Reinforcement of styrene–butadiene rubber vulcanizate by *in situ* silica prepared by the sol–gel reaction of tetraethoxysilane

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In situ silica reinforcement of styrene–butadiene rubber (SBR) has been achieved by a sol–gel process using tetraethoxysilane (TEOS). SBR was sulfur-cured and the sol–gel reaction of TEOS was carried out in TEOS or in a TEOS–tetrahydrofuran (THF) mixture. The *in situ* silica was filled homogeneously in the rubber matrix and the size of the *in situ* silica was influenced by the cross-linking density of the SBR vulcanizate. *n*-Butylamine was effective for the method using TEOS only, whereas both hydrochloric acid and *n*-butylamine worked as catalysts under the experimental conditions using THF for the *in situ* polymerization of TEOS in the SBR vulcanizate. From the viewpoint of the reinforcement of *in situ* silica and the size stability of the SBR vulcanizate, the method using only TEOS was found to be better than the mixture system. This conclusion was based on the results of tensile tests, dynamic mechanical measurements, optical and transmission electron microscopies.

Rubbers form a class of polymeric materials, which show rubbery elasticity when in use. Recently, the significance of rubber has been more widely recognized. For practical applications, most rubbers are used after mixing with inorganic materials and/or fibres. In rubber technology, therefore, the mixing of fillers is extremely important. Synthetic rubbers have become of general use after compounding of carbon black as an effective reinforcer.[1,2] Other than carbon black, only silica is known as an important reinforcing filler, in spite of many investigations to develop reinforcing fillers for synthetic rubbers.[1–3]

Conventionally, a silica–rubber composite or a silica-reinforced rubber has been prepared by mechanical mixing and compression moulding techniques followed by curing of the rubber compound. A hydrated silica, of particle size 20–80 nm, is typically used for reinforcing rubbers. Because of the small size and the large specific surface area, the incorporation of silica into rubbers *via* the normal mixing techniques gives rise to increased viscosity, which makes the processing more difficult. It can also deactivate curing agents and accelerators, which results in the reduction of the degree of cross-linking. Practically, these problems are partially overcome or minimized by using specific additives and by optimizing mixing procedures.[4]

One of the methods for overcoming these difficulties is *in situ* polymerization of tetraethoxysilane (TEOS) by a sol–gel process,[5,6] where silica is formed in the rubber matrix. This is an application of the preparation of inorganic glasses at low temperatures.[7] The reaction of TEOS takes place in two steps, hydrolysis and condensation, to produce SiO_2.

The preparation of organic–inorganic hybrid materials by using a sol–gel reaction of alkoxysilyl groups has been actively studied.[7,8] We already reported the synthesis and properties of novel networks prepared from a polyether oligomer with triethoxysilyl groups at both ends.[9–12] Utilization of so-called ‘silica coupling agents’ to enhance the effects of inorganic fillers is in a way related to the sol–gel reaction, especially when used in combination with moisture cure.[7,11,13]

Among several techniques, *in situ* silica formation in the polymer matrix is very simple and readily produces hybrid materials. *In situ* polymerizations of TEOS in silicon rubber,[14–16] polyisobutylene,[17] poly(methyl methacrylate),[18,19] poly(vinyl acetate),[20] polyimide,[21] poly(vinyl pyrrolidone),[22] polyoxazoline[23] and epoxidized natural rubber[24,25] have been reported. However, one of the conventional general-purpose diene rubbers was first subjected to the *in situ* polymerization of TEOS in our previous studies.[26,27] The better reinforcement of *in situ* silica for styrene–butadiene rubber (SBR) vulcanizates was observed when *n*-butylamine was used as the catalyst.[27]

In this report, the effect of cross-linking density on *in situ* silica formation in the SBR vulcanizates is elucidated and the difference of the reinforcement effect between *in situ* silica and conventionally mixed silica is investigated quantitatively. The effect of tetrahydrofuran (THF) on the *in situ* silica filling for the SBR vulcanizate was also studied, and in particular the influence of morphology of the *in situ* silica on the reinforcement of the rubber was discussed.

Experimental

Materials

Styrene–butadiene rubber (SBR 1502) was supplied from the Japan Synthetic Rubber (JSR) Co. and its properties are summarized in Table 1. TEOS was obtained from Shin-etu Chemical Ind. Co. The catalysts were hydrochloric acid and *n*-butylamine, which were reagent grade. Nipsil VN-3 from Nippon Silica Co., commercially available silica particles, was used for mechanical mixing with SBR, which was dried for 3 h at 150 °C before use. The specific surface area and the diameter of VN-3 are *ca.* 200 $m^2\ g^{-1}$ and *ca.* 16 nm, respectively. All reagents and solvents were used as received unless otherwise noted.

