

# Mechanical Properties of Silane-Treated, Silica-Particle-Filled Polyisoprene Rubber Composites: Effects of the Loading Amount and Alkoxy Group Numbers of a Silane Coupling Agent Containing Mercapto Groups

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**ABSTRACT:** The surface treatment of spherical silica particles with a silane coupling agent with mercapto groups was carried out. The treated silica particles were incorporated within polyisoprene and then vulcanized. The effects of the loading amount and alkoxy group number of silane on the stress-strain curve of the filled composite were investigated. For this purpose, silanes with dialkoxy and trialkoxy structures were used. The loading amount of silane on the silica surface was varied from 1 to 8 times the amount required for monolayer coverage. The stress at the same strain increased with the silane treatment, and it was higher in the dialkoxy structure than in the trialkoxy structure above 300% strain. There was no significant influence of the loading amount on the stress for the trialkoxy silane struc-

ture. However, the stress was influenced by the loading amount, and the maximum stress was observed at 4 times the silane amount required for monolayer coverage for the dialkoxy structure. The stress had a good relationship with the crosslinking density of silica-filled polyisoprene rubber (measured with a swelling test). The reinforcement effect by the silane treatment of silica was found to be affected strongly both by the entanglement of the silane chain and polyisoprene rubber matrix and by the crosslinking reaction between the mercapto group of silane and polyisoprene rubber in the interfacial region. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1507–1514, 2009

**Key words:** composites; fillers; interfaces; rubber

## INTRODUCTION

We have been investigating the effect of the interfacial adhesion between surface-treated inorganic fillers with various silane coupling agents and poly(vinyl chloride) (PVC) on the mechanical properties of their composites.<sup>1–7</sup> Glass beads were used as model filler particles, and silanes with aminopropyl and methacryloxypropyl groups as organic functional groups with dialkoxy or trialkoxy structures were used.<sup>4</sup> The amount of silane detected on the beads by a carbon analysis was about 5 times that required for monolayer coverage. The effects of the organic functional group and the number of alkoxy groups of the silanes were investigated. Higher yield stress of the filled composites was observed for the silane with aminopropyl groups than for the one with methacryloxypropyl groups.

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Furthermore, for both organic functional groups, the yield stress was higher for the silane with a dialkoxy structure than for that with a trialkoxy structure. The former was expected to form a linear chain structure of silane, whereas the latter was expected to form a network structure on the glass bead surface.<sup>8</sup> It was found that the interfacial region which formed with the dialkoxy silane was more effective than that which formed with the trialkoxy silane. Ishida and coworkers<sup>9–12</sup> and Ikuta et al.<sup>8</sup> named such an interfacial layer the interphase, which consists of mutually mixed silane chains covalently bonded on the filler surface and the matrix polymer chains.

In our previous study,<sup>7</sup> the effect of the silane chain length of a silane layer covalently bonded on the bead surface on the mechanical properties of glass-bead-filled PVC was investigated with two silane coupling agents with a dialkoxy structure having aminopropyl or methacryloxypropyl groups as organic functional groups. To obtain various silane chain lengths on the surface of the glass beads, the amount of silane added for the surface treatment

was varied. The yield stress of the composite increased and the elongation at break decreased with an increase in the silane chain length for methacryloxypropyl groups as organic functional groups. The reinforcement effect of the formed interfacial region became more effective with an increase in the silane chain length. The influence of the silane chain length was smaller for aminopropyl groups as organic functional groups than for methacryloxypropyl groups.

In this study, the effect of the loading amount of silane on the mechanical properties was examined for both dialkoxy and trialkoxy structures in a composite with a vulcanized polyisoprene rubber matrix. The deformation of the vulcanized rubber is larger than that of PVC. Larger deformation is desirable to compare the effect of the formed interfacial region by the difference in the dialkoxy or trialkoxy structure on the mechanical properties. Furthermore, spherical silica particles with a smaller mean size (3.3  $\mu\text{m}$ ) and a larger specific surface area (3.9  $\text{m}^2/\text{g}$ ), rather than those of the glass beads (14  $\mu\text{m}$ , 0.34  $\text{m}^2/\text{g}$ ) used in the previous study,<sup>7</sup> were employed. Silane coupling agents having mercapto groups with dialkoxy and trialkoxy structures were used because mercapto groups in the silane react with *cis*-1,4-polyisoprene rubber (PIR).<sup>13</sup>

