Low Molecular Weight SBR Effect on Properties of Silica-Filled SBR Compounds

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저분자량 SBR이 실리카로 보강된 SBR 배합물의 특성에 미치는 영향

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ABSTRACT : Influence of low molecular weight styrene-butadiene rubber (liquid SBR) on properties of a silica-filled styrene-butadiene rubber (SBR) compounds was studied. Viscosity of the silica-filled SBR compound decreased by adding the liquid SBR. The crosslink density decreased and the cure rate became slower as the liquid SBR content increased. The modulus and tensile strength decreased while the elongation at break became longer by increasing the liquid SBR content. The abrasion losses were nearly the same irrespective of the liquid SBR content. This might be due to the improvement of silica dispersion by adding the liquid SBR. Considering the experimental results, it was believed that addition of small amount of the liquid SBR (less than 5 phr) was desirable to improve properties of silica-filled SBR compounds.

요 약 : 저분자량 SBR (액상 SBR)이 실리카로 보강된 SBR 배합물의 특성에 미치는 영향에 대해 연구하였다. 액상 SBR을 실리카로 보강된 SBR 배합물에 첨가하면 점도가 낮아졌다. 가교밀도는 액상 SBR의 함량이 증가함에 따라 감소하였고 가황속도는 느려졌다. 모듈러스와 인장강도는 액상 SBR의 함량이 증가할수록 낮아졌고 신율은 증가하였다. 마모 특성은 액상 SBR의 함량에 따라 큰 차이를 보이지 않았다. 이는 액상 SBR의 첨가에 의해 실리카 분산이 향상되었기 때문으로 여겨진다. 실험결과를 종합해 볼 때, 5 phr 이하의 적은 양의 액상 SBR을 사용하는 것이 실리카로 보강된 SBR 배합물의 특성을 향상시키는데 바람직할 것으로 판단된다.

Keywords : silica, SBR compound, liquid SBR, dispersion

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Ⅰ. Introduction

Since silica has the strong filler-filler interactions, filler dispersion of a silica-filled rubber compound is worse than that of a carbon black-filled one.[1-3] Silane coupling agent and dispersing agent are used to improve the silica dispersion. Bis-(3-(triethoxy-silyl)-propyl)-tetrasulfide (TESPT), $(C_2H_5O)_3Si$-$(CH_2)_3$-S_x-$(CH_2)_3$-$Si(OC_2H_5)_3$, is mostly used to improve the silica dispersion as a silane coupling agent.[4-6] The silane coupling agent reacts with silanol (Si-OH) on the surface of silica and a siloxane bond (Si-O-Si) is formed. The silane molecule is bound to the silica surface.

In the previous works,[7-10] it was found that properties of a silica-filled styrene-butadiene rubber (SBR) compound were improved by adding acrylonitrile-butadiene rubber (NBR) or low molecular weight polybutadiene (liquid BR). The adsorbed NBR on the silica surface prevents adsorption of curatives. SBR consists of the four components of styrene, *cis*-1,4-, *trans*-1,4-, and 1,2-units. The 1,2-unit is more interactive with silica than the other components.[11-13] Polybutadiene (butadiene rubber, BR) can have three different components of *cis*-1,4-, *trans*-1,4-, and 1,2-units. Liquid BR with high content of the 1,2-unit improves the filler dispersion in silica-filled SBR compounds.[9,10] In this study, influence of the low molecular weight SBR (liquid SBR) on properties of silica-filled SBR compounds was investigated.

Ⅱ. Experimental

The compounds were made of SBR, liquid SBR (3, 6, and 9 phr), silica, silane coupling agent (Si69, TESPT), cure activators (stearic acid and ZnO), antidegradants (HPPD and wax), and curatives (TBBS and sulfur). Ricon 184 of Sartomer Co. was employed as a liquid SBR. The number average moleculr weights (M_n) of Ricon184 is 8600 and the styrene and 1,2-unit contents are 28 and 30 wt%, respectively. Z175 (pH = 6.9, BET = 175 m^2/g)

Table 1. Formulations of the compounds (phr) Compound No.

