Structure Development in Silica-Filled Polyacrylate Rubber Composites During Mixing

SHIGEYUKI ONO,[1] MASAYOSHI ITO,[1] HIDEYUKI TOKUMITSU,[2] KAZUHIKO SEKI[2]

[1] Department of Chemistry, Science University of Tokyo, Kagurazaka 1-3, Shinjuku-ku, Tokyo 162-8601, Japan

[2] Tsukuba Technical Laboratory, NOK Company, Wadai 25, Tsukuba, Ibaraki 300-4247, Japan

ABSTRACT: The structure of bound rubber in the composites from fumed silica (A200, Nippon Aerosil Co., Japan) and polyethylacrylate rubber (PEA) was studied as a function of mixing temperature. The fraction of bound rubber in the composites increased gradually with increasing the mixing temperature from 80 to 120°C, followed by saturation above 120°C. High-resolution solid-state NMR results revealed that there was no chemical bonding between silanol groups and PEA molecules. Scanning electron microscope and optical microscope observation of the composites indicated that, with increasing mixing temperature, the size of agglomerates formed by silica particles decreased. Further, the molecular weight retention of PEA dropped abruptly above 120°C. Dynamic viscoelastic measurements of the composites suggest that the development of network structure in the composites was greatly affected by the mixing temperature. Based on these data, structure development in composites is discussed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2529–2538, 1999

Key words: NMR; silica; polyacrylate; composite; structure

INTRODUCTION

Polyacrylate rubber (ACM) has a polar ester group on its molecular chains, which enhances heat resistance and suppresses swelling of ACM in nonpolar oil or liquid. Therefore, the ACM has been extensively used for industrial parts such as O-rings, lip seals and gaskets.[1–3] However, acrylic elastomers usually do not provide high gum strength when cured. Therefore, a reinforcing agent such as carbon black and numerous mineral fillers are used in order to provide useful properties.[3] Among the mineral fillers, silica has a hydrophilic property due to the existence of silanol groups on the silica surface. In addition, we can expect chemical interactions between si-

lanol groups on the silica surface and the ester groups of ACM. Such interactions might promote structure development in the silica-filled ACM composites. Our primary interest is the possibility of chemical interaction between polar ester groups of the acrylate rubber and the silanol groups on the silica surface, which might lead to the development of a higher-order structure in the composites. Wide-line NMR studies have provided important information on the structure of fine particle-filled rubber composites, which is useful for the understanding of mechanical reinforcement of rubber composites.[4–8] Also we can expect that high-resolution solid-state NMR gives us valuable information on the chemical interaction between fillers and rubber molecules. Recently, we reported on the high-resolution solid-state NMR and wide-line NMR data of silica-filled polyisoprene composites, which indicated that the silanol groups on the silica are not directly related

to the formation of bound rubber.[9] In this work high-resolution solid-state NMR, wide-line NMR, and viscoelastic measurements were carried out for silica-filled polyethylacrylate rubber (PEA) composites. The results are discussed in terms of structure development in the silica-filled PEA as a function of mixing temperature.

EXPERIMENTAL

Materials

Polyethylacrylate rubber (PEA) was synthesized by emulsion polymerization. The molecular weight of PEA was determined to be 1.6×10^6 by gel-permeation chromatography in tetrahydrofuran after calibration with polystyrene standards. The filler used was a fumed silica (A200) with a surface area of 200 m^2/g, manufactured by Nippon Aerosil Co. (Japan). It was dried at 100°C for 20 h under vacuum before use.

Sample Preparation

The compounding was carried out in a laboratory scale Banbury-type mixer (Laboplastomill, Toyoseiki Company, Japan) under a constant total energy (2,100 MJ/m^3), which was monitored by torque at the blades. First, PEA was masticated for 1 min in the mixer to reduce the viscosity; then 50 parts of silica were added to the mixer at 10 rpm, and the temperature of the chamber was controlled at 60, 80, 100, 120, and 150°C by air through the jackets. Bound-rubber samples were prepared from the composites by the solvent extraction method. Details of bound-rubber preparation and the determination of the bound-rubber fraction of the composites were described in our previous paper.[6]

Dynamic Viscoelastic Measurements

Dynamic mechanical measurements of the compounds were done with a Rheometrics RMS800 (Rheometric Scientific Far East Company). Measurements were made by forced dynamic shear using a 25 mm $\phi \times$ 2 mm sample. All tests were conducted at 70°C and at a frequency range of 0.05 to 50 rad/s with 0.5% strain amplitude. The data were analyzed by Winter's equation[10] in order to compensate for the inhomogeneous strain occurring between the two parallel plates.

