Effect of catalyst on *in situ* silica reinforcement of styrene–butadiene rubber vulcanizate by the sol–gel reaction of tetraethoxysilane

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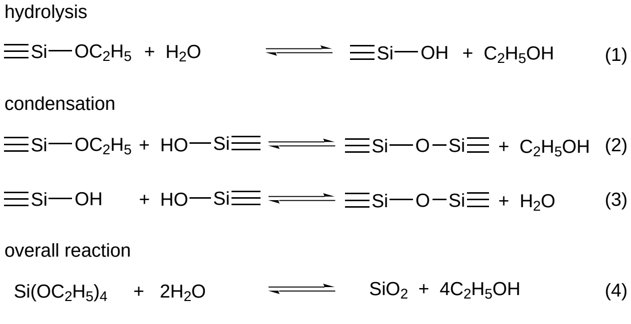
In situ silica reinforcement of styrene–butadiene rubber (SBR) vulcanizate has been achieved by the sol–gel reaction of tetraethoxysilane (TEOS) using *n*-butylamine as a catalyst. SBR was vulcanized with sulfur and soaked in TEOS and in an aqueous solution of the catalyst. When hydrochloric acid was used as a catalyst for the sol–gel reaction, silica particles were not introduced into the SBR matrix in this study. The increase of the dynamic modulus and tensile strength at break was considered to be due to the interaction between the rubber and the *in situ* silica filler in the SBR vulcanizate.

Rubber is an elastomer and the characteristic of rubber elasticity for practical applications is provided by vulcanization and the formation of compounds with fillers.[1,2] The most reinforcing filler is carbon black.[3,4] Silica is known as a 'white carbon' and has been developed as a reinforcing filler for synthetic rubbers.[3–5] Conventionally, filler-reinforced rubber is prepared by mechanical mixing of the filler followed by compression moulding for curing. However, the incorporation of silica into rubbers by normal mixing techniques increases the viscosity because of the small size and large specific surface area of the filler. Silica also deactivates curing agents and accelerators which are commonly used in rubber technology, thus resulting in an insufficient cure. These problems are partially overcome or minimized by specific additives and mixing procedures.[6] The other important difficulty is the incompatibility of inorganic silica with the organic rubber.

As a method for overcoming these difficulties, the *in situ* polymerization of tetraethoxysilane (TEOS) by the sol–gel process in the conventional diene rubber matrix has been developed and described in our earlier communications.[7,8] It is an application of the sol–gel process, for the preparation of inorganic glasses at low temperatures,[9,10] to rubber chemistry.[11] The reaction of TEOS takes place in two steps, hydrolysis and condensation, and results in SiO_2 as shown in Fig. 1. This application of the sol–gel process to rubber chemistry is somewhat related to the use of silane coupling agents and moisture or silane curing,[11,12] and it has been carried out already on silicone rubber,[13–15] polyisobutene[16] and epoxidized natural rubber.[17] However, no report has yet been made on the effect of the catalyst of the sol–gel reaction in the general-purpose grade rubbers from the viewpoint of the morphology of *in situ* silica in the rubber matrix.


hydrolysis

$$\equiv Si-OC_2H_5 + H_2O \rightleftharpoons \equiv Si-OH + C_2H_5OH \quad (1)$$

condensation

$$\equiv Si-OC_2H_5 + HO-Si\equiv \rightleftharpoons \equiv Si-O-Si\equiv + C_2H_5OH \quad (2)$$

$$\equiv Si-OH + HO-Si\equiv \rightleftharpoons \equiv Si-O-Si\equiv + H_2O \quad (3)$$

overall reaction

$$Si(OC_2H_5)_4 + 2H_2O \rightleftharpoons SiO_2 + 4C_2H_5OH \quad (4)$$

Fig. 1 Hydrolysis and condensation reactions of TEOS

In this study, the reinforcing effect of *in situ* formed silica particles in the styrene–butadiene rubber (SBR) vulcanizate was elucidated. In particular, the effect of the catalyst of the sol–gel reaction on the *in situ* silica filling in the SBR matrix is described.

