

Effects of Surface Chemistry of Silica Particles on Secondary Structure and Tensile Properties of Silica-Filled Rubber Systems

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ABSTRACT: Silica particles were treated by silane coupling agents to study the effects of surface chemistry of silica particles on the secondary structure formed by silica particles in styrene-butadiene rubber (SBR). The relation between the size of secondary structure and tensile properties of silica-filled SBR vulcanizates was also investigated. The water molecules adsorbed on the silica surface enhanced both the reactivity of the coupling agents with silanol groups on the silica surface and the condensation reaction between coupling agents. The averaged size of one agglomerate in the filled vulcanizate ($\overline{S_{agg}}$) decreased with the increase of

the hydrophobic character of silica particles, which were obtained by the introduction of coupling agents with alkyl groups. The initial slope of stress-strain curves for silica-filled vulcanizates decreased with the decrease of $\overline{S_{agg}}$. Further, a clear Payne effect was observed in all silica-filled vulcanizates, with this tendency more prominent in the larger $\overline{S_{agg}}$. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1622–1629, 2002

Key words: silica-filled SBR; coupling agent; agglomerate size; tensile property

INTRODUCTION

Recently, silica has been recognized as an important filler for rubber reinforcement.^{1–8} One reason is that the silica-filled passenger tire shows a low hysteresis compared with that of the carbon black-filled tire.^{9–12} However, a serious problem for the utilization of silica particles is their poor dispersity in the rubber matrix.^{13,14}

It is well known that the poor dispersity of silica particles in rubber matrix is caused by the formation of a secondary structure (aggregate and agglomerate) of silica particles, which is produced by hydrogen bonds between silanol groups on the silica surface.^{5–7,15–18} Donnet et al. examined the improvement of dispersity of silica particles in rubber matrix by introducing alkyl silane on the particles and found that the effect of dynamic strain amplitude on the dynamic storage modulus was smaller for the surface-modified silica-filled compound than that for the unmodified silica-filled compound.^{17–20}

We studied the effects of silanol number per unit surface area (N) and amounts of adsorbed water on

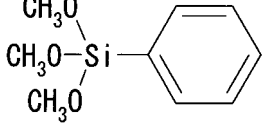
silica particles on the averaged size of agglomerates in rubber matrix, and found that the size increased with the increase in the N and the decrease in the amount of adsorbed water. This means that the averaged size is dependent on the hydrophobic character of silica particles.^{21–23} Further, it was found that stress-strain behavior of silica-filled vulcanizates was significantly affected by the size of agglomerates.²⁴

These findings suggest that we can control the mechanical properties of silica-filled vulcanizates by controlling the size of agglomerates. Further, our recent works on the quantitative analysis of transmission electron microscope (TEM) observations and NMR measurements of silica-filled vulcanizates suggested the existence of an entrapped rubber phase within the agglomerates.²⁴ Thus, a systematic study is necessary to confirm the relation between agglomerate size and tensile properties of silica-filled vulcanizates.

In this study, monofunctional silane coupling agents with different alkyl groups were used for the preparation of silica particles with different hydrophobic characters. The effects of surface chemistry of modified silica on the agglomerate size were investigated by TEM observations. Then, the stress-strain behavior and dynamic mechanical properties of the surface-modified silica-filled styrene-butadiene rubber (SBR) vulcanizates were studied in relation to the size of agglomerate.

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TABLE I
Chemical Structure of Coupling Agents

Agent	Structure
Methyl	$\begin{array}{c} \text{CH}_3\text{O} \\ \\ \text{CH}_3\text{O}-\text{Si}-\text{CH}_3 \\ \\ \text{CH}_3\text{O} \end{array}$
Phenyl	
Decyl	$\begin{array}{c} \text{CH}_3\text{O} \\ \\ \text{CH}_3\text{O}-\text{Si}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3 \\ \\ \text{CH}_3\text{O} \end{array}$

EXPERIMENTAL

Samples

Materials used were emulsion-polymerized styrene-butadiene rubber [SBR: Nipol SBR 1502, $M_w = 4.3 \times 10^5$ glass-transition temperature (T_g) = -52°C ; Nippon Zeon Co., Japan] and precipitated silica (Nipsil AQ; Nippon Silica, Japan). Coupling agents used for the surface modification of silica particles were three types of trialkoxyalkylsilane [$\text{R}-\text{Si}-(\text{OR}')_3$: KBM-13, KBM-103, and KBM-3103; Shin-Etsu Chemical Co., Japan]. The chemical structures of the coupling agents are shown in Table I.

