Preparation and Properties of a Siloxane-Containing 2-Vinylpyridine–styrene–butadiene Copolymer with Water Glass

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ABSTRACT: A siloxane-containing 2-vinylpyridine–styrene–butadiene copolymer (PSBR/WG) was prepared from a 2-vinylpyridine–styrene–butadiene copolymer (PSBR) latex and water glass. The water glass was added slowly, with stirring, to the PSBR latex. The latex mixture was stirred for 3 h at room temperature, and then, it was coagulated with 1N sulfuric acid producing a sulfate of PSBR with siloxane. The physical properties, such as the filling and stiffening effects of the hybrid polymer, and the vulcanizates were improved. An important advantage of this system is that it is possible to prepare the hybrid polymer simply, and the sodium ions formed in the reaction can also be easily removed. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 891–899, 2006

Key words: hybrid; water glass; siloxane; 2-vinylpyridine–styrene–butadiene copolymer

INTRODUCTION

Commercial silica (white carbon) is a white reinforcing filler, which is mainly composed of siloxane, and it is believed that it might replace carbon black as a filler. However, it is clear that its reinforcing effect is markedly inferior to that of carbon black. If the physical properties of a polymer containing silica were equal to those of carbon black, silica would become widely used in various fields. For example, there are applications in belts, tires,[1,2] commodities *etc.*, and it would be possible to change these products into more colorful ones. Therefore, silica would be used more widely in everyday life, in which case it would come to be considered as a valuable and useful material.

Considerable interest has been shown in silica, and it has now been extensively researched.[1–3] A significant improvement in silica technology was achieved, with the development of particle-size control and surface-modification techniques.[4,5] Furthermore, to acquire new performance and functionality, silica has also been recently utilized in organic–inorganic hybridization.[6] In the industrial field, it is already applied to producing high mileage tires and for coloring part of the tread. A typical recently developed technique for hybridization[7–13] is the sol–gel[14–17] method. Although the resulting products demonstrate excellent functionality, they also have a few problems, as follows: (1) Many factors can influence the reaction process and (2) the raw materials, such as alkyl silicate, are very expensive.

In our recent works[18] on a 2-vinylpyridine–styrene–butadiene copolymer (PSBR) hybrid composite, it was confirmed that hybridization using silanol, which was extracted by tetrahydrofuran (THF) from water glass under acid conditions (pH = 2–3), could offer a new approach to the synthesis of a hybrid composite, since water glass is structurally similar to alkyl silicate but is inexpensive by comparison. Structural characterization of those composites provided evidence that the siloxane was intercalated with the polymer, giving a uniform dispersion of polymer in the clay layer and enhancing the modulus of elasticity and thermal stability. However, this technique still leaves many things to be desired. For example, not only is a solvent required for the process of extracting the silanol[9,10] from water glass, but a drop in the extraction rate also occurs. In addition, the silanol is very unstable.

This article demonstrates the experimental results of comparisons that have been made between the characteristics of PSBR prepared by using water glass directly: PSBR resulting from the use of silanol extracted from water glass, PSBR formed by the sol–gel method

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TABLE I
Recipe and Composition of Siloxane-Containing PSBR Composites

Ingredient (phr)	PSBR/WG	PSBR/WG (THF)	Si-PSBR (sol–gel)	PSBR mix-1	PSBR mix-2
Si-PSBR	110	–	–	–	–
Si-PSBR(THF)	–	110	–	–	–
Si-PSBR (sol-gel)	–	–	110	–	–
PSBR	–	–	–	100	100
Stearic acid	1	1	1	1	1
ZnO	3	3	3	3	3
Sulfur	1	1	1	1	1
CZ[a]	1.5	1.5	1.5	1.5	1.5
Commercial silica (VN-3)	–	–	–	10	10
Si266	–	–	–	0.8	–

[a] Cyclohexylbenzothiazyl sulfenamide.

and the characteristics of copolymers obtained using the white carbon. As such, it provides a vital starting point for both the proper selection of an effective and stable composite, and also for the resolution of various technical and economical problems.

EXPERIMENTAL

Materials

Aqueous sodium silicate (water glass (Na$_2$O·nSiO$_2$·mH$_2$O):JIS third class, n = 3.23, Na$_2$O = 9.8%, SiO$_2$ = 29.67%) was supplied by Fuji Chemical Industry. The PSBR (Nipol LX605 composition: copolymer content = 40%, molar ratio of butadiene/styrene/2-vinylpyridine = 60/15/25) was supplied by Nippon Zeon. The other reagents were supplied commercially and were used without purification.

