

Influence of Molecular Size of Liquid BR on Properties of Silica-Filled SBR Compounds

Sung-Seen Choi

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

(Received July 20, 2001)

액상 BR의 분자 크기가 실리카로 보강된 SBR 배합물의 특성에 미치는 영향

최 성 신

금호산업 주식회사

(2001년 7월 20일 접수)

ABSTRACT : Low molecular weight polybutadiene (liquid BR) improves the filler dispersion in a silica-filled styrene-butadiene rubber (SBR) compound. In the present work, influence of molecular weight of the liquid BR on properties of a silica-filled SBR compound was studied. Minimum and maximum torques in the rheocurve for the compound containing the liquid BR with higher molecular weight (HLBR) are lower than those for the compound containing the liquid BR with lower one (LLBR) while the delta torques are nearly the same. Mooney scorch time of the compound containing HLBR is faster than that of the compound containing LLBR. Modulus of the compound containing HLBR is lower than that of the compound containing LLBR while tensile strength of the former is higher than that of the latter. The elongation at break of the former is also longer than that of the latter. Stability for the thermal aging at 90°C for 3 days is less favorable for the former than for the latter.

요 약 : 저분자량 폴리부타디엔 (액상 BR)은 실리카로 보강된 스티렌-부타디엔 고무 (SBR) 배합물에서 실리카 분산을 향상시킨다. 본 연구에서는 액상 BR의 분자량이 미치는 영향에 대하여 조사하였다. 레오 그래프에서 측정되는 최소 토크와 최대 토크는 액상 BR의 분자량이 큰 것 (HLBR)을 사용했을 때가 액상 BR의 분자량이 작은 것 (LLBR)을 사용했을 때 보다 더 낮지만 델타 토크는 거의 차이가 없다. 무니 스크치 시간은 HLBR을 사용했을 때 더 빨라졌다. 모듈러스는 HLBR을 사용했을 때 더 낮았지만 인장 강도는 더 강하였다. 신율은 HLBR을 사용했을 때 더 길었다. 열노화에 대한 안정성은 LLBR을 사용한 배합물이 HLBR을 사용한 것보다 더 우수하였다.

Keywords : silica, SBR compound, liquid BR, dispersion, molecular weight.

[†] 대표저자(e-mail : sschoi@swan.kumho.co.kr)

I. Introduction

Since silica has strong filler-filler interactions, filler dispersion of a silica-filled rubber compound is worse than that of a carbon black-filled one.¹⁻³ The polar surface of silica makes hydrogen bonds with polar materials in a rubber compound. Since the silica surface is acidic, especially it forms a strong hydrogen bond with basic materials. *N-tert-Butyl-2-benzothiazole sulfenamide* (TBBS) and *N-cyclohexyl benzothiazole sulfenamide* (CBS) are generally used as cure accelerators for rubbers. Since they have basic functional groups such as amide (=NH), they are adsorbed well on the silica surface. The adsorption of curatives by silica results in delay of the scorch time and reduction of the delta torque of a silica-filled rubber compound. In the previous work,⁴ it was found that properties of a silica-filled styrene-butadiene rubber (SBR) compound were improved by adding acrylonitrile-butadiene rubber (NBR). Since NBR has nitrile groups (-CN) which is basic, it can make a hydrogen bond with silica. The adsorbed NBR on the silica surface prevents the adsorption of curatives.

Since silica is polar, it is more compatible with polar materials than non-polar ones. 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.⁵⁻⁷ Polybutadiene (butadiene rubber, BR) can have three different components of *cis*-1,4-, *trans*-1,4-, and 1,2-units. Low molecular weight BR (liquid BR) with high content of the 1,2-unit improves the filler dispersion in silica-filled SBR compounds.⁸ In the present work, influence of the molecular weight of liquid BR on properties of silica-filled SBR compounds was studied.

II. Experimental

The compounds were made of SBR, liquid BR (4.0, 8.0, and 12.0 phr), silica, silane coupling agent (Si69, TESPT), cure activators (stearic acid and

ZnO), antidegradants (HPPD and wax), and curatives (TBBS and sulfur). Two types of liquid BRs with different molecular weights, Ricon 131 and Ricon 134 of Sartomer Co., were employed. The 1,2-unit contents are the same of 28% and their average molecular weights (M_n) are about 4500 and 8000, respectively. They are liquid state at room temperature. Z 175 (pH = 6.9, BET = 175 m²/g) of Kofran was used as silica. The formulations were given in Table I. 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°C 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 BR were compounded into the rubbers for 2.0 min. (3) The ingredients (cure activators and antidegradants) were

Table 1. Formulations (phr)

