Notes

Influence of Silane Coupling Agent on Pyrolysis Pattern of Styrene-Butadiene Rubber in Filled Rubber Compounds

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Received February 22, 2001

The pyrolysis-gas chromatography (pyrolysis-GC) is a useful technique for the characterization and analysis of polymers.[1-5] Styrene-butadien 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 miscrostructures depending on the component ratios of the styrene, 1,2-, *cis*-1,4-, and *trans*-1,4-units. Polymerization of SBR is performed by solution and emulsion processes.[6-8] SBR is widely used for tread compounds of a tire.[9-15] The major pyrolysis products of SBR are butadiene, 4-vinylclcyohexene, and styrene.[1,16,17] In the recent work, an important pyrolysis product formed from the 1,2-unit was reported.[18] 1,4-Cychoheptadiene is formed from only the butadiene sequence including the 1,2-unit.

Silica has been used as an important reinforcing agent in a rubber compound together with carbon black.[19-22] 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.[19,23,24] 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.[19,25-27]

The silane coupling agent in silica-filled rubber compounds is absolutely nesessary. In the present work, influence of the silane coupling agent on the pyrolysis patterns of silica-filled SBR compounds was studied using pyrolysis-GC. Si 69 (TESPT) of Degussa Co. was employed as a silane coupling agent. Not only silica-filled SBR compounds but also carbon black-filled ones were analyzed.

Both the master batch (MB) and final mixing (FM) compounds were analyzed. Figure 1 gives pyrograms of MB compounds of the Compounds C1 and C3 which are the carbon black-filled SBR compounds containing the silane coupling agent of 0.0 and 4.8 phr, respectively. The major volatile pyrolysis products are butadiene (1.66 min), C7-species (3.76 min), 4-vinylcyclohexene (4-VCH, 5.05 min), and styrene (6.37 min). The butadiene and 4-VCH are the pyrolysis products formed from the butadiene units[5,16] and the styrene is produced from the styrene unit.[16,28] The C7-species is mostly 1,4-cycloheptadiene formed from the butadiene sequence including the 1,2-unit.[18] The C7-species is a

pyrolysis product to determine the relative concentration of the 1,2-unit in SBR compounds. Relative peak intensity of the C7-species in the Compound C3 containing the silane coupling agent of 4.8 phr is higher thant that in the Compound C1 without the silane. This implies that the silane coupling agent affects the pyrolysis pattern of the SBR compound.

The peak intensity ratios of butadiene and styrene were calculated from the pyrolysis-GC chromatograms in order to investigate variation of the butadiene/styrene ratio with the silane content (Table 2). Variation of the butadiene/styrene ratio with the silane content does not show a specific trend. The butadiene/styrene ratios are nearly the same, irrespective
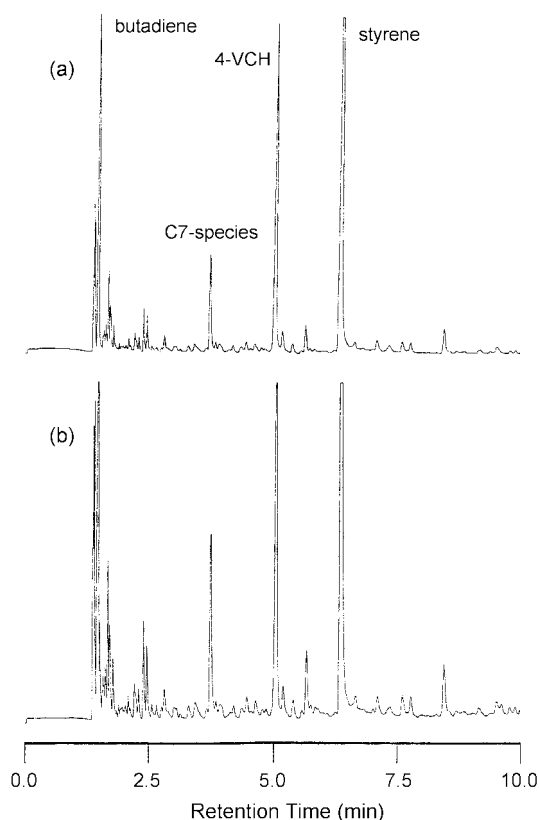

