

***In situ* formed silica particles in rubber vulcanizate by the sol–gel method**

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In situ silica filling of butadiene rubber (BR) was carried out by the sol–gel process using tetraethoxysilane (TEOS). BR was sulfur-cured, and the resultant crosslinked BR was subjected to soaking in TEOS at 30°C for 48 h. The swollen vulcanizates were kept in the aqueous solution of *n*-butylamine at 30°C for 24 h, followed by standing at 50°C for 72 h to conduct the *in situ* sol–gel reaction of TEOS. The resultant vulcanizates contained silica particles which were prepared by the *in situ* filling technique. They were subjected to tensile and dynamic mechanical measurements, differential scanning calorimetry and transmission electron microscopic observation. The *in situ* formed silica was dispersed homogeneously in the rubbery matrix. The size of *in situ* silica was influenced by the crosslinking density, probably because it was formed in the crosslinked rubber networks. Compared to the conventional silica-filled BR vulcanizate, which was prepared by mechanical mixing of the silica particles, the new vulcanizates with the *in situ* formed silica showed better mechanical properties. © 1997 Elsevier Science Ltd.

(Keywords: butadiene rubber; *in situ* sol–gel reaction; reinforcement)

INTRODUCTION

Rubber is a class of elastomeric materials, whose most important property is the ability to undergo large elastic deformations, i.e. even after large elongation to return to the original shape in a reversible way¹. Rubber elasticity, for practical applications, is generally afforded by vulcanization and mixing with reinforcing fillers. Natural rubber is noted for its versatility as an elastomeric material^{2,3}. Synthetic rubbers have become of general use after compounding of carbon black as an effective reinforcer^{4,5}. Other than carbon black, only silica has been known as an effective reinforcer, in spite of many investigations to develop reinforcing fillers for synthetic rubbers^{4–6}.

Conventionally, a silica-rubber composite or a silica-reinforced rubber is prepared by mechanical mixing and compression moulding for curing. A hydrated silica, of particle size ranging from 20 to 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 an increase of viscosity, which makes the processing more difficult. It can also deactivate curing agents and accelerators, which results in the reduction of the degree of crosslinking. Practically, these problems are partially overcome or minimized by using specific additives and by optimizing mixing procedures⁷. The other important difficulty lies in the incompatibility of the inorganic silica filler with organic rubber.

One of the methods for overcoming these difficulties is *in situ* polymerization of tetraethoxysilane (TEOS) in the crosslinked rubber. In other words, the sol–gel process^{8–10}, which brings the formation of silica, enables *in situ* silica filling in the rubber. The reaction of TEOS takes place in two steps, hydrolysis and condensation, and results in production of SiO₂ as shown in *Figure 1*. Its overall reaction is represented by the last equation.

The preparation of organic–inorganic hybrid materials using the sol–gel reaction of alkoxysilyl groups has been developed. We reported the synthesis and properties of novel amorphous networks preparing from a polyether oligomer with triethoxysilyl groups at both ends^{11–13}. Time-resolved small angle X-ray scattering analysis was also conducted, to elucidate the mechanism of the sol–gel reaction in this system¹⁴. Halogenated rubber¹⁵ and epoxidized natural rubber¹⁶ were also subjected to the sol–gel reaction with alkoxysilyl reagents.

Among several techniques to use the sol–gel reaction of alkoxysilyl reagents, *in situ* silica formation in the polymer matrix is very simple, and this makes it easy to produce composite materials. *In situ* polymerizations of TEOS in silicon rubber^{17–19}, polyisobutylene²⁰, poly(methyl methacrylate)^{21,22}, poly(vinyl acetate)²³, polyimide²⁴, poly(vinyl pyrrolidone)²⁵ and polyoxazoline²⁶ were reported. However, the study on conventional diene rubbers was first described in our preliminary reports^{13,27}.

