Properties of Silica-Filled Styrene–Butadiene Rubber Compounds Containing Acrylonitrile–Butadiene Rubber: The Influence of the Acrylonitrile–Butadiene Rubber Type

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ABSTRACT: Because silica has strong filler–filler interactions and adsorbs polar materials, a silica-filled rubber compound exhibits poor dispersion of the filler and poor cure characteristics in comparison with those of a carbon black-filled rubber compound. Acrylonitrile–butadiene rubber (NBR) improves filler dispersion in silica-filled styrene–butadiene rubber (SBR) compounds. The influence of the NBR type on the properties of silica-filled SBR compounds containing NBR was studied with NBRs of various acrylonitrile contents. The composition of the bound rubber was different from that of the compounded rubber. The NBR content of the bound rubber was higher than that of the compounded rubber; this became clearer for NBR with a higher acrylonitrile content. The Mooney scorch time and cure rate became faster as the acrylonitrile content in NBR increased. The modulus increased with an increase in the acrylonitrile content of NBR because the crosslink density increased. The experimental results could be explained by interactions of the nitrile group of NBR with silica. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 385–393, 2002

Key words: silica-filled compounds; styrene–butadiene rubber; acrylonitrile–butadiene rubber; adsorption; filler dispersion; composites

INTRODUCTION

For silica-filled rubber compounds, improvement of the filler dispersion and prevention of curative adsorption on the silica surface are very important. Because silica exhibits strong filler–filler interactions, the filler dispersion of a silica-filled rubber compound is worse than that of a carbon black-filled rubber compound. The polar surface of silica makes hydrogen bonds with polar materials in a rubber compound. Because the silica surface is acidic, it forms a strong hydrogen bond

with basic materials. *N-tert*-Butyl-2-benzothiazole sulfenamide (TBBS) and *N*-cyclohexyl benzothiazole sulfenamide are generally used as cure accelerators for rubbers. Because they have basic functional groups [e.g., amide ($=NH$)], they are adsorbed well onto the silica surface. The adsorption of curatives by silica results in a delayed scorch time and reduced crosslink density for a silica-filled rubber compound. In general, a silane coupling agent such as bis-[3-(triethoxysilyl)-propyl]-tetrasulfide (Si69) is used to improve the filler dispersion and to prevent adsorption of curatives onto the silica surface.[1–3] The silane coupling agent reacts with silanol on the surface of silica, and a siloxane bond is formed. The silane molecule is bound to the silica surface.

Table I   Formulations (phr)

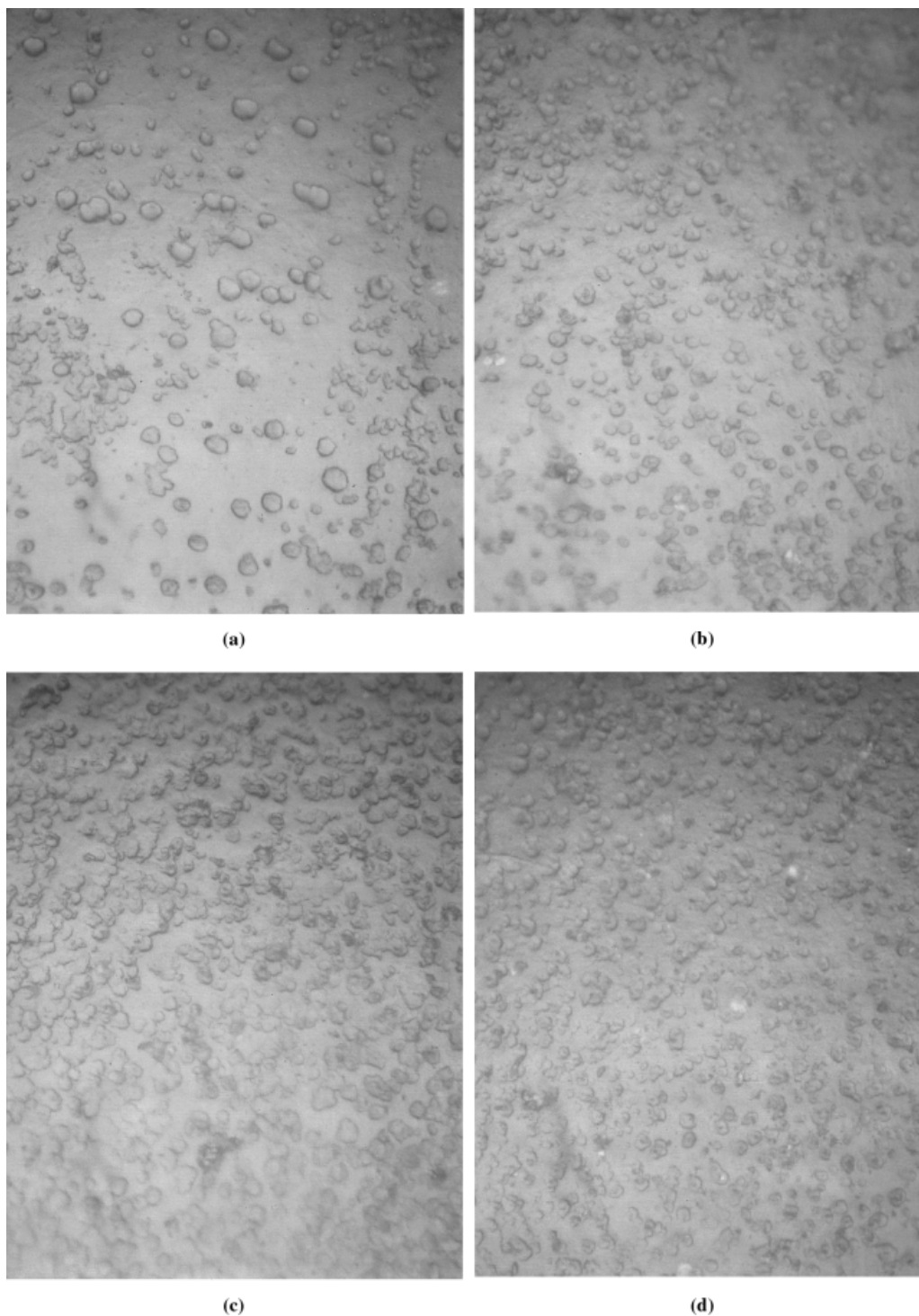|	Compound									
	1	2	3	4	5	6	7	8	9	10
SBR 1500	100.0	96.0	92.0	88.0	96.0	92.0	88.0	96.0	92.0	88.0
KNB 25M	0.0	4.0	8.0	12.0	0.0	0.0	0.0	0.0	0.0	0.0
KNB 35M	0.0	0.0	0.0	0.0	4.0	8.0	12.0	0.0	0.0	0.0
KNB 40M	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.0	8.0	12.0
Z175	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0
Si69	4.8	4.8	4.8	4.8	4.8	4.8	4.8	4.8	4.8	4.8
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

