

Improvement of Properties of Silica-Filled SBR Compounds Using NBR: Influence of Separate Load of SBR and NBR

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NBR을 이용한 실리카로 보강된 SBR 배합물의 특성 향상: SBR과 NBR의 분리 첨가 배합의 영향

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ABSTRACT : Mixing condition and procedure affect properties of a filled rubber compound such as filler dispersion, viscosity, and bound rubber formation. Influence of separate load of styrene-butadiene rubber (SBR) and acrylonitrile-butadiene rubber (NBR) on properties of silica-filled SBR compounds containing NBR was studied. Cure time and cure rate became faster as NBR content increased. The crosslink density increased with increase in the NBR content. The bound rubber content also increased as the NBR content increased. NBR content of the bound rubber was higher than that of the compounded rubber. The bound rubber content was higher when SBR and NBR were loaded separately than when loading simultaneously. The cure time and cure rate were slower for the separate load than for the simultaneous one. The crosslink density was also lower for the former case than for the latter one.

요약 : 배합 조건과 공정은 충전제 분산, 점도, 결합고무 형성 등과 같은 고무 배합물의 특성에 영향을 준다. NBR과 SBR의 분리 첨가 배합이 NBR이 함유된 실리카로 보강된 고무 배합물의 특성에 미치는 영향에 대해 연구하였다. NBR 함량이 증가할수록 가교 시간과 속도는 빨라졌다. 가교밀도는 NBR 함량이 증가할수록 증가하였다. 결합고무량도 NBR 함량이 증가할수록 증가하였다. 결합 고무 중의 NBR 함량은 배합물 고무 중의 NBR 함량보다 높았다. 결합고무량은 동시 첨가 배합의 경우보다 분리 첨가 배합의 경우 더 높았다. 가교 시간과 속도는 동시 첨가 배합의 경우보다 분리 첨가 배합 때 더 느렸다. 가교밀도도 동시 첨가 배합의 경우보다 분리 첨가 배합의 경우 더 낮았다.

Keywords : silica, SBR, NBR, Separate load

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I. Introduction

For silica-filled rubber compounds, the filler dispersion is a critical problem to solve for good products. A good dispersion of filler in a silica-filled rubber compound improves tensile strength, elongation at break, abrasion resistance, and fatigue resistance.¹ Silanol groups (Si-OH) on the silica surface make hydrogen bonds with polar materials in a rubber compound. The adsorption of curatives by silica results in delay of the scorch time and reduction of the crosslink density. In general, silane coupling agent such as bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) is used to improve the filler dispersion and to prevent the adsorption of curatives on the silica surface.²⁻⁴ The silane coupling agent reacts with silanol on the silica surface and a siloxane bond is formed. The silane molecule is bound to the silica surface.

Dispersibility of filler in a rubber compound is very important. In order to improve the filler dispersion, various processing aids are used in mixing of a rubber compound.³⁻⁸ A rubber compound with a poor filler dispersion has worse physical properties than that with a good one. The dispersibility is sensitive to mixing conditions such as mixing steps, temperature, and time. States of rubber compounds can be varied with the mixing conditions even though they have the same formulation.⁹⁻¹¹

In the previous work,¹² we scrutinized the filler dispersion in a silica-filled styrene-butadiene rubber (SBR) compound using acrylonitrile-butadiene rubber (NBR) and found that properties of a silica-filled SBR compound were improved by adding NBR. This improvement of dispersion can be interpreted with the ability of polar nitrile groups (-CN) of NBR to form a hydrogen bond with silica. However, since NBR is more compatible with silica than SBR,¹² the mixing steps, namely, simultaneous load or separate load of SBR and NBR can cause to change dispersion pattern of silica and curatives, which would result in the changes of physical properties and cure characteristics as well. As an expansion of our

previous work,¹² our study was mainly focused on the changes in properties of the compounds when NBR is loaded after mixing of silica and SBR (separate load), which was compared with the simultaneous and SBR (separate load) compared with the simultaneous load of SBR and NBR.