The rubber composites were prepared by a mechanical mixing. The composition of the composites is listed in Table II. The condition for the mixing is as follows: the SBR was put into a Banbury mixer and masticated at 60°C for 1 min, then well-dried silica (120°C for 12 h under a reduced pressure) and coupling agent were mixed with masticated SBR at 100°C for 1 min. During the mixing, the coupling agent was reacted with silanol groups on the silica particles. Next, zinc oxide, stearic acid, and antioxidant were mixed with the silica-filled rubber composites at 100°C for 2 min (first step). Then, the masterbatch obtained at the first step was mixed with sulfur and accelerator at 60°C for 3 min, followed by cooling to room temperature (second step). Finally, the masterbatch obtained at the second step was vulcanized at 160°C for 30 min.

About 1 g of the unvulcanized masterbatch obtained at the second step (mixed without curing agents) was cut into small pieces and loosely packed in a cage with a 100-size mesh. The cage was immersed in a sufficiently large amount of toluene (~ 300 mL) and extraction was carried out at room temperature for 36 h. (There was no indication of

leaching out of silica during the extraction.) The insoluble component (bound rubber) was suspended in acetone to exchange the toluene with more volatile solvent. The bound rubber was dried at room temperature under reduced pressure for 24 h.

The sample preparation for TEM observation of vulcanized composites is as follows: the vulcanized composites were cured again in melted sulfur ($\sim 125^\circ\text{C}$) for 36 h. The hardened composites were easily cut into ultrathin films (<100 nm) at room temperature by microtoming. The thin films were stuck onto the TEM grids.

Measurements

High-resolution solid-state NMR spectra were obtained by using JEOL JNM-CMX 300 (JEOL, Peabody, MA) at a resonance frequency of 59 MHz for silicon-29. Measurements were carried out by using the cross-polarization/magic-angle spinning (CPMAS) technique. The contact time for the CP process was 5 ms, and the MAS speed was set to be 3 kHz.

TABLE II
Composition of Silica-Filled Rubber Composite
(Weight per Hundred Rubber)

SBR 1502	100
Silica	50
Coupling agent	10
Zinc oxide	3
Stearic acid	2
Antioxidant 6C ^a	1
Accelerator CZ ^b	1
Accelerator DPG ^c	1.5
Sulfur	1.7

^a *N*-(1,3-dimethyl butyl)-*N'*-phenyl-*p*-phenylenediamine.

^b *N*-Cyclohexyl-2-benzothiazyl-sulfenamide.

^c Diphenyl ganidine.

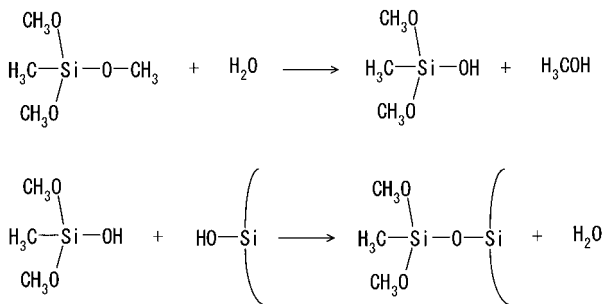


Figure 1 Reaction between silica surface and coupling agent.

The amount of bound rubber in the compound (G_r , g/g) was determined as a mass of insoluble rubber per 1 g of silica from the percentage of weight loss between 300 and 550°C. A precisely determined weight (~15 mg) of insoluble rubber was heated to 650°C by a thermal gravimetric analyzer (TGA: TG/DTA220; Seiko Instruments, Tokyo, Japan) with a heating ratio of 20°C/min.

Pulsed NMR measurements were carried out with a JEOL pulsed NMR spectrometer (JNM Mu 25), operating at 25 MHz. The solid echo sequence provided a good approximation to the free induction decay (FID), from which proton spin-spin relaxation time (T_2) was obtained. In this study, the width of 90° pulse and the pulse interval were adjusted to be 2 and 10 μs , respectively. Protons in both SBR and silica contributed to the NMR signals. Thus, the signals from silica were subtracted from observed signals to make a quantitative analysis of relaxation times of rubber molecules only.

TEM observations were carried out by using a transmission electron microscope (Hitachi H-9000 NAR Type; Hitachi, Japan). The accelerated voltage was 200 kV.

Measurements of stress-strain curves were carried out on a tensile tester (IM-20ST; Intesco, Japan) at room temperature. The strain rate was 0.5/min.

The dynamic storage modulus (E') was determined by a dynamic viscoelastometer (Rheographsolid; Toyo Seiki Seisaku-sho, Japan) at 50°C under the strain (stretching mode) of 10 ± 0.2 –9.0% and frequency of 20 Hz.

