Mechanical Properties of Silica Particle-Filled Styrene-Butadiene Rubber Composites Containing Polysulfide-Type Silane Coupling Agents: Influence of Loading Method of Silane

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ABSTRACT: Polysulfide-type silane coupling agents containing two or four sulfur atoms were incorporated into a styrene-butadiene rubber/silica composite by two different loading methods and the tensile properties were measured. The pretreatment method and the integral blend method were compared. To improve the 200% modulus of the composite, the combination of silane with four sulfur atoms and the pretreatment method was effective. Whereas, the combination of silane with four sulfur atoms and the integral blend method was effective for improving the fracture elongation. The fracture elongation of the integral blend using the silane with four sulfur atoms was higher than that of the untreated silica-filled composite. The sulfur atoms in the silane should contribute to the crosslinking of rubber in the vulcanization process. The silane with much sulfur atoms strengthens the interface effectively and raises the 200% modulus in the pretreatment method. It is considered that the unreacted silane molecules in the rubber acted as a plasticizer in the integral blend method and the effect was better with four sulfur atoms. The ^{1}H pulse nuclear magnetic resonance spectroscopy was measured for the unvulcanized rubber/silica mixture. The measured relaxation time was found to be in good correlation with the 200% modulus. It was found that the molecular mobility of rubber is lowered by the entanglement with the silane chains on the silica surface at the interfacial region, and it was more effective in the pretreatment method than in the integral blend method. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 322–329, 2013

INTRODUCTION

Silane coupling agents are widely utilized for surface modification of inorganic materials. Much research has been conducted regarding the reactivity of silane coupling agents and characterization of the resulting silane layers formed on inorganic surfaces.[1–18] 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.[19–27]

In our previous study,[25] spherical silica particles were treated with a silane coupling agent containing a mercapto group. The amount of silane loaded on the silica surface was analyzed by thermogravimetric (TG) analysis and the molecular mobility of the silane chains was analyzed using ^{1}H pulse nuclear magnetic resonance (pulse NMR) spectroscopy. Silanes with dialkoxy and trialkoxy structures were used, which formed linear chain and

network structures, respectively. 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 for the dialkoxy type than for the trialkoxy type and increased with the loading amount of the dialkoxy-type silane, although there was no influence observed on 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 effect of the linear chain and network structures on the stress-strain characteristics of the filled composite was investigated.[24] The stress at the same strain was increased by silane treatment, and was higher for the dialkoxy structure than the trialkoxy structure. This is because the linear chain silane spread into the PIR matrix easily and crosslinked with PIR molecules. Naviroj et al.,[1] Miller and Ishida,[2] Culler et al.,[3] and Ikuta et al.[4] referred to the interfacial region consisting of mutually mixed silane chains covalently

bonded to the filler surface and the matrix polymer chains as "interphase." It was found that the structure of a silane-treated layer on a particle surface had great influence on the mechanical properties of the composite.

Polysulfide-type silane coupling agents are said to be useful for tires, and many researchers are investigating the effect of these silanes on composite properties.[28–31] In this study, these silanes were incorporated into a styrene-butadiene rubber (SBR)/silica composite by two different loading methods: the pretreatment method and the integral blend method. The tensile properties of the resulting composites were measured and the influence of the loading method was examined. The two types of silanes used differed in the number of sulfur atoms, containing either two or four. The influence on the tensile properties by the number of sulfur atoms was compared. The influence of physically adsorbed silane in the treated layer on the mechanical properties of the composite was also confirmed. The interaction between the silane chains on the silica surface and the SBR molecular chains at the interfacial region in the composite was estimated using ^{1}H pulse NMR relaxation using an unvulcanized SBR/silica mixture. The relationship between the measured relaxation times and the tensile properties of the composite was discussed.

EXPERIMENTAL

Materials

Commercially available SBR (Styrene content: 23.5%, Mooney viscosity ($ML_{1 + 4}$, 100°C): 55 SL-552, JSR, Tokyo, Japan) was used as the base polymer. Spherical amorphous silica particles (mean size: 3.3 μm, specific surface area: 5.3 m^2/g, FB-3SDX, Denki Kagaku Kogyo Kabushiki Kaisha, Tokyo, Japan) and polysulfide silane coupling agents, bis[3-(triethoxysilyl)propyl]-disulfide (TESPD, Cabrus-2A, Daiso, Tokyo, Japan) and bis[3-(triethoxysilyl)propyl]-tetrasulfide (TESPT, Cabrus-4, Daiso), were used as received. Their chemical structures are shown in Figure 1.

