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Effect of silane-coupling agent on natural rubber filled with silica generated *in situ*

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The effect of silane coupling agent was investigated for the novel *in situ* silica loading to the natural rubber (*NR*) matrix. The silica was generated *in situ* by the sol-gel reaction of tetraethoxysilane in the *NR* matrix before its crosslinking. γ-mercaptopropyltrimethoxysilane (γ-MPS) significantly prevented the delay of sulfur curing and increased the wettability of *NR* onto *in situ* silica, which resulted in the increase of reinforcement effect for the *NR* vulcanizate. γ-MPS decreased the interaction between the *in situ* silica particles followed by dispersing the *in situ* silica particles homogeneously and decreasing the hardness, compression set, hysteresis loss and storage modulus at the rubbery state of *in situ* silica-filled *NR* vulcanizate. The *NR*/*in situ* silica composite with γ-MPS is a promising material for a high performance rubber product.

1. Introduction

It is well known that carbon black is the most effective reinforcing filler for rubber composites, although it always makes rubber products colored black. Besides carbon black, silica is the other important filler used in the rubber industry. This is because the compounding of silica offers a number of advantages on the vulcanizates such as good tear strength, good abrasion resistance and reduction in heat build-up, to name a few [1–3]. However, the uses of conventional silica such as VN-3 for reinforcement instead of carbon black were limited due to the several problems [4]: (1) higher compound viscosity due to the filler/filler interaction, (2) more difficult mixing and processing, (3) longer vulcanization time, and hence (4) lower network-chain density. Due to these factors, silica does not provide the same level of reinforcement when compared to carbon black of the same particle size. In order to overcome this deficiency of silica, silane coupling agents are used with silica for the reinforcement of rubber vulcanizates.

Generally, mechanical mixing is a usual processing technique to prepare silica/rubber composites or silica-reinforced rubber vulcanizates. Other than the conventional mixing, the *in situ* silica loading using the sol-gel reaction of tetraethoxysilane (TEOS) has been focused as a novel technique to reinforce the rubber vulcanizates [5–10]. The reaction of TEOS takes place in two steps, the hydrolysis and the condensation reactions, to produce SiO_2. This sol-gel process has been noted for the preparation of inorganic glasses at lower temperatures [5–11]. In the field of rubber science, silicone rubber [6, 9, 11], polyisobutylene [12] and several diene rubbers [7, 8, 10, 13–24] were subjected to the *in situ* silica loading. In these cases, the reinforcement effect of *in situ* silica was found to be considerable. However, the sol-gel silica in these studies was generated in the rubber vulcanizates, i.e., the sol-gel reaction of TEOS was conducted in the chemically crosslinked rubber vulcanizates. This technique restricts the thickness of the samples for the homogeneous loading of *in situ* silica. Then, we proposed an alternative practical preparation method of *in situ* silica loading in the rubber matrix [24]. Namely, the sol-gel reaction of TEOS produced the silica nano-particles in the unvulcanized natural rubber (*NR*) matrix, and the *in situ* silica filled *NR* compound was subjected to the mixing and heat pressing to prepare the *NR* vulcanizates. This method was found to be more practical than those of our previous reports, because various shaped vulcanizates can be prepared.

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In this article, the effect of silane coupling agent on the reinforcement of *NR* by *in situ* generated silica in the unvulcanized rubber matrix was investigated. Since the use of silane coupling agent is very common to improve the mechanical properties of rubber materials, it may be also useful for the reinforcement of *NR* vulcanizate, prepared from the *in situ* silica filled *NR* compound. The obtaining results in this study will be beneficial for the practical application of *in situ* generated silica for the reinforcement of rubber vulcanizates. *NR* is renewable and can be produced even after the depletion of fossil fuels (petroleum and coal). Therefore, the composite composed of silica generated *in situ* and "green" (uncured) *NR* is a preferred material from the viewpoint of environmental issues such as possibilities of renewal and recycling, use of biomass, and saving of energy for the processing. Thus, we call it a "green" (eco-friendly) composite.

2. Experimental

2.1. Materials

The grade of used *NR* was RSS#1. The crosslinking agent was sulfur, and cyclohexylbenzothiazyl sulfenamide (CZ-G) was used as an accelerating agent. Nipsil VN-3 from Nippon Silica Ind. Co., whose specific surface area was ca. 200 m^2/g, was used as commercially available silica. It was for the preparation of control sample by the conventional milling method. Other reagents for the vulcanization were commercial grade ones. TEOS was obtained from Katayama Chemical Co. The catalyst for sol-gel reaction was *n*-butylamine, which was of reagent grade purity. γ-mercaptopropyltrimethoxysilane (γ-MPS) from Nippon Unicar Co. was used as a silane coupling agent. All reagents were used as received.

2.2. Preparation

2.2.1. Preparation of the silica-filled rubber compound by the sol-gel method

One kilogram of *NR* was subjected to tight milling to prepare the *NR* sheet of ca. 1 mm thickness, and the sheet was immersed in TEOS for 48 h at room temperature (r.t.). The swollen *NR* sheet was then immersed in the aqueous solution of *n*-butylamine at 40°C for 72 h to follow the sol-gel reaction of TEOS. The amount of *n*-butylamine was 1/20 mol against the amount of TEOS in the swollen sample. The sample was air-dried for 24 h and further dried under vacuum at 30°C for 48 h.

