

Influence of 1,2-Unit Contents on Retraction Behaviors of SBR Vulcanizates

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ABSTRACT: Styrene-butadiene rubber (SBR) has four different repeat units of styrene, *cis*-1,4-, *trans*-1,4-, and 1,2-units. Influence of the 1,2-unit content on the retraction behaviors of SBR vulcanizates reinforced with silica or carbon black was studied. The retraction behaviors were compared in terms of the filler systems and the microstructures of SBR. The silica-filled vulcanizates containing a coupling agent showed nearly the same retraction behaviors as the carbon black-filled ones, but the silica-filled vulcanizates without a coupling agent were recovered slower than the carbon

black-filled ones. The vulcanizates with lower 1,2-unit content started to recover at lower temperature than that with higher 1,2-unit content. The recovery rate increased with increase of the 1,2-unit content of SBR. The experimental results were explained with the polymer-filler interactions, filler dispersion, glass transition temperature, and modulus. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4707–4711, 2006

Key words: retraction behaviors; SBR vulcanizate; 1,2-unit content; polymer-filler interaction

INTRODUCTION

Styrene-butadiene rubber (SBR) is a copolymer of styrene and butadiene. The butadiene units have three different microstructures of *cis*-1,4-, *trans*-1,4-, and 1,2-units. Grades of SBR are determined by ratios of the four components. Rubber materials have been widely used for vibration damping. The low glass transition temperature (T_g) property of rubber 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}

Carbon black and silica are the most popular reinforcing agents in rubber compounds.^{7–13} Silica has a number of hydroxyl groups (silanol, Si-OH), which results in strong filler–filler interactions and adsorption of polar materials by hydrogen bonds.^{12,14} Since intermolecular hydrogen bonds between silanol groups on the silica surface are very strong, it can aggregate tightly.^{13,15} Its property can cause a poor dispersion of silica in a nonpolar rubber compound. In general, a silane coupling agent such as bis(3-(triethoxysilyl)propyl)-tetrasulfide (TESPT) is used to improve the

filler dispersion and to prevent adsorption of curatives on the silica surface.^{16,17}

Some researchers^{18–22} reported that the 1,2-unit is more interactive with carbon black and silica than the other components of *cis*-1,4- and *trans*-1,4-units. One can expect that retraction behaviors of SBR vulcanizates will be varied with the microstructures of SBR since properties of SBR depend on the ratios of the four components. In the present work, we studied influence of the 1,2-unit contents on the retraction behaviors of SBR vulcanizates. Variation of the retraction behaviors of SBR vulcanizates with the filler systems was also investigated.

EXPERIMENTAL

The filled 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). SBR 1502 of Korea Kumho Petroleum, VSL 2525 of Lanxess, and NS 116 of Nippon Zeon were employed as SBR. The 1,2-unit contents are 18, 25, and 60 wt %, respectively. Si69 of Degussa (TESPT) was used as a silane coupling agent. The formulations are given in Table I. The Compounds 1–3 were carbon black-filled compounds and the Compounds 4–9 were silica-filled ones. The Compounds 4–6 do not contain Si69, while the Compounds 7–9 contain the silane coupling agent.

Mixing was performed in a Banbury type mixer at a rotor speed of 40 and 25 rpm for master batch (MB) and final mixing (FM) stages, respectively. The

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TABLE I
Formulations (phr)

Compound no	1	2	3	4	5	6	7	8	9
SBR 1502	100.0	0.0	0.0	100.0	0.0	0.0	100.0	0.0	0.0
VSL 2525	0.0	100.0	0.0	0.0	100.0	0.0	0.0	100.0	0.0
NS 116	0.0	0.0	100.0	0.0	0.0	100.0	0.0	0.0	100.0
N220	50.0	50.0	50.0	0.0	0.0	0.0	0.0	0.0	0.0
Z175	0.0	0.0	0.0	50.0	50.0	50.0	50.0	50.0	50.0
Si69	0.0	0.0	0.0	0.0	0.0	0.0	3.0	3.0	3.0
Stearic acid	2.0	2.0	2.0	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	2.0	2.0	2.0
HPPD	2.0	2.0	2.0	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	2.0	2.0	2.0
TBBS	1.4	1.4	1.4	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	1.4	1.4	1.4

SBR1502: styrene 23.5 wt %, 1,2-unit 18 wt %; VSL 2525: styrene 25.0 wt %, 1,2-unit 25 wt %; NS 116: styrene 21.0 wt %, 1,2-unit 60 wt %; 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 sulfonamide.

initial temperatures of the mixer were 110 and 80°C for MB and FM stages, respectively. The MB compounds were prepared as follows: (1) The rubber was loaded into the mixer and preheated for 0.5 min. (2) The fillers and silane coupling agent were compounded into the rubber for 2.0 min. (3) The cure activators and antidegradants were mixed for 2.0 min and the compounds were discharged. The FM compounds were prepared by mixing the curatives with the MB compounds for 2.0 min.