Experimental

Materials

Styrene–butadiene rubber (SBR 1502) was supplied by the Japan Synthetic Rubber (JSR) Co. and its properties are summarized in Table 1. Tetraethoxysilane (TEOS) was obtained from Shin-etu Chemical Ind. Co. The catalysts were hydrochloric acid and *n*-butylamine, which were reagent grade. All reagents were used as received unless otherwise noted.

Preparation of the rubber vulcanizates

SBR and reagents were mixed in a two-roll mill; the proportions of reagents are shown in Table 2. Rubber vulcanizates were prepared by curing at 150 °C for a curing time of 50 min, which was determined from the cure curve obtained with a JSR Curelastometer III.

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

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 in 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 reduced pressure. The amounts of TEOS and the catalyst solution were ten times the mass of the sample film. The *in situ* silica-filled vulcanizate prepared using the acid catalyst and that prepared using the base catalyst are hereafter abbreviated as SBR-a and SBR-b, respectively.

Characterization of the silica-filled vulcanizates

Swelling. The sample was soaked in TEOS at 30 °C for 48 h, and the degree of swelling was calculated using eqn. (5)

$$\text{degree of swelling} = 100\ [(M_1 - M_2)/M_2] \qquad (5)$$

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

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 vulcanizate (phr[a])

SBR 1502	100
ZnO	5.0
stearic acid	1.5
MSA-G[b]	0.5
sulfur	0.5

[a]Parts per hundred rubber in terms of mass. [b]*N*-Oxydiethylene-2-benzothiazole sulfenamide.

Thermogravimetry. Thermogravimetry (TG) was carried out using a Rigaku TG Instrument. A sample (*ca.* 100 mg) was placed in a platinum pan and heated in 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, *i.e.* calculated using eqn. (6)

$$\text{silica content (\%)} = 100\ (M_3/M_4) \qquad (6)$$

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 *ca.* 600 °C. It was corrected by using the residual mass of non-filled vulcanizate.

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

Dynamic mechanical analysis. Dynamic mechanical analysis (DMA) was carried out with 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 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 KLB 14800 Cryokit. The specimen was placed on a copper grid, which was coated with Folmbar® and evaporated carbon in advance. Then, transmission electron microscopy (TEM) observation was carried out with a JEOL TEM-100U instrument, without staining. The accelerating voltage was 80 kV.

Results and Discussion

Conversion of TEOS into silica in the SBR matrix

Table 3 shows the results of swelling of the vulcanizates in TEOS and the silica content after the sol–gel reaction. The conversion of TEOS into silica in the SBR vulcanizates was

Table 3 Results of swelling and the sol–gel reaction

sample	residue at 800 °C in TG (%)	degree of swelling in TEOS (%)	SiO_2 content (%)	degree of sol–gel reaction (%)
SBR-g	3.4	145.9	—	—
SBR-a	22.2	—	19.5	59.6
SBR-b	25.9	—	23.3	74.8

evaluated from the degree of swelling in TEOS and from the silica content by using eqn. (7)

$$\text{degree of sol–gel reaction (\%)} = 100\,(M_3/M_5) \qquad (7)$$

where M_5 is the mass of silica calculated from the incorporated TEOS in the vulcanizate.

The conversion of TEOS of SBR-b was *ca.* 75%, while that of SBR-a was *ca.* 60%. The conversion of TEOS is controlled by the temperature and time of the sol–gel reaction.

Effect of catalyst on the reinforcement of the SBR vulcanizates filled with *in situ* formed silica

Tensile stress–strain curves of SBR-a and SBR-b vulcanizates are illustrated in Fig. 2, together with that of SBR gum (SBR-g) vulcanizate. The effect of *in situ* silica reinforcement was significant in SBR-b, *i.e.* its modulus and its tensile strength at break increased greatly compared to those of SBR-g. However, the mechanical properties of SBR-a were only slightly improved, although the silica content of SBR-a was *ca.* 20%. In order to evaluate the difference of the tensile properties of SBR-a and SBR-b, the morphology of silica in these SBR vulcanizates was elucidated.

