Influence of Filler Systems and Microstructures of SBR on Stress Softening Effect of SBR Vulcanizates

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SBR의 미세 구조와 보강 시스템이 SBR 가황물의 응력 풀림 효과에 미치는 영향

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ABSTRACT : Stress softening behaviors of SBR vulcanizates reinforced with silica or carbon black were studied. Two types of SBR with different 1,2-unit contents of 18 and 60 wt% were used and three filler systems of carbon black and silica with/without silane coupling agent were employed. Stress softening behaviors of the SBR vulcanizates were varied with the SBR types as well as the filler systems. The silica-filled rubber specimens had higher residual strains than the carbon black-filled ones. The residual strains of silica-filled vulcanizates were remarkably reduced by adding a silane coupling agent. The maximum loads at 50% maximum stretch of the carbon black-filled vulcanizates were lower than those of the silica-filled ones. On the contrary, the maximum loads at 200% maximum stretch of the carbon black-filled vulcanizates were higher than those of the silica-filled ones. The maximum loads of the specimens with the 1,2-unit content of 60 wt% are higher than those with the 1,2-unit content of 18 wt% irrespective of the filler systems.

요 약 : 실리카 또는 카본블랙으로 보강된 SBR 가황물의 응력 풀림 거동을 연구하였다. 1,2-단위체 함량이 18과 60 wt%인 두 가지 SBR을 사용하였으며 보강 시스템으로 카본블랙과 실리카에 실란 결합제가 없는 것 그리고 실리카에 실란 결합제가 있는 것 등 세 가지를 사용하였다. SBR 가황물의 응력 풀림 거동은 보강 시스템뿐만 아니라 SBR 종류에 따라서도 달라졌다. 실리카로 보강된 시료는 카본블랙으로 보강된 시료보다 잔류 변형률이 높았다. 실리카로 보강된 가황물의 잔류 변형률은 실란 커플링제를 첨가함으로써 크게 감소하였다. 카본블랙으로 보강된 가황물의 50% 최대 신장에서의 최대 하중은 실리카로 보강된 가황물의 경우보다 낮았다. 이와는 반대로 카본블랙으로 보강된 가황물의 200% 최대 신장에서의 최대 하중은 실리카로 보강된 가황물의 경우보다 높았다. 1,2-단위체 함량이 60 wt%인 시료의 최대 하중은 1,2-단위체 함량이 18 wt%인 시료의 경우보다 보강 시스템에 상관없이 높았다.

Keywords : stress softening; SBR composite; filler system; microstructure

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I. Introduction

Under tensile strain, rubber vulcanizates exhibit a reduction in stress on the second and subsequent extensions, a phenomenon that has come to be known as the Mullins effect.[1,2] Mullins and Tobin[1] proposed a model that in which the filled polymer was assumed to exist in two phases, one is soft phase having a lower modulus and the other is hard phase with a higher modulus. They postulated that hard phase regions were converted to soft ones under strain and the stress was reduced. The origin of Mullins effect is still considered as one of the most important problems in rubber elasticity. Dorfmann and Ogden[3] studied stress softening of rubber vulcanizates reinforced with carbon black and reported that the residual strain was increased with increase of the carbon black content.

Carbon black and silica are the most popular reinforcing agents in rubber composites.[4-10] 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.[9,11] Since intermolecular hydrogen bonds between silanol groups on the silica surface are very strong, it can aggregate tightly.[10,12] Its property can cause a poor dispersion of silica in a 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.[13]

Styrene-butadiene rubber (SBR) is a copolymer of styrene and butadiene. The butadiene sequence has three different microstructures of *cis*-1,4-, *trans*-1,4-, and 1,2-units. Properties of SBR are determined by ratios of the four components. Some studies reported that the 1,2-unit was more interactive with fillers, especially silica, than the other components of *cis*-1,4- and trans-1,4-units.[14-17] It can be expected that stress softening behaviors of filled SBR vulcanizates will be varied with the microstructures of SBR as well as the filler systems. In the present work, we studied the influence of the filler systems

and the 1,2-unit contents on the stress softening behaviors of filled-SBR vulcanizates. Silica and carbon black were used as fillers and two types of SBRs with different 1,2-unit contents were employed.