Compound No.	1	2	3	4	5	6
SBR1500	96.0	92.0	88.0	96.0	92.0	88.0
Ricon 131	4.0	8.0	12.0	0.0	0.0	0.0
Ricon 134	0.0	0.0	0.0	4.0	8.0	12.0
Z175	60.0	60.0	60.0	60.0	60.0	60.0
Si69	4.8	4.8	4.8	4.8	4.8	4.8
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0
ZnO	4.0	4.0	4.0	4.0	4.0	4.0
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	1.6	1.6	1.6	1.6	1.6	1.6
Sulfur	1.4	1.4	1.4	1.4	1.4	1.4

SBR1500: styrene-butadiene rubber with 23.5% of styrene content

Ricon 131: liquid polybutadiene with 28% of 1,2-unit and M_n of 4500

Ricon 134: liquid polybutadiene with 28% of 1,2-unit and M_n of 8000

Z175: silica

Si 69: 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

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°C with a Mooney viscometer MV 2000 of Alpha Technologies. Cure characteristics were obtained using a Flexsys rheometer (MDR 2000) at a frequency of 100 cycles/min and ± 1.5 arc at 160°C. The vulcanizates were prepared by curing at 160°C 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

1. Cure characteristics

Cure characteristics of the compounds were investigated at 160°C. Figure 1 gives variations of the minimum torque, maximum torque, and delta torque (difference between the maximum and minimum torques) with the liquid BR content. The minimum torque reflects viscosity of the compound. The higher the minimum torque is, the higher the viscosity is. The minimum torque decreases with increase in the liquid BR content. This implies that the viscosity decreases with increase in the liquid BR content. This may be due to the improved filler dispersion and the role of the liquid BR as plasticizer. The filler dispersion is improved in a silica-filled SBR compound by adding the liquid BR having a higher content of the 1,2-unit since the 1,2-unit is compatible with silica.⁸ The raw liquid BR has a much lower viscosity compared to the raw SBR, which leads to lower the viscosity of compounds. The average molecular weights (M_n) of SBR 1500, Ricon 131, and Ricon 134 were about 160000, 4500, and 8000, respectively. Minimum torque of the

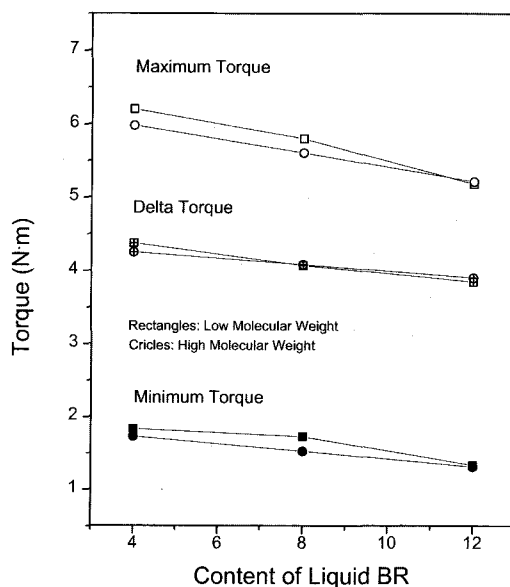


Figure 1. Variation of the torques in rheocurves as a function of the liquid BR content. Rectangles and circles indicate Ricon 131 (low molecular weight) and Ricon 134 (high molecular weight), respectively. Solid, open, and crossed symbols stand for the minimum torque, maximum torque, and delta torque (maximum torque minus minimum torque), respectively.

compound containing the liquid BR with higher molecular weight (HLBR, Ricon 134) is lower than that of the compound containing the liquid BR with lower molecular weight (LLBR, Ricon 131). This is an unexpected result since the molecular weight of HLBR is larger than that of LLBR. This may be due to the filler dispersion. This can imply that the HLBR improves the filler dispersion better than the LLBR.

The delta torque is correlated closely with the crosslink density since the torque is increased by crosslinking reactions. The delta torque decreases by increasing the liquid BR content. This can be explained by the big difference in molecular weights between SBR and liquid BR and by prevention of crosslink formations between SBRs or between SBR and silica by the liquid BR. Crosslinks between long polymer chains are more efficient to increase the crosslink density than those between short chains. Lots of the liquid BR are located around silica since

the liquid BR is more compatible with silica than the SBR as discussed above. Thus, the liquid BR molecules prevent the SBR chains from contacting with silica so crosslinking reactions between the SBR and silica will be reduced. The liquid BR molecules between the SBR chains will also prevent the crosslinking reactions between the SBRs.