2.2.2. Crosslinking of silica-filled NR

Using the *in situ* silica-filled *NR*, compounds for vulcanization were mechanically prepared by the conventional mixing on a two-roll mill. The recipe of the compounds with and without *in situ* generated silica and γ-MPS is shown in Table I. As a control sample, the *NR* vulcanizate filled with commercial silica (VN-3) was also prepared by the conventional mixing technique. Diethylene glycol (DEG) was also added for mixing of commercial silica. *NR* vulcanizate was prepared by curing the each compound at 150°C for 20 min under pressure in the mold. The thickness of the vulcanizates was *ca.* 2 mm. Here, *NR* vulcanizates without silica, with commercial silica and γ-MPS, and with *in situ* silica and γ-MPS are abbreviated as "*NR-V*," "*NR-mix-γ-V*" and "*NR-in situ-γ-V*", respectively. The abbreviation of *NR* vulcanizate added with commercial silica is "*NR-mix-V*" and that with *in situ* silica is "*NR-in situ-V*," respectively. "*V*" means the vulcanizate, and the sample code without "*V*" means the *NR* compound before crosslinking.

2.3. Material characterizations

2.3.1. Measurements of viscosity

The viscosity of *NR* compounds was measured on a Capillary rheometer Capirograph 1C of Toyo Seiki Seisaku-sho at 100°C, and the scorch time was determined by a Mooney viscometer of Toyo Seiki Seisaku-sho at 121°C.

2.3.2. Thermogravimetry

Thermogravimetric analysis was carried out using a Shimazdu TGA-50 in order to measure the silica

TABLE I Recipes of *NR* compounds and their properties

Sample code	*NR*	*NR-mix*	*NR-mix-γ*	*NR-in situ*	*NR-in situ-γ*
Ingredient (phr)					
NR	100	100	100	0	0
Stearic acid	1	1	1	1	1
ZnO	5	5	5	5	5
Sulfur	2	2	2	2	2
CZ-G[a]	1	1	1	1	1
Diethylene glycol	0	2	2	0	0
Commercial silica (VN-3)	0	33	33	0	0
γ-MPS[b]	0	0	0.5	0	0.5
NR with *in situ* silica	0	0	0	133	133
Properties					
ML_{1+3} (121°C)	19.5	60.5	42.7	44.2	37.0
Viscosity (Pa · s)	3.4×10^4	1.3×10^5	8.0×10^4	9.5×10^4	7.5×10^4
Scorch time (min) (5 points, 121°C)	49.2	>60	39.3	42.7	23.2

[a] Cyclohexylbenzothiazyl sulfenamide.

[b] γ-mercaptopropyltrimethoxysilane.

content in the *in situ* silica-filled *NR* compound and the vulcanizates [22, 23]. A sample (ca. 20 mg) was placed in a platinum pan and heated under air up to 900°C at a temperature increase of 20°C/min.

2.3.3. Measurement of network-chain density

The network-chain density (ν) of the vulcanizates was determined by the micro-compression method [22, 23] using a Thermo-Mechanical Analyzer (TG-50TMA of Shimadzu Co.). The small specimen, with a size ca.1 mm × 2 mm × 2 mm, was soaked in the 1/1 (by volume) mixture of tetrahydrofuran and benzene for 10 h at 25°C. Then, the swollen sample was placed in the instrument, and was compressed by loading at 180 g/min. The degree of deformation was measured for the calculation of the network-chain number (n) by Equation (1) [25, 26],

$$f = kT(n/V_0')(\alpha - 1/\alpha^2)A_0\{[(L_{S0}/L_0)^3 - \phi] \times (1-\phi)^{-1}\}^{1/3} \qquad (1)$$

where f is the compression stress, k is the Boltzmann constant, L_0 is the sample height before swelling, L_{S0} is the sample height after swelling, L_S is the height of swollen sample after the compression, A_0 is the cross-sectional area of the sample before swelling, α is "L_S/L_{S0}," V_0 is the total volume of the sample, V_0' is "$V_0(1-\phi)$" and ϕ is the volume fraction of filler. The n values reported were based on the average of three measurements for each sample, and the ν was determined using Avogadro's number and the n value.

2.3.4. Tensile measurement

Tensile properties of the vulcanizates were measured on a tensile tester (Strograph-R2 from Toyo Seiki Seisaku-sho) at 25°C, with a strain rate of 500 mm/min, using dumbbell type specimens in accord with JIS K6301. The length between the benchmarks was 20 mm. Values reported were based on the average of three measurements for each sample. Hysteresis behavior of the vulcanizates was also elucidated on this tensile tester with a strain rate of 100 mm/min by repeating the stretching up to 50% five times.

2.3.5. Measurement of compression set

Compression set was measured according to JIS K6262 at 70°C. The rate of compression strain was 25% and compression time was 168 h.

2.3.6. Measurement of rebound resilience

Rebound resilience was measured on a Lupke pendulum tester of Kobunshi Keiki Seisaku-sho according to JIS K6255.