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). SBR 1502 of Kumho Petroleum Co. and NS 116 of Nippon Zeon Co. were employed as SBR. The 1,2-unit contents are 18 and 60 wt%, respectively. Si69 of Degussa Co. (TESPT) was used as a silane coupling agent. The formulations are given in Table 1. The Compounds S1, S2, SC1, and SC2 were silica-filled compounds and the Compounds C1 and C2 were carbon black-filled ones. The Compounds S1 and S2 do not contain Si69, while the Compounds SC1 and SC2 contain the silane coupling agent.

The vulcanizates were prepared by curing at 160

Table 1. Formulations (phr).

Compound No.	S1	S2	SC1	SC2	C1	C2
SBR 1502	100.0	0.0	100.0	0.0	100.0	0.0
NS 116	0.0	100.0	0.0	100.0	0.0	100.0
Z175	50.0	50.0	50.0	50.0	0.0	0.0
N220	0.0	0.0	0.0	0.0	50.0	50.0
Si69	0.0	0.0	3.0	3.0	0.0	0.0
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

SBR 1502: styrene 23.5 wt%, 1,2-unit 18.0 wt%
NS 116: styrene 21.0 wt%, 1,2-unit 60.0 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 sulfenamide

℃. Dumbbell-shaped samples were prepared from the cured sheets of 2 mm thickness. The stress-strain experiments were performed with the Universal Testing Machine (Instron 6021) at a cross-head speed of 200 mm/min. The maximum strains were 50 and 200%. Swelling ratios (Q) of the stretched and unstretched zones were measured. 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 equation of $Q = (W_s-W_u) / W_u$, where W_s and W_u are weights of the swollen and unswollen samples.

III. Results and Discussion

The stress-strain experiments were performed with two modes. One is that after completion of the tenth loading-unloading cycles at the maximum strain of 50%, each specimen was then loaded up to the maximum stretch of 200% and again subjected to tenth cycles. The other one is the tenth loading-unloading cycles only at the maximum strain of 200%. Figure 1 shows the stress-strain responses for the SBR vulcanizates reinforced with carbon black and silica without and containing the silane coupling agent. There are large differences in the stresses corresponding to the same strain level under loading and unloading during the first cycle in periodic tests with a fixed strain. The stress softening behaviors are varied with the filler system. The stress reduction is the largest on the first and second loading-unloading cycles. The stress reduction on the second cycle for the silica-filled vulcanizate without the silane coupling agent is bigger than for the other specimens. The carbon black-filled specimens show the smaller reduction in stress on the second cycle than the silica-filled ones. This can be explained with the filler dispersion and
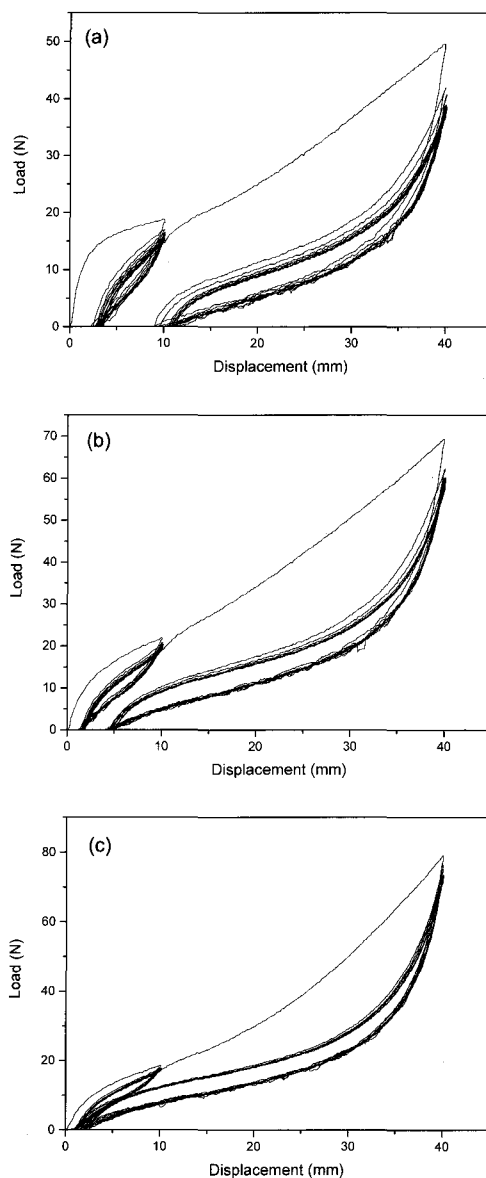