Measurements

The concentration of SiO$_2$ was determined by a combustion test and by infrared spectroscopy (IR). The combustion test was carried out at a temperature of 800°C (heating rate, 20°C/min) in air using an EYELA electric furnace TMF-100, and the weight of the resulting residue was measured. Fourier transform infrared (FTIR) spectra were recorded on a SHIMAZ spectrophotometer (FT/IR5300) over the wave number range 4000–400 cm^{-1}, using the KBr method. Solid-state CP/MAS ^{13}C NMR spectra were obtained using a Varian Unity plus 300 MHz spectrometer at 75.41 MHz. A zirconium rotor was used at a constant spin-speed of 4 kHz. ESCA spectra were obtained using an Axis His 165 Ultra (Kratos Analytical, UK), with an electron gun power of 150 W (Al anode). The tensile properties of dumbbell-shaped samples were measured at room temperature (23 ± 2)°C and 40–60% humidity, using an Orientec RTC-1225A, having a contact-type elongation indicator between Gauge Marks (Model U-4310), at a cross-head speed of 500 mm/min. The fractured surface of the composite was imaged using a transmission electron microscope (FE-TEM, HF-2000, HITACHI), which was operated with a high-tension voltage of 10 kV. Atomic force microscopy (AFM) experiments of the dried films were carried out at room temperature in air using an SPI3800N (Seiko Instruments). Most of the images were obtained in DMF mode, with a spring constant of 40 N/m and a resonating frequency of 300 kHz.

Preparation of siloxane-containing PSBR using water glass

The 10 wt % siloxane-containing PSBR (PSBR/WG) was prepared from PSBR latex and water glass. PSBR latex (300 g) was placed in a 3-L disposable PP beaker, and then, an appropriate amount (44 g) of water glass was added slowly, by dropping with vigorous stir-
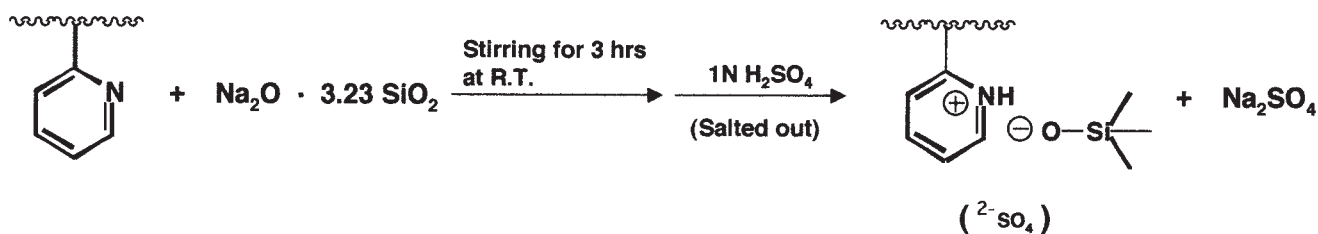
Scheme 1 Preparative procedure of PSBR/WG composites, using water glass.

TABLE II
SiO$_2$ Content of Siloxane-Containing PSBR Composites[a]

Sample	SiO$_2$ content[b] (wt %)
PSBR/WG	10.6
PSBR/WG (THF)	10.9
Si-PSBR (sol-gel)	11.0
PSBR mix-1	10.8
PSBR mix-2	11.2

[a] Theoretical values of SiO$_2$ content are 10.0 wt % for all.
[b] Observed final wt % residue obtained after heating at 800°C in air.

ring. The reaction mixture was stirred for 3 h at room temperature (23 ± 2)°C. The 10 wt % PSBR/WG was produced by coagulation and was salted out with 1N sulfuric acid (1 L). The resulting material was washed with water overnight, to remove the sodium sulfate completely, and was then dried for 48 h at 60°C under reduced pressure (1 mmHg).

Vulcanization

Vulcanization was performed with 3 per hundred rubber (phr) of zinc oxide, 1 phr of stearic acid, 1.5 phr of cyclohexylbenzothiazyl sulfenamide, and finally 1 phr of sulfur at 170°C, as shown in Table I. The time required for vulcanization was determined from the maximum torque of a curastmeter curve.

RESULTS AND DISCUSSION

Siloxane-loading behavior

When water glass was used for the hybridization, it was necessary to consider the existence of sodium ions, given the undesirable effects, e.g., cracking, that Na$^+$ can have on the physical properties. It is possible to remove Na$^+$ by various methods, for example, extraction of silanol using a solvent (THF) and the use of an ion-exchange membrane. However, the removal of sodium ions in a reaction solution is difficult. In this case, when the PSBR latex was coagulated and salted out with dilute sulfuric acid (1N H$_2$SO$_4$), sodium ions were removed simultaneously as sodium sulfate (Scheme 1).