2.3.7. Dynamic mechanical analysis

Dynamic mechanical properties were evaluated using a Rheospectolar DVE-4 instrument (Rheology Co.) at a frequency of 10 Hz and a heating rate of 2°C/min. Storage modulus (E') and loss tangent (tanδ) were measured as a function of temperature. The tensile mode was used, and the applied static force was automatically controlled. The size of the specimen was 20 mm × 5 mm × 2 mm, and the dynamic strain was ±10 μm.

2.4. Morphological analysis

2.4.1. Atomic force microscopy (AFM)

The sample films were frozen in liquid nitrogen and broken and the obtained cross sections were subjected to observation by AFM using an SPM-9500J2 of Shimadzu Inc., Japan. The AFM measurement was carried out in the dynamic mode, where the cantilever is oscillated close to its response. The change of the vertical cantilever oscillation amplitude is detected, which is caused by the interaction of the tip with the surface. A silicon cantilever (type NCHR-16, NANOSENSORS Dr. Olaf Wolter GmbH, Germany; typical length, 125 μm; width, 30 μm; thickness, 4 μm; spring constant, 42 N/m; response frequency, 330 kHz) was used. The cantilever was excited at 312.9–313.0 kHz in air. The height signal was recorded. Imaging was performed by displaying a three-dimensional (3D) image computer from the height data. The AFM scanner was placed on an air-spring vibration insulator. Before recording the data, the instrument and the samples were aged more than two hours by the scanning operation. This aging serves to reduce the specimen drift that is induced thermally. However, it should be noted that small crumples running parallel in the same direction are artifacts. In order to reduce the intensity of these artifacts, the images have been processed by the Fourier filtering technique.

2.4.2. Transmission electron microscopy (TEM)

Ultra thin films of the samples were prepared using a microtome (KLB 4800A Ultrotome) in liquid nitrogen of LKB 14800 Cryokit. The specimen was placed on a copper grid, which was coated in advance with Folmvar^R and evaporated carbon. Then, TEM observation was carried out with a transmission electron JEOL TEM-100U instrument of Hitachi Ltd. The accelerating voltage was 80 kV.

3. Results and discussions

3.1. Effect of γ-MPS on the viscosity of *in situ* silica-filled *NR*

The effect of silane coupling agent (γ-MPS) on the viscosities of *NR-in situ-*γ was clearly appeared as shown in Table I: the addition of γ-MPS decreased the viscosity at 100°C and Mooney viscosity (ML_{1+3} (121°C)) of *in situ* silica filled *NR* compound similarly with the effect of γ-MPS on the conventional silica-filled *NR* compound. The degree of decrease of viscosity was smaller in *NR-in situ-*γ than in *NR-mix-*γ. Since the aggregation of silica in the rubber compound is assumed to bring about the formation of pseudo-network structure followed by increasing its viscosity in general, the results of viscosity in this study qualitatively suggest that the degree of aggregation of *in situ* silica in *NR-in situ-γ* was less than *NR-in situ* and *NR-mix-γ*. Namely, the interaction between the *in situ* silica particles is considered to become weak by adding γ-MPS, probably due to the decrease of silanol groups on the *in situ* silica surface. This result will be favorable for the processing.

3.2. Effect of γ-MPS on the vulcanization of *in situ* silica-filled *NR*

The scorch times of *NR* compounds are summarized in Table I. The scorch time of *NR* with *in situ* silica was shorter than those of *NR* with conventional silica VN-3, and the addition of γ-MPS made the scorch time of *NR-in situ-γ* shorter for both *NR*'s with *in situ* silica as well as *NR-mix-γ*. The scorch time of *NR-in situ-γ* was the shortest among the samples, which implies that the minimum deactivation (due to adsorption) of crosslinking reagents was achieved by the simultaneous use of *in situ* silica and γ-MPS.

The vulcanization to prepare the sheet was carried out at 150°C for 20 min in a mold. The network-chain density of *NR-in situ-V* was higher than that of *NR*-mix-V as shown in Table II. The presence of γ-MPS increased the network-chain density of *in situ* silica-filled *NR* similarly with the case of conventional silica VN-3 (*NR*-mix-γ-V). The degree of increase of network-chain density was smaller in the system of *in situ* silica than that of VN-3. This suggests that the number of silanol groups of *in situ* silica particles was less than that of VN-3. Generally, DEG is mixed in the rubber compound with the conventional silica, because the silanol groups on the surface of VN-3 retard the crosslinking reaction of rubber by sulfur. However, the addition of PEG is not necessary for the *in situ* silica-filled *NR* compound.