II. Experimental

The silica-filled SBR compounds were made of SBR, NBR (0.0, 4.0, 8.0, and 12.0 phr), silica, silane coupling agent (TESPT), cure activators (stearic acid and ZnO), antidegradants (HPPD and wax), and curatives (TBBS and sulfur). HPPD and TBBS are *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine and *N*-*tert*-butyl-2-benzothiazole sulfenamide, respectively. SBR 1500 with 23.5 wt% of styrene content of Korea Kumho Petroleum Co. was used as SBR. Three NBRs of KNB 25M, KNB 35M, and KNB 40M with acrylonitrile contents of 28.4, 34.9, and 41.2 wt%, respectively, of Korea Kumho Petroleum Co. were used as NBR. Z175 (pH = 6.9, BET = 175 m²/g) 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 °C for the MB and FM stages, respectively. The separately loaded MB compounds were prepared as the following sequence: (1) The SBR was loaded into the mixer and pre-mixed for 0.5 min. (2) The silica and silane coupling agent were compounded into the rubber for 2.0 min. (3) The NBR and 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.

Contents of bound rubber were determined by extraction of unbound materials such as ingredients and free rubbers with toluene for 7 days and *n*-hexane for 1 day and drying for 2 days at room

Table 1. Formulations (weight parts) and Mooney Viscosity

| Compound No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|--|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| SBR 1500 | 100.0 | 96.0 | 92.0 | 88.0 | 96.0 | 92.0 | 88.0 | 96.0 | 92.0 | 88.0 |
| Z175 | 60.0 | 60.0 | 60.0 | 60.0 | 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 | 4.8 | 4.8 | 4.8 | 4.8 |
| KNB 25M | 0.0 | 4.0 | 8.0 | 12.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| KNB 35M | 0.0 | 0.0 | 0.0 | 0.0 | 4.0 | 8.0 | 12.0 | 0.0 | 0.0 | 0.0 |
| KNB 40M | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 4.0 | 8.0 | 12.0 |
| Stearic acid | 2.0 | 2.0 | 2.0 | 2.0 | 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 | 4.0 | 4.0 | 4.0 | 4.0 |
| HPPD | 2.0 | 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 | 2.0 |
| TBBS | 1.6 | 1.6 | 1.6 | 1.6 | 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 | 1.4 | 1.4 | 1.4 | 1.4 |
| Mooney Viscosity (ML1+4 at 100 °C, MU) | 111.0 | 112.2 | 115.3 | 116.1 | 114.2 | 114.2 | 118.5 | 112.8 | 112.5 | 112.0 |

temperature. Weights of the samples before and after the extraction were measured and the bound rubber contents were calculated. The bound rubber contents were measured three times and averaged. Bound rubber composition was determined using pyrolysis-gas chromatography (pyrolysis-GC). Pyrolysis-GC chromatograms of the samples were acquired with a Curie point pyrolyzer JHP-22 and an HP 5890 gas chromatograph. The sample (0.5 ± 0.1 mg) was pyrolyzed at 590 °C for 5 sec. An HP-5 capillary column (length 21 m) was used. The analysis conditions for the pyrolysis-GC have been described in detail elsewhere.¹³ Quantitative analysis of the rubber composition of the bound rubber was carried out using the FM compounds as the references. Cure characteristics were obtained using a Monsanto rheometer (R100) at 160 °C. Viscosities and Mooney cure times of the compounds were measured at 100 and 125 °C, respectively, using a Mooney MV 2000 of Alpha Technologies.

The vulcanizates were prepared by curing at 160 °C for 30 min. Crosslink densities of the samples were measured by swelling method. Organic addi-

tives 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 *n*-decane for 2 days and the weights of the swollen samples were measured. Physical properties of the vulcanizates were measured with the universal testing machine (Instron 6021). The physical properties were measured three times and averaged.

