

Improvement of Properties of Silica-Filled Styrene–Butadiene Rubber Compounds Using Acrylonitrile–Butadiene Rubber

SUNG-SEEN CHOI

Kumho Research and Development Center, 555, Sochon-dong, Kwangsan-gu, Kwangju 506-040, South Korea

Received 13 August 1999; accepted 14 January 2000

ABSTRACT: Since silica has strong filler–filler interactions and adsorbs polar materials, a silica-filled rubber compound has a poor dispersion of the filler and poor cure characteristics. Improvement of the properties of silica-filled styrene–butadiene rubber (SBR) compounds was studied using acrylonitrile–butadiene rubber (NBR). Viscosities and bound rubber contents of the compounds became lower by adding NBR to the compound. Cure characteristics of the compounds were improved by adding NBR. Physical properties such as modulus, tensile strength, heat buildup, abrasion, and crack resistance were also improved by adding NBR. Both wet traction and rolling resistance of the vulcanizates containing NBR were better than were those of the vulcanizate without NBR. The NBR effects in the silica-filled SBR compounds were compared with the carbon black-filled compounds. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1127–1133, 2001

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

INTRODUCTION

Silica¹ has a number of hydroxyl groups on the surface, which results in strong filler–filler interactions and adsorption of polar materials by hydrogen bonds.¹ Since silica has the strong filler–filler interactions, filler dispersion of a silica-filled rubber compound is worse than that of a carbon-filled one. 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 func-

tional groups such as amide (=NH), they are adsorbed well on the silica surface.¹ 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 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.^{1–4} 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.

Acrylonitrile–butadiene rubber (NBR) has nitrile groups (—CN). Since the nitrile group is basic, one can expect that it will make a hydrogen bond with silica. In this work, the influence of NBR on the properties of silica-filled styrene–butadiene rubber (SBR) compounds was studied by adding 5.0–15.0 phr of NBR to the silica-filled

Table I Formulations (phr)

Ingredients	Compound No.							
	S1	S2	S3	S4	C1	C2	C3	C4
SBR 1500	100.0	95.0	90.0	85.0	100.0	95.0	90.0	85.0
KNB 35L	0.0	5.0	10.0	15.0	0.0	5.0	10.0	15.0
Z 175	50.0	50.0	50.0	50.0	0.0	0.0	0.0	0.0
Si 69	3.0	3.0	3.0	3.0	0.0	0.0	0.0	0.0
N 330	0.0	0.0	0.0	0.0	50.0	50.0	50.0	50.0
Stearic acid	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
HPPD	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
TBBS	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
Sulfur	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
DPG	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

SBR 1500: styrene-butadiene rubber with 23.5% of styrene content; KNB 35L: acrylonitrile-butadiene rubber with 35% acrylonitrile content; Z 175: silica; Si 69: silane coupling agent, bis-(3-(triethoxysilyl)propyl)tetrasulfide (TESPT); N 330: carbon black; HPPD: *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine; DPG: diphenylguanidine; TBBS: *N*-*tert*-butyl-2-benzothiazole sulfenamide.

SBR compounds. The study was focused on the reduction of the curative adsorption and improvement of the filler dispersion by the addition of NBR. Properties of carbon black-filled SBR compounds containing NBR were also investigated to compare with the silica-filled ones.

EXPERIMENTAL

The silica-filled SBR compounds were made of SBR, NBR (0.0–15.0 phr), silica, the silane coupling agent, cure activators (stearic acid and ZnO), antidegradants (HPPD and wax), and curatives (TBBS, DPG, and sulfur). KNB 35L with an acrylonitrile content of 35 wt % (Korea Kumho Petroleum Co., South Korea) was used as the NBR. Z 175 (pH 6.9, BET = 175 m²/g) of Kofran was used as silica. In general, silica-filled rubber compounds contain poly(ethylene glycol) to prevent adsorption of curatives on the silica surface. In this work, poly(ethylene glycol) was not used in order to enlarge the NBR effect. The formulations are given in Table I. Carbon black-filled compounds did not contain the silane coupling agent or DPG. The master-batch (MB) stage was performed in a Banbury-type mixer at a rotor speed of 40 rpm, while final mixing (FM) was carried out in a two-roll mill. The initial temperature of the mixer was 110°C. The two-roll mill was kept at 100°C during the mixing. The MB compounds

