

## Mechanical Properties of Silane-Treated Silica Particle-Filled Polyisoprene Composites: Influence of the Alkoxy Group Mixing Ratio in Silane Coupling Agent Containing Mercapto Group

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**ABSTRACT:** Spherical silica particles were treated with a mixture of silane coupling agents with mercapto functional groups and dialkoxy or trialkoxy groups. The surface coverage, which indicates the number of layers covering the silica surface, was in the range from 1.6 to 6.0. The molecular mobility of the treated layer was analyzed with <sup>1</sup>H-NMR spectroscopy. The silane chain became more flexible with increasing dialkoxy structures in the mixture and with increasing surface coverage. The stress–strain behavior was measured for a composite consisting of the treated silica and vulcanized polyisoprene rubber (PIR). There was no influence of the dialkoxy and trialkoxy mixing ratio for near monolayer coverage. In the case of the pure dialkoxy and low trialkoxy contents, a higher stress was observed at the same strain for surface coverages of 2.4–3.8. However, a longer length flexible silane chain, that is, with a surface coverage of 6.0, was disadvantageous for the reinforcement effect. The results of pulse NMR analysis of the unextracted PIR on the particle surface and swelling test indicate that the reinforcement effect was strongly affected both by entanglement and the crosslinking reaction between the silane chain and PIR at the interfacial region. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 128: 2548–2555, 2013

**KEYWORDS:** composites; fillers; interfaces; rubber

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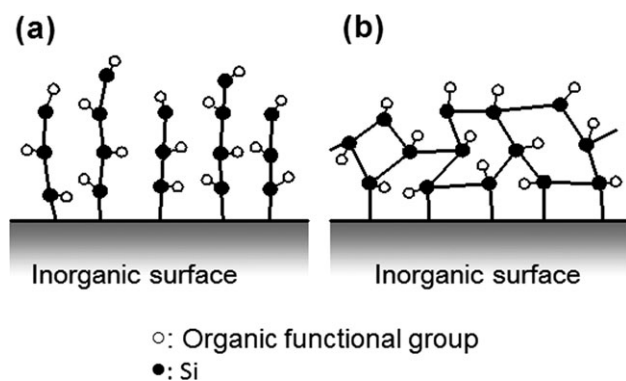
### INTRODUCTION

Silane coupling agents are widely used for the surface modification of inorganic materials. Much research has been conducted on the reactivity of silane coupling agents and characterization of the silane layer formed on an inorganic surface.<sup>1–25</sup> We have also characterized the silane layer on inorganic particle surfaces and the effect of interfacial adhesion between fillers and a matrix polymer on the mechanical properties of a composite of the treated inorganic particles with various silane coupling agents.<sup>26–32</sup>

In our previous study,<sup>32</sup> spherical silica particles were treated with a silane coupling agent having mercapto groups, and the structure of the silane-treated layer and the loading amount were analyzed with pulse <sup>1</sup>H-NMR spectroscopy and thermogravimetric (TG) analysis. The principle of pulse NMR is as follows.<sup>33–35</sup> The nuclear spin of protons in the polymer is first oriented in a magnetic field, and the relaxation time of the nuclear spin is measured. The spin–spin ( $T_2$ ) relaxation time obtained by measurement of the free induction decay (FID) is dependent on the molecular mobility. Silanes with dialkoxy and

trialkoxy structures were used. As shown in Scheme 1, the dialkoxy and trialkoxy structures form linear-chain and network structures, respectively. The loading amount of silane on the silica surface was varied from one to nine times that required for monolayer coverage. The effects of the loading amount and the silane structure on the molecular mobility were investigated. The relaxation time measured by pulse NMR was longer in the dialkoxy type than in the trialkoxy type and increased with increasing loading amount of dialkoxy type silane, although there was no influence observed for the trialkoxy type silane. The dialkoxy type silane structure was flexible, whereas the trialkoxy type silane structure was rigid.

The treated silica particles were mixed with a polyisoprene rubber (PIR) matrix and vulcanized, and the effects of the linear-chain and network structures on the stress–strain characteristics of the filled composite were investigated.<sup>31</sup> The stress at the same strain was increased by silane treatment and was higher for the dialkoxy structure than the trialkoxy structure. The stress characteristics showed good correlation with the crosslinking density of the silica-filled PIR, as measured by a swelling test.



**Scheme 1.** Schematic image of the silane-treated layer on an inorganic surface. Alkoxy group number: (a) 2 and (b) 3.

This was because the linear-chain silane spread into the PIR matrix easily and crosslinked with the PIR molecules. Naviroj et al.,<sup>3</sup> Miller and Ishida,<sup>4</sup> Culler et al.,<sup>5</sup> and Ikuta et al.<sup>6</sup> referred to the interfacial region consisting of mutually mixed silane chains covalently bonded to the filler surface and the matrix polymer chains as the *interphase*. The molecular mobility of the silane chains also influenced the interphase formation.

In this study, silica particles were treated with various mixing ratios of dialkoxy and trialkoxy structures and various loading amounts to form silane network structures with different network densities on the silica surface. The molecular mobility of silane chains on the silica surface was characterized by pulse NMR and TG analysis. The treated silica particles were incorporated into a PIR matrix, and the effect of the crosslinking structure of the silane-treated layer on the mechanical properties of the treated silica/PIR composite was investigated. The lightly crosslinked network structure of silane chains on the silica surface may have formed an interpenetrating polymer network<sup>36</sup> structure with PIR chains, which would have resulted in an improvement of the reinforcement effect of filler addition. Furthermore, the entanglement of silane and PIR chains at the silica particle/PIR interface was again estimated with pulse NMR.

## EXPERIMENTAL

### Materials

For the vulcanization of PIR, we used the following compounds as received: commercially available *cis*-1,4-polyisoprene (PIR; IR-2200, JSR Corp., Tokyo, Japan) as the base polymer, sulfur (Sigma-Aldrich Japan, Tokyo, Japan) as a vulcanizing agent, zinc oxide (Sigma-Aldrich Japan), *N*-cyclohexyl-2-benzothiazolylsulfenamide (Tokyo Chemical Industries Co., Ltd., Tokyo, Japan) as a vulcanization accelerator, 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.