In a previous study,[4] we studied the improvement of the filler dispersion in a silica-filled styrene–butadiene rubber (SBR) compound with acrylonitrile–butadiene rubber (NBR) and found that properties of a silica-filled SBR compound were improved by the addition of NBR to the compound. NBR has nitrile groups (—CN). Because the nitrile group is basic, it can make a hydrogen bond with silica, and the filler dispersion is improved. In this work, the influence of the NBR type on the properties of silica-filled SBR compounds was studied with NBRs of various acrylonitrile contents. The study was focused on reducing the curative adsorption and improving the filler dispersion by the addition of NBR.

EXPERIMENTAL

The silica-filled rubber compounds were made of SBR, NBR (0.0–12.0 phr), silica, a silane coupling agent (Si69), cure activators (stearic acid and ZnO), antidegradants [N-phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine (HPPD) and wax], and curatives (TBBS and sulfur). Three NBRs with acrylonitrile contents of 28.4, 34.9, and 41.2% (KNB 25M, KNB 35M, and KNB 40M, respectively) from Korea Kumho Petroleum Co. (Korea) were used. Z175 (pH = 6.9, Brunauer-Emmett-Teller = 175 m^2/g) from Kofran Co. (Korea) was used as silica. The formulations are given in Table I. The mixing of the compounds was performed in a Banbury-type mixer at rotor speeds 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 follows: the rubbers were loaded into the mixer and premixed for 0.5 min, the silica and silane coupling agent were compounded into the rubbers for 2.0 min, the ingredients (cure activators and antidegradants) were mixed for 2.0 min, and the compounds were discharged. The FM compounds were prepared by the curatives being mixed with the MB compounds for 2.0 min.

The contents of bound rubber were determined by the extraction of unbound materials (ingredients and free rubbers) with toluene for 7 days and n-hexane for 1 day and by 2 days of drying at room temperature. Weights of the samples before and after the extraction were measured, and the bound-rubber contents were calculated. Bound-rubber compositions were determined with pyrolysis gas chromatography (GC). Pyrolysis GC chromatograms of the samples were acquired with a Curie JHP-22 point pyrolyzer (JAI Co., Japan) and an HP5890 gas chromatograph (Hewlett-Packard Co., USA). The sample (0.5 ± 0.1 mg) was pyrolyzed at 590°C for 5 s. An HP-5 capillary column (length = 21 m) was used. The analysis conditions for the pyrolysis GC have been described in detail elsewhere.[5] A quantitative analysis of the rubber compositions of the bound rubber was carried out by calibration with the FM compounds. Cure characteristics were obtained with a Flexsys rheometer (MDR 2000; USA) at a frequency of 100 cycles/min and ±1.5 arc at 160°C. Viscosities and Mooney cure times of the compounds were measured at 100 and 125°C, re-

Figure 1 Photographs of the vulcanizate surfaces of compounds (a) 1, (b) 3, (c) 6, and (d) 9 obtained with a optical microscope (original magnification, 1000×).

spectively, with a Mooney MV 2000 of Alpha Technologies (USA).

