

Influence of Silane Coupling Agent on Properties of Filled Styrene-Butadiene Rubber Compounds

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Abstract : Influence of silane coupling agent, bis-(3-(triethoxysilyl)-propyl)-tetrasulfide, on cure characteristics and bound rubber content of filled styrene-butadiene rubber (SBR) compounds and on physical properties of the vulcanizates was studied. Carbon black-filled and silica-filled compounds were compared. Content of the bound rubber increased with increased content of the silane coupling agent and this trend was shown more clearly in the silica-filled compounds. Optimum cure time of the carbon black-filled compound increased with increase of the silane content, while that of the silica-filled one decreased. Cure rate of the carbon black-filled compound became slower as the silane content increased while that of the silica-filled one became faster. By increasing the silane content, the minimum torque decreased and the delta torque increased. Physical properties of the silica-filled vulcanizate were found to be improved by adding the silane coupling agent. However, for the carbon black-filled vulcanizates, the tensile strength and tear resistance decreased with increase of the silane content. The differences between the carbon black-filled and silica-filled compounds were explained by difference in the reactivities of the fillers with the silane.

Introduction

Dispersibility of filler in a rubber compound is very important. In order to improve the dispersibility, various processing aids are used in mixing of a rubber compound.^{1,4} A rubber compound with a poor dispersibility of a filler will have worse physical properties than that with a good one. The dispersibility is sensitive to mixing conditions such as mixing steps, temperature, and time. Thus, properties of rubber compounds will be different each other depending on the mixing conditions even though they have the same formulation.⁵⁻⁷

Silica has been used as an important reinforcing agent in a rubber compound together with carbon black.⁸⁻¹¹ 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.^{8,12,13} Since intermolecular hydrogen bonds between hydroxyl groups on the surface of

silica are very strong, it can aggregate tightly.^{9,13} Its property can cause a poor dispersion of silica in a rubber compound.

For silica-filled rubber compounds with accelerated sulfur cure system, the curatives are adsorbed on the surface which leads to slow cure characteristics. Since the silica surface is acidic, especially it forms a strong hydrogen bond with basic materials. 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, silane coupling agent such as bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) is used in order to improve the silica dispersion and in order to prevent adsorption of curatives on the silica surface.^{8,14-16}

In the present work, variation of cure characteristics and bound rubber content with the content of silane coupling agent was studied using filled styrene-butadiene rubber (SBR) compounds. Variation of the physical properties was also investigated. Properties of the silica-filled compounds were compared to the carbon black-filled ones.

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Experimental

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. Bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) 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 were given in Table I.

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. The MB compounds were prepared as follow. (1) The rubber was loaded into the mixer and premixed for 0.5 min. (2) The filler 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 compounds were dumped. The FM compounds were prepared by mixing the curatives with the MB

compounds for 1.5 min.

Contents of the bound rubber were determined by extracting the 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. Cure characteristics were obtained using Flexsys rheometer (MDR 2000) at a frequency of 100 cycles/min and ± 1.5 arc at 160°C. Mooney viscosity and Mooney scorch time were measured using a Mooney MV 2000 of Alpha Technologies at 100 and 125°C, respectively. Vulcanizates were prepared by curing at 160°C for 30 min. Physical properties of the vulcanizates were measured with the Universal Testing Machine (Instron 6021). $\tan \delta$ of the vulcanizates were measured according to ASTM D2231-87.

Results and Discussion

Bound Rubber and Viscosity. Bound rubber contents of the MB and FM compounds were measured. The results were summarized in Table II. The bound rubber content increases as the silane coupling agent increases. This is due to the formation of chemical bonds between rubber and filler. The silane, $(C_2H_5O)_3Si-(CH_2)_3-S_x-(CH_2)_3-Si-$

Table I. Formulations (phr)

Compound No.	1	2	3	4	5	6	7	8
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.