Figure 1. Pyrolysis-GC chromatogram of the MB compounds of the Compound No. C1 (a) and C3 (b).
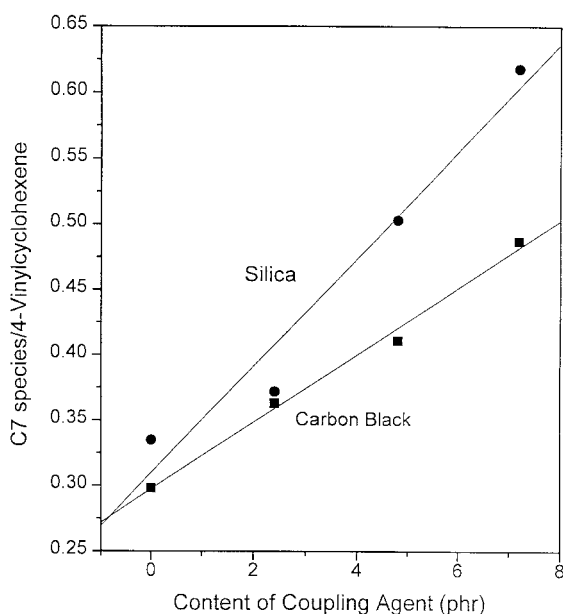
Figure 2. Variation of the peak intensity ratio of c7 species and 4-vinylcyclohexene of the MB compounds as a function of content of the silane coupling agent. Rectangles and circles indicate the carbon black-filled and silica-filled compounds, respectively.

Figure 3. Variation of the peak intensity ratio of c7 species and 4-vinylcyclohexene of the FM compounds as a function of content of the silane coupling agent. Rectangles and circles indicate the carbon black-filled and silica-filled compounds, respectively.
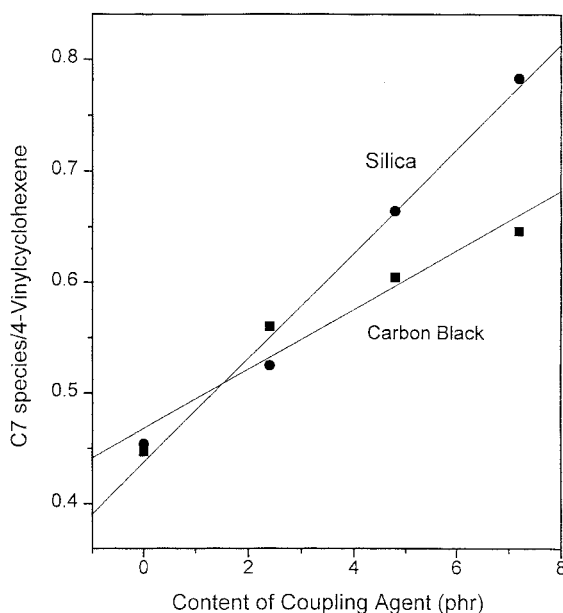
of the silane contents. This implies that the silane does not affect the relative peak intensity ratio of butadiene and styrene.

