Silica Reinforcement of Synthetic Diene Rubbers by Sol–Gel Process in the Latex

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ABSTRACT: Styrene–butadiene rubber (SBR) and nitrile rubber (NBR) were reinforced with silica by the sol–gel method of tetraethoxysilane (TEOS) in latex. The sol–gel reaction proceeded in the mixture of latex, TEOS, water, and a catalyst. The compound that involved silica was crosslinked with the curing agent at 150°C. The amount of TEOS added and the molar ratio of TEOS to water ($[H_2O]/[TEOS]$) in the mixture were related to the silica content in the compounds, particle size, and reinforcing behavior of silica. The particle size and reinforcing behavior of the silica were greatly influenced by the amount of TEOS and $[H_2O]/[TEOS]$. The diameter of the dispersed silica particles in cured rubbers was controlled by the amount of TEOS and $[H_2O]/[TEOS]$, which were smaller than 100 nm. By the dispersion of the fine silica in the nanometer-order level, the tensile strength of the compound was drastically improved. The tensile strength of SBR was over 30 MPa, and of NBR, over 25 MPa. Compounds with a high tensile strength had a high bound rubber fraction and a very strong interaction of the fine silica with rubber. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2053–2063, 2002

Key words: silica; reinforcement; sol–gel method; rubber; latex

INTRODUCTION

Silica occupies an important position in the rubber industry as an indispensable material, because it has a high reinforcement effect and an excellent functionality for rubbers.[1–5] However, various contrivances are necessary for silica to compound with the rubber without hurting the performance and function, since the dispersion to the rubber is poor. The well-known methods for improvement of the reinforcement effect are the treatment of the silica surface by silane coupling agents to promote the interaction with rubber.[6–10] Recently, *in situ* synthesis of silica using the sol–gel method has been widely studied as a compounding method of silica.[11–20] The sol–gel method is a synthetic method of metal oxide by the hydrolysis and the condensation of metallic alkoxide.[21] This method had originally developed as a new synthetic method for glass and ceramics. It was applied to the reaction of alkoxide with organic polymers as a synthetic method for new organic inorganic hybrid materials.[22–27] Tetraethoxysilane (TEOS), as a metallic alkoxide, was primarily used in this method. The sol–gel method is recognized as a novel method for controlling the particle size and dispersion of the silica by the condition of the reaction. Several

compounding procedures of rubber with silica are used in the sol–gel method. A representative procedure is a method in which water and a catalyst are impregnated into rubber swollen in TEOS and silica synthesis in the rubber matrix is carried out.[11–19] In another procedure, the sol–gel reaction is promoted by the addition of alcohol, water, TEOS, and a catalyst to the rubber swollen in organic solvents such as THF.[20] Both procedures are also completely different from the compounding method of conventional silica. However, these procedures are not conventional because of the use of a large amount of organic solvent and a long reaction time.

Authors have studied the synthesis of silica by the sol–gel method of TEOS in latex for compounding rubber and silica.[28–30] The latex can mix with TEOS and emulsify easily. Therefore, the sol–gel reaction in this procedure is faster than that in swollen rubber. The advantage of this procedure is that no organic solvent is used, since the system consists of emulsified rubber, TEOS, water, and a catalyst. Additional advantage is that many rubbers are prepared as latex. In this article, silica reinforcement for styrene–butadiene rubber (SBR) and nitrile rubber (NBR) was studied using the sol–gel reaction of TEOS in the corresponding latexes.

EXPERIMENTAL

Materials

The SBR latex used was a commercial SBR latex (SBR 0561; 69 wt % solid element, 24.5% styrene content; JSR Co., Tokyo, Japan). The NBR latex used was LX-531 (64% solid element, 25–35% nitrile content; Nippon Zeon Co., Tokyo, Japan). TEOS and a 25% ammonia aqueous solution as a catalyst were special-grade reagents (Wako Pure Chemical Ind., Ltd., Osaka, Japan). Zinc oxide, stearic acid, sulfur, N-cyclohexyl-2-benzothiazyl sulfenamide (CBS), diphenylguanidine (DPG), organic amines as various curing agents, and dibenzothiazyl disulfide (MBTS) were commercial products used as received. Toluene and 2-butanone (MEK), used for the bound rubber measurement, were special-grade reagents (Wako Pure Chemical Ind., Ltd., Osaka, Japan).

Preparation of the Silica in the Latex by the Sol–Gel Method

The silica in the latex was prepared by the following procedure: Latex, 50 g, was weighed in a 300

Table I   Recipe of Curing Agents

Material	Content (phr)	
SBR	100	
NBR		100
Zinc oxide	3.00	5.00
Stearic acid	1.00	1.00
Sulfur	1.75	1.50
CBS	2.00	
DPG	0.65	
Organic amine[a]	0.65	
MBTS		1.00

[a] Acting SL (Yoshitomi Pharmaceutical Industries Ltd.)

mL beaker. TEOS, water, and the catalyst of the required amount were added. These reagents were mixed at an ambient temperature at 760 rpm and uniformly emulsified. The reactant mixture stood for 24 h in an oven at 40°C to progress the sol–gel reaction. Then, the reaction products were dried under reduced pressure at 80°C for 8 h. The amounts of TEOS, water, and the catalyst were variously changed.

Preparation of Silica-reinforced Rubber

The curing agents were mixed into the obtained rubber compound by use of a roll mill. The compound that contained the curing agents was cured by a hot press at 150°C. A rubber sheet of about 1-mm thickness was produced. The curing time was determined by measurement of the crosslink time–torque curve of each sample. Table I shows the recipe of the curing agents.