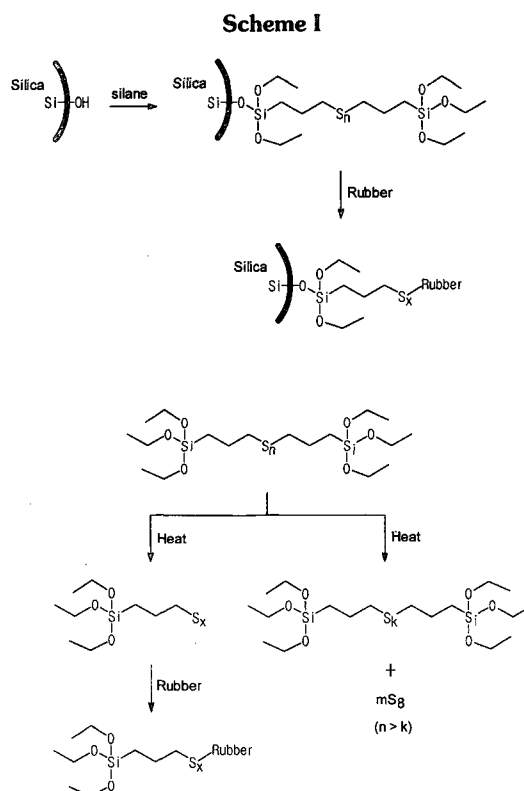
Table II. Bound Rubber Contents and Mooney Viscosities of the Compounds

Compound No.	1	2	3	4	5	6	7	8
Bound Rubber Content (%)								
MB Compounds	22.73	25.38	26.05	26.46	21.54	29.11	33.46	35.26
FM Compounds	25.02	27.35	27.46	27.54	25.00	30.97	34.80	35.76
Mooney Viscosity (ML1+4 at 100°C)								
	98.1	91.6	87.5	83.9	>200	167.7	141.4	115.3

$(OC_2H_5)_3$, reacts with the filler surface to form a siloxane bond since carbon black and silane have functional groups such as hydroxy, carboxyl, and so forth. Sulfide group of the silane bonded to the filler is dissociated and reacts with the rubber molecule to form a crosslink between the filler and rubber. This chemical bond enhances formation of the bound rubber.

For the compounds without the silane, bound rubber content of the silica-filled compound is lower than for the carbon black-filled one. But, for the compounds containing the silane, bound rubber content of the silica-filled compound is much higher than for the carbon black-filled one. This can be explained by the difference in reactivities of the fillers (silica and carbon black) with rubber. Since silica surface has lots of silanol groups, they react easily with ethoxy groups of the silane to form siloxane bonds. Sulfide group of the silane bonded to the silica reacts with the rubber molecule to form a crosslink between the silica and the rubber (Scheme I). Rubber molecules chemically bonded to the silica through the silane become the bound rubber. Since carbon black surface has functional groups such as acid, aldehyde, quinone, and so forth, it also reacts with the silane to form a crosslink between the carbon black and rubber. However, carbon black has less functional groups so level of the chemical bonds between filler and rubber is much lower than for the silica-filled compound.

The viscosity is also affected by the silane content. The Mooney viscosity decreases with increase of the silane content (Table II). Decrement of the Mooney viscosity of the silica-filled compound is higher than for the carbon black-filled one. The Mooney viscosity of the carbon black-filled compound decreases from 98.1 to 83.9 as the silane



content increases from 0.0 to 7.2 phr, respectively, and that of the silica-filled one decreases from over 200 to 115.3, respectively. This implies that the silane is more effective to the silica-filled compound to decrease the viscosity and the silane improves the dispersion of silica. This may be due to the surface modification of silica by the silane. There are rubber and the silane on the modified silica surface. The silanes exist on the silica surface by reactions between the silane and silica. The rubber can also exist on the silica surface by reactions between the silica and rubber through the silane as discussed above. The silane and rubber

molecule on the silica surface can prevent intermolecular hydrogen bonds between silica particles and the filler-filler interactions will be diminished. The reduced filler-filler interactions lead to a good dispersion and reduction of the viscosity.

Cure Characteristics. Cure times, t_{02} (scorch time), t_{40} , and t_{90} (optimum cure time), are varied with the silane content as shown in Figure 1. For both the carbon black-filled and silica-filled compounds, the t_{02} and t_{40} decrease slightly as the silane content increases. This is due to the increased sulfur content in the compound by adding the silane. The silane coupling agent has a sulfidic linkage of di- to octa-sulfides and the average number of $-S_x-$ is about 3.8.¹⁵ The sulfur content of the silane is about 20 wt%. Elemental sulfur (S_8) is formed by heating the silane.¹⁷ Therefore, the t_{02} and t_{40} become shorter since the total sulfur content increases with increasing the silane. For the t_{90} , the silica-filled compound shows a different trend to the carbon black-filled one. The t_{90} of the silica-filled compound decreases with increasing the silane, while that of the carbon black-filled one increases. Shortening of the t_{90} of the silica-filled compound by adding the silane can be explained both by the reaction between silica and