NMR Measurements

High-resolution solid-state NMR spectra were obtained by a JEOL JMN CMX 300 at resonance frequencies of 75 and 59 MHz for carbon-13 and silicon-29, respectively, by using high-power decoupling, cross polarization (CP), and magic-angle spinning (MAS) techniques. MAS was routinely carried out at a 3-KHz spinning rate in a double-bearing probe head. Measurement temperatures were set at room temperature for ^{29}Si–CP/MAS–NMR, and 70°C for ^{13}C–DD/MAS–NMR,[11,12] respectively. The data of CP–MAS spectra were transferred to the computer and analyzed by a curve-fitting program. Synthetic spectra were generated using a function consisting of three overlapping Gaussian lines. The nine associated variables, such as width, area, and chemical shift, for each of the three peaks were adjusted to minimize the root–mean–square error.

Pulsed NMR measurements were performed with a pulsed NMR spectrometer (CXP90, Brucker Co.) at a resonance frequency of 60 MHz. The proton spin–spin relaxation time (T_2) and the fraction of each component were determined by a solid echo sequence.[13] The 90°C pulse width and the pulse interval were adjusted to be 2 and 9 μs, respectively. The spin–spin relaxation time (T_2) and the fraction of each component were determined by fitting the solid echo signal to the Weibull function[14];

$$M(t) = \sum_i M_{oi} \exp\lfloor -(t/T_{2i})^{E_i} \rfloor \qquad (1)$$

where t is the time, E_i is the Weibull coefficient, M_{0i} is the signal intensity of the ith component at $t = 0$, $M(t)$ is the signal intensity at t, and T_{2i} is the spin–spin relaxation time of the ith component. The fraction of the jth component (f_j) is given by

$$f_j = M_{0j}/\sum M_{0i} \qquad (2)$$

RESULTS AND DISCUSSION

Temperature Dependence of Mixing

Figure 1 shows the torque curves at different mixing temperatures from 60 to 150°C. The mixing time of 0 min corresponds to the time when silica was added into a mixing chamber in which there already was rubber. Just after the addition
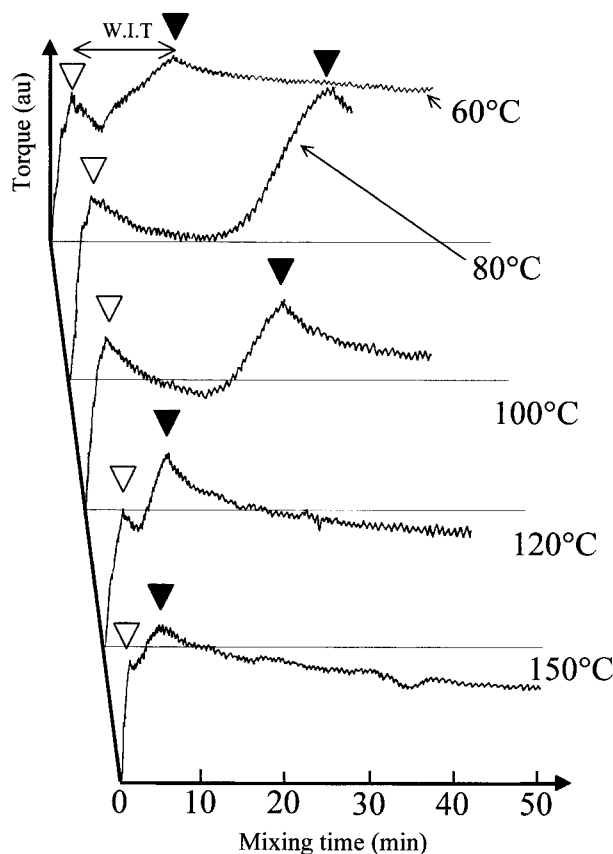
Figure 1 Mixing torque curves of the silica-filled PEA at different temperatures.

incorporation time (BIT).[15] In this study we named the corresponding time as a white incorporation time (WIT).