Sulfur (Sigma-Aldrich Japan, Tokyo, Japan) as a vulcanizing agent, zinc oxide (Sigma-Aldrich Japan, Tokyo, Japan), N-cyclohexyl-2-benzothiazolylsulfenamide (CBS, Nocceler CZ, Ouchi Shinko Chemical Industrial, Tokyo, Japan) and 1,3-diphenylguanidine (D, Sigma-Aldrich Japan) as vulcanization accelerators, stearic acid (Sigma-Aldrich Japan) as an accelerator activator, and polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ, Kawaguchi Chemical Industries, Tokyo, Japan) as an antioxidant were used as received for the vulcanization of SBR. The oil (Sunthene 415, naphthenic type oil, Japan Sun Oil Company, Tokyo, Japan) was used as a softening agent.

Surface Treatment of Silica

The amount of silane required for monolayer coverage of silica particles was calculated as previously described.[23–25] The amount of silane was determined by the surface coverage, which indicates the number of layers covering the silica surface. The added amount of silane for the surface treatment was equivalent to 2.5 layers as surface coverage.

The surface treatment of silica particles was carried out by the dry treatment method. The silane coupling agent of predetermined quantity was added little by little to the silica particles of 100 g in a polyethylene bag, and mixed by hand from outside the bag for 10 min. The mixture was mixed for an additional 5 min at 23°C using a mixer for home use (Nakasa, Osaka, Japan). The treated silica particles were left at room temperature for 24 h, and then heated at 120°C for 24 h in an oven.

To remove the physically adsorbed silane molecules, ethanol washing was performed. The surface-treated silica and ethanol were mixed in an eggplant type flask and stirred for 30 min using an evaporator, followed by suction filtration using filter paper (No. 7, Toyo Roshi Kaisya, Tokyo, Japan). The obtained washed silica particles were left at room temperature for 24 h, and then heated at 120°C for 24 h in an oven.

Quantitative Analysis of Loading Amount

The amount of silane loaded on the treated silica surface was measured using TG analysis (TG/DTA-6300, SII NanoTechnology, Chiba, Japan). Dried silane-treated silica particles were heated to 1000°C with a heating rate of 10°C/min in air atmosphere (flow rate: 300 mL/min). The typical TG curves were shown in Figure 2. They are the TG curves of TESPD-treated silica particles before and after washing. The weight reduction began above 20°C and the constant value was shown above 600°C. The amount of silane loaded on the treated silica surface was calculated from the difference with the values of 30 and 1000°C, and was shown by the surface coverage.

When treated silica is burned in the presence of oxygen, C, H, and S atoms in the silane-coupling agent are removed as CO_2, H_2O, and SO_2 gases, respectively. However, Si atoms will remain as solid SiO_2 on the silica surface. Thus, the weight loss determined by TG analysis is based on the C, H, and S atoms and not the Si and O atoms in SiO_2. To calculate the surface coverage, a correction in consideration of this point was performed as previously reported.[24,25]
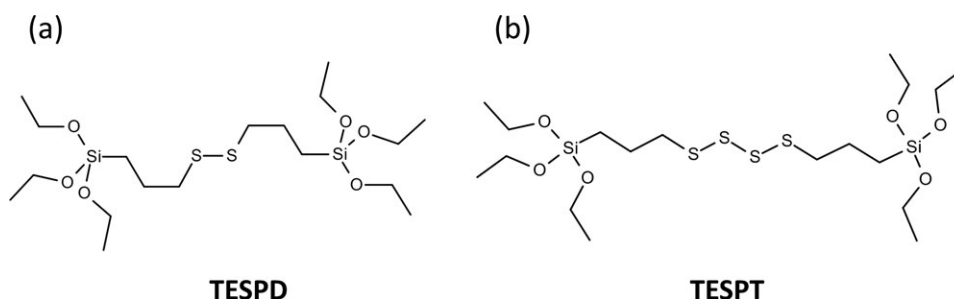
(a)   (b)