RESULTS AND DISCUSSION

Reaction of coupling agent

The reaction of coupling agent with silanol group on the silica surface was divided into two steps, as shown in Figure 1.^{25–27} At the first step, the coupling agents react with water molecules that exist on the surface of silica particles and produces dimethoxymethylhydroxylsilane (DMHS). At the second step, the silanol group of DMHS reacts with silanol groups on the

surface of silica particles. This means that the reaction of coupling agent with silanol groups on silica particles is significantly affected by the water molecules adsorbed on the silica surface.

Detailed thermal gravimetric analyses of silica particles revealed that the weight loss up to 120°C resulted from the loss of adsorbed water on the silica particles and that the loss above 120°C resulted from the dehydration of silanol groups.^{1,23} In this work, first of all, the effect of water molecules on the reaction of coupling agent was evaluated by using as-received and dry silicas. The dry silica was obtained by the treatment of as-received silica at 120°C for 12 h under reduced pressure. By this treatment, the weight loss during heating from 30 to 120°C, which corresponds to the loss of adsorbed water, decreased from 5 wt % of as-received silica to 2 wt % of dry silica.

Figure 2 shows solid-state ^{29}Si -CPMAS NMR spectra of bound rubbers. For the spectrum of bound rubber from unmodified dry silica (I), three peaks [assigned to silicon atoms with no OH group (Q_4), one OH group (Q_3), and two OH groups (Q_2) attached] were observed, as previously reported in the literature.^{27–29} The bound rubbers from modified silica by methyl (II, III) showed additional peaks at –50 to –70 ppm. The peak intensities were smaller for dry silica (II) than those for as-received silica (III). As shown in Figure 2, there are two different reaction sites of silanol groups on the silica particles: one is a geminal silanol group (Q_2) and the other is a single silanol group (Q_3). The reactivity of each silanol group with the coupling agent was evaluated from the spectrum, in which the deconvolution of the NMR spectra in the range of –90 to –120 ppm into separate peaks of Q_2 , Q_3 , and Q_4 was examined. The fractions of each com-

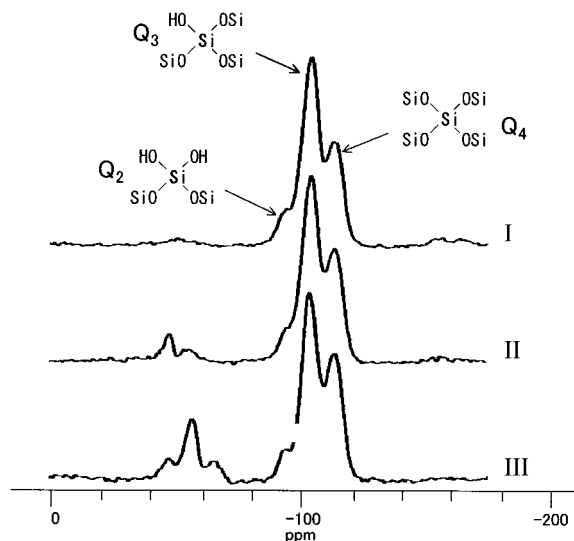


Figure 2 ^{29}Si -CPMAS NMR spectra of bound rubbers (I: dry silica; II: dry silica + methyl; III: as-received silica + methyl).

TABLE III
Function of Each Component Around -90 to -120 ppm
in ^{29}Si -CPMAS NMR Spectra of Bound Rubbers

Sample ^a	FQ ₂	FQ ₃	FQ ₄
I	0.099	0.580	0.321
II	0.093	0.562	0.344
III	0.083	0.547	0.370

^a I, dry silica; II, dry silica + methyl; III, as-received silica + methyl.

ponent (FQ₂, FQ₃, FQ₄) were determined from the fraction of each peak area of deconvoluted spectrum, the results of which are shown in Table III. It is clear that fractions of Q₂ (FQ₂) and Q₃ (FQ₃) decreased and that of Q₄ (FQ₄) increased by the reaction, with this tendency more prominent in the case of as-received silica (III). The results indicate that water molecules adsorbed on the silica surface enhance the reactivity of coupling agent with silanol groups on the silica surface, in accordance with the findings of Hunshe et al.^{26,27} Through the reaction, a part of the geminal silanol groups (Q₂) might be changed into single silanol groups (Q₃). If so, FQ₃ should be increased by the reaction. However, a large decrease of FQ₃ and the increase of FQ₄ by the reaction suggest that the reactivity of single silanol groups is higher than that of geminal silanol groups.