were dumped at 3.0 and 4.0 min for the silica- and carbon black-filled compounds, respectively. The silica-filled MB compounds were prepared as follows: (1) The rubbers were loaded into the mixer and premixed for 0.5 min. (2) The silica and the silane coupling agent were compounded into the rubbers for 2.0 min. (3) The cure activators and antidegradants were mixed for 1.5 min and the compounds were dumped. The carbon black-filled MB compounds were prepared as follows: (1) The rubbers were loaded into the mixer and preheated for 0.5 min. (2) The carbon black and ingredients were compounded into the rubbers for 2.5 min and the compounds were dumped. The FM compounds were prepared by mixing the curatives with the MB compounds for 4.0 min in a two-roll mill.

Viscosities of the compounds were measured using a Mooney MV 2000 of Alpha Technologies. The contents of the 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 temperature. Weights of the samples before and after the extraction were measured and the bound rubber contents were calculated. The bound rubber composition was determined using pyrolysis gas chromatography (pyrolysis-GC). The analysis conditions for the pyrolysis-GC were described in detail elsewhere.⁵ Quantitative analysis of the rubber composition of the bound rubber

Table II Viscosities, Contents, and Compositions of Bound Rubber and Total Sulfur Contents

Measurements	Compound No.							
	S1	S2	S3	S4	C1	C2	C3	C4
Mooney viscosity (ML 1 + 4) at 100 and 130°C for MB and FM compounds								
MB compounds	97.7	92.1	91.5	94.4	70.5	71.3	70.6	70.7
FM compounds	98.0	93.0	90.8	92.0	72.3	72.9	72.1	72.2
Bound rubber contents (%)								
MB compounds	30.50	26.24	27.03	27.33	18.73	19.84	20.24	20.91
FM compounds	36.36	34.63	34.85	36.46	22.68	21.78	21.84	23.98
NBR content of the bound rubber (%)								
MB compounds	0	9	>15	>15	0	4	9	13
FM compounds	0	6	>15	>15	0	5	9	>15
Total sulfur content obtained using a sulfur determinator (wt %)	1.43	1.47	1.40	1.42	1.42	1.44	1.44	1.46

was carried out by calibration using the FM compounds. The cure characteristics were obtained using a Flexsys rheometer (MDR 2000) at a frequency of 100 cycles/min and ± 1.5 arc at 145 and 160°C. The vulcanizates were prepared by curing at 160°C for 30 min. The 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. $\tan \delta$ of the vulcanizates were measured according to ASTM D2231-87 with a Qualimeter Eplexor 150N of Gabo Co. Flex cracking resistance was measured with a DMFC tester (FT-1503, 300 cpm).

RESULTS AND DISCUSSION

Besides the physical properties of the vulcanizates, properties of the compounds such as viscosity, bound rubber content, bound rubber composition, and cure characteristics were investigated.

Mooney Viscosity

The viscosity of a rubber compound is a very important property in the manufacturing of rubber goods. Filled rubber compounds should have proper viscosities to meet good extrusion and calendaring properties. Viscosities of rubber compounds become lower during the mixing by shear force,⁶⁻¹⁰ which leads to scission of rubber chains.