3.3. Effect of γ-MPS on the mechanical properties of *NR* vulcanizates

The results of tensile measurements of *NR-in situ-γ-V* and *NR-mix-γ-V* are shown in Fig. 1 and Table II with those of *NR-V*, *NR-mix-V* and *NR-in situ-V*. The stresses at 50%, 100%, 300% and 500% elongations (M_{50}, M_{100}, M_{300} and M_{500}, respectively), tensile strength at break (T_B) and elongation at break (E_B) are summarized together with the hardness, compression set and rebound resilience. γ-MPS increased the stress of *in situ* silica-filled vulcanizate as well as the effect of γ-MPS on the conventional silica-filled vulcanizate. It is attributable to the increase of network-chain density of the *NR* vulcanizates by adding the silane coupling agent. Interestingly, *NR-in situ-γ-V* showed the highest stresses at 300% and 500% elongations among all *NR* vulcanizates, whereas its stress at low elongation was comparable with those of *NR-mix-γ-V*. This result is discussed in the section on the morphology. The degree of increase on the stress of *in situ* silica-filled vulcanizate by adding γ-MPS, however, was smaller than that of conventional silica-filled vulcanizate, which is ascribed in the difference of numbers of silanol groups on the silica surfaces between *in situ* silica and VN-3. It is worth noting that the tensile properties of *NR-in situ-V* were comparable to those of *NR-mix-γ-V*, even though the silane coupling agent was not added to *NR-in situ-V*. This observation clearly displays the usefulness of *in situ* silica loading for the rubber technology.

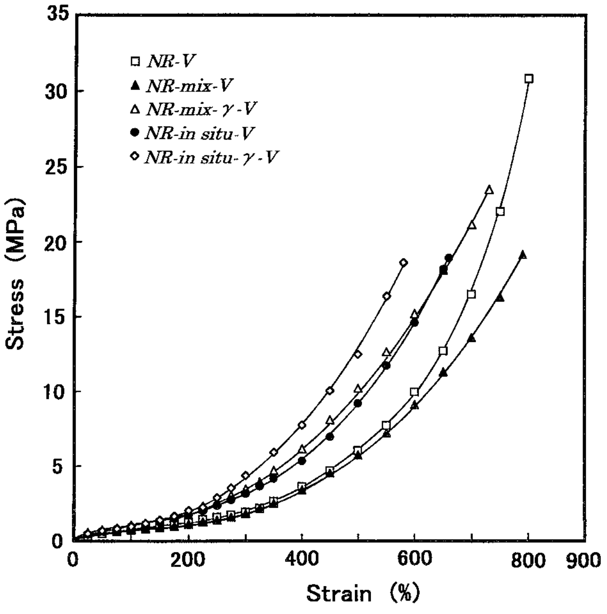


Figure 1 Stress-strain curves of *NR* vulcanizates at 25°C.

TABLE II Physical properties of *NR* vulcanizates

Sample code	*NR-V*	*NR-mix-V*	*NR-mix-γ-V*	*NR-in situ-V*	*NR-in situ-γ-V*
Silica content (%)	0	20.1	20.1	21.4	21.3
ν[a] (mol/cm^3)	1.41×10^{-4}	7.83×10^{-5}	1.30×10^{-4}	1.32×10^{-4}	1.58×10^{-4}
M_{50} (MPa)	0.48	0.66	0.75	0.64	0.68
M_{100}(MPa)	0.74	0.76	1.08	0.95	0.97
M_{300} (MPa)	1.92	1.83	3.45	3.14	4.36
M_{500}(MPa)	6.00	5.70	10.2	9.17	12.5
T_B (MPa)	30.8	19.2	23.5	18.9	18.6
E_B (%)	800	790	730	660	580
Hardness[b]	39	54	58	50	48
Compression set (%)	39	92	73	63	45
Rebound resilience (%)	82	58	62	67	70

[a] Network-chain density measured by the micro-compression method.
[b] Shore A.