TESPD   **TESPT**

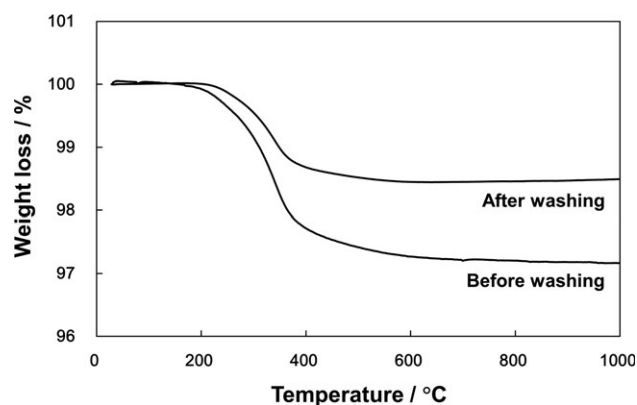**Figure 1.** Chemical structures of (a) TESPD and (b) TESPT.

Figure 2. TG curves of TESPD-treated silica particles before and after washing measured under air flow and atmospheric pressure.

Preparation of SBR/Silica Compound

The recipe of the SBR/silica compound is shown in Table I. The SBR was masticated at room temperature (23°C) for 2 min using a mixing roll (191-TM, Yasuda Seiki Seisakusho, Hyogo, Japan) beforehand. The oil was added to the mixture gradually over 8 min while mixing and further mixing was performed for 2 min at 23°C. The SBR/silica compound was prepared as described below using two different methods. All kneading was done at 23°C.

The Pretreatment Method. First, all additives in Table I such as the vulcanizing agent (sulfur), the vulcanization accelerators, the accelerator activator, and the antioxidant were mixed in the powdered state. The oil and SBR mixture was kneaded by the mixing roll, and the treated silica particles were added to the mixture gradually over 8 min. The mixture of additives was added over 3 min, and mixed an additional 5 min. The total mixing time was 28 min.

The Integral Blend Method. The oil and SBR mixture was kneaded by the mixing roll, and the silane coupling agent was

added gradually over 3 min. Untreated silica particles were added to the mixture gradually over 5 min. The mixture of additives was added in the same way as in the pretreatment method. The total mixing time was 28 min.

Preparation of Vulcanized SBR Composite Sheet

The obtained SBR compound was pressed and vulcanized simultaneously at 160°C under a pressure of 20 MPa for 20 min using a pressing machine (Mini test press, MP-WNL 250, Toyo Seiki Seisaku-Sho, Tokyo, Japan). SBR composite sheets of ~2 mm thickness were then prepared.

Tensile Test

The above prepared sheet of vulcanized SBR/silica composites with ~2 mm thickness was punched using a dumbbell-shaped blanking die and a handpress. Tensile testing was conducted with dumbbell-shaped specimens (Japanese Industrial Standard, JIS-K6301-3) of ~2 mm thickness with a cross-head rate of 200 mm/min using a tensile testing machine (AG-5KNIS, Shimadzu, Kyoto, Japan) to record stress-strain curves. The distance between specimen grip tools was 40 mm (=actual specimen length). The 200% modulus and the fracture elongation were measured.

Preparation of Unvulcanized SBR/Silica Mixture

To measure the interaction between the silane layer on the silica particle surface and SBR by pulse NMR spectroscopy, an unvulcanized SBR/silica mixture was prepared. For this purpose, the SBR compound without sulfur, all the vulcanization accelerators and oil in Table I was prepared (Only stearic acid and TMQ were added as additive). First, the stearic acid and TMQ were mixed in the powdered state. After the mastication of SBR for 2 min, the mixture of stearic acid and TMQ was added gradually over 3 min, and further mixing was done for 3 min at 23°C using the mixing roll. Hereinafter, the obtained mixture is referred to as the SBR/additives mixture.