The chain scission results in decrease of the molecular weight distributions.^{9,10}

Table II gives the Mooney viscosities of the MB and FM compounds. In general, the Mooney viscosity is measured at 100°C. In this study, the Mooney viscosities of the FM compounds were measured at 100°C while those of the MB compounds were measured at 130°C because their initial viscosities were very high. Mooney viscosities of the carbon black-filled compounds containing NBR (compounds C2–C4) are nearly the same as that of the carbon black-filled one without NBR (compound C1). For the silica-filled compounds, however, Mooney viscosities of the compounds are lower when they contain NBR (compounds S2–S4) than when without NBR (compound S1). If the filler is dispersed well in polymers, its viscosity will be lowered. Thus, this implies that the NBR makes the silica dispersion improve. This may be due to the adsorption of NBR on the silica surface by hydrogen bonds between hydroxyl groups of silica and acrylonitrile groups of NBR. The adsorption of NBR results in weakness of the filler–filler interactions, which leads to a good dispersion of the filler. Detailed evidence for the improvement of the dispersion of silica in the silica-filled compounds containing NBR are discussed in the later section.

Content and Composition of Bound Rubber

Carbon black becomes incorporated and dispersed in the rubber during the mixing process. In gen-

eral, the incorporation process refers to the wetting of carbon black with rubber and squeezing out entrapped air. It is suggested that during the initial stages of carbon black incorporation the filler becomes compressed by the polymer into many discrete cavities. At that time, the carbon black is being crushed by the shearing and compressive forces. Subsequently, rubber is forced into those voids and air expelled. The contents of the bound rubber in filled rubber compounds are important because they affect the physical properties of their vulcanizates.^{11,12}

The bound rubber contents of the MB and FM compounds were measured. The bound rubber contents of the FM compounds are more abundant than are those of the MB ones (Table II). This is due to the reaction between the polymer and filler activated by sulfur and TBBS. Carbon black reacts with sulfur and the cure accelerator and $\equiv\text{CS}\cdot$ radicals or $\equiv\text{CX}$ (X is SH or residues of a cure accelerator) are formed.¹³ These radicals react with polymers, and chemical bonds between the filler and polymer are formed. The bound rubber contents of the silica-filled compounds are more abundant than are those of the carbon black-filled ones. This may be due to the silane coupling agent (Si 69) which has ethoxy groups to react with hydroxyl groups of silica and also has a polysulfide linkage to react with rubber molecules. The silane coupling agent reacts with hydroxyl groups of the silica, so it is bonded to the silica. A polysulfide of the silane coupling agent is dissociated with ease at high temperatures. The sulfide radicals react with the rubber molecules so the polymers are bound to the silica.

The bound rubber contents of the carbon black-filled compounds containing NBR are more abundant than are those of the compound without NBR. However, the bound rubber contents of the silica-filled MB compounds containing NBR are less abundant than are those of the compound without NBR. This may be due to the adsorption of NBR to the silica. Since NBR has nitrile groups ($-\text{C}\equiv\text{N}$) which form hydrogen bonds with hydroxyl groups of the silica, it will be adsorbed well to the silica. The adsorption of NBR on the silica surface can prevent the silane coupling agent from reacting with the silica. Thus, reactions between the silica and SBR by the silane coupling agent are reduced, which results in reduction of the bound rubber contents.

The rubber composition of the bound rubber was measured using pyrolysis-GC to investigate the influence of NBR on properties of the silica-



Figure 1 Photograph of the silica-filled rubber vulcanizate for the compound S1 obtained using an optical microscope ($\times 1000$).

filled compounds. The FM compounds were used as reference samples to determine the NBR content of the bound rubber. The NBR contents of the samples were determined using the relative peak intensity of acrylonitrile and styrene in the pyrolysis-GC chromatograms compared those of the references. Thus, the NBR content of the bound rubber with more than 15% NBR could not be determined exactly. The results are listed in Table II. For the carbon black-filled compounds, the NBR contents of the bound rubbers do not exceed the NBR contents of the compounds except for the FM compound of compound C4 and the difference in the NBR contents of the bound rubbers and the compounds is very small. The rubber composition of the bound rubbers of the silica-filled compounds shows a different trend to the carbon black-filled compounds. The NBR contents of the bound rubbers of the silica-filled compounds are much larger than are those of the compounds. These phenomena appear more clearly in the MB compounds. The NBR contents of the bound rubbers of the silica-filled MB compounds are about twice as much as are the NBR content of the compounds. This may be also due to the good adsorption of NBR on the silica as discussed above.