The peak intensity ratios of C7-species and 4-VCH were calculated from the pyrograms in order to investigate variation of the C7-species/4-VCH ratio with the silane content (Figures 2 and 3). Variation of the C7-species/4-VCH ratio with the silane content shows a specific trend. The C7-species/4-VCH ratio increases linearly with increasing the
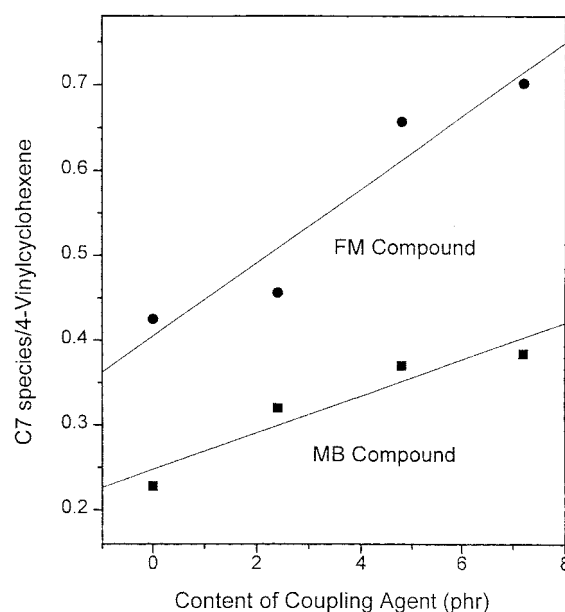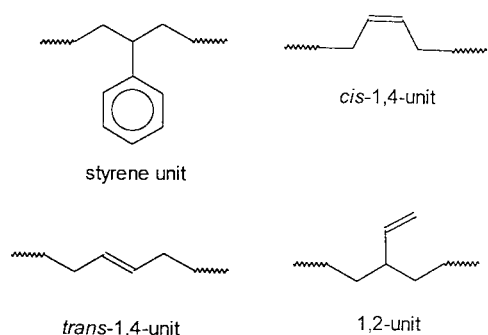

Figure 4. Variation of the peak intensity ratio of c7 species and 4-vinylcyclohexene of the unfilled compounds as a function of content of the silane coupling agent. Rectangles and circles indicate the MB and FM compounds, respectively.

silane content in the compound. This implies that the silane affects formation of the C7-species and 4-VCH.
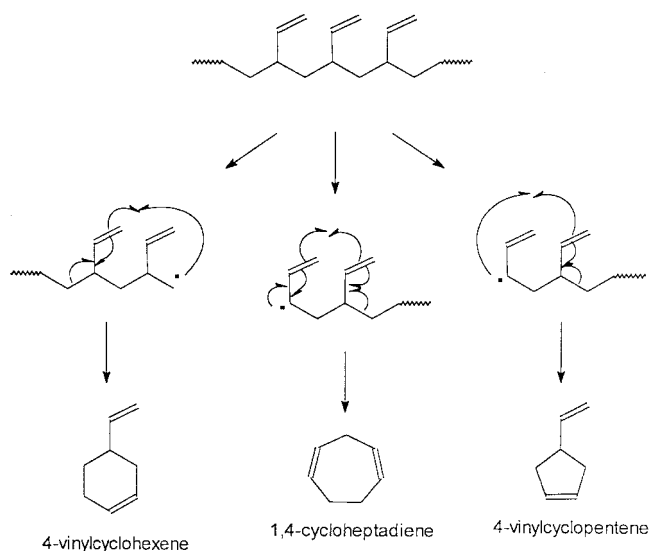
In order to investigate the influence of the filler on the formation of C7-species and 4-VCH, unfilled SBR compounds (without any fillers) were analyzed. The C7-species/4-VCH ratio of the unfilled compounds also increases with an increase in the silane content (Figure 4). This implies that the filler hardly affect the formation of C7-species and 4-VCH. The C7-species/4-VCH ratios of the unfilled FM compounds are higher than those of the MB compounds. This implies that the C7-species/4-VCH ratio is affected by the cure accelerator (TBBS) as well as the silane coupling agent.

Both TBBS and Si 69 can react with rubber chains to form a pendent group. The silane coupling agent has polysulfide linkage so can be dissociated at high temperature with ease to form a sulfide radical. The sulfide radical will reacts with a rubber molecule to form a pendent group terminated by the silane residue (Scheme 1). TBBS is dissociated into mercaptobenzothiazole (MBT) and *t*-butylamine radicals by heating.[29] The MBT radical will be a pendent group formed by pending to a rubber chain.[30-32] The *t*-butylamine radical can be also a pendent group formed by pending to a rubber chain.[31] The C-S bond between the rubber and the pendent goup is weaker than the C-C bonds in the backbone of the polymer so the C-S bonds are dissociated more easily than the C-C ones. It can be considered that radicals formed by dissociation of the C-S bonds during heating in the pyrolyzer affect formation of the pyrolysis prodcuts.

