

Filler-Polymer Interactions in Filled Styrene-Butadiene Rubber Compounds

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Abstract : Formation of bound rubber depends on the filler-polymer interactions including physical adsorption, chemisorption, and mechanical interaction. Bound rubbers consist of tightly and loosely bound ones. Styrene-butadiene rubber (SBR) is composed of styrene, 1,2-, *cis*-1,4-, and *trans*-1,4-units. Filler-polymer interactions of each components of SBR with fillers, carbon black and silica, were studied by analysis of microstructure of the bound rubber. Filler-polymer interaction of the 1,2-unit with the fillers was found to be stronger than those of the other components and this phenomenon was shown more clearly in the tightly bound rubber.

Introduction

Bound rubber, filler gel, phenomenon and its effect on properties of filled rubber compounds and vulcanizates have been studied.¹⁻¹⁰ The early concept for bound rubber, which is a gel of carbon black particles held together in a three-dimensional lattice by polymer molecules, is still valid. The bound rubber depends on characteristics of filler such as surface area, structure or morphology, and surface activity. With regard to the polymer, the chemical structure (saturated vs. unsaturated, polar vs. nonpolar) and the microstructure (configuration, molecular weight, and molecular weight distribution) influence the level of bound rubber content.

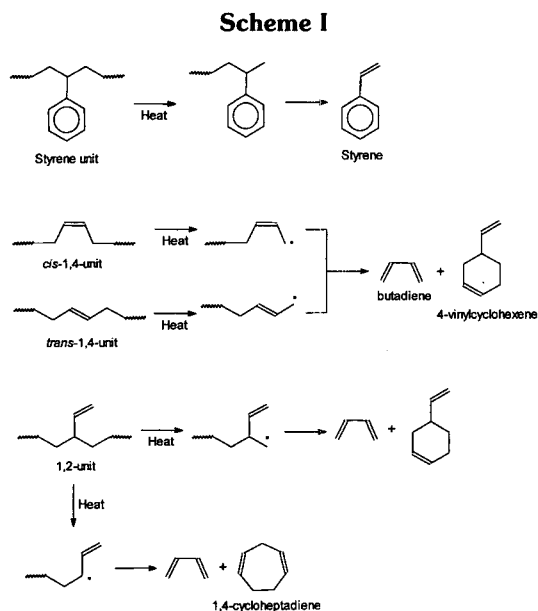
Bound rubber is a parameter which is simple to measure but the factors which influence the test results are very complicated. The filler-polymer interaction leading to the formation of bound rubber involves physical adsorption, chemisorption, and mechanical interaction. Moreover, bound rubber also depends on the processing conditions of the compound, such as mixing and storage times. Factors affecting the bound rubber content during the measurement are the nature of the solvent and the

temperature of extraction.

Silica has been used as an important reinforcing agent in a rubber compound together with carbon black.¹¹⁻¹⁴ Silica has a number of hydroxyl groups on the surface, which results in strong filler-filler interactions and adsorption of polar materials by hydrogen bonds.^{11,15,16} In general, silane coupling agent such as bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) is used to improve the silica dispersion and to prevent adsorption of curatives on the silica surface.^{11,17-19} Styrene-butadiene rubber (SBR) is a copolymer of styrene and butadiene. Butadiene unit can have three different components, 1,2-, *cis*-1,4-, and *trans*-1,4-units. Thus, SBR can have various microstructures depending on the component ratios of the styrene, 1,2-, *cis*-1,4-, and *trans*-1,4-units. Scheme I shows the four components.

The use of pyrolysis-gas chromatography (pyrolysis-GC) has been used for the characterization and analysis of polymers.²⁰⁻²⁴ Pyrolysis products of SBR were analyzed and the major pyrolysis products are butadiene, 1,4-cycloheptadiene, 4-vinylcyclohexene, and styrene.^{20,25-27} Pyrolysis pattern of SBR depends on the microstructures. In the present work, filler-polymer interactions of each components of SBR with fillers, carbon black and

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silica, were studied by analysis of microstructure of the bound rubber using pyrolysis-GC. Difference in rubber composition of the loosely and tightly bound rubbers was investigated.