Spherical amorphous silica particles (mean size = 3.3  $\mu\text{m}$ , specific surface area = 5.3  $\text{m}^2/\text{g}$ , FB-3SDX, Denki Kagaku Kogyo Kabushiki Kaisha, Tokyo, Japan) and silane coupling agents, 3-mercaptopropylmethyldimethoxysilane (MrPDMS; dialkoxy type, KBM-802, Shin-Etsu Chemical Co., Ltd., Tokyo, Japan) and 3-mercaptopropyltrimethoxysilane (MrPTMS; trialkoxy type,

KBM-803, Shin-Etsu Chemical Co.), were used as received. Reagent-grade 2-propanol (2-PA) was used as a solvent.

### Surface Treatment

The surface treatment was conducted in the same way as described in our previous report.<sup>31</sup> The silane coupling agents and silica particles were mixed for 5 min in 2-PA, after which the 2-PA solvent was removed with an evaporator. After the complete evaporation of 2-PA, the treated silica particles were left at room temperature for 24 h and were then heated at 120°C for 24 h in an oven. The amount of silane required for the monolayer coverage of the silica particles was calculated in the same way as previously described<sup>30–32</sup> with the area occupied by a single silane molecule (0.13  $\text{nm}^2$ )<sup>37,38</sup> and the specific surface area of the silica particles. The amount of silane required for the monolayer coverage of a silica particle was equivalent to a surface coverage of 1.

### Polycondensation of the Silane Coupling Agents

Polycondensation of MrPDMS, MrPTMS, and the MrPDMS/MrPTMS mixtures was carried out as follows. The mixture of silane coupling agent and water (1:2 w/w) was stirred with a magnetic stirrer for 24 h. The pH of the mixture was adjusted to 10 by the addition of a 1.0 wt % sodium hydroxide aqueous solution, and the mixture was poured into a polytetrafluoroethylene vessel, where it was left at room temperature for 1 week. Polycondensed silane coupling agents were obtained as a result and are denoted here as PMrPDMS, PMrPTMS, and P(MrPDMS/MrPTMS) for MrPDMS, MrPTMS, and MrPDMS/MrPTMS mixture, respectively.

### Quantitative Analysis of the Loading Amount

The loading amount of silane on the treated silica surface was measured with thermogravimetry/differential thermal analysis (TG/DTA-6300, SII NanoTechnology, Inc., Chiba, Japan). Dried silane-treated silica particles were heated at 1000°C for 3 h in an air atmosphere (flow rate = 500 mL/min) at a heating rate of 10°C/min. The loading amount of silane on the treated silica surface was measured by the weight loss on heating and was shown by the surface coverage, which indicated the number of layers covering the silica surface.

When the treated silica was burned in the presence of O<sub>2</sub>, C, H, and S atoms in the silane coupling agent were removed as CO<sub>2</sub>, H<sub>2</sub>O, and SO<sub>2</sub> gases, respectively. On the other hand, Si atoms remained as solid SiO<sub>2</sub> on the silica surface. So, the weight loss determined by TG analysis was based on the C, H, and S atoms, except Si and O, which corresponded to SiO<sub>2</sub>. To calculate the surface coverage, a correction in consideration of this point was done.

### Analysis of the Molecular Mobility

The molecular mobility of silane chains was investigated with pulse <sup>1</sup>H-NMR (resonance frequency = 25 MHz, JNM-MU25, JEOL, Ltd., Tokyo, Japan) by the solid echo method at 35°C with a sampling time of 2 ms, as previously described,<sup>32</sup> and the T<sub>2</sub> relaxation behavior was measured.

### Sample Preparation

We previously reported the formulation of the PIR-silica composite.<sup>31</sup> The silica particle content used in the PIR matrix was 23.1 wt %. First, the PIR was masticated at room temperature

for 3 min with a mixing roll (191-TM, Yasuda Seiki Seisakusho, Ltd., Hyogo, Japan). The mixture of other components, except silica, was then added to the PIR and mixed for 5 min. Silica particles were gradually added for 7 min with mixing. The total mixing time was 20 min. Sheets approximately 1 mm thick were prepared and vulcanized at the same time by compression of the mixed compounds at 145°C under a pressure of 20 MPa for 20 min with a pressing machine (Mini Test Press, MP-WNL 250, Toyo Seiki Seisaku-Sho, Ltd., Tokyo, Japan).

### Tensile Testing

Tensile testing was conducted with dumbbell-type specimens (Japanese Industrial Standard JIS-K6301-3) approximately 1 mm thick with a crosshead rate of 200 mm/min with a tensile testing machine (AG-5KNIS, Shimadzu Corp., Kyoto, Japan) to record stress-strain curves. The distance between the specimen grip tools was 40 mm (the actual specimen length).

### Swelling Test

The crosslinking density of the PIR sheet was measured in the same way as previously described.<sup>31</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 was measured. The crosslinking density ( $\nu_e$ ) was calculated with the following equations:<sup>39</sup>

$$\nu_e = \frac{\rho_p N_A}{M_c} \quad (1)$$

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

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 solvent,  $\phi_p$  is the volume fraction of polymer in the swollen specimen with solvent, and  $\chi_1$  is the Flory-Huggins polymer/solvent interaction parameter.

### Extraction Test

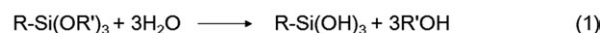
The interaction between the silane chains covalently bonded on the silica surface and the unvulcanized PIR molecules was examined on the basis of the conditions reported by Pliskin and Tokita.<sup>40</sup> The PIR (15 g) and silane-treated silica particles (9 g) were mixed at room temperature for 15 min with a mixing roll. The free PIR in the mixture was extracted by toluene dipping at room temperature in the same way as previously described.<sup>31</sup> The molecular mobility of the mixture of silane and PIR chains remaining on the silica particle surface was then analyzed with pulse NMR.

