

Influence of Filler Composition Ratio on Properties of Both Silica and Carbon Black-Filled Styrene-Butadiene Rubber Compounds

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실리카와 카본블랙으로 보강된 SBR 고무 배합물의 특성에 보강제 조성비가 미치는 영향

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ABSTRACT: Influence of the filler composition ratio on cure characteristics and bound rubber content of the compounds and on physical properties of the vulcanizates were studied using both silica and carbon black-filled styrene-butadiene rubber (SBR) compounds with the total filler content of 80.0 phr. The bound rubber content increased slightly with increase of the silica content ratio. The viscosity also increased with increasing the silica content ratio, especially increased steeply after the silica content of 60.0 phr. The cure times obtained with a rheometer, t_2 , t_{40} , and t_{90} , are increased by increasing the silica content ratio and the cure rate decreased. The delta torque increased with the increased silica content ratio. Variation of the modulus with the silica content ratio showed a decreased trend though the delta torque increased. The $\tan\delta$ at 60°C decreased with increase of the silica content ratio.

요 약: 실리카와 카본블랙으로 보강된 SBR 배합물의 가황 특성과 bound rubber 함량 그리고 가황물의 물성에 보강제의 조성비가 미치는 영향을 연구하였다. 고무 배합물의 보강제 총 함량은 80.0 phr 이다. Bound rubber 함량은 실리카 함량비가 증가할수록 증가하였고 점도 역시 증가하였는데, 특히 실리카 함량이 60.0 phr 이상일 때는 점도의 증가폭이 두드러지게 높아졌다. 가황 시간은 실리카 함량이 증가할수록 느려졌고 가황 속도도 느려졌다. 실리카 함량비가 증가할수록 델타 토크가 증가함에도 불구하고 모듈러스는 감소하는 경향을 보였다. 60°C에서의 $\tan\delta$ 값은 실리카 함량이 증가할수록 감소하였다.

Keywords : silica, carbon black, SBR compound, filler content ratio.

I. Introduction

Silica has been used as an important reinforcing agent in a rubber compound together with carbon

black.¹⁻⁴ 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.^{1,5,6} Since intermolecular hydrogen bonds between hydroxyl groups on the surface of

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silica are very strong, it can aggregate tightly.^{2,6} 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.^{1,7-9}

In the present work, influence of the filler composition ratio on cure characteristics and bound rubber content of both silica and carbon black-filled styrene-butadiene rubber (SBR) compounds were studied. Variation of the physical properties with the filler composition ratio was also investigated.

II. Experimental

The both silica and carbon black-filled compounds were made of SBR, silica, carbon black, silane coupling agent, cure activators (stearic acid and zinc oxide), antidegradants (HPPD and wax), and curatives (DPG, TBBS, and sulfur). The total filler content was 80.0 phr. The content ratio of silica/carbon black was varied from 10.0/70.0 to 70.0/10.0 phr. Bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) of Degussa Co. was employed as a silane coupling agent. The silane coupling agent of 8.0 wt% of the silica content was added. The formulations were 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. The MB compounds were dumped at 4.0 min. The MB 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

Table 1. Formulations (phr)

Compound No.	1	2	3	4	5	6	7
SBR 1500	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Z 175	10.0	20.0	30.0	40.0	50.0	60.0	70.0
Si 69	0.8	1.6	2.4	3.2	4.0	4.8	5.6
N 330	70.0	60.0	50.0	40.0	30.0	20.0	10.0
ZnO	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
HPPD	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
DPG	0.5	0.5	0.5	0.5	0.5	0.5	0.5
TBBS	1.6	1.6	1.6	1.6	1.6	1.6	1.6
Sulfur	1.0	1.0	1.0	1.0	1.0	1.0	1.0

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

Z 175: silica

Si 69: silane coupling agent, bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT)

N 330: carbon black

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

DPG: diphenylguanidine

TBBS: *N*-*tert*-butyl-2-benzothiazole sulfenamide

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 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. The bound rubber contents were calculated by $R_b (\%) = 100 [W_{fg} - W_t [m_f / (m_f + m_r)]] / W_t [m_r / (m_f + m_r)]$, where R_b is the bound rubber content, W_{fg} the weight of filler and gel, W_t the weight of the sample, m_f the fraction of the filler in the compound, m_r the fraction of the rubber in the compound. 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 was measured using a Mooney MV 2000 of Alpha Technologies at 100°C. Vulcanizates were

prepared by curing at 160 °C for 20 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.