Experimental

The silica-filled compound (Compound 1) was made of SBR, silica, silane coupling agent, cure activators (stearic acid and ZnO), and anti-degradants (HPPD and wax). The silane coupling agent (Si 69) of 8.0 wt% of the silica content was

added. The carbon black-filled compound (Compound 2) contains carbon black instead of silica. The both silica and carbon black-filled compounds (both-filled compounds, Compounds 3-5) contain both silica and carbon black. The content ratios of silica/carbon black were 20.0/60.0, 40.0/40.0, and 60.0/20.0 phr. The silane coupling agent of 8.0 wt% of the silica content was added. The formulations were given in Table I.

Mixing was performed in a Banbury type mixer at a rotor speed of 40 rpm. The initial temperature of the mixer was 110°C. The both-filled compounds were prepared as follow. (1) The rubber was loaded into the mixer and preheated for 0.5 min. (2) The silica and silane coupling agent were compounded into the rubber for 1.5 min. (3) The carbon black and the ingredients were mixed for 2.0 min and the compounds were dumped. The silica-filled compound was prepared as follow. (1) The rubber 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 1.5 min. (3) The cure activators and anti-degradants were mixed for 2.0 min and the compound was dumped. The carbon black-filled compound was prepared as follow. (1) The rubber was loaded into the mixer and pre-mixed for 0.5 min. (2) The carbon black and the ingredients were compounded into the rubber for 2.5 min and the compound was dumped.

Content of bound rubber was determined by extracting the unbound materials such as ingredi-

Table I. Formulations (phr)

Compound No.	1	2	3	4	5
SBR 1500	100.0	100.0	100.0	100.0	100.0
Z 175	60.0	0.0	20.0	40.0	60.0
Si 69	4.8	0.0	1.6	3.2	4.8
N 330	0.0	60.0	60.0	40.0	20.0
ZnO	4.0	4.0	4.0	4.0	4.0
Stearic acid	2.0	2.0	2.0	2.0	2.0
HPPD	2.0	2.0	2.0	2.0	2.0
Wax	2.0	2.0	2.0	2.0	2.0

SBR 1500: Styrene-butadiene rubber with 23.5 wt% styrene content.

Z 175: Silica.

Si 69: Silane coupling agent, bis-(3-(triethoxysilyl)-propyl)-tetrasulfide.

N 330: Carbon black.

HPPD: *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine.

ents and free rubbers with toluene for 7 days and *n*-hexane for 1 day and drying for 2 days at room temperature. Measurement of the bound rubber content was performed about 2 months after the mixing of the compounds in order to stabilize sufficiently the samples. The experiments were performed at 30 and 90°C using a convection oven.

Rubber composition of the bound rubbers obtained by extracting the unbound materials at 30 and 90°C was analyzed with Pyrolysis-GC. Pyrolysis-GC chromatograms of the samples were acquired with Curie point pyrolyzer (JHP-22) and gas chromatograph (HP5890). The sample (0.6 ± 0.1 mg) was pyrolyzed for 5 sec. The pyrolysis temperature was 590°C. HP-5 capillary column (length 21m) was used. Temperatures of the injector and detector of the GC were 200°C. The GC oven temperature program was as follows. (1) The initial temperature was 60°C and keeping for 3 min. (2) Increasing the temperature from 60 to 160°C with a rate of 8°C/min.