Table I summarizes the characteristics of mixing. Except for the mixing temperature of 60°C, the WIT decreased with increasing mixing temperature. As described in the experimental section, all the compoundings were performed under a constant total energy. Therefore, the mixing time required for the constant total energy of 2,100 MJ/m³ increased with the decreasing of the mixing torque. Except for the mixing temperature of 60°C, the mixing torque decreased with increasing mixing temperature, leading to the increase of mixing time (see Table I). It is generally recognized that aggregated carbon black disperses rapidly until the BIT, followed by uniform dispersion with the mixing time. As seen in Figure 1 and Table I, the mixing energy consumed after the BIT increased with the increasing of the mixing temperature. However, the increase was almost independent of molecular weight change of PEA during mixing, as will be discussed later. The mixing behavior at 60°C is slightly different from that at 80–150°C. This is probably due to a heterogeneous dispersion of silica in rubber. The details are currently under study.

Interaction between Silica and PEA

Figure 2 shows ^{29}Si–CP/MAS–NMR spectra of the original silica and bound rubbers from the composites obtained at mixing temperatures of 100 and 150°C. For all spectra, three peaks were observed around 100 ppm, which could be assigned to silicon atoms with geminal silanol, Q^2, single silanol, Q^3, and siloxane bridge, Q^4 (see Table II).[16] Although the relative intensities of Q^2, Q^3, and Q^4 for both bound rubbers were different from that of the original silica, the corresponding

of the silica into the mixing chamber, the mixing torque rapidly increased with time. With increasing mixing time, the first and second peaks appeared in the torque curves at every mixing temperature. These curve profiles are similar to those for the mixing of carbon black with rubber.[15] The mixing time at the second peak for the mixing of carbon black with rubber is the so-called black

Table I Characteristics of Mixing

Temperature (°C)	Total Mixing Time (min)	WIT (min)	Mixing Torque (N m)		
			at 1st Peak	at 2nd Peak	at End
60	44.2	14.0	35.2	42.1	46.1
80	32.4	28.1	40.2	66.6	59.8
100	38.5	21.3	39.2	49.0	36.3
120	44.5	6.8	31.4	44.1	26.5
150	51.1	6.5	27.4	37.2	22.5

All samples tested; 10 rpm of rotor speed, same total energy calculated by torque onto blade (2,100 MJ/m³) and same fill factor (0.75).
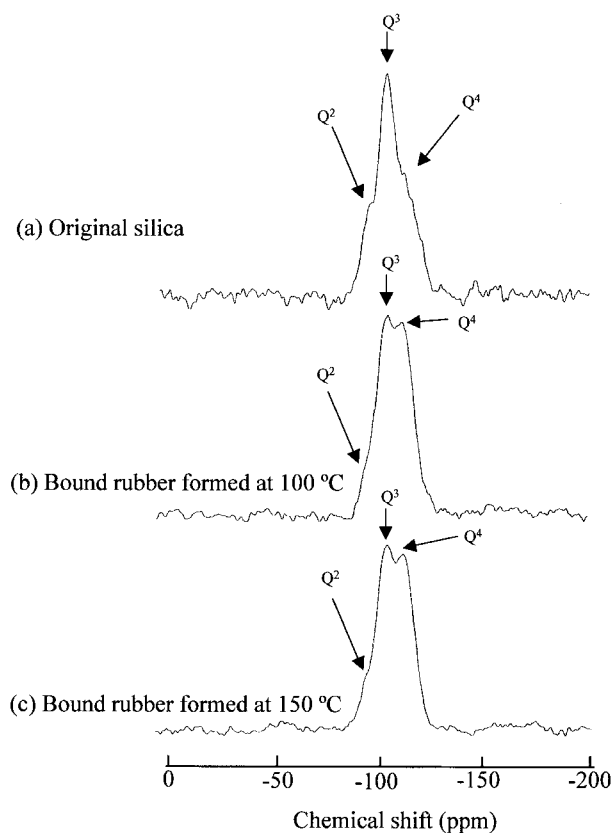
Figure 2 ^{29}Si–CP/MAS–NMR spectra of original silica and bound rubbers formed at 100 and 150°C.