## RESULTS AND DISCUSSION

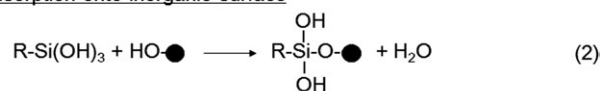
### Reaction of the Silane Coupling Agent

Scheme 2 shows the reaction of the silane coupling agent. {SCHEME2} The hydrolysis reaction of the silane coupling agent occurred in an aqueous phase; as a result, a silanol group formed (part 1). The formed silanol group reacted to an inorganic surface (part 2). The self-condensation reaction of silane coupling agents also occurred simultaneously (part 3). When this reaction occurred on the inorganic particle surface, the silane treated layer, as shown in Scheme 1, was expected to be formed, depending on the alkoxy group number.

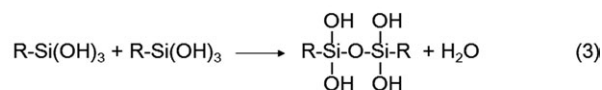
### Formation of silanol group via hydrolysis



### Adsorption onto inorganic surface



### Self-condensation of hydrolyzed silane molecules



R: Organic functional group

R': CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>

•: Inorganic particle

Scheme 2. Reactions of the silane coupling agent.

### Characterization of Silane-Treated Layer

Figure 1 shows the surface coverage measured by TG analysis for silica particles treated with MrPDMS/MrPTMS mixtures. The added silane surface treatments, shown as surface coverage, were (○) 1.5, (△) 3.5, (□) 5, and (◇) 7. In the case of the amount of added silane at a surface coverage of 7 (◇), the measured surface coverage was in the range from 5.2 to 6.7, and the average value was 6.0. Therefore, hereafter, the surface coverage for four different amounts of added silane at the surface of the treated systems shown in Figure 1 are expressed as the average measured surface coverages, as follows: (○) 1.6, (△) 2.4, (□) 3.8, and 6.0 (◇). Silane-treated silica particles with different MrPDMS/MrPTMS mixing ratios and with almost the same surface coverages were successfully obtained.

The amount of physically adsorbed silane may have been contained in this result. To confirm this, TG analysis was done for the MrPDMS- and MrPTMS-treated silica particles after they were washed with methanol three times. As a result, there was no influence of washing on the amount of silane on the silica surfaces. In this study, the surface treatment of silica particles was carried out through a 2-PA solution and heated at 120°C for 24 h after the evaporation of 2-PA. It was found that this treatment condition never generated the physically adsorbed

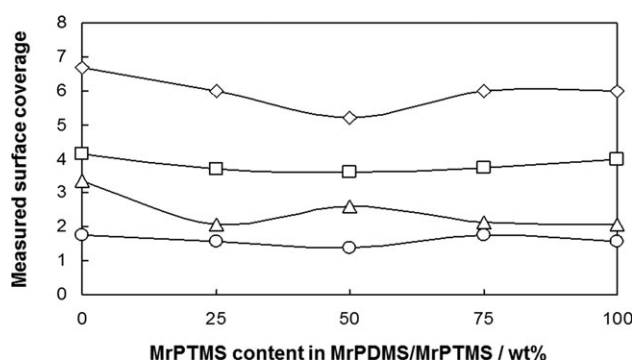
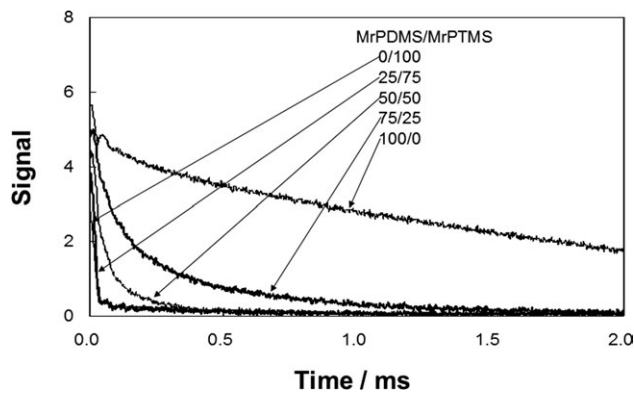


Figure 1. Measured surface coverage for silica particles treated with MrPDMS/MrPTMS mixtures determined by TG analysis. Average measured surface coverage: (○) 1.6, (△) 2.4, (□) 3.8, and (◇) 6.0.



**Figure 2.** FID signals for silica particles treated with MrPDMS/MrPTMS mixtures measured by pulse NMR with the solid echo method at 35°C (average measured surface coverage = 3.8).

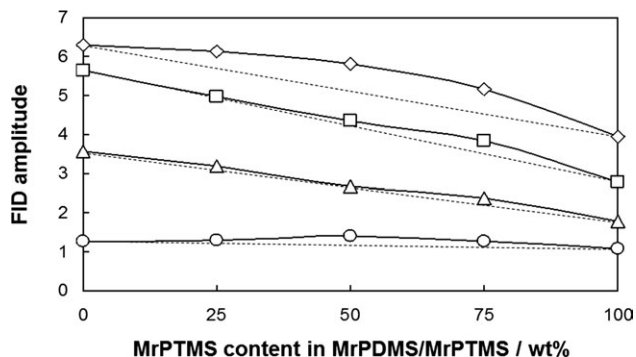
silane. So, this article shows only the result of the silica particles treated without washing.

The surface coverage was calculated with the occupied area of a single silane coupling agent molecule of 0.13 nm<sup>2</sup>,<sup>37,38</sup> this is the common value used for all silane coupling agents. However, the value should differ according to the type of organic functional group in the silane. For this reason, the surface coverage in this study was only a relative standard.

Figure 2 shows the FID curves of  $T_2$  relaxation for silica particles treated with MrPDMS/MrPTMS mixtures as measured by pulse NMR. The average surface coverage was measured as 3.8. The signal intensity decreased significantly immediately after measurement initiation for the pure MrPTMS-treated silica, whereas it decreased gradually for the pure MrPDMS-treated silica. This was caused by the difference in the silane structure: the former was expected to form a rigid network structure, and the latter was expected to form a flexible linear-chain structure, as we previously reported.<sup>19</sup> The relaxation behaviors of the MrPDMS/MrPTMS-mixture-treated systems were between that for the MrPDMS- and MrPTMS-treated systems, and the relaxation became more gradual with increasing MrPDMS content in the mixture.

