

Effects of Rubber/Filler Interactions on the Structural Development and Mechanical Properties of NBR/Silica Composites

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ABSTRACT: A study was carried out on the effects of interactions between nitrile-butadiene rubber (NBR) and silica on the developments of agglomerates by silica particles and of bound rubber in NBR/silica composites. The mechanical properties of the composites were also investigated in relation to the structure development. Transmission infrared spectra revealed the existence of hydrogen bonding between nitrile groups in NBR and silanol groups on the silica surface. The number of hydrogen bonds increased with the increasing nitrile group content of NBR. Transmission electron microscopy observations and thermal analysis revealed that the averaged size of agglomerates in composites decreased, and simultaneously the amount of filler-gel in silica-filled NBR decreased with increasing nitrile group content of NBR. These results suggest that the hydrogen bonding between nitrile groups and silanol groups sup-

presses the development of agglomerates by silica particles, that is, the dispersion of silica is improved by the hydrogen bonding. At a given nitrile group content of NBR, the storage modulus and the initial slope of stress-strain curves for vulcanized composites increased with increasing the amount of filler-gel. Further, at a larger strain, the composites showed a clear pseudo-yielding point on the stress-strain curves, with this tendency more prominent in the larger agglomerate size. These results suggest that the mechanical properties for NBR/silica composites are affected by the content of filler-gel. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 74–81, 2005

Key words: rubber; silicas; mechanical properties; agglomerates; hydrogen bonding

INTRODUCTION

Silica has been used as an important filler for rubber to obtain highly reinforced rubber composites.^{1–4} It is well known that the rubber reinforcement is closely related to the formation of bound rubber,^{5–7} which corresponds to insoluble rubber molecules in common organic solvents. Thus, extensive works have been devoted to clarify the formation mechanism of bound rubber in rubber/silica composites.

For rubber/carbon black composite, it is generally accepted that the bound rubber is divided into two components. The one is formed by the rubber/filler interactions around the filler (filler-gel),^{8–11} and the other is formed by crosslinking of rubber molecules during the mixing (rubber-gel).^{12,13} For rubber/silica composites, however, the details of bound rubber have not been clarified up to now. Kravlevich et al.¹⁴ investigated rubber/silica interactions for natural

rubber (NR)/silica composites, and found the existence of a small amount of rubber component that could not be extracted from the composites. They suggested that such a rubber component was formed by chemical bondings between rubber molecules and the silica surface. On the other hand, Wagner¹⁵ investigated the tensile strength of styrene-butadiene rubber (SBR)/silica composites as a function of surface chemistry of silica particles, and reported that the tensile strength was not affected by the surface chemistry. Based on the results, he suggested that the interactions between rubber molecules and silica surface were weak and adsorptive ones.

We studied the effects of rubber/silica interactions on the formation of bound rubber. High-resolution solid-state NMR results for polyisoprene (PIR) and polyacrylate rubber (ACM)/silica showed no evidence for direct chemical coupling between silanol groups on a silica surface and rubber molecules.^{16,17} Further, transmission electron microscopy (TEM) observations suggested that the bound rubber might correspond to the rubber component entrapped within the secondary structure formed by silica particles (agglomerates).^{18–20}

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TABLE I
Characteristics of NBRs

Sample	AN content (wt %)	T_g (°C)	M_w
NBR①	28.5	-36.5	3.50×10^5
NBR②	33.5	-30.3	3.45×10^5
NBR③	36.5	-26.8	3.27×10^5
NBR④	40.5	-21.6	3.04×10^5

Because the nitrile-butadiene rubber (NBR) has nitrile groups in its molecular chain, we can expect interactions between nitrile groups and silanol groups, which might influence the formation of bound rubber in the NBR/silica composite. FTIR is a powerful technique to evaluate the possibility of hydrogen bonding between nitrile groups and silanol groups.^{21,22} Thus, we expect that rubber/filler interactions can be evaluated from FTIR spectra for NBR/silica composites.