III. Results and Discussion

1. Bound Rubber

Bound rubber content was measured at room temperature and its rubber composition was analyzed with a pyrolysis-GC technique. Figure 1 shows variation of the bound rubber content (%) as a function of the NBR content (phr). For the separate load, the bound rubber content of the NBR-containing compounds is higher than that of the compounds without NBR, and the bound rubber content in

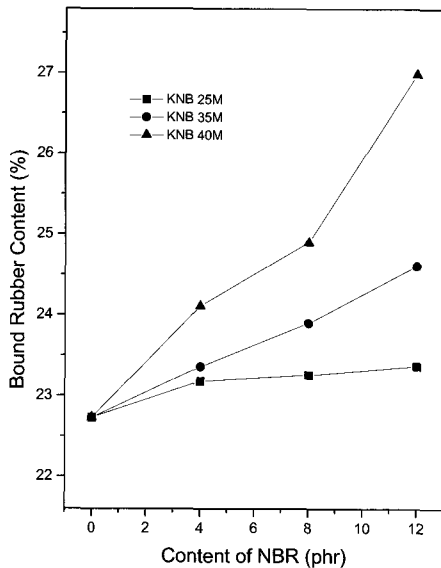


Figure 1. Variation of the bound rubber content as a function of the NBR content. The squares, circles, and triangles indicate the KNB 25M, KNB 35M, and KNB 40M, respectively.

increases in NBR content-dependent manner. The augmentation of the bound rubber content is especially obvious when high acrylonitrile content of NBR is used. However, our previous work shows that bound rubber content of the compound without NBR is, on the whole, higher than those of the NBR-containing compounds for the simultaneous load.¹⁴ This difference may be interpreted with the lower compatibility of SBR with silica compared to NBR. NBR is more compatible with silica than SBR since it has basic nitrile group (-CN). So, when NBR and SBR are loaded simultaneously, SBR does not contact sufficiently with silica because NBR contacts faster with silica than SBR. When NBR is loaded after loading of SBR and silica, SBR has sufficient contact time with silica and then formation of bound rubber between SBR and silica increases.

Figure 2 shows variation of NBR content in the bound rubber as a function of the NBR content in the compound in the separate load. NBR content of the bound rubber also increases in the NBR content-dependent manner and the acrylonitrile content of

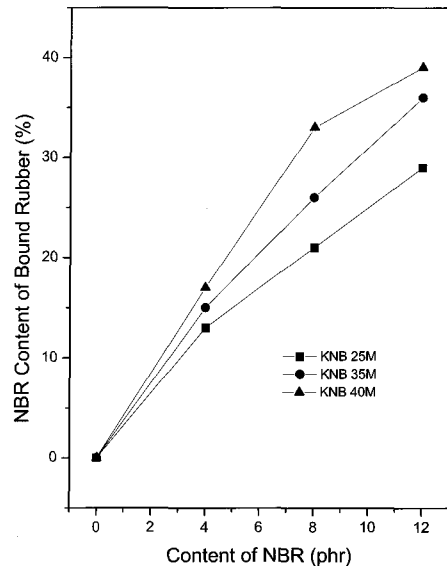


Figure 2. Variation of NBR content in the bound rubber as a function of the NBR content in the compound. The squares, circles, and triangles indicate the KNB 25M, KNB 35M, and KNB 40M, respectively.

NBR-dependent manner as well. However, NBR contents in the bound rubber for the separate load are nearly the same with those for the simultaneous load. The NBR contents of the bound rubber are described below. For the simultaneous load, NBR contents of the bound rubber were 10, 21, and 29% for the compounds containing KNB 25M of 4, 8, and 12 phr, respectively, and were 17, 34, and 51% for the compounds containing KNB 40M, respectively.¹⁴ For the separate load (Figure 2), the NBR contents are 13, 21, and 29% for the compounds containing KNB 25M, respectively, and are 17, 33, and 39% for the compounds containing KNB 40M, respectively.