The vulcanizates were prepared by curing at 160°C for the t_{\max} in a press mold ($2 \times 140 \times 140 \text{ mm}^3$). 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 was performed as follows: (1) The sample was strained by 50% and kept in 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). $\tan \delta$ s of the vulcanizates were measured according to the procedure in ASTM D2231-87 with a qualimeter plexor 150N of Gabo.

RESULTS AND DISCUSSION

TR test was started at -75°C and finished at the temperature of 90% recovery. The retraction behaviors were compared depending on the filler systems as well as the 1,2-unit contents. Figures 1–3 show the differences in retraction behaviors of the vulcanizates reinforced with different filler systems. The vulcanizate with higher 1,2-unit content begins to

recover at higher temperature than that with lower 1,2-unit content. The vulcanizates with the 1,2-unit contents of 18, 25, and 60 wt % start to recover around -50, -45, and -25°C, respectively. This is due to the glass transition temperature (T_g). T_g s of the vulcanizates were measured with dynamic mechanical analysis (DMA). T_g s of the vulcanizates with the 1,2-unit contents of 18, 25, and 60 wt % are about -36, -32, and -12°C, respectively. The starting temperatures to recover are nearly the same irrespective of the filler systems when the vulcanizates are made of the same SBR. Let the 10% recovery be R_{10} . The temperatures at R_{10} (T_{10}) of the vulcanizates with the 1,2-unit content of 18 wt % are -44.3, -45.6, and -45.3°C for the filler systems of carbon

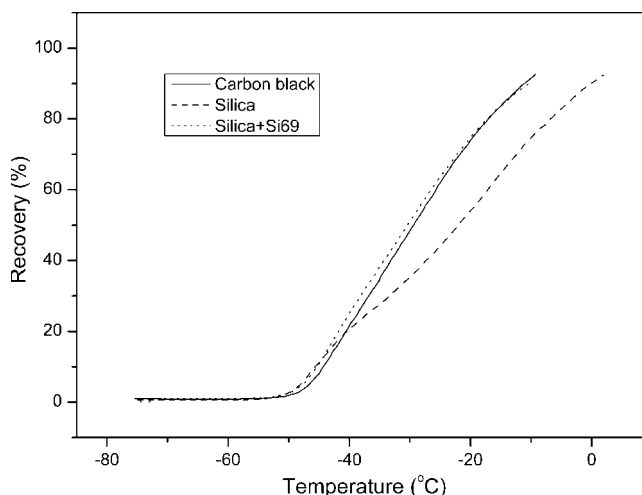


Figure 1 Recovery curves of the SBR vulcanizates with the 1,2-unit content of 18 wt %. Solid, dash, and dot lines indicate the vulcanizates reinforced with carbon black, silica without Si69, and silica containing Si69, respectively.

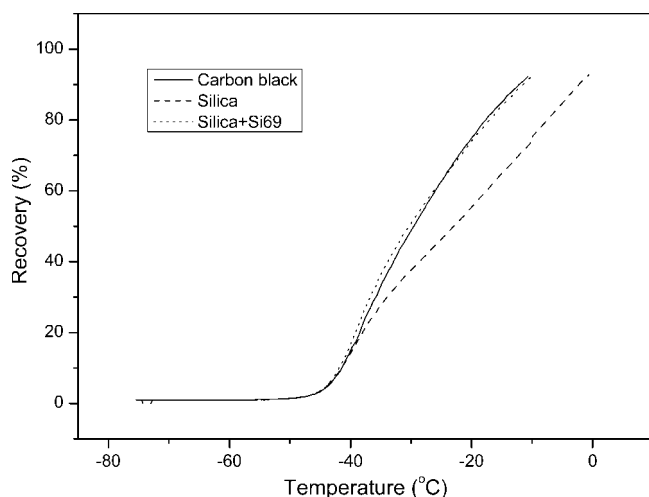


Figure 2 Recovery curves of the SBR vulcanizates with the 1,2-unit content of 25 wt %. Solid, dash, and dot lines indicate the vulcanizates reinforced with carbon black, silica without Si69, and silica containing Si69, respectively.

black, silica without Si69, and silica containing Si69, respectively. The T_{10} s of the vulcanizates with the 1,2-unit content of 25 wt % are -41.4 , -41.5 , and -41.7°C , respectively. For the vulcanizates with the 1,2-unit content of 60 wt %, the T_{10} s are -19.7 , -20.6 , and -21.6°C , respectively.