The FID amplitude (the signal intensity of the FID at 0 ms) was dependent on the magnetic dipole density of the sample, namely, the proton content. Our previous study<sup>32</sup> showed that the FID amplitude was dependent on the loading amount of silane on the silica surface.

Figure 3 shows the relation between the FID amplitude from Figure 2 and the MrPTMS content in the mixture. The FID amplitude decreased with decreasing measured surface coverage and with increasing MrPTMS content in the MrPDMS/MrPTMS mixture. The FID amplitude was different for MrPDMS and MrPTMS because MrPTMS had three methoxy groups, whereas MrPDMS had two methoxy groups and one methyl group so that the proton content was higher in the hydrolyzed MrPDMS than in the hydrolyzed MrPTMS. The measured surface coverage of the treated silica was almost constant and independent of the MrPDMS/MrPTMS ratio, as shown in Figure 1. The dashed lines in Figure 3 indicate the FID amplitude calculated according to the rule of mixture (Fox equation)<sup>41</sup> with the FID amplitude val-

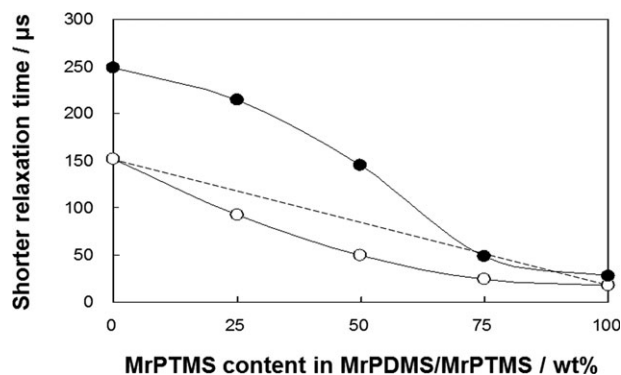


**Figure 3.** Relationship between FID amplitude measured by pulse NMR with the solid echo method at 35°C and the MrPTMS content in the MrPDMS/MrPTMS mixture used for the surface treatment of the silica particles. Average measured surface coverage: (○) 1.6, (△) 2.4, (□) 3.8, and (◇) 6.0. The dashed lines indicate the FID amplitude calculated according to the rule of mixture (Fox equation).

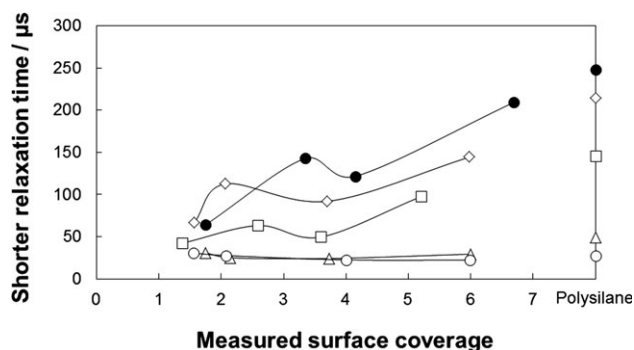
ues for the MrPDMS- and MrPTMS-treated systems. The measured values were larger than the calculated values and were most pronounced for the system with an average measured surface coverage of 6.0, which indicated that the actual MrPDMS ratio in the MrPDMS/MrPTMS-mixture-treated layer was slightly higher than the nominal added ratio.

The FID curves in Figure 2 indicate that there were two different silane chains; one showed an immediate relaxation, that is, relatively rigid silane chains, and the other showed a gradual relaxation, that is, relatively flexible silane chains. The FID curves were divided into these two components in the same way as reported previously<sup>32</sup> in accordance with the method proposed by Tanaka and Nishi.<sup>34,35</sup> Hereafter, the relaxation time for the component that shows immediate relaxation is called the *shorter relaxation time* and that for the component that shows gradual relaxation is called the *longer relaxation time*.

Figure 4 shows the relation between the shorter relaxation time and the MrPTMS content in the mixture. The average measured



**Figure 4.** Shorter relaxation time determined for silica particles treated with (○) MrPDMS/MrPTMS mixtures and (◌) for polysilane [P(MrPDMS/MrPTMS)] as a function of the MrPTMS content in the MrPDMS/MrPTMS mixture measured by pulse NMR with the solid echo method at 35°C (average measured surface coverage = 3.8). The dashed line indicates the relaxation time calculated according to the rule of mixture (Fox equation).



**Figure 5.** Shorter relaxation time determined for silica particles treated with MrPDMS/MrPTMS mixtures and polysilane [P(MrPDMS/MrPTMS)] as a function of the measured surface coverage measured by pulse NMR with the solid echo method at 35°C. MrPDMS/MrPTMS mixing ratio: (○) 0/100, (△) 25/75, (□) 50/50, (◇) 75/25, and (●) 100/0.

surface coverage was 3.8. The relaxation times of the MrPDMS/MrPTMS-mixture-treated systems (○) were in the range between those of the MrPDMS- and the MrPTMS-treated systems. The dashed line indicates the relaxation time calculated according to the Fox equation<sup>41</sup> with the shorter relaxation times of the MrPDMS- and MrPTMS-treated systems. The measured values were lower than the predicted values because the actual incorporated ratio of MrPDMS in the MrPDMS/MrPTMS-mixture-treated layer was slightly higher than the nominal added ratio from Figure 3. However, the measured relaxation times were lower than the calculated values, although the MrPDMS component resulted in a more flexible mixed silane chain. This showed that network formation by the MrPTMS component strongly restricted the molecular mobility.

The ratio of proton number belonging to each component could be measured by pulse NMR. The proton component ratio of the shorter relaxation time was in the range from 0.6 to 0.9. The shorter relaxation time reflected the molecular mobility of the majority of silane chains; therefore, the data for longer relaxation times were omitted in this article.

The plotted points shown by black circles in Figure 3 are the shorter relaxation times for PMrPDMS, PMrPTMS, and P(MrPDMS/MrPTMS). PMrPTMS and P(MrPDMS/MrPTMS) at 25/75 and 50/50 were in the solid state, whereas PMrPDMS was in the liquid state. Although the greater portion of P(MrPDMS/MrPTMS) at 75/25 was in the liquid state, a part of the polysilane was also in the solid state. Therefore, pulse NMR was measured by the solid echo method for all samples and was suitable for solid samples.