2. Cure Characteristics

For the separated load, the variations of the Mooney cure times with the NBR content are shown in Figure 3, which were measured at 125 °C using a Mooney viscometer. The t_5 (Mooney scorch time), t_{35} , and Δt (cure rate index) were measured. The t_5 and t_{35} mean the times taken for the viscosity to

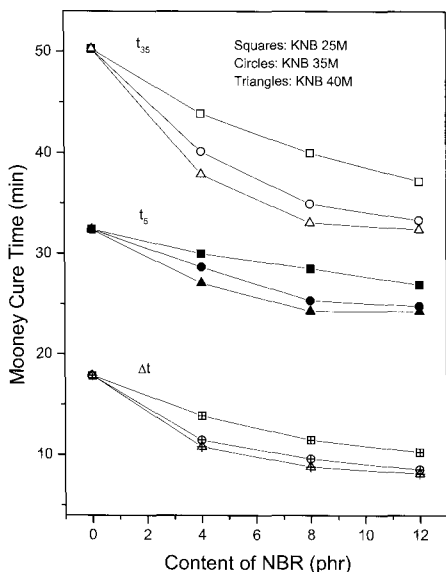


Figure 3. Variation of the Mooney cure times as a function of the NBR content. The solid, open, and crossed symbols stand for the t_5 , t_{35} , and Δt (cure index, $t_{35} - t_5$), respectively. The squares, circles, and triangles indicate the KNB 25M, KNB 35M, and KNB 40M, respectively.

reach from the minimum point to increases of 5 and 35 MU (Mooney unit), respectively. The Δt is the difference between the t_{35} and t_5 . The reciprocal of the Δt is used as a cure rate. The bigger the Δt , the slower the cure rate. The t_5 and t_{35} become faster as the NBR content increases. The Δt also becomes faster by increasing the NBR content. This implies that the scorch time and cure rate become faster as the NBR content increases due mainly to the preventive effect of NBR against the curative adsorption on the silica surface. The cure time and cure rate also become faster as the acrylonitrile content in NBR increases. This phenomenon is interpreted with the increased interaction between NBR and silica as the the acrylonitrile content of NBR increases. The t_5 and cure rate are slightly slower for the separate load than for the simultaneous load. This may be associated with slightly lower NBR content of the bound rubber for the separate load than for the simultaneous load. So, the prevention of the curative adsorption becomes less effective for the

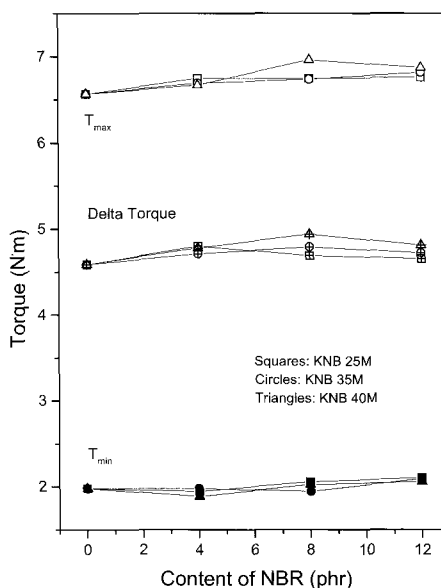


Figure 4. Variation of torques in the rheocurves as a function of the NBR content. The solid, open, and crossed symbols stand for the minimum torque, maximum torque, and delta torque (maximum torque - minimum torque), respectively. The squares, circles, and triangles indicate the KNB 25M, KNB 35M, and KNB 40M, respectively.

separat load.

