Effect of Silica Reinforcement on Natural Rubber and Butadiene Rubber Vulcanizates by a Sol–Gel Reaction with Tetraethoxysilane

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ABSTRACT: The effect of silica reinforcement was studied for natural rubber (NR) and butadiene rubber (BR) vulcanizates by a sol–gel reaction with tetraethoxysilane at different temperatures. The formation of silica in the rubber vulcanizates was investigated analytically with Fourier transform infrared spectroscopy and energy-dispersive X-ray analysis. The variations of the mechanical and dynamic properties were measured in the NR and BR vulcanizates with silica filling. The hardness of the rubber vulcanizates increased with silica filling in the rubber matrix. The tensile strength and elongation at break decreased with silica filling in the NR vulcanizates.

The moduli at 50, 100, and 300% elongation increased with silica filling in the rubber matrix. The storage modulus of silica-filled rubber vulcanizates became higher than that of pure rubber vulcanizates. The temperature dependence of the loss modulus also increased with silica filling. The temperature dependence of the loss tangent was maintained, regardless of silica filling in the BR vulcanizates. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3952–3959, 2008

Key words: reinforcement; rubber; silicas; strain; vulcanization

INTRODUCTION

Tires have a great influence on revolution resistance, braking properties, and driving stability.[1,2] Efforts to develop tires that meet the increasing ecological requirements of lowest rolling resistance and high durability, without sacrifices in handling and skid properties, led to the concept of the green tire.[3,4] The tread compounds of green tires are commonly based on blends of solution styrene–butadiene rubber, butadiene rubber (BR), and natural rubber (NR). They are filled with high quantities of silica.

Silica is an economical reinforcing filler used in rubber chemistry.[5] Silica has been lacking in one prerequisite for all rubber-reinforcing capability, that is, silica–rubber bonding. The addition of BR will improve abrasion resistance and cold flexibility, whereas NR can have a positive influence on processing and grip. Only with the help of silane coupling agents can high quantities of silica filler be reasonably incorporated into tread compounds and provide an excellent reinforcing effect.[6,7] Various methods used to modify the surface properties of silica have been introduced largely in terms of thermal, chemical, electrochemical, and coupling agent treatments.[8–10] The rubber–silica adhesion is increased, and consequently, the reinforcing effect of the silica is enhanced.[11–13] It has been found that the use of coupling agents that promote covalent bounds between rubber and fillers reduces the amplitude of the nonlinear phenomenon.[14]

Silica-reinforced rubber has been prepared by mechanical mixing and molding techniques followed by the curing of the rubber compounds.[15,16] The mechanical mixing process, however, is difficult because of the small size and large specific surface area of the hydrated silica.[17,18] The polymerization of tetraethoxysilane (TEOS) by a sol–gel process can overcome the difficulties.[19,20] The reaction of TEOS takes place in two steps, hydrolysis and condensation, in which silica is formed in the rubber matrix.[21–25]

In this study, the effect of silica reinforcement was studied for NR and BR vulcanizates by a sol–gel reaction of TEOS. The formation of silica in the rubber vulcanizates was confirmed analytically. The variations of the mechanical properties were investigated with silica filling in the NR and BR vulcanizates. The dynamic properties of the storage modulus (E'), loss modulus (E''), and loss tangent (tan δ) were also evaluated with silica filling in the rubber vulcanizates.

EXPERIMENTAL

Preparation of the materials by the sol–gel reaction

The NR and BR vulcanizates were prepared according to ASTM D 3184-89. Table I lists the proportions of the reagents used in the preparation of the rubber vulcanizates.

NR and BR vulcanizates sheets (15 cm × 15 cm) were swollen in 1 L of tetraethylorthosilicate (TEOS; Aldrich, St. Louis, MO; 98%) for 48 h at 30, 50, and 70°C, respectively. They were soaked in a 10 wt % aqueous solution of *n*-butylamine (Aldrich; 98%) for 24 h at the same temperature with swelling. The weight of the sample sheets was measured before and after each process. The sample sheets were dried for 3 days at 50°C under reducing pressure to 10^{-2} Torr.

Material characterization

Analysis of silica incorporation into rubber vulcanizates

A sample of the reaction solution was collected at every hour in the soaking process, and then it was analyzed with gas chromatography (M680D, Young-In, Ansan, Korea) to confirm the formation of ethyl alcohol. The silica-filled vulcanizates are abbreviated with the soaking temperature hereafter [i.e., SiO_2/NR(#) or SiO_2/BR(#), where # designates the soaking temperature].