Preparation of the rubber vulcanizates

SBR and reagents were mixed on a two-roll mill. The proportions of reagents are shown in Table 2. In order to evaluate the effect of cross-linking density on the *in situ* silica formation in the rubber vulcanizate, the amounts of sulfur and *N*-oxydiethylene-2-benzothiazolylsulfenamide (MSA-G) were changed. Thus, the master batch technique was used for the preparation of the compounds. The SBR compounds physically

Table 1 Properties of SBR 1502

type	cold
bound styrene (mass%)	23.5
Mooney viscosity (ML_{1+4}, 100 °C)	52
product stain	non-staining

Table 2 Reagents used in the preparation of SBR vulcanizates (phr[a])

	SBR-1	SBR-2	SBR-1-VN
SBR 1502	100	100	100
ZnO	5.0	5.0	5.0
stearic acid	1.5	1.5	1.5
MSA-G[b]	0.5	1.0	0.5
sulfur	0.5	1.0	0.5
silica (VN-3)[c]	0	0	30

[a]Part per hundred in mass. [b]*N*-Oxydiethylene-2-benzothiazolylsulfenamide. [c]Commercial silica.

mixed with silica particles (VN-3) were prepared by a conventional method using a two-roll mill; the product of this procedure is abbreviated as SBR-1-VN. Rubber vulcanizates were prepared by curing at 150 °C for a given time under a pressure of 100 kg cm^{-2}. Curing times were 50 min for SBR-1 and 30 min for SBR-2, which were determined from the cure curves using a JSR Curelastometer III.

Preparation of the *in situ* silica-filled vulcanizates by the sol–gel method

Two methods were used for the preparation of *in situ* silica-filled vulcanizates.

Method A. The SBR vulcanizates were swollen in TEOS at 30 °C for 48 h and soaked in an aqueous solution of 1 mol dm^{-3} hydrochloric acid or a 10 mass% aqueous solution of *n*-butylamine at 30 °C for 24 h. Then, the samples were heated at 50 °C for 72 h and dried for several days at 50 °C under a reduced pressure. The amounts of TEOS and the catalyst solution were ten times the mass of the sample film. The *in situ* silica-filled vulcanizates formed by acid catalyst and by base catalyst are abbreviated hereafter, for example, as SBR-1-A-acid and SBR-1-A-base, respectively, where A means method A.

Method B. The SBR vulcanizates were swollen in THF for 30 min at 30 °C. Then, TEOS and the aqueous solution of 1 mol dm^{-3} hydrochloric acid or 10 mass% aqueous solution of *n*-butylamine were added, and the samples were kept immersed at 30 °C for 48 h. The amount of TEOS used was six times the mass of the sample. Hydrochloric acid and *n*-butylamine were 1/50 the molarity and 1/10 the molarity of TEOS, respectively. The volumes of the solution of THF and the aqueous solution of catalyst were equal to that of TEOS. Then, the samples were heated at 50 °C for 72 h and dried for several days at 50 °C under reduced pressure. The *in situ* silica-filled vulcanizates by acid and base catalyst were abbreviated as SBR-1-B-acid and SBR-1-B-base, respectively, where B means method B.

Material characterization of the *in situ* silica-filled vulcanizates

Thermogravimetry. Thermogravimetric analysis (TG) was carried out by using a Rigaku TG Instrument. A sample (*ca.* 100 mg) was placed in a platinum pan and heated under air to 1000 °C at a rate of 20 °C min^{-1}. The silica contents of the *in situ* silica-filled vulcanizates were determined by TG.

Swelling. The degree of swelling of the sample was measured by soaking in solvent at 30 °C for 48 h, and was calculated using eqn. (1).

$$\text{Degree of swelling (\%)} = 100[(M_1 - M_2)/M_2] \quad (1)$$

where M_1 is the mass of film after swelling and M_2 is the mass of film before swelling.

Tensile test. Tensile properties of the silica-filled vulcanizates were measured on a tensile tester at room temperature at a strain rate of 100 mm min^{-1} using ring-shaped specimens. Values reported are based on the average of five measurements for each sample.

Dynamic mechanical analysis. Dynamic mechanical analysis (DMA) was carried out using a Rheospectoler DVE-4 instrument (Rheology Co., Kyoto) at a frequency of 10 Hz and a heating rate of 2 °C min^{-1}.

Optical microscopy. The optical microscopic observation was carried out by using a Nikon Polarizing Microscope (Model POH 3).

Transmission electron microscopy. Ultrathin films of the samples were prepared using a microtome (KLB 4800A Ultrotome) in liquid nitrogen of LKB 14800 Cryokit. The specimen was placed on a copper grid, which was coated with Folmvar and evaporated carbon in advance. Then, transmission electron microscopy (TEM) observations were carried out with a transmission electron JEOL TEM-100U instrument without staining. The accelerating voltage was 80 kV.

Results and Discussion

Effect of cross-linking density on *in situ* silica formation in the SBR vulcanizate

In order to elucidate the sol–gel reaction of TEOS in the SBR matrix, the effect of cross-linking density of the SBR vulcanizates on *in situ* silica formation was investigated. The proportions of the reagents, *i.e.* the amounts of sulfur and curing accelerator (MSA-G) were changed for the preparation of the SBR vulcanizates as shown in Table 2. The cross-linking densities of the sulfur-cured films were determined from the Mooney–Rivlin plots shown in Fig. 1. The Mooney–Rivlin equation[28,29] is as follows:

$$\sigma/(\alpha - 1/\alpha^2) = 2(C_1 + C_2/\alpha) \quad (2)$$

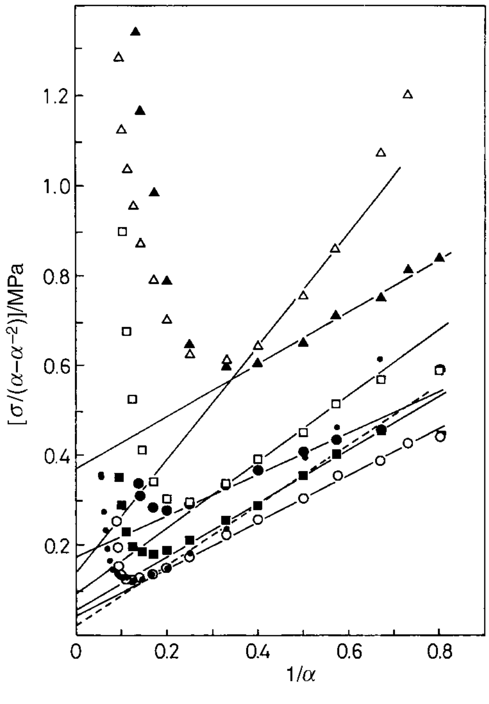


Fig. 1 Mooney–Rivlin plots of SBR vulcanizates with and without silica. SBR-1 (○), SBR-1-A-base (△), SBR-2 (●), SBR-2-A-base (▲), SBR-1-VN (•), SBR-1-B-acid (■), SBR-1-B-base (□).

where σ is the tensile modulus, α is the strain and C_1 and C_2 are constants. Mooney–Rivlin plots of the reduced stress against reciprocal elongation are represented using the results of the tensile test. In the low elongation region of the Mooney–Rivlin plot, a straight line can be drawn, and its intercept and slope correspond to $2C_1$ and $2C_2$, respectively. C_1 can be defined by eqn. (3).

$$2C_1 = vkT \tag{3}$$

where v is the cross-linking density, k is Boltzmann's constant and T is the absolute temperature. From this relation, the cross-linking density was determined; the results are shown in Table 3. Two kinds of SBR vulcanizates were prepared whose cross-linking densities were 1.6×10^{-5} and 7.0×10^{-5} mol cm^{-3} for SBR-1 and SBR-2, respectively. In order to determine clearly the reinforcement effect of *in situ* silica, the sulfur curing was set to be suppressed compared with that of practical SBR vulcanizates.

In the case of SBR-2-A-acid and SBR-1-A-acid,[27] silica was not formed in the SBR matrix, but formed in the surface layer of the vulcanizate as depicted in Fig. 2. Thus, the samples prepared using *n*-butylamine as a catalyst are discussed here. The TEM photographs of SBR-1-A-base and SBR-2-A-base are shown in Fig. 3. The dark portions were *in situ* silicas. It is clear that the particles dispersed homogeneously and did not aggregate in the rubber matrix, which is much different from the silica particles of SBR-1-VN as shown in the figure. Interestingly, the size of the *in situ* silica of SBR-2-A-base was smaller than that of SBR-1-A-base. The diameter of the former was *ca.* 10–17 nm and that of the latter was *ca.* 20–35 nm. The particle size is concluded to be influenced by the cross-linking density, *i.e.* the smaller the molecular mass between the cross-linking sites, the smaller the *in situ* silica particles.

On the other hand, the silica content of SBR-2-A-base was less than that of SBR-1-A-base as shown in Table 4. This is due to the difference of the degree of swelling in TEOS for the SBR vulcanizates, *i.e.* the degree of swelling of SBR-2 in TEOS was lower than that of SBR-1, because of the difference of their cross-linking densities. The amount of sulfur used in the vulcanization of SBR-2 was twice that used for SBR-1. The silica content was determined from the TG results, *i.e.* the residual mass at 800 °C by eqn. (4),[27]

$$\text{silica content (\%)} = 100(M_3/M_4) \tag{4}$$

where M_3 is the mass of *in situ* formed silica and M_4 is the mass of the silica-filled vulcanizate. The value was based on the residual mass at 800 °C, which was an appropriate temperature since the mass was observed to be constant at around 600 °C. It was corrected using the residual mass of non-filled vulcanizate.

The conversion of TEOS in the sol–gel reaction was larger in SBR-2-A-base than in SBR-1-A-base as shown in Table 4.

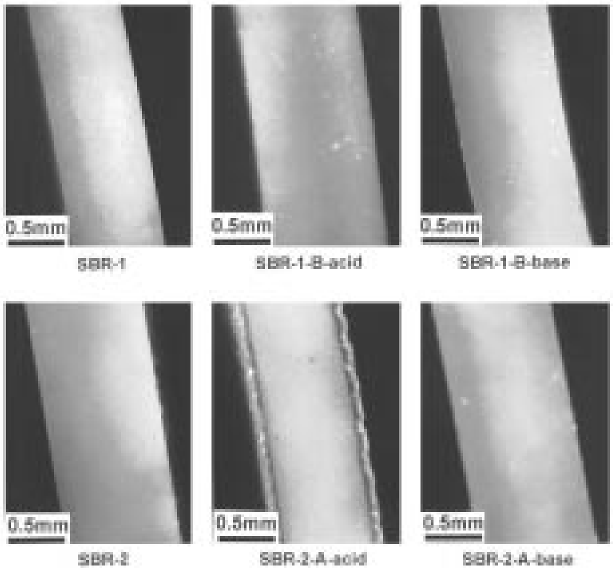


Fig. 2 Optical microscopy images of SBR vulcanizates with and without *in situ* silica

The conversion of TEOS into silica by the sol–gel reaction was evaluated by using eqn. (5),[27]

$$\text{Conversion (\%)} = 100(M_3/M_5) \tag{5}$$

where M_3 has appeared in eqn. (4) and M_5 is the mass of silica calculated from the swollen TEOS into the vulcanizate assuming quantitative conversion.