The vulcanizates were prepared by 30 min of curing at 160°C. Crosslink densities of the sam-ples were measured by the swelling method. Or-ganic additives in the samples were removed by extraction with tetrahydrofuran and *n*-hexane for 3 and 2 days, respectively, and they were dried for

Table II   Content and Composition of the Bound Rubber and Viscosity

	Compound									
	1	2	3	4	5	6	7	8	9	10
Bound rubber content (%)	26.28	24.07	25.70	26.55	23.52	25.98	26.21	26.33	27.72	30.95
Bound rubber composition (content of NBR, %)	0	10	21	29	14	27	38	17	34	51
Viscosity (ML1 + 4* at 100°C, MU)	111.0	107.4	117.1	119.8	109.9	114.8	114.4	112.3	117.7	113.9

* Measurement of Mooney viscosity with a large rotor at 4 min after preheating for 1 min.

2 days at room temperature. The weights of the organic material-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 a universal testing machine (Instron 6021). Abrasion loss was measured according to ASTM Standard 2228 with a Pico abrasion tester from BF Goodrich for 80 cycles.

RESULTS AND DISCUSSION

Dispersion of Silica

To investigate the NBR effect on the dispersion of silica, we investigated the degree of filler dispersion with optical microscopy. Figure 1(a–d) shows photographs of the vulcanizate surfaces of compounds 1, 3, 6, and 9, respectively. Compound 1 does not contain NBR, whereas compounds 3, 6, and 9 contain 8.0 phr KNB 25M, KNB 35M, and KNB 40M, respectively. For the silica-filled compound without NBR, silica agglomerates are clustered, as shown in Figure 1(a). The silica agglomerates in the silica-filled compound without NBR are larger than those in the compounds containing NBR. For the silica-filled compounds containing NBR, silica is dispersed to some extent, as shown in Figure 1(b–d). This can be explained by the adsorption of NBR onto the silica. The NBR adsorbed onto the silica surface reduces the filler–filler interactions so that the silica is dispersed well in the rubber. However, there is no big difference in the silica dispersion for the compounds containing NBR.