The results of combustion tests for a variety of PSBR/WGs are given in Table II. The value of the SiO$_2$ content revealed by the combustion test is seemingly
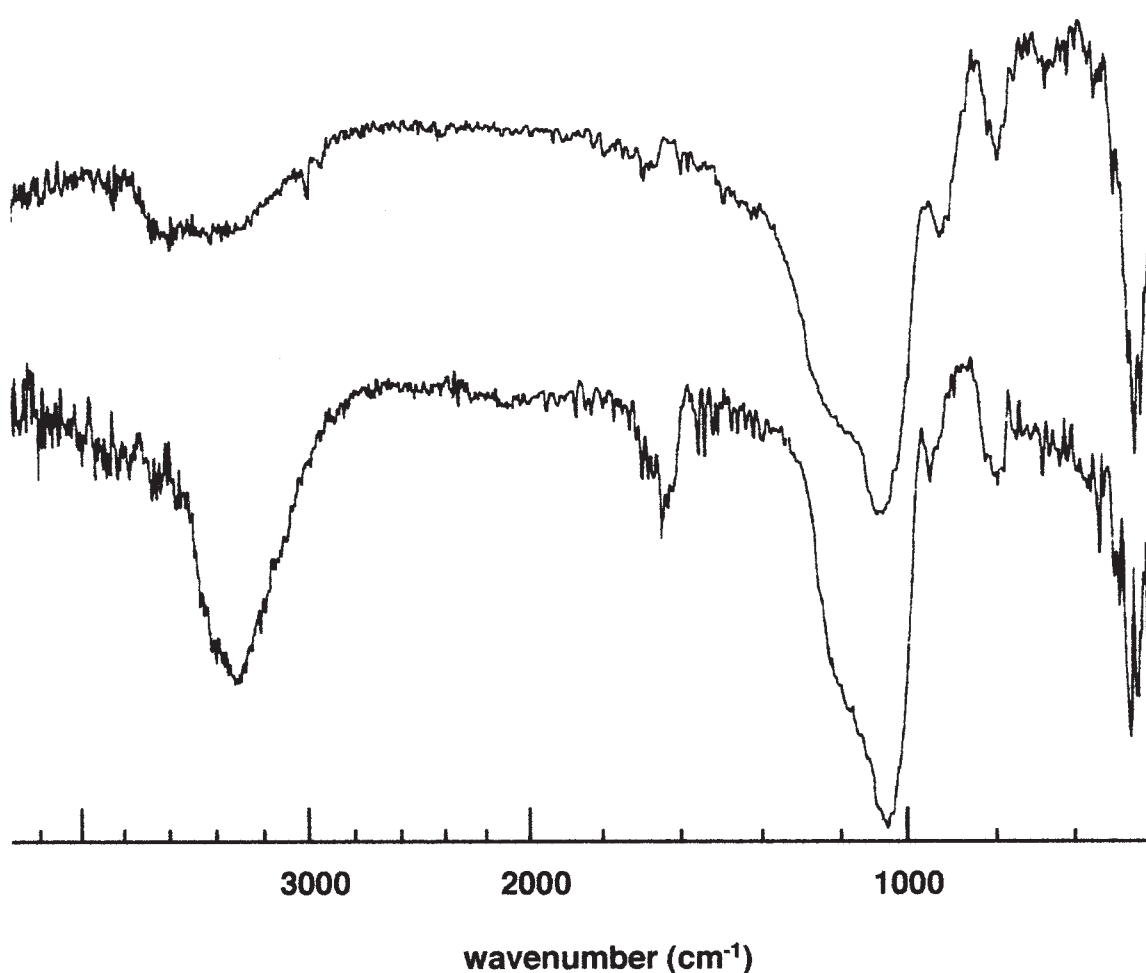
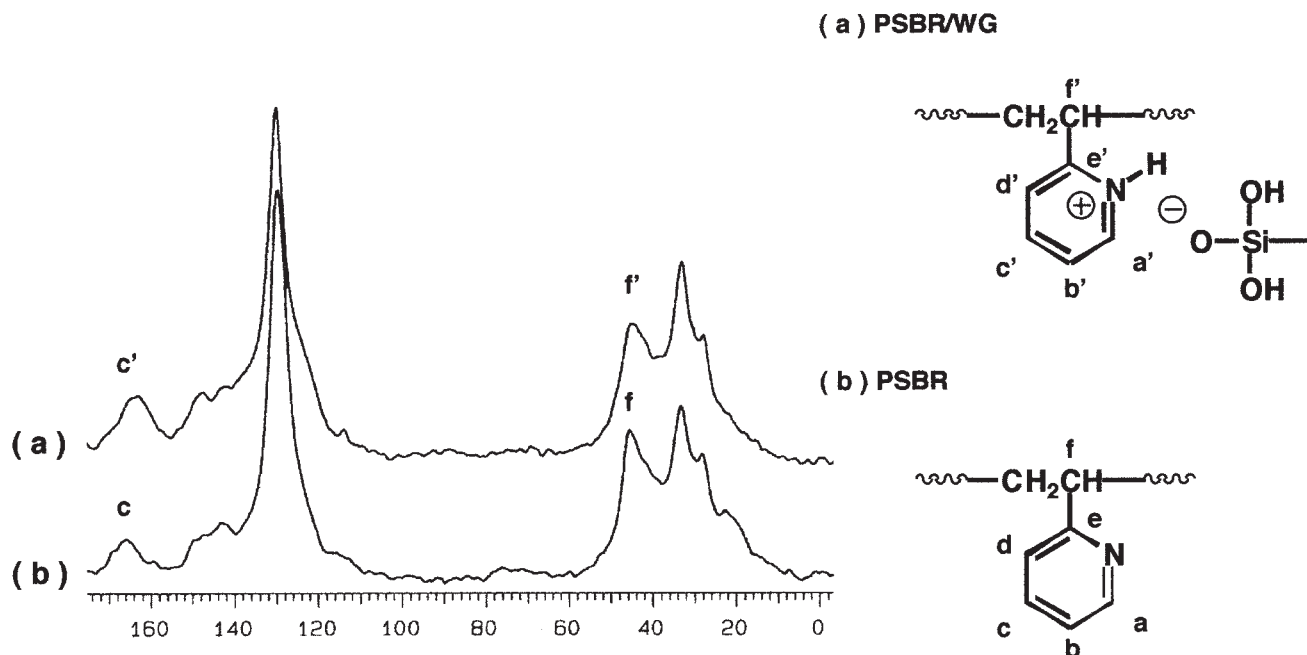**Figure 1** IR spectra of commercial SiO$_2$ (top) and residue of combustion test (bottom).