The peaks for unreacted coupling agents should appear around -40 ppm.²⁵⁻²⁷ Thus, the peaks around -50 to -70 ppm might be assigned to the silicon atoms of coupling agents, which reacted with the silanol groups on the silica surface. For sample III, the spectrum of reacted coupling agent was separated into three peaks. These peaks were assigned to the silicon atoms with one reacted methoxyl group (S), two reacted methoxyl groups (D), and three reacted methoxyl groups (T)²⁵⁻²⁷ (see Fig. 3). If the reaction of coupling agent with silanol groups on the silica surface is represented by the mechanism as shown in Figure 1, the spectrum should show a single peak of S. The appearance of D and T in the spectrum indicates that the residual methoxyl groups in the coupling agent react with water molecules, leading to the formation of silanol groups in the coupling agent. Then, the silanol groups react with silanol groups on the silica surface and/or silanol groups of DMHS. In this case, three reaction mechanisms might be considered as follows:

- Case I. The condensation of adjacent silanol groups on the silica particles
- Case II. The condensation within the coupling agents
- Case III. The condensation within the coupling agents followed by the condensation with the adjacent silanol groups on the silica particles

These are illustrated in Figure 4. The distance between adjacent silanol groups on the silica surface and the length of the O—Si—O bond have been evaluated to be 5.41 and 3.13 Å, respectively.²⁵⁻²⁷ The data suggest the difficulty of case I.

As revealed in Figure 3, the peak intensities of D and T were greatly reduced by the utilization of dry silica. This means that the existence of water molecules enhances the condensation within the coupling agents. Therefore, the control of water content on silica surface is important to balance the reaction between coupling agent and silanol groups on the silica surface and the condensation reaction within the coupling agent. Too many water molecules primarily lead to the condensation reaction within coupling agents. As a result, the reaction between coupling agent and silanol group on the silica is suppressed, which is not preferable for increasing the hydrophobic character of silica particles.

Figure 5 shows ^{29}Si -CPMAS NMR spectra of bound rubbers from modified dry silica by phenyl (IV) and decyl (V). The spectrum of bound rubber from modified dry silica by methyl (II) was also shown in this figure for the comparison. For both samples (IV and V), the spectra showed peaks at -90 to -120 ppm and -50 to -80 ppm, which were assigned to the silicon atoms of modified silica particles and reacted coupling agents, respectively, similar to the case of sample II. For sample IV, the peaks that were assigned to the reacted coupling agent shifted to higher field compared with those for sample II. This is attributed to the existence of a phenyl group. Lower intensities of D for

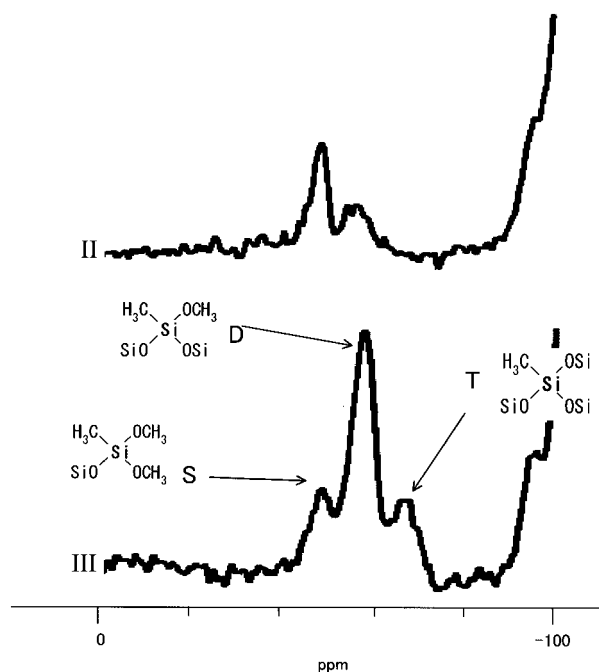


Figure 3 ^{29}Si -CPMAS NMR spectra of reacted silane coupling agents.

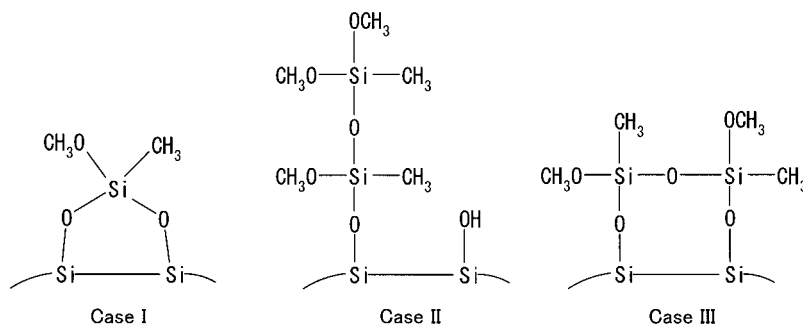


Figure 4 Schematic representation of the condensation of coupling agents.

samples IV and V revealed the low level of condensation reaction between the coupling agents. This arose from the utilization of dry silica as described above.