In method A, the content of introduced silica is restricted first by the swelling degree of the vulcanizate in TEOS, and next by the reactivity of TEOS in the sol–gel reaction. The differences of the silica content and the morphology of silica particles had a marked influence on the mechanical properties of SBR vulcanizates.

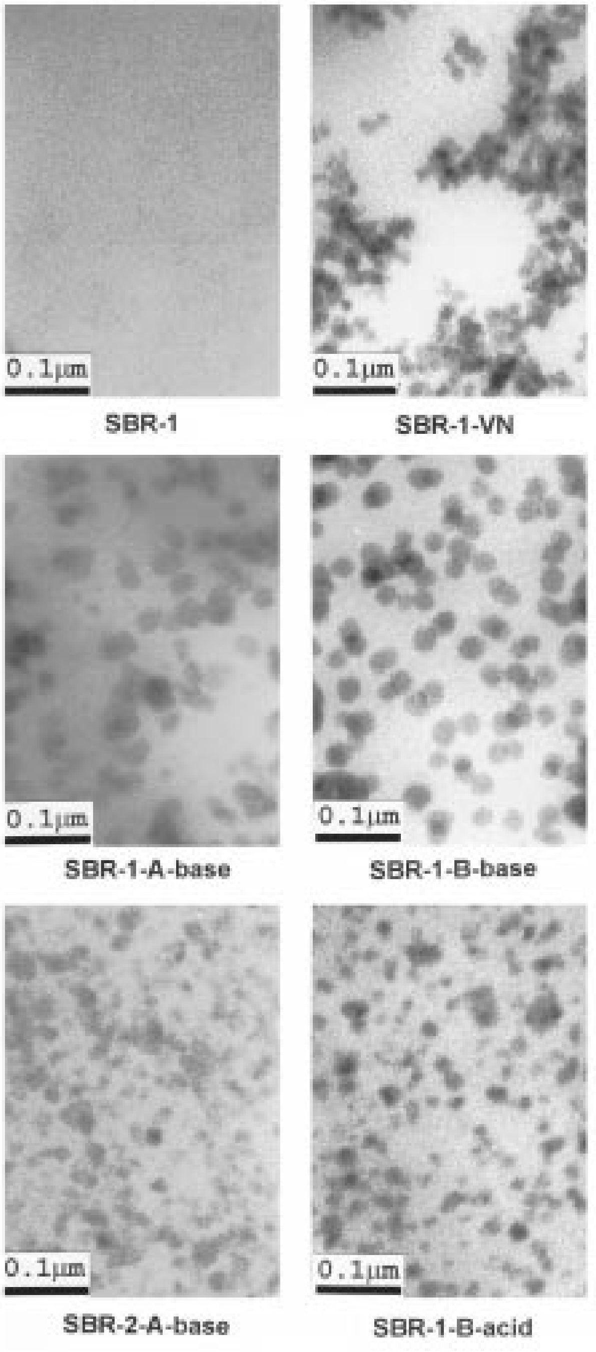
Effect of *in situ* silica on the mechanical properties of the SBR vulcanizate

Stress–strain curves of SBR-1 and SBR-2 vulcanizates with and without *in situ* silica are shown in Fig. 4 and 5, respectively. The tensile properties of SBR-1-VN are also illustrated in Fig. 4. The moduli at 50, 100, 300 and 500% elongations (M_{50}, M_{100}, M_{300}, and M_{500}, respectively), the tensile strength at break (σ_B) and the elongation at break (ε_B) determined from these curves are summarized in Table 3. The results of SBR-1-A-acid[27] and SBR-2-A-acid are included in this table for comparison, although the *in situ* silica was not formed in the rubber matrix, as reported previously.[27]

Table 3 Mechanical properties of SBR vulcanizates with and without silica

sample	silica content (%)	M_{50}[a]		M_{100}[a]		M_{300}[a]		M_{500}[a]		σ_B[b]		ε_B[c] (%)	v[d]/10^{-5} mol cm^{-3}
		MPa	RI[e]	MPa	RI[e]	MPa	RI[e]	MPa	RI[e]	MPa	RI[e]		
SBR-1[f]	0	0.41	—	0.53	—	0.67	—	0.80	—	3.01	—	1150	1.6
SBR-1-A-acid[f]	19.5	0.57	—	0.74	—	0.91	—	1.05	—	1.30	—	710	—
SBR-1-A-base[f]	23.3	1.22	12.8	1.32	10.7	2.46	15.8	4.70	25.2	16.60	23.7	1080	5.3
SBR-1-VN	21.8	0.65	7.3	0.70	6.1	0.72	4.9	0.84	4.8	6.27	9.6	1660	1.0
SBR-2	0	0.48	—	0.71	—	1.15	—	1.68	—	2.46	—	630	7.0
SBR-2-A-acid	13.7	0.58	—	0.84	—	1.33	—	—	—	1.87	—	470	—
SBR-2-A-base	19.0	0.79	8.7	1.13	8.4	2.54	11.6	5.86	18.4	10.64	22.8	690	15.0
SBR-1-B-acid	12.8	0.48	9.1	0.62	9.1	0.83	9.7	1.06	10.4	3.73	9.7	970	2.1
SBR-1-B-base	24.4	0.60	6.0	0.79	6.1	1.17	7.2	2.03	10.4	10.39	14.1	940	3.6