Dispersion of Silica

To investigate the NBR effect on the dispersion of silica, the degree of dispersion of silica was investigated by optical microscopy. Figures 1–4 are photographs of the silica-filled SBR vulcanizates

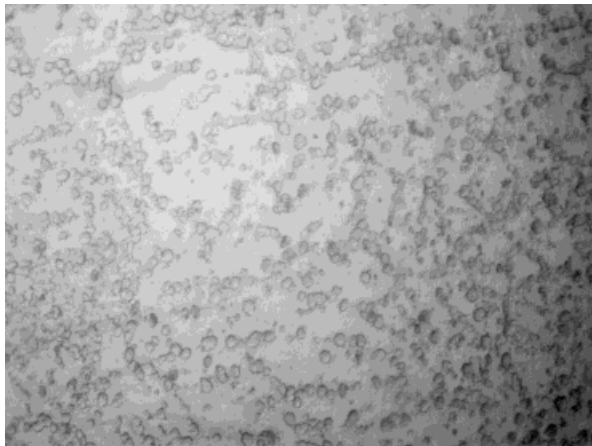


Figure 2 Photograph of the silica-filled rubber vulcanizate for the compound S2 obtained using a optical microscope ($\times 1000$).

for compounds S1–S4, respectively. The silica-filled compound without NBR has a very poor dispersion of silica. Figure 1 shows that silica agglomerates are clustered. The sizes of the silica agglomerates in the silica-filled compound without NBR are larger than are those in the compounds containing NBR. For the silica-filled compounds containing NBR, silica agglomerates are not clustered and silica is dispersed to some extent. This can be explained by the adsorption of NBR on the silica. The NBR adsorbed on the silica surface reduces the filler–filler interactions so that the silica is dispersed well into the rubber.

Cure Characteristics

The cure characteristics of the compounds were investigated at 160 and 170°C. Delta torque (dif-



Figure 3 Photograph of the silica-filled rubber vulcanizate for the compound S3 obtained using a optical microscope ($\times 1000$).



Figure 4 Photograph of the silica-filled rubber vulcanizate for the compound S4 obtained using a optical microscope ($\times 1000$).

ference between the maximum and minimum torques), scorch time (t_{02}), medium cure time (t_{40}), and optimum cure time (t_{90}) are listed in Table III. The delta torques of the carbon black-filled compounds containing NBR are nearly the same as that of the compound without NBR. For the silica-filled compounds, the delta torques of the compounds containing NBR are higher than that of the compound without NBR by over 6%. This is a very interesting fact. To prove that this does not result from experimental errors, the total sulfur contents of the compounds were measured with a sulfur determinator (LECO SC-132). The analysis results are summarized in Table II. The total sulfur contents of all the silica-filled compounds are nearly the same. Thus, the difference in the delta torques of the silica-filled compounds due to the addition of NBR does not result from the experimental errors. This is because the NBR adsorbed on the silica prevents the silica from adsorbing the curatives. The delta torques depend mainly on amounts of the free curatives in the compounds.

The t_{02} , t_{40} , and t_{90} of the carbon black-filled compounds become faster as the NBR content of the compound increases. This may be due to the nitrile groups of NBR. Since the nitrile groups are polar, they can serve as a ligand of zinc complexes. The zinc complexes activated by the nitrile groups can react fast so that crosslinking reactions will also proceed fast. For the silica-filled compounds, the t_{40} and t_{90} of the compounds become faster by increasing the NBR content. This may be due to the reduction of the curative adsorption and the activation of the zinc complexed