The present study reports one phase of ongoing research aimed to elucidate the features of *in situ* formed silica by the reaction of TEOS in a rubber

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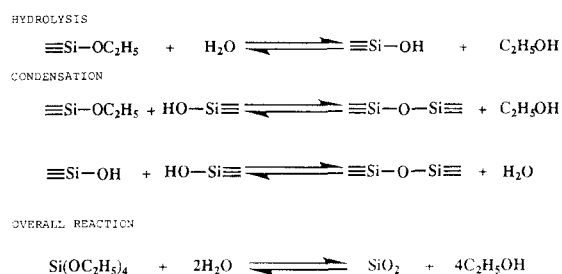


Figure 1 Hydrolysis and condensation reactions of TEOS

Table 1 Properties of BR-01

Cis-1,4 content (%)	96
Mooney viscosity (ML ₁₊₄ , 100°C)	44
Product stain	Non-staining ^a

^a Not containing any staining reagents (amines)

Table 2 Compounding recipe (phr)

	BR-1	BR-2	BR-1-VN
BR-01	100	100	100
ZnO	3.0	3.0	3.0
Stearic acid	1.0	1.0	1.0
MSA-G ^a	0.5	1.0	0.5
Sulfur	0.5	1.0	0.5
DEG ^b	—	—	3.0
Silica ^c	—	—	30

^a N-Oxydiethylene-2-benzothiazolylsulfenamide

^b Diethylene glycol

^c Commercial silica, VN-3

vulcanizate. The particular system studied herein is *in situ* polymerization of TEOS in the butadiene rubber (BR) vulcanizates. The mechanical properties, the dispersion of silica particles and the relationship between them were investigated compared to the conventional silica-filled vulcanizate, in order to evaluate the effect of *in situ* silica on physical properties.

EXPERIMENTAL

Materials

Cis-1,4-polybutadiene (BR-01) was supplied by Japan Synthetic Rubber (JSR) Company. The properties of BR-01 are summarized in Table 1. TEOS was used as a precursor of silica, which was obtained from Shin-Etsu Chemical Ind. Co. The catalyst was *n*-butylamine, which was reagent grade. Nipsil VN-3 from Nippon Silica Co., commercially available silica particle, was used for mechanical mixing with BR, which was dried for 3 h at 150°C before use. All reagents and solvents were used as received unless otherwise stated.

Preparation of the rubber vulcanizate

The compounding recipe for BR vulcanizates is shown in Table 2. BR and these reagents were mixed on a two-roll mill. In order to evaluate the effect of crosslinking density of the BR vulcanizate, the amounts of sulfur and *N*-oxydiethylene-2-benzothiazolylsulfenamide (MSA-G) were changed. Here, sulfur is a crosslinker and MSA-G is a sulfur-cure accelerator. Two samples of different crosslinking density are abbreviated as BR-1 and BR-2. The master batch technique was used for the preparation

of the compounds. The BR compounds physically mixed with silica particle (VN-3) were prepared by a conventional method using a two-roll mill. This is abbreviated as BR-1-VN.

Rubber vulcanizates were prepared by curing at 150°C for a prescribed time; curing time was 120 min for BR-1, 85 min for BR-2 and 120 min for BR-1-VN, respectively, which were determined from the results for cure rate measured by a JSR Curelastometer III.

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

Rubber vulcanizates were swollen in TEOS at 30°C for 48 h, followed by soaking in the 10 wt% aqueous solution of *n*-butylamine at 30°C for 24 h. Then the samples were subjected to heating at 50°C for 72 h after removal from the catalyst solution. The drying of the samples was conducted for several days at 50°C under a reduced pressure. The amounts of TEOS and the catalyst solution were ten times the weight of the sample film. *In situ* silica-filled vulcanizates are abbreviated as BR-1-sol-gel and BR-2-sol-gel for BR-1 and BR-2, respectively.

Material characterization of silica-filled vulcanizates

Differential scanning calorimetry measurements. Differential scanning calorimetry (d.s.c.) measurement was carried out on a DSC-20 Seiko Instruments under air. The sweep rate of temperature was 10°C min⁻¹. The sample loaded was *ca.* 10 mg and the temperature range was -140°C through 100°C. The measurement was repeated twice.

Swelling. The degree of swelling of the sample was measured by soaking in TEOS at 30°C for 48 h. The degree of swelling was calculated by equation (1).

$$\text{Degree of swelling (\%)} = \frac{W_1 - W_2}{W_2} \times 100 \quad (1)$$

where W_1 is the weight of the swollen film and W_2 is the weight of the film before swelling.

Thermogravimetric measurements. Thermogravimetric analysis (t.g.a.) was carried out using a Rigaku TG Instrument. *Ca* 100 mg of a sample was placed in a platinum pan and heated under air to 1000°C. The sweep rate of temperature was 20°C min⁻¹. The silica content of the *in situ* silica-filled vulcanizates was determined from the results of t.g.a. by equation (2).

$$\text{Silica content (\%)} = \frac{W_3}{W_4} \times 100 \quad (2)$$

where W_3 is the residual weight at 800°C, which corresponds to the weight of *in situ* formed silica, and W_4 is the initial weight. 800°C was an appropriate temperature since the weight was observed to be constant at around 600°C. Values from equation (2) were corrected by the residual weights of vulcanizates without silica.