Table 2. Viscosity and Content of Bound Rubber

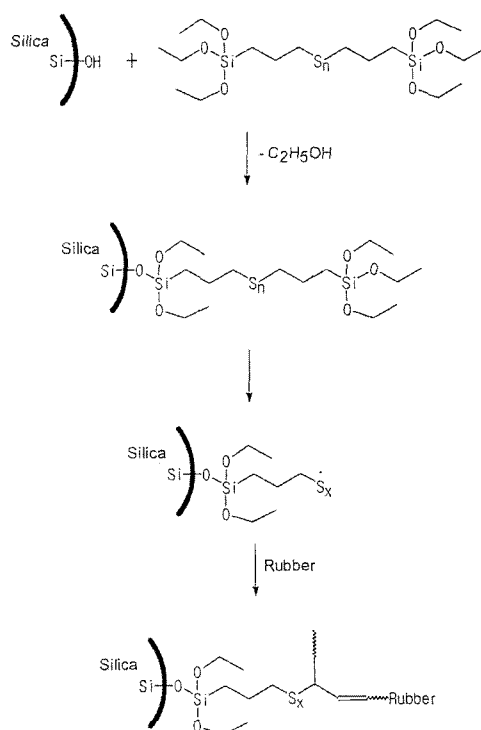
Compound No.	1	2	3	4	5	6	7
Mooney viscosity (ML 1+4 at 100°C)							
	135.0	141.7	141.3	141.7	145.4	158.8	174.6
Content of bound rubber (%)							
MB compounds	30.25	30.56	31.58	32.10	34.18	33.96	34.05
FM compounds	33.16	34.22	34.59	34.56	35.60	35.23	36.32

III. Results and Discussion

1. Bound rubber content and viscosity

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. Bound rubber phenomenon and its effect on properties of filled rubber compounds and vulcanizates have been studied.¹⁰⁻¹⁵ 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 (polarity and saturation/unsaturation) and the microstructure (configuration, molecular weight, and molecular-weight distribution) influence the level of bound rubber content. The filler-polymer interactions involving physical adsorption, chemisorption, and mechanical interaction lead to the formation of bound rubber.

Bound rubber contents of the MB and FM compounds were measured. The results were summarized in Table 2. The bound rubber content increases slightly as the silica content ratio increases. This is due to the formation of chemical bonds between the silica and rubber by the silane coupling agent. The



Scheme 1

silane coupling agent, (C₂H₅O)₃Si-(CH₂)₃-S_x-(CH₂)₃-Si(OC₂H₅)₃, has a sulfidic linkage between triethoxysilylpropyl groups. Ethoxy group of the coupling agent reacts with silanol group of the silica to form a siloxane bond, silica ≡ Si-OSi(OC₂H₅)₂-(CH₂)₃-S_x-(CH₂)₃-Si(OC₂H₅)₃, as shown in Scheme 1. 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 rubber. The chemical bonds enhance the bound rubber formation. If the silane is not added to the compound, the bound rubber content will be decreased by increasing the silica content ratio because carbon black is more interactive with the rubber than silica. Silica surface is very polar, while carbon black and the rubber is less polar.

Bound rubber contents of the FM compounds are higher than those of the respective MB ones. This is due to the formation of chemical bonds between

the carbon black and rubber by curatives. Carbon black reacts with sulfur and cure accelerator so that $\equiv\text{CS}\cdot$ radicals or $\equiv\text{CX}$ (X is SH or residues of a cure accelerator) are formed.¹⁶ The radicals or $\equiv\text{CX}$ on the filler surface can react with rubber chains and this will result in formation of chemical bonds between the rubber and filler.

The viscosity increases with increase of the silica content ratio. (Table 2) The viscosity increases slightly as the silica content ratio increases from 10.0 to 50.0 phr and then increases steeply. This can be explained by the formation of filler networks by silica. Since silica has lots of silanol groups on the surface, the filler-filler interactions are very strong and the filler networks can be formed by strong intermolecular hydrogen bonds when the silica content is high. From the experimental results, it can lead to a conclusion that, for the both silica and carbon black-filled compounds, strong filler networks of silica are formed by the intermolecular hydrogen bonds when the silica content is over 50.0 phr.

2. Cure characteristics

Figure 1 shows variation of the cure times, t_2 (scorch time), t_{40} , and t_{90} (optimum curetime). The cure times increase with increasing the silica content ratio. This is due to the adsorption of curatives on the silica surface. The polar surface of silica can make hydrogen bonds well with polar organic materials in a rubber compound. Since the silica surface is acidic, especially it forms a strong hydrogen bond with basic materials. In this study, *N-tert-butyl-2-benzothiazole sulfenamide*(TBBS) and diphenylguanidine (DPG) were used as cure accelerators. Since the cure accelerators have basic functional groups such as amide ($=\text{NH}$) and secondary amine, they are adsorbed well on the silica surface. The adsorption of curatives on the silica surface results in delay of the cure times. For the t_{90} , the increment between the compounds with the silica contents of 40.0 and 50.0 phr is much higher than