Results and Discussion

Bound rubbers consist of tightly and loosely bound ones. The loosely bound rubber exists in an outer shell around the filler while the tightly bound rubber is in the immediate vicinity of the filler particle. The tightly bound rubber is much less mobile than the loosely bound rubber.²⁸⁻³⁰ In general, measurement of the bound rubber content is performed under the restricted conditions: at low temperature (near room temperature) and under the static condition, in order to prevent the bound rubber (especially the loosely bound one) from extracting. If the extracting temperature is high or the vessel containing the sample and solvent is shaken, some loosely bound rubber will be extracted. The loosely bound rubber can be extracted by the solvent at high temperature since binding energy of the loosely bound rubber is low. In this study, the tightly bound rubber was obtained by extracting the unbound and loosely

bound rubbers at high temperature of 90°C.

Bound rubber contents of the compounds were listed in Table II. The bound rubber content of the silica-filled compound (Compound 1) is higher than for the carbon black-filled one (Compound 2). For the both silica and carbon black-filled compounds (both-filled compounds, Compounds 3-5), the bound rubber content increases with increase of the silica content ratio. This may be due to the formation of chemical bonds between silica and rubber by the silane coupling agent, Si 69, $(C_2H_5O)_3Si-(CH_2)_3-S_x-(CH_2)_3-Si(OC_2H_5)_3$. The structure of Si 69 is a sulfidic linkage between triethoxysilylpropyl groups. Ethoxy group of the coupling agent reacts with silanol group of the silica to form a siloxane bond. Sulfide group of the coupling agent bonded to the silica is dissociated and reacts with the rubber molecule to form a crosslink between the silica and the rubber. The chemical bonds between silica and rubber enhance the bound rubber formation.

The bound rubber contents measured at 90°C are lower than those measured at 30°C as listed in Table II. This is due to the extraction of loosely bound rubber at the high temperature. Of the total bound rubber content, the loosely bound rubber content can be calculated by the difference between the bound rubber contents measured at 30 and 90°C. The loosely bound rubber contents are 9.91, 7.88, 7.33, 7.26, and 7.81% for the Compounds 1, 2, 3, 4, and 5, respectively. The absolute content of the loosely bound rubber of the silica-filled compound is higher than for the carbon black-filled one. However, portion of the loosely bound rubber content of the total bound rubber content shows a different trend. The portion of loosely bound rubber content is obtained by dividing the absolute content of the loosely bound rubber by the total bound rubber content. The loosely bound rubber portions are 23.38, 31.75, 22.19, 19.35, and 19.14% for the Compounds 1, 2, 3, 4, and 5, respectively. The loosely bound rubber portion of the silica-filled com-

Table II. Bound Rubber Contents (%)

Compound No.	1	2	3	4	5
at 30°C	42.57	24.82	33.03	37.52	40.80
at 90°C	32.66	16.94	25.70	30.26	32.99

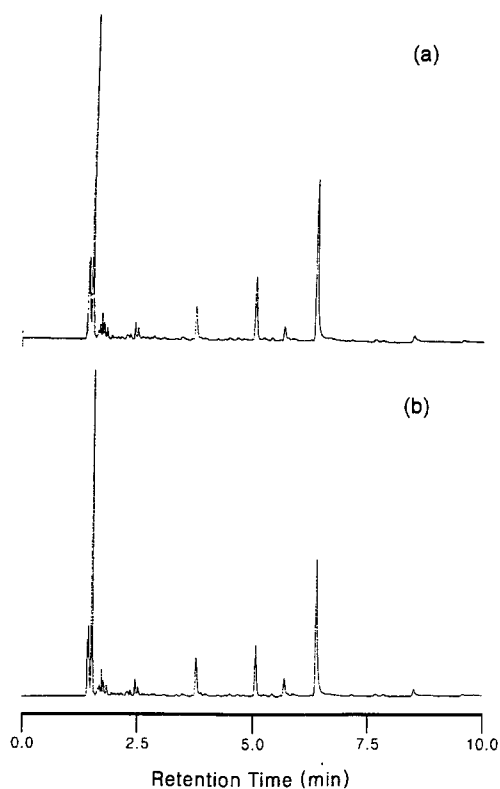


Figure 1. Pyrolysis-GC chromatograms of bound rubbers of the Compound 1. The extracting temperatures are 30°C (a) and 90°C (b).

pound is lower than that of the carbon black-filled one. For the both-filled compounds, the loosely bound rubber portion decreases with increasing the silica content ratio. This is because of formation of chemical bonds between silica and rubber by the silane coupling agent as discussed previously.