Characterization

The Silica content of the compound was determined by thermogravimetric analysis (TGA). The measurement of TG/DTA (TG/DTA 200, Seiko Instrument Co., Japan) was carried out under the following conditions: sample weight of 10 mg, flow rate of 200 mL/min under an air atmosphere, temperature range from 30 to 815°C, and heating rate of 20°C/min. After the temperature of sample in the TGA analysis reached 815°C; the sample was held for 5 min at this temperature.

The mechanical properties of the silica-reinforced rubbers were measured using an Instron-type tensile tester (Shimadzu-Autograph DSS5000, Shimadzu Co. Japan). The temperature dependence of the dynamic viscoelasticity was measured by a dynamic viscoelastometer

Table II   Preparation Conditions of SBR–Silica Compound

Sample No.	Latex (g)	TEOS (g)	H_2O (g)	25% NH_3 (g)	$[H_2O]/[TEOS]$ (Molar Ratio)
S30-1	50	30	5.3	0.39	8.1
S30-2	50	30	11.8	0.44	10.6
S30-3	50	30	23.8	0.54	15.3
S40-1	50	40	12.2	0.52	8.1
S40-2	50	40	20.9	0.59	10.6
S40-3	50	40	36.9	0.71	15.3
S50-1	50	50	19.0	0.65	8.1
S50-2	50	50	30.0	0.73	10.6
S50-3	50	50	50.0	0.89	15.3
S60-1	50	60	26.0	0.78	8.1
S60-2	50	60	39.0	0.88	10.6
S60-3	50	60	63.0	1.07	15.3
S80-1	50	80	40.0	1.05	8.1
S80-2	50	80	57.3	1.18	10.6
S80-3	50	80	90.0	1.44	15.3

(DMS210, Seiko Instrument Co., Japan) at a heating rate of 2°C/min from −80 to 60°C at 10 Hz and in the tension mode. The morphology was observed using a scanning electron microscope (SEM) (JSM-840F; JEOL Co.). The specimens observed were compounds and samples obtained by fracture of the silica-reinforced rubbers frozen in liquid nitrogen. The fraction of the bound rubber that occurred in the compounds was determined by the following procedures: Shear force was applied to the compound of about 2 g by passing it through the roll mill with a nip length of 0.1 mm at 100 times. This shear force was equal to the shear applied to the rubber when the rubber compound was prepared. Then, the compound applied to the shear force was cut off to the size of a 2 × 2-mm square. It was put into a cage made by stainless wire gauze of 280 mesh (aperture: 53 μm). The cage was soaked in the solvent of 60 mL at 23°C for 72 h. The cage was taken out after 72 h and air-dried at 23°C for 24 h, then dried for 1 h under reduced pressure at 60°C. Toluene was used for SBR and MEK was used for NBR as the solvent. The insoluble rubber fraction was calculated from the weight of the residual sample. By eq. (1), the bound rubber fraction was calculated from the insoluble rubber fraction:

Bound rubber fraction (wt %)

$$= \frac{\text{insoluble rubber fraction} - \text{silica quantity in the sample}}{\text{rubber quantity in the sample}} \times 100 \quad (1)$$

RESULTS AND DISCUSSION

Silica Content of Compound

The amount of TEOS added to latex of 50 g in this study was changed between 30 and 80 g to examine the change of the silica content of the compound. The molar ratio of water to TEOS ($[H_2O]/[TEOS]$) in the mixture was also changed at three levels. The quantity of the catalyst with the change of $[H_2O]/[TEOS]$ was adjusted to become a specific quantity for the total weight of water and TEOS in the mixture. The preparation conditions of the compounds are shown in Tables II and III. Latexes of SBR and NBR were easily mixed with TEOS without both phase separation and flocculation. However, phase separation in the case of NBR was observed under a reaction with a large amount of TEOS.

Figures 1 and 2 show the relationship between the amount of TEOS and the silica content in the SBR or NBR compounds. The square value of the correlation coefficient (R^2) and the regression line are shown in Figure 1 and 2. The data of the both samples that greatly deviated from linearity were not used for calculating R^2 and the regression line in the case of NBR. The silica content in SBR increased with increase of the amount of TEOS. Since R^2 between the amount of TEOS and the silica content was 0.956, the relationship between the amount of TEOS and the silica content was approximately well in the regression line shown in the figures. The difference of $[H_2O]/[TEOS]$ did

Table III   Preparation Conditions of NBR–Silica Compound

Sample No.	Latex (g)	TEOS (g)	H_2O (g)	25% NH_3 (g)	$[H_2O]/[TEOS]$ (Molar Ratio)
N30-1	50	30	2.8	0.39	8.1
N30-2	50	30	8.0	0.43	10.1
N30-3	50	30	20.9	0.53	15.1
N40-1	50	40	9.7	0.52	8.1
N40-2	50	40	16.6	0.58	10.1
N40-3	50	40	33.9	0.71	15.1
N50-1	50	50	16.6	0.65	8.1
N50-2	50	50	25.3	0.72	10.1
N50-3	50	50	46.9	0.89	15.1
N60-1	50	60	23.5	0.78	8.1
N60-2	50	60	33.9	0.86	10.1
N60-3	50	60	59.9	1.07	15.1
N70-1	50	70	30.5	0.92	8.1
N70-2	50	70	42.6	1.01	10.1
N70-3	50	70	72.9	1.24	15.1

not remarkably influence the silica content. The silica content of the compounds was at a high content about of 40 wt %. These results led to that the silica content of the compounds was almost controlled by the amount of TEOS.