## EXPERIMENTAL

### Materials

Commercially available PIR (IR-2200, Kraton JSR Elastomers K.K., Tokyo, Japan), sulfur (Sigma-Aldrich Japan K.K., Tokyo, Japan) as a vulcanizing agent, zinc oxide (Sigma-Aldrich Japan) and *N*-cyclohexyl-2-benzothiazolylsulfenamide (Tokyo Chemical Industries Co., Ltd., Tokyo, Japan) as vulcanization accelerators, stearic acid (Sigma-Aldrich Japan) as an accelerator activator, and polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (Kawaguchi Chemical Industries Co., Ltd., Tokyo, Japan) as an antioxidant were used as received. Spherical amorphous silica particles (median mean size = 3.3  $\mu\text{m}$ , specific surface area = 3.9  $\text{m}^2/\text{g}$ ; FB-3SDX, Denki Kagaku Kogyo Kabushiki Kaisya, Tokyo, Japan) as fillers, 3-mercaptopropyl methyltrimethoxysilane (MrPDMS; KEM-802, Shin-Etsu Chemical Co., Ltd., Tokyo, Japan) and 3-mercaptopropyl trimethoxysilane (MrPTMS; KBM-803, Shin-Etsu Chemical) as silane coupling agents, and reagent-grade 2-propanol as a solvent were also used as received.

### Surface treatment

The surface treatment was carried out in the same way described in the previous article.<sup>7</sup> The amount

**TABLE 1**  
Recipes for the PIR/Silica Composites

	Unfilled PIR (phr)	PIR/silica composite (phr)
PIR	100	100
Silica	—	30
Sulfur <sup>a</sup>	2.0	2.0
Zinc oxide <sup>b</sup>	5.0	5.0
CBS <sup>c</sup>	1.2	1.2
Stearic acid <sup>d</sup>	2.0	2.0
TMQ <sup>e</sup>	1.0	1.0

<sup>a</sup> Vulcanizing agent.

<sup>b</sup> Vulcanization accelerator.

<sup>c</sup> Vulcanization accelerator, *N*-cyclohexyl-2-benzothiazolylsulfenamide (CBS).

<sup>d</sup> Accelerator activator.

<sup>e</sup> Antioxidant, polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ).

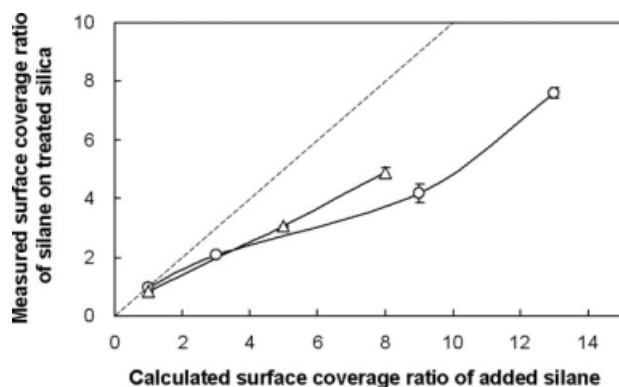
of silane required for monolayer coverage of silica particles was calculated in the same way used in the previous studies<sup>1-7</sup> with the area occupied by a single silane molecule (0.13  $\text{nm}^2$ )<sup>14,15</sup> and the specific surface area values of silica particles. The amount of silane required for monolayer coverage of silica particle is equal to a surface coverage ratio of 1. The amount of silane in the treatment is shown as the surface coverage ratio in this article. The silane, the silica particles, and 2-propanol were mixed for 5 min in an evaporator. Soon after this mixing, the drying of the solvent in the mixture was carried out in an evaporator. After this drying process was completed, all the treated silica particles were left at room temperature for 24 h, and then they were heated at 120°C for 24 h in an oven.