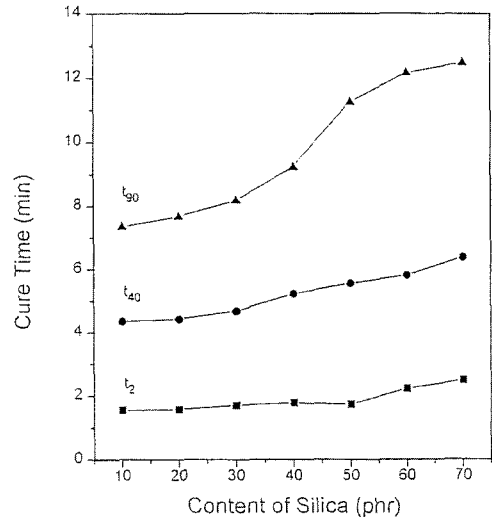


Figure 1. Variation of the cure times as a function of the silica content ratio. (Rectangles, circles, and triangles indicate the t_2 , t_{40} , and t_{90} , respectively.)

for the other regions.

Variation of the cure rate with the silica content ratio was also investigated. Difference between the t_{90} and t_2 was used as a cure rate index ($\Delta t = t_{90} - t_2$). The shorter the Δt is the faster the cure rate is. The Δt are 5.80, 6.10, 6.47, 7.44, 9.42, 9.94, and 9.99 min for the Compounds 1 through 7, respectively. The cure rate (Δt^{-1}) decreases with increase of the silica content ratio. This is also due to the adsorption of curatives on the silica surface. The adsorbed curatives can not role as crosslinking agents at the beginning of cure and some of the adsorbed materials are desorbed slowly as the cure time elapses. Thus, the cure times and cure rate become slower as the silica content ratio increases.

Figure 2 shows variation of the torques obtained from the rheographs, the minimum torque (T_{\min}) and delta torque, with the silica content ratio. Delta torque is the difference between the maximum and minimum torques, which is correlated closely with the crosslink density. The higher the delta torque is the higher the crosslink density is. The T_{\min} increases with increase of the silica content ratio. The T_{\min} in a rheograph is related closely with the

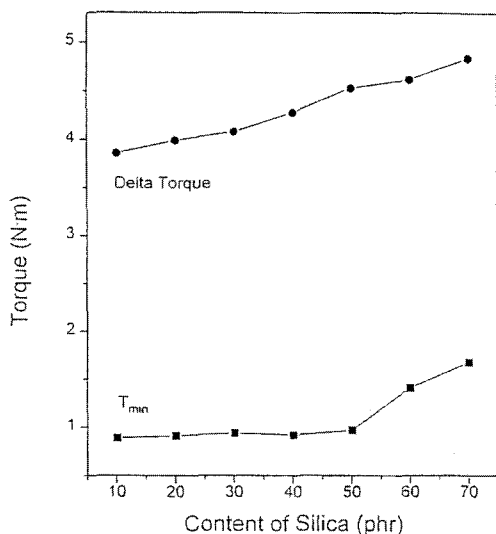


Figure 2. Variation of the torques as a function of the silica content ratio.(Rectangles and circles indicate the minimum torque (T_{min}) and delta torque, respectively.)

viscosity. The higher the viscosity is the higher the T_{min} is. The T_{min} increases slightly as the silica content increases from 10.0 to 50.0 phr and then increases steeply. This trend is similar to the viscosity. This can be also explained by the formation of filler networks when the silica content is high as discussed previously. The delta torque increases linearly with the increased silica content ratio. This can be explained both by the increase of sulfur content in the compound with the increased silane content and by the formation of crosslinks between the silica and rubber chain through the silane. The silane coupling agent has a sulfidic linkage of di- to octasulfides and the average number of S_x is about 3.8. The sulfur content of the silane is about 20 wt%. Elemental sulfur (S_8) is formed by heating the silane.¹⁷ The increased sulfur content implies the increased crosslink density (delta torque). By increasing the silica content, the silane content also increases. Since the silane reacts with silica and rubber to form a crosslink between them as shown in Scheme 1, the crosslinks formed by the silane increase with increase of the silica and silane.

Table 3. Physical Properties

Compound No.	1	2	3	4	5	6	7
Hardness (Shore A)	80.0	80.0	81.0	82.0	82.0	83.0	83.0
Tensile strength (kg/cm ²)	245.9	239.8	243.1	244.8	251.3	235.2	240.9
Elongation at break (%)	385.7	375.8	400.2	383.9	399.1	368.5	369.2
Heat build-up (°C)	52.9	53.6	53.3	50.1	49.9	50.0	48.7