Compound No.	1	2	3	4
SBR1500[a]	100.0	97.0	94.0	91.0
Ricon184[b]	0.0	3.0	6.0	9.0
Z175[c]	60.0	60.0	60.0	60.0
Si69[d]	3.6	3.6	3.6	3.6
Stearic acid	2.0	2.0	2.0	2.0
ZnO	4.0	4.0	4.0	4.0
HPPD[e]	2.0	2.0	2.0	2.0
Wax	2.0	2.0	2.0	2.0
TBBS[f]	1.8	1.8	1.8	1.8
Sulfur	1.4	1.4	1.4	1.4

a) SBR1500: styrene-butadiene rubber with 23.5% of styrene content
b) Ricon184: liquid styrene-butadiene copolymer with 30% of 1,2-unit content, 28% of styrene content, and 8600 of M_n
c) Z175: silica
d) Si69: silane coupling agent, bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT)
e) HPPD: *N*-phenyl-*N*′-(1,3-dimethylbutyl)-*p*-phenylenediamine
f) TBBS: *N-tert*-butyl-2-benzothiazole sulfenamide

of Kofran Co. was used as silica. The formulations were given in Table 1. Mixing of the compounds was performed in a Banbury type mixer at a rotor speed of 40 and 30 rpm for the master batch (MB) and final mixing (FM) stages, respectively. The initial temperatures of the mixer were 110 and 80℃ for the MB and FM stages, respectively. The MB compounds were prepared as follow. (1) SBR was loaded into the mixer and premixed for 0.5 min. (2) The silica, silane coupling agent, and liquid SBR were compounded into the rubbers for 2.0 min. (3) The ingredients (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.

Mooney scorch times of the compounds were measured at 125℃ with a Mooney viscometer MV 2000 of Alpha Technologies. Cure characteristics were obtained using a Flexsys rheometer (MDR

2000) at 180℃. The vulcanizates were prepared by curing at 160℃ for 40 min. Physical properties of the vulcanizates were measured with a universal testing machine (Instron 6021). Abrasion loss was measured according to ASTM 2228 with a Pico abrasion tester of BF Goodrich for 80 cycles. Flex cracking resistance was measured with a DMFC tester (FT-1503, 300 cpm).

Ⅲ. Results and Discussion

Cure characteristics of the compounds were investigated at 180℃. Figure 1 gives variations of the rheograph with the liquid SBR content. Variations of the minimum torque (T_{min}), maximum torque (T_{max}), and delta torque with the liquid SBR content were plotted in Figure 2. The minimum torque reflects viscosity of the compound. The higher the minimum torque is, the higher the viscosity is. The minimum torque decreases linearly by increasing the liquid SBR content (correlation coefficient = -0.994). The T_{min} decreases by 0.06 N·m for every 1 phr increase of the liquid SBR. This implies that the viscosity decreases by the liquid SBR content. This may be due to the improved filler dispersion and the role of the liquid SBR as plasticizer. The minimum torque also decreases linearly with increse of the liquid SBR content (correlation coefficient = -0.996). The T_{max} decreases by 0.13 N·m for every 1 phr increase of the liquid SBR.

The delta torque (ΔT) is the difference between the maximum and minimum torque ($\Delta T = T_{max} - T_{min}$). The delta torque is correlated closely with the crosslink density since the torque is increased by crosslinking reactions. The delta torque also decreases linearly by increasing the liquid SBR content (correlation coefficient = -0.992). The delta torque decreases by 0.07 N·m for every 1 phr increase of the liquid SBR. This can be explained by the big difference in molecular weights between SBR and liquid SBR It can be also explained by prevention of crosslink formations between the matrix SBR
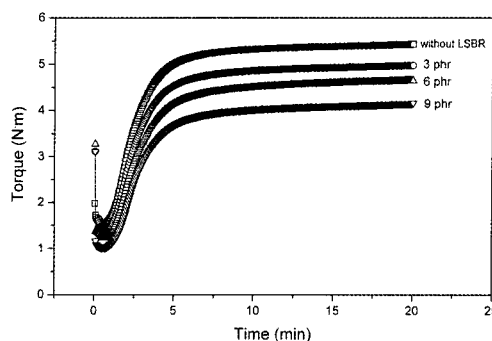