The incorporation of silica into rubbers was confirmed with Fourier transform infrared (FTIR) spectra (model FTS 175C FTIR spectrometer, Bio-Rad, Hercules, CA). Energy-dispersive X-ray (EDX) analysis (SII 1609, Noran, Middleton, WI) was also carried out to define the incorporation of silica into the external surface and internal matrix of the silica-filled NR vulcanizates. The dispersion and size of the silica in the rubber vulcanizates were examined with a Hitachi S-4900 scanning electron microscope (Nishishimbashi, Japan). The sample of the internal matrix was obtained from scratching of the cross-sectional fracture of NR vulcanizates. Thermogravimetry (model 951, DuPont Instrument, Wilmington, DE) was measured in air to 800°C at a rate of 20°C/min. The amount of silica filling was determined from thermogravimetric analysis.

Analysis of the mechanical and dynamic properties

The tensile properties of the silica-filled vulcanizates were measured on a tensile tester (model 6021, Instron, USA) based on ASTM D 412 at room temperature and at a crosshead speed of 500 mm/min with dumbbell-shaped specimens. The values reported here are based on averages of three measurements for each sample. The hardness of the rubber vulcani-

TABLE I
Reagents Used in the Preparation of NR and BR Vulcanizates

NR vulcanizate		BR vulcanizate	
Material	phr[a]	Material	phr[a]
NR[b]	100	BR	100
CURE-NS[c]	0.6	Zinc oxide	3.0
Stearic acid	3.0	Sulfur	1.5
Zinc oxide	5.0	Stearic acid	2.0
Carbon black	50.0	Oil furnace black	60.0
Sulfur	2.5	TBBS[d]	0.9
		ASTM type 103 petroleum oil	15.0
Total	161.1	Total	182.4

[a] Parts per hundred parts of rubber in terms of mass.
[b] SMR-CV60 from Lee Rubber Co. (Kaohsiung, Hsien, Taiwan)
[c] Vulcanizing accelerator (*N*-oxydiethylene-2-benzethiazole sulfenamide, Kumho Co., Gwangju, Korea).
[d] *n-tert*-Butyl-2-benzothiazolsulfenamide (Kumho Co., Gwangju, Korea).

zates was measured with a Shore A durometer (*N*-oxydiethylene-2-benzethiazole sulfenamide, Kumho Co., Gwangju, Korea) based on ASTM D 2240. The dynamic properties of the rubber vulcanizates were measured on a dynamic tester (Eplexer 150N, GABO Co., Ansan, Korea) at a frequency of 10 Hz. The heating rate of the dynamic test was maintained at 3°C/min from −110 to 70°C.

RESULTS AND DISCUSSION

Sol–gel reaction mechanism

The sol–gel process for the preparation of inorganic glasses at low temperatures was adopted according to rubber chemistry.[26] The sol–gel reaction of TEOS involves the swelling of a precured rubber in TEOS and then subjection of the TEOS-swollen rubber to a sol–gel process, that is, hydrolysis and condensation. 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,[27] and it has been carried out already on silicon rubber.[28] The TEOS contained in the rubber is converted into silica upon hydrolysis and condensation according to the following equation:

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH \quad (1)$$
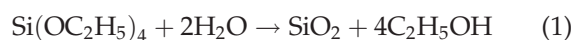
Formation of silica in the rubber matrix

The formation of silica can be found indirectly from the detection of ethyl alcohol that forms in the reaction solution during the soaking process according to
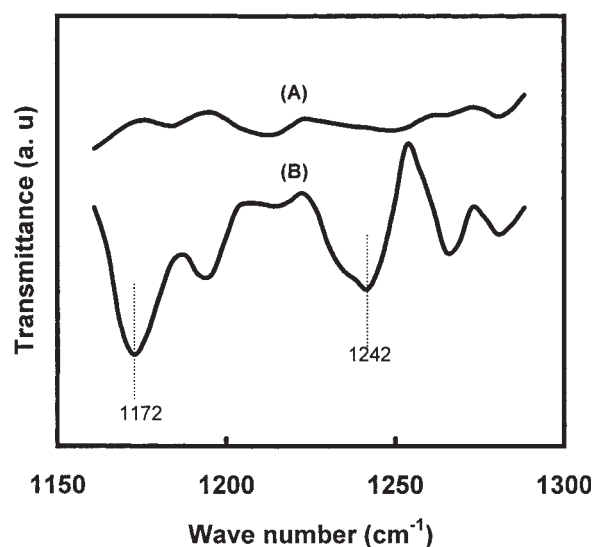
Figure 1 FTIR spectra of the pure BR and silica-filled BR vulcanizates: (A) BR and (B) SiO_2/BR(70).

eq. (1). In this sol–gel reaction, ethyl alcohol was detected from the results of gas chromatography analysis for the reaction solution. The amount of ethyl alcohol increased with the progression of the reaction. However, it was difficult to determine the amount of ethyl alcohol quantitatively on the basis of stoichiometry according to the reaction mechanism.