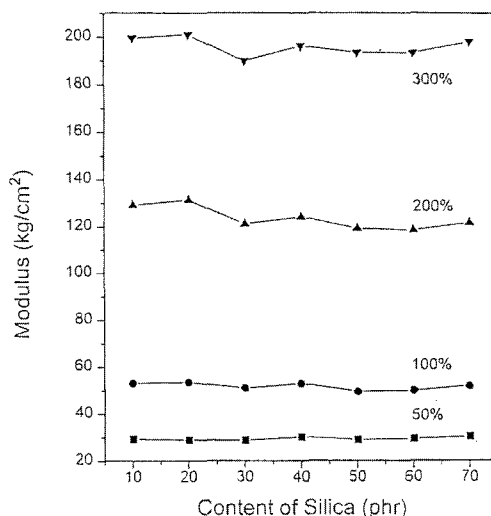


Figure 3. Variation of the modulus as a function of the silica content ratio.(Rectangles, circles, up-triangles, and down-triangles indicate the moduli at 50, 100, 200, and 300% strains, respectively.)

3. Physical properties

Physical properties of the vulcanizates were summarized in Table 3 and Figures 3 and 4. The hardness increases with increase of the silica content ratio. This may be due to the increased crosslink density. Since the total sulfur content is increased by adding the silane and crosslinks between the filler and rubber are also increased, the crosslink density is increased. Variation of the modulus with the silica content ratio does not show a clear trend as shown in Figure 3. Modulus of a rubber vulcanizate is a proportional property to the degree of crosslink

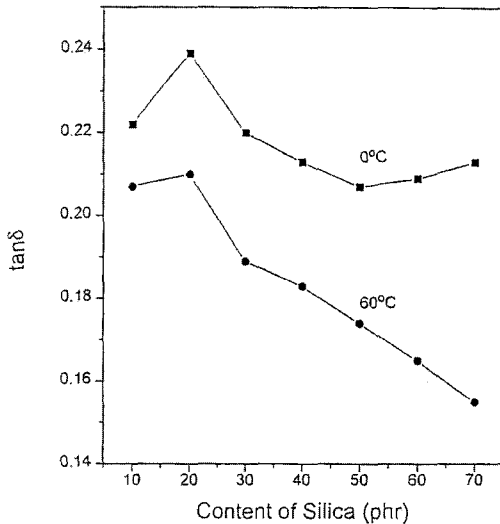


Figure 4. Variation of the $\tan \delta$ as a function of the silica content ratio. (Rectangles and circles indicate the $\tan \delta$ at 0 and 60°C, respectively.)

density. If the vulcanizates follow this trend, the modulus should be increased with increase of the silica content ratio. However, variation of the modulus shows the reverse trend. The moduli at 100, 200, and 300% strains, on the whole, decrease slightly with increase of the silica content ratio. This can be explained by the difference in degree of reinforcing effect between carbon black and silica. The carbon black and SBR are less polar and the silica has a polar surface. Thus, intermolecular interactions between the carbon black and SBR are stronger than for the silica and reinforcing effect of the carbon black is better than for the silica.

Variation of the tensile strength with the silica content ratio does not show a specific trend. The tensile strengths are nearly the same within 5% irrespective of the filler composition ratio. Variation of the elongation at break with the silica content ratio also does not show a specific trend. Only the elongations at break of the vulcanizates with the silica contents of 60.0 and 70.0 phr are shorter than for the others. This can be explained by the silica networks. As discussed previously, the silica networks can be formed by strong intermolecular

hydrogen bonds of silanol groups on the silica surface when the silica content is high. According to the results for viscosity and minimum torque, the silica networks will be highly developed when the silica content is over 50 phr. This is consistent with the variation of elongation at break. The heat build-up, on the whole, decreases with the increased silica content. This is due to the increase of crosslink density. Heat build-up of a rubber vulcanizate is an inversely proportional property to the degree of crosslink density.

Figure 4 gives variations of the $\tan \delta$ at 0 and 60°C with the silica content ratio. The $\tan \delta$ at 0 and 60°C, on the whole, decrease with the silica content ratio. This may be due to the increase of crosslink density. For the $\tan \delta$ at 0°C, the value decreases as the silica content increases from 20.0 to 50.0 phr and then increases slightly. The point to start increasing the $\tan \delta$ at 0°C is corresponding to the point which the silica networks are highly developed. Thus, it can be considered that the silica networks improve the $\tan \delta$ at 0°C.

IV. Conclusion

The bound rubber content increases with increase of the silica content ratio due to the formation of chemical bonds between the silica and rubber through the silane. The viscosity also increases with increasing the silica content ratio, especially increases steeply when the silica content is high. This is due to the silica networks formed by strong intermolecular hydrogen bonds of the silanols. The cure times, t_2 , t_{40} , and t_{90} , become slower as the silica content ratio increases and the cure rate decreases. This is because the curatives are adsorbed on the silica surface by hydrogen bonding between the silica and curatives. The delta torque increases with the increased silica content ratio. The modulus, on the whole, decreases with increase of the silica content ratio though the delta torque increases.

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