[a] Moduli at 50, 100, 300 and 500 elongations, respectively. [b] Tensile strength at break. [c] Elongation at break. [d] Cross-linking density determined from Mooney–Rivlin plot. [e] Reinforcement index calculated by eqn. (6). [f] Taken from ref. 27.



SBR-1 SBR-1-VN

SBR-1-A-base SBR-1-B-base

SBR-2-A-base SBR-1-B-acid

Fig. 3 TEM photographs of SBR vulcanizates with and without silica

Table 4 Results of the sol–gel reaction

sample	residue at 800 °C (%)	SiO_2 content (%)	conversion of sol–gel reaction (%)
SBR-1[a]	3.4	0	—
SBR-1-A-acid[a]	22.2	19.5	59.6
SBR-1-A-base[a]	25.9	23.3	74.8
SBR-2	4.2	0	—
SBR-2-A-acid	17.3	13.7	55.7
SBR-2-A-base	22.4	19.0	82.2
SBR-1-B-acid	15.8	12.8	—
SBR-1-B-base	27.0	24.4	—

[a] Taken from ref. 27.

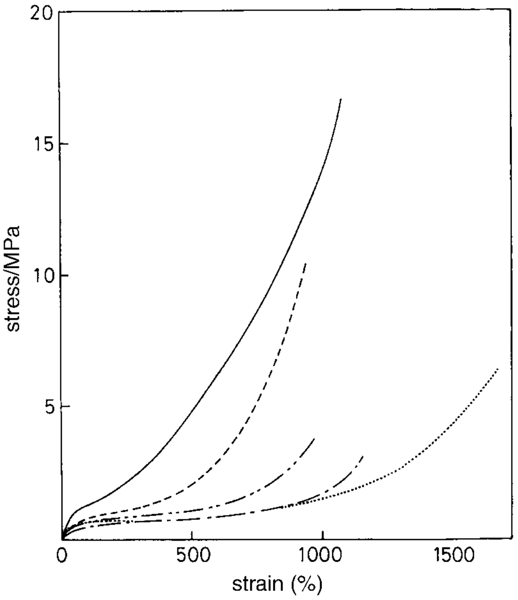


Fig. 4 Stress–strain curves of SBR-1 vulcanizates with and without silica. SBR-1 (— – —), SBR-1-A-base (—), SBR-1-VN (---), SBR-1-B-acid (—··—), SBR-1-B-base (– – –).

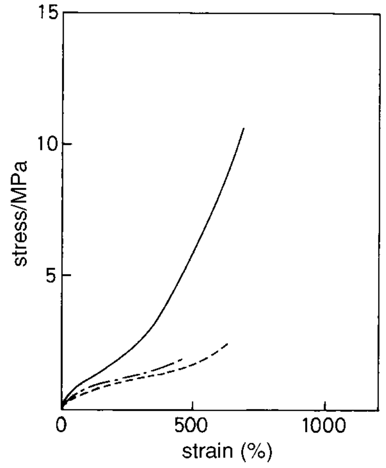


Fig. 5 Stress–strain curves of SBR-2 vulcanizates with and without *in situ* silica. SBR-2 (– – –), SBR-2-A-acid (— – —), SBR-2-A-base (—).

In both the SBR-1 and the SBR-2 vulcanizates, the effect of *in situ* silica reinforcement was clear, *i.e.* the modulus and σ_B of the rubber vulcanizates which were subjected to the sol–gel reaction increased markedly compared to those of SBR-1 and SBR-2, respectively. For SBR-1-A-base, SBR-1-VN was used as a control sample. Generally, industrial products of silica-reinforced rubbers contain from 30 parts per hundred in mass (phr) to 100 phr silica. In this study, 30 phr silica was compounded in SBR-1 by conventional mixing using a two-roll mill. The silica content of SBR-1-VN calculated from the recipe was *ca.* 22%, which was comparable to that of SBR-1-A-base (*ca.* 23%). SBR-1-A-base clearly shows higher modulus and higher σ_B than does SBR-1-VN. From Fig. 3, the homogeneous dispersion of *in situ* silica particles in the rubber matrix is concluded to result in the excellent reinforcement effect of the SBR vulcanizate. In addition, the *in situ* polymerization of TEOS in the networks was found to create the homogeneous morphology of silica particles under the reaction conditions described in this study. These observations are expected to develop a novel aspect in the field of rubber science for studying the relationship between a filler and a reinforcement.

