

# Synthesis of Polychloroprene–Silica Composites by Sol-Gel Method in the Presence of Modified Polychloroprene Containing Triethoxysilyl Group

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**ABSTRACT:** Triethoxysilyl-modified polychloroprene (CR) latex was synthesized by the emulsion copolymerization of 2-(3-triethoxysilylpropyl)-1,3-butadiene with chloroprene. This latex was mixed with unmodified CR latex and tetraethoxysilane to obtain CR–silica composites by sol-gel reaction in the latex. SEM observation showed that the silica particles in unvulcanized composites have various diameters ranging from 0.1 to 0.6  $\mu$  m, and their size became larger with the decrease of

the silica content. Vulcanized CR–silica composites showed that the tensile modulus and tear strength improved with an increase of the amount of modified CR. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1545–1552, 2005

**Key words:** polychloroprene; rubber; silicas; composites; mechanical properties

## INTRODUCTION

Recently, many polymer–silica hybrid materials prepared by sol-gel approach were rapidly developed. Several investigations were also made for diene polymers. Kohjiya et al. and Ikeda et al. studied the preparation of silica-hybrid vulcanized styrene-butadiene rubber (SBR),<sup>1,2</sup> vulcanized polybutadiene rubber (BR),<sup>3,4</sup> or unvulcanized natural rubber (NR)<sup>5–7</sup> by soaking and swelling the raw materials into tetraethoxysilane followed by hydrolysis. Yoshikai et al.<sup>8–10</sup> prepared SBR–silica composites by progressing sol-gel reaction after dispersing tetraethoxysilane into polymer latex. In all the reports, they confirmed that those composites in which minute silica particles were uniformly dispersed showed higher mechanical properties than those prepared by the conventional mixing method.

Polychloroprene (CR) is also an important material in various fields, such as weather, ozone, heat, flame, and chemical resistance, because of its excellent performance. So we have come to be interested in the possibility of CR–silica composite to improve these performances with sol-gel approach. To the best of our knowledge, there are no reports of CR–silica composite synthesized by sol-gel method.

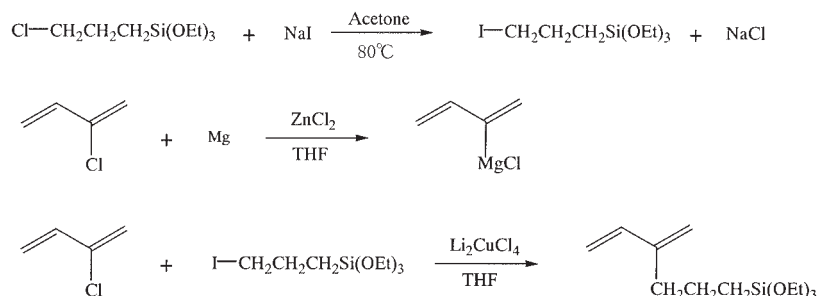
On the other hand, it is known that the reinforcing effect can be improved by the interaction between polymer phase and silica phase. In this respect, there is various research such as hydrogen bond,<sup>11</sup> covalent bond,<sup>12</sup>  $\pi$ – $\pi$  stacking effect,<sup>13</sup> ionic bond,<sup>14</sup> and interpenetrating polymer network (IPN).<sup>15,16</sup> Particularly in the rubber processing field, Ikeda<sup>17</sup> and Murakami et al.<sup>18</sup> reported polycondensation of tetraalkoxysilanes in the presence of a silane-coupling agent. Recently, we have found that the modified styrene-butadiene rubber (Si-SBR) latex containing triethoxysilyl group could improve the mechanical and dynamic properties of SBR–silica composites.<sup>19</sup> This modified rubber latex could be used for the polymeric silane-coupling agent, by which the silica surface can be modified more effectively. To elucidate that this technique is useful for CR–silica composite, the modified polychloroprene (Si-CR) containing triethoxysilyl group was synthesized. In this article, we report the effect of Si-CR on various properties of CR–silica composites.

## EXPERIMENTAL

### Materials

2-Chloro-1,3-butadiene (chloroprene, purity 99.8%) and polychloroprene rubber (Denka Chloroprene M-40) were supplied by Denki Kagaku Kogyo K.K. (Omi, Itoigawa, Niigata, Japan) and used as received. CR latex (Denka Chloroprene M-40 latex before drying process) was also supplied by Denki Kagaku Ko-

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Scheme 1 Synthesis of 4-methylene-5-hexenyltriethoxysilane.

gyo K.K. The solid content of the latex was adjusted to 25% prior to use. Silica powder, Nipsil VN-3 Tosoh Silica Corporation (Kaisei, Shunan, Yamaguchi, Japan), was used as received. Other materials were commercially available and used as received.