Figure 1. Periodic uniaxial extension tests of the SBR 1502 vulcanizates reinforced with silica (a), silica and coupling agent (b), and carbon black (c).

filler-filler interactions. In general, filler dispersion of a carbon black-filled rubber compound is better than that of a silica-filled one and filler dispersion of a silica-filled rubber compound is improved by adding a silane coupling agent.[18-21] Strong hydrogen bonds by lots of silanol groups on the silica surface

lead to strong filler-filler interactions as described previously. The silane coupling agent makes the strong filler-filler interactions of silica reduced by modifying of the silica surface. Silanol groups of silica react with ethoxy groups of the silane coupling agent to form siloxane bonds (~Si-O-Si~). Polarity of the modified silica surface reduces and hydrogen bonds between silica particles will be prevented by the silane coupling agent.

Figures 2 - 4 show the accumulation of residual strain with the number of loading-unloading cycles. The major part of the residual strain in each case is generated during the first loading-unloading cycle. The accumulated residual strain depends on the maximum stretch of the specimen, i. e. larger stretch translates into larger residual strain. The residual strains of the silica-filled vulcanizates without the coupling agent are larger than those of the other specimens. This may be due to the filler dispersion. Filler dispersion of a rubber compound reinforced with silica is worse than that reinforced with carbon black as discussed above. For silica-filled compounds, the filler dispersion is improved when containing a silane coupling agent. The residual strains at 50% stretch on the whole slightly increase
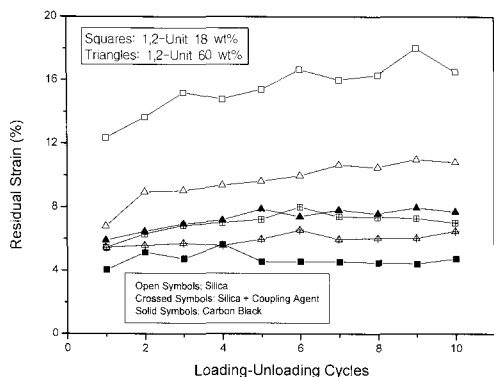

Figure 3. Accumulation of residual strain. Periodic loading-unloading was performed with maximum stretch of 200% after the 10 cycles of 50% stretch. Squares and triangles stand for the SBR vulcanizates with the 1,2-unit contents of 18 and 60 wt%, respectively. Open, crossed, and solid symbols indicate the vulcanizates reinforced with silica, silica and coupling agent, and carbon black, respectively.
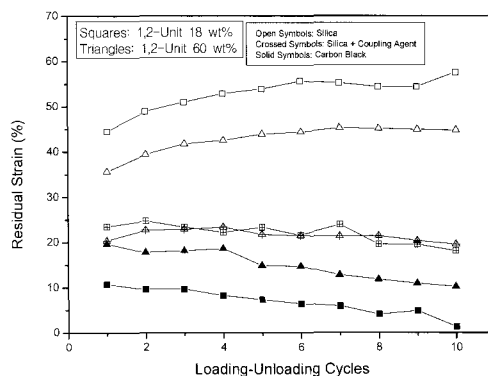