For the vulcanizates with the 1,2-unit contents of 18–25 wt %, the vulcanizates reinforced with carbon black and silica containing Si69 show nearly the same retraction behaviors as shown in Figures 1 and 2. However, retraction behaviors of the silica-filled vulcanizates without the silane coupling agent are different with those of the vulcanizates reinforced

with carbon black and silica containing the coupling agent. This may be due to the filler dispersion. In general, filler dispersion of a silica-filled rubber compound without a silane coupling agent is worse than that containing a silane coupling agent.^{23–26}

The vulcanizates recover steeply after 5–10% recovery and show the fast recovery behaviors until 80–90% recovery. The recovery rate, $\Delta T = T_{80} - T_{10}$, was calculated and compared, where the T_{80} and T_{10} indicate the temperatures at 80 and 10% recoveries, respectively. For the vulcanizates with the 1,2-unit contents of 18–25 wt %, the ΔT s of the silica-filled vulcanizates without Si69 are slower than those of the other ones. The ΔT s of the vulcanizates with the 1,2-unit content of 18 wt % are 27.2, 38.8, and 28.1 $^\circ\text{C}$ for the filler systems of carbon black, silica without Si69, and silica containing Si69, respectively. The ΔT s of the vulcanizates with the 1,2-unit content of 25 wt % are 23.7, 33.9, and 24.7 $^\circ\text{C}$, respectively. For the vulcanizates with the 1,2-unit content of 60 wt %, difference in the ΔT s with the filler systems is relatively small. For the vulcanizates with the 1,2-unit content of 60 wt %, the ΔT s are 15.4, 20.5, and 15.1 $^\circ\text{C}$, respectively. The slower recovery rates of the silica-filled vulcanizates without Si69 can be explained with the lower modulus. The detail discussion was in the latter.

The recovery rate becomes faster as the 1,2-unit content of SBR increases. This can be explained with the T_g and modulus. The T_g becomes higher as the 1,2-unit content increases as described previously. The modulus also increases with increasing 1,2-unit content. Moduli at 50% strain of the vulcanizates with the 1,2-unit content of 18 wt % are 15.6, 14.8, and 18.6 kg/cm^2 for the filler systems of carbon

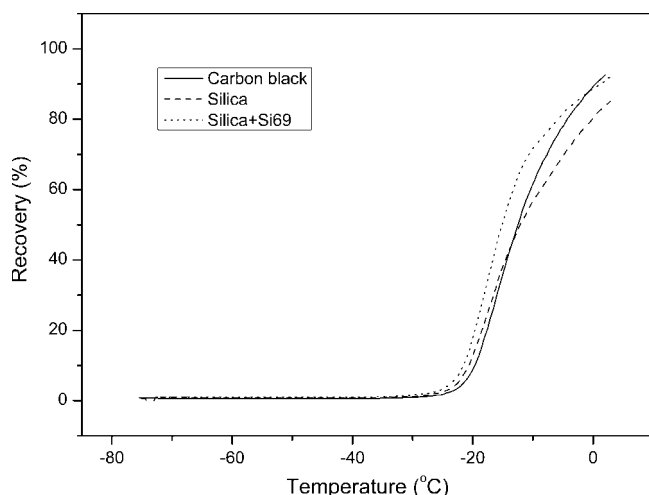


Figure 3 Recovery curves of the SBR vulcanizates with the 1,2-unit content of 60 wt %. Solid, dash, and dot lines indicate the vulcanizates reinforced with carbon black, silica without Si69, and silica containing Si69, respectively.