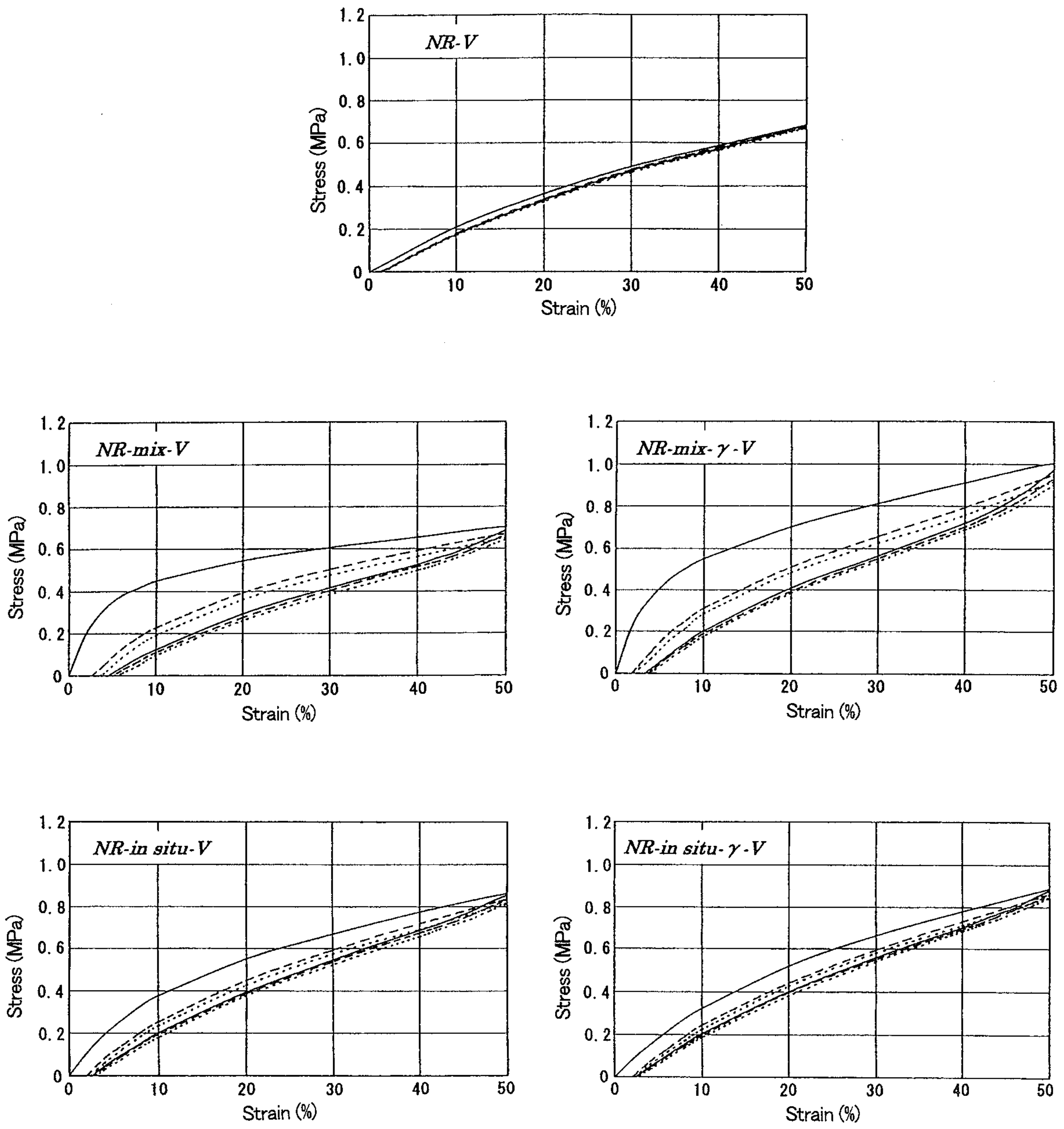


Figure 2 Hysteresis behaviors of *NR* vulcanizates at 25°C. 1st (———), 2nd (-------) and 5th (······).

The hardness of *NR-in situ-γ-V* was smaller than that of other silica-filled vulcanizates in spite of its high network-chain density, as shown in Table II. The silane coupling agent increases the hardness of *NR-mix-γ-V*, whereas the opposite phenomenon was observed in *NR-in situ-γ-V*. These results were equal with those of the tensile measurement, i.e., the stress at the small deformation of *NR-in situ-γ-V* was lower than those of the others. On the other hand, the rebound resilience of *NR-in situ-γ-V* was largest among the silica-filled vulcanizates. The effect of γ-MPS on the rebound resilience of *NR-in situ-γ-V* was similar with that of *NR-mix-γ-V*, i.e., the silane coupling agent increased the rebound resilience of both *NR* vulcanizates.

TABLE III Hysteresis behavior and dynamic mechanical properties of *NR* vulcanizates

Sample code	*NR-V*	*NR-mix-V*	*NR-mix-γ-V*	*NR-in situ-V*	*NR-in situ-γ-V*
Hysteresis behavior					
1st HL[a] (%)	6.2	37.8	34.8	21.3	17.2
2nd HL[a] (%)	2.6	21.5	17.8	10.0	7.7
5th HL[a] (%)	2.3	19.2	15.1	8.7	6.7
Dynamic mechanical properties					
tanδ peak position (°C)	−52.1	−50.7	−49.8	−50.2	−47.5
tanδ peak height	1.56	1.05	1.06	1.24	1.37
E' at 25°C (MPa)	1.81	7.20	10.5	7.08	3.91

[a] HL denotes the percent of hysteresis loss relative to the stored energy.

Totally, the physical properties of *NR-in situ-γ-V* were more close to those of *NR* vulcanizate without silica except the tensile properties. These unique characteristics of *NR-in situ-γ-V* also appeared in the hysteresis behavior. The hysteresis measurement up to 50% are shown in Fig. 2 and the percents of the hysteresis loss relative to the stored energy (HL), by repeating the stretching up to 50% elongation, are summarized in Table III. The HL of *NR-in situ-γ-V* was lowest among the samples. Since the amounts of silica of all samples were nearly equal and the network-chain density of *NR-in situ-γ-V* was largest among the samples, the difference of properties of the silica-filled *NR* vulcanizates should result in the characteristics of morphology and the interactions between silica particles and between silica and rubber. In order to elucidate this point, the samples were subjected to the dynamic mechanical and morphological analyses.

3.4. Effect of γ-MPS on the dynamic mechanical properties of *NR* vulcanizates

The temperature dispersions of E' and tanδ of the samples are illustrated in Fig. 3 and the tanδ peak position, tanδ height and E' at 25°C are summarized in Table III. In our previous article [24], the *in situ* silica-filled vulcanizate was reported to show the lower E' at 25°C than *NR-mix-V*, although the observed reinforcement effect of silica particles at the large deformation of the former was larger than the latter. It was assumed to be due to the larger aggregates of silica particles forming the pseudo-network structure in *NR-mix-V* than *NR-in situ-V*, because the pseudo-network of silica particles give a reinforcement effect at the small deformation but it is not stable for the large deformation. As shown in Table III, the E' at 25°C were in order of *NR-mix-V* > *NR-mix-γ-V* > *NR-in situ-V* > *NR-in situ-γ-V* and the E' at 25°C of *NR-in situ-γ-V* was lowest among the samples, although the amounts of silica between them were similar with each other and the order of network-chain density was opposite (*NR-mix-V* < *NR-mix-γ-V* < *NR-in situ-V* < *NR-in situ-γ-V*). This means that the formation of pseudo-network structure became less in *NR-in situ-γ-V* than the others by adding of γ-MPS to the *in situ* silica-filled *NR*. This consideration is consistent with the results of hardness and stress at the small deformation of the samples.