### Preparation of Si-Bd monomer

4-Methylene-5-hexenyltriethoxysilane [i.e., 2-(3-triethoxysilylpropyl)-1,3-butadiene (Si-Bd)] was synthesized via three steps, as shown in Scheme 1.

### Preparation of 3-iodopropyltriethoxysilane

In a 1000-mL round-bottom flask, 135.0 g (0.9 mol) of sodium iodide was placed and dried under vacuum at 80°C. Then 900 mL of anhydrous acetone was added into the flask to dissolve the salt. Then 72.2 g (0.3 mol) of 3-chloropropyltriethoxysilane, commercially available as silane-coupling agent, was added to the mixture and refluxed for 100 h with stirring. After 3-chloropropyltriethoxysilane was completely converted to 3-iodopropyltriethoxysilane, which was confirmed by gas chromatography analysis, the resulting solution was cooled and poured into hexane (500 mL) to precipitate the salt. Then the salt was filtrated and 3-iodopropyltriethoxysilane was isolated by distillation under reduced pressure [boiling point (bp), 54°C/3 mmHg, yield, 86%].

### Preparation of 2-(1,3-butadienyl) magnesium chloride

In a 300-mL three-neck round-bottom flask equipped with a Dimroth condenser, a dropping funnel, and a magnetic stirrer, 50 mL of anhydrous tetrahydrofuran (THF) and 12.4 g (0.51 mol) of magnesium turnings were placed and purged with nitrogen. The mixture of chloroprene 30.1 g (0.34 mol) and THF 70 mL was placed in the dropping funnel. A small amount of methyl iodide was added to the flask to activate the magnesium surface. Then about 30 mL of the resulting white turbid solution of methyl magnesium iodide was taken out with a syringe, and it was poured into

the dropping funnel to dehydrate chloroprene solution. Confirming that the surface of magnesium turnings turned to black, a 0.27 g (0.002 mol) of anhydrous zinc chloride was added to the flask as catalyst. Finally, chloroprene solution was slowly added over 30 min with gentle refluxing to obtain the solution of 2-(1,3-butadienyl) magnesium chloride.

### Preparation of Si-Bd

In a 300-mL three-neck round-bottom flask equipped with a Dimroth condenser, a dropping funnel, and a magnetic stirring bar, 0.64 g (0.015 mol) anhydrous lithium chloride and 1.01 g (0.0075 mol) copper (II) chloride were added and dissolved in 75 mL THF to prepare  $\text{Li}_2\text{CuCl}_4$  catalyst solution.<sup>19</sup> To this solution, 49.8 g (0.15 mol) of 3-iodopropyltriethoxysilane was added and 2-(1,3-butadienyl) magnesium chloride in THF was slowly added at 30°C over 30 min. After 3-iodopropyltriethoxysilane was completely consumed, which was confirmed by gas chromatography analysis, the resulting solution was poured into a 20 wt % solution of ammonium chloride in water. The organic layer was extracted thrice with diethylether and the combined organic layer was dried with anhydrous magnesium sulfate. After the usual work-up, Si-Bd was isolated by distillation under reduced pressure (bp, 54°C/3 mmHg, yield, 86%).

### Preparation of Si-modified CR latex

In a 3000-mL four-necked round-bottom flask equipped with a mechanical stirrer, a Dimroth condenser, and a dropping funnel, 40.0 g (0.139 mol) sodium lauryl sulfate and 1150 mL distilled water were charged and maintained at 30°C for 30 min. To this soap solution, 1150 g (13.0 mol) chloroprene (98 mol %), 40.0 g (0.155 mol) Si-Bd (2 mol %), and 2.2 g ( $10.9 \times 10^{-3}$  mol) 1-dodecanethiol were added and stirred at 200 rpm at 35°C. Then 98.1 mL of the aqueous solution containing 1 wt % potassium peroxydisulfate (KPS) was added into the mixture from the dropping funnel under nitrogen atmosphere over 5.8 h. Poly-

TABLE I  
Recipe of Emulsion Copolymerization

Ingredients	Amount
2-Chloro-1,3-butadiene (Chloroprene)	13.0 mol
4-Methylene-5-hexenyltriethoxysilane (Si-Bd)	0.155 mol
1-Dodecanethiol	$10.9 \times 10^{-3}$ mol
Distilled water	1150 ml
Sodium lauryl sulfate	0.139 mol
Phenothiazine	$0.642 \times 10^{-3}$ mol
4- <i>tert</i> -Butylcatechol	$0.770 \times 10^{-3}$ mol
Aqueous solution containing 1% of potassium peroxydisulfate (KPS)	98.1 ml

merization was quenched by the addition of phenothiazine and 4-*tert*-butylcatechol at 59% of conversion. Si-CR latex was obtained after removal of unreacted monomers at 60°C under reduced pressure (~ 580 mmHg). The recipe of emulsion copolymerization is shown in Table I.