First, SBR-a and SBR-b were examined by optical microscopy. The sections of the samples, which were prepared by cutting the sheets, are shown in Fig. 3 with that of SBR-g. The state of SBR-b was almost similar to that of SBR-g. However, the picture of SBR-a clearly shows the presence of silica on the surface layer of the SBR vulcanizate.

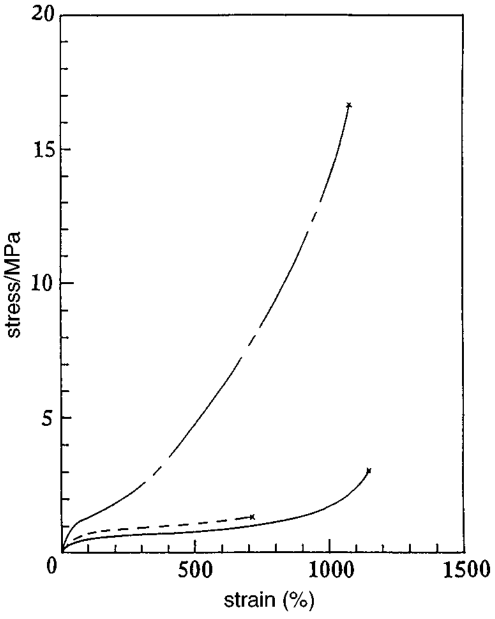
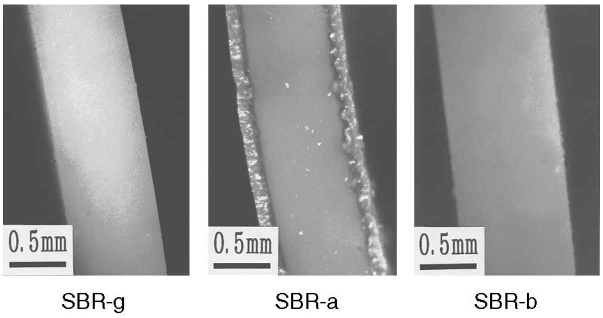
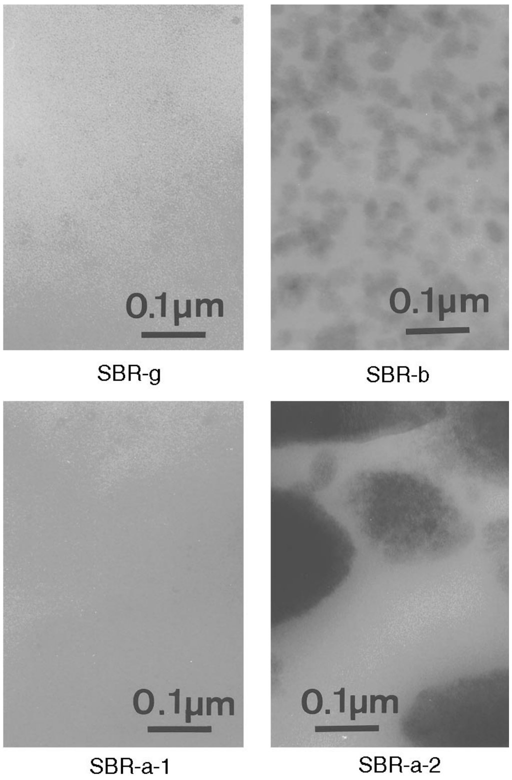


Fig. 2 Stress–strain curves of SBR vulcanizates with and without *in situ* formed silica. ——, SBR-g; - - - -, SBR-a; — - —, SBR-b.