Table III Cure Characteristics

Characteristics	Compound No.							
	S1	S2	S3	S4	C1	C2	C3	C4
At 160°C								
T_{\min} (N m)	0.60	0.61	0.61	0.62	0.46	0.48	0.49	0.51
T_{\max} (N m)	4.00	4.23	4.28	4.28	3.73	3.89	3.75	3.70
Delta torque (N m)	3.40	3.62	3.67	3.66	3.27	3.41	3.26	3.19
t_{02} (min)	1.03	1.10	1.00	0.75	3.35	3.18	2.68	1.90
t_{40} (min)	7.82	5.55	4.87	4.52	9.55	7.92	6.58	4.87
t_{90} (min)	11.72	8.55	7.72	7.323	14.60	11.70	9.73	7.68
At 170°C								
T_{\min} (N m)	0.45	0.46	0.46	0.48	0.34	0.35	0.36	0.37
T_{\max} (N m)	3.26	3.50	3.54	3.57	2.95	3.09	3.02	2.99
Delta torque (N m)	2.81	3.04	3.08	3.09	2.61	2.74	2.66	2.62
t_{02} (min)	0.67	0.72	0.72	0.63	1.57	1.52	1.42	1.18
t_{40} (min)	4.38	3.33	2.95	2.75	5.75	4.83	4.02	2.97
t_{90} (min)	7.17	5.55	5.12	4.98	8.78	7.58	6.27	4.85

by NBR. The t_{02} 's of the silica-filled compounds containing NBR of 5.0 and 10.0 phr are slightly slower than that of the compound without NBR. This implies that for the silica-filled SBR compounds the addition of NBR makes the cure rate fast without acceleration of the scorch time when the NBR content is equal or less than 10 phr.

Physical Properties

The physical properties of the vulcanizates such as hardness, modulus, tensile strength, elongation at break, heat buildup, and crack resistance were measured. Their wear property and dynamic

property ($\tan \delta$) were also measured. The results are listed in Table IV. For the carbon black-filled vulcanizates, the hardnesses and moduli of the vulcanizates containing NBR are higher than are those of the vulcanizate without NBR, but the tensile strengths of the former are lower than that of the latter. The heat buildup, crack resistance, and wear property of the former are worse than those of the latter.

For the silica-filled vulcanizates, the hardnesses, moduli, and tensile strengths of the vulcanizates containing NBR are higher than are those of the vulcanizate without NBR, while the elongation at break of the former are lower than

Table IV Physical Properties

Properties	Compound No.							
	S1	S2	S3	S4	C1	C2	C3	C4
Hardness (shore A)	64.0	67.0	68.0	69.0	65.0	66.0	67.0	69.0
50% modulus (kg/cm ²)	14.2	15.8	16.4	17.1	15.2	15.6	16.4	17.0
100% modulus (kg/cm ²)	21.0	23.5	24.4	26.4	24.4	25.6	26.9	28.7
200% modulus (kg/cm ²)	45.5	52.4	55.5	59.6	64.3	66.7	70.1	72.3
300% modulus (kg/cm ²)	80.9	93.7	98.5	105.0	117.4	122.1	123.0	125.0
Tensile strength (kg/cm ²)	229.2	250.0	243.8	249.9	253.9	246.5	235.4	243.9
Elongation at break (%)	586.3	582.1	559.3	555.3	551.4	529.4	516.6	535.9
Heat buildup (°C)	35.1	33.7	35.0	34.4	37.0	37.0	38.3	40.3
Dematia flex-cracking test (20,000 cycles)								
Crack size (mm)	12.7	12.6	8.4	8.8	6.4	12.7	16.3	11.4
Abrasion loss (mg)	32.0	29.0	31.0	30.0	26.0	30.0	29.5	31.0