Figure 1 shows FTIR spectra of the pure BR vulcanizate and silica-filled BR vulcanizate. For the pure BR vulcanizate, there was no significant infrared vibration band from 1100 to 1300 cm^{-1}, whereas two infrared bands were revealed at 1172 and 1242 cm^{-1} for the silica-filled BR vulcanizate. The infrared vibration bands of the silica combination from 1020 to 1250 cm^{-1} were attributed to asymmetrical Si—O—Si stretching.[25,29] It is evident that the silica was combined into the rubber matrix by the reaction.

An EDX analysis of the silica-filled NR vulcanizate is shown in Figure 2. Some metals (platinum, zinc, etc.), loaded as metal oxides in the vulcanizing process, were detected with sulfur. Silicon was also detected in the EDX analysis of both the external surface and inner matrix of the silica-filled rubber vulcanizate. The formation of silica was derived from silica filling through the sol–gel reaction. It is concluded that silica was incorporated evenly into the internal matrix as well as external surface of the rubber vulcanizates, and this led to the results of FTIR and EDX. SEM photos of the rubber vulcanizates to their external surface and internal matrix are shown in Figure 3. The silica formed by the reaction was well dispersed on the external surface as well as the internal matrix in NR and BR vulcanizates. Even big size of silica was below 4 μm.
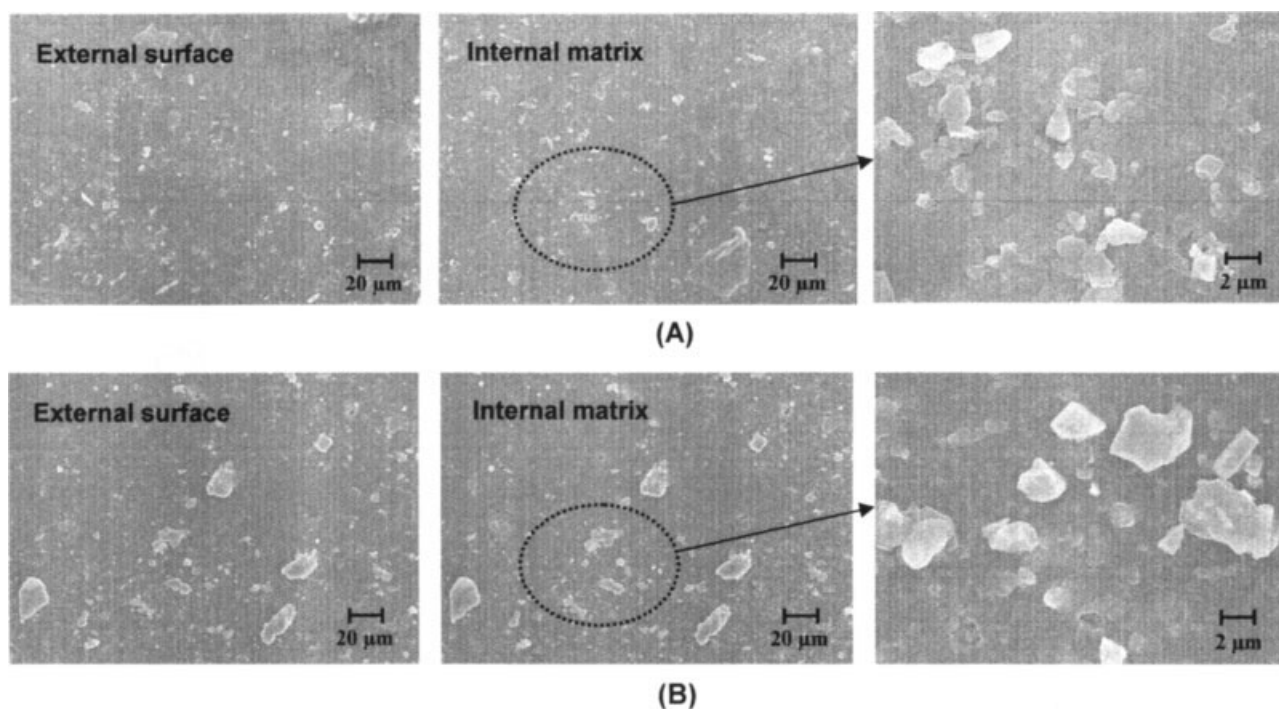
The results of thermogravimetry of rubber vulcanizates with different sol–gel reaction temperatures are

shown in Figure 4. The weight loss of the rubber vulcanizates from 100 to 300°C was derived from the combustion of organic compounds employed in the preparation of rubber vulcanizates as a vulcanizing accelerator and crosslinking agent. The second weight loss appeared from 300 to 400°C. It was due to the combustion of polymers contained in the rubber vulcanizates. Carbon black in the rubber vulcanizates burned from 500 to 600°C. Some unburned components remained above 600°C after the third weight loss was finished.