Contents and Compositions of Bound Rubber

Contents of bound rubber in filled rubber compounds are important because they affect physi-
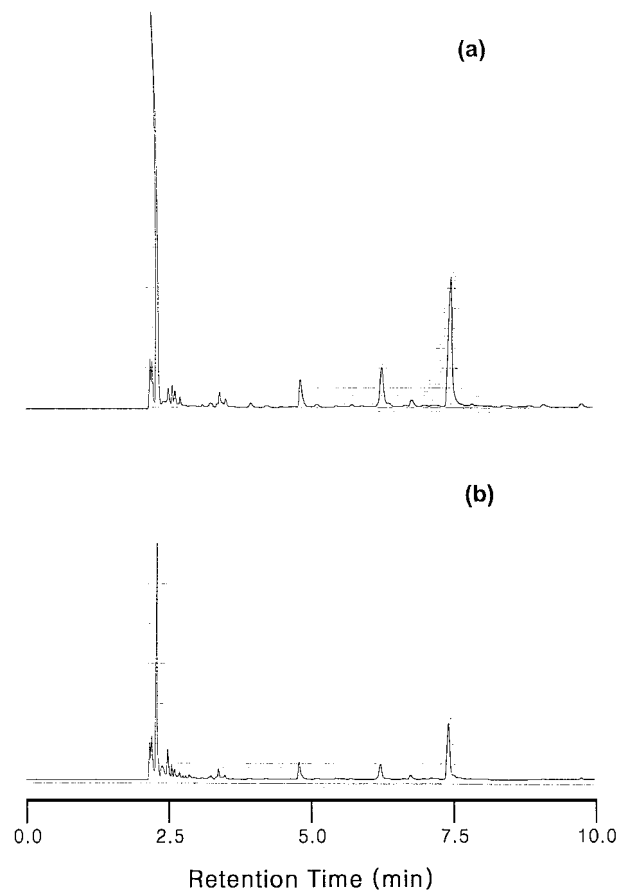
cal properties of their vulcanizates.[6,7] The bound-rubber contents are summarized in Table II. Bound-rubber contents of the compounds containing NBR with low acrylonitrile contents (KNB 25M and KNB 35M) are, on the whole, less abundant than that of the compound without NBR.
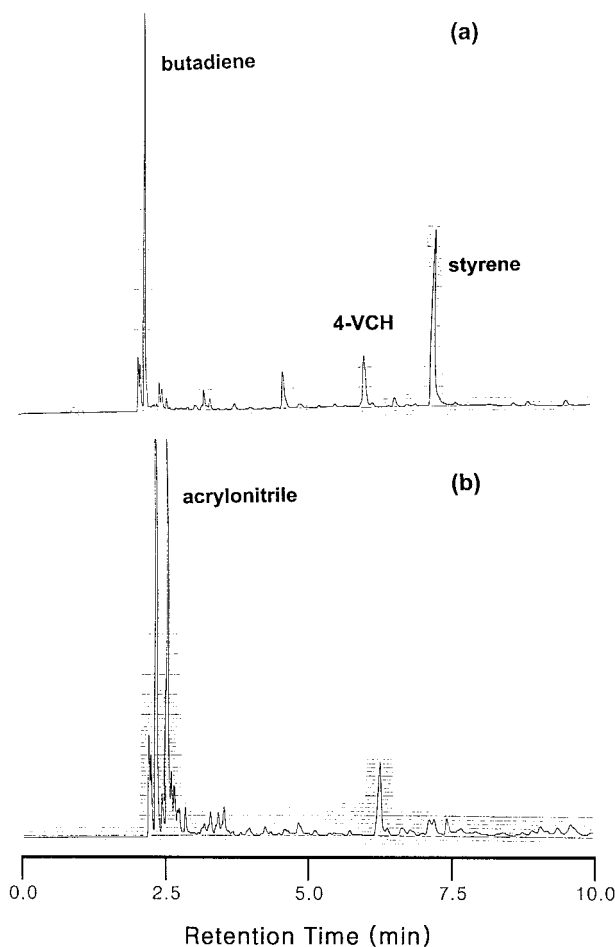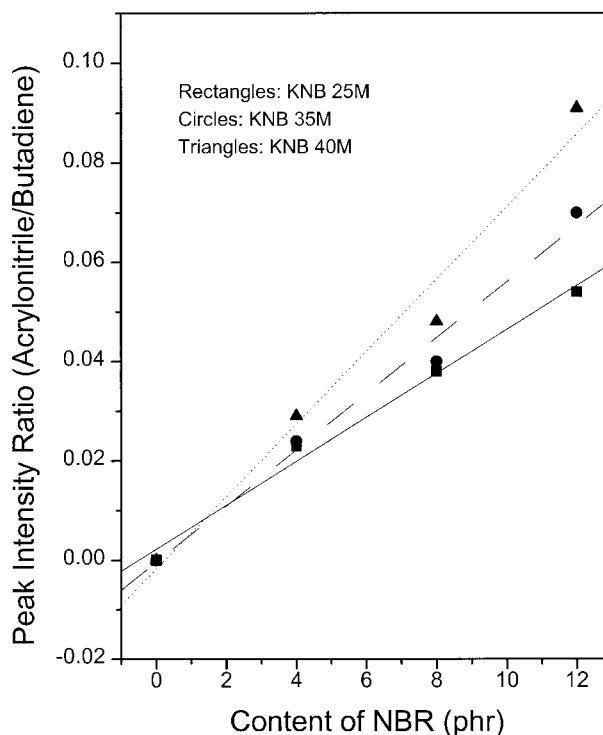

Figure 2 Pyrolysis gas chromatograms of (a) raw SBR 1500 and (b) KNB 35M.

However, for the NBR with a high acrylonitrile content (KNB 40M), bound-rubber contents of the compounds containing NBR are higher than that of the compound without NBR. For the compounds containing NBR, the bound-rubber content increases with an increase in the NBR content. The bound-rubber content also, on the whole, increases with the acrylonitrile content increasing in NBR.

The rubber compositions of the bound rubber was measured with pyrolysis GC to investigate the influence of the NBR type on the formation of the bound rubber. The FM compounded rubbers were used as reference samples to determine the NBR content of the bound rubber. NBR contents of the bound rubber were determined with the relative peak intensity ratio of acrylonitrile and butadiene in the pyrolysis GC chromatogram compared with those of the references. Figure 2 gives the pyrolysis GC chromatograms of raw SBR 1500 (SBR with a 23.5% styrene content)
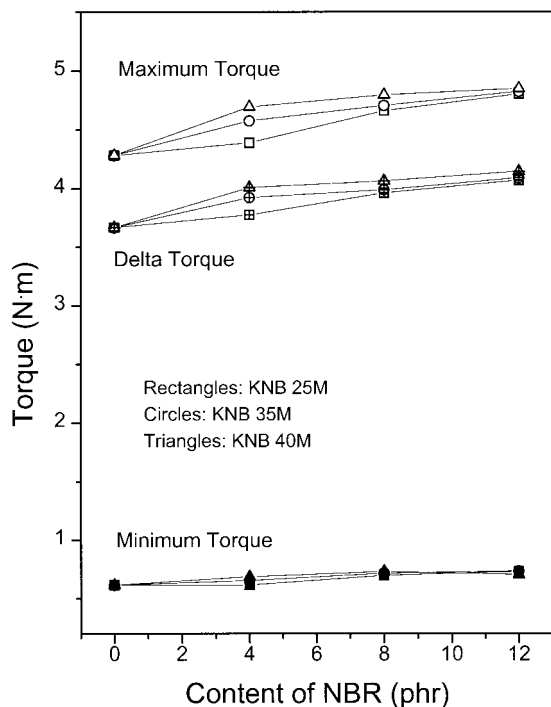