In this study, the effects of interactions between NBR and silica surface on the formation of agglomerate and bound rubber were investigated by FTIR measurements and TEM observations by using NBRs with different nitrile group contents and precipitated silica. Static and dynamic mechanical properties of NBR/silica composites were also studied in relation to the structure development in the composites.

EXPERIMENTAL

Samples

The raw rubbers used were four kinds of nitrile-butadiene rubbers (NBR) with different nitrile group contents (AN). These were designated NBR① (DN2850): AN = 28.5 wt %, NBR② (DN3350): AN = 33.5 wt %, NBR③ (DN3650): AN = 36.5 wt %, and NBR④ (DN4050): AN = 40.5 wt % (Nippon Zeon Co., Tokyo, Japan). The filler used was a precipitated silica (Nipsil AQ; Nippon Silica, Nanyo, Japan). Characteristics of NBRs and silica are shown in Tables I and II, respectively.

The composites were prepared by both solution mixing and mechanical mixing. The composition of the composites is listed in Table III. Mixing conditions for the solution mixing were as follows: 2 g of NBR and curing agents (zinc oxide, stearic acid, antioxi-

TABLE II
Characteristics of Precipitated Silica

Diameter (nm)	Surface area ($\text{m}^2 \text{g}^{-1}$)	SiOH (mmol g^{-1})	N^a (nm^{-2})
18	187	1.86	6.0

^a N (nm^{-2}) = SiOH (mmol g^{-1})/Surface area ($\text{m}^2 \text{g}^{-1}$) $\times N_a$, where N_a is the Avogadro number.

TABLE III
Composition of NBR/Silica Composites

Component	Weight per hundred rubber
NBR	100.0
Silica	50.0
Zinc oxide	5.0
Stearic acid	1.5
Antioxidant 6C ^a	5.0
Accelerator ^b	2.4
Sulfur	1.8

^a *N*-(1,3-Dimethyl butyl)-*N'*-phenyl-*p*-phenylenediamine.

^b *N*-Cyclohexyl-2-benzothiazyl-sulfenamide.

dant, sulfur, and accelerator) were dissolved in 150 mL of benzene/acetone mixed solvent (9/1:v/v). Then, the solution was mixed with 1 g of well-dried silica, dispersed in 100 mL of the mixed solvent, and gently stirred at room temperature for 3 h. Finally, the unvulcanized composite was obtained from the mixed solution by a freeze-dry method. Conditions for mechanical mixing were as follows: NBR was put into a Banbury mixer and masticated at 60°C for 1 min, then well-dried silica (120°C for 12 h under a reduced pressure) was mixed with masticated NBR at 100°C for 1 min. Next, zinc oxide, stearic acid, and antioxidant were mixed with NBR/silica composites at 100°C for 2 min. Finally, the masterbatch was mixed with sulfur and accelerator at 60°C for 3 min. The unvulcanized composites prepared by the solution and mechanical mixings were sheeted on a roll mill followed by a vulcanization at 165°C for 15 min under a pressure of 400 kg/cm².

About 1.5 g of unvulcanized rubber, prepared by solution and mechanical mixing (mixed without curing agents), was cut into small pieces and loosely packed in a cage with 100-size mesh. The cage was immersed in about 300 mL of methyl-ethyl ketone (MEK) and extraction was carried out at room temperature for 36 h. The insoluble component (bound rubber) was suspended in methanol with more volatile solvent. The bound rubber was dried at room temperature under a reduced pressure for 24 h.

The mixture of NBR and silica prepared by the solution mixing was dropped onto the TEM grid coated by carbon. The composite was obtained by removing the solvent from the mixture on the mesh at room temperature under a reduced pressure for 24 h. The composite on the mesh was immersed in a large amount of the solvent and extraction was carried out at room temperature for 144 h. The solvent for extraction was the benzene/acetone mixed solvent to protect the carbon coat of TEM grid. The remaining materials on the mesh were the bound rubber and silica for TEM observations.