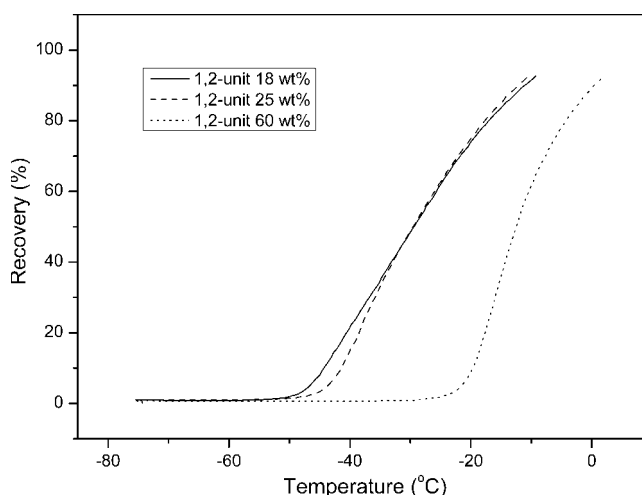


Figure 4 Recovery curves of the carbon black-reinforced vulcanizates. Solid, dash, and dot lines indicate the SBR vulcanizates with the 1,2-unit contents of 18, 25, and 60 wt %, respectively.

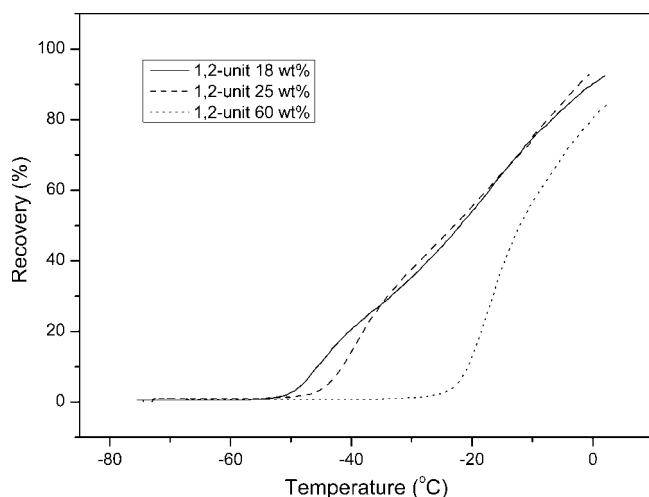


Figure 5 Recovery curves of the silica-reinforced vulcanizates without Si69. Solid, dash, and dot lines indicate the SBR vulcanizates with the 1,2-unit contents of 18, 25, and 60 wt %, respectively.

black, silica without Si69, and silica containing Si69, respectively. The 50% moduli of the vulcanizates with the 1,2-unit content of 25 wt % are 16.4, 19.6, and 20.7 kg/cm², respectively. For of the vulcanizates with the 1,2-unit content of 60 wt %, the 50% moduli of the vulcanizates are 18.8, 24.9, and 25.6 kg/cm², respectively. Ability to return to the original form from the deformed state becomes higher as the modulus increases. A rubber vulcanizate also has elastic property more and more as the temperature increases. Since the vulcanizates start to recover around their T_g s, the starting temperature to recover becomes higher as the 1,2-unit content increases.

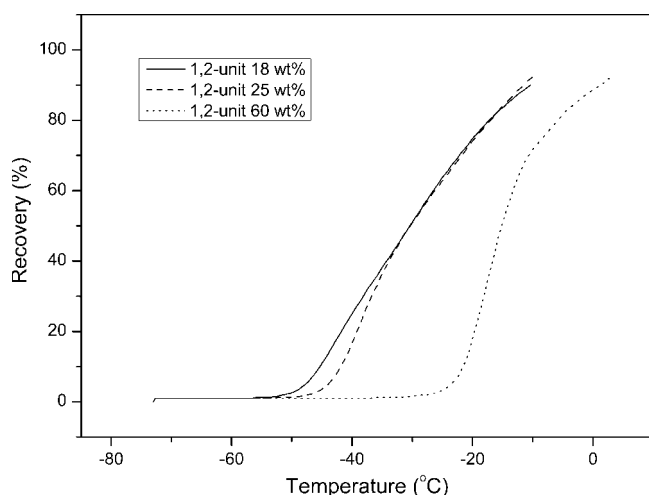


Figure 6 Recovery curves of the silica-reinforced vulcanizates containing Si69. Solid, dash, and dot lines indicate the SBR vulcanizates with the 1,2-unit contents of 18, 25, and 60 wt %, respectively.