Figure 4   Variation of the relative peak intensity ratio of acrylonitrile and butadiene as a function of the NBR content. The straight, dashed, and dotted lines indicate KNB 25M, KNB 35M, and KNB 40M, respectively.

and KNB 35M. The pyrolysis of SBR and NBR has been studied by many workers.[8–12] Major pyrolysis products of SBR are butadiene, 4-vinylcyclohexene (4-VCH), and styrene, whereas those of NBR are butadiene, acrylonitrile, and 4-VCH. Of the pyrolyzates, acrylonitrile is formed from NBR, not SBR. With the relative peak intensities of acrylonitrile and butadiene, the NBR content of the bound rubber was determined.

Figure 3 gives the pyrolysis GC chromatograms of compounded rubber and bound rubber of compound 7 containing 12.0 phr KNB 35M. The relative intensity of the acrylonitrile peak in the

Figure 3   Pyrolysis gas chromatograms of (a) compounded rubber and (b) bound rubber of the compound containing 12.0 phr KNB 35M.

Table III   Curve-Fitting Equations for the Calibration Curve of Figure 3

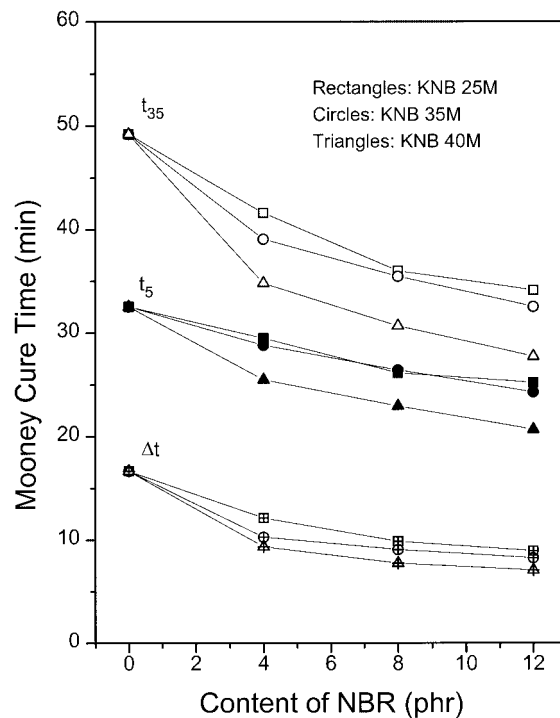| NBR Type	Equation	Correlation Coefficient
KNB 25M	$y = 0.00443x + 0.0022$	0.995
KNB 35M	$y = 0.00565x - 0.0004$	0.994
KNB 40M	$y = 0.00730x - 0.0018$	0.988

Figure 5 Variation of the torque in rheocurves as a function of the NBR content. The solid, open, and crossed symbols stand for the minimum torque, maximum torque, and Δ torque, respectively.
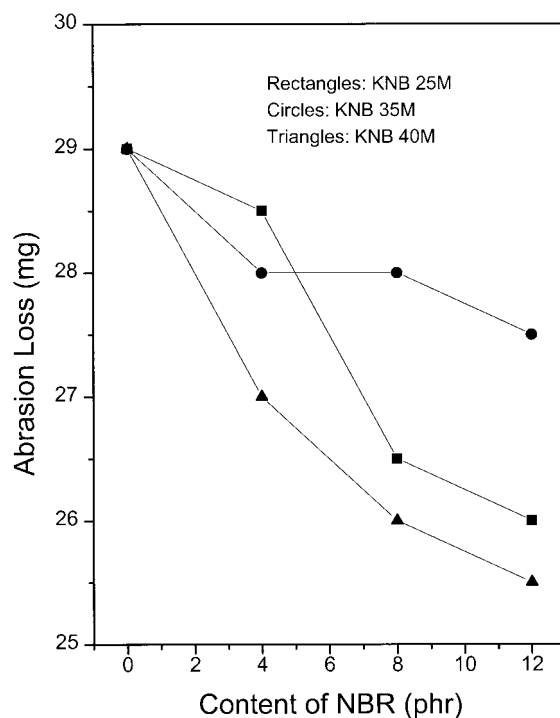