Figure 1 gives pyrograms of the bound rubbers obtained at 30 and 90°C. The major volatile pyrolysis products are butadiene (1.49 min), C7 species (3.76 min), 4-vinylcyclohexene (5.05 min), and styrene (6.36 min). The butadiene and 4-vinylcyclohexene are the pyrolysis products formed from all the butadiene units^{24,25} and the styrene is produced from the styrene unit.^{25,31} The C7 species is mostly 1,4-cycloheptadiene which is formed from the butadiene sequence including the 1,2-unit.²⁷ Scheme I shows the mechanism for formation of the major pyrolysis products. Relative peak intensities of the major pyrolysis products

formed from the bound rubber at 30°C is different to those from the bound rubber at 90°C as shown in Figure 1. The relative peak intensities of the bound rubbers obtained at 30°C are 25.64, 4.79, 5.57, and 21.05% for the butadiene, C7 species, 4-vinylcyclohexene, and styrene peaks, respectively, while those at 90°C are 24.52, 6.77, 4.67, and 21.79%, respectively. This implies that rubber compositions of the bound rubbers obtained at 30 and 90°C are different. This also implies that rubber compositions of the loosely and tightly rubbers are different since the bound rubber obtained at 30°C includes the loosely bound one as well as the tightly bound one.

The level of bound rubber formation is basically dependent on the filler-polymer interaction. The stronger the filler-polymer interaction is, the more the bound rubber is formed. It was reported that of the bound rubbers in filled SBR compounds the butadiene units were more abundant than the styrene unit.³² In order to investigate the difference in rubber compositions of the tightly and loosely bound rubbers in detail, peak intensity ratios of the butadiene/styrene and C7 species/4-vinylcyclohexene were calculated from the pyrograms. The results were Figures 2 and 3, respectively. The butadiene/styrene peak intensity ratios indicate the difference in filler-polymer interactions of the butadiene units and the styrene unit since the butadiene is formed from all the butadiene units and the styrene is formed from only the styrene unit. The C7 species/4-vinylcyclohexene peak intensity ratios indicate the difference in filler-polymer interactions of the 1,2-unit and the *cis*-1,4-unit/*trans*-1,4-unit since the C7 species, 1,4-cycloheptadiene, is formed only from the butadiene sequence including the 1,2-unit.

The butadiene/styrene peak intensity ratios of the bound rubbers obtained at 90°C are lower than those of the bound rubbers obtained at 30°C as shown in Figure 2. This implies that the loosely bound rubber contains more butadiene units. The C7 species/4-vinylcyclohexene peak intensity ratios of the bound rubbers (Figure 3) are higher than those of the compounded rubbers (less than 0.6). This implies that the 1,2-unit interacts with the filler stronger than the other components. The C7 species/4-vinylcyclohexene peak intensity ratios

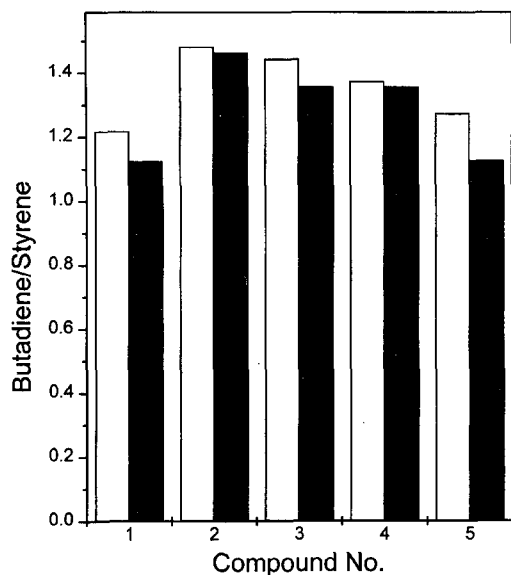


Figure 2. Peak intensity ratios of the butadiene/styrene of the bound rubbers obtained at 30 and 90°C. Open and closed columns indicate the extracting temperatures of 30 and 90°C, respectively.