The vulcanized composites were cured again in melted sulfur ($\approx 125^\circ\text{C}$) for 36 h. The hardened com-

posites were easily cut into ultrathin films (<100 nm) at room temperature by microtoming. The thin films were stuck onto the TEM grids for TEM observations.

Measurements

Amounts of bound rubber in the composites (G_t , g/g) were determined as a mass of insoluble rubber per 1 g of silica from the percentage of weight loss between 300 and 550°C. A precisely determined weight (≈ 15 mg) of insoluble rubber was heated to 650°C by a thermal gravimetric analyzer (TGA: TG/DTA220; Seiko Instruments, Chiba, Japan) with a heating rate of 20°C/min.

Transmission FTIR measurements of NBRs and bound rubbers were carried out by using a FTIR spectrometer (Spectrum One; Perkin Elmer Cetus Instruments, Norwalk, CT). Measurements were carried out by using cast films of NBR and KBr disks of bound rubbers.

The dynamic storage modulus (E') was determined by a dynamic viscoelastometer (Reovibron DDV II-C; Orientec, Tokyo, Japan) at -20 – 120°C under a fine strain amplitude (5.3×10^{-3} %) and frequency of 110 Hz.

Measurements of stress–strain curves were carried out in an air oven equipped with a tensile tester (RTC-1210; Orientec) at above 100°C of T_g for pure NBR. The strain rate was 0.5/min.

RESULTS AND DISCUSSION

Structure development in solution-mixed composites

In this study, two mixing methods (solution and mechanical) were used for sample preparation. As stated, bound rubber in the rubber/silica composites is expected to be composed of filler–gel and rubber–gel, similar to the case of rubber/carbon black composites. For mechanical mixing, a large shear force was applied to the systems during mixing that might influence the dispersion of silica particles in the rubber matrix and might enhance the scission and recombination of rubber molecules.^{12,13} In this case, a certain amount of rubber–gel might be produced. For solution mixing, on the other hand, the shear force applied to the systems is quite small, resulting in the negligibly small amount of rubber–gel. Thus, most of the bound rubber prepared by the solution mixing might correspond to the filler–gel, which is formed by the filler/polymer interactions. Thus, we evaluated the interactions between fillers and rubber molecules by the FTIR method.

Silica particles show an absorption peak at about 3750 cm^{-1} in the IR spectrum assigned to the stretching vibrations of isolated silanol groups.^{23–25} How-

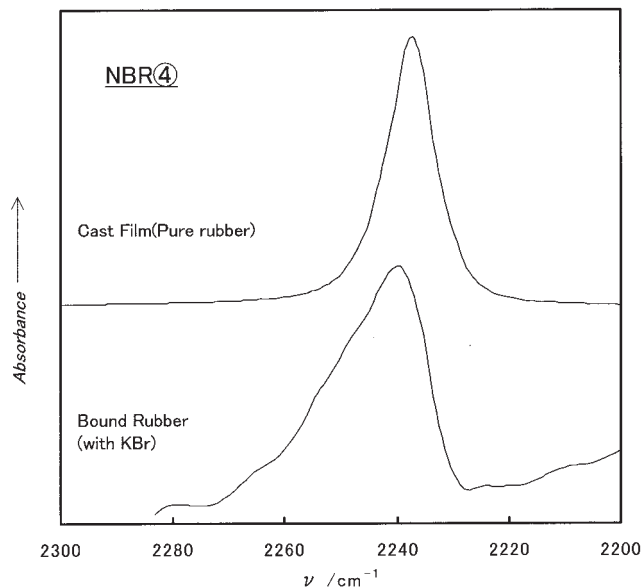


Figure 1 FTIR spectra, at 2200 – 2300 cm^{-1} , for pure unvulcanized NBR④ and bound rubber prepared from solution-mixed unvulcanized NBR④/silica composite.

ever, the peak position is affected by water molecules adsorbed on the silica surface. Thus it is not likely that one can evaluate NBR/silica interactions from the absorption peak of silanol groups. On the other hand, NBR shows an absorption peak at about 2250 cm^{-1} in the IR spectrum assigned to the stretching vibrations of isolated nitrile groups.^{26–28} This peak shifts to higher wavenumber by the formation of hydrogen bonding with silanol groups^{21,22}; further this peak is hardly affected by water molecules. In this study the NBR/silica interactions were thus investigated by the shifts of the adsorption peak for nitrile groups.

