBR, silica (Z175), carbon black (N220), cure activators (stearic acid and ZnO), antidegradants (HPPD and wax), and curatives (TBBS and sulfur). SL 574 of Japan Synthetic Rubber Co. and NS 116 of Nippon Zeon Co. were employed as SBR. The styrene contents are 15 and 21 wt%, respectively. Si69 of Degussa Co. was used as a silane coupling agent. The formulations are given in Table 1. The compounds were reinforced with various filler systems of carbon black, silica without a coupling agent, and silica containing a coupling agent.

Table 1. Formulations (phr)

Compound No.	1	2	3	4	5	6
SL 574	100.0	100.0	100.0	0.0	0.0	0.0
NS 116	0.0	0.0	0.0	100.0	100.0	100.0
N220	50.0	0.0	0.0	50.0	0.0	0.0
Z175	0.0	50.0	50.0	0.0	50.0	50.0
Si69	0.0	0.0	3.0	0.0	0.0	3.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0
ZnO	2.0	2.0	2.0	2.0	2.0	2.0
HPPD	2.0	2.0	2.0	2.0	2.0	2.0
Wax	2.0	2.0	2.0	2.0	2.0	2.0
TBBS	1.4	1.4	1.4	1.4	1.4	1.4
Sulfur	1.4	1.4	1.4	1.4	1.4	1.4

SL 574: styrene 15.0 wt%, 1,2-unit 57.0 wt%, ML(1+4) = 50

NS 116: styrene 21.0 wt%, 1,2-unit 60.0 wt%, ML(1+4) = 45

N220: carbon black

Z175: silica

Si69: silane coupling agent, bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT)

HPPD: *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine

TBBS: *N*-*tert*-butyl-2-benzothiazole sulfenamide

The vulcanizates were prepared by curing at 160 °C. The sample dimension for the temperature retraction (TR) test was 50 mm of length, 2 mm of width, and 2 mm of thickness. The TR test according to the ASTM D1329 with a TR tester ET01 of Elastocon Co. was performed as follow. (1) The sample was strained by 50% and kept in a low temperature chamber (about -75 °C) for 30 min. (2) The elongated sample was released and the temperature was increased at 1 °C/min. (3) Variation of the recovery with the temperature was measured. Physical properties of the vulcanizates were measured with the Universal Testing Machine (Instron 6021). Tan δ s of the vulcanizates were measured according to the procedure in ASTM D2231-87 with a Qualimeter Eplexor 150 N of Gabo Co.

III. Results and Discussion

Figures 1, 2, and 3 show the retraction behaviors of SBR vulcanizates with the filler systems of carbon black, silica without Si69, and silica containing Si69, respectively. The vulcanizates with low styrene content of 15 wt% begin to recover at lower temperature than those with high one of 21 wt%, irrespective of the filler systems. The vulcanizates with the styrene contents of 15 and 21 wt% begin to recover around -50 and -25 °C, respec-

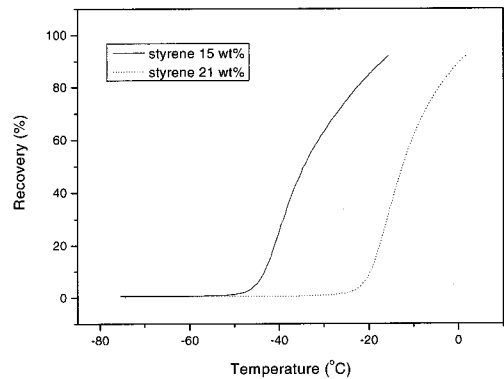


Figure 1. Recovery curves of the carbon black-filled SBR vulcanizates. Solid and dot lines indicate the vulcanizates with the styrene contents of 15 and 21 wt%, respectively.

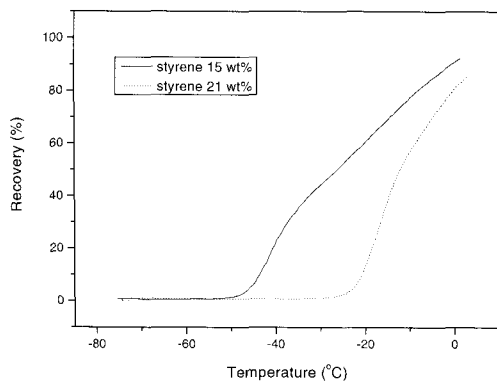


Figure 2. Recovery curves of the silica-filled SBR vulcanizates without the silane coupling agent. Solid and dot lines indicate the vulcanizates with the styrene contents of 15 and 21 wt%, respectively.