In the pure rubber vulcanizates, the residual components may be composed mainly of metal oxides employed in the preparation of the rubber vulcanizates. The residual components in the thermogravimetry of the silica-filled rubber vulcanizates increased in comparison with those of the pure rubber vulcanizates. As a result, the silica combined in the rubber matrix was added to residual components
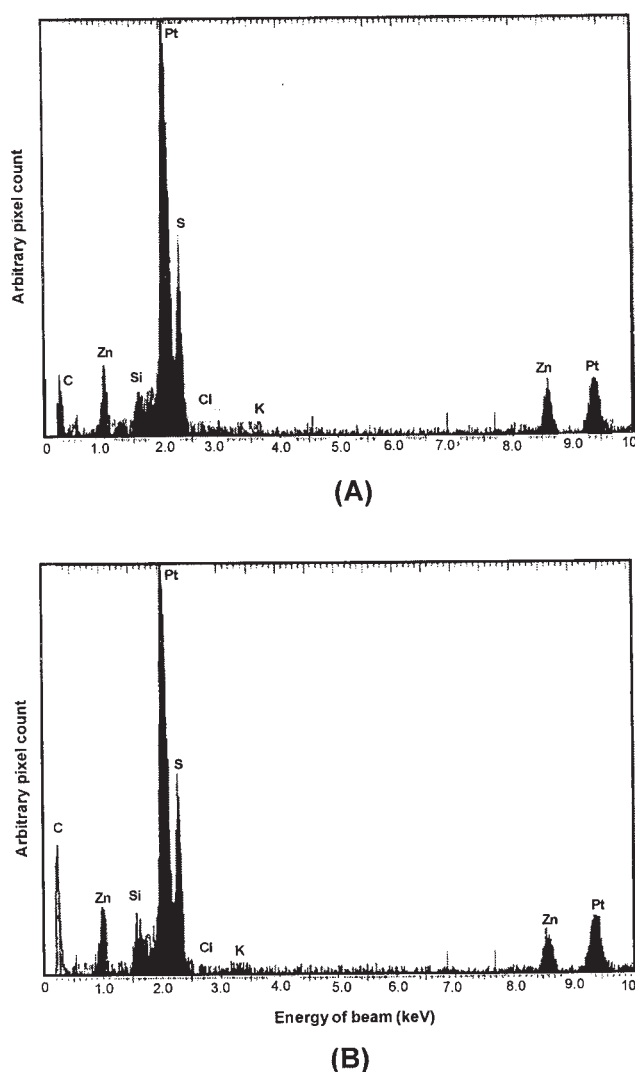
Figure 2 EDX spectra of the silica-filled NR vulcanizate: (A) external surface and (B) internal matrix.

Figure 3 Scanning electron microscopy photographs of the external surface and internal matrix of the silica-filled rubber vulcanizates: (A) NR vulcanizate and (B) BR vulcanizate.

by the thermogravimetry of the pure rubber vulcanizates. The result means that the residual components in the thermogravimetry of the silica-filled rubber vulcanizates included the silica and the metal oxides contained in the pure rubber vulcanizates initially.

Table II lists the results of thermogravimetry for the pure rubber vulcanizates and silica-filled rubber vulcanizates with different sol–gel reaction temperatures. The weight percentages of the remaining component in the thermogravimetry with respect to the pure NR and BR vulcanizates were 6.8 and 4.3%, respectively. As mentioned previously, the amount of the residual component in the thermogravimetry for the silica-filled rubber vulcanizates increased because silica was added to the residual component in the thermogravimetry of the pure rubber vulcanizates. The silica was obtained from incorporation into the rubber matrix by the sol–gel reaction. Therefore, the silica content can be defined as the weight percentage of silica with respect to the total weight. The amount of combined silica became large with the reaction temperature increasing in the silica-filled NR vulcanizate, whereas a reverse trend was observed for BR vulcanizates.

### Reinforcement of the mechanical properties

The hardness, tensile strength, and glass-transition temperature of the rubber vulcanizates are listed in Table III. The hardness increased in the silica-filled rubber vulcanizates. In particular, a significant increase in the hardness appeared in the silica-filled NR vulcanizates. The hardness of the pure rubber vulcanizates of NR and BR was 59 and 68 kg/m^2, respectively. The hardness of the silica-filled rubber vulcanizates increased with the silica filling in the rubber matrix. The enhancement of hardness with silica filling induced the improvement of the resistance to abrasion of the rubber. However, the enhancement of hardness was apart from the reaction temperature.