The dependence of the silica content on the amount of TEOS in NBR was also similar to that of SBR except for the case of phase separation in the reaction. The data that deviated from linearity in Figure 2 indicate the phase separation in the reaction. The phase separation in the reaction brought about a drastic lowering of the silica content. A number of silica particles with a large particle size were observed by SEM when the
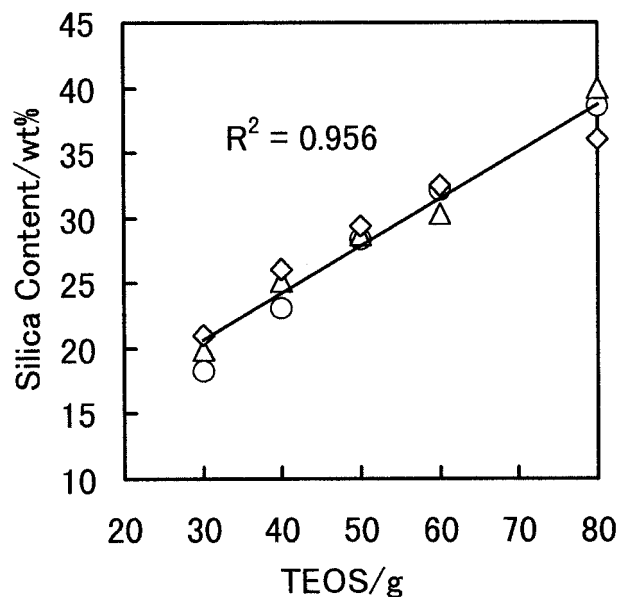

Figure 1   Relationships between the amount of added TEOS and the silica content of the SBR–silica compound: ($\bigcirc$, $\triangle$, $\diamondsuit$) $[H_2O]/[TEOS]$ = 8.1, 10.6, and 15.3, respectively.
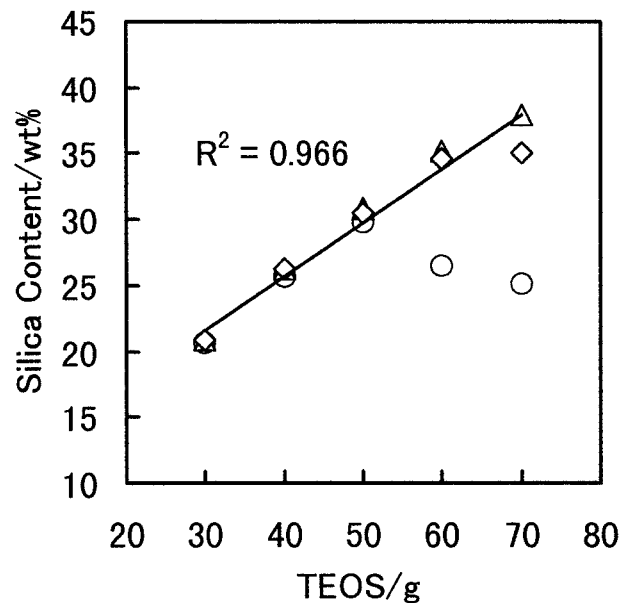
Figure 2   Relationships between the amount of added TEOS and the silica content of the NBR–silica compound: ($\bigcirc$, $\triangle$, $\diamondsuit$) $[H_2O]/[TEOS]$ = 8.1, 10.1, and 15.1, respectively.
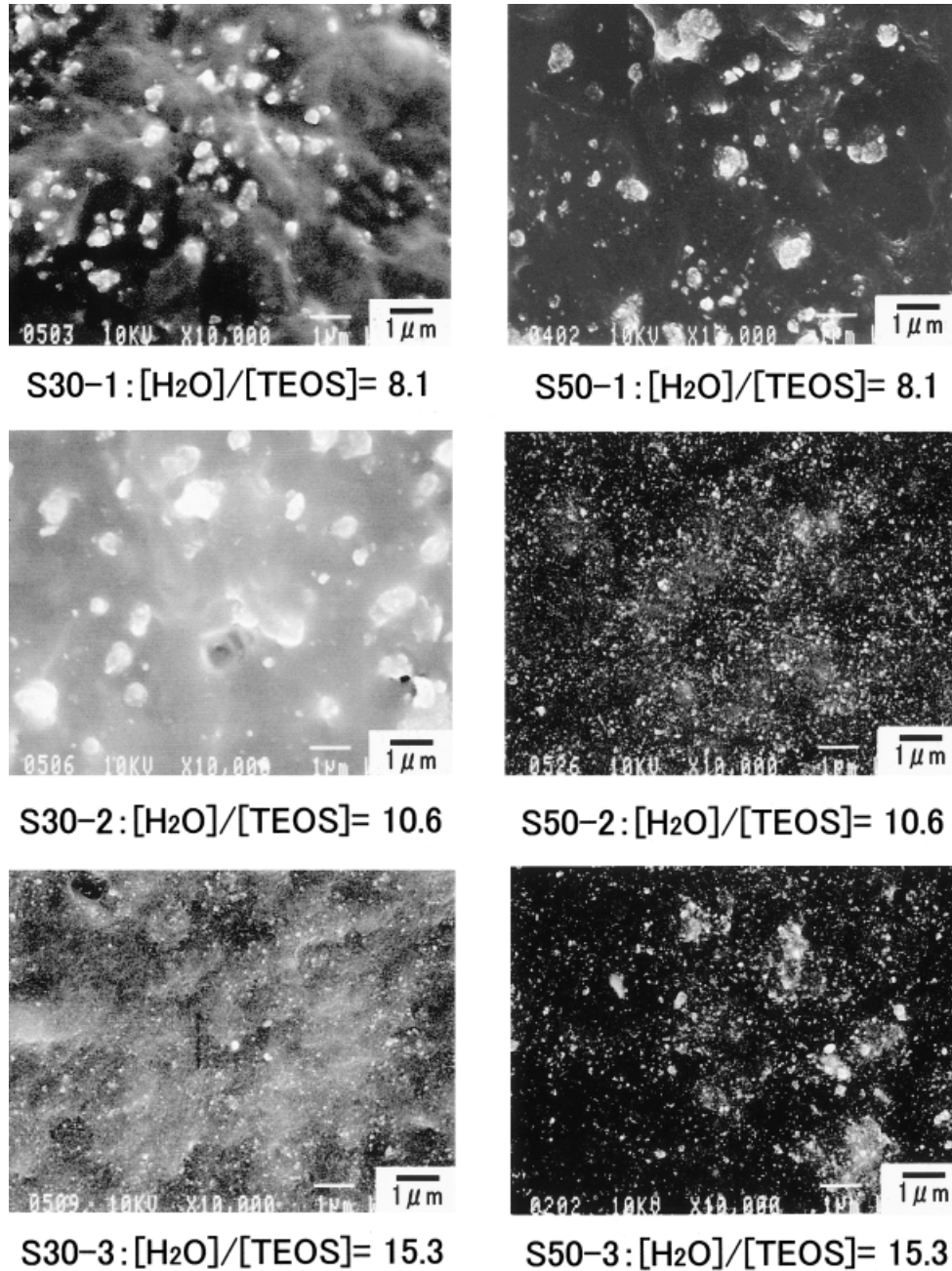
Figure 3 SEM pictures of the fracture surface of SBR compounds.