Figure 4. Accumulation of residual strain. Periodic loading-unloading was performed with maximum stretch of 200%. Squares and triangles stand for the SBR vulcanizates with the 1,2-unit contents of 18 and 60 wt%, respectively. Open, crossed, and solid symbols indicate the vulcanizates reinforced with silica, silica and coupling agent, and carbon black, respectively.
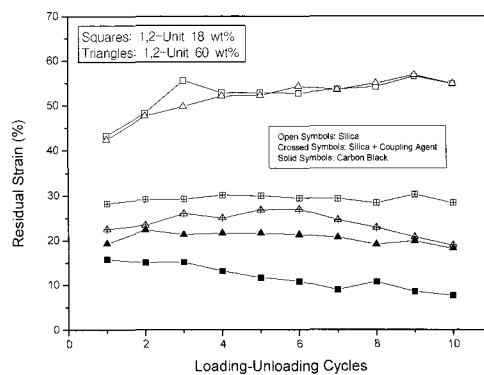

Figure 2. Accumulation of residual strain. Periodic loading-unloading was performed with maximum stretch of 50%. Squares and triangles stand for the SBR vulcanizates with the 1,2-unit contents of 18 and 60 wt%, respectively. Open, crossed, and solid symbols indicate the vulcanizates reinforced with silica, silica and coupling agent, and carbon black, respectively.

as the loading-unloading cycle increases irrespective of the filler systems. However, for the residual strains at the direct 200% and the successive 50-200% stretches, the trends are varied with the filler systems. For the silica-filled vulcanizates without the silane coupling agent, the residual strains at the direct 200% stretch and the successive 50-200%

stretches also increase with increase of the loading-unloading cycle, but the residual strains at the 200% and 50-200% stretches of the carbon black-filled vulcanizates tend to decrease. The silica-filled vulcanizates containing the silane coupling agent also show the decreased trends. The residual strains are also varied with the 1,2-unit content of SBR. For the silica-filled rubber vulcanizates, the residual strain is decreased by increasing the 1,2-unit content as shown in Figures 2 - 4. The reduced residual strain of the silica-filled specimens with the 1,2-unit content can be explained by the polymer-filler interactions. The 1,2-units are more interactive with silica than the cis-1,4- and trans-1,4-units.[14-17] On the contrary, for the carbon black-filled rubber vulcanizates, the residual strain increases with increase of the 1,2-unit content.

The stresses and residual strains obtained for specimens loaded cyclically up to 50% stretch and successively to 200% stretch (50-200% stretches) should be compared with those loaded directly to 200% stretch. The residual strains for the direct 200% stretch are relatively higher than those for the 50-200% successive stretches. The residual strains are also varied with the SBR types as well as the filler systems. For the silica-filled vulcanizates without the silane coupling agent, the difference in the residual strains of the specimens with the different 1,2-unit contents of 18 and 60 wt% (ΔS_R) are comparable. The ΔS_R for the 50-200% successive stretches are much larger than those at the direct 200% stretch. The average ΔS_R for the 50-200% successive stretches and the direct 200% stretch are 10.1 and 0.6%, respectively. This can be explained with the presoftening at the 50% stretch and the poor silica dispersion. When the specimen is stretched, the filler agglomerates are destroyed and it will be hard for the destroyed structures to recover. Especially, the silica-filled vulcanizates without the silane coupling agent has poor filler dispersion and lots of agglomerates. For the silica-filled vulcanizates containing the silane coupling agent, the average ΔS_R for the 50-200% successive stretches

and at the direct 200% stretch are 0.5 and 5.5%, respectively. Reasons for the opposite trends between the silica-filled specimens without and containing the silane coupling agent can not be exactly explained at this point. Further study is needed. For the carbon black-filled vulcanizates, the ΔS_R for the 50-200% successive stretches and at the direct 200% stretch is not big. The average ΔS_R for the 50-200% successive stretches and the direct 200% stretch are 8.1 and 8.8%, respectively.