chemical shifts of the three samples were almost the same (see Table III). During the mixing at high temperatures of 100 or 150°C, dehydration
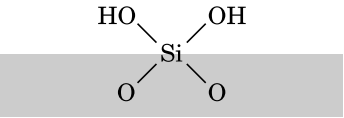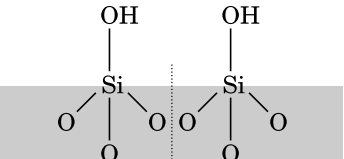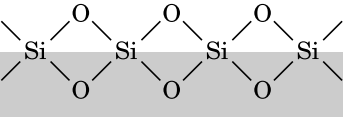
Table III   Chemical Shift of the Samples

Samples	Q^2 (ppm)	Q^3 (ppm)	Q^4 (ppm)
Original silica (A200)	−90.3	−100.0	−109.7
Bound rubber formed at 100°C	−90.8	−101.2	−110.8
150°C	−90.8	−100.2	−110.5

might occur on the silica surface,[17] which induced the changes of relative intensities of Q^2, Q^3, and Q^4. No difference of chemical shift among the samples suggests that a silanol group is not responsible for the formation of bound rubber.

Figure 3 shows ^{13}C–DD/MAS–NMR spectra of the original PEA and the two bound rubbers formed at 100 and 150°C. The spectrum of the original PEA shows five peaks. These peaks are assigned as shown in Table IV.[18] As seen in the figure, the chemical shift and relative intensity of these peaks for the bound rubbers were consistent with those for the original PEA. A small but new peak appeared at 54 ppm for both bound rubbers, which could be assigned to the carbonyl group in the side chain of PEA, which had polar interactions or hydrogen bonding with other groups. The lack of appearance of a new peak in the higher magnetic field of 0–10 ppm corresponding to ≡Si—O—R and ≡Si—O—CO—R (R: alkyl groups) bonds[19] suggests that we can't expect direct chemical coupling between silanol groups and

Table II   Assignment of ^{29}Si–CP/MAS–NMR Spectra

Type	Name	^{29}Si Chemical Shift
Q^2	geminal	−90 ppm
Q^3	single	−100 ppm
Q^4	siloxane	−110 ppm

(a) Original PEA

(b) Bound rubber formed at 100 °C

(c) Bound rubber formed at 150 °C

Chemical shift (ppm)
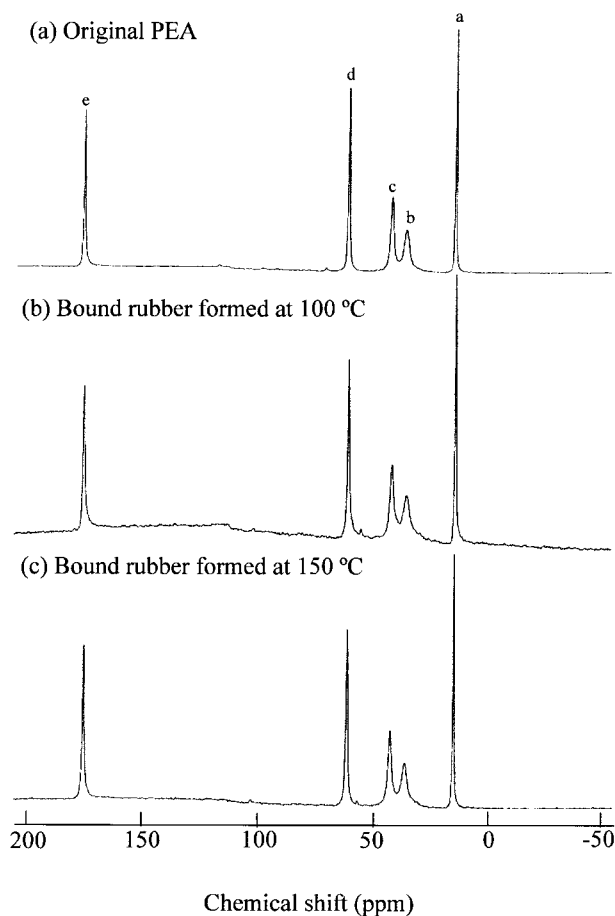
Figure 3 ^{13}C–DD/MAS–NMR spectra of original PEA and bound rubbers formed at 100 and 150°C.