amount of TEOS was over 60 g. The formation condition of the silica in the NBR latex at a high TEOS content was clearly different from that of the other samples.

Particle Size of the Dispersed Silica in Compound

SEM photographs of the fracture surface of the compounds prepared under conditions shown in Tables I and II are shown in Figures 3 and 4. The silica particles were uniformly dispersed in the compound, but the particle size was greatly different according to the preparation conditions. The particle size was affected by the amount of TEOS and $[H_2O]/[TEOS]$ in the mixture. The fineness of silica particle in the compound prepared under the optimum condition was 100 nm or less. This fact showed that the particle size of silica is controlled by $[H_2O]/[TEOS]$ at an ambient con-
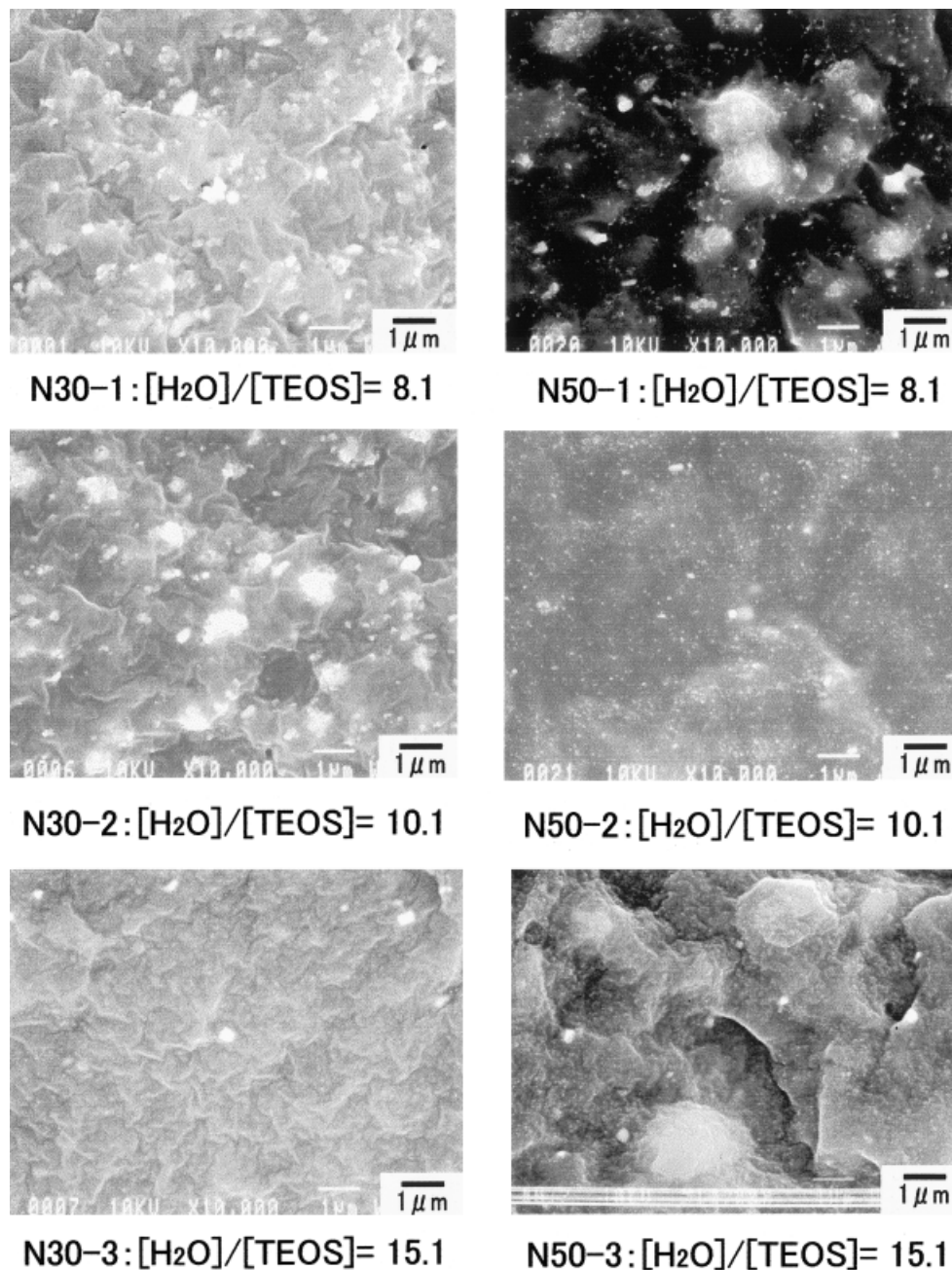
Figure 4 SEM pictures of the fracture surface of NBR compounds.

stant value of the silica content, because the silica content depends only on the added TEOS. For example, a very small silica particle of nanometer diameter was produced by [H$_2$O]/[TEOS] of about 10 at the silica content of 30 wt %. The particle size of the reinforcing filler is the important factor that determines the mechanical properties and the viscoelasticity of the cured rubber. Therefore, these results mean that control of the preparation

conditions control the mechanical properties and the viscoelasticity.