The shorter relaxation times for PMrPTMS and P(MrPDMS/MrPTMS) at 25/75 were almost the same as those for the treated layer on the silica surface. On the other hand, those for PMrPDMS and P(MrPDMS/MrPTMS) above 50/50 were longer than those for the treated layer on the silica surface. The molecular motion of the silane chains chemically bonded on the silica surface was restrained by the influence of the surface. PMrPTMS and P(MrPDMS/MrPTMS) at 25/75 were rigid network structures; therefore, they were not influenced by the surface.

Figure 5 shows the relation between the shorter relaxation time for the MrPDMS/MrPTMS-mixture-treated silica with various mixing ratios and surface coverages. For a surface coverage of approximately 1.5 (near monolayer coverage), the relaxation time was shortest for all mixing ratios. The relaxation time increased with increasing surface coverage for MrPDMS/MrPTMS ratios above 50/50.

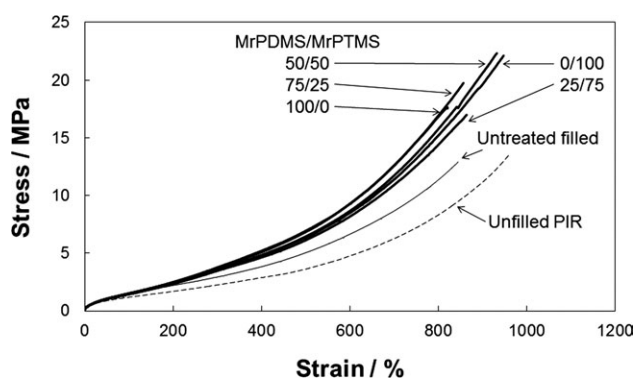
The relaxation times for PMrPTMS and P(MrPDMS/MrPTMS) at 25/75 were short, and they were almost the same as those for the treated layer on the silica surface. Those for P(MrPDMS/MrPTMS) above 50/50 became longer with increasing MrPDMS content in the mixture; that is, the silane chain became more flexible, whereas those for PMrPDMS and P(MrPDMS/MrPTMS) above 50/50 were longer than those for the treated layer on the silica surface.

The proton component ratio of the shorter relaxation time for the MrPDMS/MrPTMS-mixture-treated silica decreased with increasing MrPDMS content in the mixture and the surface coverage. The result also indicates that the silane chain became more flexible with increasing relaxation time compared to those with shorter relaxation times shown in Figure 5, and the data were omitted in this article.

As shown by these results, the network density and flexibility of the silane chain could be controlled by changes in the mixing ratio of silane coupling agents with dialkoxy and trialkoxy structures and the loading amount. The silane chain became more flexible with increasing dialkoxy structure in the mixture, and this was more significant with increasing loading amount.

### Mechanical Properties of the Filled PIR Composite

Figure 6 shows stress–strain curves of the unfilled and silica-filled vulcanized PIR at a filler content of 23.1 wt %. The average measured surface coverage was 2.4. Each curve shown is the typical one chosen from five measured results. The stress with the same strain of vulcanized PIR was increased by untreated silica filling and increased further with silane treatment of the silica particles. The results also indicate that the stress was affected by the MrPDMS/MrPTMS mixing ratio.



**Figure 6.** Stress–strain curves of unfilled, vulcanized PIR and those filled with untreated silica particles and silica particles treated with MrPDMS/MrPTMS mixtures at a particle content of 23.1 wt % (average measured surface coverage = 2.4).

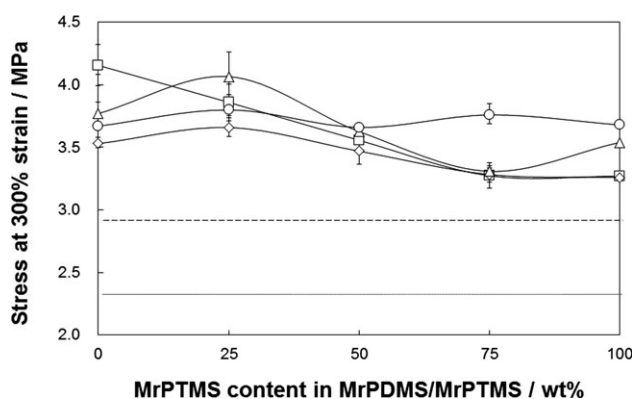
**Table I.** Tensile Properties of the MrPDMS/MrPTMS-Mixture-Treated, Silica-Filled PIR

Composite	Mixing ratio	Stress (MPa)					Fracture stress (MPa)	Elongation at break (%)
		50% strain	100% strain	300% strain	500% strain	700% strain		
Unfilled PIR	—	0.90 ( $\pm 0.03$ )	1.22 ( $\pm 0.04$ )	2.32 ( $\pm 0.08$ )	3.78 ( $\pm 0.13$ )	6.61 ( $\pm 0.33$ )	19.1 ( $\pm 1.7$ )	1097 ( $\pm 53$ )
Untreated silica-filled PIR	—	1.10 ( $\pm 0.02$ )	1.52 ( $\pm 0.02$ )	2.93 ( $\pm 0.04$ )	5.03 ( $\pm 0.09$ )	8.62 ( $\pm 0.20$ )	19.6 ( $\pm 2.0$ )	992 ( $\pm 32$ )
MrPDMS/MrPTMS-mixture-treated, silica-filled PIR	100/0	1.07 ( $\pm 0.01$ )	1.53 ( $\pm 0.02$ )	3.77 ( $\pm 0.06$ )	6.99 ( $\pm 0.12$ )	12.8 ( $\pm 0.29$ )	18.5 ( $\pm 2.6$ )	826 ( $\pm 58$ )
	75/25	1.10 ( $\pm 0.03$ )	1.57 ( $\pm 0.03$ )	4.07 ( $\pm 0.11$ )	7.89 ( $\pm 0.33$ )	14.2 ( $\pm 0.57$ )	22.2 ( $\pm 0.81$ )	882 ( $\pm 28$ )
	50/50	1.00 ( $\pm 0.01$ )	1.44 ( $\pm 0.01$ )	3.63 ( $\pm 0.13$ )	6.99 ( $\pm 0.45$ )	13.0 ( $\pm 1.2$ )	17.1 ( $\pm 0.20$ )	800 ( $\pm 62$ )
	25/75	1.01 ( $\pm 0.02$ )	1.42 ( $\pm 0.02$ )	3.31 ( $\pm 0.03$ )	6.02 ( $\pm 0.04$ )	10.6 ( $\pm 0.02$ )	23.7 ( $\pm 2.6$ )	1026 ( $\pm 48$ )
	0/100	1.03 ( $\pm 0.03$ )	1.49 ( $\pm 0.02$ )	3.54 ( $\pm 0.04$ )	6.35 ( $\pm 0.09$ )	11.3 ( $\pm 0.01$ )	21.9 ( $\pm 1.6$ )	939 ( $\pm 25$ )

Average measured surface coverage = 2.4.