In the pretreatment method, the treated silica particles were added to the SBR/additives mixture gradually over 8 min while

Table I. Compounding Recipes of Vulcanized SBR/Silica Composite

	Untreated system (g)	Integral blend system (g)	Pretreated system (g)
SBR	100	100	100
Oil (softening agent)	15	15	15
Silica	60	60	–
Silane coupling agent	–	4.8[a] or 5.5[b]	–
Pretreated silica	–	–	64.8[c] or 65.5[d]
Sulfur (vulcanizing agent)	1.5	1.5	1.5
Zinc oxide (vulcanization accelerator)	4.0	4.0	4.0
CBS (vulcanization accelerator)	1.8	1.8	1.8
D (vulcanization accelerator)	2.0	2.0	2.0
Stearic acid (accelerator activator)	2.0	2.0	2.0
TMQ (antioxidant)	1.0	1.0	1.0

[a]For TESPD.
[b]For TESPT.
[c]TESPD-treated silica.
[d]TESPT-treated silica.

mixing using the mixing roll. Total mixing time was 18 min. In the integral blend method, the silane coupling agent was added to the SBR/additives mixture gradually over 3 min, then the untreated silica particles were added gradually over 5 min while mixing using the mixing roll. Total mixing time was 18 min.

Analysis of Molecular Mobility

The molecular mobility of the silane chains was investigated using ^{1}H pulse NMR[32–34] (JNM-MU25, resonance frequency of 25 MHz, Jeol, Tokyo, Japan) by the solid echo method at 120°C with a sampling time of 2 ms as previously described,[25–27] and the T_2 relaxation behavior was measured.

Molecular Modeling

Molecular modeling calculations by the molecular orbital method were performed using MOPAC7 with the AM1 method (the semi-empirical quantum chemistry method) in Winmostar software.[35] The energy of the molecule with various conformation was calculated and compared, and the conformation with minimum energy was estimated.

RESULTS AND DISCUSSION

Comparison of Pretreatment Method and Integral Blend Method

In the pretreated system, the amount of loaded silane for surface treatment was equivalent to 2.5 layers as surface coverage. The measured silane on the silica surface by TG analysis was 2.5 layers for TESPD-treated silica and 2.0 layers for TESPT-treated silica, respectively. In the integral blend system, the amount of loaded silane was equivalent to 2.5 layers.

First, the influence of the different silane loading methods was compared. For this investigation, the silica before washing was used for the pretreated system. The stress-strain curves for silica particle-filled SBR containing TESPD are shown in Figure 3. The stress was higher in the pretreated system, whereas the fracture elongation was higher in the integral blend system.