Figure 1. Rheocurves of the compounds at 180℃. Squares, circles, up-triangles, and down-triangles indicate the compound without liquid SBR, the compound containing liquid SBR of 3 phr, the compound containing liquid SBR of 6 phr, and the compound containing liquid SBR of 9 phr, respectively.
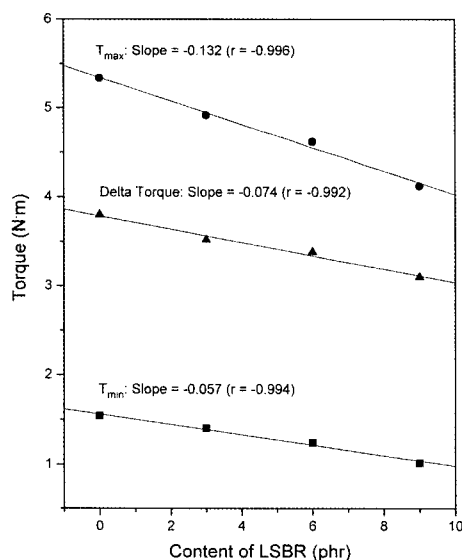

Figure 2. Variations of the minimum torque (T_{min}), maximum torque (T_{max}), and delta torque at 180℃ with the liquid SBR content. Squares, circles, and triangles indicate the minimum torque (T_{min}), maximum torque (T_{max}), and delta torque, respectively.

molecules or crosslink formations of the matrix SBR with silica by the liquid SBR. Crosslinks between long polymer chains are more efficient to increase the crosslink density than those between short chains. Lots of the liquid SBR molecules will be located around silica since the liquid SBR is more
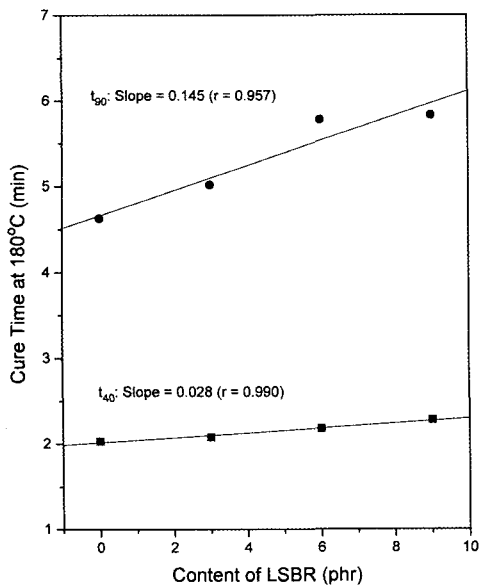
Figure 3. Variations of the t_{40} and t_{90} at 180℃ with the liquid SBR content. Squares and circles indicate the t_{40} and t_{90}, respectively.

Table 2. Mooney viscosity and Mooney cure times of the compounds

Content of Liquid SBR (phr)	0	3	6	9
Viscosity (ML 1+4 at 100℃)	118.12	105.13	97.2	86.94
Mooney Cure Times at 125℃				
t_5 (min)	24.00	26.53	29.60	35.87
t_{35} (min)	38.27	42.00	48.53	59.33
Δt	14.27	15.47	18.93	23.46

mobile than the matrix SBR. Thus, the liquid SBR molecules prevent the matrix SBR chains from contacting with silica so crosslinking reactions between the matrix SBR and silica will be reduced. The liquid SBR molecules between the matrix SBR chains will also prevent the crosslinking reactions between the matrix SBR molecules.