Figure 6 Variation of the Mooney cure time as a function of the NBR content. The solid, open, and crossed symbols stand for t_5, t_{35}, and Δt, respectively.

bound rubber (ca. 6.1%) is higher than that in the compounded rubber (ca. 2.8%). This implies that the bound rubber has a higher NBR content than the compounded rubber. Figure 4 shows the variation of the relative peak intensity ratio of acrylonitrile and butadiene with the NBR content in the compounded rubber. The variation exhibits a good linear correlation (Table III). With the curve-fitting equations, the NBR contents in the bound rubbers were calculated. The results are summarized in Table II. The NBR contents of the bound rubbers are more than 2 times greater than those of the respective compounded rubbers. This phenomenon appears more clearly in the compounds containing NBR with higher acrylonitrile contents. This may be due to the good interaction that NBR has with silica. Because the nitrile group (—C≡N) of NBR is basic and the silanol group (≡Si—OH) of silica is acidic, they can make a good hydrogen bond. These hydrogen bonds between NBR and silica weaken the filler–filler interactions of silica, so the silica dispersion will be improved.
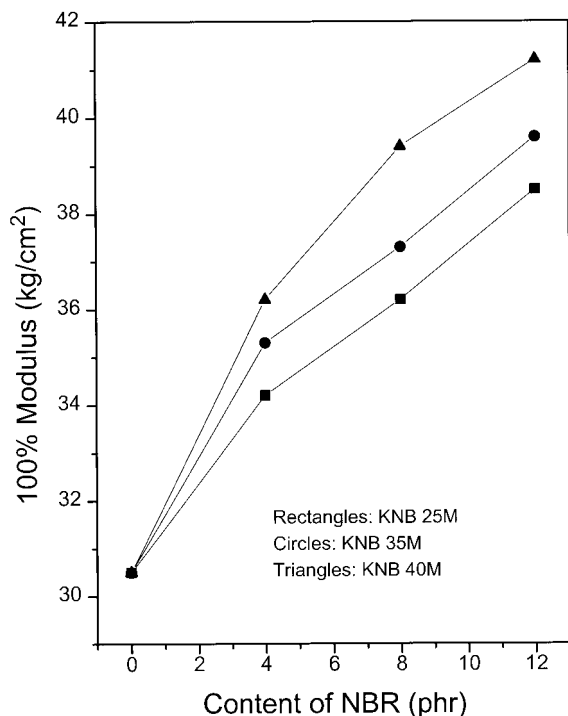
Cure Characteristics

Cure characteristics of the compounds were investigated at 160°C. Variations of the minimum

Figure 7 Variation of the abrasion loss as a function of the NBR content.
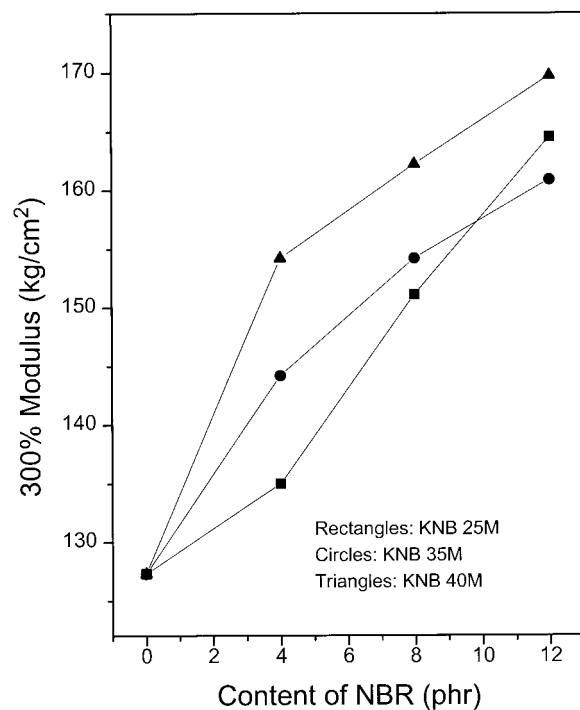
Figure 8 Variation of the 100% modulus as a function of the NBR content.

torque, maximum torque, and Δ torque (maximum torque $-$ minimum torque) as a function of the NBR content are demonstrated in Figure 5. The minimum torque, on the whole, increases with an increase in the NBR content. The minimum torque of a rubber compound is related to the viscosity. Table II gives the Mooney viscosities of the compounds. The viscosity of the compound without NBR is lower than those of the compounds containing NBR, except for the compounds containing 4.0 phr KNB 25M and KNB 35M. This may be due to the raw polymer viscosity. The viscosity of the raw NBR is much 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 Δ torque increases with an increase in the NBR content. This implies that the crosslink density increases with increasing NBR content. The Δ torque of a rubber compound mainly depends on the amounts of free curatives in the compounds. Therefore, it can lead to the conclusion that the NBR coated on silica prevents the adsorption of curatives. The Δ torque of the compound containing NBR with a higher acrylonitrile content is higher than that of the compound containing NBR with a lower content. This means that the NBR with a higher

acrylonitrile content prevents the adsorption of curatives more effectively than the NBR with a lower content.