Figure 2 CP/MAS ^{13}C NMR spectra of PSBR/WG composite (a) and normal PSBR (b).

comparable with the SiO_2 content in water glass. The siloxane contents of the PSBRs were between 85 and 96% and were nearly quantitative. The residue that resulted from the combustion test was confirmed to be SiO_2 by IR spectroscopy (Fig. 1). When using this method, it is necessary to consider the possibility of sodium ions, imparting undesirable effects on the product. Although sodium ions in water glass can generally be removed by a variety of methods, such as extraction of silanol,[18,19] the use of an ion-exchange membrane,[20] and alkylation reactions,[21–24] extraction would be difficult from this latex mixture by these methods. However, in this case, the sodium ions can dissolve in water as sodium sulfate, and so, the sodium ions can be simply removed without the need for any of the methods described earlier.

Characterization of PSBR/WG

Figure 2 shows the CP/MAS ^{13}C NMR spectra obtained from PSBR/WG and composites (PSBR), which were prepared without water glass. Both the PSBR and PSBR/WG exhibit peaks characteristic of carbons on a pyridine ring, the *ortho*-position at 126.8 ppm, the *meta*-position at 140.5 ppm, and the *para*-position at 166.2 ppm and 163.1 ppm. The peaks for the *ortho*- and *meta*-positions were nearly the same, but the peaks for the *para*-position were different. The peak for the *para*-position on the pyridine ring in PSBR/WG shifted by 3.1 ppm in a high magnetic field. Observation of the spectra shown in Figure 2 gives strong evidence that formation of a salt occurs.[25]

The results obtained so far from analysis of the NMR spectrum led to the conclusion that siloxane can be incorporated with PSBR, whether or not it is modified with a silicate salt. However, in the case of this hybridization, it is also possible to produce the sulfate salt. Therefore, elemental analysis was undertaken. The results for PSBR/WG and the composite, which was salted out without water glass, are shown in Table III. The sulfur content was confirmed in each of the samples. The ratio (S:N) of sulfur content to nitrogen content was about 1:2. Also, the ionic valence ratio of the sulfur content to the nitrogen content was about 1:1.