Figure 1 shows transmission FTIR spectra from 2200 to 2300 cm^{-1} for pure NBR④ and bound rubber from NBR④. The absorption curve for pure NBR④ was symmetric, centered at 2237 cm^{-1} . However, the curve for the bound rubber was asymmetric, which was able to deconvolute into two components. Figure 2 shows the result of deconvolution for bound rubber from NBR④. The wavenumbers at the absorption peaks for the two components were 2237 and 2248 cm^{-1} , respectively. It is reported that the peak at 2237 cm^{-1} shifts to higher wavenumber by the formation of hydrogen bonding.^{21,22} Thus, the peak at 2248 cm^{-1} was assigned to the stretching vibration of hydrogen-bonded nitrile groups. The fraction of the hydrogen bonded nitrile group in the total nitrile group of NBR (F_{HB}) was evaluated from the deconvoluted spectra. The absorption coefficient for nitrile groups increases with increasing wavenumber of the absorption peak.^{27,28} Thus, the F_{HB} does not completely correspond to the fraction of hydrogen-bonded nitrile groups in all the nitrile groups. In this study, however, the difference of

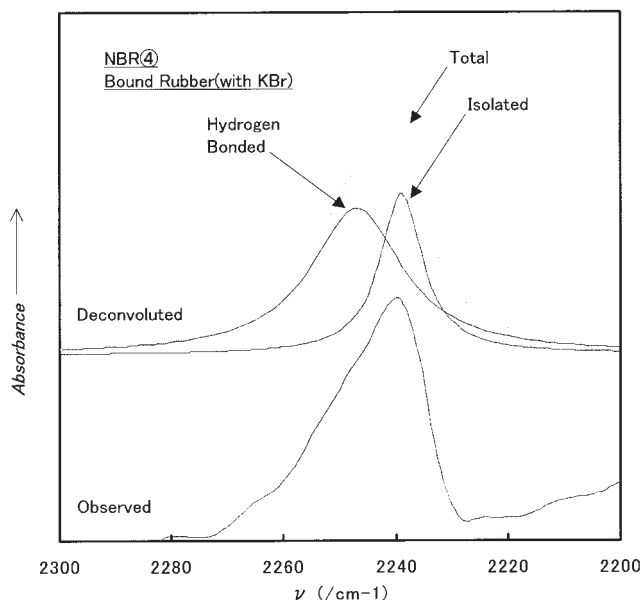


Figure 2 Deconvolution of spectrum for bound rubber from NBR④.

wavenumber is only 11 cm^{-1} , which means that the difference of absorption coefficient is quite small. Table IV shows the F_{HB} values for the bound rubbers from all NBRs. It is clear that the F_{HB} was not affected by the nitrile group content of NBR. The result suggests that the number of hydrogen-bonded nitrile groups in the filler-gel increased with increasing nitrile group content of NBR. With the increase of the number of hydrogen-bonded nitrile groups, the number of hydrogen bonded silanol groups also increases.

We investigated the formation of agglomerates in solution-mixed PIR/silica composites by TEM observations, and reported that the size of agglomerate decreased with decreasing number of silanol groups per unit surface area of the particles.^{18,19} The size of agglomerate in the composites also might change with the nitrile group content, given that the number of isolated silanol groups that control the size of agglomerate decreased with increasing nitrile group content. This was confirmed by TEM observations of agglomerate in solution-mixed NBR/silica composites. The observations revealed the distribution of the size. However, the distribution was quite narrow, and it was clear that the averaged size decreased with increasing nitrile

TABLE IV
 F_{HB} Values for Bound Rubber from Solution-Mixed NBR/Silica Composites