Figure 6 gives variations of the Mooney cure times with the NBR content. t_5 (Mooney scorch time), t_{35}, and Δt (cure-rate index) were measured at 125°C. t_5 and t_{35} are the times taken for the viscosity to increase from the minimum point to an additional 5 and 35 MU, respectively. Δt is the difference between t_{35} and t_5. The reciprocal of Δt is used as a cure rate. The bigger Δt is, the slower the cure rate is. t_5 and t_{35} become faster as the NBR content increases. Δt also becomes faster with increasing NBR content. This implies that the scorch time and cure rate become faster as the NBR content increases. This is due to the prevention of curative adsorption onto silica by NBR. NBR is more abundant around the silica than SBR because it is more compatible with silica than SBR. NBR placed on the silica can prevent the adsorption of curatives. The fast cure characteristics are clearer in the compound containing NBR with a higher acrylonitrile content. This can be explained by the increased interaction between NBR and silica with an increase in the acrylonitrile content. The NBR content of the bound rubber increases as the acrylonitrile content in NBR
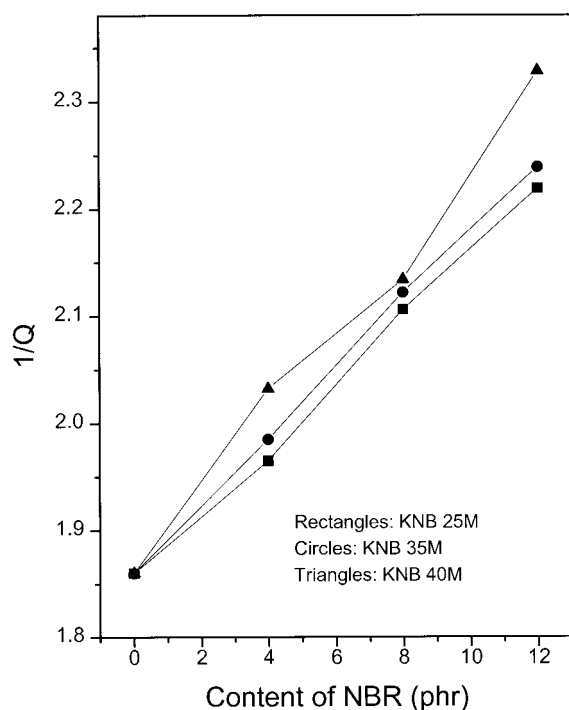

Figure 9 Variation of the 300% modulus as a function of the NBR content.

increases, as discussed previously. The curative adsorption is prevented more and more effectively as the amount of NBR around silica increases.
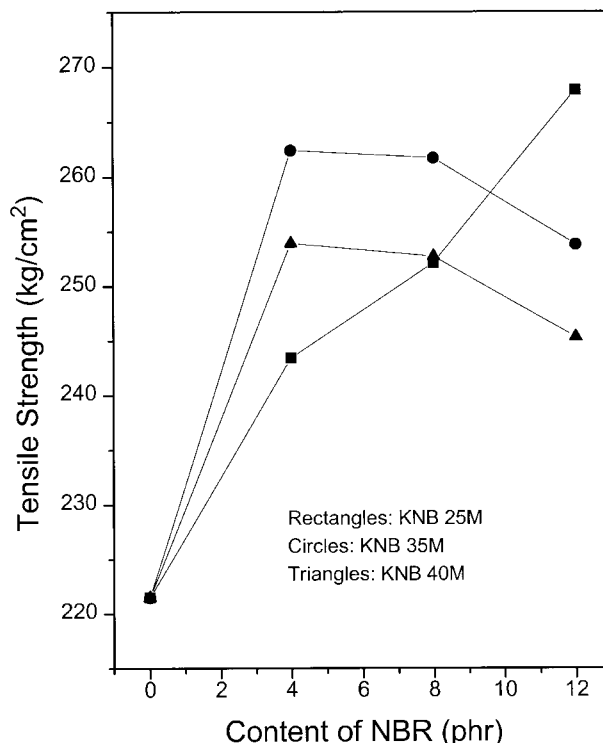
Physical Properties

The wear properties are improved by the addition of NBR to the silica-filled SBR compound. The abrasion loss decreases as the NBR content increases (Fig. 7). This may be due to the increased crosslink density and improved silica dispersion from the addition of NBR. The abrasion loss of the vulcanizate containing KNB 40M is lower than those of the vulcanizates containing KNB 25M and 35M. This is because the crosslink density (Δ torque) of the former is higher than those of the latter, as shown in Figure 5. The variation of the crosslink density with the type and content of NBR is discussed in detail next.