Tensile measurements. Tensile properties of the rubber vulcanizate were measured at room temperature at a strain rate of 100 mm min⁻¹ using a ring type specimen. Values reported in this study were the average of five measurements for each sample.

Dynamic mechanical analysis. Dynamic mechanical analysis (d.m.a.) was carried out by using a Rheospectoler

DVE-4 (Rheology Co., Kyoto) at 10 Hz by the tensile mode. Temperature dependence was measured with the heating rate of $2^{\circ}\text{C min}^{-1}$.

Transmission electron microscopy. Ultra-thin films of the samples were prepared using a microtome (KLB 4800A ULTRATOME) in liquid nitrogen of LKB 14800 CRYOKIT. The specimen was placed on a copper grid, which was coated with Folbar[®] and evaporated carbon in advance. Then, transmission electron microscopic (TEM) observation was carried out with a JEOL TEM-100U without staining. The accelerating voltage used here was 80 kV.

RESULTS AND DISCUSSION

In situ silica formation in BR vulcanizates

Table 3 shows the results of swelling of the BR vulcanizates in TEOS and the silica content after the sol-gel reaction for them. The silica content was determined from the results of t.g.a.

The conversion of TEOS into silica in the BR vulcanizates was evaluated from equation (3).

$$\text{Conversion of TEOS (\%)} = \frac{W_3}{W_5} \times 100 \quad (3)$$

where W_3 has appeared in equation (2) and W_5 is the weight of silica calculated from the swollen TEOS into the vulcanizate assuming quantitative conversion.

The silica content of BR-1-sol-gel was 15.8%, and that of BR-2-sol-gel was 14.1%. There was not a big difference in silica content between them, although the conversion of TEOS for BR-1-sol-gel was lower than that for BR-2-sol-gel. This is because the swelling of BR-1 was larger than that of BR-2, which is due to the difference in crosslinking density. Twice as much sulfur was used in the vulcanization of BR-2. In the method reported here, the degree of silica introduction is firstly restricted by the swelling degree of the vulcanizate in TEOS, and next by the degree of reaction of TEOS in the sol-gel process.

Mechanical properties of in situ silica-filled BR vulcanizates

Tensile stress-strain curves of the sample films are illustrated in Figures 2 and 3. As a control sample, the conventional silica-filled BR vulcanizate (BR-1-VN) was prepared by mechanical mixing. Its stress-strain curve is shown in Figure 2, together with the result of BR-1-sol-gel. The compounding recipe for vulcanization was the

Table 3 Results of swelling and the *in situ* sol-gel reaction of TEOS

Sample code	Residue at 800°C (%)	Degree of swelling in TEOS (%)	SiO ₂ content (%)	Conversion of TEOS (%)
BR-1	2.97	—	0	—
BR-1-sol-gel	15.31	204.5	15.8	65.7
BR-1-VN	—	—	21.7 ^a	—
BR-2	3.14	—	0	—
BR-2-sol-gel	13.77	180.3	14.1	75.5

^a Calculated from the recipe shown in Table 2

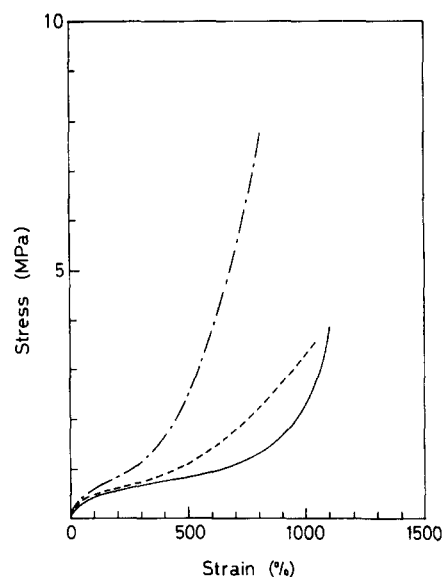


Figure 2 Stress-strain curves of BR-1 (—), BR-1-sol-gel (---) and BR-1-VN (- - -)