Sample	NBR①	NBR②	NBR③	NBR④
F_{HB}	0.63 ± 0.1	0.65 ± 0.1	0.66 ± 0.1	0.65 ± 0.1

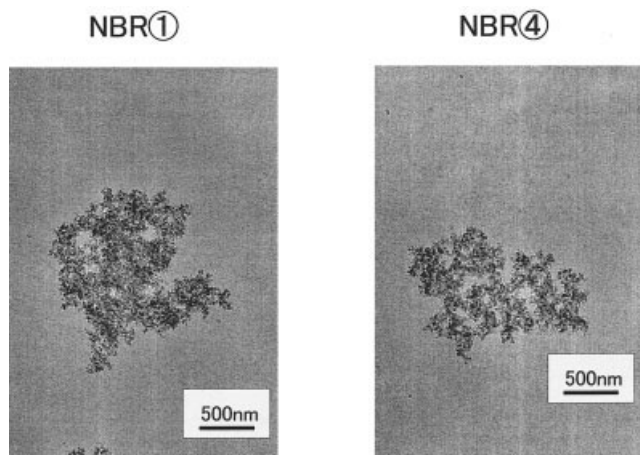


Figure 3 TEM microphotographs of bound rubber and silica particles from solution-mixed unvulcanized NBR/silica composites.

group content of NBR. Figure 3 shows the TEM microphotographs of the agglomerates. The one is the agglomerate in the NBR with the smallest nitrile group content (NBR①) and the other one is the NBR agglomerate with the largest nitrile group content (NBR④). We checked the effects of extraction conditions on the shape of agglomerates in silica-filled polyisoprene, and found that the shape was not affected by the extraction conditions.¹⁸ From these results, it is clear that the agglomeration of silica particles is suppressed by the existence of the nitrile group; in other words, the dispersity of silica particles was improved by the nitrile groups, in accordance with the report by Choi.²⁹ The agglomerate is formed by the hydrogen bonding between silanol groups on silica surfaces.^{16–20} However, the agglomeration is suppressed by the nitrile groups of NBR because silanol groups form hydrogen bondings with nitrile groups. Thus, the size of agglomerate decreased with the increase of nitrile group content of NBR. These are explained schematically in Figure 4.

Table V shows the content of bound rubber (Gt) in composites from all NBRs. As stated, for the composites prepared by solution mixing, the Gt corresponds to the amount of filler-gel in the composites. Therefore, the results shown in Table V indicate that the content of filler-gel was likely to decrease with the increasing nitrile group content of NBR. However, the content of filler-gel for NBR③ was larger than that for NBR②. The difference of nitrile group content between NBR② and NBR③ was only 3.0 wt %. Thus, this might include the experimental error. That is, the larger the agglomerate size, the higher the Gt value, similar to the case of PIR/silica composites.^{18,19} It is reported that the amount of filler-gel is affected by the molecular weight of rubber

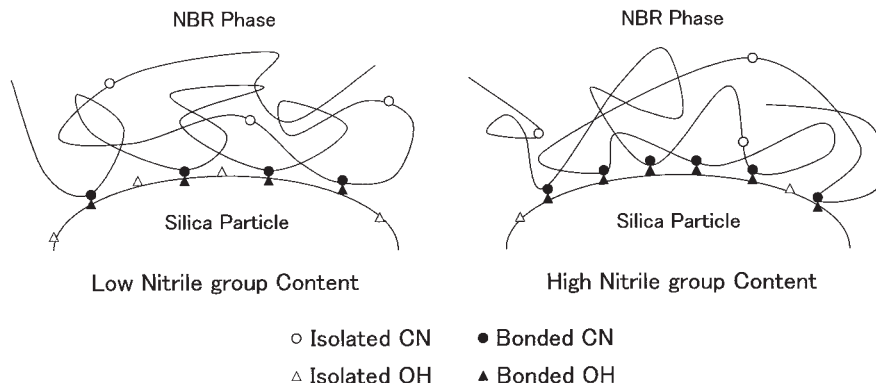


Figure 4 Schematic representation of hydrogen bonding between unvulcanized NBR and silica surface.

molecules.³⁰ However, in this study, the effects of molecular weight on the amount of filler–gel can be neglected, given that the composites were prepared by using NBRs with a similar molecular weight.