ESCA measurements

The results of ESCA measurement of PSBR/WG prepared by the water-glass method and PSBR are shown in Figure 3. A difference in the chemical states of the PSBR/WG and the PSBR emerged. The N atom on the PSBR/WG appeared at 403 eV, whereas the N atom on

TABLE III
Elemental Analysis of PSBR/WG Coagulated by Sulfuric Acid

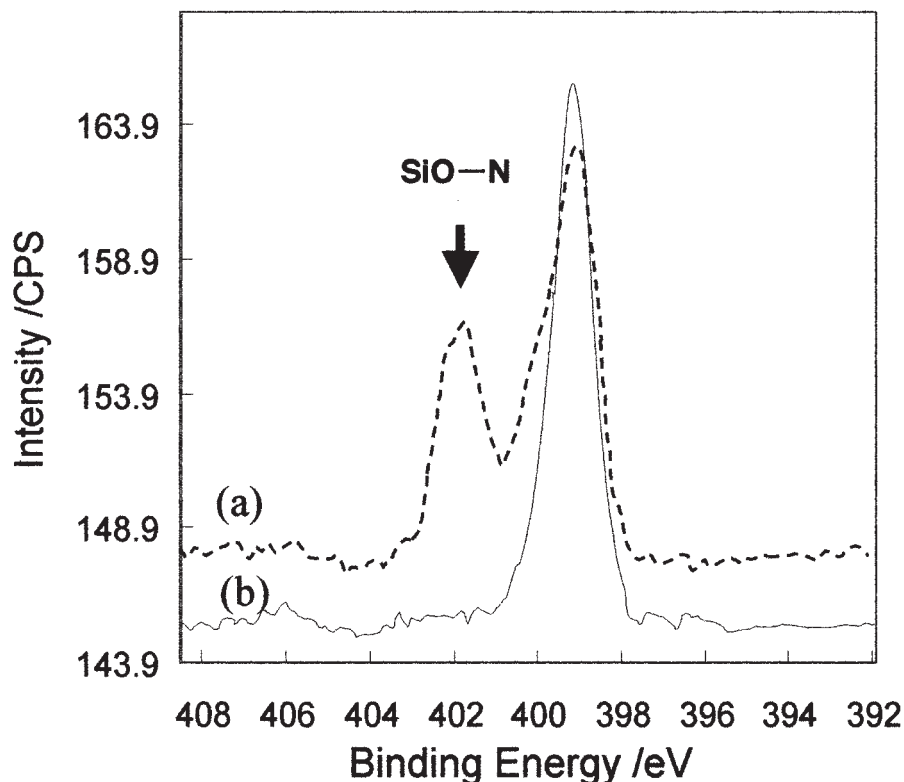| PSBR/WG analysis	Element (%)
C	26.4
H	37.3
N	1.0
S	0.5

Figure 3 ESCA measurements of (a) PSBR/WG (dotted line) and (b) normal PSBR (solid line) composites.

the PSBR was at 309 eV. Since the N atom originating from a pyridine ring on PSBR/WG was at higher energy than the N atom originating from a normal pyridine ring, some combination featuring high electronegativity is suggested. As shown in Figure 3, a linkage between the N atom, originating from the pyridine ring on the PSBR/WG, and the O atom on the silanol generated from the water glass is presumed.

It is clear that the composite, resulting from the PSBR (N atom connect polymer) and the water glass (charge of nonequipments with silanol machine), had joined together by an interaction between the hydroxide group on the silanol and the pyridine ring. Also, it is surmised that this combination is much weaker than

a typical ionic bond. The composite has a large hysteresis loss. Even if the bond between the O atom on the silanol and the N atom on the pyridine is broken, energy must be consumed in order for an O atom on the silanol to immediately recombine with a N atom on a pyridine group in the lattice. As a result, the composite exhibits a large hysteresis loss.

Tensile properties

Table IV shows the influence of the silica content on the tensile properties of the composite, prepared from the PSBR latex and the water glass, and also summarizes the tensile modulus. In terms of the stress–strain

TABLE IV
Tensile Properties[a] of Vulcanized Siloxane-Containing PSBR Composites

Sample	M_{100} (MPa)	M_{200} (MPa)	M_{300} (MPa)	M_{400}[b] (MPa)	TS[c] (MPa)	EL[d] (%)	Hysteresis loss (%)
PSBR/WG	0.9	1.4	2.8	–	11.3	378	61
PSBR/WG (THF)	0.8	1.4	2.6	–	8.3	300	51
Si-PSBR (sol-gel)	0.8	1.4	3.3	–	7.5	402	43
PSBR mix-1	0.6	0.8	1.5	2.5	4.2	403	35
PSBR mix-2	0.6	0.9	1.8	2.7	3.7	400	31