Solid content and conversion were measured after drying the latex at 200°C for 60 min in an oven. A small part of the latex was withdrawn prior to the drying and poured into methanol to precipitate the polymer. The precipitated polymer was dried under vacuum. The composition of copolymer was determined by <sup>1</sup>H-NMR.

### Preparation of CR-silica composite

CR-silica composites having various silica contents and diameters were prepared by changing the amount of Si-CR latex and ammonia. In a 5000-mL kettle, tetraethoxysilane (TEOS) and aqueous ammonia (28 wt %) were added into the mixture of Si-CR latex and unmodified CR (M-40) latex under stirring at 200 rpm. The amount of aqueous ammonia was 1% to the total weight of TEOS and water in the mixed latex. Then, the emulsion was transferred to a 5000-mL polyethylene bottle. It was vigorously shaken for 1 h and then left standing still for 24 h at 23°C for sol-gel reaction to be completed. Complete conversion of TEOS to silica was confirmed by measuring the solid content of the emulsion. After this emulsion was frozen at -60°C, CR-silica composite was obtained by vacuum drying at 30°C below 0.5 mmHg. The recipe of sol-gel reaction is shown in Table II. The sample code such as CR-*x*-*y* in Table II indicates the Si-CR content (*x*% by weight, solid) and the silica content (*y*% by weight).

### Measurement of silica content

The silica content in CR-silica composites was determined by TG/DTA20 (Seiko Instruments Co.). It was calculated from residual sample weight at 150 and 800°C, respectively, as shown in the equation

Silica content (wt %)

$$= \frac{\text{Residual sample weight at } 800^{\circ}\text{C}}{\text{Residual sample weight at } 150^{\circ}\text{C}} \times 100 \quad (1)$$

### Observation of silica by scanning electron microscope (SEM)

SEM observation of silica particles was performed for both the fractured surface of CR-silica composites prepared by crushing in liquid nitrogen and the ash remaining after TG/DTA measurement. The specimens were fixed on the stage with carbon tape and coated Au-Pd. A Hitachi S-800 scanning electron microscope as used at a magnification of  $\times 20,000$  and acceleration voltage of 10 kV.

### Preparation of vulcanized composites

Two kinds of formulations, pure gum compound (Formulation A) and carbon-filled compound (Formulation B), were used to prepare vulcanizates of CR-silica composites as shown in Tables III and IV, respectively. Generally, the curing rate became later as more filler is added, because the filler hinders the reaction between polymer and curing agent. So, the amount of ethylene thiourea as curing agent in Table IV must be more than that in Table III. Rubber and compounding agents were mixed at 50°C on a two-roll mixer. The compound was sheeted out from the mixer and pressed for 30 min at 170°C to make the vulcanized sheet have a thickness of 2 mm. The suitable conditions for vulcanization were determined from the shape of curing curves measured by cure meter.

### Evaluation of vulcanized composites

Tensile stress at elongations of 100% ( $M_{100}$ ) to 300% ( $M_{300}$ ), tensile strength ( $T_B$ ), and elongation at break ( $E_B$ ) was evaluated according to Japanese Industrial Standard (JIS) K 6251 procedures. Tearing strength (TR) was determined according to JIS K 6252. Com-

TABLE II  
Preparation of CR-Silica Composite by Sol-Gel Method

Sample code	Ingredients (g)			
	M-40 latex <sup>a</sup>	Si-CR latex <sup>b</sup>	TEOS	28% NH <sub>3</sub> aq
CR-0-10	3840.0	—	832.2	37.1
CR-0-20	4320.0	—	416.1	36.6
CR-2-10	4253.7	66.3	416.1	36.6
CR-2-20	3781.1	58.9	832.2	37.1
CR-5-10	4154.4	165.6	416.1	36.6
CR-5-20	3692.7	147.3	832.2	37.1

<sup>a</sup> Solid content 25.0%.

<sup>b</sup> Solid content 32.6%.