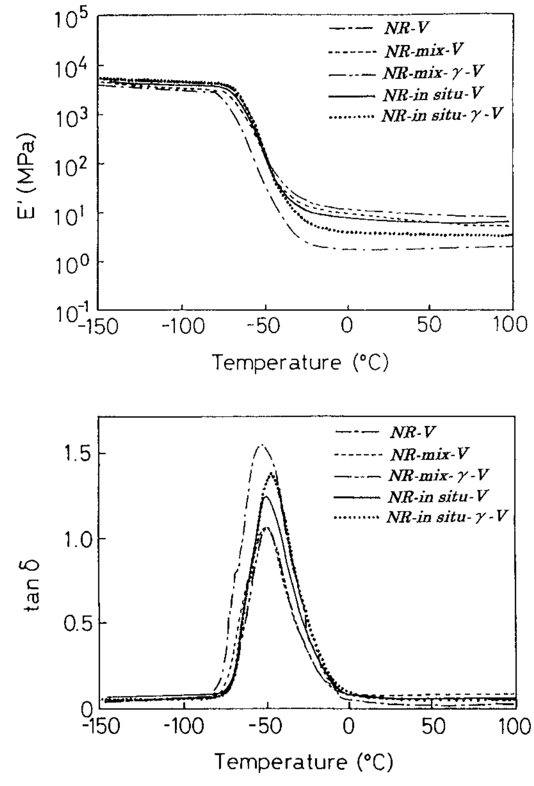


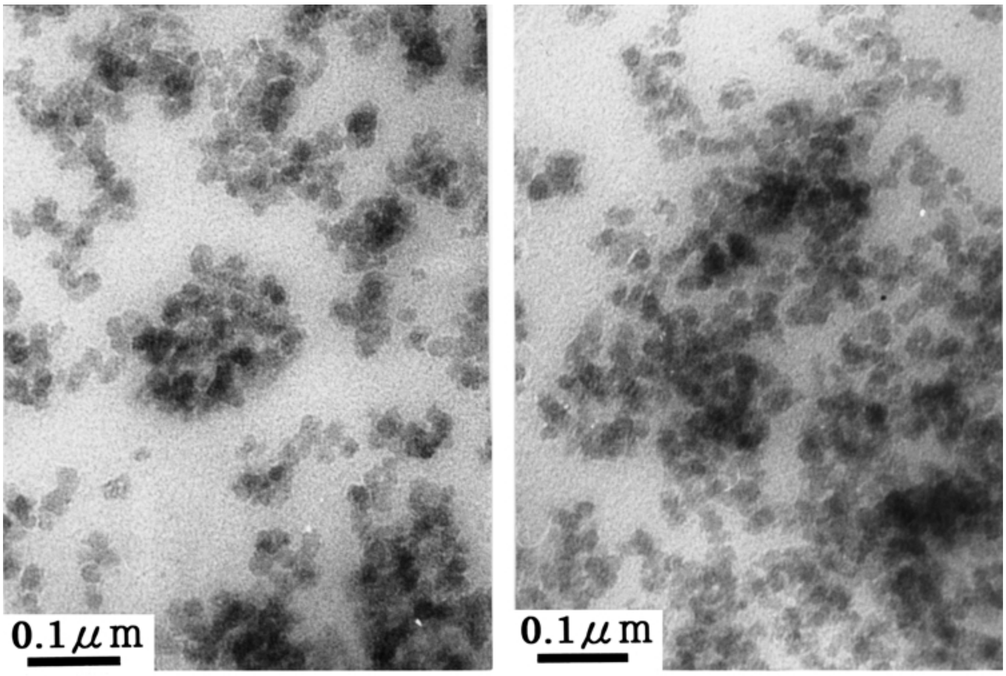
Figure 3 Temperature dispersions of E' and tanδ of *NR* vulcanizates.

The comparison among the tanδ peaks of *NR* vulcanizates gave the information on the interaction between the rubber and silica particles. It is known that the increases of network-chain density and amount of reinforcing filler give rise to the shift of tanδ peak top to the higher temperature region and to make the tanδ peak broad and low in general. These changes are accepted to be mainly due to the combination of two factors from the network structure and the interaction between the rubber and filler. In the case of conventional silica VN-3, the tanδ peak of *NR-mix-γ-V* became sharp by adding the silane coupling agent. Namely, the shoulder peak in the tanδ curve of *NR-mix-V* disappeared by adding γ-MPS, which means that the interaction between the rubber molecule and silica particle of *NR-mix-γ-V* increased by adding γ-MPS. The position and height of tanδ peak top of *NR-mix-γ-V* were almost equal with those of *NR-mix-V*.