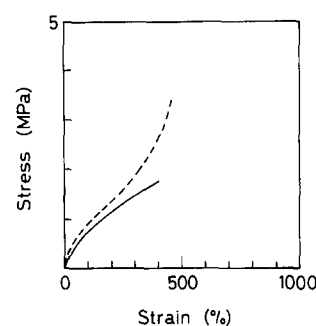


Figure 3 Stress-strain curves of BR-2 (—) and BR-2-sol-gel (---)

same for the two. The moduli at 50, 100, 300 and 500% elongations (M_{50} , M_{100} , M_{300} and M_{500} , respectively), the tensile strength at break (T_B) and the elongation at break (E_B) determined from these curves are summarized in Table 4. Both modulus and T_B increased greatly by *in situ* silica filling, i.e. the effect of *in situ* silica reinforcement was demonstrated.

Dynamic modulus (E') at 20°C, which was measured by d.m.a., is shown in Table 5. The moduli of the *in situ* silica-filled vulcanizates were larger than those of the non-filled vulcanizates both in the cases of BR-1 and BR-2. These results for d.m.a. were in agreement with those of the tensile test. The degree of reinforcement by *in situ* silica filling was larger for the BR-1 vulcanizate than for BR-2 vulcanizate. This is considered to be due to differences in the silica content and in the size of the silica particles, which are discussed later.

Industrial products of silica reinforced rubbers usually contain from 30 phr to 100 phr silica. In this study, a control sample was prepared by the compounding recipe as shown in Table 2. The silica content of BR-1-VN calculated from the recipe was 21.7%. It is clear that BR-1-sol-gel with 15.7% *in situ* silica shows the higher modulus and T_B than does BR-1-VN. The excellent reinforcement effect of *in situ* silica for the BR vulcanizate is again manifested.

The stress-strain behaviours are presented in the Mooney-Rivlin plots. The Mooney-Rivlin equation^{28,29}

Table 4 Mechanical properties of the BR vulcanizates with and without *in situ* silica

Sample code	Silica content (%)	M_{50}^a (MPa)	M_{100}^a (MPa)	M_{300}^a (MPa)	M_{500}^a (MPa)	T_B^b (MPa)	E_B^c (%)	C_1^d (MPa)	C_2^d (MPa)	ν^e ($\times 10^{-4}$ mol cm $^{-3}$)
BR-1	0	0.28	0.43	0.65	0.85	3.87	1100	0.043	0.155	0.35
BR-1-sol-gel	15.8	0.44	0.61	1.10	2.50	7.80	810	0.076	0.200	0.63
BR-1-VN	21.7	0.36	0.46	0.69	1.09	3.58	1040	0.044	0.175	0.36
BR-2	0	0.47	0.79	1.46	-	1.74	390	0.148	0.150	1.22
BR-2-sol-gel	14.1	0.64	0.95	1.89	-	3.47	460	0.172	0.205	1.43

^a Modulus at 50, 100, 300 or 500% elongation, respectively

^b Tensile strength at break

^c Elongation at break

^d Constant determined by Mooney–Rivlin plots

^e Crosslinking density determined from equation (5)

Table 5 Results of d.m.a. and d.s.c. measurements

Sample code	Silica content (%)	D.m.a.			D.s.c.			
		Tan δ max (°C)	Peak height of tan δ max	E' at 20°C ($\times 10^7$ dyn cm $^{-2}$)	First		Second	
					T_g (°C)	T_m (°C)	T_g (°C)	T_m (°C)
BR-1	0	-97.6	0.275	1.33	-104.3	-17.0	-105.0	-16.9
BR-1-sol-gel	15.8	-94.0	0.216	3.41	-107.0	-16.4	-105.0	-17.5
BR-1-VN	21.7	-102.2	0.178	5.20	-103.5	-18.5	-103.5	-19.0
BR-2	0	-91.3	0.273	2.33	-105.5	-22.2	-105.5	-22.3
BR-2-sol-gel	14.1	-95.8	0.267	2.92	-106.5	-21.7	-105.3	-22.8