The peak intensity of S, which corresponds to the silicon atoms, with one reacted methoxyl group in the coupling agent was of the order of methyl > phenyl > decyl. The result suggests that the reactivity of decyl with silanol groups on the silica surface is low compared with that for methyl and phenyl. The decyl has a long alkyl group with a hydrophobic character. Thus, decyl seems to have a weak affinity for the silica surface, which might reduce the reactivity with silica.

Network structure of silica particles in the rubber

Figure 6 shows TEM photographs of the silica-filled SBR system and the digital binary images of the photos. The transformation of TEM photographs to digital binary images (DBI) was accomplished by adjusting the contrast of TEM photographs so that the interface between silica and rubber matrix would be easily recognized by eye. The silica and rubber phases were

thus determined by a black and a white image, respectively. The details are described in our previous study.²⁴

The averaged area of black-colored phase, which corresponds to the averaged size of one agglomerate in the filled rubber systems ($\overline{S_{agg}}$), and the area fraction of the black phase in the DBI (F_B) were calculated from the DBI. The results are shown in Table IV. It is clearly seen that the $\overline{S_{agg}}$ is decreased by the introduction of coupling agent. The size is the order of unmodified > methyl > decyl. It is well known that the secondary structure such as aggregate and agglomerate formed by silica particles is formed by hydrogen bonding between silanol groups on silica particles.^{5-7,21-23} By the reaction of silanol groups on silica particles with coupling agent, the number of silanol groups decreases, which suppresses a formation of the secondary structure. As stated in the previous section, the reactivity of decyl with silanol groups is poor compared with that of methyl; however, the size of the secondary structure is the smallest among the three. The decyl has a long alkyl group within the molecule. Thus, the increase of hydrophobic character by the introduction of one molecule of coupling agent on the silica surface might be greater for decyl than for methyl, which might suppress the formation of a secondary structure of the modified silica by decyl.

The silica content in all samples was adjusted to be 24 wt %. Thus, all samples should have a similar value of F_B ; however, the F_B increased with increasing the $\overline{S_{agg}}$. In this study, the TEM images were converted into the digital binary images as two-dimensional information. However, TEM images actually involved three-dimensional information because of the sample thickness. Thus, there is a possibility that the observed F_B value is greater than the calculated value of 0.26, which was obtained under the assumption that all silica particles were spheres. As seen in Table IV, the difference between F_B and the calculated value of 0.26 decreased with decreasing the $\overline{S_{agg}}$. Sawanobori et al.²³ reported that certain amounts of rubber molecules were entrapped in the agglomerates as bound rubber in silica-filled polyisoprene systems. Further,

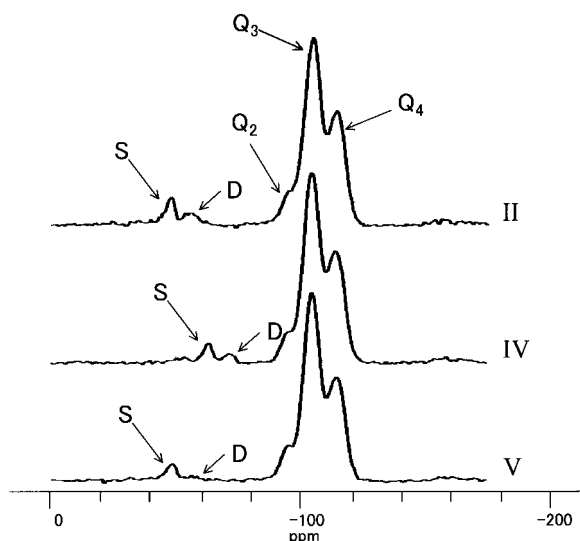


Figure 5 ²⁹Si-CPMAS NMR spectra of bound rubbers obtained from surface-modified silica-filled rubber composites (II: methyl; IV: phenyl; V: decyl).