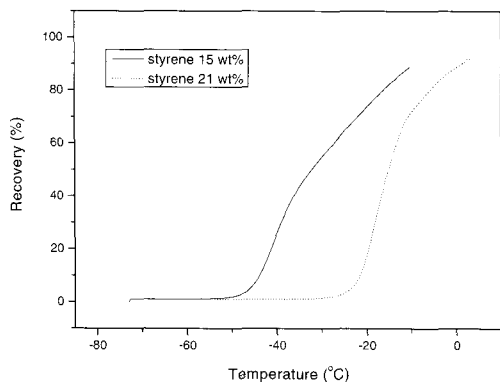


Figure 3. Recovery curves of the silica-filled SBR vulcanizates containing the silane coupling agent. Solid and dot lines indicate the vulcanizates with the styrene contents of 15 and 21 wt%, respectively.

tively. This is related to the glass transition temperature (T_g). T_g s of the vulcanizates with the styrene contents of 15 and 21 wt% are about -30 and -12 °C, respectively. Letting the temperature to reach 10% recovery be T_{10} . The T_{10} s of the carbon black-filled vulcanizates with the styrene contents of 15 and 21 wt% are -43.4 and -19.7 °C, respectively. The T_{10} s of the silica-filled vulcanizates without the silane coupling agent are -43.6 and -20.6 °C, respectively. For the vulcanizates containing the silane coupling agent, the T_{10} s are -43.9 and -21.6 °C, respectively. The T_{10} s of the vulcanizates with

same styrene contents are nearly the same, irrespective of the filler system. The T_{10} s of the vulcanizates with the styrene content of 15 wt% are lower than those with the styrene content of 21 wt% by about 13 °C. This is due to the difference of T_g discussed above.

The recovery rate was defined as $\Delta T = T_{80} - T_{10}$, where the T_{80} and T_{10} indicate the temperatures at 80% and 10% recoveries, respectively. The ΔT s of the carbon black-filled vulcanizates with the styrene contents of 15 and 21 wt% are 20.8 and 15.4 °C, respectively. The ΔT s of the silica-filled vulcanizates without the coupling agent are 35.4 and 20.5 °C, respectively. For the vulcanizates containing the coupling agent, the ΔT s are 27.8 and 15.1 °C, respectively. The recovery rates of the vulcanizates with the high styrene content are faster than those with the low one. This is due to the modulus. Moduli at 50 / 100 / 200% of the vulcanizates with the styrene content of 15 wt% are 1.73 / 2.94 / 7.22, 1.94 / 2.37 / 3.42, and 2.20 / 3.43 / 6.21 MPa for the filler systems of carbon black, silica without the coupling agent, and silica containing the coupling agent, respectively. Moduli at 50 / 100 / 200% of the vulcanizates with the styrene content of 21 wt% are 1.88 / 3.26 / 7.95, 2.49 / 3.57 / 5.57, and 2.56 / 4.22 / 7.71 MPa, respectively. Moduli of the vulcanizates with the high styrene content are larger than those with the low one. When a sample has higher modulus, the applied stress will be larger at the same strain rate. The larger stress will lead to faster return to its original form.⁷

Graphs of the temperature vs the recovery difference (Figure 4) and the recovery vs the temperature difference (Figure 5) were plotted in order to compare the differences of the retraction behaviors in detail. The recovery difference is the difference in recoveries at the same temperature between the vulcanizates with the styrene contents of 15 and 21 wt% (recovery difference = $R(21) - R(15)$, where $R(21)$ and $R(15)$ indicate the recoveries of the vulcanizates with the styrene contents of 21 and 15 wt%, respectively). All of the recovery difference

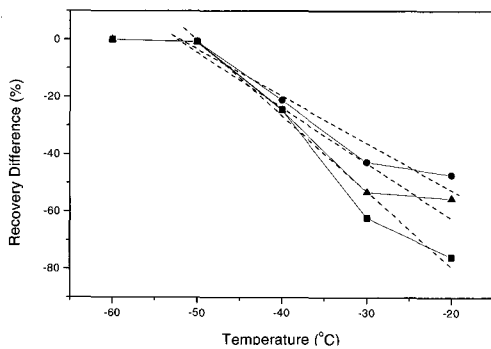


Figure 4. Variation of the recovery difference as a function of the temperature. Squares, circles, and triangles indicate the vulcanizates with the filler systems of carbon black, silica without Si69, and silica containing Si69, respectively.