Table IV Assignment of ^{13}C–DD/MAS–NMR Spectra

		^{13}C Chemical Shift (ppm)
—(^{b}CH$_2$—^{c}CH$_2$)$_{\overline{n}}$—	a	14
^{e}CO	b	35
O	c	41
^{d}CH$_2$	d	60
^{a}CH$_3$	e	174

Scanning electron microscopy (SEM) and optical microscope (OM) photographs of the composites mixed at 60, 100, and 150°C are shown in Figures 5 and 6, respectively. The SEM observation of the composite prepared at 60°C showed that silica in the composite existed as agglomerates with 10–100 μm large [Fig. 5(a)]. These agglomerates formed irregular band tails and blocks in the direction of the shared stress. This means that, at the mixing temperature of 60°C, the state
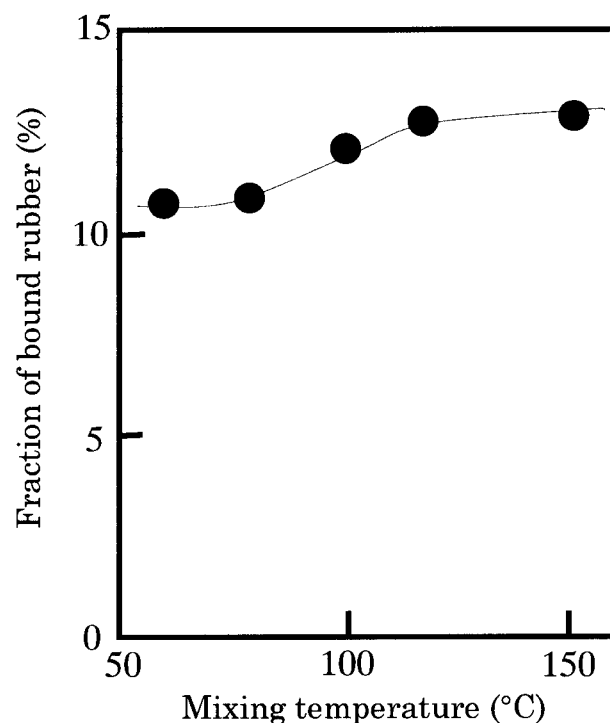
rubber molecules, in accordance with the ^{29}Si–CP/MAS–NMR results.

Change in Bound-Rubber Content with Mixing Temperature

Figure 4 shows the fraction of bound rubber in the composites as a function of mixing temperature. The fraction increased gradually with increasing mixing temperature from 80 to 120°C, followed by a saturation above 120°C.

As was discussed in the previous section, we could not expect chemical coupling between silanol groups on the silica surface and PEA molecules. This means that formation of bound rubber is not directly related to the chemical interaction between fillers and rubber molecules. Also the bound-rubber formation can't be simply explained by a physical adsorption of rubber onto silica judging from the relation between the fraction of bound rubber and mixing temperature,[20] as shown in Figure 4.