### Carbon analysis

The carbon content of the silane-treated silica was measured with a carbon analyzer (EMIA-110, Horiba, Ltd., Kyoto, Japan) to estimate the amount of silane on its surfaces.<sup>1-7</sup>

### Sample preparation

Table I shows the recipe for the preparation of the PIR/silica composite. The silica particle content was 30 parts per hundred parts of rubber by weight (phr). First, the mastication of PIR was conducted at room temperature for 3 min with a mixing roll (191-TM, Yasuda Seiki Seisakusho, Ltd., Nshinomiya, Hyogo, Japan). Second, a mixture of the other components, except for silica, was added to the PIR and kneaded for 5 min. Third, silica particles were added little by little for 7 min with kneading. The total kneading time was 20 min. Sheets with a thickness of approximately 1 mm were prepared and were vulcanized at the same time by compression of the



**Figure 1** Relationship between the amount of silane measured on the silica surface for (○) MrPDMS- and (△) MrPTMS-treated silica particles by a carbon analysis and the amount of added silane for surface treatment. The amount of silane is shown as the surface coverage ratio. The broken line indicates the amount of silane calculated under the assumption that the added silane is completely adsorbed onto the silica surface.

kneaded compounds at 145°C under a pressure of 20 MPa for 20 min with a pressing machine (MP-WNL 250 mini test press, Toyo Seiki Seisaku-Sho, Ltd., Tokyo, Japan).

#### Tensile test

A tensile test was carried out with dumbbell-type specimens (Japanese Industrial Standard JIS-K6301-3) about 1 mm thick with a crosshead speed of 200 mm/min and a chuck distance of 40 mm with a tensile testing machine (AG-5KNIS, Shimadzu Corp.). The stress–strain curves were recorded.

#### Swelling test

To characterize the crosslinking density of the PIR sheet, a swelling test with a sample sheet was carried out.<sup>16</sup> The strip specimen (10 × 20 × 1 mm<sup>3</sup>) was dipped in toluene for 6 h at room temperature, and the equilibrium degree of swelling ( $Q$ ) was measured in accordance with eq. (1):

$$Q = \frac{m - m_0}{m_0} \times 100 \quad (1)$$

where  $m_0$  and  $m$  are the masses of the unswollen and swollen specimens, respectively.

The crosslinking density ( $\nu_e$ ) was calculated with the following equations:<sup>17</sup>

$$\nu_e = \frac{\rho_p N_A}{M_c} \quad (2)$$

$$M_c = -V_1 \rho_p \frac{\phi_p^{1/3} - \frac{\phi_p}{2}}{\ln(1 - \phi_p) + \phi_p + \chi_1 \phi_p^2} \quad (3)$$

where  $\rho_p$  is the density of the polymer,  $N_A$  is Avogadro's constant,  $M_c$  is the molecular weight between crosslinking points,  $V_1$  is the molar volume of the solvent,  $\phi_p$  is the volume fraction of the polymer in the specimen swollen with the solvent, and  $\chi_1$  is the Flory–Huggins interaction parameter for the polymer and solvent.