A careful TEM observation was done to find rubber phases around the agglomerates. However, we could not find the rubber phases even under a highly magnified condition. The result suggests that the insoluble rubber phase is within the agglomerates, similar to the case of PIR/silica composites.^{18,19}

Structure development in mechanically mixed composites

FTIR spectra for bound rubbers prepared from mechanically mixed unvulcanized composites were also deconvoluted into two components. Further, the relation between F_{HB} and nitrile content was qualitatively similar to that for bound rubbers from solution-mixed composites (Table VI). However, the difference was that the F_{HB} for mechanically mixed samples at a given nitrile group content of NBR was almost half of the F_{HB} for the solution-mixed one. To understand the difference, TEM observations of bound rubber in mechanically mixed unvulcanized composites were examined. However, the bound rubber from mechanically mixed composites involved large amounts of rubber–gel, which made it difficult to prepare the filler–gel for TEM observations. Thus, we prepared ultrathin films from hardened NBR/silica composites to carry out TEM observations.

Figures 5 and 6 show TEM microphotographs of mechanically mixed and hardened NBR/silica composites and their digital binary images, respectively.

The transformation of TEM microphotograph to digital binary image (DBI) was as follows: the contrast of TEM microphotographs was adjusted to be able to easily recognize the interface between silica and rubber matrix by eyes. Then silica and rubber phases were explained by a black and a white, respectively. The details are described in our previous article.²⁰ The averaged area of black-colored phase, which corresponds to the averaged size of one agglomerate in the composites ($\overline{S_{agg}}$), was calculated from the DBI. The results are shown in the lower part of Figure 6. It is clearly seen that the $\overline{S_{agg}}$ for NBR with lower nitrile group content is larger than that for NBR with larger nitrile group content. The comparison of Figure 6 with Figure 3 clearly indicates that the agglomerate size is smaller for mechanically mixed composites than for the solution-mixed one. During the mechanical mixing, large agglomerates were broken into small blocks by the shear force. This might lead to the decrease of the amount of filler–gel in mechanically mixed composites, as discussed in the previous section.

Table VII shows the Gt values for mechanically mixed composites. The Gt increased with the increase of $\overline{S_{agg}}$, similar to the case of solution-mixed composites. However, the Gt values for mechanically mixed composites were about 10-fold larger than Gt values for solution-mixed ones (see Table V), although the agglomerate size in the mechanically mixed composites was much smaller than that in the solution-mixed one. As stated, rubber–gel was formed by a large shear force applied to samples during mechanical mixing. This might cause a substantial difference of Gt

TABLE V
 Gt Values for Solution-Mixed Composites

Sample	NBR①	NBR②	NBR③	NBR④
Gt g/g	0.061 ± 0.003	0.045 ± 0.004	0.051 ± 0.004	0.035 ± 0.002

TABLE VI
 F_{HB} Values for Bound Rubber from Mechanically Mixed
 NBR/Silica Composites

Sample	NBR①	NBR②	NBR③	NBR④
F_{HB}	0.36 ± 0.1	0.37 ± 0.1	0.35 ± 0.1	0.36 ± 0.1

values between solution and mechanically mixed composites.

Effects of bound rubber structure on mechanical properties of composites

Figure 7 shows the temperature dependency of storage modulus (E') for vulcanized pure NBR and vulcanized NBR/silica composites prepared by the mechanical and solution mixings. At the rubbery region ($>30^\circ\text{C}$), the E' for composites was larger than that for pure rubber. Further, the E' for solution mixed composite was larger than that for the mechanically mixed one. Priskin and Tokita¹³ studied the effect of bound rubber on the E' for SBR/carbon black composites, and reported that the E' increased with the increasing volume fraction of bound rubber in the composite. Wang^{4,31} suggests that the rubber molecules entrapped in the filler lose their identity as an elastomer and behave as a filler in terms of stress-strain properties. As stated in the previous section, at a given nitrile group content, the content of filler-gel was larger for the solution-mixed one than for the mechanically mixed one. Thus, the difference of E' between the two mixing techniques can be explained by the difference of the content of filler-gel. The mechanically mixed composites involved large amount of rubber-gel. It is generally accepted that the segmental mobility of rubber-gel is higher than that of filler-gel, and that the elasticity of rubber-gel is much lower than that