The quantity of the catalyst was also varied. However, this effect to the silica content, the particle size, and the reinforcing behavior of silica can be neglected, because the effect on the silica content, the particle size, and the reinforcing behavior of silica could not be recognized, even if the catalyst quantity was changed
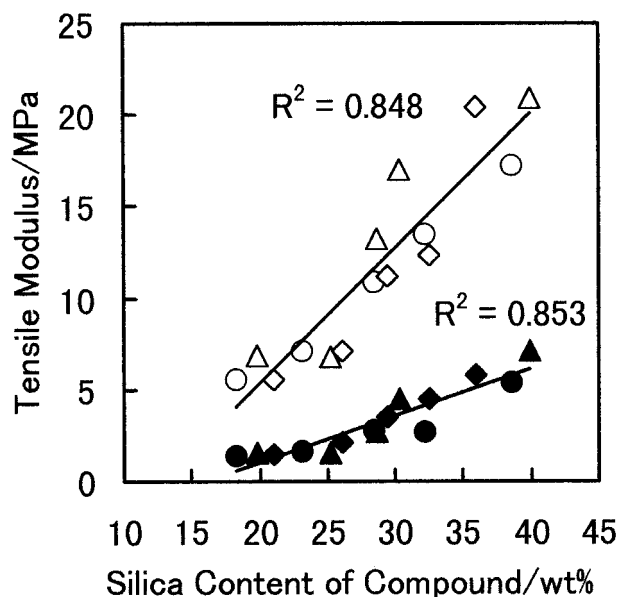
Figure 5 Relationships between the silica content and the tensile modulus of the SBR–silica compound: (●, ▲, ◆) 100% tensile modulus of compounds prepared with $[H_2O]/[TEOS]$ = 8.1, 10.6, and 15.3, respectively; (○, △, ◇) 300% tensile modulus of compounds prepared with $[H_2O]/[TEOS]$ = 8.1, 10.6, and 15.3, respectively.
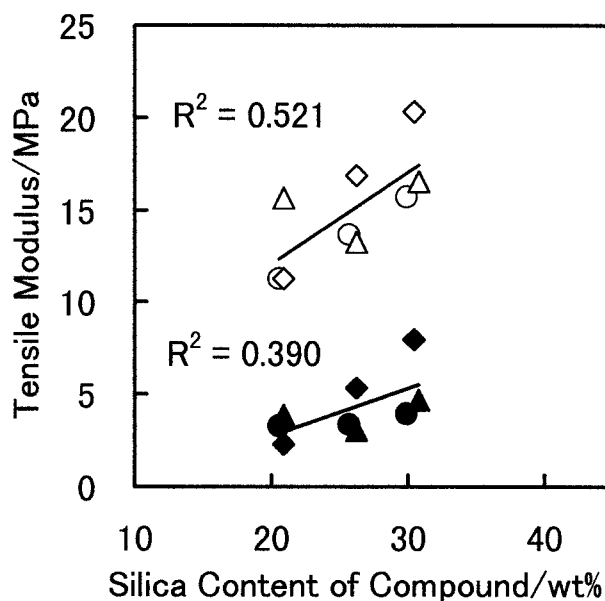

Figure 6 Relationships between the silica content and the tensile modulus of the NBR–silica compound: (●, ▲, ◆) 100% tensile modulus of compounds prepared with $[H_2O]/[TEOS]$ = 8.1, 10.1, and 15.1, respectively; (○, △, ◇) 300% tensile modulus of compounds prepared with $[H_2O]/[TEOS]$ = 8.1, 10.1, and 15.1, respectively.

as in previous research[29] over twice that of the present case.

Mechanical Properties of Compound

The relationships between the tensile modulus and the silica content of SBR and NBR-cured rubbers are, respectively, shown in Figures 5 and 6. Figures 7 and 8 show the relationship between the tensile strength and the silica content in SBR and NBR, respectively. R^2 and the regression line are shown in the figures. The tensile modulus in SBR almost monotonously increased with increase of the silica content. The dependence of the tensile modulus on the silica content had a high correlation with R^2 of about 0.85. As a result, the relationship between the tensile modulus and the silica content approximately was well in the regression line shown in Figure 5. The effect of $[H_2O]/[TEOS]$ in the mixture on the tensile modulus was not significantly recognized. These results mean that the synthesized silica improves the tensile modulus but the $[H_2O]/[TEOS]$ in the mixture does not affect the tensile modulus.