rubber and by the increased sulfur content. The increased t_{90} of the carbon black-filled compound by adding the silane may be due to prevention of crosslinking reaction by the silane residues. When the silane reacts with filler and rubber, it becomes a linkage between them. Otherwise, length of the sulfidic linkage of the silane can be reduced to mono- or disulfide by the elimination of elemental sulfur as shown in Scheme I. The silane residue which has a short sulfidic linkage can inhibit the crosslinking reaction. Since carbon black has less functional groups than silica, the silane residues exist more in the carbon black-filled compound than in the silica-filled one. This is discussed in more detail in the later section.

Mooney cure times of the compounds were also measured. In general, the Mooney scorch time, t_5 , is employed as the scorch time in rubber industries. The t_5 means the time taken for the Mooney viscosity to increase by 5 MU from the minimum point. The t_{35} means the time taken for the Mooney viscosity to increase by 35 MU from the minimum point. The difference between the t_{35} and the t_5 , $\Delta t = t_{35} - t_5$, is used as the cure rate index. That is, if the Δt is longer the cure rate is slower. Figure 2 gives variations of the Mooney

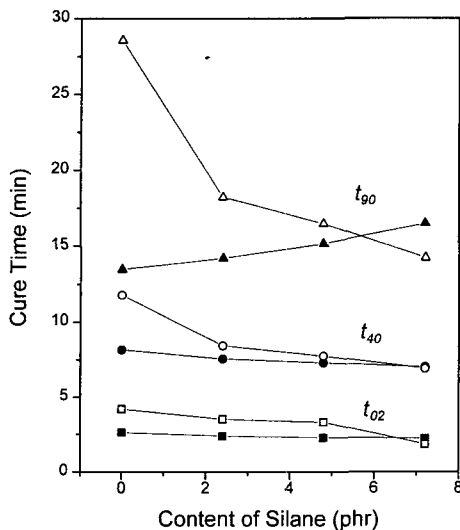


Figure 1. Variation of the cure times at 160°C as a function of content of the silane coupling agent. Closed and open symbols indicate the carbon black-filled and silica-filled compounds, respectively. Rectangles, circles, and triangles stand for the t_{02} , t_{40} , and t_{90} , respectively.

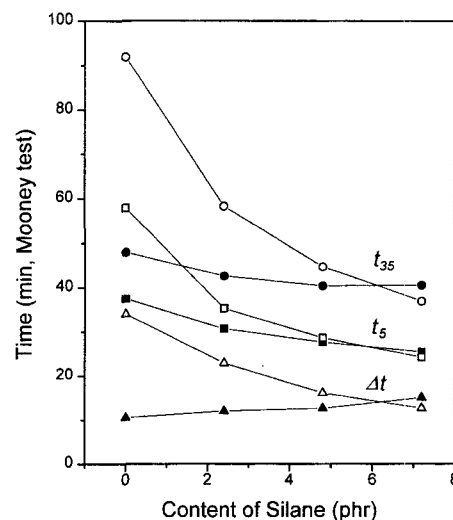


Figure 2. Variation of the Mooney cure times at 125°C as a function of content of the silane coupling agent. Closed and open symbols indicate the carbon black-filled and silica-filled compounds, respectively. Rectangles, circles, and triangles stand for the t_5 , t_{35} , and Δt , respectively.

cure times with the silane content. The t_5 and t_{35} decrease with increasing the silane content irrespective of the filler type. This is due to the increased total sulfur content in the compound by adding the silane as discussed previously. The variations of Δt show a different trend with the filler type. The Δt of the silica-filled compound decreases with increase of the silane content, while that of the carbon black-filled one increases. This implies that the cure rate of the silica-filled compound increases as the silane content increases while that of the carbon black-filled one decreases. This can be explained by the difference in reactivities of the fillers (silica and carbon black) with the silane. Since silica has lots of silanol groups on the surface, the silane reacts easily with silica. Thus, by increasing the silane content, the reaction of the silane with silica will be faster and faster. On the other hand, since carbon black has much less functional groups on the surface, most of the silane in the carbon black-filled compound remain not to react with the filler. The remained silane reacts with rubber to form a pending group of the silane or becomes a new silane with shorter sulfidic linkage (Scheme 1). The pendent group terminated by the silane residue and the shorter silane can inhibit the crosslinking reaction of curatives.