Moduli of pure and silica-filled rubber vulcanizates are also listed in Table III. The moduli of the silica-filled rubber vulcanizates increased in the whole elongation in comparison with those of the pure rubber vulcanizates. However, there was not a significant variation trend of the modulus increasing with the sol–gel reaction temperature. The increase in the modulus in the silica-filled rubber vulcanizates was independent of the reaction temperature, like the increase in the hardness of the silica-filled rubber vulcanizates in the range of reaction temperatures.

Figure 5 shows the stress–strain curves of the pure rubber vulcanizates and silica-filled rubber vulcanizates. In both NR and BR silica-filled vulcanizates, the moduli at 50%, 100%, and 300% elongation were higher than those of the pure rubber vulcanizates. The elongation–stress curves were almost the same at reaction temperatures of 30 and 50°C for both NR
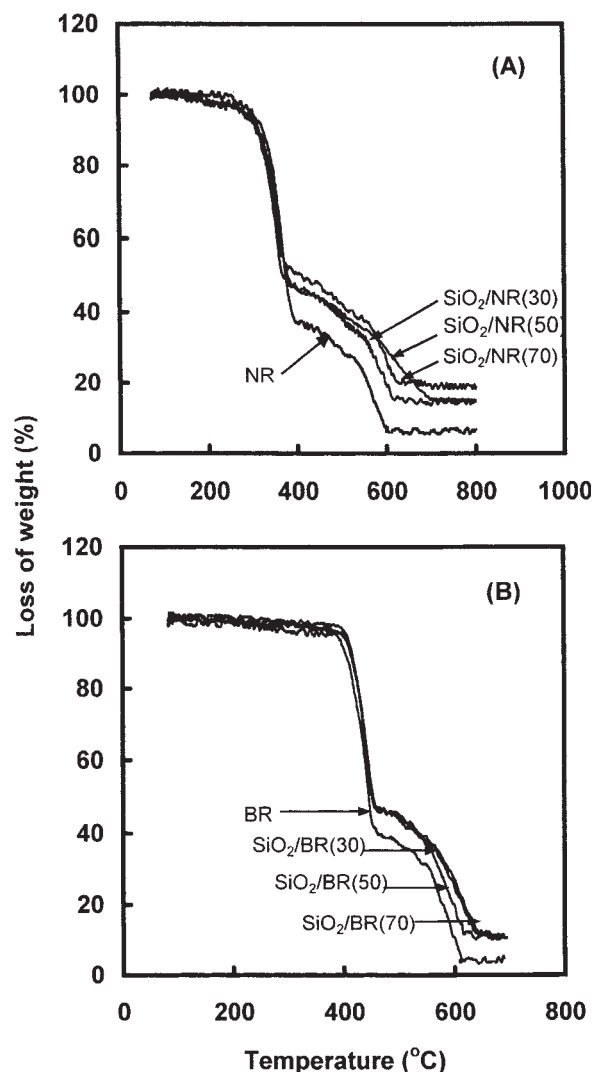
Figure 4 Thermogravimetry results for the silica-filled rubber vulcanizates and pure rubber vulcanizates: (A) NR vulcanizate and (B) BR vulcanizate.

and BR silica-filled vulcanizates. On the contrary, the stress–strain curves of $SiO_2/NR(70)$ and $SiO_2/BR(70)$ vulcanizates decreased after 250% elongation more than those of the pure rubber vulcanizates. It seems that the rubber matrix became weakened in

$SiO_2/NR(70)$ and $SiO_2/BR(70)$ vulcanizates because of the high reaction temperature. It has been known that humid aggravation takes place because of a high temperature and humidity. The decrease in the elongation stress for the $SiO_2/NR(70)$ and $SiO_2/BR(70)$ vulcanizates after 250% elongation may have resulted from the high sol–gel reaction temperature, which could induce humid aggravation.

Reinforcement of the dynamic properties

E' of pure rubber vulcanizates and silica-filled rubber vulcanizates is shown in Figure 6. E' is determined from the stored elastic energy in materials.[30] E' is related to a traction property. If the value of E' becomes higher, the traction property is becoming excellent.[31] The E' values of the silica-filled rubber vulcanizates were larger than those of the pure rubber vulcanizates. This result indicates that the elastic and storage properties of the rubber were enhanced with the silica filling of the pure rubber vulcanizates. The E' values of the silica-filled rubber vulcanizates were similar, although the reaction temperature was different. It seems that the reaction temperature did not affect them.