The C-S bond between the rubber and pendent group is dissociated by pyrolysis to form a radical on the rubber molecule. The radaical is rearranged to form a pyrolysis product. When the pendent group is formed between the 1,2-

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Bull. Korean Chem. Soc. **2001**, Vol. 22, No. 10   1147

Scheme 1

Scheme 2

Table 1. Formulations (phr)

Compound No.	C1	C2	C3	C4	S1	S2	S3	S4
SBR 1500	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
N 330	60.0	60.0	60.0	60.0	0.0	0.0	0.0	0.0
Z 175	0.0	0.0	0.0	0.0	60.0	60.0	60.0	60.0
Si 69	0.0	2.4	4.8	7.2	0.0	2.4	4.8	7.2
ZnO	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
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	1.6	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

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

Table 2. Peak intensity ratios of the butadiene and styrene (butadiene/styrene)

Content of Si 69 (phr)	0.0	2.4	4.8	7.2
Carbon black-filled compounds				
MB compounds	1.52	1.56	1.55	1.54
FM compounds	1.42	1.40	1.44	1.45
Silica-filled compounds				
MB compounds	1.47	1.56	1.60	1.59
FM compounds	1.40	1.39	1.38	1.37

unit and the *cis*-1,4-unit (or *trans*-1,4-unit), the C7-species can be formed by rearrangement as shown in Scheme 2. The pendent groups will be increased with increasing the silane coupling agent and the cure accelerator. Thus, the 4-VCH increases with an increase in the silane content.

The C7-species/4-VCH ratios of the silica-filled compounds are higher than those of the carbon black-filled ones for both the MB and FM compounds. Variation of the C7-species/4-VCH ratio with the silane content for the silica-filled compounds is more sensitive than for the carbon black-filled ones. For the MB compounds, the slopes calculated from the curve fitting equations are 0.041 and 0.026 for the silica-filled and carbon black-filled compounds, respectively. For the FM compounds, the slopes are 0.047 and 0.027, respectively. This implies that the silica-filled compounds are more sensitive to the silane content than the carbon black-filled ones. This may be due to the fact that silica is more reactive with the silane coupling agent than carbon black.

From the experimental results, it can lead to a conclusion that the formation of C7-species and 4-VCH is affected by content of the silane. When a SBR compound has a high silane content, results of the pyrolysis analysis will say that the 1,2-unit content in the sample is higher than the real 1,2-unit content.

Experimental Section

Carbon black-filled and silica-filled SBR compounds were prepared. They were made of SBR, filler (carbon black or silica), silane coupling agent, cure activators (stearic acid and ZnO), antidegradants (HPPD and wax), and curatives (TBBS and sulfur). The filler content was 60.0 phr. Si 69 of Degussa Co. was employed as a silane coupling agent. The silane coupling agents of 0.0, 4.0, 8.0, and 12.0 wt% of the filler content were added. The formulations are given in Table 1. Mixing was performed in a Banbury type mixer at a rotor speed of 40 and 30 rpm for 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.

Analysis of pyrolysis products of the compounds was performed with pyrolysis-GC. Pyrolysis-GC chromatograms of the samples were acquired with a Curie point pyrolyzer JHP-22 and an HP5890 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. Temperatures of the injector and detector (FID) 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 °C to 160 with a rate of 8 °C/min. The analysis conditions for the pyrolysis-GC were described in detail elsewhere.[33]