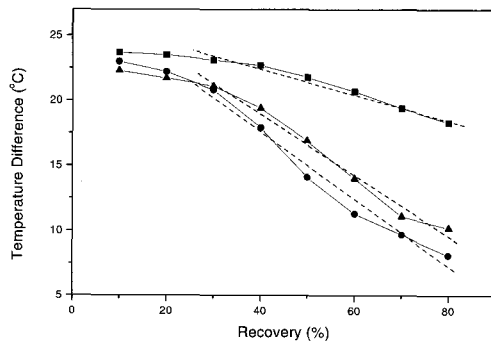


Figure 5. Variation of the temperature difference as a function of the recovery. Squares, circles, and triangles indicate the vulcanizates with the filler systems of carbon black, silica without Si69, and silica containing Si69, respectively.

values are negative. This means that the vulcanizate with the 15 wt% styrene content is recovered more than that with 21 wt% one at the same temperature. Absolute values of the recovery differences increase continuously with increase of the temperature, irrespective of the filler systems (Figure 4). The plots of Figure 4 in range from $-50\text{ }^{\circ}\text{C}$ to $-20\text{ }^{\circ}\text{C}$ show good linear relations. The curve fitting equations in the temperature range were calculated and listed in Table 2. The change of the recovery difference of the carbon black-filled vulcanizate is larger than those of the silica-filled ones. For the silica-filled vulcanizates, the change of the recovery

Table 2. Curve Fitting Equations for the Plot of Temperature vs Recovery Difference with the Linear Region from $-50\text{ }^{\circ}\text{C}$ to $-20\text{ }^{\circ}\text{C}$ in Figure 4.

Filler system	Curve fitting equation	Correlation coefficient (r)
Carbon black	$y = -2.63x - 133$	0.99
Silica without Si69	$y = -1.61x - 84$	0.97
Silica containing Si69	$y = -1.92x - 101$	0.96

difference of the vulcanizate containing the silane coupling agent is larger than that of the vulcanizate without one. Absolute values of the recovery differences increase about 2.6, 1.9, and 1.6% every $1\text{ }^{\circ}\text{C}$ for the vulcanizates with the filler systems of carbon black, silica containing the silane coupling agent, and silica without the silane coupling agent, respectively.

Figure 5 shows variation of the temperature difference with the recovery. The temperature differences decrease continuously as the recovery increases. The temperature difference is the difference in temperatures to reach the same recovery between the vulcanizates with the styrene contents of 15 and 21 wt% (temperature difference = $T(21) - T(15)$, where $T(21)$ and $T(15)$ indicate the temperatures of the vulcanizates with the styrene contents of 21 and 15 wt%, respectively). All of the temperature difference values are positive. This also means that the vulcanizate with the 21 wt% styrene content is recovered less than that with 15 wt% one. The temperature differences decrease continuously with increase of the temperature, irrespective of the filler systems. The plots of Figure 5 in range from 30% to 80% show good linear relations. The curve fitting equations in the recovery range were calculated and listed in Table 3. The change of the temperature difference of the carbon black-filled vulcanizate is smaller than those of the silica-filled ones. For the silica-filled vulcanizate, the change of the temperature difference of the vulcanizate containing the silane coupling agent is smaller than that of the vulcanizate without one. The temperature differences decrease about 1.0, 2.4, and 2.6 $^{\circ}\text{C}$ every

Table 3. Curve Fitting Equations for the plot of Recovery vs Temperature Difference with the Linear Region from 30% to 80% in Figure 5.

Filler system	Curve fitting equation	Correlation coefficient (r)
Carbon black	$y = -0.10x + 27$	0.99
Silica without Si69	$y = -0.26x + 28$	0.99
Silica containing Si69	$y = -0.24x + 28$	0.99

10% recovery for the vulcanizates with the filler systems of carbon black, silica containing the silane coupling agent, and silica without the silane coupling agent, respectively.

IV. Conclusion

The vulcanizate with the low styrene content started to recover at lower temperature than that with the high one due to the lower glass transition temperature. The glass transition temperature of the vulcanizate with the styrene content of 15 wt% was lower than that with the styrene content of 21 wt%. The recovery rate of the vulcanizate with the low styrene content was slower than that with the high one due to the modulus difference. The modulus of the vulcanizate with the styrene content of 15 wt% was lower than that with the styrene content of 21 wt%.

Acknowledgements

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