Table I shows the tensile properties of the MrPDMS/MrPTMS-mixture-treated, silica-filled PIR. The highest stress was observed for the MrPDMS/MrPTMS mixing ratio of 75/25 at all strain values. The influence of the MrPDMS/MrPTMS mixing ratio on the stress was then examined for other surface coverages.

Figure 7 shows the influence of the MrPDMS/MrPTMS mixing ratio on the stress at 300% strain for the mixture-treated, silica-filled, vulcanized PIR. There was the smallest influence of the mixing ratio on the stress for a surface coverage of 1.6 (○) because the mixing ratio had little effect on the structure of the silane molecule in the case of near monolayer. At a surface coverage of 2.4 or more, the stress was significantly affected by the MrPDMS/MrPTMS mixing ratio. In the case of a MrPDMS/MrPTMS mixing ratio of 50/50 or more, the stresses were lower than that at a surface coverage of 1.6. However, the stresses were higher than those at a surface coverage of 1.6 for the

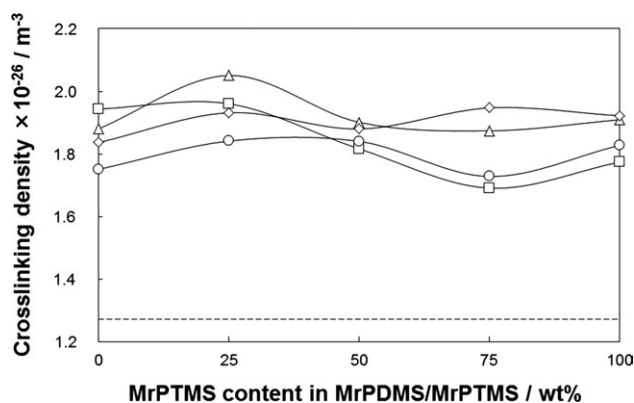


**Figure 7.** Stress at 300% strain for the MrPDMS/MrPTMS-mixture-treated, silica-filled, vulcanized PIR measured by tensile testing as a function of the MrPTMS content in MrPDMS/MrPTMS mixture. The dotted and dashed lines indicate the stress at 300% strain for the unfilled, vulcanized PIR and the untreated, silica-filled, vulcanized PIR, respectively. Average measured surface coverage: (○) 1.6, (△) 2.4, (□) 3.8, and (◇) 6.0 (silica particle content = 23.1 wt %).

MrPDMS/MrPTMS mixing ratios of 100/0 (surface coverage = 3.8) and 75/25 (surface coverage = 2.4). Stress beyond that for monolayer coverage could be obtained by multilayer coverage with an increased ratio of MrPDMS. Moreover, the results indicate that a loading amount that was too high (surface coverage = 6.0) and a greater ratio of MrPTMS in the mixture were not effective in imparting reinforcement to the composite.

The mercapto group in the silane was expected to react with rubber like the sulfur as a vulcanizing agent.<sup>42</sup> Therefore, there was a possibility that the loading amount of silane and the chain structure affected the crosslinking structure. Therefore, a swelling test of the silica-filled, vulcanized PIR was conducted, and the crosslinking density was calculated.

Figure 8 shows the crosslinking density of filled PIR as a function of the MrPDMS/MrPTMS mixing ratio. The dashed line indicates the crosslinking density of the untreated, silica-filled,



**Figure 8.** Crosslinking density of the MrPDMS/MrPTMS-mixture-treated, silica-filled, vulcanized PIR as a function of the MrPTMS content in MrPDMS/MrPTMS mixture. The dashed line indicates the crosslinking density of the untreated, silica-filled, vulcanized PIR. Average measured surface coverage: (○) 1.6, (△) 2.4, (□) 3.8, and (◇) 6.0 (silica particle content = 23.1 wt %).

vulcanized PIR. The crosslinking density of the unfilled, vulcanized PIR was  $1.16 \times 10^{26} \text{ m}^{-3}$ . The crosslinking density of the untreated, silica-filled PIR was lower than that of the unfilled, vulcanized PIR because the PIR component that could be crosslinked was decreased by silica addition. However, the crosslinking density of the silane-treated, silica-filled PIR was higher than that of untreated, silica-filled, vulcanized PIR; this indicated that a crosslinking reaction occurred between the mercapto group in the silane and the PIR. Therefore, this crosslinking reaction improved the reinforcement effect and explained the increased stress shown in Figures 6 and 7. The tendency of the crosslinking density shown in Figure 8 was in good agreement with the stress at 300% strain shown in Figure 7. It was expected that the increase of stress was dependent on the degree of crosslinking reaction between the mercapto group in the silane and PIR at the interfacial region. That is, the results indicate that entanglement of the silane chain on the silica surface and the PIR molecular chain was expected to occur most effectively for the MrPDMS/MrPTMS mixing ratios of 75/25 (surface coverage = 2.4) and 100/0 (surface coverage = 3.8).