The tensile strength also increased with increase of the silica content. However, the correlation between the tensile strength and the silica

content of the compound was low as shown R^2 of 0.297. This was different from the case of the tensile modulus. There was a large difference in
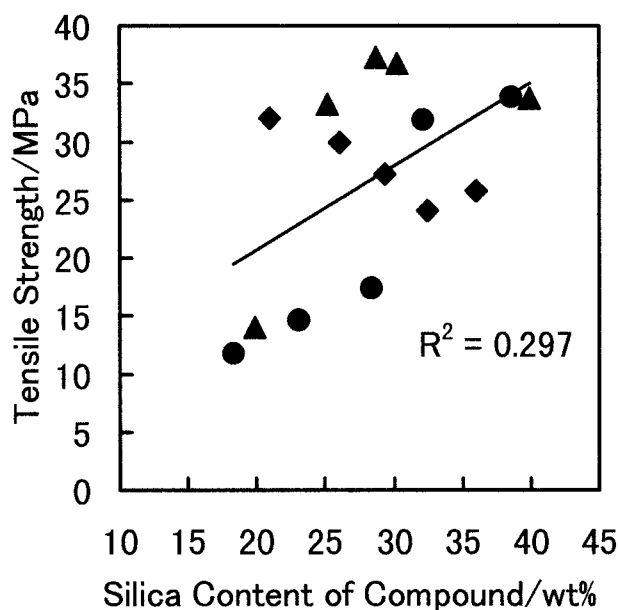

Figure 7 Relationships between the silica content and the tensile strength of the SBR–silica compound: (●, ▲, ◆) $[H_2O]/[TEOS]$ = 8.1, 10.6, and 15.3 respectively.

the tensile strength, even if it was almost the same silica content. For example, the highest tensile strength was twice the lowest value when the silica content was about 30 wt %.

The different symbols which show the data in the figures indicate the difference of $[H_2O]/[TEOS]$ in the mixture. This seems to show that the tensile strength of a compound is largely affected by changing the $[H_2O]/[TEOS]$ in the mixture. The dependence of the tensile modulus and the tensile strength on the silica content of a compound in NBR was also similar to that of SBR. The monotonous increase of the tensile modulus with increase of the silica content and the effect of $[H_2O]/[TEOS]$ on the tensile strength did not appear clearly in NBR since the data were very scattered in addition to the small amount of data. However, it is reasonable that the features of the mechanical properties were similar to those of SBR, because the results on the particle size and bound rubber described later were similar to the results in SBR.

The effect of $[H_2O]/[TEOS]$ on the tensile strength is shown in Figure 9. In this case, the amount of added TEOS was fixed at 50 g to the silica content of the compound of about 30 wt %. The preparation conditions of the curing rubbers are shown in Table IV. It was clearly proven that the tensile strength was largely affected by the
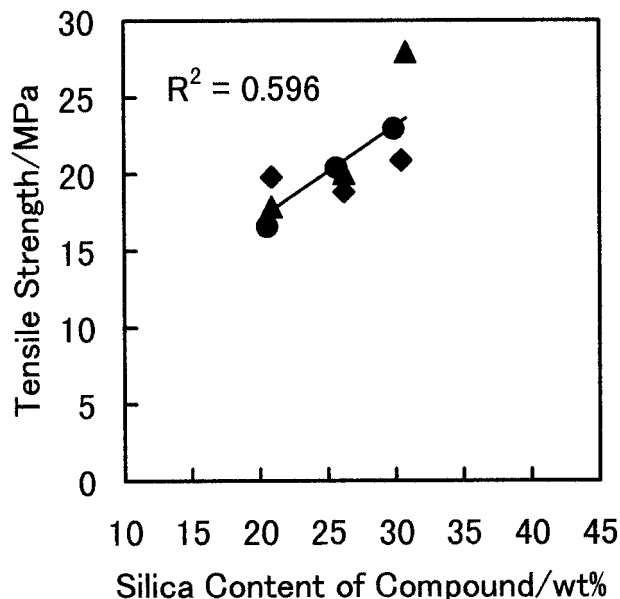

Figure 9 Dependence of the tensile strength of the compound on the molar ratio of $[H_2O]/[TEOS]$ in the latex mixture.

change of the $[H_2O]/[TEOS]$. In SBR, the tensile strength was extremely improved from about 15 to 30 MPa by changing the $[H_2O]/[TEOS]$. The maximum tensile strength was shown near $[H_2O]/[TEOS]$ of 10. Although it was not remarkable as for the case of SBR, the effect of $[H_2O]/[TEOS]$ on the tensile strength was also similar in NBR.

The SEM photographs of the fracture surface of the compounds prepared under the conditions in Table 4 are shown in Figure 10. The particle size of the silica dramatically changed between the compounds of which the tensile strength greatly differed. The fineness of the silica particle in the compound shown in high tensile strength was the size of 100 nm or less. The tensile strength is affected by the particle size of the influencing reinforcing filler.[31,32] In the meantime, the tensile modulus is greatly influenced by the content of the reinforcing filler.[2] Therefore, the tensile strength greatly differs between the compounds with the same silica content because the particle size of the silica changes dramatically by the $[H_2O]/[TEOS]$.

Bound Rubber of the Compound

Figures 11 and 12 show the change of the bound rubber fraction of the compound with the change of the tensile strength of the compound. It was proven that the tensile strength and the bound