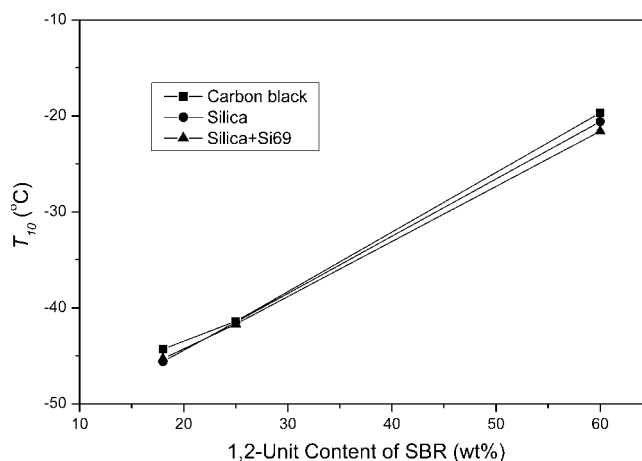


Figure 7 Variation of the starting temperature to recover (T_{10}) as a function of the 1,2-unit content of SBR. Squares, circles, and triangles indicate the carbon black-filled, silica-filled (without Si69), silica-filled (containing Si69) vulcanizates, respectively.

Recovery curves of the vulcanizates with the same filler system were plotted in one figure to investigate the influence of the 1,2-unit contents on the retraction behaviors in detail (Figs. 4–6). The vulcanizates with the 1,2-unit content of 18 wt % show nearly the same retraction behaviors as the vulcanizates with the 1,2-unit content of 25 wt %, irrespective of the filler systems. But the retraction behaviors of the vulcanizates with the 1,2-unit content of 60 wt % show very different trends to the others. The starting temperature to recover (T_{10}) increases as the 1,2-unit content increases, irrespective of the filler systems as shown in Figure 7. This is because of the T_g as

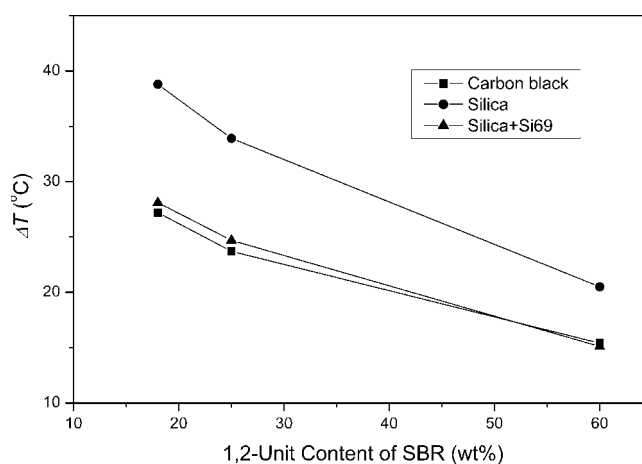


Figure 8 Variation of the recovery rate (ΔT) as a function of the 1,2-unit content of SBR. Squares, circles, and triangles indicate the carbon black-filled, silica-filled (without Si69), silica-filled (containing Si69) vulcanizates, respectively.

discussed previously. The T_{10} variations with the 1,2-unit content of SBR show the same trends irrespective of the filler system. The T_{10} increases about 0.6% every 1 wt % of the 1,2-unit.

Although the vulcanizate with the 1,2-unit content of 60 wt % starts to recover later (at higher temperature) than the others, its recovery rate is faster than the others after starting to recover, irrespective of the filler systems, as shown in Figures 4–6. Variations of the recovery rate (ΔT) with the 1,2-unit content were plotted in Figure 8. The recovery rate becomes faster as the 1,2-unit content of SBR increases. The ΔT decreases 0.27, 0.42, and 0.30% every 1 wt % of the 1,2-unit for the filler systems of carbon black, silica without Si69, and silica containing Si69, respectively. This may be due to the modulus. Modulus of the vulcanizate with the 1,2-unit content of 60 wt % is higher than those with the 1,2-unit content of 18–25 wt % as described previously.

CONCLUSIONS

Retraction behaviors of the SBR vulcanizates with different 1,2-unit content were investigated. The starting temperature to recover became higher as the 1,2-unit content of SBR increases due to the glass transition temperature. The glass transition temperature of SBR becomes higher with increase of the 1,2-unit content. The T_{10} increased about 0.6% every 1 wt % of the 1,2-unit. The recovery rate became faster as the 1,2-unit content of SBR increases. This can be explained with the modulus. The ΔT decreased 0.28–0.44% every 1 wt % of the 1,2-unit.

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