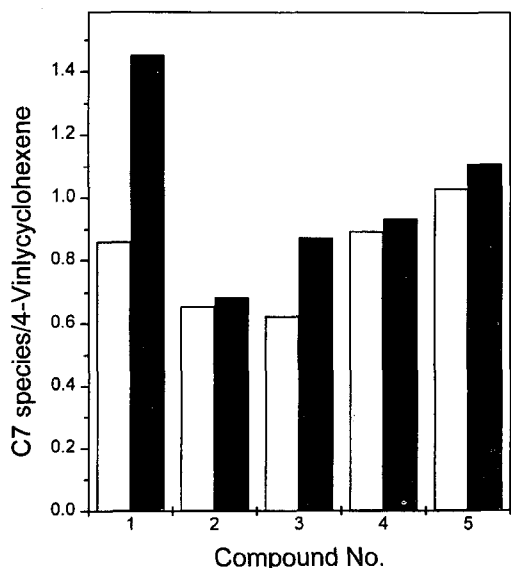


Figure 3. Peak intensity ratios of the C7 species/4-vinylcyclohexene of the bound rubbers obtained at 30 and 90°C. Open and closed columns indicate the extracting temperatures of 30 and 90°C, respectively.

of the bound rubbers obtained at 90°C are higher than those of the bound rubbers obtained at 30°C as shown in Figure 3. This implies that content of

the 1,2-unit is higher of the tightly bound rubber content than of the total bound rubber content. This is also an evidence that the filler-polymer interaction of the 1,2-unit is stronger than that of the *cis*-1,4-unit or *trans*-1,4-unit. The C7 species/4-vinylcyclohexene peak intensity ratio of the silica-filled compound is higher than for the carbon black-filled one by about 30 and 110% for the bound rubbers obtained at 30 and 90°C, respectively. Thus, it can lead to a conclusion that intermolecular interaction of the 1,2-unit with silica is stronger than with carbon black. The difference in filler-polymer interactions of the 1,2-unit and the *cis*-1,4-unit/*trans*-1,4-unit shows more clearly in the tightly bound rubber than in the bound rubber including both loosely and tightly ones.

Conclusion

The bound rubber content of the silica-filled compound is higher than for the carbon black-filled one due to the formation of chemical bonds between silica and rubber by the silane coupling agent. The loosely bound rubber portion of the silica-filled compound is lower than that of the carbon black-filled one. For the both-filled compounds, the loosely bound rubber portion decreases with increasing the ratio of silica content. The loosely bound rubber has a rubber composition of rich butadiene units. Intermolecular interaction of the 1,2-unit with the filler is stronger than for the *cis*-1,4- and *trans*-1,4-units. The filler-polymer interaction of the 1,2-unit with silica is stronger than with carbon black. The difference in filler-polymer interactions of the 1,2-unit and the *cis*-1,4-unit/*trans*-1,4-unit shows more clearly in the tightly bound rubber than in the bound rubber including both loosely and tightly ones.