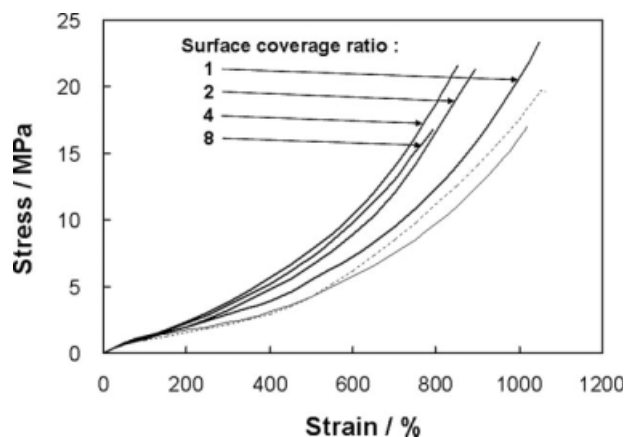
#### Extraction test

The interaction between the silane chain covalently bonded on the silica surface and the unvulcanized PIR molecules was examined as follows.<sup>18</sup> In the first procedure, PIR (15 g) and silane-treated silica particles (9 g) were mixed at room temperature for 15 min with a mixing roll. The obtained mixture was dipped in toluene in a glass vessel at room temperature for 24 h to extract the free PIR in the mixture via shaking with a shaker (BR-3000LF, Taitec Corp., Saitama, Japan) at a rate of 140 cycles per minute. In the second procedure, the PIR/toluene mixture in a glass vessel was vibrated in an ultrasonic cleaner (Bransonic 221, Yamato Scientific Co., Ltd., Tokyo, Japan) for 30 min, and then it was centrifuged with a centrifugal precipitator (H-100BC, Kokusan Co., Ltd., Tokyo, Japan) at 1000 rpm for 10 min. The separated precipitate was mixed with toluene (200 mL) in a glass vessel. The vessel was shaken with the shaker at a rate of 140 cycles per minute again for at least 6 h. The second procedure was repeated six times. In each repetition, methanol as a poor solvent of PIR was added to the clear supernatant of toluene obtained by centrifugal precipitation to confirm that there was extracted PIR. As a result, a deposit of PIR was formed. After the sixth centrifugal precipitation, no deposit of PIR was formed in the clear supernatant of toluene with the addition of methanol. In the third procedure, the shaken precipitate and toluene mixture was filtered with a membrane filter (mean pore size = 0.8 μm; T080A, Toyo Roshi Kaisha, Ltd., Tokyo, Japan), and the separated solid was dried at 40°C in an oven for 1 week. The amount of unextracted PIR on the silica surface was measured by carbon analysis.

## RESULTS AND DISCUSSION

The effect of the amount of adsorbed silane on the mechanical properties of the PIR/silica composite was investigated. For this purpose, the amount of silane added for the surface treatment was varied to prepare silica particles with different amounts of adsorbed silane on the surface.

Figure 1 shows the relationship between the measured surface coverage ratio of silane on MrPDMS- and MrPTMS-treated silica particles and the surface coverage ratio calculated with the added silane for



**Figure 2** Stress–strain curves of unfilled vulcanized PIR (dashed line) and PIR filled with untreated silica particles (thin, solid line) or MrPDMS-treated silica particles (thick, solid line) with a particle content of 30 phr. The mean particle size was 3.3  $\mu\text{m}$ . The surface coverage ratios of silane were 1, 2, 4, and 8.

the surface treatment. The measured surface coverage ratio of silica increased gradually with an increase in the amount of added silane, and this indicates that MrPDMS- and MrPTMS-treated silica particles with different silane loadings were obtained. The broken line indicates the amount of silane calculated under the assumption that the added silane was completely covalently bonded on the silica surface. In this study, the measured surface coverage ratio values of 0.94, 2.08, 4.17, and 7.56 are shown as 1, 2, 4, and 8 for the MrPDMS-treated particles, and those of 0.84, 3.04, and 4.90 are shown as 1, 3, and 5 for the MrPTMS-treated particles.

Figure 2 shows the stress–strain curves of unfilled vulcanized PIR with no silica particles and PIR filled with untreated or MrPDMS-treated silica particles with various silane loadings with a particle content of 30 phr. Each curve is one of five measured results. The stress increased with an increase in the strain for the unfilled vulcanized PIR. The stress for the untreated silica-filled PIR was higher below 600% strain but lower above 600% strain versus that for the unfilled PIR. This result indicates that there was no reinforcement effect by the untreated silica particles at a higher strain. The interface between the silica particles and PIR seems to be debonded at about 600% strain. The stress increased with the silane treatment for MrPDMS-treated silica-filled PIR. There was a significant difference with the loading amount of silane in the stress, and the stress was independent of the loading amount of silane.

Figure 3 shows the stress–strain curves of MrPTMS-treated silica with various loading amounts of silane with a particle content of 30 phr. The stress increased with the silane treatment for MrPTMS-treated silica-filled PIR. However, there was no sig-

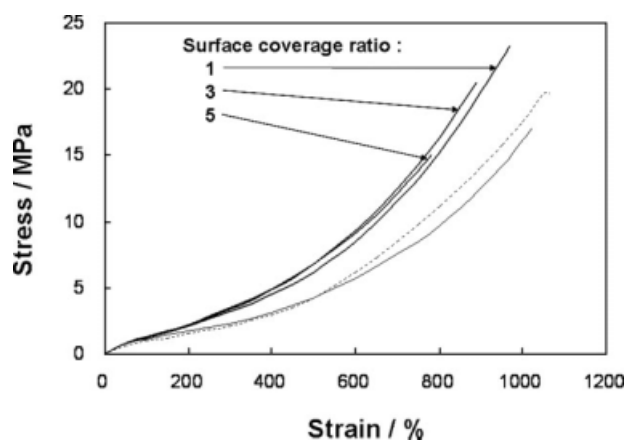
nificant difference with the loading amount of silane in the stress.