Figure 3 shows variation of the torques, the minimum torque (T_{min}), maximum torque (T_{max}), and delta torque, with the silane content. The T_{min} of the carbon black-filled compound decreases slightly with increase of the silane content and that of the silica-filled one decreases notably. The minimum torque in a rheograph is related closely with the viscosity. The higher the viscosity is the higher the minimum torque is. The viscosity decrement of the silica-filled compound is much larger than for the carbon black-filled one as listed in Table II. The T_{max} increases with increase of the silane content. This is due to the increased sulfur content. Since some sulfur is isolated from the silane by heating, total sulfur content in the compound increases with the increased silane content. The delta torque of the carbon black-filled compound increases with increase of the silane content and that of the silica-filled one increases notably. For the compounds without the silane,

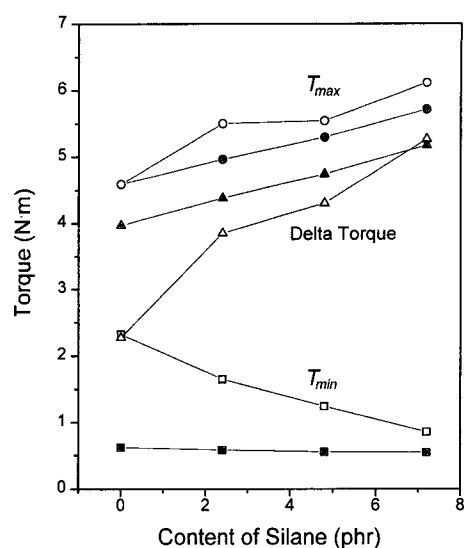


Figure 3. Variation of the torques as a function of content of the silane coupling agent. Closed and open symbols indicate the carbon black-filled and silica-filled compounds, respectively. Rectangles, circles, and triangles stand for the minimum torque (T_{min}), maximum torque (T_{max}), and delta torque, respectively.

the delta torque of the silica-filled compound is much lower than that of the carbon black-filled one. This is due to adsorption of the curatives on the silica surface. Since the silica surface has lots of silanol groups and is acidic, especially it forms a strong hydrogen bond with basic materials. *N-tert-Butyl-2-benzothiazole sulfenamide* (TBBS) has a basic functional group such as amide ($=NH$), it is adsorbed well on the silica surface which results in delay of the scorch time and reduction of the delta torque of a silica-filled rubber compound. However, for the compounds with the silane of 7.2 phr, the delta torques of the both kind compounds are nearly same. For the silica-filled compound with high content of the silane, the silane reacts with silica to form a siloxane bond and prevent the adsorption of curatives as discussed previously.

Physical Properties. Physical properties of the vulcanizates were summarized in Table III and Figures 4 and 5. The hardness increases with increase of the silane content. This is due to the increased crosslink density. Since the total sulfur content is increased by adding the silane and crosslinks between the filler and rubber, the cross-

link density is also increased. The modulus also increases with increase of the silane as shown in Figure 4. Especially, modulus of the silica-filled vulcanizate increases linearly. This implies that the total sulfur content and the number of chemical bonds between the silica and rubber are increased linearly by increasing the silane content.

For variations of the tensile strength and tear resistance with the silane content, the carbon black-filled and silica-filled vulcanizates show different trends each other. The tensile strength and tear resistance of the silica-filled vulcanizate increases with increase of the silane content, while those of the carbon black-filled one decreases. This is very interesting fact. One can expect that the tensile strength and tear resistance of the carbon black-filled vulcanizate also increases by adding the silane because the sulfur content increases and the chemical bonds between filler and rubber are formed. However, the experimental results are opposite. This may be due to the slippage effect by the silane residues remaining in the carbon black-filled vulcanizates. As discussed above, lots of the silane residues, the pending silane residue to a rubber chain and the silane with lower sulfidic linkage as shown in Scheme I, exist in the carbon black-filled vulcanizates so they will reduce interactions of rubber chains to result in weakness of the physical properties.