Figure 4 shows the result for SBRs containing TESPT. The observed tendency was similar to the result for SBRs containing TESPD shown in Figure 3. The 200% modulus and the fracture elongation in both SBR/silica composites containing TESPD
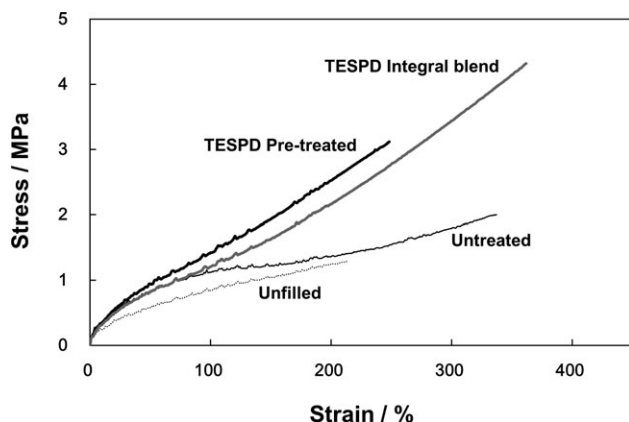
Figure 4. Stress-strain curves of raw silica particle-filled SBR (silica content: 32 wt %) and those incorporated with TESPT by integral blend method and pretreatment method (silica content: 31 wt %).
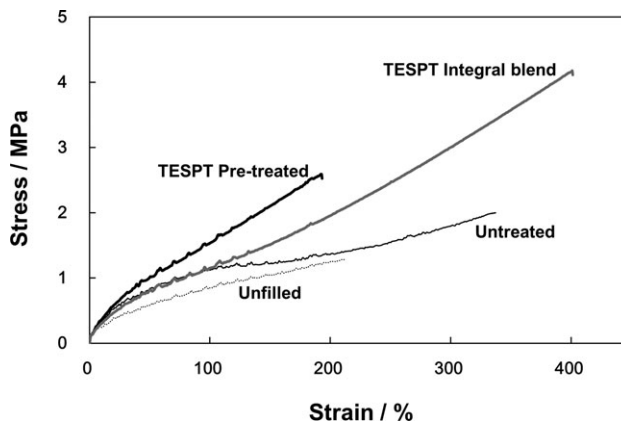
and TESPT are compared in Figure 5. The 300% modulus is usually used to assess the mechanical properties of rubber. However, some samples in this research had a fracture elongation below 300%, so the 200% modulus was used. The 200% modulus for the pretreated systems was nearly twice that for untreated silica-filled systems by the addition of TESPD and TESPT. The values for the integral blend systems were lower than those for the pretreated silica-filled systems. The fracture
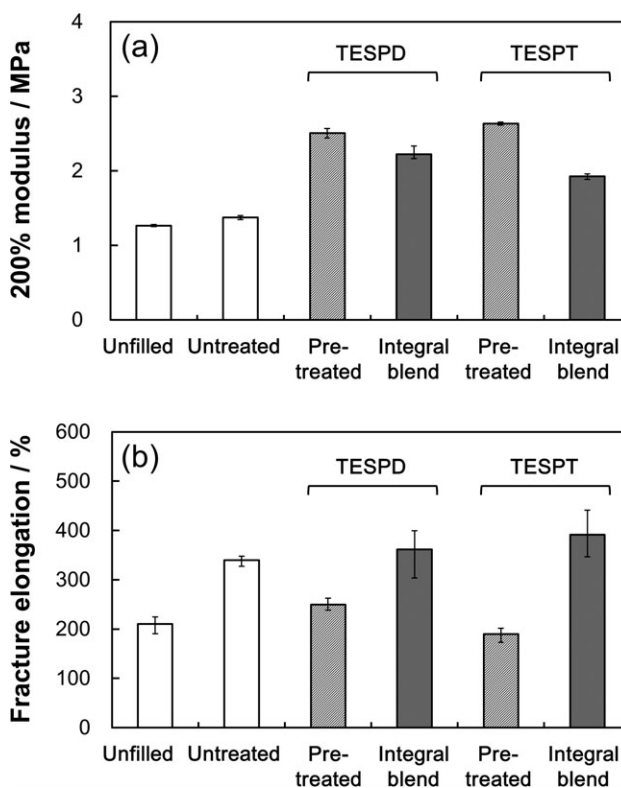
Figure 5. (a) 200% modulus and (b) fracture elongation of raw silica particle-filled SBR (silica content: 32 wt %) and those incorporated with TESPD and TESPT by integral blend method and pretreatment method (silica content: 31 wt %).

Figure 3. Stress-strain curves of raw silica particle-filled SBR (silica content: 32 wt %) and those incorporated with TESPD by integral blend method and pretreatment method (silica content: 31 wt %).

elongations of the integral blend system were higher than those of the untreated silica-filled systems; whereas, the fracture elongations of the pretreated silica-filled systems were lower than those of the untreated silica-filled systems.

These results indicate that the amount of the SBR molecular chains bound on the silica particle surface was larger in the pretreated silica-filled systems than in the integral blend systems. From the above results, it may be observed that the pretreatment method improves the 200% modulus effectively, but decreases the fracture elongation. However, the integral blend method improves the 200% modulus to some extent, without reducing the fracture elongation. The reason for this is proposed as follows: since some unreacted silane molecules should remain in the SBR in the integral blend method. Such silane molecules in the SBR continuous phase act as a plasticizer.

Influence of Number of Sulfur Atoms

Figure 5 also shows the influence of the number of sulfur atoms in polysulfide-type silanes on the mechanical properties of filled SBR. The 200% modulus for TESPT-treated silica-filled SBR was slightly higher than that for TESPD-treated silica-filled SBR in the pretreated silica-filled systems. The trend was opposite in the integral blend systems. The fracture elongation for TESPD-treated silica-filled SBR was higher than that for TESPT-treated silica-filled SBR in the pretreated silica-filled systems. The trend was again opposite in the integral blend systems. Thus, to improve the 200% modulus of the composite, the combination of TESPT and the pretreatment method was effective. Whereas, the combination of TESPT and the integral blend method was effective for improving the fracture elongation.