Table II shows the results of tensile testing, such as the stress values at various strains. The averages of five measured values and the differences between the average and maximum or minimum values are shown in this table. The following figures are plotted from the data in Table II.

Figure 4 shows the effect of the surface coverage ratio of MrPDMS- and MrPTMS-treated silica on the fracture stress of the silica-filled vulcanized PIR. The broken line indicates the fracture stress of the unfilled vulcanized PIR. The fracture stress increased with the surface treatment and decreased with an increase in the surface coverage ratio for both MrPDMS- and MrPTMS-treated systems. The fracture stress was slightly higher in the MrPDMS-treated system than in the MrPTMS-treated system.

Figure 5 shows the effect of the surface coverage ratio on the elongation at break. The broken line indicates the elongation at break of the unfilled vulcanized PIR. The elongation at break decreased with an increase in the surface coverage ratio for both MrPDMS- and MrPTMS-treated systems.

Figure 6 shows the effect of the surface coverage ratio on the stress at 300% strain. The broken line indicates the stress of the unfilled vulcanized PIR. The stress of the untreated silica-filled PIR (measured surface coverage ratio of silane = 0) showed almost the same level, whereas the stress increased with the silane treatment. There was no significant influence of the loading amount of silane on the stress for the MrPTMS-treated system. However, the stress increased with an increase in the loading amount for the MrPDMS-treated system, and the maximum stress value was obtained with the

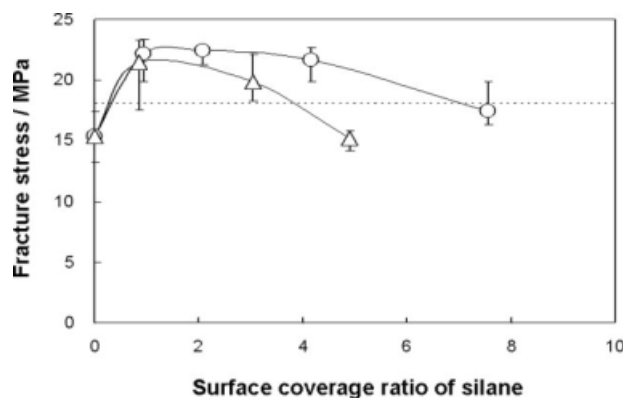


**Figure 3** Stress–strain curves of unfilled vulcanized PIR (dashed line) and PIR filled with untreated silica particles (thin, solid line) or MrPTMS-treated silica particles (thick, solid line) with a particle content of 30 phr. The mean particle size was 3.3  $\mu\text{m}$ . The surface coverage ratios of silane were 1, 3, and 5.

**TABLE II**  
**Tensile Properties of the PIR/Silica Composites**

Composite	Surface coverage ratio	Stress (MPa) <sup>a</sup>										Fracture stress (MPa)	Elongation at break (%)		
		50% strain	100% strain	300% strain	500% strain	700% strain	700% strain	700% strain	700% strain	700% strain	700% strain				
Unfilled PIR	—	0.67	+0.07	0.98	+0.08	2.18	+0.16	4.14	+0.38	8.08	+0.51	18.02	+4.84	1027	+123
Untreated silica-filled PIR	—	0.80	+0.01	1.15	+0.02	2.33	+0.03	4.28	+0.08	7.58	+0.26	15.36	+2.10	977	+58
MrPDMS-treated silica-filled PIR	1	0.82	+0.03	1.21	+0.04	2.99	+0.07	5.54	+0.20	9.64	+0.62	22.14	+1.22	1043	+37
	2	0.68	+0.02	1.08	+0.03	3.27	+0.03	6.63	+0.17	12.21	+0.43	22.44	+0.45	926	+19
	4	0.84	+0.13	1.30	+0.03	3.92	+0.27	7.83	+0.39	14.35	+0.93	21.66	+1.06	845	+28
	8	0.82	+0.01	1.24	+0.01	3.58	+0.05	7.15	+0.10	13.03	+0.30	17.40	+2.47	811	+51
MrPTMS-treated silica-filled PIR	1	0.83	+0.02	1.24	+0.02	3.27	+0.08	6.34	+0.21	11.56	+0.39	21.49	+1.79	939	+55
	3	0.83	+0.01	1.25	+0.02	3.40	+0.03	6.76	+0.08	12.36	+0.36	19.84	+2.30	881	+23
	5	0.83	+0.02	1.26	+0.03	3.42	+0.07	6.71	+0.14	12.14	+0.18	15.12	+0.59	783	+13
			-0.02		-0.03		-0.09		-0.17		-0.11		-1.01		-25

<sup>a</sup> The values shown are the average of five measured values. Upper right of the average: difference between the average and the maximum value. Lower right of the average: difference between the average and the minimum value.