Elongation at break is an inversely proportional property to the degree of crosslink density. Since crosslink density of the vulcanizate increases with the increased silane content, the elongation at break decreases as the silane content increases. Heat build-up is also an inversely proportional property to the degree of crosslink density. Thus, the heat build-up decreases as the silane content increases as listed in Table III. Decrement of the

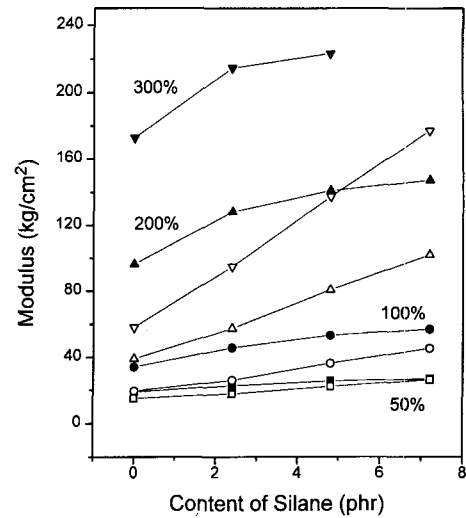


Figure 4. Variation of the modulus as a function of content of the silane coupling agent. Closed and open symbols indicate the carbon black-filled and silica-filled compounds, respectively. Rectangles, circles, up-triangles, and down-triangles stand for the moduli at 50, 100, 200, and 300% strains, respectively.

heat build-up between the silica-filled vulcanizates with the silane contents of 0.0 and 2.4 phr is notable (about 10°C). This is due to the large increment of the crosslink density. The delta torque (crosslink density) of the silica-filled compound increases remarkably with increase of the silane content from 0.0 to 2.4 phr as shown in Figure 3.

Figure 5 gives variations of the $\tan\delta$ at 0°C and 60°C with the silane content. For the silica-filled vulcanizate, the $\tan\delta$ at 0°C increases by adding the silane coupling agent. The $\tan\delta$ at 0°C of the carbon black-filled vulcanizate is hardly affected by the silane. Variations of the $\tan\delta$ at 60°C of the carbon black-filled and silica-filled vulcanizates show the same trend. The $\tan\delta$ at 60°C decreases

Table III. Physical Properties of the Vulcanizates

Compound No.	1	2	3	4	5	6	7	8
Hardness (Shore A)	70.0	72.0	75.0	75.0	75.0	75.0	76.0	79.0
Tensile Strength (kg/cm ²)	248.6	240.7	224.8	208.7	160.1	231.7	237.7	237.1
Elongation at Break (%)	419.9	338.1	301.1	272.3	801.0	612.2	463.5	376.4
Tear Resistance (kg/cm ²)	92.5	82.5	74.5	70.0	66.0	82.0	89.5	90.0
Heat Build-up (°C)	34.9	33.7	30.8	30.2	53.4	43.7	34.4	32.1

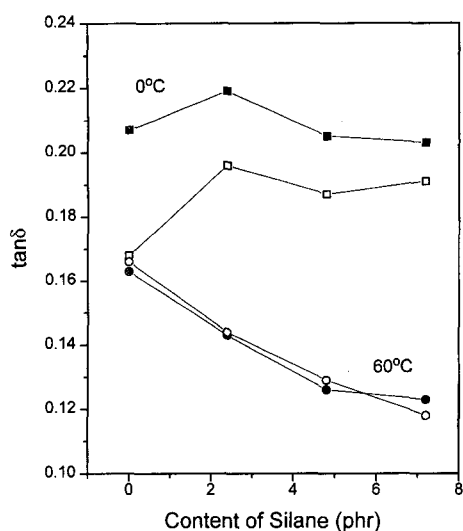


Figure 5. Variation of the $\tan\delta$ as a function of content of the silane coupling agent. Closed and open symbols indicate the carbon black-filled and silica-filled compounds, respectively. Rectangles and circles stand for the $\tan\delta$ at 0 and 60°C, respectively.

as the silane content increases. This is due to the increased crosslink density by adding the silane.

Conclusions

The bound rubber content increases with increase of the silane content since chemical bonds between the rubber and filler are formed by the silane. The scorch time becomes shorter by increasing the silane content. Cure rate of the carbon black-filled compound decreases as the silane content increases while that of the silica-filled one increases. By increasing the silane content, the minimum torque decreases and the delta torque increases. This is due to formation of the silane crosslinks between the filler and rubber and the increased sulfur content in the compound by

elimination of elemental sulfur from the silane. Physical properties of the silica-filled vulcanizates are improved by adding the silane coupling agent. However, for the carbon black-filled vulcanizates, the tensile strength and tear resistance decrease with increase of the silane content. This is due to the silane residues such as the pending silane residue to a rubber chain and the silane with lower sulfidic linkage.

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