Figure 7 shows the temperature dependence of E'' for the pure rubber vulcanizates and silica-filled rubber vulcanizates. E'' is derived from a viscous dissipation.[30] E'' influences the viscoelasticity of rubber. The E'' values of the silica-filled rubber vulcanizates were higher than those of the pure rubber vulcanizates. This result means that the viscoelasticity improved with the silica filling of the pure rubber vulcanizates. The E'' values of the silica-filled NR vulcanizates were much higher than those of the pure NR vulcanizate from −50 to 70°C. The values of the silica-filled NR vulcanizates were also similar, being independent of the reaction temperature. For silica-filled BR vulcanizates, the E'' values were higher from −40 to 70°C than those of the pure BR vulcanizate. A difference in the E'' values in the silica-filled BR vulcanizates did not appear with different reaction temperatures.

TABLE II
Results of Thermogravimetry for the Pure Rubber Vulcanizates and Silica-Filled Rubber Vulcanizates

Reaction temperature (°C)	NR		BR	
	Residual component (wt %)	Silica combined in the rubber (wt %)[a]	Residual component (wt %)	Silica combined in the rubber (wt %)[a]
Pure rubber vulcanizate	6.8	—	4.3	—
30	15.1	8.2	11.7	7.4
50	15.3	8.5	10.8	6.5
70	19.7	12.9	10.1	5.8

[a] Weight percentage of silica combined in the rubber = (Weight percentage of the residual component remaining after thermogravimetry in the silica-filled rubber vulcanizate) − (Weight percentage of the residual component remaining after thermogravimetry in the pure rubber vulcanizate).

TABLE III
Results of the GABO Test with the Pure Rubber Vulcanizates and Silica-Filled Rubber Vulcanizates

Rubber	Hardness (kg/cm^2)	Modulus (kg/cm^2)				Tensile strength (kg/cm^2)	Elongation at break (%)	Glass-transition temperature (°C)
		50%	100%	200%	300%			
NR	59	13.7	23.5	59.3	120	287	526	−54.1
SiO$_2$/NR(30)	82	37.2	52.2	100	160	208	394	−54.9
SiO$_2$/NR(50)	86	39.9	53.7	98.4	153	203	400	−55.0
SiO$_2$/NR(70)	87	43.1	50.8	80.1	117	165	410	−55.6
BR	68	19.3	31.8	74.1	134	169	358	−98.6
SiO$_2$/BR(30)	82	34.2	48.8	93.1	151	158	318	−102
SiO$_2$/BR(50)	85	37.3	50.9	92.1	147	159	316	−101
SiO$_2$/BR(70)	81	31.0	41.7	76.9	124	158	365	−102

The temperature dependence of tan δ for the pure rubber vulcanizates and the silica-filled rubber vulcanizates is shown in Figure 8. Tan δ is the function of the viscoelasticity defined as E''/E'. The driving stability, handling stability, and rolling resistance are related to the viscoelasticity of rubber. The viscoelasticity of rubber should be optimized with tempera-

ture variation. In the results for the NR vulcanizates, tan δ of the silica-filled NR vulcanizates was lower than that of the pure NR vulcanizates below 0°C. However, tan δ of the silica-filled NR vulcanizates above 0°C became higher than that of the pure NR vulcanizates. The traction became better as tan δ became higher below 0°C. However, the rolling
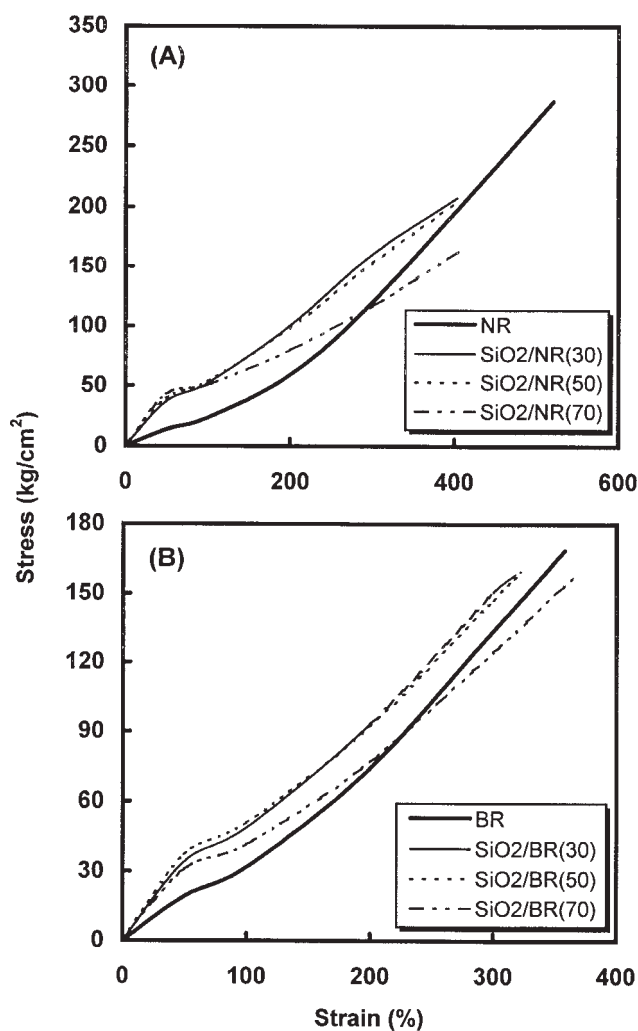