Table V Tan δ

Temperature	Compound No.							
	S1	S2	S3	S4	C1	C2	C3	C4
-20°C	0.378	0.350	0.369	0.377	0.368	0.359	0.374	0.369
0°C	0.182	0.198	0.227	0.229	0.202	0.220	0.235	0.256
10°C	0.159	0.162	0.178	0.176	0.194	0.204	0.212	0.220
50°C	0.122	0.118	0.121	0.120	0.150	0.152	0.160	0.162
60°C	0.118	0.113	0.117	0.114	0.145	0.147	0.155	0.157
70°C	0.114	0.109	0.113	0.110	0.141	0.143	0.151	0.153

are those of the latter. This is because the crosslink densities of the vulcanizates containing NBR are higher than is that of the vulcanizate without NBR. The heat buildup, crack resistance, and wear property of the former are also better than are those of the latter. This can be also explained by the higher crosslink densities of the vulcanizates containing NBR. Thus, it can lead to a conclusion that the addition of NBR to the silica-filled SBR compounds make the physical properties of the vulcanizates improve. The elongation at break of the vulcanizate containing NBR of 5.0 phr is longer than are those of the vulcanizates containing NBR of 10.0 and 15.0 phr. The heat buildup and abrasion property of the former are better than are those of the latter.

Tan δ values at 0 and 60°C reflect the wet traction and the rolling resistance, respectively (Table V). The larger the tan δ value at 0°C, the better is the wet traction property of a vulcanizate. The smaller the tan δ value at 60°C, the better is the wear property of a vulcanizate. Tan δ at 0°C of the silica-filled vulcanizates containing NBR are higher than is that of the vulcanizate without NBR, while the tan δ 's at 60°C of the former are lower than is that of the latter. This means that the properties for the wet traction and the rolling resistance of the silica-filled SBR vulcanizates are improved by adding NBR. The improvement of the rolling resistance may be due to the increase of the crosslink densities. The improvement of the wet traction may be due to the increase of the hydrophilic groups of the nitrile groups by adding NBR. For the carbon black-filled vulcanizates, both the tan δ at 0 and 60°C of the vulcanizates containing NBR are higher than are those of the vulcanizate without NBR. This implies that the wet traction properties of the former are better than are that of the latter, while the rolling resistance properties of the former are worse are that of the latter.

CONCLUSIONS

By adding NBR to the silica-filled SBR compounds, dispersion of the filler was improved notably and the cure rates (t_{40} and t_{90}) became faster without acceleration of the scorch time (t_{02}). The delta torques of the silica-filled compounds containing NBR were higher than was that of the compound without one due to the reduction of the curative adsorption on the silica. The physical properties of the silica-filled vulcanizates were, on the whole, improved by the addition of NBR. Properties for the wet traction and the rolling resistance of the silica-filled vulcanizates containing NBR were better than was that of the vulcanizate without NBR. It was found that the properties of the silica-filled SBR compounds and vulcanizates were improved by adding only NBR of 5.0 phr.

REFERENCES

1. Byers, J. T. *Rubber World* 1998, 219(2), 38.
2. Görl, U.; Hunsche, A. In *Proceedings of the Rubber Division 150th Meeting*, American Chemical Society, Paper No. 76, 1996.
3. Görl, U.; Hunsche, A. In *Proceedings of the Rubber Division 151st Meeting*, American Chemical Society, Paper No. 38, 1997.
4. Hashim, A. S.; Azahari, B.; Ikeda, Y.; Kohjiya, S. *Rubb Chem Technol* 1998, 71, 289.
5. Choi, S.-S. *J Anal Appl Pyrolysis* 1999, 52, 105.
6. Ahagon, A. *Rubb Chem Technol* 1996, 69, 742.
7. Bhatnagar, S. K.; Banerjee, S. *Rubb Chem Technol* 1965, 38, 961.
8. Angier, D. J.; Chambers, W. T.; Watson, W. F. *Rubb Chem Technol* 1958, 31, 73.
9. Imoto, M. *Rubb Chem Technol* 1952, 25, 234.
10. Bristow, G. M. *Rubb Chem Technol* 1962, 35, 896.
11. Sperberg, L. R.; Svetlik, J. F.; Bliss, L. A. *Ind Eng Chem* 1949, 41, 1607.
12. Brennan, J. J.; Jermyn, T. E. *Rubb Chem Technol* 1967, 40, 817.
13. Gessler, A. M. *Rubb Chem Technol* 1969, 42, 858.