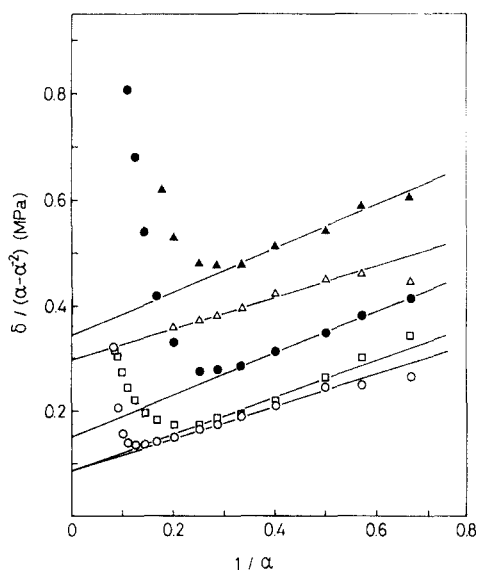


Figure 4 Mooney–Rivlin plots of BR-1 (○), BR-1-sol-gel (●), BR-1-VN (□), BR-2 (△) and BR-2-sol-gel (▲)

is

$$\sigma = 2 \left(C_1 + \frac{C_2}{\alpha} \right) \left(\alpha - \frac{1}{\alpha^2} \right) \quad (4)$$

where σ is tensile modulus, α is strain, and C_1 and C_2 are constants. The results for the BR vulcanizates with and without silica are given in *Figure 4*. The upturns at a higher elongation clearly demonstrate the reinforcing effect. Such reinforcement was absent in the BR vulcanizates without silica.

At initial and intermediate elongation regions of the Mooney–Rivlin plot, a straight line is drawn, and $2C_2$

and $2C_1$ are calculated from its slope and intercept, respectively. C_1 is defined by equation (5).

$$2C_1 = \nu kT \quad (5)$$

where ν is crosslinking density, k is the Boltzmann constant, and T is absolute temperature. From this relation, the crosslinking density is determined even on filled vulcanizates. The crosslinking density calculated from equation (5) are summarized in *Table 4*. The ν of BR-1-VN was similar to that of non-filled BR-1, but interestingly the ν s of the *in situ* silica-filled BR vulcanizates were larger than those of the non-filled BR vulcanizates. This result suggests the presence of some interaction between *in situ* silica particles and BR chains, and the interaction is effective to the increase of stress. Additionally, the degree of increase in the ν value after the sol–gel reaction was higher in BR-1-sol-gel than in BR-2-sol-gel, which means that the more interaction between *in situ* silica and rubber is in the former than in the latter due to the smaller crosslinking density.

Dispersion of *in situ* silica in the BR vulcanizates

Photographs of BR-1-sol-gel and BR-2-sol-gel as observed by TEM, are shown in *Figure 5* with that of BR-1-VN. The dark portions in the photos represent the SiO $_2$ particles. The observed particles were spherically shaped silicas with diameters of 20 nm to 33 nm for BR-1-sol-gel and of 15 nm to 20 nm for BR-2-sol-gel. These particles did not aggregate in the rubber matrix, which is very different from BR-1-VN, the rubber mechanically mixed with conventional silica particles. The image obtained for BR-1-VN showed two regions, i.e. the SiO $_2$ -rich and SiO $_2$ -poor phases, and the observed single silica particle had diameters from 13 to 17 nm. These particles aggregated to form clusters having various shapes and sizes. Thus, the dispersion of *in situ* silica