TABLE III  
Formulation of Pure Gum Compound (Formulation A) (phr)

Sample code	1A	2A	3A	4A	5A	6A	7A	8A
CR-0-10	111	—	—	—	—	—	—	—
CR-0-20	—	125	—	—	—	—	—	—
CR-2-10	—	—	111	—	—	—	—	—
CR-2-20	—	—	—	125	—	—	—	—
CR-5-10	—	—	—	—	111	—	—	—
CR-5-20	—	—	—	—	—	125	—	—
M-40 (solid) <sup>a</sup>	—	—	—	—	—	—	100	100
Silica <sup>b</sup>	—	—	—	—	—	—	11	25
Phenyl-1-naphtylamine <sup>c</sup>	1	1	1	1	1	1	1	1
Magnesium oxide <sup>d</sup>	4	4	4	4	4	4	4	4
Zinc oxide <sup>e</sup>	5	5	5	5	5	5	5	5
Ethylene thiourea <sup>f</sup>	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37

<sup>a</sup> Denka Chloroprene M-40 (Denki Kagaku Kogyo K.K., Itoigawa, Niigata, Japan).

<sup>b</sup> Nipsil VN-3 (Tosoh Silica Corporation, Kaisei, Shunan, Yamaguchi, Japan).

<sup>c</sup> Nocrac PA (Ouchishinko Chemical Industrial Co.,Ltd., Itabashi-ku, Tokyo, Japan).

<sup>d</sup> Kyowamag 30 (Kyowa Chemical Industry Co.,Ltd., Takamatsu, Kagawa, Japan).

<sup>e</sup> Zinc Oxide #2 (Sakai Chemical Industry Co.,Ltd., Sakai, Osaka, Japan).

<sup>f</sup> Accel 22S (Kawaguchi Chemical Industry Co.,Ltd., Chiyoda-ku, Tokyo, Japan).

pression set (CS) and permanent set (Ps) were determined according to JIS K 6262. Tensile stress at low elongation ( $M_{25}$ ) and static shear modulus (GS) was measured according to JIS K 6254. Hardness (HS) was measured by A-method according to JIS K 6253. A specimen having 4.5-mm width, 20-mm length, and 2-mm thickness, cut from cured sheet, was tested to check viscoelastic behavior. Both storage elastic modulus ( $E'$ ) and  $\tan \delta$  were estimated by using Rheovibron DDV-25FP (Orientec Co.,Ltd.) at a vibration frequency of 15 Hz and an amplitude of 10  $\mu$  m, a heating rate of 5°C/min range.

## RESULTS AND DISCUSSION

### Characterization of si-modified CR latex

Conversion and the composition of the copolymer, solid content of Si-CR latex are shown in Table V. The copolymer became partly insoluble in organic solvent after repeating precipitation, although the copolymer isolated from latex after polymerization was soluble in organic solvent. Partial condensation of triethoxysilyl groups in the copolymer might have occurred in the reprecipitation process.

TABLE IV  
Formulation of Carbon-Filled Compound (Formulation B) (phr)

Sample code	1B	2B	3B	4B	5B	6B	7B	8B
CR-0-10	111	—	—	—	—	—	—	—
CR-0-20	—	125	—	—	—	—	—	—
CR-2-10	—	—	111	—	—	—	—	—
CR-2-20	—	—	—	125	—	—	—	—
CR-5-10	—	—	—	—	111	—	—	—
CR-5-20	—	—	—	—	—	125	—	—
M-40 (solid) <sup>a</sup>	—	—	—	—	—	—	100	100
Silica <sup>b</sup>	—	—	—	—	—	—	11	25
Phenyl-1-naphtylamine <sup>c</sup>	1	1	1	1	1	1	1	1
Magnesium oxide <sup>d</sup>	4	4	4	4	4	4	4	4
Carbon black <sup>e</sup>	15	15	15	15	15	15	15	15
Zinc oxide <sup>f</sup>	5	5	5	5	5	5	5	5
Ethylene thiourea <sup>g</sup>	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

<sup>a</sup> Denka Chloroprene M-40 (Denki Kagaku Kogyo K.K.).

<sup>b</sup> Nipsil VN-3 (Nippon Silica Industrial Co.,Ltd.).

<sup>c</sup> Nocrac PA (Ouchishinko Chemical Industrial Co.,Ltd.).

<sup>d</sup> Kyowamag 30 (Kyowa Chemical Industry Co.,Ltd.).

<sup>e</sup> Semi-reinforcing furnace black, Asahi 50 (Asahi Carbon Co.,Ltd.).

<sup>f</sup> Zinc Oxide #2 (Sakai Chemical Industry Co.,Ltd.).