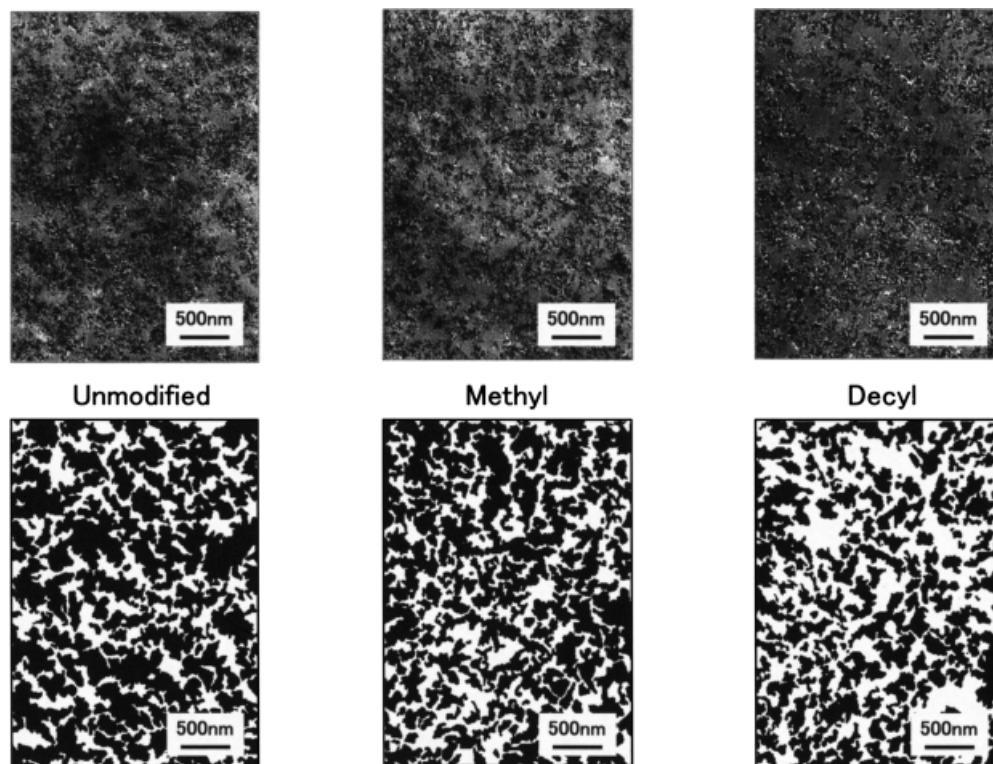


Figure 6 TEM photographs and digital binary images of surface-modified silica-filled rubber systems.

the content of bound rubber increased with increasing the size of agglomerate. In this study, the content of bound rubber (G_t) was also determined. The G_t and the spin–spin relaxation time (T_2) for the highly mobile rubber phase of bound rubber at 30°C are shown in Table V. The G_t increased with the increase of $\overline{S_{agg}}$, similar to the case of silica-filled polyisoprene.²³ The data reveal that T_2 for bound rubber is considerably short compared with that for pure SBR (about 800 μ s). This means that the segmental mobility of bound rubber is highly constrained by silica particles. The result that the content of highly constrained rubber phase increased with the increase of $\overline{S_{agg}}$ suggests that certain amounts of rubber molecules are entrapped within the agglomerates, leading to a value of F_B larger than the calculated value of 0.26.

In the case of unmodified silica-filled vulcanizate, the G_t was large compared with that reported in our previous study.²⁴ In our earlier works, as-received silica was used. As-received silica has a large amount of adsorbed water compared with that for dry silica.

The adsorbed water suppresses the hydrogen bonding between the silica particles, leading to the decrease of $\overline{S_{agg}}$.²³ Thus, the difference of G_t value obtained in this and previous studies was obtained from the difference in values of $\overline{S_{agg}}$.

Tensile properties of modified silica-filled rubber systems

Figure 7 shows the stress–strain curves for silica-filled SBR vulcanizates with different agglomerate sizes and unfilled vulcanizate. The initial slopes of the curves for filled vulcanizates decreased with decreasing the $\overline{S_{agg}}$, which means that the initial moduli of the filled vulcanizates decrease with the decrease of $\overline{S_{agg}}$. Pliskin and Tokita³⁰ studied the effect of the bound rubber on the storage modulus (E') for carbon black-filled SBR systems, and reported that the E' increased with the increase of volume fraction of bound rubber in the composite. Wang^{31,32} suggests that the rubber molecules entrapped in the filler lose their identity as

TABLE IV
Averaged Agglomerate Size ($\overline{S_{agg}}$) and Area Fraction of Silica Phase (F_B) for Silica-Filled Rubber Systems

	Unmodified	Methyl	Decyl
$\overline{S_{agg}}$ (nm ²) $\times 10^4$	12.4	9.2	4.0
F_B	0.65	0.61	0.50

TABLE V
Bound Rubber Content (G_t) and Spin–Spin Relaxation Time (T_2) for the Highly Mobile Rubber Phase of Bound Rubber at 30°C