The comparison of the reinforcement effect of the *in situ* silica filling for SBR-1 and SBR-2 was not easy because their silica contents were not equal. Thus, the results of tensile tests were normalized by the following equation.

$$\text{Reinforcement index (RI)} = (N_1/N_2)/(\text{Silica content}/100) \quad (6)$$

where N_1 and N_2 are nominal values obtained by mechanical measurements of the samples with and without silica, respectively. The RI at each elongation are summarized in Table 3. The RI values of SBR-1-A-base at each elongation were larger than those of SBR-2-A-base. This result can be explained from the viewpoint of the particle size, where the diameter of the *in situ* silica of SBR-1-A-base was larger than that of SBR-2-A-base.

As the gels prepared by the sol–gel reaction of TEOS were swollen gels, SiO_2 networks would shrink during drying and some SBR chains could be entrapped in the *in situ* silica particles. Therefore, we speculate that the larger particles trapped more SBR chains. Consequently, the interaction between the *in situ* silica particles and SBR chains must become stronger in SBR-1-A-base than in SBR-2-A-base. This consideration was supported by the apparent cross-linking density obtained from the Mooney–Rivlin plots of the samples.

In the Mooney–Rivlin plots of both SBR-1-A-base and SBR-2-A-base, the upturns at high elongations were clearly detected as shown in Fig. 1 and demonstrated the desired reinforcing effects. Such upturns are absent in both the silica-unfilled SBR vulcanizates. Cross-linking densities of the *in situ* silica-filled SBR vulcanizates were larger than those of the non-filled SBR vulcanizates. This result suggests that some interaction between *in situ* silicas and SBR chains was present in the *in situ* silica-filled vulcanizates and it worked as a physical cross-linking site. In addition, the degree of increase in the v value was higher in SBR-1-A-base than SBR-2-A-base, which means that more interactions were present in the former than the latter.

The large reinforcement effect of *in situ* silica filling for SBR vulcanizates and the influence of the particle size therein also appeared in DMA. Fig. 6, 7 and 8 display the temperature dependence of E' and tan δ for the samples. The maximum of tan δ, the maximum of loss modulus (E''), the height of tan δ, dynamic modulus (E') at 20 °C and E'' at 20 °C are summarized in Table 5. The reinforcement effect was normalized using E' and the E'', and the RI values are also displayed in this table. The E' at 20 °C of the *in situ* silica-filled vulcanizates were larger than those of the non-filled vulcanizates. Moreover, the RI of E' of SBR-1-A-base was larger than that of SBR-2-A-base.

In general, the glass transition temperature (T_g) of the rubber shifts to the higher temperature region upon addition of the filler to the rubber matrix, when the interaction between the rubber and the fillers occurs. Concurrently, the tan δ peak which is attributable to T_g also becomes broader and its height becomes lower compared to those of the non-filled vulcanizate. In this study, the maximum of tan δ of the *in situ* silica-filled vulcanizates is not greatly changed by the presence of *in situ* silica. The same tendency was observed in the change of maximum of E'' as shown in Table 5. Interestingly, these maximum peaks, *i.e.*, T_gs of every sample were found to decrease by about 2–4 °C, in contrast to the general trend. This is considered to be due to the swelling in TEOS, which may contribute to the disentanglement of the SBR chains in the vulcanizate followed by lowering of T_g. The plasticization of the rubber by residual oligomers from the sol–gel reaction might contribute to this lowering of T_g.

On the other hand, the breadth of the tan δ peaks increased slightly both in SBR-1-A-base and SBR-2-A-base. The degree of broadness for the *in situ* silica-filled vulcanizates of this study was very low compared to the mechanically silica-filled vulcanizate. Between SBR-1-A-base and SBR-2-A-base, the decrease of height of the tan δ peak of the former was larger than that of the latter. This means that the interaction was strong between the rubber and the *in situ* filled silicas of SBR-1-A-base. The difference of E'' at 20 °C also supported this consideration. The RI of E'' at 20 °C of SBR-1-A-base was larger than that of SBR-2-A-base.

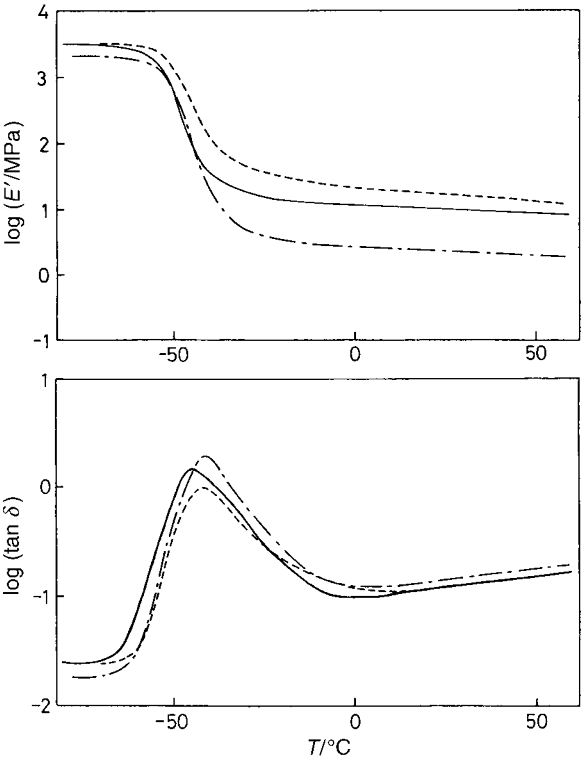


Fig. 6 Temperature dependence of E' and tan δ for SBR-1 vulcanizates with and without silica. SBR-1 (— – —), SBR-1-A-base (—), SBR-1-VN (– – –).