By stress softening, some of the agglomerate structures and some of connections between fillers and rubbers will be destroyed and level of solvent swelling will be increased. Table 2 shows results for the swelling ratio measurements of the stretched and unstretched regions. The swelling ratios of the stretched regions are higher than those of the unstretched ones. The swelling ratio changes after the periodic uniaxial extension test of the carbon black-filled vulcanizates are lower than those of the silica-filled ones. For the specimens having the 1,2-unit content of 18 wt%, the swelling ratio changes for the 50-200% successive stretches are smaller than those for the direct 200% stretch. On the other hand, for the specimens having the 1,2-unit content of 60 wt%, the swelling ratio changes for the 50-200% successive stretches are larger than those at the direct 200% stretch.

Table 2. Swelling ratios (Q) of the stretched and unstretched regions after the periodic uniaxial extension tests.

Compound No.		S1	S2	SC1	SC2	C1	C2
Stretched region	50-200%	3.35	2.75	2.30	2.01	2.18	2.16
	200%	3.41	2.73	2.32	1.98	2.20	2.15
Unstretched region		3.18	2.61	2.15	1.77	2.11	2.08

Swelling ratio change of the stretch and unstretched regions (%)*							
Stretched region	50-200%	5.35	5.36	6.98	13.56	3.32	3.85
	200%	7.23	4.60	7.91	11.86	4.27	3.37

* Swelling ratio change (%) = $100 \times (Q^{st}-Q^{un})/Q^{un}$, where Q^{st} and Q^{un} are the swelling ratios of the stretched and unstretched regions, respectively.

Figures 5 - 7 show variations of the maximum stress with the loading-unloading cycles. For the maximum stress at the 50% strain, the stresses tend to decrease with increase of the loading-unloading cycle. The 50% stresses of the carbon black-filled specimens are lower than those of the silica-filled
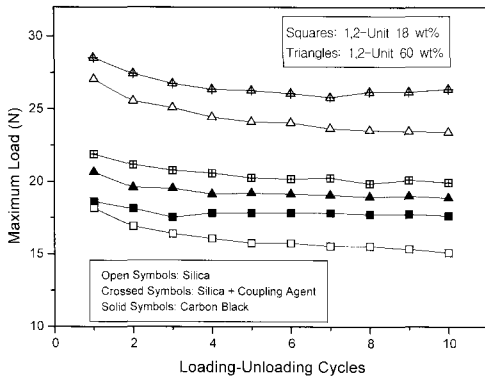

Figure 5. Accumulation of maximum stress. Periodic loading-unloading was performed with maximum stretch of 50%. Squares and triangles stand for the SBR vulcanizates with the 1,2-unit contents of 18 and 60 wt%, respectively. Open, crossed, and solid symbols indicate the vulcanizates reinforced with silica, silica and coupling agent, and carbon black, respectively.
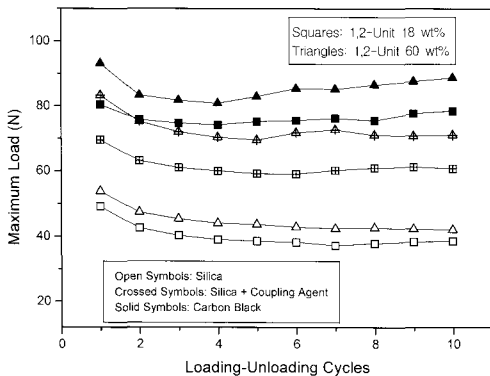

Figure 6. Accumulation of maximum stress. Periodic loading-unloading was performed with maximum stretch of 200% after the 10 cycles of 50% stretch. Squares and triangles stand for the SBR vulcanizates with the 1,2-unit contents of 18 and 60 wt%, respectively. Open, crossed, and solid symbols indicate the vulcanizates reinforced with silica, silica and coupling agent, and carbon black, respectively.