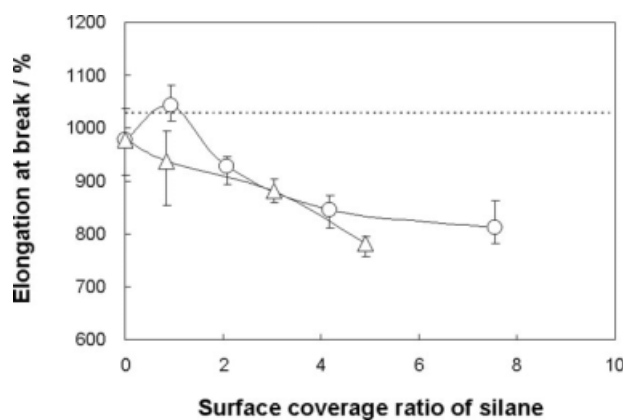


**Figure 4** Effect of the surface coverage ratio of (○) MrPDMS- and (△) MrPTMS-treated silica particles on the fracture stress of the silica-filled vulcanized PIR (measured with a tensile test). The broken line indicates the fracture stress of the unfilled vulcanized PIR. The silica particle content was 30 phr.

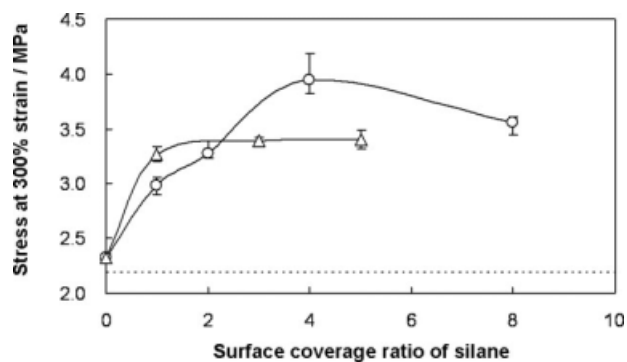
surface coverage ratio of 4. Above the surface coverage ratio of 4, the stress decreased. The reinforcement effect was strongly affected by the loading amount and the alkoxy group numbers of silane. The tendency of Figure 6 was observed above 300% strain, as shown in Table II.

The mercapto group in the silane reacts with PIR in a similar way with sulfur as a vulcanizing agent.<sup>13</sup> Therefore, there is a possibility that the loading amount of silane and the chain structure affect the crosslinking structure. Next, a swelling test of the silica-filled vulcanized PIR was carried out.

Figure 7 shows the degree of swelling of filled PIR. The broken line indicates the degree of swelling of unfilled vulcanized PIR. These results indicate that the degree of swelling was affected by both the loading amount of silane and the alkoxy group num-



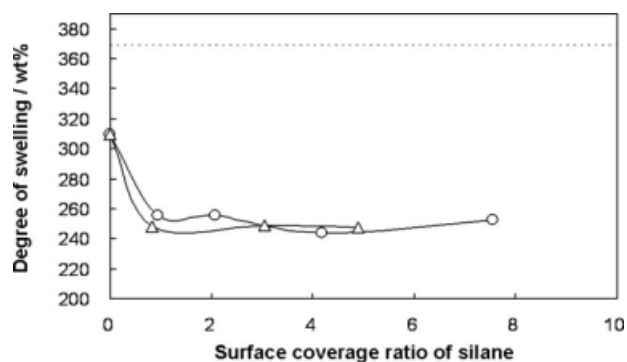
**Figure 5** Effect of the surface coverage ratio of (○) MrPDMS- and (△) MrPTMS-treated silica particles on the elongation at break of the silica-filled vulcanized PIR (measured with a tensile test). The broken line indicates the elongation at break of the unfilled vulcanized PIR. The silica particle content was 30 phr.