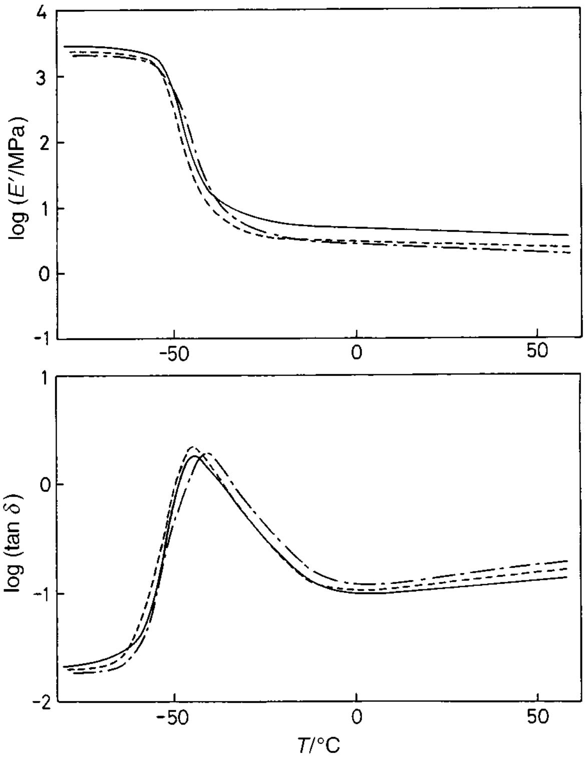


Fig. 7 Temperature dependence of E' and tan δ for SBR-1 vulcanizates with and without silica. SBR-1 (— – —), SBR-1-B-acid (– – –), SBR-1-B-base (—).

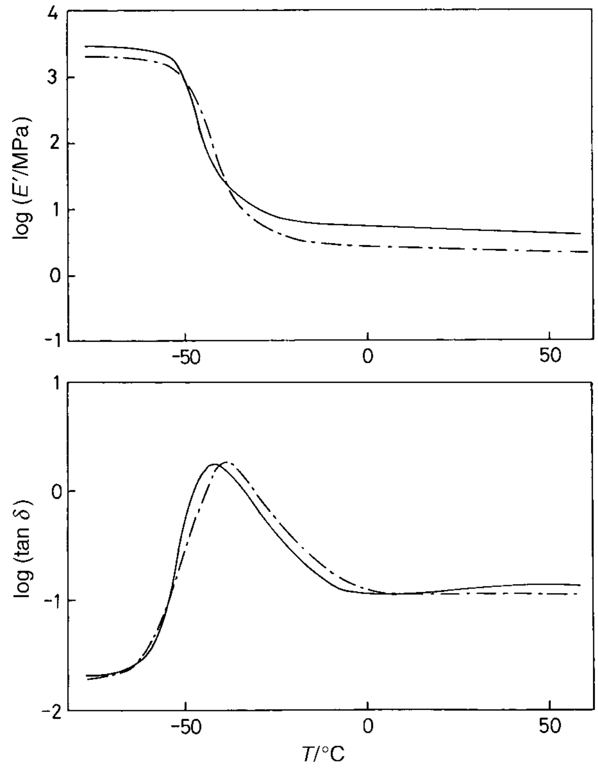


Fig. 8 Temperature dependence of E' and tan δ for SBR-2 vulcanizates with and without *in situ* silica. SBR-2 (— — —), SBR-2-B-base (—)

Effect of THF on *in situ* silica formation in the SBR vulcanizate

In our previous paper,[27] hydrochloric acid was reported to be inadequate as a catalyst for the sol–gel reaction of TEOS in the SBR vulcanizate which was swollen in TEOS (*i.e.* by method A). This is because the aqueous solution of hydrochloric acid was not well dissolved in TEOS. Thus, silica was formed only in the surface layer of the vulcanizate as shown in the example of SBR-2-A-acid of Fig. 2. In order to avoid these difficulties of acid catalysis, pre-swelling of the vulcanizate was carried out before the sol–gel reaction. THF was chosen as the solvent for the swelling of the SBR vulcanization. As shown in Fig. 2, the silica layer was not formed on the surface of SBR-1-B-acid, and the silica particles were found to disperse in the SBR vulcanizate by the TEM observation which is displayed in Fig. 3. In both the acidic and the basic aqueous solutions mixed with THF, the *in situ* formation of silica occurred in the rubber matrix.

Compared with SBR-1-B-base, however, the content of *in situ* silica of SBR-1-B-acid was less. Characteristically, the shape and the size of the *in situ* silica of SBR-1-B-acid were very different from those of SBR-1-B-base, *i.e.* spherical particles of diameter 25–35 nm were formed when *n*-butylamine was used in method B, but small irregularly shaped particles were formed in SBR-1-B-acid as shown in Fig. 3. These characteristics greatly influenced the mechanical properties of the SBR vulcanizates as shown in Fig. 4 and 5 and Table 3. Therefore, it is concluded that *n*-butylamine is superior to hydrochloric acid as a catalyst for the sol–gel reaction of TEOS in the SBR vulcanizate in both method A and method B.