Figure 7. Accumulation of maximum stress. Periodic loading-unloading was performed with maximum stretch of 200%. Squares and triangles stand for the SBR vulcanizates with the 1,2-unit contents of 18 and 60 wt%, respectively. Open, crossed, and solid symbols indicate the vulcanizates reinforced with silica, silica and coupling agent, and carbon black, respectively.
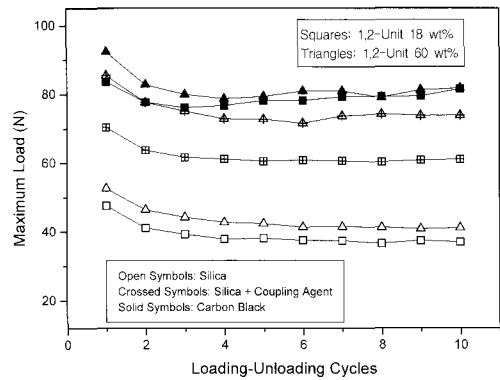
ones except the S1 vulcanizate. This is an interesting result because the crosslink densities of the carbon black-filled vulcanizates are higher than those of the silica-filled ones except the SC2 specimen. In general, modulus of a rubber vulcanizate is a proportional property to its crosslink density. The experimental results say that the other factors affect the modulus. Major factors influenced on the modulus are the crosslink density, filler-filler interactions, and polymer-filler interactions. The higher 50% stresses of the silica-filled specimens can be explained with the strong filler-filler interactions of silica as discussed previously. The 50% stresses of the specimens with the 1,2-unit content of 60 wt% are larger than those with the 1,2-unit content of 18 wt%. This is due to the higher crosslink density as listed in Table 2. Difference in the 50% stresses of the specimens with the 1,2-unit contents of 60 and 18 wt% is differing with the filler systems. The 50% stress difference of the silica-filled specimens is much larger than that of the carbon black-filled ones. Especially, the 50% stress difference of the silica-filled vulcanizates without the silane coupling agent is very big.

The maximum stresses for the successive 50%-200% stretches and those for the direct 200% stretch

show similar trends as shown in Figures 6 and 7. For the silica-filled specimens, the stresses tend to reduce with the loading-unloading cycle. For the carbon black-filled ones, however, the stresses decrease until third or fourth cycle and then tend to increase. The 200% stresses of the specimens with the 1,2-unit content of 60 wt% are also larger than those with the 1,2-unit content of 18 wt%. The 200% stresses of the carbon black-filled specimens are higher than those of the silica-filled ones. This is reverse to the 50% stresses. This may be due to the crosslink density and polymer-filler interactions. Polymer-filler interaction is one of the major factors influenced on the modulus.[23] Though crosslink densities of the carbon black-filled vulcanizates are slightly lower than those of the silica-filled vulcanizates containing the silane coupling agent, the polymer-filler interactions of carbon black with the rubber are higher than those of silica.

Ⅳ. Conclusions

The residual strains at 50% stretch on the whole slightly increased with increase of the loading-unloading cycle irrespective of the filler systems. However, for the residual strains at the 200% and 50-200% stretches, the trends were varied with the filler systems. The residual strains for the 50-200% successive stretches were on the whole smaller than those for the direct 200% stretch. The 50% stresses of the carbon black-filled specimens were lower than those of the silica-filled ones except the S1 vulcanizate. Difference in the maximum loads of the specimens with the 1,2-units of 60 and 18 wt% was varied with the filler systems. The difference in the maximum loads at the 50% strain of the silica-filled specimens was much larger than that of the carbon black-filled ones due to the strong filler-filler interactions of silica. Especially, the 50% stress difference of the silica-filled vulcanizates without the silane coupling agent was very big. The 200% stresses (both the direct 200% and successive 50-200% stretches) of the carbon black-filled speci-

mens were higher than those of the silica-filled ones due to the higher crosslink densities of the carbon black-filled SBR vulcanizates.

Acknowledgements

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