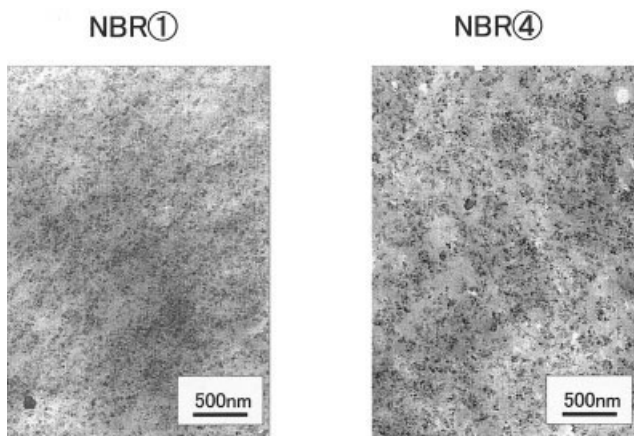


Figure 5 TEM microphotographs of mechanically mixed and hardened vulcanized NBR/silica composites.

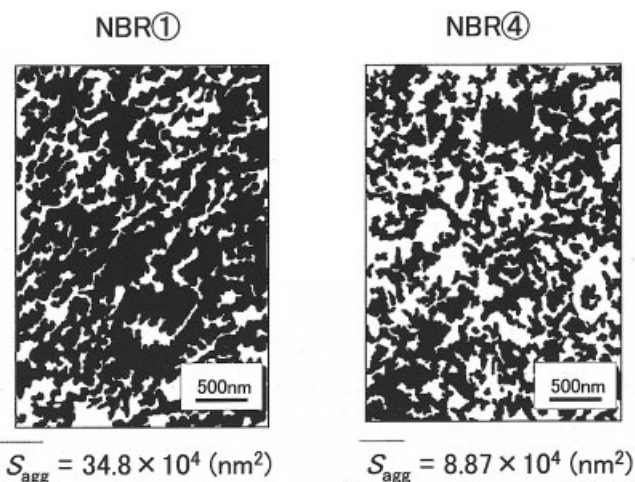


Figure 6 Digital binary images of Figure 5.

of filler-gel. Therefore, the E' for NBR/silica composites was primarily controlled by the content of filler-gel rather than the content of rubber-gel.

Figure 8 shows the stress-strain curves for vulcanized NBR/silica composites prepared by both solution and mechanical mixing and NBR/ CaCO_3 composite prepared by mechanical mixing. The NBR used was NBR①. The measurement temperature was set to be 60°C , which corresponds to the rubbery region of NBR. The volume fraction of CaCO_3 in the composite was similar to that for NBR/silica composites. The initial slope of the curve for NBR/silica composites was larger than that for the NBR/ CaCO_3 composite. Further, this tendency was more prominent in the composite with larger agglomerate size, in accordance with the results shown in Figure 7. It is well known that CaCO_3 does not form any agglomerate in composite. Thus, the NBR/ CaCO_3 composite does not form any filler-gel. Based on these facts, it is suggested that the initial slope was controlled by the amount of filler-gel.

At a larger strain, around 0.2, NBR/silica composites showed a large pseudo-yielding. However, NBR/ CaCO_3 composite did not show any yielding point. This tendency was more prominent in the sample with larger agglomerate size.