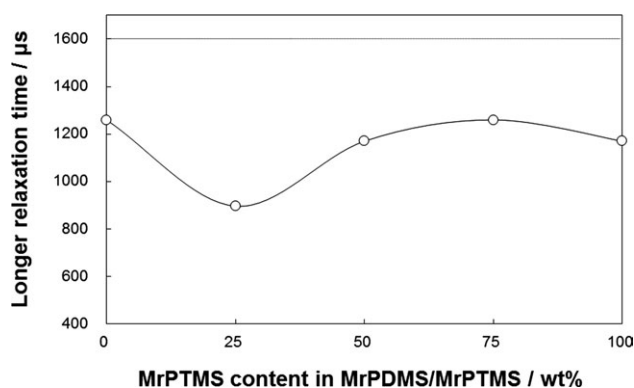
To confirm the entanglement of the silane network and PIR molecules at the interfacial region, the silane-treated silica (measured surface coverage = 2.4) and PIR were mixed with a mixing roll at room temperature without curing agents; then, the PIR was extracted. Under this temperature condition, the reaction between the mercapto group in the silane and PIR should not have occurred.

After the extraction of free PIR with toluene, the amount of unextracted component was measured by TG analysis, and the loading amount of silane was subtracted. The amount of unextracted PIR was about 3–4 wt % at MrPTMS contents of 0, 50, 75, and 100 wt %, whereas it was about 6 wt % at a MrPTMS content of 25 wt %.

The molecular mobility of the silane and PIR chains remaining on the silica particle surface was measured with pulse NMR. There was insufficient PIR on the untreated silica surface for pulse NMR measurement after the extraction of PIR from the untreated silica and PIR mixture.

Figure 9 shows the longer relaxation time as a function of the MrPTMS content in the mixture measured by pulse NMR for the silica particles after extraction from the mixture with unvulcanized PIR. The longer relaxation time of the pure unvulcanized PIR was 1600  $\mu\text{s}$ . The lowest relaxation time was observed at an MrPTMS content of 25 wt %. The longer relaxation time showed the molecular mobility for the entangled silane and PIR chains at the interfacial region. These results indicate that the entanglement of silane and PIR chains, that is, the formation of an interpenetrating polymer network structure, occurred most effectively at this ratio.

The proton component ratios for the shorter relaxation time component were 0.55 or greater, and the ratio showed about 0.75 of the maximum at an MrPTMS content of 25 wt %. This result indicates that the proton that belonged to the shorter relaxation time was more preferred. However, the shorter relaxation time was in the range from 20 to 30  $\mu\text{s}$  and was almost constant.



**Figure 9.** Longer relaxation time determined for the silica particles after extraction from the mixture with unvulcanized PIR as a function of MrPTMS content in the MrPDMS/MrPTMS mixture measured by pulse NMR with the solid echo method at 35°C. The dotted line indicates the longer relaxation time of the unvulcanized PIR. The silica particles used were treated beforehand with the MrPDMS/MrPTMS mixture (average measured surface coverage = 2.4).

Figure 7 also shows that the reinforcement effect was reduced for a high surface coverage. This was considered to be caused by the self-agglomeration of silane chains in the case of such long chains.

We previously investigated<sup>30</sup> the effect of silane chain length on glass bead surfaces on the mechanical properties of glass-bead-filled poly(vinyl chloride) (PVC) with 3-methacryloxypropyl methyl dimethoxysilane (MPDMS). The silane chain length was varied from 1 to 9 of the surface coverage. As a result, the yield stress of the composite increased and the elongation at break decreased with increasing silane chain length. The reinforcement of the formed interfacial region became more effective with increasing silane chain length; this suggested that the entanglement of the silane chains and PVC tended to increase with increasing silane chain length. The results were different from those obtained in this study, and the difference seemed to be caused by the compatibility of the silane chain and matrix polymer. The solubility parameter (SP) value of PVC was 19.5 (MPa)<sup>1/2</sup>.<sup>43</sup> The SP values of the hydrolyzed single MPDMS and that of the condensed 5-hydrolyzed MPDMS molecules, which were calculated by Fedors's method,<sup>44</sup> were approximately 22.0 and 20.1 (MPa)<sup>1/2</sup>, respectively. On the other hand, the SP value of PIR was 15.2 (MPa)<sup>1/2</sup>.<sup>43</sup> The calculated SP of the hydrolyzed single MrPDMS and the condensed 5-hydrolyzed MrPDMS molecules were 22.2 and 19.7 (MPa)<sup>1/2</sup>, respectively; this indicated that the self-agglomeration of silane chains tended to occur in the MrPDMS/PIR system more than in the MPDMS/PVC system.

As shown by these results, the reinforcement of the silane treatment was strongly affected by the entanglement of silane chains bonded on the silica particle surfaces and the PIR matrix in the interfacial region. Highly crosslinked silane networks and flexible silane chains with lengths that were too long were disadvantageous for this effect.

## CONCLUSIONS

The treatment of spherical silica particles surfaces with MrPDMS/MrPTMS mixtures was conducted, and the structure

of the silane-treated layer on the silica particle surface was analyzed with pulse NMR. The effect of the loading amount and the MrPDMS/MrPTMS mixing ratio on the stress-strain curve of the filled PIR composite were also investigated. The following results were obtained.

1. The relaxation time was longer in the MrPDMS-treated system than in the MrPTMS-treated system. The relaxation time for the MrPDMS/MrPTMS-mixture-treated system was between those for the MrPDMS- and MrPTMS-treated systems and was dependent on the mixing ratio. The network density of the silane chains on silica particles could be controlled by variation of the mixing ratio of MrPDMS and MrPTMS.
2. In the case of near monolayer coverage, there was no influence of the MrPDMS/MrPTMS mixing ratio on the stress at the same strain. The pure-MrPDMS- or low-MrPTMS-content-mixture-treated systems exhibited higher stress at the same strain for surface coverages of 2.4–3.8. The reinforcement effect was strongly affected both by entanglement and the crosslinking reaction between silane and PIR at the interfacial region. However, flexible silane chains with longer lengths (surface coverage = 6.0) were disadvantageous for the reinforcement effect.