[a] Tensile properties are measured at room temperature, with strain speed of 50 mm/min.
[b] M_x is tensile strength at a strain of x %.
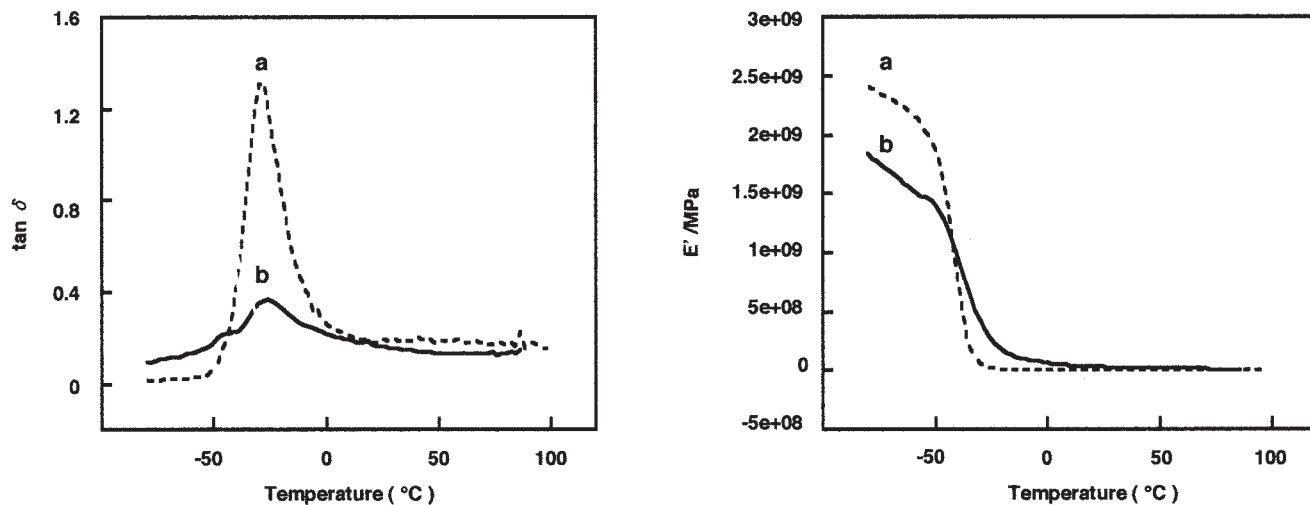[c] Tensile strength at breaking point.
[d] Elongation of breaking point.

Figure 4 Temperature dependence of storage modulus (E') and tan δ of PSBR/WG (b) (solid line) and PSBR mix-1 composites (a) (dotted line).
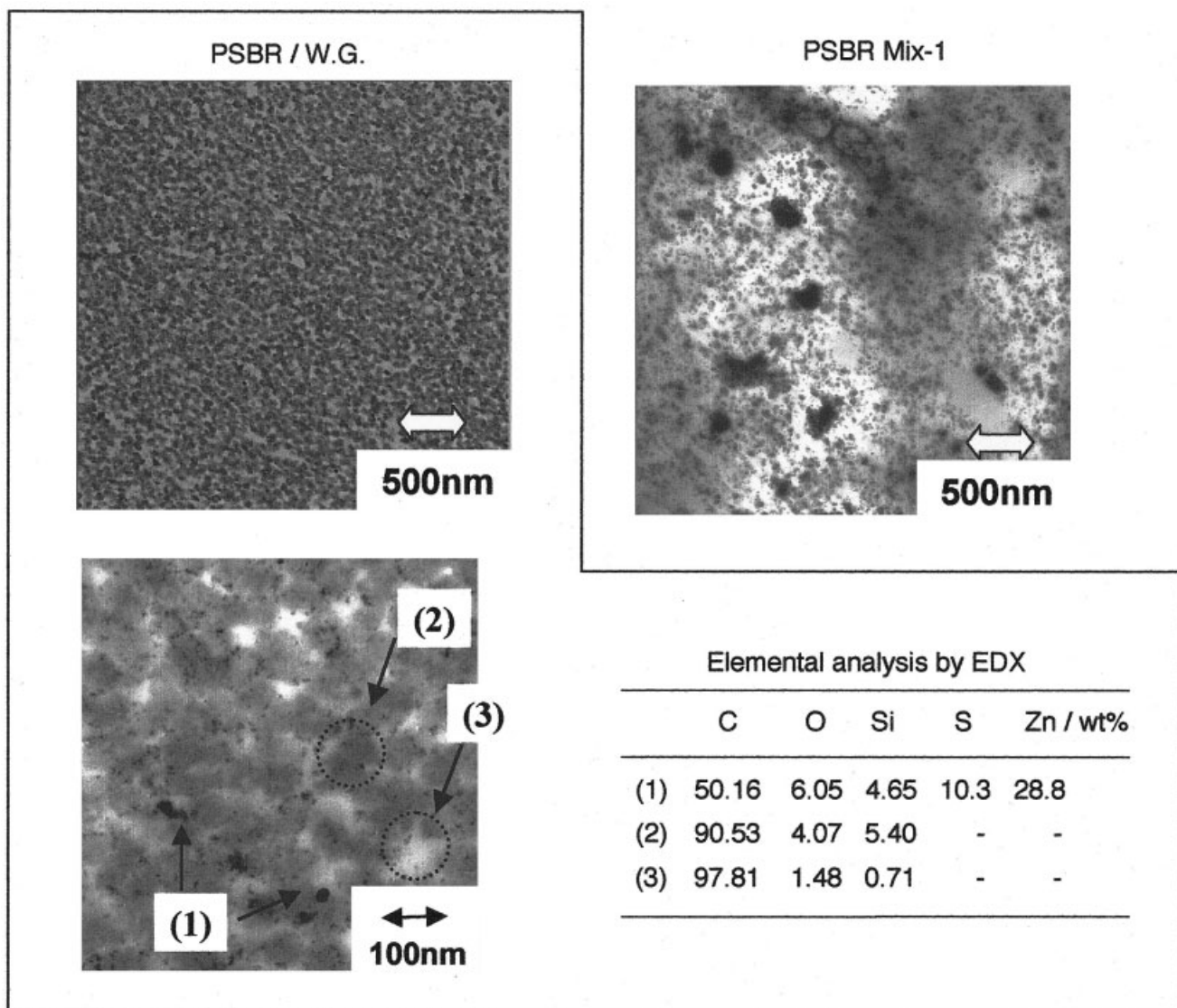