	Unmodified	Methyl	Decyl
G_t (g/g)	0.988	0.518	0.430
T_2 (μ s)	106.8	194.9	310.2

an elastomer and behave as a filler in terms of stress-strain properties. As stated in the previous section, the segmental mobility of entrapped rubber molecules in the agglomerates is highly constrained compared with that of rubber matrix. Thus, the entrapped rubber phase is expected to show a higher elasticity compared with that of the rubber matrix. Taking these outcomes into consideration, it is suggested that the initial modulus for silica-filled SBR vulcanizates can be controlled by the $\overline{S_{agg}}$ and the content of entrapped rubber molecules.

All the samples (except for unfilled vulcanizate) showed a pseudoyielding point around 20% of strain. The yield phenomenon at a low strain has been observed in the carbon black-filled rubber systems and is thought to be the result of a breakdown of aggregates.^{33,34} Payne studied the effect of dynamic strain amplitude on the dynamic storage modulus (E') for carbon black-filled vulcanizate and reported that the E' of the vulcanizate decreased with increasing strain amplitude, with this tendency more prominent in higher concentrations of filler in the vulcanizate. Further, at a large strain, the effects of filler concentration on the E' decrease significantly.^{33,34} These results were explained by the breakdown of the aggregated secondary network or agglomerates of filler particles formed by van der Waals-London attraction forces. The aggregates and agglomerates in the silica-filled SBR vulcanizates are primarily formed by hydrogen bonding, which is stronger than van der Waals-London attraction forces. Thus, the possibility of a breakdown of the secondary structure in the silica-filled rubber system was evaluated from the effects of dynamic strain amplitude (DSA) on the E' of the samples, and the results are shown in Figure 8. The E' decreased with increasing the DSA. This tendency was more prominent in the samples that had larger agglomerate size. These results indicate that the secondary structure formed by silica particles is destroyed by

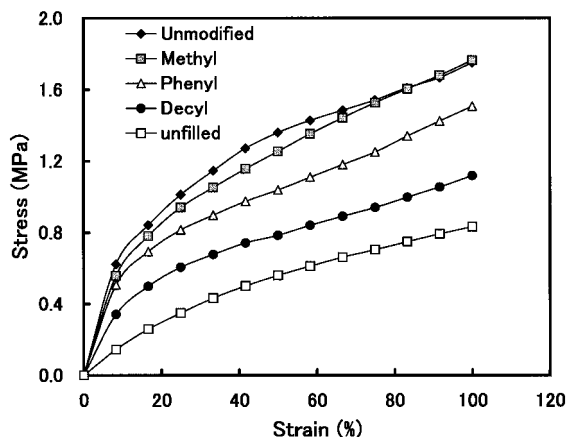


Figure 7 Stress-strain curves of silica-filled and unfilled vulcanizates.

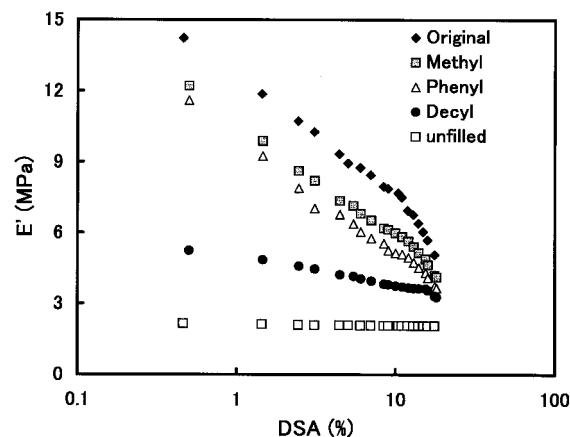


Figure 8 Dynamic strain dependency on the storage modulus for silica-filled and unfilled vulcanizates.

a strain, similar to the case of carbon black, leading to the appearance of a pseudoyielding point on the stress-strain curve of silica-filled vulcanizates.