<sup>g</sup> Accel 22S (Kawaguchi Chemical Industry Co.,Ltd.).

**TABLE V**  
Result of Emulsion Copolymerization

Sample no.	Copolymer <sup>a</sup> (mol %)		Yield (%)	Solid content <sup>b</sup> (%)
	CP	Si-Bd		
Si-CR	98.7	1.3	59	32.6

<sup>a</sup> Determined by <sup>1</sup>H-NMR (soluble part in CDCl<sub>3</sub>).

<sup>b</sup> After removal of unreacted monomer.

### Measurement of silica content

Silica content determined from the results of TG/DTA measurement for CR-silica composites are summarized in Table VI. In all the samples, observed silica content by TG/DTA measurement was higher than those of the theoretical value. One likely explanation for this is a formation of nonvolatile silicon carbide derived from the siloxane linkage between silica and modified CR.

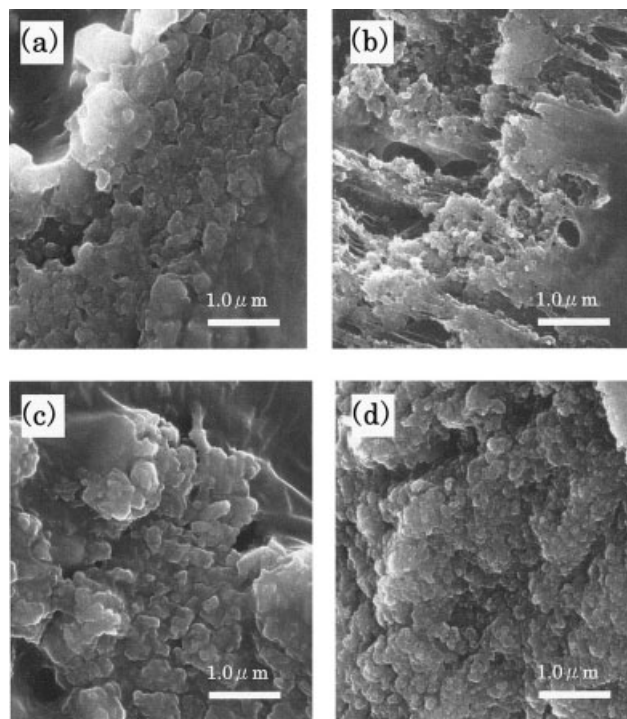
### Observation of silica

SEM images of the freeze-fractured surface of CR-silica composites which differ in silica content and Si-CR content are shown in Figure 1. The convex shapes in SEM images are silica particles. The silica particles in CR-2-10 and CR-5-10 have various diameters ranging from 0.3 to 0.6  $\mu$  m, whereas the silica particles in CR-2-20 and CR-5-20 have various diameters ranging from 0.1 to 0.3  $\mu$  m. This difference in particle size might be caused by the increased probability of reaction between the triethoxysilyl group in TEOS and that in Si-CR, leading to the growth inhibition of silica particles by Si-CR latex particles.

To estimate the size of silica particles formed in latex, SEM observation of the ash after TG/DTA measurement for CR-silica composites was also carried out. Their SEM images are shown in Figure 2. In all the images, all silica particles were adhered each other to form porous glass. This may be on account of sintering<sup>20</sup> among many particles during combustion or the above-mentioned formation of silicon carbide. As can

**TABLE VI**  
Silica Content Determined from the Results of TG/DTA Measurement

Sample no.	Silica content (wt. %)	
	Theoretical	Actual
CR-0-10	10.0	11.2
CR-0-20	20.0	23.1
CR-2-10	10.0	13.3
CR-2-20	20.0	22.4
CR-5-10	10.0	12.6
CR-5-20	20.0	22.4



**Figure 1** SEM images of the dispersed silica in nonsheared unvulcanized composites which differ in silica content and Si-CR content. (a) CR-2-10, (b) CR-2-20, (c) CR-5-10, (d) CR-5-20.

be seen, the size of silica particles decreased with an increase in silica content. Si-CR content had almost no significant influence on primary particle size.