Figure 2 gives variations of the Mooney cure times with the liquid BR content. 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 BR content increases. The Δt also becomes slower by increasing the liquid BR content. This can be explained by the difference in mobility between SBR and liquid BR and prevention of crosslink formations between SBRs or between

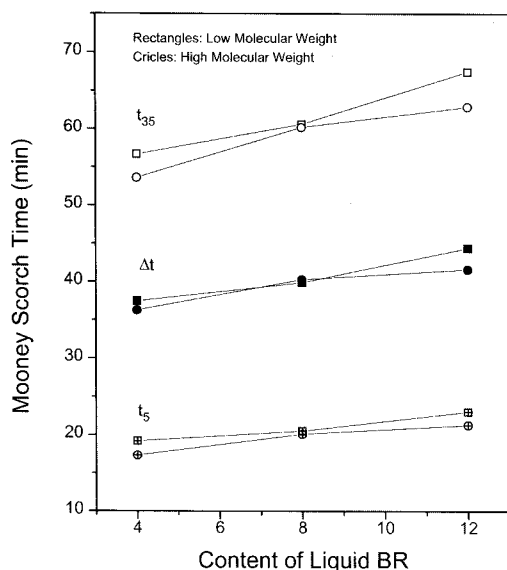


Figure 2. Variation of the cure times in rheocurves as a function of the liquid BR content. Rectangles and circles indicate Ricon 131 (low molecular weight) and Ricon 134 (high molecular weight), respectively. Solid, open, and crossed symbols stand for the t_{35} , t_5 , and cure rate index ($\Delta t = t_{35} - t_5$), respectively.

SBR and silica by the liquid BR. Long chain molecule moves slower than short one and sulfur crosslinking reactions occur faster in less movable long chains than in mobile short chains. The t_5 and t_{35} of compounds containing LLBR are also slower than those of compounds containing HLBR. The liquid BR molecules also prevent the crosslinking reactions between SBRs. Prevention of the crosslinking reactions will be more effective as the number of the liquid BR molecules. Since molecular weight of the HLBR (Ricon 134) is larger than that of the LLBR (Ricon 131) by about twice, the number of the HLBR molecules is smaller than that of the LLBR molecules by about twice in the same content. Thus, the LLBR is more efficient for delay of the cure time than the HLBR.

2. Physical properties

Physical properties of a rubber vulcanizate cured by accelerated sulfur cure system depend on the crosslink density.⁹ 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 vulcanizates were thermally aged at 90°C for 3 days to investigate the influence of thermal aging on the tensile properties (modulus, tensile strength, and elongation at break).

Figures 3 and 4 show variations of the moduli at 100% and 300% strains with the liquid BR content. The moduli decrease with increase in the liquid BR content. This is due to the decreased crosslink density. The decreased crosslink density with the increased liquid BR content was discussed previously. There is no big difference in the 100% moduli of vulcanizates containing the LLBR and HLBR before the thermal aging. However, after the thermal aging, the 100% moduli of vulcanizates containing the HLBR become higher than those of vulcanizates containing the LLBR. This phenomenon was also observed in the 300% modulus. The 300% moduli of vulcanizates containing the HLBR of 4.0 and 8.0 phr are lower than those of vul-

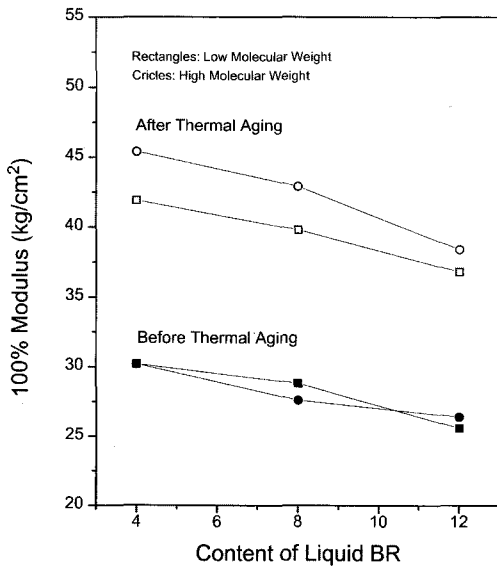


Figure 3. Variation of the 100% modulus as a function of the liquid BR content. Rectangles and circles indicate Ricon 131 (low molecular weight) and Ricon 134 (high molecular weight), respectively. Solid and open symbols stand for before and after the thermal aging at 90°C for 3 days, respectively.