It is well known that SBR/silica composite shows the reduction of E' with dynamic strain amplitude (Payne effect), with this tendency more prominent in the composite with larger agglomerate size.^{20,32} This

TABLE VII
 Gt Values for Mechanically Mixed Composites

Sample	NBR①	NBR②	NBR③	NBR④
$Gt, \text{g/g}$	0.44 ± 0.01	0.40 ± 0.01	0.36 ± 0.02	0.29 ± 0.02

result was explained by the breakdown of the agglomerates and release of filler-gel. Similar structural changes might happen during stress-strain measurements of vulcanized NBR/silica composite, leading to the appearance of the pseudo-yielding point on the stress-strain curve.

CONCLUSIONS

NBR/silica composites, with different nitrile group contents of NBR, were obtained from both solution and mechanical mixing. Based on the FTIR spectra and TEM observations, the effects of NBR/silica interactions on structural development of composites were investigated. Then, dynamic mechanical properties and stress-strain behavior were investigated in relation to structure development of the composites. The following conclusions were derived from the experimental results:

1. FTIR spectra suggested the existence of hydrogen bonding between nitrile groups of NBR and silanol groups on the silica surface. Further, the number of hydrogen bonds increased with increasing nitrile group content of NBR.
2. The hydrogen bonding between NBR and silica suppressed the development of agglomerates in the composites.
3. Bound rubber in the NBR/silica composite prepared by mechanical mixing was composed of both filler-gel and rubber-gel. The amount of filler-gel decreased with decreasing agglomerate size.
4. The E' and the initial slope of stress-strain curves for NBR/silica composites increased with increasing amounts of filler-gel in the composites.

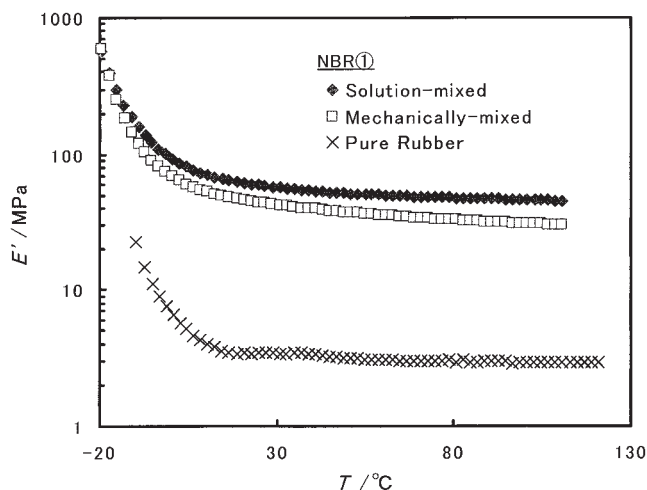


Figure 7 Temperature dependency on dynamic storage modulus for pure vulcanized NBR and solution and mechanically mixed vulcanized NBR/silica composites.

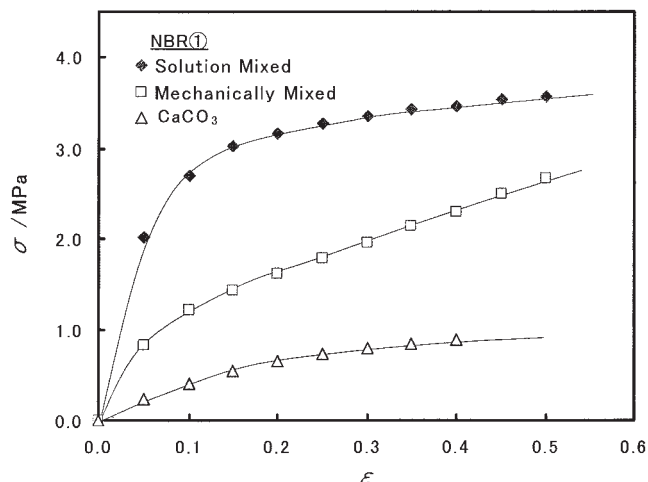


Figure 8 Stress-strain curves for solution and mechanically mixed vulcanized NBR/silica composites at 60°C.

Further, at a larger strain, NBR/silica composites showed a clear pseudo-yielding point on the stress-strain curves, with this tendency more prominent in the larger agglomerate size. These results suggest that the tensile properties of NBR/silica composites are affected by the content of filler-gel.

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