SBR-g SBR-a SBR-b

Fig. 3 Optical photographs of SBR-g, SBR-a and SBR-b



SBR-g SBR-b

SBR-a-1 SBR-a-2

Fig. 4 TEM photographs of SBR-g, SBR-a and SBR-b (SBR-a-1, the inside; SBR-a-2, the interface between the silica layer and the rubber)

Next, the samples were subjected to TEM analysis. Fig. 4 is the result of TEM observation for SBR-g, SBR-a and SBR-b. The dark portions in the photograph of SBR-b are silica particles. Interestingly, the diameter of the *in situ* silica particles was *ca.* 20–35 nm and they were dispersed homogeneously in the matrix. On the other hand, silica particles were not detected within the SBR-a sample as shown in Fig. 4 (SBR-a-1). The TEM photograph (SBR-a-2) of the interface between the silica layer and the rubber is also shown. These observations suggest that hydrochloric acid is not an adequate catalyst for the reinforcement of the SBR vulcanizate by the technique described in the Experimental section. This is due to the non-solubility of hydrochloric acid into the swollen rubber with TEOS.

Silica was formed and filled in the vulcanizate when *n*-butylamine was used as a catalyst for the sol–gel reaction of TEOS in the SBR matrix. The morphology of the *in situ* filled silica in SBR-b is considered to bring excellent reinforcement to the SBR vulcanizate.

Dynamic mechanical properties of SBR-b

The temperature dependence of the dynamic modulus (E') and tan δ for SBR-b and SBR-g are illustrated in Fig. 5. The E' of the *in situ* silica filled SBR vulcanizate was larger than that of the non-filled SBR vulcanizate. This result agrees with that of the tensile test. The tan δ peak of SBR-b, which is attributed to the glass transition temperature, was detected as well as SBR-g, but its peak height was decreased compared to that of SBR-g. This observation suggests the presence of the interaction between the rubber and the *in situ* formed silica in the SBR vulcanizate. Interestingly, the tan δ peak of SBR-b was shifted to the lower temperature region after the sol–gel reaction. It is considered that the swelling in TEOS may contribute to the disentanglement of the polymer chains in the vulcanizate. Moreover, the plasticization of the rubber by residual oligomers from the sol–gel reaction might contribute to this phenomenon.

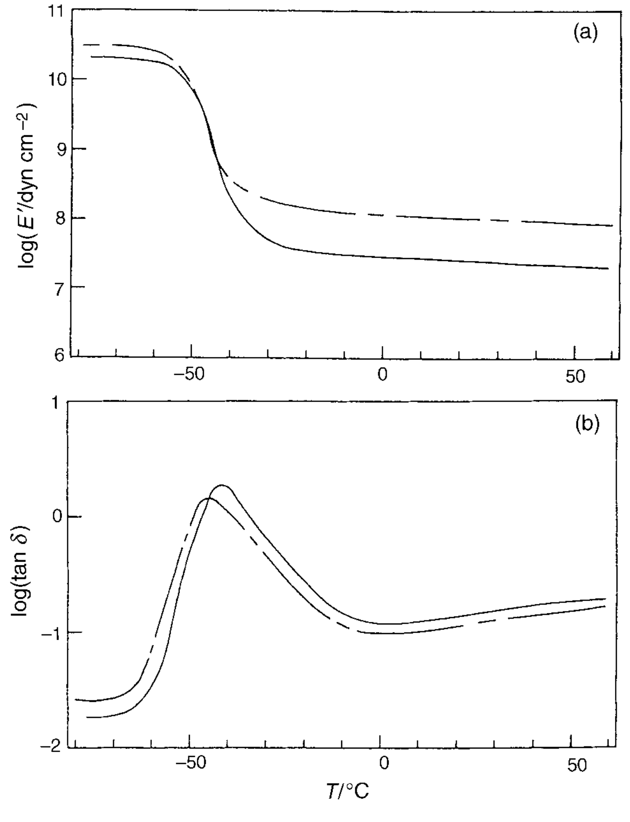


Fig. 5 Temperature dependence of E' (a) and tan δ (b) for SBR vulcanizates with and without *in situ* formed silica. ——, SBR-g; — - —, SBR-b.

Conclusions

In situ silica reinforcement of SBR vulcanizates was carried out by the sol–gel process using TEOS. *n*-Butylamine was a good catalyst for *in situ* silica filling of the SBR vulcanizate. The silica particles formed in the SBR vulcanizate were dispersed homogeneously in the matrix and the diameter of the particles was *ca.* 20–35 nm. This study represents a simple and effective method for compounding silica particles into rubber vulcanizates for its reinforcement.

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