The sulfur atoms in the polysulfide-type silanes should contribute to the crosslinking of SBR in the vulcanization process just like added sulfur.[36] Thus, TESPT with more sulfur atoms has a higher effect on binding the SBR molecules on the silica particle surface in the pretreated system. As mentioned above, some unreacted silanes in the SBR continuous phase are expected to act as a plasticizer in the integral blend system. The plasticizer effect of TESPT is higher than that of TESPD.
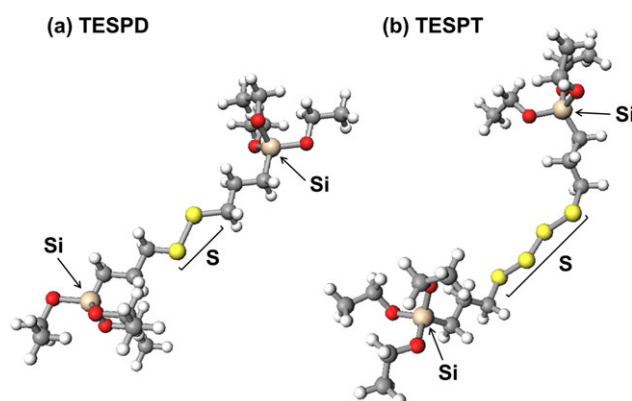
Figure 6 shows the molecular modeling outcomes for TESPD and TESPT by the molecular orbital method. TESPD is a linear structure and TESPT is a curved structure. This result indicates that TESPT is bulkier than TESPD. The unreacted silane molecule with a bulkier structure in SBR weakens the intermolecular interaction of SBR, and the plasticizer effect becomes higher. However, the degree of binding of the SBR molecular chains by the silane molecules on the silica surface may also influence the fracture elongation. To confirm this, the influence of physically adsorbed silane on the mechanical properties of SBR/silica composite was investigated.

Influence of Physically Adsorbed Silane

The TESPD-treated silica particles were washed by ethanol to remove the physically adsorbed silane molecules. The stress-strain curves for SBR filled with TESPD-treated silica particles before and after ethanol washing are shown in Figure 7. The stress was almost the same, whereas the fracture elongation was higher before washing the system than after washing the system.

Figure 8 shows the influence of washing the treated-silica on the 200% modulus and the fracture elongation. The fracture elongation was higher before washing than after washing. In the system before washing, the physically adsorbed silane molecules dispersed into the SBR continuous phase, and acted as a plasticizer. As a result, the fracture elongation was higher in the system before washing. The 200% modulus was slightly lower in the system after washing as seen in Figure 8. This may be caused by the change in the amount of TESPD molecules. The amount of TESPD molecules in the surface coverage measured by TG analysis was 2.5 layers before washing and 0.9 layers after washing.

Binding of SBR by Silane Molecules on Silica Surface

The effect of binding of SBR molecular chains by the silane molecules on the silica surface was measured by pulse NMR relaxation. First, the vulcanized SBR/silica composite was measured. However, there was no clear difference. It was considered that the influence of the decrease of molecular mobility of SBR chains by crosslinking was far higher than the binding by the silane molecules on the silica surface. Therefore, this
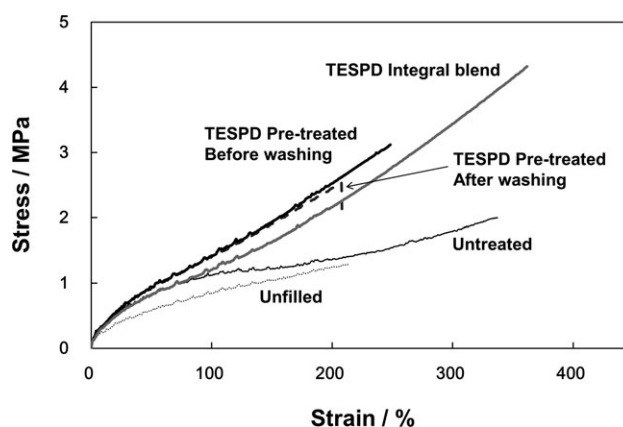