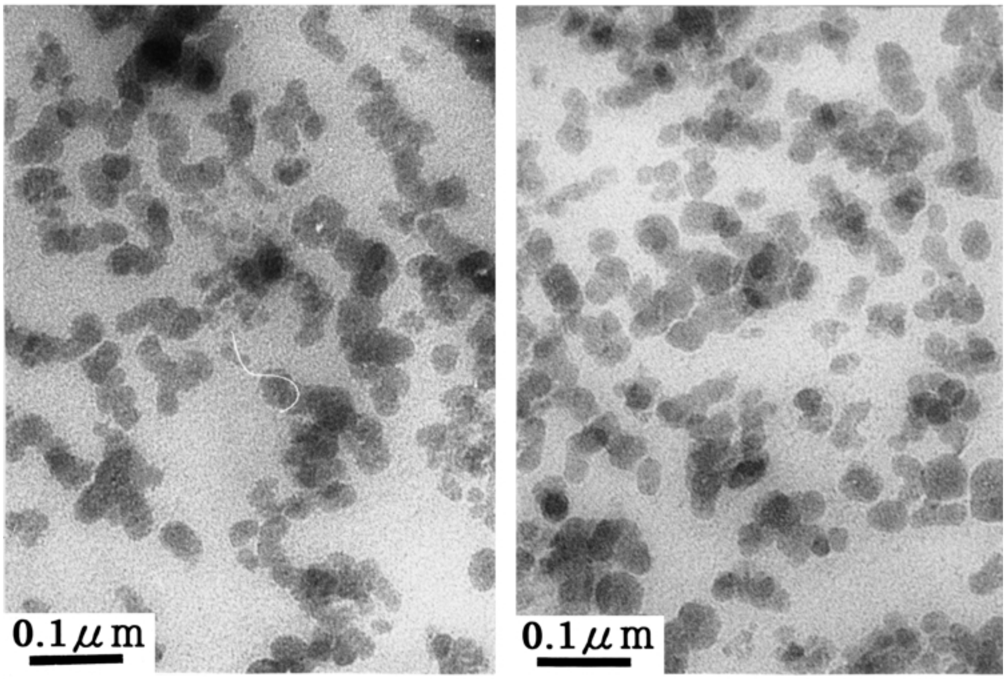
On the other hand, both position and height of tanδ peak of *NR-in situ-γ-V* was changed by adding the silane coupling agent: its peak position shifted to the higher temperature region and its height became higher when compared with those of *NR-in situ-V*. Additionally, the shape of tanδ peak of *NR-in situ-γ-V* was very similar with that of *NR-V*, i.e., one peak top and shoulder peak were detected in both *NR-V* and *NR-in situ-γ-V*. The effect of γ-MPS on the tanδ curves was different between the *in situ* silica-filled vulcanizate and the conventional silica-filled vulcanizate as well as the results of E'. Then, why was the reinforcement effect by *in situ* silica with γ-MPS detected under the large deformation?

3.5. Effect of γ-MPS on the morphology of *in situ* silica in *NR* vulcanizates

The results of TEM observations are shown in Fig. 4. It is clear that the *in situ* silica particles in *NR-in situ-V* were larger than VN-3 and their diameter were ca. 20–45 nm. *In situ* silica was found to disperse more homogeneously in the *NR* matrix than VN-3. This clearly implies that the inter-particle interaction among *in situ* silica particles in *NR-in situ-V* was smaller than that between VN-3 silica particles in *NR*-mix-V, as expected from the results of viscosity and mechanical analyses. As shown in Fig. 4, the addition of γ-MPS to the *in situ* silica-filled *NR* seems to bring about more



NR-mix-V *NR-mix-γ-V*



NR-in situ-V *NR-in situ-γ-V*

Figure 4 TEM photographs of *NR* vulcanizates.

homogeneously dispersed *in situ* silica particles in the *NR* matrix.

AFM photographs are shown in Fig. 5, where the unevenness on the surface of broken sample was displayed. Interestingly, the silica aggregates were clearly reflected in the AFM photograph of *NR-mix-V*, whereas the smoother surface was detected in *NR-in situ-V* than in *NR-mix-V*. Moreover, the adding of γ-MPS to *NR-in situ-γ-V* made its surfaces smoother than to *NR-in situ-γ-V*. This observation suggests that the wettability of *NR* onto *in situ* silica was increased by the silane coupling agent which modified the *in situ* silica surface to more compatible one with *NR*, and γ-MPS linked the *in situ* silica particles to the rubber molecules. As the results of them, the number of crevasse between *NR* and *in situ* silica became much less in *NR-in situ-γ-V* than *NR-in situ-V*.

From the results of TEM and AFM, the factors for these unique characteristics of *NR-in situ-γ-V* appeared: the good reinforcement effect at the large deformation is attributable to the high wettability between the *in situ* silica and *NR* molecules and to the homogeneous dispersion of *in situ* silica particles whose diameter was ca. 20–45 nm in *NR* matrix.