Figure 3 shows variations of the cure times (t_{40} and t_{90}) with the liquid SBR content. The cure times become longer as the liquid SBR content increases. The t_{40} and t_{90} increases by 0.03 and 0.15 min for every 1 phr increase of the liquid SBR, respectively (correlation coefficients are 0.990 and 0.957, respectively). This can be also explained with the prevention of crosslink formations by the liquid SBR as discussed above. The liquid SBR molecules between the matrix SBR chains will also prevent the crosslinking reactions between the matrix SBRs.

The Mooney viscosities were measured at 100℃ (Table 2). The viscosity decreases by increasing of the liquid SBR content. This can be explained by the improved filler dispersion and the role of the

liquid SBR as plasticizer. Figure 4 shows the degree of the silica dispersion. The filler dispersions of the compounds containing the liquid SBR is, on the whole, slightly better than that of the compound without the liquid SBR. Since the liquid SBR molecules are much smaller than the matrix SBR molecules, they can role as a plasticizer.

The Mooney cure times were measured at 125℃ (Table 2). The t_5 (Mooney scorch time), t_{35}, and Δt (cure rate index) were obtained. The t_5 and t_{35} mean the times taken for the viscosity to reach from the minimum point to increases of 5 and 35 MU, respectively. The Δt is the difference between the t_{35} and t_5. The reciprocal of Δt is used as a cure rate. The bigger the Δt is, the slower the cure rate is. The t_5 and t_{35} become slower as the liquid SBR content increases. The Δt also becomes slower by increasing the liquid SBR content. This can be explained by the difference in mobility between matrix SBR and liquid SBR. It can be also explained by the prevention of crosslink formations between the matrix SBRs or crosslink formations of the matrix SBR with silica by the liquid SBR. Long chain molecule moves slower than short one and sulfur crosslinking reactions occur faster in less movable long chains than in mobile short chains.

In general, silica-filled rubber compounds have high viscosities since the filler-filler interactions are very strong. Thus, it is necessary to decrease the viscosity. It is believed that a rubber compound having a faster cure system is more desirable than
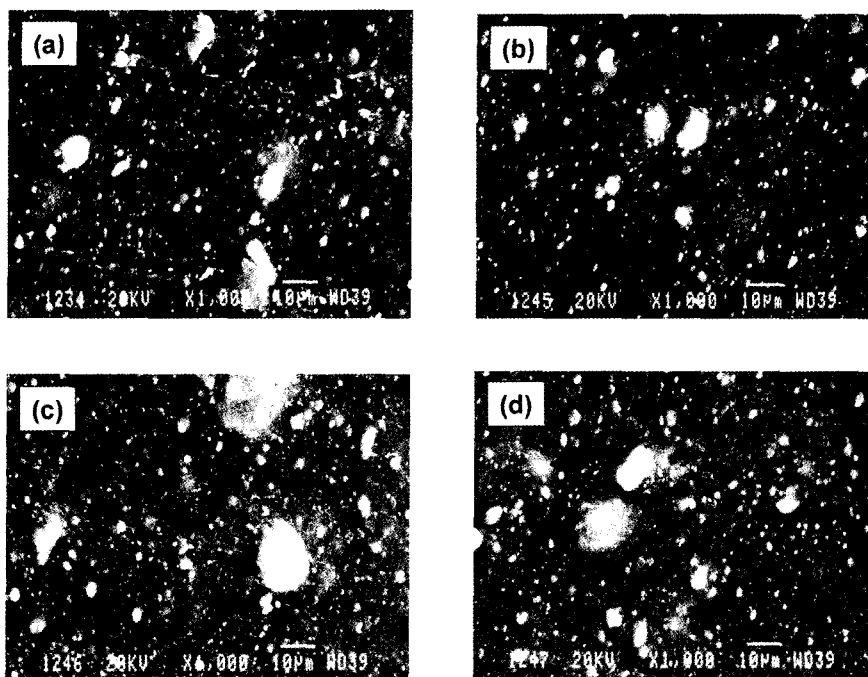
Figure 4. Scanning electron microscopy (SEM) photographs (× 1000) of the vulcanizate surfaces. (a) the vulcanizate without liquid SBR, (b) the vulcanizate containing 3 phr of liquid SBR, (c) the vulcanizate containing 6 phr of liquid SBR, and (d) the vulcanizate containing 9 phr of liquid SBR.