CONCLUSIONS

The surface-modified silicas were obtained by the reaction of three types of trialkoxyalkylsilane with silanol groups on silica particles. Based on the solid-state ^{29}Si -CPMAS NMR spectra of the samples, the reaction mechanisms between silane coupling agents and silanol groups on silica particles were evaluated. TEM observations and mechanical properties were also investigated for silica-filled vulcanizates that were prepared from SBR and silicas with different surface chemistries. The following conclusions were derived from the experimental results:

1. The reaction of coupling agents with silanol groups on silica surface was significantly affected by water molecules adsorbed on the silica particles.
2. The averaged size of one agglomerate in the filled vulcanizates ($\overline{S_{agg}}$) decreased with the increase of hydrophobic character of silica particles that were obtained by the introduction of coupling agents with alkyl groups.
3. Certain amounts of rubber molecules are suggested to be entrapped within the agglomerates in silica-filled SBR vulcanizates, similar to the case of silica-filled polyisoprene compounds.
4. The initial slope of stress-strain curves for silica-filled vulcanizates decreased with the decrease in the $\overline{S_{agg}}$.
5. A clear Payne effect was observed in all silica-filled vulcanizates, with this tendency more prominent in the larger $\overline{S_{agg}}$, which suggested the breakdown of the secondary structure of silica particles in rubber matrix by a strain.

References

1. Bachmann, J. H.; Sellers, J. W.; Wagener, M. P.; Wolf, R. F. *Rubber Chem Technol* 1959, 32, 1286.
2. Dogadkin, B.; Pechkovskaya, K.; Goldman, E. *Rubber Chem Technol* 1957, 30, 639.
3. Wagner, M. P. *Rubber Chem Technol* 1976, 49, 703.
4. Okamoto, H. *J Soc Rubber Ind Jpn* 1989, 62, 819.
5. Eggers, H.; Schümmer, P. *Rubber Chem Technol* 1996, 69, 253.
6. Wolff, S. *Rubber Chem Technol* 1996, 69, 325.
7. Kravlevich, M. L.; Koenig, J. L. *Rubber Chem Technol* 1998, 71, 300.
8. Tokita, N.; Wang, M.-J.; Chung, B.; Mahmud, K. *J Soc Rubber Ind Jpn* 1998, 71, 522.
9. Waddell, W. H.; Beauregard, P. A.; Evans, L. R. *Tire Technol Int* 1995, 24.
10. Kobayashi, N.; Furuta, I. *J Soc Rubber Ind Jpn* 1997, 70, 147.
11. Fujimaki, T.; Morita, K. *J Soc Rubber Ind Jpn* 1998, 71, 563.
12. Makiura, M. *J Soc Rubber Ind Jpn* 1998, 71, 583.
13. Kojiya, S.; Ikeda, Y. *Rubber Chem Technol* 2000, 73, 534.
14. Doi, A. *J Soc Rubber Ind Jpn* 1998, 71, 102.
15. Wolff, S.; Donnet, J. B. *Rubber Chem Technol* 1990, 63, 32.
16. Donnet, J. B.; Wang, M.-J.; Papirer, E.; Vidal, A. *Kautsch Gummi Kunstst* 1986, 39, 510.
17. Wang, M.-J.; Wolff, S. *Rubber Chem Technol* 1991, 64, 559.
18. Wolff, S.; Wang, M.-J. *Rubber Chem Technol* 1992, 65, 329.
19. Wang, M.-J.; Wolff, S. *Rubber Chem Technol* 1992, 65, 715.
20. Wolff, S.; Wang, M.-J.; Tan, E.-H. *Kautsch Gummi Kunstst* 1994, 47, 102.
21. Ono, S.; Ito, M. *Rep Progr Polym Phys Jpn* 1998, 41, 547.
22. Ono, S.; Kiuchi, Y.; Sawanobori, J.; Ito, M. *Polym Int* 1999, 48, 1035.
23. Sawanobori, J.; Ono, S.; Ito, M. *Kobunshi Ronbunshu* 2000, 57, 356.
24. Yatsuyanagi, F.; Suzuki, N.; Ito, M.; Kaidou, H. *Polymer* 2001, 42, 9523.
25. Sindorf, D. W.; Maciel, G. E. *J Am Chem Soc* 1983, 105, 3767.
26. Hunsche, A.; Görl, U.; Müller, A.; Knaack, M.; Göbel, Th. *Kautsch Gummi Kunstst* 1997, 50, 881.
27. Görl, U.; Hunsche, A. *J Soc Rubber Ind Jpn* 1998, 71, 550.
28. Maciel, G. E.; Sindorf, D. W. *J Am Chem Soc* 1980, 102, 7607.
29. Sindorf, D. W.; Maciel, G. E. *J Am Chem Soc* 1983, 105, 1487.
30. Pliskin, I.; Tokita, N. *J Appl Polym Sci* 1972, 16, 473.
31. Wang, M.-J. *Rubber Chem Technol* 1998, 71, 520.
32. Wang, M.-J. *Rubber Chem Technol* 1999, 72, 430.
33. Payne, A. R. *J Appl Polym Sci* 1962, 19, 57.
34. Payne, A. R.; Whittaker, R. E. *Rubber Chem Technol* 1971, 44, 440.