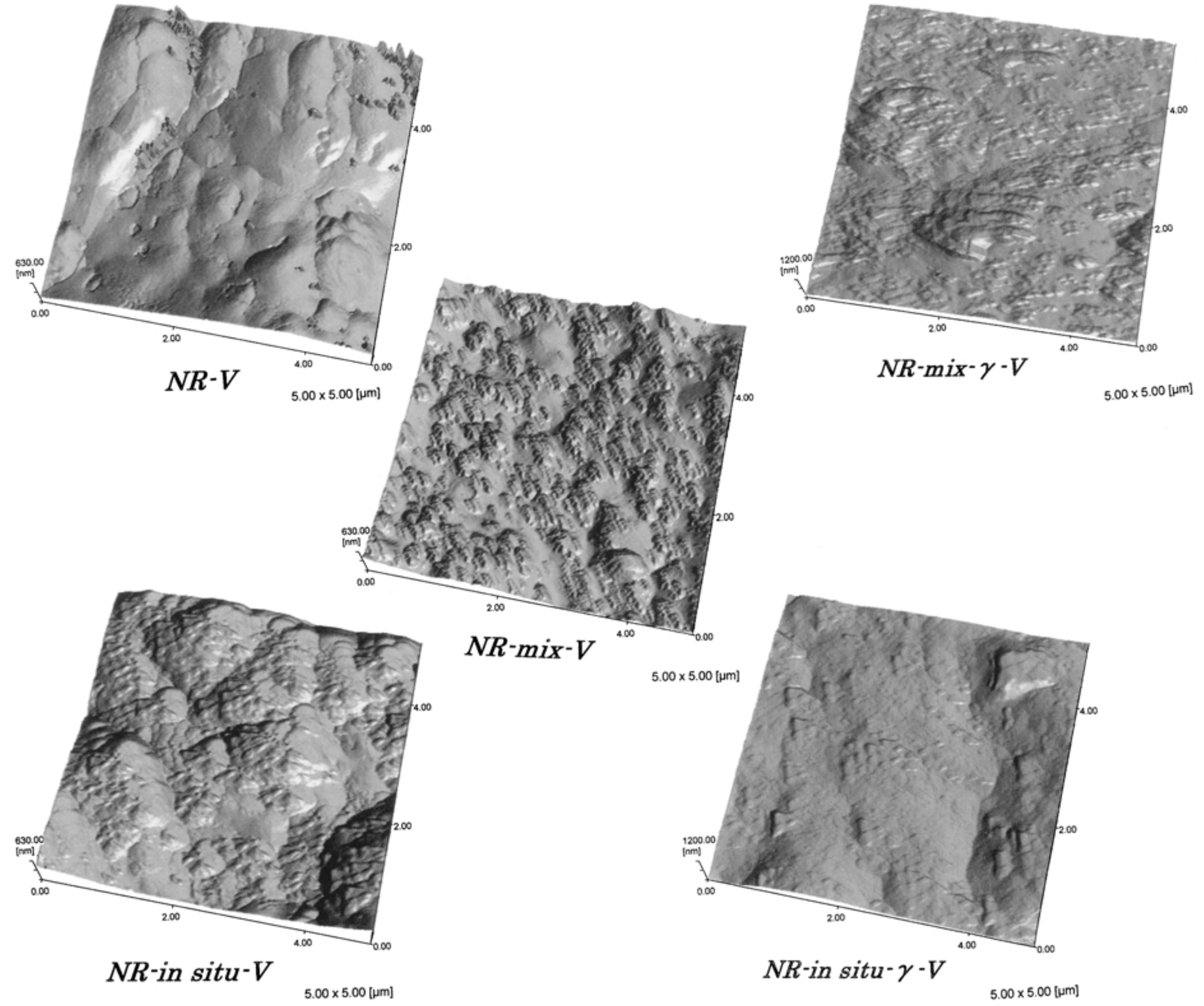


Figure 5 AFM photographs of *NR* vulcanizates.

4. Conclusions

The silane coupling agent (γ-MPS) was found to increase the reinforcement effect of *in situ* silica for the *NR* vulcanizate. In addition, it decreased the hardness, compression set, hysteresis loss and E' at the rubbery state of *in situ* silica-filled *NR* vulcanizate. The diameter of *in situ* silica particles was ca. 20–45 nm and the dispersion of *in situ* silica in the *NR* matrix became homogeneous by adding γ-MPS. The low number of silanol group of *in situ* silica particles is considered to bring about not only the unique physical properties but also the characteristic morphology of *in situ* silica-filled *NR* vulcanizate, where γ-MPS further decreased the number of silanol groups of *in situ* silica and made the interaction between the *in situ* silica particles weak. The simultaneous use of *in situ* silica and silane coupling agent significantly prevented the delay of sulfur curing and increased the wettability of *NR* onto *in situ* silica, which resulted in the increase of reinforcement effect of *in situ* silica for the *NR* vulcanizates. Therefore, the utilization of *in situ* silica, which is generated in the "green" *NR* matrix by the sol-gel reaction of TEOS before vulcanization, can be concluded to be useful as a new loading method of silica in the rubber technology. Especially, *NR* (a renewable resource) with *in situ* silica may have much potential as an ecologically "green" material. Since the mechanism of reinforcement effect of filler has not been appeared sufficiently [27, 28], the study on *in situ* silica loading into rubber will be meaningful for developing the filler science and technology.

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