Figure 5 Stress–strain curves for the silica-filled rubber vulcanizates and pure rubber vulcanizates: (A) NR vulcanizate and (B) BR vulcanizate.
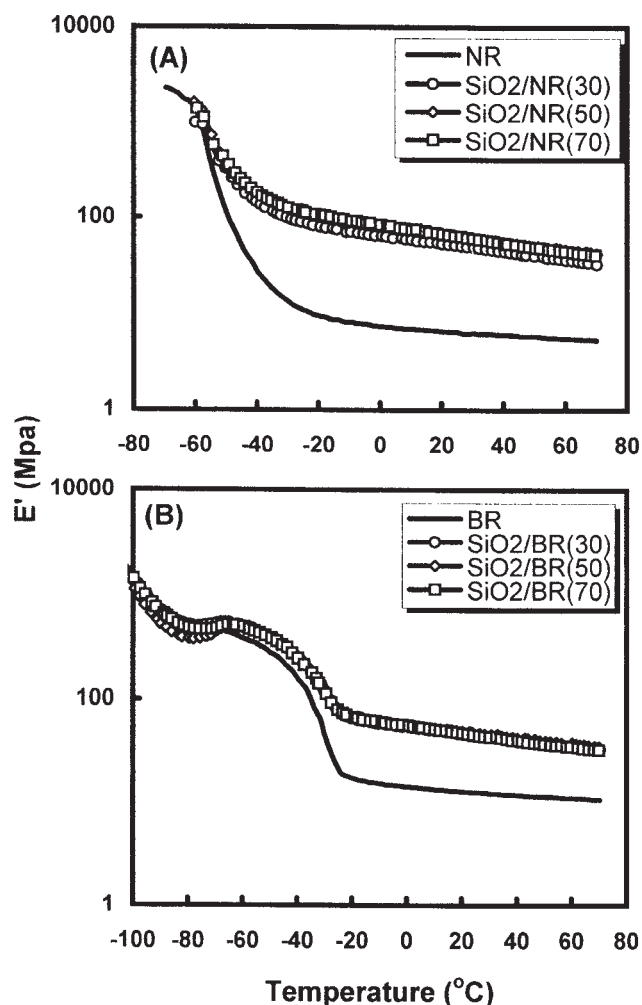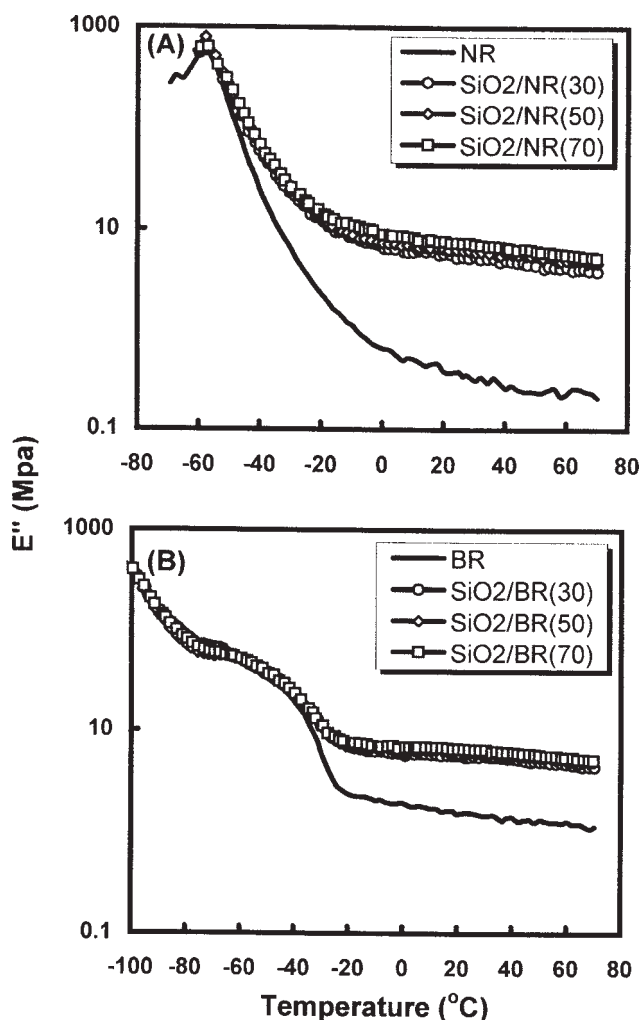