Figure 4 gives variations of the minimum torque (T_{min}), maximum torque (T_{max}), and delta torque (difference between the maximum and minimum torques) measured at 160 °C as a function of the NBR content. The T_{min} , which is related with the viscosity of a rubber compound, increases with increase of the NBR content even though slightly (Table 1). The viscosity of the compound without NBR is lower than those of the compounds containing NBR. This is due to the raw polymer viscosity and the bound rubber content. Viscosity of the raw NBR is higher than that of the raw SBR. The Mooney viscosities of SBR 1500, KNB 25M, KNB 35M, and KNB 40M were 52, 62, 61, and 59, respectively. The bound rubber content increases by increasing the NBR content (Figure 1). The increased bound rubber content results in the increased viscosity. The delta torque increases with increase of the NBR content. This implies that the

crosslink density increases with increasing the NBR content. The delta torque of a rubber compound mainly depends on amounts of the free curatives in the compounds. Since NBR makes a role of prevention of the curative adsorption on the silica surface, the delta torque of the compound containing NBR with higher acrylonitrile content is higher than that of the compound containing NBR with lower one.

3. Physical Properties

Physical properties of a vulcanizate such as modulus, tensile strength, elongation at break, and so on depend on degree of crosslink density.¹⁵ Modulus is a proportional property to degree of crosslink density, while elongation at break is an inversely proportional property to degree of crosslink density. Crosslink densities of the vulcanizates were measured with a swelling method. Figure 5 shows variation of the reciprocal swelling ratio ($1/Q$) with the NBR content. The swelling ratio is correlated closely to the crosslink density. The swelling ratio was calculated as follow equation (1)

$$Q = 100 \times (W_s - W_u) / W_u \quad (1)$$

where W_s and W_u are weights of the swollen and unswollen samples. The reciprocal swelling value, $1/Q$, was used as crosslink density. The crosslink density increases with increase of the NBR content. Crosslink density of the vulcanizate containing NBR with higher acrylonitrile content is higher than that of the vulcanizate containing NBR with lower one. Crosslink density of a vulcanizate prepared by the separate load is slightly lower than that of a vulcanizate prepared by the simultaneous load. This can be explained by the relatively less effective prevention of the curative adsorption for the separate load compared to the simultaneous load.

Figure 6 gives variation of the moduli with the NBR content. The moduli increase with increasing the NBR content since the crosslink density increases with increasing the NBR content as shown in Figure 5. Figure 7 gives variation of the elonga-

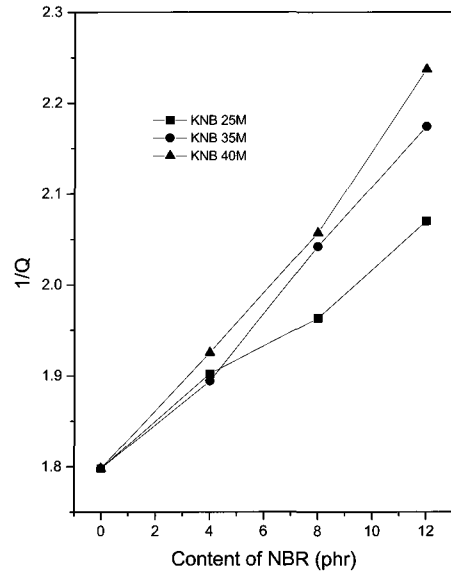


Figure 5. Variation of the reciprocal swelling ratio ($1/Q$) as a function of the NBR content. The squares, circles, and triangles indicate the KNB 25M, KNB 35M, and KNB 40M, respectively.