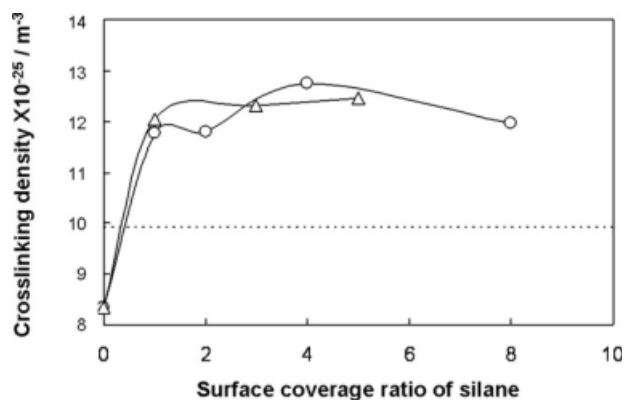
**Figure 6** Effect of the surface coverage ratio of (○) MrPDMS- and (△) MrPTMS-treated silica particles on the stress at 300% strain of the silica-filled vulcanized PIR (measured with a tensile test). The broken line indicates the stress of the unfilled vulcanized PIR. The silica particle content was 30 phr.

bers of silane. From these results, the crosslinking density was calculated.

Figure 8 shows the calculated crosslinking density. The broken line indicates the crosslinking density of unfilled vulcanized PIR. The crosslinking density of untreated silica-filled PIR was lower than that of unfilled vulcanized PIR because the PIR component, which could be crosslinked, decreased with the addition of silica. However, the crosslinking density of silane-treated silica-filled PIR was higher than that of unfilled vulcanized PIR. This result indicates that a crosslinking reaction between the mercapto group in the silane and PIR occurred. That is, this crosslinking reaction increased the reinforcement effect, and then the stress shown in Figure 6 was increased. The tendency of the crosslinking density shown in Figure 8 was in good agreement with the stress at 300% strain shown in Figure 6. It was expected that the increase in stress would be dependent on the degree of the crosslinking reaction between the mercapto group in the silane and PIR at the interfacial region.



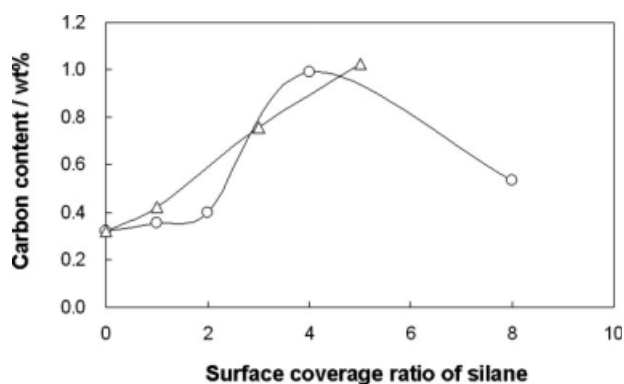
**Figure 7** Degree of swelling of vulcanized PIR filled with (○) MrPDMS- and (△) MrPTMS-treated silica particles. The broken line indicates the degree of swelling of the unfilled vulcanized PIR. The silica particle content was 30 phr.



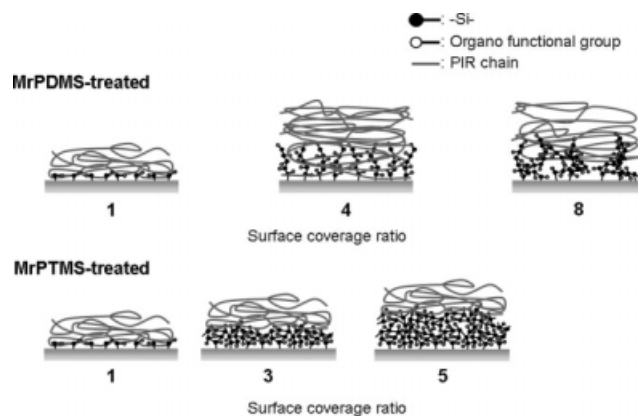
**Figure 8** Measured crosslinking density of vulcanized PIR filled with (○) MrPDMS- and (△) MrPTMS-treated silica particles. The broken line indicates the crosslinking density of the unfilled vulcanized PIR. The silica particle content was 30 phr.