that aving a slower one. Decrements of the viscosities of the compounds containing 3 and 9 phr of the liquid SBR, compared to the compound without the liquid SBR, are about 11 and 26%, respectively. Decrements the Δt of the compounds containing 3 and 9 phr of the liquid SBR are about 8 and 64%, respectively. Thus, it can lead to a conclusion that the compound containing smaller amount of the liquid SBR has better cure property than the compound containing larger one.

Physical properties of a rubber vulcanizate cured by accelerated sulfur cure system depend on the crosslink density.[14] Modulus is a proportional property to the degree of crosslink density, while elongation at break is an inversely proportional property to the degree of crosslink density. The physical properties were summarized in Table 3. The modulus decreases linearly with increase of the liquid SBR content. This is due to the decreased

Table 3. Physical properties of the vulcanizates Content of Liquid SBR (phr)

Content of Liquid SBR (phr)	0	3	6	9
Hardness (Shore A)	77	76	76	72
100% Modulus (kg/cm^2)	26.7	25.0	22.5	19.6
300% Modulus (kg/cm^2)	98.2	86.3	74.7	62.3
Tensile Strength (kg/cm^2)	224.2	219.1	209.0	190.3
Elongation at Break (%)	577.2	627.1	678.1	671
Heat Build-Up($^\circ$C)	43.5	42.2	50.0	52.8
Dematia Cracking Test Crack Size (mm)	16.5	11.4	11.4	3.0
Abrasion Loss (mg)	39.5	40.0	40.5	40.0

crosslink density. The decreased crosslink density with the increased liquid SBR content was discussed previously. The 100% and 300% moduli decrease by 0.79 and 3.98 kg/cm^2 for every 1 phr increase of the liquid SBR, respectively.

The tensile strength also decreases with increase of the liquid SBR content and the elongation at break becomes longer as the liquid SBR content increases. This may be due to the decreased cross-link density. The hardnesses of the vulcanizates containing 3 and 6 phr of the liquid SBR are nearly the same with the vulcanizate without the liquid SBR. Heat build-up of the vulcanizate containing 3 phr of the liquid SBR is lower than that of the vulcanizate without the liquid SBR, while those of the vulcanizates containing 6 and 9 phr of the liquid SBR are much higher than that of the vulcanizate without the liquid SBR. The lower heat build-up of the vulcanizate containing 3 phr of the liquid SBR may be due to the better silica dispersion compared to the vulcanizate without the liquid SBR as shown in Figure 4. Crack-resistance of the vulcanizate containing the liquid SBR is better than that of the vulcanizate without the liquid SBR. This can be explained by the decreased crosslink density and the improved silica dispersion of the vulcanizates containing the liquid SBR. The abrasion losses are nearly the same irrespective of the liquid SBR content. It is an interesting result because the wear property of a rubber vulcanizate is a proportional property to the degree of crosslink density. This is another evidence that the liquid SBR makes the filler dispersion improved in a silica-filled SBR compound.

Ⅳ. Conclusion

By adding liquid SBR to a silica-filled SBR compound, the viscosity decreases and the cure rate becomes slower. Due to the decreased crosslink density, the modulus and tensile strength decrease as the liquid SBR increases. The wear property does not become worse due to the improved silica dispersion by adding the liquid SBR though the crosslink density decreases with increase of the liquid SBR. Considering the whole experimental results, it is believed that the compound containing smaller amount of the liquid SBR is more desirable

than the compound containing larger amount of the liquid SBR.

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