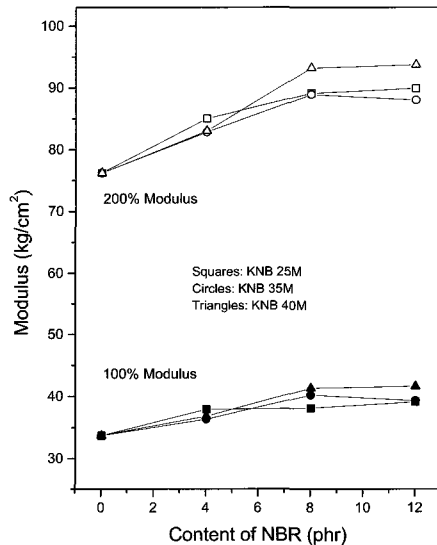


Figure 6. Variation of moduli as a function of the NBR content. The solid and open symbols indicate 100% and 200% moduli, respectively. The squares, circles, and triangles indicate the KNB 25M, KNB 35M, and KNB 40M, respectively.

tion at break with the NBR content. Elongation at

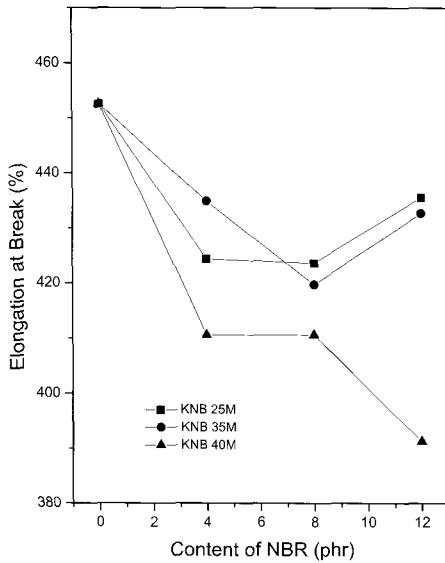


Figure 7. Variation of the elongation at break as a function of the NBR content. The squares, circles, and triangles indicate the KNB 25M, KNB 35M, and KNB 40M, respectively.

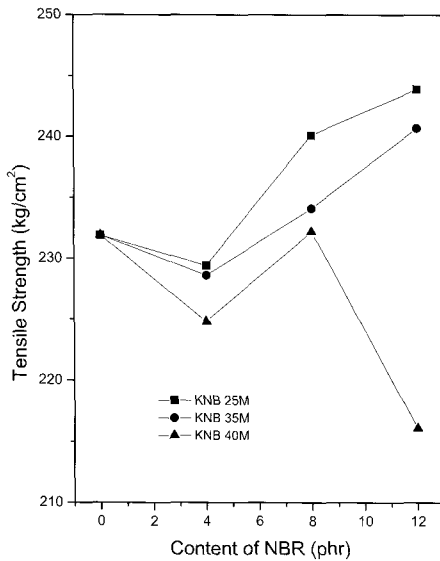


Figure 8. Variation of the tensile strength as a function of the NBR content. The squares, circles, and triangles indicate the KNB 25M, KNB 35M, and KNB 40M, respectively.

break of the vulcanizate without NBR is longer than those of the vulcanizates containing NBR since

crosslink density of the former is lower than those of the latter. Figure 8 gives variation of the tensile strength with the NBR content. For the vulcanizates containing KNB 25M or KNB 35M, tensile strength of the vulcanizate containing the NBR of 4.0 phr is lower than that of the vulcanizate without NBR, while those of the vulcanizates containing the NBR of 8.0 and 12.0 phr are higher than that of the vulcanizate without NBR. The higher tensile strength may be due to the improved silica dispersion.

IV. Conclusions

The filler dispersion in a silica-filled SBR compound was improved by adding NBR. The bound rubber content increased with increasing the NBR content of the compound and the acrylonitrile content of NBR. NBR content in the bound rubber also increased with increasing the NBR content of the compound and the acrylonitrile content of NBR. The cure time and cure rate became faster as the NBR content of the compound and the acrylonitrile content of NBR increased. Bound rubber content of the compound prepared by the separate load was higher than that of the compound prepared by the simultaneous one. NBR content of the bound rubber was slightly lower for the compound prepared by the separate load process than for the compound prepared with the simultaneous one. The vulcanizate prepared with the separate load process had a relatively lower crosslink density compared to the vulcanizate prepared with the simultaneous one.

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