References

- (1) D. F. Twiss, *J. Soc. Chem. Ind.*, **44**, 1067 (1925).
- (2) A. K. Sircar and A. Voet, *Rubber Chem. Technol.*, **43**, 973 (1970).
- (3) L. R. Sperberg, J. F. Svetlik, and L. A. Bliss, *Ind. Eng. Chem.*, **41**, 1607 (1949).
- (4) E. M. Dannberg, *Rubber Chem. Technol.*, **59**, 512 (1986).
- (5) P. B. Stickney and R. D. Falb, *Rubber Chem. Tech-*

- nol.*, **37**, 1299 (1964).
- (6) B. Meissner, *Rubber Chem. Technol.*, **48**, 810 (1975).
- (7) S. Wolff and M.-J. Wang, *Rubber Chem. Technol.*, **65**, 329 (1992).
- (8) S. Wolff, M.-J. Wang, and E.-H. Tan, *Rubber Chem. Technol.*, **66**, 163 (1993).
- (9) F. Yatsuyanagi, H. Kaidou, and M. Ito, *Rubber Chem. Technol.*, **72**, 657 (1999).
- (10) S.-S. Choi, *Kor. Polym. J.*, **7**, 244 (1999).
- (11) J. T. Byers, *Rubber World*, **218**(6), 38 (1998).
- (12) S. Wolff and M.-J. Wang, *Rubber Chem. Technol.*, **65**, 329 (1992).
- (13) B. B. Boonstra, H. Cochrane, and E. M. Dannenberg, *Rubber Chem. Technol.*, **48**, 558 (1975).
- (14) A. Voet, J. C. Morawski, and J. B. Donnet, *Rubber Chem. Technol.*, **50**, 342 (1977).
- (15) Y.-C. Ou, Z.-Z. Yu, A. Vidal, and J. B. Donnet, *Rubber Chem. Technol.*, **67**, 834 (1994).
- (16) Y. Li, M. J. Wang, T. Zhang, F. Zhang, and X. Fu, *Rubber Chem. Technol.*, **67**, 693 (1994).
- (17) U. Görl and A. Hunsche, in *Proceedings of the Rubber Division 150th Meeting, American Chemical Society*, Paper No. 76 (1996).
- (18) U. Görl and A. Hunsche, in *Proceedings of the Rubber Division 151st Meeting, American Chemical Society*, Paper No. 38 (1997).
- (19) A. S. Hashim, B. Azahari, Y. Ikeda, and S. Kohjiya, *Rubber Chem. Technol.*, **71**, 289 (1998).
- (20) S.-S. Choi, *J. Anal. Appl. Pyrolysis*, **55**, 161 (2000).
- (21) S.-S. Choi, *Bull. Kor. Chem. Soc.*, **20**, 1348 (1999).
- (22) H. Ohtani, S. Ueda, Y. Tsukahara, C. Watanabe, and S. Tsuge, *J. Anal. Appl. Pyrolysis*, **25**, 1 (1993).
- (23) P. Bradna and J. Zima, *J. Anal. Appl. Pyrolysis*, **21**, 207 (1991).
- (24) T. S. Radhakrishnan and M. R. Rao, *J. Polym. Sci.: Polym. Chem. Ed.*, **19**, 3197 (1981).
- (25) J. Hacaloglu, T. Ersen, N. Ertugrul, M. M. Fares, and S. Suzer, *Eur. Polym. J.*, **33**, 199 (1997).
- (26) G. N. Ghebremeskel, J. K. Sekinger, J. L. Hoffpauir, and C. Hendrix, *Rubber Chem. Technol.*, **69**, 874 (1996).
- (27) S.-S. Choi, *J. Anal. Appl. Pyrolysis*, **57**, 249 (2001).
- (28) J. O'Brien, E. Cashell, G. E. Wardell, V. J. McBrierty, *Macromolecules*, **9**, 653 (1976).
- (29) J. C. Kenny, V. J. McBrierty, Z. Rigbi, and D. C. Douglass, *Macromolecules*, **24**, 436 (1991).
- (30) A. P. Legrand, N. Lecomte, A. Vidal, B. Haidar, and E. Papiper, *J. Appl. Polym. Sci.*, **46**, 2223 (1992).
- (31) M. Guaita, *Br. Polym. J.*, **18**, 226 (1986).
- (32) S.-S. Choi, *J. Anal. Appl. Pyrolysis*, **55**, 161 (2000).