Figure 6 Temperature dependence of E' for the silica-filled rubber vulcanizates and pure rubber vulcanizates: (A) NR vulcanizate and (B) BR vulcanizate.

resistance improved as tan δ became lower from 60 to 80°C. Therefore, the traction and rolling resistance became worse with silica filling of the NR vulcanizates. On the contrary, tan δ of the silica-filled BR vulcanizates agreed mostly with the value of pure BR vulcanizates in the whole temperature range. It can be concluded that the mechanical properties of the silica-filled BR vulcanizates were enhanced. In addition, the viscoelasticity and rolling resistance were maintained, regardless of the silica filling. It seems that the reaction temperature did not affect the tan δ value of the silica-filled BR vulcanizates.

CONCLUSIONS

The amount of silica filling in the rubber vulcanizates was 6–13 wt % for the rubber vulcanizates manufactured by a sol–gel reaction of TEOS at temperatures of 30–70°C. The hardness of the silica–rubber complex was enhanced with silica filling. The

Figure 7 Temperature dependence of E'' for the silica-filled rubber vulcanizates and pure rubber vulcanizates: (A) NR vulcanizate and (B) BR vulcanizate.
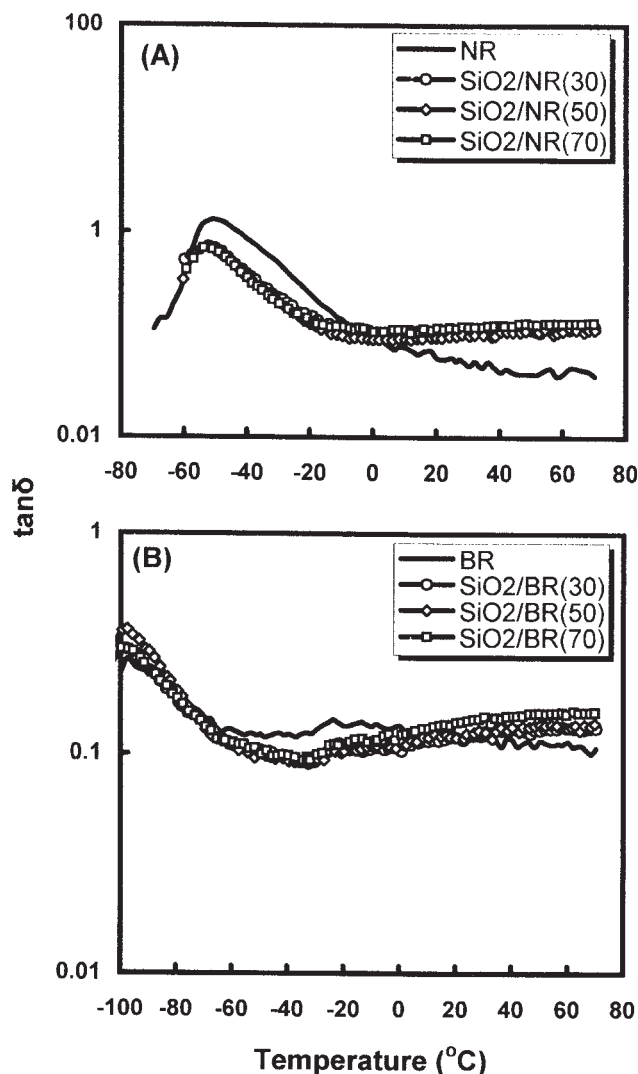
Figure 8 Temperature dependence of tan δ for the silica-filled rubber vulcanizates and pure rubber vulcanizates: (A) NR vulcanizate and (B) BR vulcanizate.

hardness of the silica-filled NR vulcanizate improved significantly compared with that of the pure NR vulcanizate. The moduli at 50, 100, and 300% elongation increased with silica filling in the rubber matrix in comparison with those of the pure rubber vulcanizates. The E' values of the silica-filled rubber vulcanizates with temperature variation became higher than those of the pure rubber vulcanizates. E', however, did not depend on the sol–gel reaction temperature. E'' of the silica-filled rubber vulcanizates also increased in comparison with that of the pure rubber vulcanizates. The tan δ value did not change in the silica-filled BR vulcanizates.

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