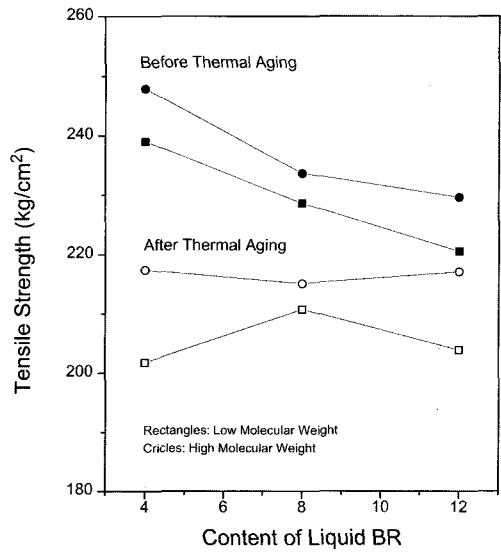


Figure 5. Variation of the tensile strength as a function of the liquid BR content. Rectangles and circles indicate Ricon 131 (low molecular weight) and Ricon 134 (high molecular weight), respectively. Solid and open symbols stand for before and after the thermal aging at 90°C for 3 days, respectively.

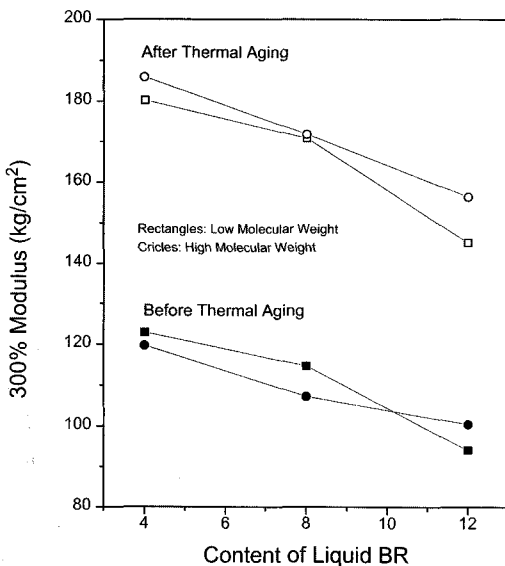


Figure 4. Variation of the 300% modulus as a function of the liquid BR content. Rectangles and circles indicate Ricon 131 (low molecular weight) and Ricon 134 (high molecular weight), respectively. Solid and open symbols stand for before and after the thermal aging at 90°C for 3 days, respectively.

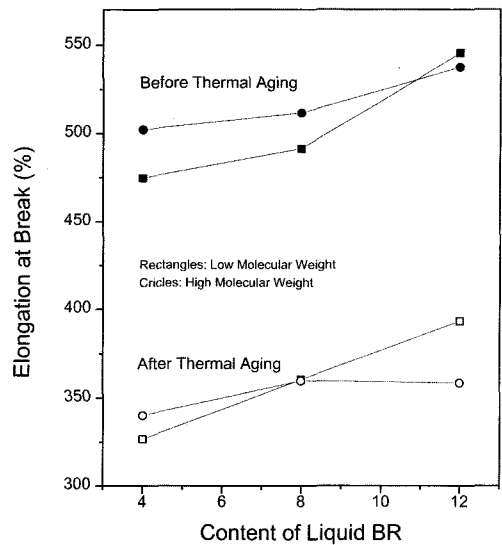


Figure 6. Variation of the elongation at break as a function of the liquid BR content. Rectangles and circles indicate Ricon 131 (low molecular weight) and Ricon 134 (high molecular weight), respectively. Solid and open symbols stand for before and after the thermal aging at 90°C for 3 days, respectively.

canizates containing the LLBR before the thermal aging. After the thermal aging, the 300% moduli of vulcanizates containing the HLBR become higher than those of vulcanizates containing the LLBR as shown in Figure 4. This implies that the vulcanizates containing the LLBR are thermally more stable than the vulcanizates containing the HLBR since the increased modulus by the thermal aging for the vulcanizate containing the LLBR is lower than for the vulcanizate containing the HLBR. The tensile strength decreases with increase in the liquid BR content before the thermal aging (Figure 5). The tensile strength becomes low after the thermal aging. This is due to the decreased elongation at break by the thermal aging. The elongation at break becomes shorter after the thermal aging (Figure 6). This is due to the increased crosslink density by the thermal aging.