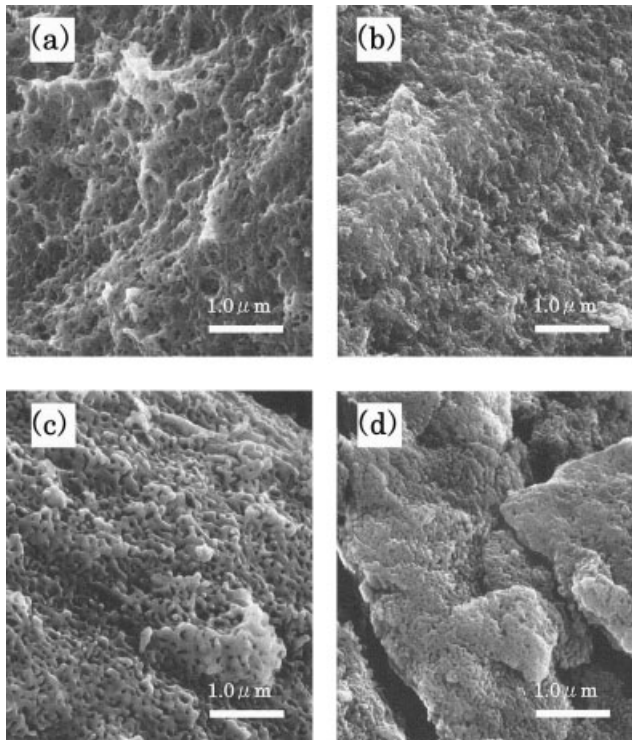
### Effect of silica content on mechanical properties

Mechanical properties of vulcanized composites are summarized in Table VII.

Tensile stress, tearing strength, and hardness of the vulcanized composites containing 20% of silica were higher than those of the samples containing 10% of silica. It is well known that silica phase is less deformable than polymer phase. So, the energy required to deform composites might have increased with an increase of silica content. Compression set and permanent set of the vulcanized composites containing 20% of silica were inferior to those of the samples containing 10% of silica. This might be due to the finding that the surface area where adsorption or reaction between polymer and silica occurs during strain or compression increased in proportion to silica content.

### Effect of sol-gel method on mechanical properties

Table VII summarized the mechanical properties of the vulcanized silica-CR composite with pure-gum compound prepared by a different method. Sample 7A and 8A were prepared by conventional mechanical

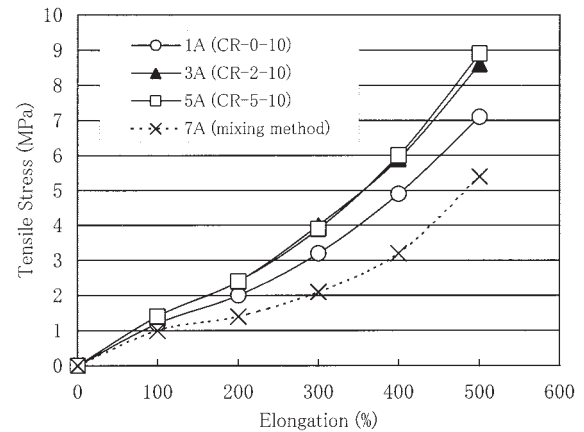


**Figure 2** SEM images of the ash of nonsheared unvulcanized composites which differ in silica content and Si-CR content. (a) CR-2-10, (b) CR-2-20, (c) CR-5-10, (d) CR-5-20.

mixing of solid rubber with silica powder, whereas others were prepared by the *in situ* silica filling using sol-gel method. Comparing tensile stress, tearing strength, and hardness of the composites having the same silica content, the composites by the sol-gel method showed better properties than those prepared by normal mixing method. This might be due to the finding that the silica formed by sol-gel method is finer than the conventional silica used for normal mixing method. However, the sol-gel method showed lower tensile strength and elongation at break than the mixing method.

#### Effect of adding Si-CR on mechanical properties

Table VII also shows the effect of Si-CR addition on the mechanical properties. It is obvious that tensile



**Figure 3** Elongation-stress curves for vulcanized composites containing 10% silica.

stress, tearing strength, and hardness of the composites, having the same silica content prepared by sol-gel method, increased with an increase in the amount of Si-CR. The influence of Si-CR on the relationship between elongation and stress for vulcanized composites with 10 and 20% of silica content are shown in Figures 3 and 4, respectively.

As shown in Figures 3 and 4, tensile stress increased with an increase of Si-CR for the samples containing 10 and 20% of silica. It was clarified that the reinforcing effect of silica was improved by adding Si-CR. Addition of Si-CR had no influence on compression set and permanent set.