Figure 8 Relationships between the silica content and the tensile strength of the NBR–silica compound: (●, ▲, ◆) $[H_2O]/[TEOS]$ = 8.1, 10.1, and 15.1 respectively.
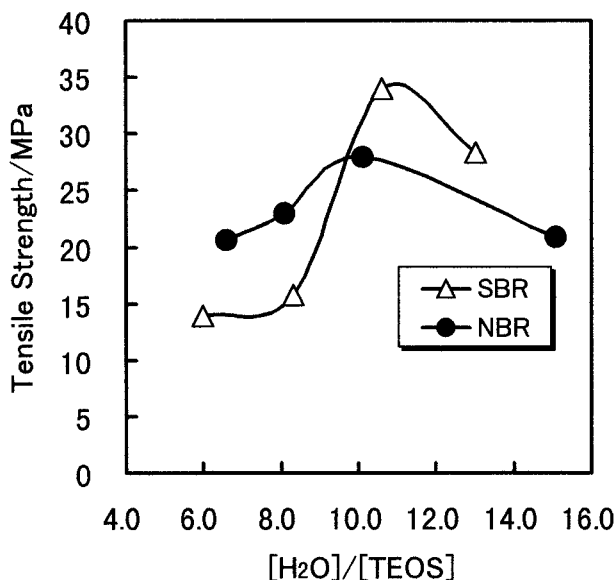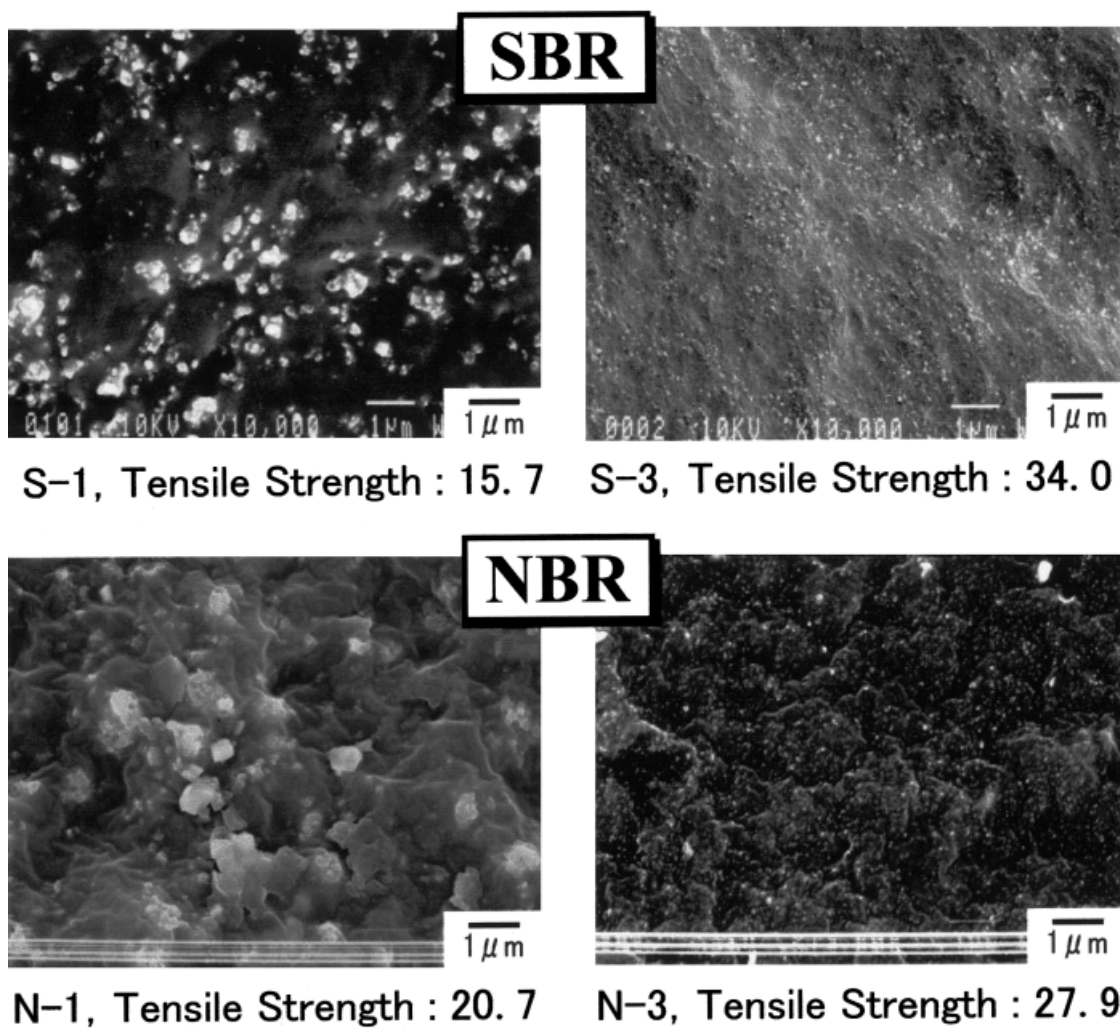
Table IV   Preparation Conditions of SBR and NBR–Silica Compound Under Different [H$_2$O]/[TEOS] Contents

Sample No.	Rubber	Latex (g)	TEOS (g)	H$_2$O (g)	25% NH$_3$ (g)	[H$_2$O]/[TEOS] (Molar Ratio)
S-1	SBR	50	50	10.0	0.58	6.0
S-2	SBR	50	50	20.0	0.65	8.3
S-3	SBR	50	50	30.0	0.73	10.6
S-4	SBR	50	50	40.0	0.81	13.0
N-1	NBR	50	50	10.0	0.60	6.6
N-2	NBR	50	50	16.6	0.65	8.1
N-3	NBR	50	50	25.3	0.72	10.1
N-4	NBR	50	50	46.9	0.89	15.1

Figure 10   SEM pictures of the fracture surface of compounds prepared under the conditions, in Table IV.
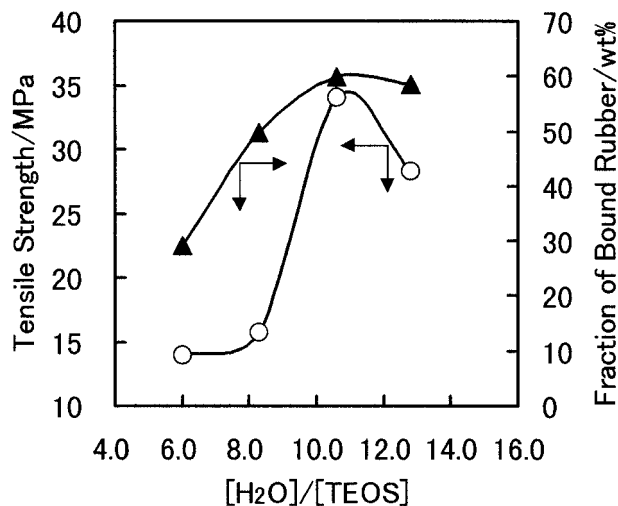
Figure 11 Dependence of the fraction of bound rubber and the tensile strength of the SBR–silica compound on the molar ratio of $[H_2O]/[TEOS]$ in the latex mixture.