Figure 6. Molecular models of (a) TESPD and (b) TESPT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 7. Stress-strain curves of raw silica particle-filled SBR (silica content: 32 wt %) and those incorporated with TESPD by integral blend method and pretreatment method before and after washing (silica content: 31 wt %).
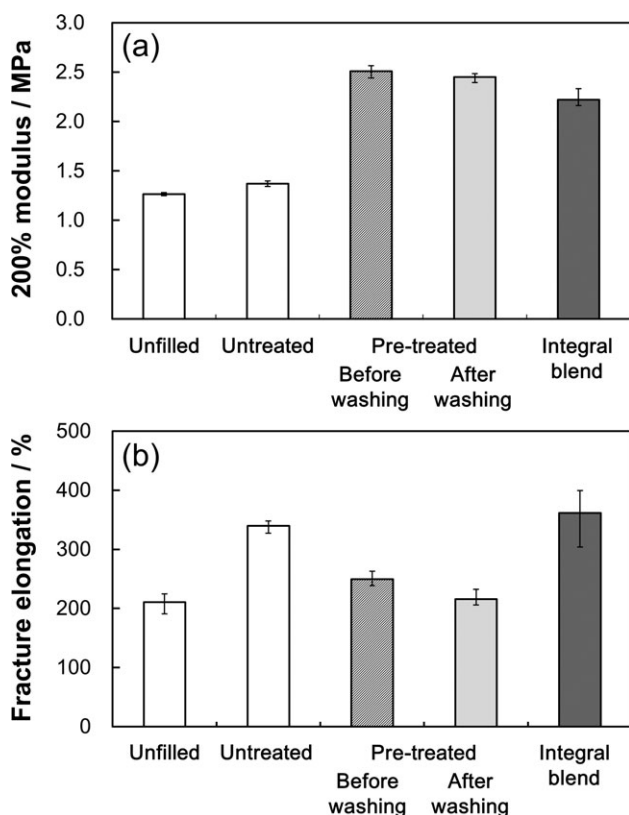
Figure 8. (a) 200% modulus and (b) fracture elongation of raw silica particle-filled SBR (silica content: 32 wt %) and those incorporated with TESPD by integral blend method and pretreatment method before and after washing (silica content: 31 wt %).

investigation was performed on an unvulcanized system. The measured pulse NMR free induction decay (FID) data were normalized and differentiated as proposed by Urahama[37] in the same way as previously reported.[38] In this manner, the relaxation time and distribution of specific components were clearly shown.
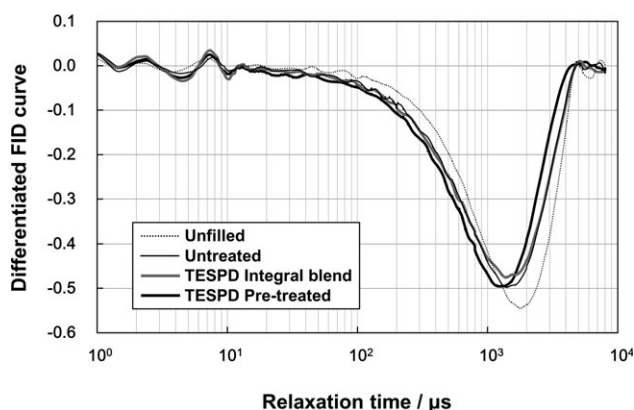

Figure 9. Differentiated FID curves measured by pulse NMR of raw silica particle-filled unvulcanized SBR (silica content: 37 wt %) and those incorporated with TESPD by integral blend method and pretreatment method (silica content: 36 wt %).
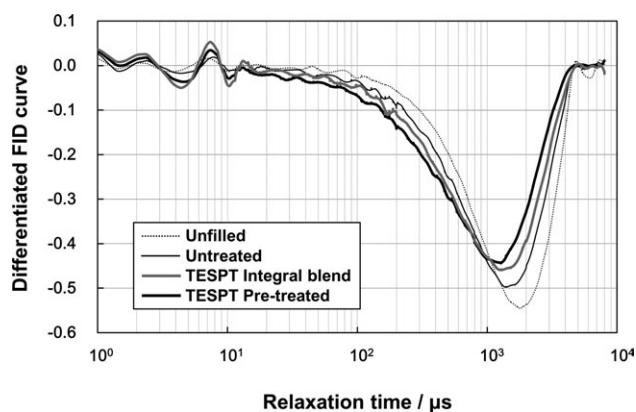

Figure 10. Differentiated FID curves measured by pulse NMR of raw silica particle-filled unvulcanized SBR (silica content: 37 wt %) and those incorporated with TESPT by integral blend method and pretreatment method (silica content: 36 wt %).