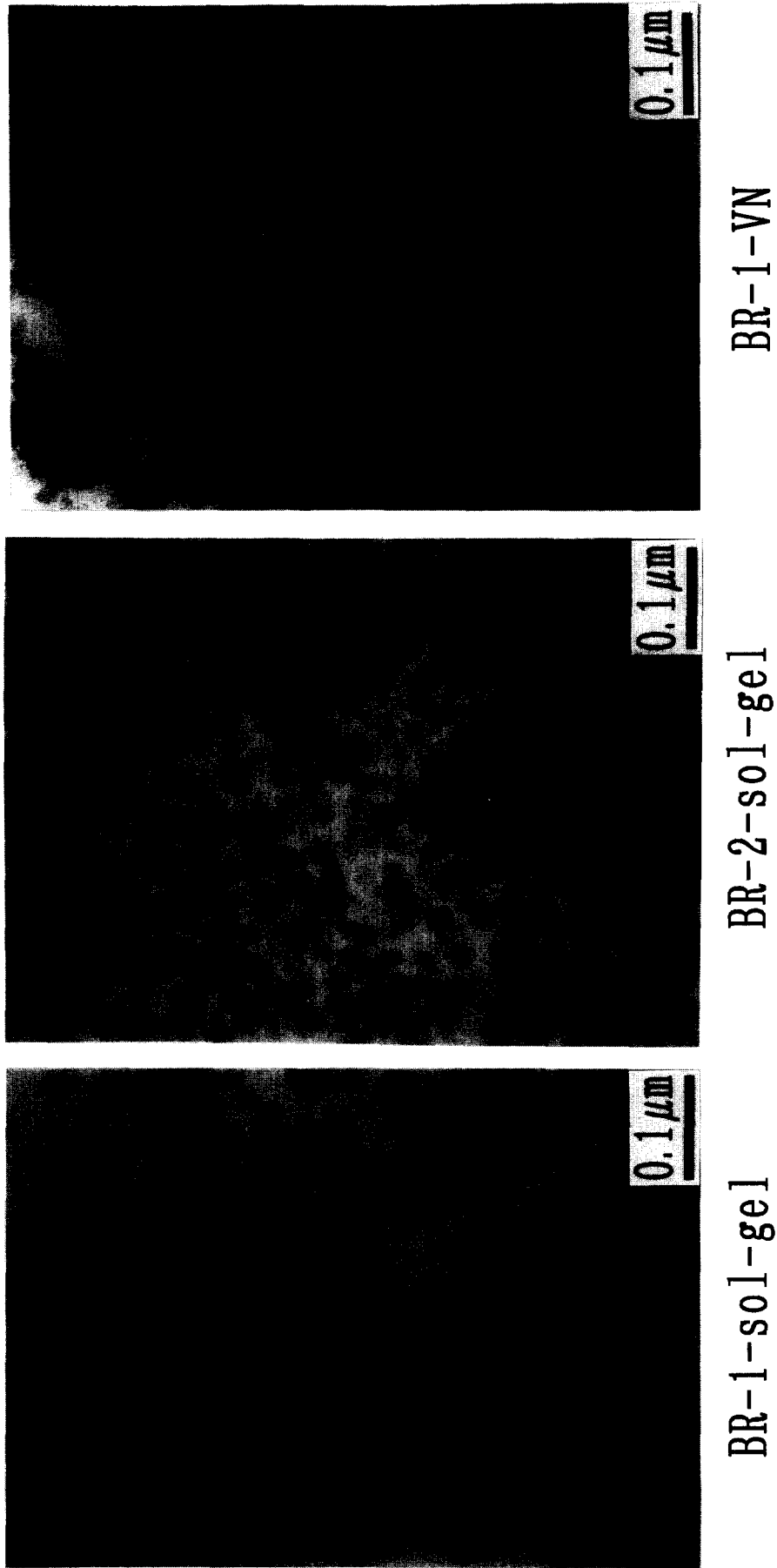


Figure 5 TEM photographs of BR-1-sol-gel, BR-2-sol-gel and BR-1-VN

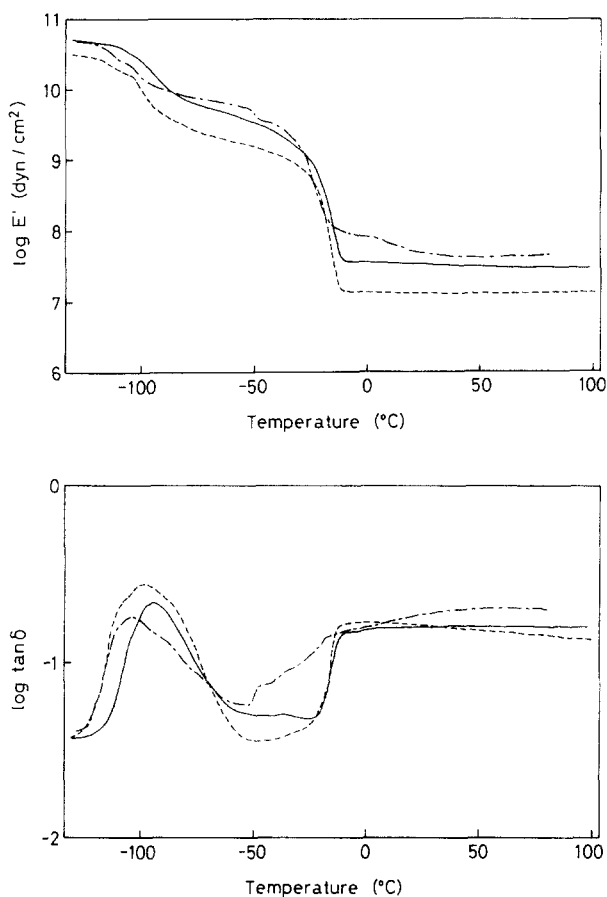


Figure 6 Temperature dispersions of E' and $\tan \delta$ for BR-1 (---), BR-1-sol-gel (—) and BR-1-VN (— · —)