Figure 4 Mixing-temperature dependence on the fraction of bound rubber in the composites.
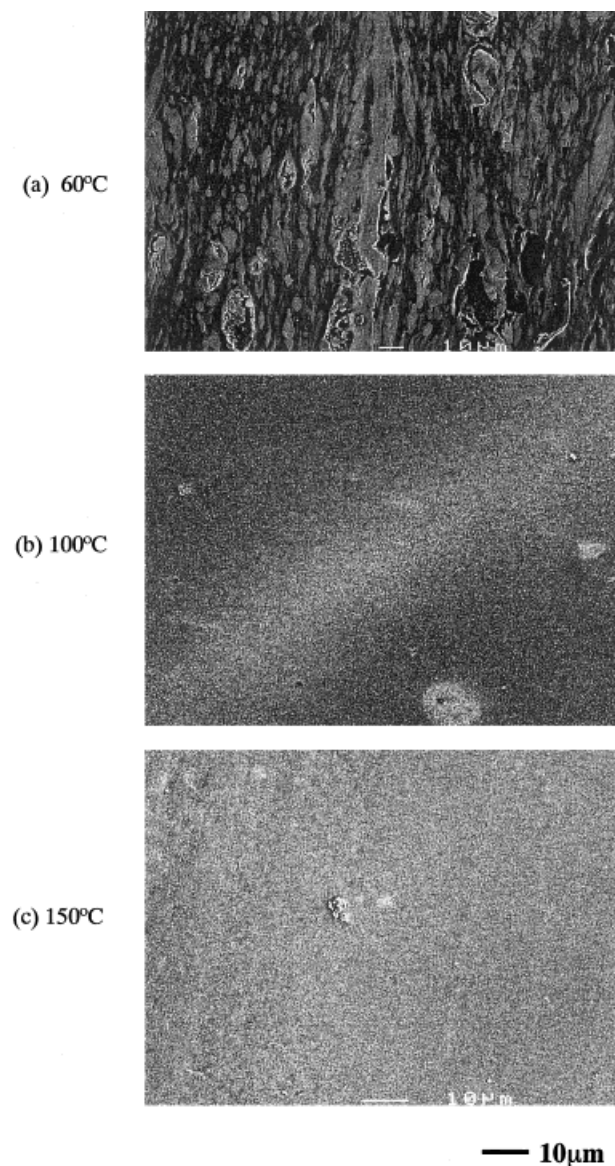
Figure 5 SEM photographs of thin section of composites obtained at (a) 60, (b) 100, and (c) 150°C.

Figure 6 OM photograph of the composites: mixing temperature at (a) 60°C and (b) 100°C.

of dispersion does not change much even after the WIT. On the other hand, in the composites prepared at 100 and 150°C, the agglomerates disappeared, and silica particles were dispersed homogeneously in the PEA matrix [Fig. 5(b,c)]. The differences of dispersibility of silica in the composites are clearly recognized in the optical microscopic photographs (Fig. 6). The PEA sheet–prepared compression molding at room temperature gives a transparent body. On the other hand, the composite prepared at 60°C, which had a poor dispersion of silica in the PEA, gave an opaque 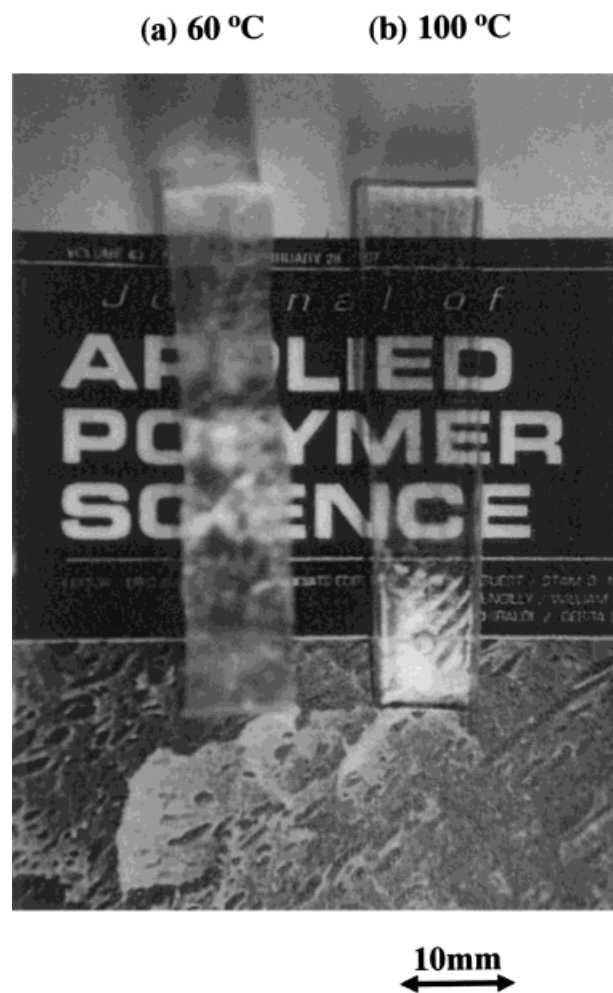sheet [Fig. 6(a)]. When the mixing temperature increased to 100°C, the composites became transparent [Fig. 6(b)]. Such OM observation is in good agreement with the results of SEM observation. These results indicate that the dispersibility of silica in the composites is dependent on the mixing temperature.