rubber fraction was significantly affected by $[H_2O]/[TEOS]$. Figures 11 and 12 indicate that the compound with a high tensile strength has a high bound rubber fraction. The bound rubber fraction and tensile strength in SBR correlated comparatively well with $R^2 = 0.695$. On the other hand, a clear correlation in NBR was not obtained, as R^2 was 0.379. However, compounds with a high tensile strength had a high bound rubber as shown in Figure 12. Therefore, these
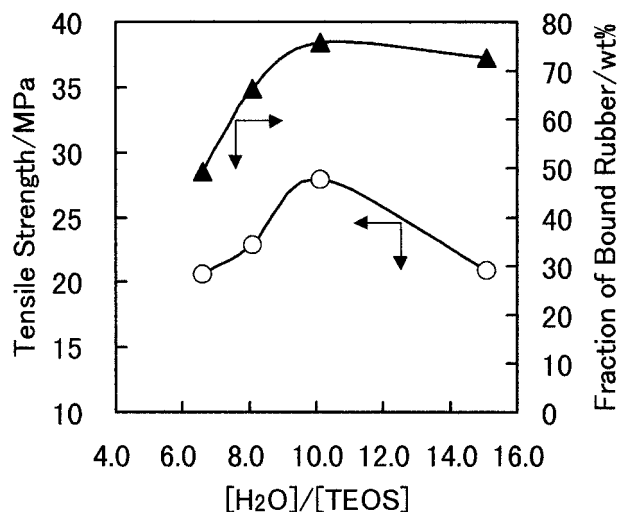

Figure 12 Dependence of the fraction of bound rubber and the tensile strength of the NBR–silica compound on the molar ratio of $[H_2O]/[TEOS]$ in the latex mixture.
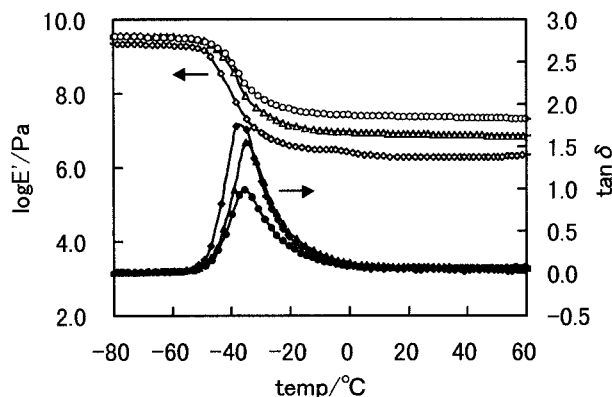

Figure 13 Temperature dependence of log E' and tan δ of the SBR–silica compound and nonfilling SBR: ($\blacktriangle$, $\bullet$, $\blacklozenge$) log E' of S-1, S-3, and nonfilling SBR, respectively, ($\triangle$, $\bigcirc$, $\diamond$) tan δ of S-1, S-3, and nonfilling SBR, respectively.

suggest that the $[H_2O]/[TEOS]$ in the mixture also controls not only the particle size of the silica but also the formation of bound rubber in the compound. The change of the bound rubber fraction reflects the change of the interface interaction of the rubber and filler.[2,31,33,34] In the rubber with a high bound rubber fraction; the interface interaction between the rubber and the silica was strong. Therefore, the peeling of the interface by the stress as an origin of the destruction was difficult in the compounds with a high bound rubber fraction. A high bound rubber fraction played a role in the suppression effect of the crack growth by fine silica. These results led to the high tensile strength of the compounds due to increase of the fineness of the silica particle.

Dynamic Mechanical Properties

The temperature dependence of the dynamic modulus (E') and the loss tangent (tan δ) of crosslinked SBR is shown of Figure 13. The storage modulus at room temperature increased with incorporation of silica and it further increased at the S-3 with silica of 100 nm or less. This is attributed to that the interaction of the interparticle increases with an increasing number of particles. The contribution of this interaction appears when a very low strain was applied, but it does not contribute to the tensile modulus. Therefore, the result of the storage modulus does not contradict the result of the tensile modulus.

The peak intensity of tan δ decreased and the peak temperature increased to the high-temperature side by the incorporated silica. The lowering

of the peak intensity for S-3 was more remarkable than that of S-1. This behavior shows that the amount of rubber molecules bound in S-3 is larger than that of S-1. The result agrees with the result of bound rubber. This result also displays the strong interaction between rubber and silica with a fine particle sizes.

CONCLUSIONS

The synthesis of silica in the latex of a diene synthetic rubber by the sol–gel method and the properties of reinforced rubbers were studied. The results led to the following conclusions:

1. Fine silica particles were compounded to SBR and NBR by the sol–gel reaction of TEOS in the latex.
2. The amount of silica compounded was almost proportional to the amount of added TEOS to the latex.
3. The silica particle size in the crosslinked rubber dramatically changed with variation of the amount of TEOS added to the latex and the [H_2O]/[TEOS] in the mixture. The ratio of [H_2O]/[TEOS] in the mixture controlled the fineness of the silica particles of a nanometer-order level in the compounds.
4. By the dispersion of the fine silica of the nanometer-order level, the tensile strength of the compound was drastically improved.
5. The particle size hardly affected the tensile modulus, and the tensile modulus almost monotonously increased with the silica content.
6. Compounds with a high tensile strength had a high bound rubber fraction.
7. The result of the dynamic viscoelasticity measurement showed that a strong interaction existed between rubber and silica with a fine particle size.

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