Figure 9 shows the amount of the unextracted organic component (shown as the carbon content) from the PIR/silica mixture for the treated silica-filled systems. The tendency of the amount of unextracted PIR was similar to the tendency of the stress at 300% strain shown in Figure 6 and the tendency of the crosslinking density shown in Figure 8. This result indicates that the entanglement of the silane chain and PIR matrix at the interfacial region tends to occur in accordance with this order.

The amount of the unextracted organic component shown in Figure 9 contains the amount of silane deposited on the silica surface. When the carbon content based on the silane was subtracted from the carbon content shown in Figure 9, the resultant values became negative. However, the tendency agreed completely with that shown in Figure 9. The negative values seemed to be caused for the following reason. The spherical silica particles used in this study contained submicrometer-sized fine particles.



**Figure 9** Amount of the unextracted organic component from a PIR/silica mixture for (○) MrPDMS- and (△) MrPTMS-treated silica-filled systems (measured with a carbon analysis). The amount of the unextracted organic component is shown as the carbon content.



**Figure 10** Schematic views of the interfaces of the MrPDMS- and MrPTMS-treated silica particles and vulcanized PIR matrix.

These silane-treated fine particles were hardly centrifuged and remained in the supernatant.

Figure 10 shows schematic views of the interfaces of the treated silica and vulcanized PIR matrix. In the case of the dialkoxy structure, silane should form a linear chain structure. The amount of mercapto groups increases with an increase in the silane chain, so the crosslinking reaction between the silane chain and PIR matrix should increase. However, in the case of too long silane chains, such as a surface coverage ratio of 8, the crosslinking reaction between the silane chain and PIR matrix decreases with the self-agglomeration of silane chains.

In the case of the trialkoxy structure, silane forms a network structure. The matrix polymer chain hardly penetrates the silane network, so the crosslinking reaction between the silane chain and PIR matrix should occur only in the surface region of the silane network, and the degree of interaction is independent of the loading amount of silane.

In our previous study,<sup>7</sup> the effect of the silane chain length on the glass bead surface on the mechanical properties of glass-bead-filled PVC was investigated with 3-methacryloxypropyl methyltrimethoxysilane (MPDMS). The silane chain length was varied with surface coverage ratios of 1–9. As a result, the yield stress of the composite increased and the elongation at break decreased with an increase in the silane chain length. The reinforcement effect of the formed interfacial region became more effective with an increase in the silane chain length. This suggests that the entanglement of the silane chain and PVC tends to increase with an increase in the silane chain length. The result was different from the result of this study. The difference seemed to be caused by the compatibility of the silane chain and the matrix polymer; therefore, their solubility parameters (SPs) were considered. The SP value of PVC was 19.5 (MPa)<sup>1/2</sup>.<sup>17</sup> The SP values of

hydrolyzed MPDMS and the condensate of five hydrolyzed MPDMS molecules, which were calculated with the Fedors method,<sup>19</sup> were 23.7 and 20.6 (MPa)<sup>1/2</sup>, respectively. They showed the approximate values. On the other hand, the SP value of PIR was 15.2 (MPa)<sup>1/2</sup>.<sup>17</sup> The calculated SP value of hydrolyzed MrPDMS and that of the condensate of five hydrolyzed MrPDMS molecules were 24.4 and 19.7 (MPa)<sup>1/2</sup>, respectively. These results indicate that the self-agglomeration of silane chains tends to occur more in the PIR matrix than in the PVC matrix.

On the basis of the aforementioned results, the reinforcement effect by the silane treatment is strongly affected by the entanglement of silane chains bonded onto the silica particle surface and PIR matrix in the interfacial region.

### CONCLUSIONS

The surface treatment of spherical silica particles with MrPDMS and MrPTMS was carried out. The effects of the loading amount and alkoxy group number of the silane on the mechanical properties of the PIR/silica composite were investigated. The following results were obtained:

1. The stress value observed at the same strain increased with the silane treatment of silica particles.
2. There was no significant influence of the loading amount for the MrPTMS-treated system on the stress at the same strain.
3. The stress at the same strain was higher for the MrPDMS-treated system than for the MrPTMS-treated system. The stress was dependent on the loading amount, and the maximum stress was observed at 4 times the surface coverage ratio for the MrPDMS-treated system.
4. There was a good relation between the stress at the same strain and the crosslinking density measured by a swelling test for silica-filled PIR.

5. The reinforcement effect by the silane treatment was strongly affected by the entanglement of the silane chain and PIR matrix in the interfacial region.

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