References

1. Choi, S.-S. *J. Anal. Appl. Pyrolysis* **2000**, *55*, 161.
2. Choi, S.-S. *Bull. Korean Chem. Soc.* **1999**, *20*, 1348.
3. Ohtani, H.; Ueda, S.; Tsukahara, Y.; Watanabe, C.; Tsuge, S. *J. Anal. Appl. Pyrolysis* **1993**, *25*, 1.
4. Bradna, P.; Zima, J. *J. Anal. Appl. Pyrolysis* **1991**, *21*, 207.
5. Radhakrishnan, T. S.; Rao, M. R. *J. Polym. Sci.: Polym. Chem. Ed.* **1981**, *19*, 3197.
6. Hsieh, H. L. *Rubber Chem. Technol.* **1966**, *39*, 491.
7. Weissert, F. C.; Johnson, B. S. *Rubber Chem. Technol.* **1965**, *40*, 590.
8. Bouton, T. C.; Futamura, S. *Rubber Age* **1974**, *106*(3), 33.
9. Wilder, R.; Haws, J. R.; Middle, T. C. In *Proceedings of the Rubber Division 124th Meeting*; American Chemical Society: 1983; Paper No. 81.
10. Brantley, Jr. H. L.; Day, G. L. In *Proceedings of the Rubber Division 129th Meeting*; American Chemical Society: 1986; Paper No. 33.
11. Tsutsumi, F.; Sakakibara, M.; Oshima, N. In *Proceedings of the Rubber Division 134th Meeting*; American Chemical Society: 1988; Paper No. 9.
12. Kobe, Y. S. *Kautsch. Gummi Kunstst.* **1986**, *39*, 30.
13. Laflair, R. T. In *Proceedings of the Rubber Division 149th Meeting*; American Chemical Society: 1996; Paper No. 39H.
14. Bomal, Y.; Touzet, S.; Barruel, R.; Cochet, Ph.; Dejean, B. *Kautsch. Gummi Kunstst.* **1997**, *50*, 434.
15. Hattori, I.; Sakakibara, M.; Furuta, I.; Makino, K.; Hongu, Y. In *Proceedings of the Rubber Division 143rd Meeting*; American Chemical Society: 1993; Paper No. 22.
16. Hacaloglu, J.; Ersen, T.; Ertugrul, N.; Fares, M. M.; Suzer, S. *Eur. Polym. J.* **1997**, *33*, 199.
17. Ghebremeskel, G. N.; Sekinger, J. K.; Hoffpauir, J. L.; Hendrix, C. *Rubber Chem. Technol.* **1996**, *69*, 874.
18. Choi, S.-S. *J. Anal. Appl. Pyrolysis* **2001**, *57*, 249.
19. Byers, J. T. *Rubber World* **1998**, *218*(6), 38.
20. Wolff, S.; Wang, M.-J. *Rubber Chem. Technol.* **1992**, *65*, 329.
21. Boonstra, B. B.; Cochrane, H.; Dannenberg, E. M. *Rubber Chem. Technol.* **1975**, *48*, 558.
22. Voet, A.; Morawski, J. C.; Donnet, J. B. *Rubber Chem. Technol.* **1977**, *50*, 342.
23. Ou, Y.-C.; Yu, Z.-Z.; Vidal, A.; Donnet, J. B. *Rubber Chem. Technol.* **1994**, *67*, 834.
24. Li, Y.; Wang, M. J.; Zhang, T.; Zhang, F.; Fu, X. *Rubber Chem. Technol.* **1994**, *67*, 693.
25. Görl, U.; Hunsche, A. In *Proceedings of the Rubber Division 150th Meeting*; American Chemical Society: 1996; Paper No. 76.
26. Görl, U.; Hunsche, A. In *Proceedings of the Rubber Division 151st Meeting*; American Chemical Society: 1997; Paper No. 38.
27. Hashim, A. S.; Azahari, B.; Ikeda, Y.; Kohjiya, S. *Rubber Chem. Technol.* **1998**, *71*, 289.
28. Guaita, M. *Br. Polym. J.* **1986**, *18*, 226.
29. Gradwell, M. H. S.; McGill, W. J. *J. Appl. Polym. Sci.* **1994**, *51*, 169.
30. Gradwell, M. H. S.; McGill, W. J. *J. Appl. Polym. Sci.* **1996**, *61*, 1131.
31. Gradwell, M. H. S.; McGill, W. J. *J. Appl. Polym. Sci.* **1996**, *61*, 1515.
32. Morrison, N. J. *Rubber Chem. Technol.* **1984**, *57*, 97.
33. Choi, S.-S. *J. Anal. Appl. Pyrolysis* **1999**, *52*, 105.