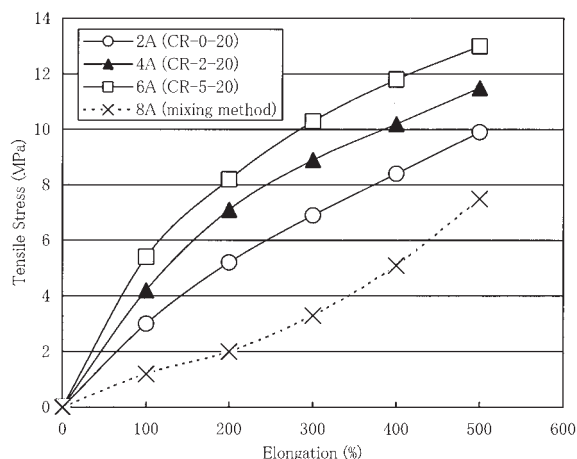
#### Dynamic properties

Storage modulus of vulcanized composites containing 20% of silica is shown in Figure 5.

In the absence of Si-CR, storage modulus of the composite by sol-gel method was lower than that by the mixing method in the rubberlike region. On the other hand, when Si-CR was added to some extent, storage modulus in the rubberlike region increased with an increase of Si-CR content. As shown in Figure 1, the silica size of the sample prepared by 5% of Si-CR was almost same with that by 5% of Si-CR. It is known

**TABLE VII**  
Properties of Vulcanized CR-Silica Composites Prepared with Pure Gum Compound (Formulation A)

Sample code	$M_{100}$ [MPa]	$M_{200}$ [MPa]	$M_{300}$ [MPa]	$T_B$ [MPa]	$E_B$ [%]	TR [MPa]	CS [%]	Ps [%]	$M_{25}$ [MPa]	GS [MPa]	HS [JIS A]
1A	1.2	2.0	3.2	21.1	815	44	16	18	0.40	0.66	51
2A	3.0	5.2	6.9	12.9	646	64	22	36	0.81	1.34	69
3A	1.4	2.4	4.0	21.5	778	53	17	28	0.50	0.81	53
4A	4.2	7.1	8.9	11.8	529	66	21	36	1.06	1.73	74
5A	1.4	2.4	3.9	22.6	786	57	14	27	0.51	0.83	54
6A	5.4	8.2	10.3	13.0	492	73	23	38	1.33	2.19	77
7A	1.0	1.4	2.1	24.5	820	48	14	17	0.37	0.61	50
8A	1.2	2.0	3.3	31.5	933	61	25	34	0.46	0.76	58

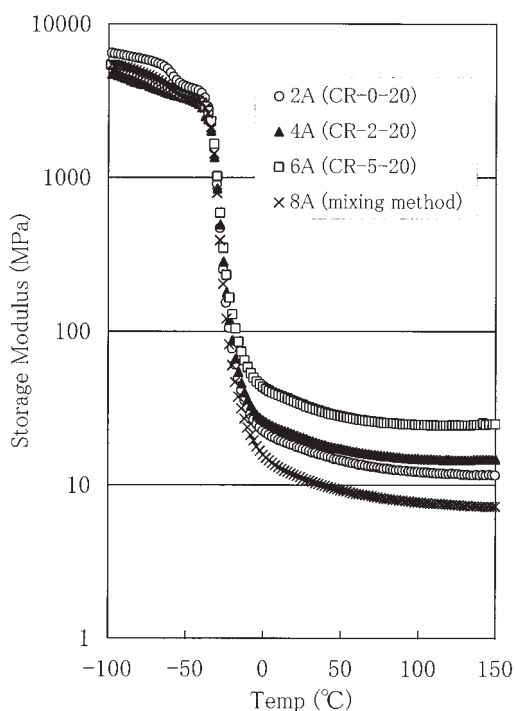


**Figure 4** Elongation-stress curves for vulcanized composites containing 20% silica.

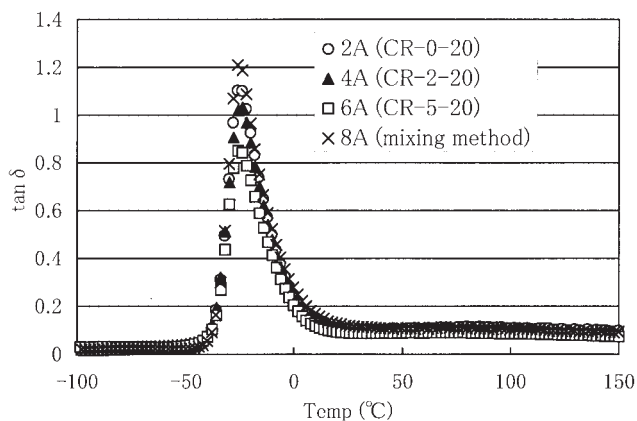
that the silica size did not depend on the amount of Si-CR. Thus, the improvement of these physical properties is presumably due to the increased affinity of silica surface with matrix polymer by the added Si-CR.