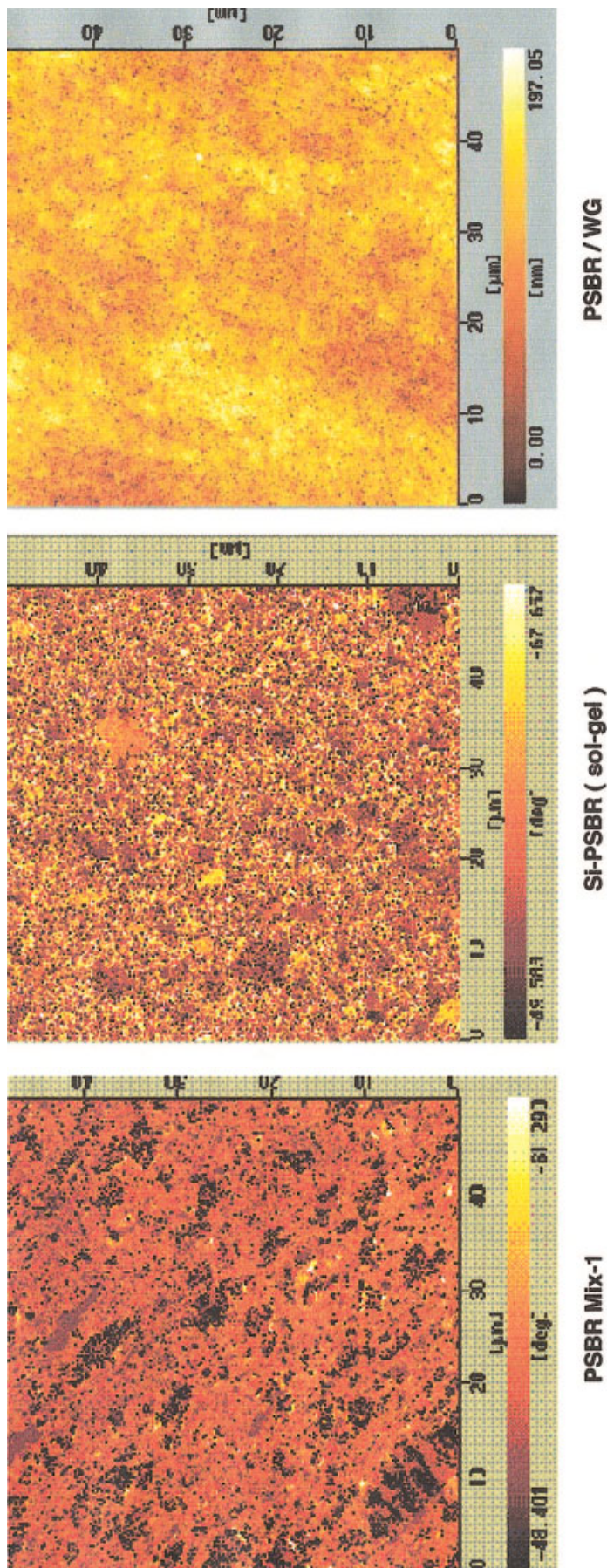**Figure 5** TEM photographs of PSBR/WG and PSBR mix-1 vulcanizates.