Effect of shape of *in situ* silica on reinforcement of the SBR vulcanizate

In the case of *n*-butylamine as a catalyst for the sol–gel reaction of TEOS, the *in situ* polymerization of TEOS in the SBR vulcanizate occurred in the reactions both with and without THF (*i.e.* in both method A and method B). Interestingly, the presence of THF influenced the shape of the silica particles which were dispersed in the SBR vulcanizates. In method B, spherical particles were formed, but less spherical shape than SBR-1-B-base was observed in method A, although the amounts and the sizes of *in situ* silica formed were similar. The reaction system with THF and *n*-butylamine appears to result in spherical silica particles in the SBR matrix. However, we also observed spherical particles of *in situ* silica in the matrix of the butadiene rubber vulcanizate formed by method A.[30] Therefore, the formation of spherical particles might depend on complex factors to give *in situ* polymerization of TEOS in the rubber vulcanizates.

The shape of the *in situ* silica had a marked effect on the mechanical properties of the vulcanizates, *i.e.* the modulus and the σ_B of SBR-1-A-base were higher than those of SBR-1-B-base as shown in Fig. 4. The ε_B values showed the same tendency. The cross-linking density determined from the Mooney–Rivlin plots gave a larger ν value in SBR-1-A-base than in SBR-1-B-base. This means that the interaction between the rubber chains and the *in situ* silica particles was greater in the former than the latter, because this ν value includes the physical cross-linking sites.

The DMA results supported this consideration. The degree of decrease of the tan δ peak for SBR-1-A-base was larger than that of SBR-1-B-base, and the tan δ peak of the former became broader than that of the latter. In addition, the E'' at 20 °C of the former was also higher than that of the latter. Therefore, the less spherical shaped silica appears to result in a larger reinforcement effect on the rubber vulcanizate than the spherical shaped silica. This is also considered to be due to the shrinking during drying, which was explained in the previous section. SBR chains could be entrapped during drying and the amount of entrapped SBR chains was probably larger in the irregularly shaped silica than the spherical shaped silica. This must cause the stronger interactions between the SBR chains and the *in situ* silicas in SBR-1-A-base.

Table 5 Results of DMA measurements

		DMA						
					E' at 20 °C		E'' at 20 °C	
sample	silica content (%)	tan δ_{max}/°C	E''_{max}/°C	peak height of tan δ	MPa	RI[a]	MPa	RI[a]
SBR-1	0	−41.7	−49.3	1.92	2.6	—	0.35	—
SBR-1-A-base	23.3	−45.7	−51.9	1.45	10.8	17.8	1.22	15.0
SBR-1-VN	21.8	−41.5	−50.2	0.98	18.6	32.8	2.10	27.6
SBR-2	0	−37.8	−47.8	1.85	2.6	—	0.30	—
SBR-2-A-base	19.0	−42.0	−49.9	1.78	5.1	10.3	0.61	10.7
SBR-1-B-acid	12.8	−43.6	−51.9	2.05	2.9	8.7	0.35	7.8
SBR-1-B-base	24.4	−43.2	−51.8	1.82	4.4	6.9	0.48	5.6

[a] Reinforcement index calculated from eqn. (6).

Moreover, the size stability of the SBR vulcanizate in method A is superior to method B. This stability was affected by the degree of swelling, *i.e.* the degree of swelling of SBR-1 in THF was 990% and it was about seven times larger than in TEOS (150%). Therefore, method A can be concluded to be much better for *in situ* silica reinforcement of the SBR vulcanizate than method B.

Conclusions

In situ silica reinforcement of SBR vulcanizates was achieved in the swollen vulcanizate in TEOS by the sol–gel reaction of TEOS using *n*-butylamine. The *in situ* silica was formed homogeneously in the rubber matrix. The size of *in situ* silica was observed to be influenced by the cross-linking density, *i.e.* the larger the cross-linking density, the smaller the size of *in situ* silica particles formed.

Comparing with the silica-filled vulcanizates prepared by conventional mixing, the homogeneity of dispersion of the silica particles was found to be important for the reinforcement of rubber vulcanizates. In addition, the size of silica particles obviously affects the reinforcement of the vulcanizate. The larger the *in situ* silica particles, the better the mechanical properties found in this study.

When THF was used as the solvent in the sol–gel reaction of TEOS, both hydrochloric acid and *n*-butylamine acted as catalysts to produce the *in situ* silica in the matrix of the SBR vulcanizate. In the system using THF, *n*-butylamine was concluded to be a more useful catalyst for the *in situ* silica reinforcement of the SBR vulcanizate. Spherical particles were formed in the SBR matrix when *n*-butylamine and THF were used for the *in situ* sol–gel reaction of TEOS. On the other hand, irregularly shaped particles were formed by the method using *n*-butylamine in TEOS only. The irregularly shaped *in situ* silica particles were found to be effective for the reinforcement of the SBR vulcanizate.

The method described herein represents a simple and effective means for adding silica particles to the SBR vulcanizate for its reinforcement. The *in situ* sol–gel reaction of TEOS could be applied to the industry technique, especially, it is adequate for the reinforcement of some shapes such as thin films.

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