The wear property becomes worse as the liquid BR content increases (Figure 7). This is because the crosslink density decreases with increase in the liquid BR content. For the vulcanizates containing the liquid BR of 4.0 phr, abrasion loss of the vulcanizate containing the LLBR is lower than that of the vulcanizate containing the HLBR. However, for the vulcanizates containing the liquid BR of 12.0 phr, abrasion loss of the vulcanizate containing the LLBR is higher than that of the vulcanizate containing the HLBR. This is correspondent well with the delta torque in Figure 1. Delta torque of the vulcanizate containing the LLBR is higher than that of the vulcanizate containing the HLBR when the liquid BR content is 4.0 phr, while that of the former is lower than that of the latter when the liquid BR content is 12.0 phr. The flex cracking property is improved by adding the liquid BR. The crack size decreases with increase in the liquid BR content (Figure 8). This is due to the improved silica dispersion and decreased crosslink density by adding liquid BR. Crack sizes of the vulcanizates containing the HLBR are smaller than those of the respective vulcanizates containing the LLBR. This can imply that the HLBR improves the silica

dispersion better than LLBR.

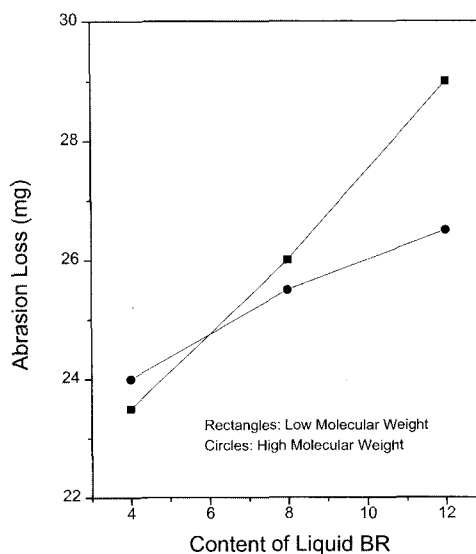


Figure 7. Variation of the abrasion loss as a function of the liquid BR content. Rectangles and circles indicate Ricon 131 (low molecular weight) and Ricon 134 (high molecular weight), respectively.

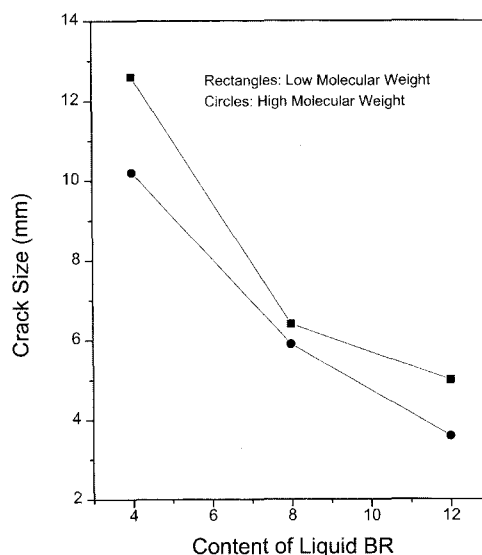


Figure 8. Variation of the crack size (Dematia flex-cracking test) as a function of the liquid BR content. Rectangles and circles indicate Ricon 131 (low molecular weight) and Ricon 134 (high molecular weight), respectively.

IV. Conclusion

The filler dispersion in a silica-filled SBR compound is improved by the liquid BR. The viscosity and crosslink density decrease with increase in the liquid BR content. The scorch time and cure rate become slower as the liquid BR content increases. This is more clear in the compound containing the liquid BR with higher molecular weight (HLBR) rather than the liquid BR with low one (LLBR). The observed cure characteristics can be explained by the improved silica dispersion, much lower molecular weight of the liquid BR compared to SBR, and prevention of crosslink formation between the SBRs or between the SBR and silica. The vulcanizates containing the LLBR were found to be thermally more stable than those containing the HLBR. From the results for elongation at break and flex-cracking test, it was found that the silica

dispersion was more improved when the HLBR was used than when the LLBR was used.

References

1. S. Wolff and M. J. Wang, *Rubber Chem. Technol.*, **65**, 329 (1992).
2. Y.-C. Ou, Z.-Z. Yu, A. Vidal, and J. B. Donnet, *Rubber Chem. Technol.*, **67**, 834 (1994).
3. Y. Li, M. J. Wang, T. Zhang, F. Zhang, and X. Fu, *Rubber Chem. Technol.*, **67**, 693 (1994).
4. S.-S. Choi, *J. Appl. Polym. Sci.*, **79**, 1127 (2001).
5. S.-S. Choi, *J. Polym. Sci.: Part B: Polym. Phys.*, **39**, 439 (2001).
6. S.-S. Choi, *Kor. Polym. J.*, **9**, 45 (2001).
7. S.-S. Choi, *J. Anal. Appl. Pyrolysis*, **55**, 161 (2000).
8. S.-S. Choi, manuscript in preparation.
9. N. J. Morrison and M. Porter, *Rubber Chem. Technol.*, **57**, 63 (1984).