The effect of sol-gel method and addition of Si-CR on  $\tan \delta$  at 20% content of silica was shown in Figure 6.

In the absence of Si-CR, the sol-gel sample showed a lower peak  $\tan \delta$  value compared with that of the conventional mixing sample. Furthermore, peak height of  $\tan \delta$  became lower with an increase in additive amount of Si-CR. This may be due to the



**Figure 5** Storage modulus of vulcanized composites containing 20% silica.



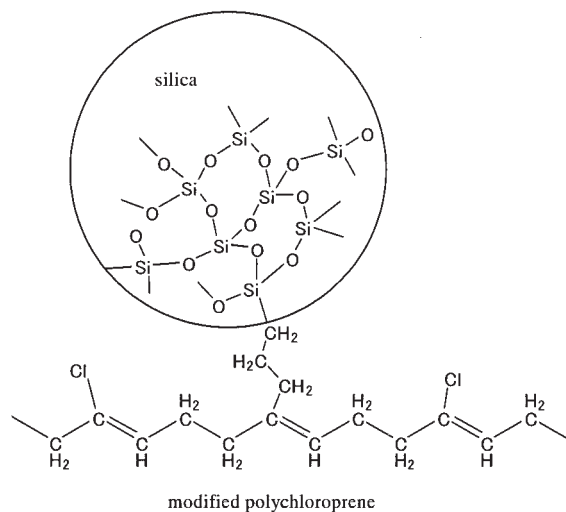
**Figure 6** Effect of sol-gel method and addition of Si-CR on  $\tan \delta$  at 20% content silica.

finding of the formation of siloxane bond between Si-CR and silica, and the restriction of rearrangement for polymer chain in the neighborhood of silica surface, as shown in Figure 7. The amount of the siloxane bond between Si-CR and silica might be too small to change the position of peak top of  $\tan \delta$  (i.e., glass transition point).

#### Effect of compounding carbon black with silica

Mechanical properties of vulcanized CR-Silica composites prepared with formulation containing carbon black (Formulation B) are given in Table VIII.

Comparing the properties for carbon-filled compound in Table VIII with the properties for pure-gum compound in Table VII, it was shown that tensile stress and hardness increased, whereas elongation decreased by compounding carbon black. The composite by the sol-



**Figure 7** Illustration of the combination between Si-CR and silica.

TABLE VIII  
Properties of Vulcanized CR-Silica Composites Prepared with Carbon-Filled Compound (Formulation B)

Sample code	$M_{100}$ [MPa]	$M_{200}$ [MPa]	$M_{300}$ [MPa]	$T_B$ [MPa]	$E_B$ [%]	TR [MPa]	CS [%]	Ps [%]	$M_{25}$ [MPa]	GS [MPa]	HS [JIS A]
1B	3.0	6.7	11.1	18.1	454	65	12	6	0.87	1.43	65
2B	7.1	10.8	—	12.7	279	54	21	11	1.69	2.78	84
3B	2.8	6.8	12.0	19.4	452	66	15	8	0.86	1.41	64
4B	8.0	12.0	—	13.4	254	56	18	11	1.72	2.82	83
5B	3.6	8.0	13.6	19.0	402	66	12	6	0.99	1.62	68
6B	8.2	13.4	—	15.4	358	65	20	15	1.82	2.99	86
7B	2.0	4.6	8.6	23.5	587	78	7	6	0.64	1.05	59
8B	2.3	5.6	9.9	24.8	633	90	19	15	0.71	1.17	65

gel method was superior to the one by the normal mixing method in tensile stress and hardness. Tensile stress and hardness increased with the increase in the amount of Si-CR. It was shown that the addition of Si-CR can improve the reinforcement effect of silica on the formulation containing carbon black, too.

### CONCLUSION

CR-silica composites were synthesized by sol-gel method in the presence of unmodified CR latex (M-40) and modified polychloroprene latex (Si-CR) containing triethoxysilyl group. SEM observation for the unvulcanized composites showed that the silica particles have various diameters ranging from 0.1 to 0.6  $\mu$  m, and their size became larger with decreases in silica content. The vulcanizates prepared by sol-gel method have higher tensile stress, elastic modulus, and hardness than the those prepared by conventional mixing method and have lower tensile strength and lower elongation. Addition of Si-CR resulted in improvement of tensile stress, elastic modulus, tearing strength, and hardness. It was clarified that adding Si-CR was effective in reinforcing CR-silica composites.

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