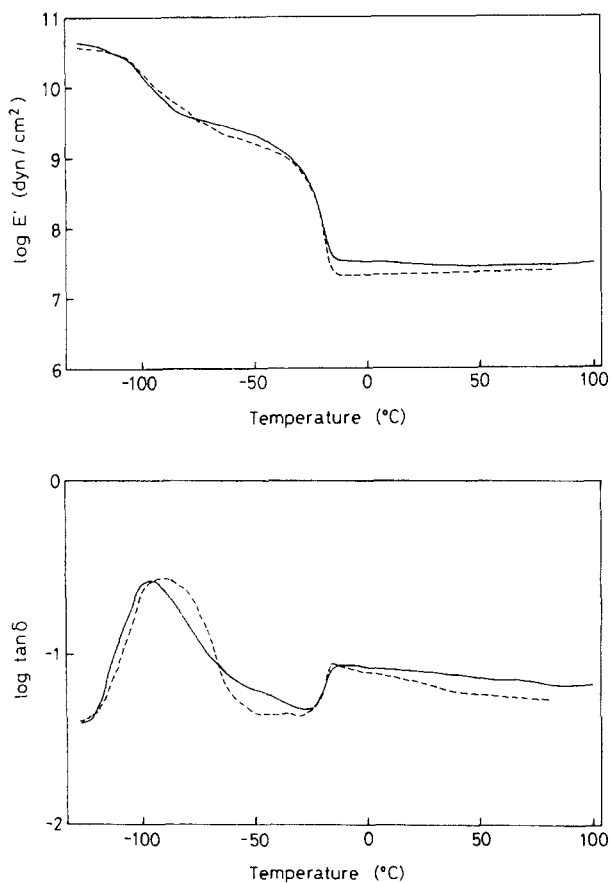


Figure 7 Temperature dispersions of E' and $\tan \delta$ for BR-2 (---) and BR-2-sol-gel (— · —)

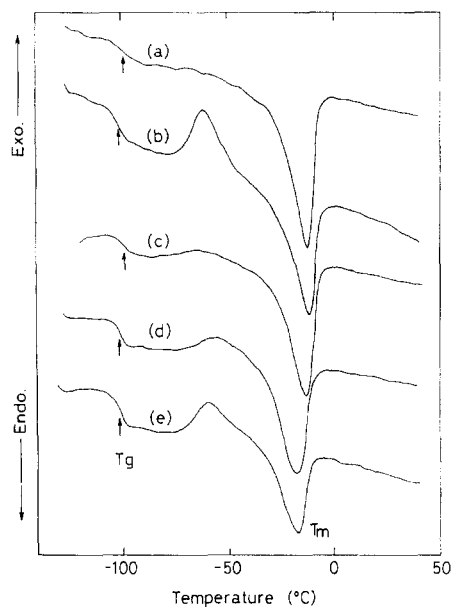


Figure 8 D.s.c. curves for BR-1 (a), BR-1-sol-gel (b), BR-1-VN (c), BR-2 (d) and BR-2-sol-gel (e)

particles was much more homogeneous than the conventional silica particles.

It is noteworthy that the particle size was influenced by the crosslinking density, i.e. the larger the molecular weight between the crosslinking sites was, the larger the *in situ* silica particles were. Judging from the monodispersity of *in situ* formed silica, the crosslinking reaction seems to have progressed rather homogeneously under the sulfur cure conditions in this study. To our knowledge, up to now, this is the first visual observation for the homogeneous distribution of silica particles in the conventional diene rubber, with such a small diameter.

From these observations, it is concluded that the uniform dispersion of silica particles in the BR matrix was one of the reasons for the excellent reinforcement of the BR vulcanizate by *in situ* silica filling using the sol-gel reaction of TEOS.