Figure 6 AFM images of Si-PSBR (sol–gel) (center), PSBR mix-1 (left), and PSBR/WG (right). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

behavior of the PSBR/WG, although no remarkable telescopic motion as an elastomer was obtained, the maximum tensile strength of the breaking point increased in comparison with PSBR/WG (THF) and Si-PSBR (sol–gel); it is about 2.5 times that of unmodified PSBR. The elongation at breaking point of PSBR/WG is higher than that of PSBR/WG (THF) and lower than that of Si-PSBR (sol–gel).

The values of the tensile modulus at strains of 100 and 200 for PSBR/WG are almost the same as those of PSBR/WG (THF) and Si-PSBR (sol–gel), but at a strain of 300 it is higher than that of PSBR/WG (THF) and lower than that of Si-PSBR (sol–gel).

The hysteresis loss of PSBR/WG is higher than that of PSBR/WG (THF), Si-PSBR (sol–gel), and PSBR mix-1 and mix-2. This data supports the results of the ESCA measurements.

Dynamic mechanical properties

The results of DMA for PSBR/WG and PSBR mix-1 are shown in Figure 4. The main transition is observed for PSBR/WG and PSBR mix-1 in Figure 4. The transition (T_g^S) appearing below 0°C is attributed to the relaxation of the PSBR. On the basis of the tan δ peak, T_g^S for PSBR/WG and PSBR mix-1 are −29.2 and −30.1°C, respectively. Accordingly, the results for T_g^S suggested that the formation of the silica composite has little influence on the additional side of silica.

In the standard silica mixture (PSBR mix-1), E′ decreases with T_g^S. On the other hand, lowering of the elastic modulus is observed, even in the high-temperature region. The shape of tan δ for PSBR/WG is broad, and its value is low (about 0.5) in comparison with normal PSBR. It is considered that micro-Brownian motion in the siloxane network is suppressed by combination in the PSBR.

Morphological comparison

The morphology of the PSBR/WG was analyzed by energy dispersive X-ray (EDX) analysis at several spots (<5 nm in diameter), using the apparatus installed in a TEM. The results are shown in Figure 5.

As for the mixing method (PSBR mix-1; commercial silica), about 250 nm of siloxane condensation was observed everywhere, from TEM measurements on the frozen side of the samples. However, although siloxane condensation was not observed at all for the PSBR/WG produced with water glass, a layer of about 100–200 nm was observed over the whole area in this case. Since the diameter of an average particle of PSBR in latex is 140 nm (measured value), this is considered to be the structure in which the PSBR particles condensed. In the enlarged picture of the PSBR/WG, the black part (1) is zinc oxide, the gray part (2) is rubber-containing siloxane, and the white part (3) is normal

rubber. This means that the siloxane condensate is dispersed uniformly in the PSBR copolymer. PSBR/WG has a unique morphological form, based on the reaction between silanol generated from water glass and the machine pyridine, originating from the PSBR.

The surface morphology and homogeneity of the PSBR/WG, the Si-PSBR (sol–gel) and the PSBR mix-1 were estimated for the film samples by three transformations of the AFM images (Fig. 6). In comparison with the Si-PSBR (sol–gel) and the PSBR mix-1, the PSBR/WG shows a flattening of the particles and the formation of a more homogeneous surface. This result is consistent with the TEM measurements.

CONCLUSION

PSBR/WG was successfully prepared using a PSBR latex and water glass. Their mechanical and thermal properties were investigated.

The PSBR/WG composite was obtained by the water-glass method. Sodium ions in water glass were completely removed. FTIR analysis of the residue of the combustion test confirmed that the measured value of the SiO_2 content in the PSBR/WG composite agreed well with the theoretical value.

The resulting PSBR/WG composite showed the unique features described as follows:

1. The reinforcement effect with respect to hardness and modulus was excellent, and the hysteresis loss was also very good.
2. The cohered particles were approximately 100–200 nm in size.
3. It was suggested that the N atom on the pyridine ring in PSBR latex combined weakly with the O atom on the silanol generated from the water glass.

The water-glass method is expected to be more advantageous in cost than did the conventional sol–gel method, and is simple and easy.

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