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#### REFERENCES

1. Graf, R. T.; Koenig, J. L.; Ishida, H. *J. Adhes.* **1983**, *16*, 97.
2. Ishida, H.; Miller, J. D. *Macromolecules* **1984**, *17*, 1659.
3. Naviroj, S.; Koenig, J. L.; Ishida, H. *J. Adhes.* **1985**, *18*, 93.
4. Miller, J. D.; Ishida, H. *Langmuir* **1986**, *2*, 127.
5. Culler, S. R.; Ishida, H.; Koenig, J. L. *J. Colloid Interface Sci.* **1986**, *109*, 1.
6. Ikuta, N.; Maekawa, Z.; Hamada, H.; Ichihashi, M.; Nishio, E. *J. Mater. Sci.* **1991**, *26*, 4663.
7. Krasnoslobodtsev, A. V.; Smirnov, S. N. *Langmuir* **2002**, *18*, 3184.
8. Miller, A. C.; Berg, J. C. *Compos. A* **2003**, *34*, 327.
9. Marrone, M.; Montanari, T.; Busca, G.; Conzatti, L.; Costa, G.; Castellano, M.; Turturro, A. *J. Phys. Chem. B* **2004**, *108*, 3563.
10. Benkoski, J. J.; Kramer, E. J.; Yim, H.; Kent, M. S.; Hall, J. *Langmuir* **2004**, *20*, 3246.
11. Suzuki, N.; Ishida, H. *Compos. Interfaces* **2005**, *12*, 769.
12. Griswold, C.; Cross, W. M.; Kjerengtroen, L.; Kellar, J. J. *J. Adhes. Sci. Technol.* **2005**, *19*, 279.
13. Abel, M.-L.; Allington, R. D.; Digby, R. P.; Porritt, N.; Shaw, S. J.; Watts, J. F. *Int. J. Adhes. Adhes.* **2006**, *26*, 2.
14. Jensen, R. E.; Palmese, G. R.; McKnight, S. H. *Int. J. Adhes. Adhes.* **2006**, *26*, 103.
15. Rattana, A.; Abel, M.-L.; Watts, J. F. *Int. J. Adhes. Adhes.* **2006**, *26*, 28.
16. Castellano, M.; Conzatti, L.; Turturro, A.; Costa, G.; Busca, G. *J. Phys. Chem. B* **2007**, *111*, 4495.
17. Abdelmouleh, M.; Boufi, S.; Belgacem, M. N.; Dufresne, A. *Compos. Sci. Technol.* **2007**, *67*, 1627.
18. Dohi, H.; Horiuchi, S. *Langmuir* **2007**, *23*, 12344.
19. Liu, X.; Zhao, S. *J. Appl. Polym. Sci.* **2008**, *108*, 3038.
20. Brochier, M.-C.; Salon, B.; Bayle, P.-A.; Abdelmouleh, M.; Boufi, S.; Belgacem, M. N. *Colloids Surf. A* **2008**, *312*, 83.
21. Salon, M.-C. B.; Bayle, P.-A.; Abdelmouleh, M.; Boufic, S.; Belgacem, M. N. *Colloids Surf. A* **2008**, *312*, 83.
22. Han, J.; Zuo, C.; Gu, Q.; Li, D.; Wang, X.; Xue, G. *Appl. Surf. Sci.* **2008**, *255*, 2316.
23. Garcia, N.; Benito, E.; Guzman, J.; de Francisco, R.; Tiemblo, P. *Langmuir* **2010**, *26*, 5499.
24. Stockelhuber, K. W.; Svistkov, A. S.; Pelevin, A. G.; Heinrich, G. *Macromolecules* **2011**, *44*, 4366.
25. Zhao, Z.; Zhao, X.; Gong, G.; Zheng, J.; Liang, T.; Yin, C.; Zhang, Q. *Polym. Plast. Technol. Eng.* **2012**, *51*, 268.
26. Nagata, K.; Nigo, H.; Nakamura, Y.; Okumura, H.; Nishimura, A.; Tobita, Y.; Iida, T.; Yoshitani, H.; Nishino, T.; Nakamae, K. *Compos. Interfaces* **2002**, *9*, 273.
27. Nakamura, Y.; Nagata, K.; Tobita, Y.; Yokouchi, N.; Nigo, H.; Iida, T. *J. Adhes. Sci. Technol.* **2002**, *16*, 523.
28. Nakamura, Y.; Yokouchi, N.; Tobita, Y.; Iida, T.; Nagata, K. *Compos. Interfaces* **2005**, *12*, 669.
29. Nakamura, Y.; Usa, T.; Gotoh, T.; Yokouchi, N.; Iida, T.; Nagata, K. *J. Adhes. Sci. Technol.* **2006**, *20*, 1199.
30. Nakamura, Y.; Harada, A.; Gotoh, T.; Yokouchi, N.; Iida, T. *Compos. Interfaces* **2007**, *14*, 117.
31. Nakamura, Y.; Honda, H.; Harada, A.; Fujii, S.; Nagata, K. *J. Appl. Polym. Sci.* **2009**, *113*, 1507.
32. Nakamura, Y.; Nishida, Y.; Honda, H.; Fujii, S.; Sasaki, M. *J. Adhes. Sci. Technol.* **2011**, *25*, 2703.
33. Mansfield, P. *Phys. Rev.* **1965**, *137*, 961.
34. Tanaka, H.; Nishi, T. *J. Chem. Phys.* **1985**, *82*, 4326.
35. Tanaka, H.; Nishi, T. *J. Chem. Phys.* **1986**, *85*, 6197.
36. Sperling, L. H. *Interpenetrating Polymer Networks and Related Materials*; Plenum: New York, **1981**.
37. Yoshioka, H. *J. Adhes. Soc. Jpn.* **1985**, *21*, 252.
38. Hozoji, H.; Horie, O.; Ogata, M.; Numata, S.; Kinjo, N. *Kobunshi Ronbunshu* **1990**, *47*, 483.
39. Gwaily, S. E.; Badawy, M. M.; Hassan, H. H.; Madani, M. *Polym. Test* **2003**, *22*, 3.
40. Pliskin, I.; Tokita, N. *J. Appl. Polym. Sci.* **1972**, *16*, 473.
41. Fox, T. G. *Bull. Am. Phys. Soc. Ser. II* **1956**, *1*, 123.
42. Hewitt, N. L. *Elastomerics* **1981**, *3*, 33.
43. *Polymer Handbook*; Brandrup, J.; Immergut, E. H., Eds.; Wiley: New York, **1989**.
44. Fedors, R. F. *Polym. Eng. Sci.* **1974**, *14*, 147.