Figures 8 and 9 give variations of the 100 and 300% moduli with the NBR contents, respectively. Moduli of the vulcanizates containing NBR are much higher than those of the vulcanizate without NBR. The modulus increases with an increase in the NBR content. The modulus also increases as the acrylonitrile content increases. The variation of the modulus with the content

Figure 11 Variation of the tensile strength as a function of the NBR content.
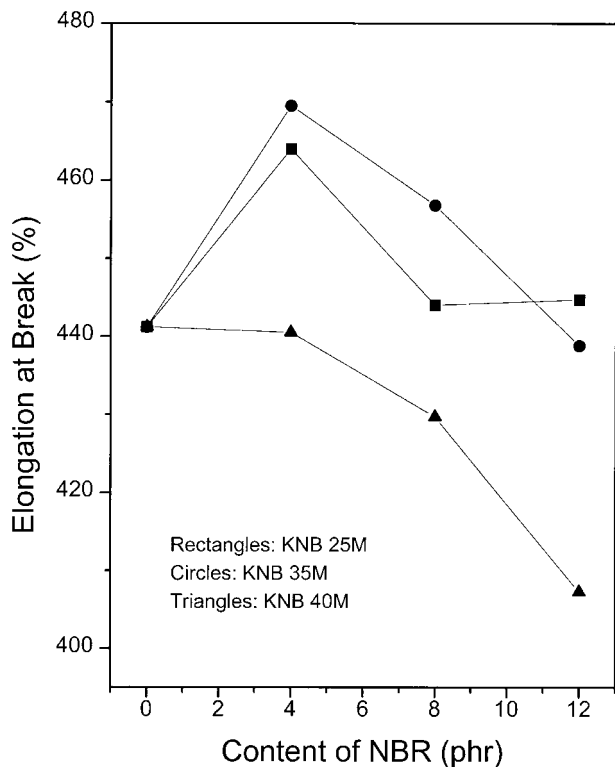

Figure 10 Variation of $1/Q$ as a function of the NBR content.

and type of NBR can be explained by the crosslink density. Figure 10 shows the 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 follows: $Q = 100 \times (W_s - W_u)/W_u$, where W_s and W_u are weights of the swollen and unswollen samples, respectively. $1/Q$ was used as the crosslink density.[13] The crosslink density increases with an increase in the NBR content. The crosslink density of the vulcanizate containing NBR with a high acrylonitrile content is higher than that of the vulcanizate containing NBR with a low content. The modulus of a rubber vulcanizate is a property proportional to the degree of crosslink density.[14] The modulus of a rubber vulcanizate with a high crosslink density is higher than that of a rubber vulcanizate with a low one.

Figure 11 gives the variation of the tensile strength with the NBR content. The tensile strength of the vulcanizate containing NBR is higher than that of the vulcanizate without NBR. For the vulcanizate containing KNB 25M, the tensile strength increases linearly with an increase in the NBR content. However, for the vulcanizates containing KNB 35M and KNB 40M,

Figure 12 Variation of the elongation at break as a function of the NBR content.

the tensile strengths increases with the addition of 4.0 phr NBR and then decreases slightly with increasing NBR content. This may be due to the decreased elongation at break (Fig. 12).

For the vulcanizates containing KNB 25M and KNB 35M, the elongation at break increases with the addition of 4.0 phr NBR and then decreases with increasing NBR content. In general, the elongation at break of a vulcanizate with a high crosslink density is shorter than that of a vulcanizate with a low density because elongation at break is an property inversely proportional to the degree of crosslink density.[14] However, the elongations at break of the vulcanizates containing KNB 25M and KNB 35M are higher than that of the vulcanizate without NBR. This may be due to the improved silica dispersion from the addition of NBR.

CONCLUSIONS

With the addition of NBR to the silica-filled SBR compounds, the silica dispersion is improved, the cure rate becomes faster, and the physical properties are improved. NBR is more compatible with silica than SBR, and the compatibility increases with an increase in the acrylonitrile content of NBR. The cure rate becomes faster and the crosslink density increases with an increase in the acrylonitrile content of NBR. On account of the viscosity of the compound and the physical properties of the vulcanizates, the advisable NBR content will be about 5 phr because the compound has a lower viscosity and the vulcanizate has a longer elongation at break, higher tensile strength, improved wear properties, and higher modulus.

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