Interaction between the *in situ* formed silica and the rubber

Generally, the glass transition temperature (T_g) of the rubber is shifted to a high temperature region by adding a filler in a rubber matrix by mechanical mixing, when the interaction between the rubber and the filler is strong. Concurrently, the $\tan \delta$ peak, which is attributable to T_g in d.m.a. also becomes broader, and its height becomes lower. In this study, the results of d.s.c. and d.m.a. for the conventional silica-filled BR vulcanizate (BR-1-VN) substantially agreed with the general tendency stated above, as shown in Table 5. Figures 6 and 7 illustrated the temperature dependency of E' and $\tan \delta$ for the samples, and d.s.c. curves of the first scanning for the samples are shown in Figure 8. The T_g of BR-1-VN was not clearly detected in the d.s.c. measurement, but the $\tan \delta$ peak attributable to the T_g of BR-1-VN appeared at ca. -102°C . The height of the $\tan \delta$ peak of BR-1-VN is lower than that of BR-1, and its $\tan \delta$ curve is very broad. Additionally, the $\tan \delta$ curve attributable to the melting of BR segments increases more slowly in the wide temperature region, compared to that of BR-1.

However, the BR vulcanizates with *in situ* silica particles gave different results. In the measurement of

d.s.c., the T_g of the *in situ* silica-filled vulcanizates became lower than that of non-filled vulcanizates. Characteristically, the endothermic peak attributable to the recrystallization of BR segments clearly appeared after the sol-gel reaction of TEOS, as shown in Figure 8. These phenomena can be explained by rearrangement of BR chains in the vulcanizates during swelling in TEOS. The endothermic peak of recrystallization of BR segments became larger for BR-1-sol-gel than for BR-2-sol-gel. This is considered to be due to the difference of the crosslinking density between BR-1 and BR-2, i.e. the degree of swelling of BR-1 was larger than that of BR-2, and the BR chains became more mobile in the case of BR-1. The rearrangement of BR chains was also detected by d.m.a.. Tan δ peaks attributable to T_g s for both *in situ* silica filled vulcanizates became sharper, i.e. the shoulder in the tan δ curves became much smaller after the sol-gel reaction of TEOS. The tan δ peak attributable to the melting for BR-1-sol-gel was also much smaller than that of BR-1-VN.

On the other hand, the height of the tan δ peak at ca. -100°C for BR-2-sol-gel showed little decrease compared to that of BR-2, whereas the height of the tan δ peak of BR-1-sol-gel decreased more than that of BR-1 by *in situ* filling of silica. This means that the interaction between the *in situ* silica particles and BR chains were stronger in BR-1-sol-gel than in BR-2-sol-gel. Apparently, this result agreed with that of the tensile test. The reason for the difference in interaction between them can be accounted for by considering the particle size of *in situ* silica.

As the gels which have been just prepared by the sol-gel reaction of TEOS were swollen gels, SiO_2 networks would shrink during drying under a reduced pressure at 50°C , and some PB chains could be entrapped in the *in situ* silica particles during drying. As observed in TEM photographs, it was already confirmed that the sol-gel reaction progressed to form the larger silica particles in the BR-1 vulcanizate than in the BR-2 vulcanizate. Therefore, the larger particles are speculated to have trapped more BR chains. Consequently, the interaction between the *in situ* silica particles and BR chains might become stronger in BR-1-sol-gel than in BR-2-sol-gel. Of course, the slightly higher silica content of BR-1-sol-gel than that of BR-2-sol-gel is also one of the reasons for the above results detected in the measurements. The effect of particle size of *in situ* silica on the physical properties of the vulcanizate will be studied more in the near future.

CONCLUSION

Silica particles were introduced in the BR networks by using the *in situ* sol-gel reaction of TEOS. From the TEM observation, the *in situ* silica was found to be homogeneously dispersed in the rubber vulcanizate, and its size was ca. 15–33 nm. Interestingly, the size of *in situ* formed silica was influenced by the crosslinking density, i.e. the larger the crosslinking density, the smaller the size of *in situ* silica formed in the rubber vulcanizate. Concurrently, the interaction between the *in situ* silica particles and the BR chains seemed to become larger.

The considerable reinforcement effect of the *in situ* silica for the BR vulcanizate was observed by the tensile test and d.m.a. Comparing to the BR vulcanizate, which was mechanically filled with conventional silica particles,

the dispersion of silica was considered to be important for the reinforcement of the rubber vulcanizate.

This work has afforded some results on the interaction between the organic polymers and fillers. However, study on the interface between *in situ* silica particles and rubber chains is necessary, to know the relationship between *in situ* silica and the reinforcement effect in more detail. The method described herein represents a simple and effective means for mixing silica particles into rubber vulcanizate for its reinforcement.

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