Figure 9 shows normalized and differentiated FID curves for the unvulcanized SBR/silica mixture using TESPD measured by pulse NMR relaxation at 120°C. The peak for the unfilled SBR was observed at about 2×10^3 μs and the peak shifted to a shorter relaxation time by the addition of silica particles. A further shift to shorter relaxation was observed by the incorporation of TESPD. The shift to a shorter relaxation time was stronger in the pretreated system than in the integral blend system. The peak for the pretreated system was observed at about 1.2×10^3 μs. It was found that the binding of SBR molecular chains by silica particles was stronger in the order of pretreated > integral blend > untreated. This result has good correlation with the stress in the stress-strain curve (Figure 3) and the 200% modulus (Figure 5).

Figure 10 shows the normalized and differentiated FID curves for the unvulcanized SBR/silica mixture using TESPT measured by pulse NMR relaxation at 120°C. The tendency was the same as that in Figure 9. The peak for the pretreated system was observed at about 1.2×10^3 μs. It was same as that for TESPD
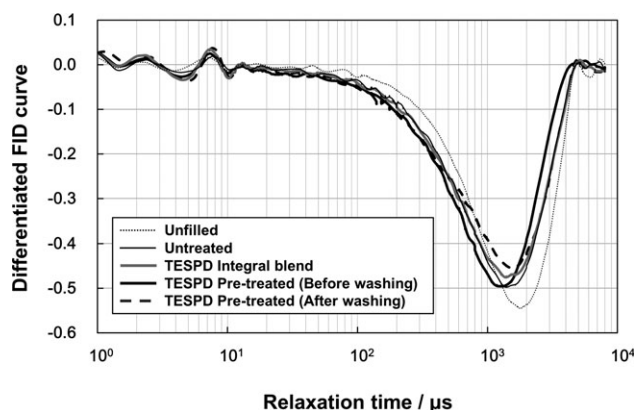

Figure 11. Differentiated FID curves measured by pulse NMR of raw silica particle-filled unvulcanized SBR (silica content: 37 wt %) and those incorporated with TESPD by integral blend method and pretreatment method before and after washing (silica content: 36 wt %).

(Figure 9). However, the distribution of the FID signals in the range from about 5×10^1 μs to 4×10^2 μs was more for TESPT (Figure 10) than for TESPD (Figure 9). This indicates that the binding of SBR molecular chains in the pretreated silica-filled system was slightly higher for TESPT than that for TESPD. As a result, the 200% modulus in the pretreated silica-filled system for TESPT was slightly higher than that for TESPD as shown in Figure 5.

Figure 11 shows the influence of physically adsorbed silane on the molecular mobility of the unvulcanized SBR/silica mixture using TESPD. The peak after washing occurred at a longer relaxation time. This indicates that the binding of SBR molecular chains is lower after washing. This seemed to be influenced by the fewer amount of silanes after washing as mentioned above.

CONCLUSIONS

Polysulfide-type silane coupling agents were incorporated into a SBR/silica composite by the pretreatment method or the integral blend method and the mechanical properties of the resulting composites were measured. The influences of the loading method and the number of sulfur atoms in the silanes on the tensile properties were investigated. The interaction between the silane chains on the silica surface and the SBR molecular chains at the interfacial region in the SBR/silica composite was estimated using pulse NMR spectroscopy. The following results were obtained.

1. To improve the 200% modulus of the composite, the combination of TESPT and the pretreatment method was effective. The sulfur atoms in the silane should contribute to the crosslinking of rubber in the vulcanization process. TESPT strengthens the interface effectively and raises the 200% modulus in the pretreatment method.
2. Whereas, the combination of TESPT and the integral blend method was effective for improving the fracture elongation. It is considered that the unreacted silane molecules in the SBR acted as a plasticizer in the integral blend method and the effect was better for TESPT than for TESPD. It was estimated from the molecular modeling that TESPT is bulkier than TESPD.
3. Removing physically adsorbed silane from the pretreated layer on the silica surface does not improve the 200% modulus and reduced the fracture elongation.
4. From pulse NMR spectroscopy for the unvulcanized SBR/silica mixture, the measured relaxation time was found to be in good correlation with the 200% modulus. It was found that the molecular mobility of rubber is lowered by the entanglement with the silane chains on the silica surface at the interfacial region, and it was more effective in the pretreatment method than in the integral blend method.

ACKNOWLEDGMENTS

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