Table 5 shows the relative peak area of Q^2/Q^4 and Q^3/Q^4 obtained from the ^{29}Si–CP/MAS–NMR spectra, as shown in Figure 2. The ratio of Q^2/Q^4

Table V   Ratio of Q^2/Q^4 and Q^3/Q^4 for the Samples

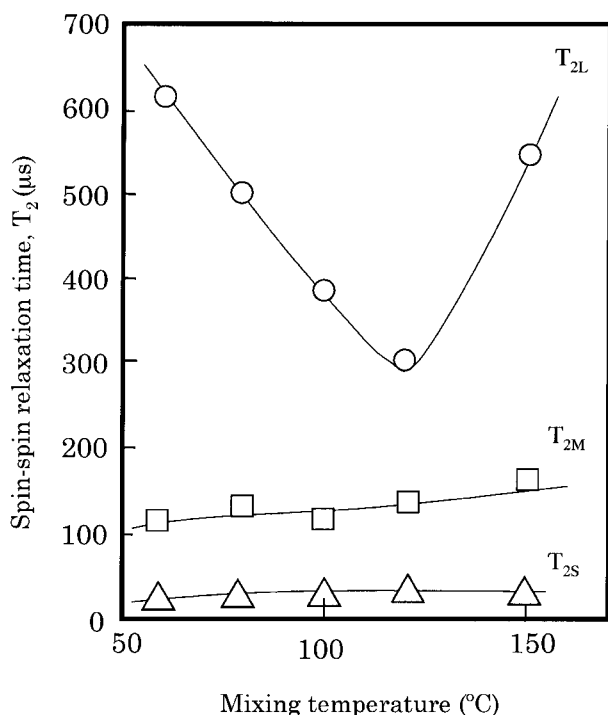| Samples	Q^2/Q^4	Q^3/Q^4
Original silica (A200)	0.47	1.23
Bound rubber formed at 100°C	0.08	1.19
150°C	0.25	0.71

Figure 7 Mixing-temperature dependence on the spin–spin relaxation time, T_2, of the composites.

and Q^3/Q^4 indicates the number of geminal and single silanol groups, respectively, based on the siloxane skeleton bond. Both geminal and single silanol groups decreased with increasing mixing temperature. Our previous paper revealed that the ratios of Q^2/Q^4 and Q^3/Q^4 were not affected by the elimination of adsorbed water on the silica surface.[9] Further, the changes in the chemical shift with mixing temperature were not observed in ^{29}Si–CP/MAS–NMR spectra of bound rubbers (see Fig. 2).

These results suggest that the decrease of geminal and single silanol groups might be derived from the dehydration from inter- or intrasilanol groups on the silica surface during mixing at high temperatures of 100°C or above. That is, surface chemistry of silica particles changes with temperature, especially above 100°C.[16] Such changes might induce the structural change of silica aggregates, leading to the change in the dispersibility in the rubber matrix. The change of dispersibility of silica might induce the change in the fraction of bound rubber in the composites.

Higher Order Structure of the Composites

Above room temperature, NMR decay signals of all composites indicated the existence of three T_2

components. This means that the composites are composed of three phases with different chain mobilities.[7,8] That is, a highly mobile rubber phase with the largest T_2 (T_{2L}) and a glassy rubber phase with the shortest T_2 (T_{2S}). The intermediate T_2 (T_{2M}) arises from the interface between the T_{2L} and T_{2S} phases. Both T_2 and fraction of each T_2 component were dependent on the measurement temperature. Above 60°C, the fraction of each T_2 was weakly dependent on the measurement temperature. Thus, the structural analysis of bound rubber was carried out at 60°C to minimize the structural change of the composite by heat.

Spin–spin relaxation time (T_2) and the fraction of T_2 from the composite are plotted as a function of mixing temperature in Figures 7 and 8, respectively. As seen in Figure 8, the component fraction of T_{2L} for all samples exceeded 80%. Thus, the discussion relates only to the T_{2L} component. The T_{2L} decreased with increasing mixing temperature, showing a minimum at 120°C, then increasing with the temperature. The decrease of T_{2L} with the mixing temperature is due to the increase of the fraction of bound rubber. The T_{2L} is responsible for the segmental mobilities of the highly mobile phase in the bound rubber and of
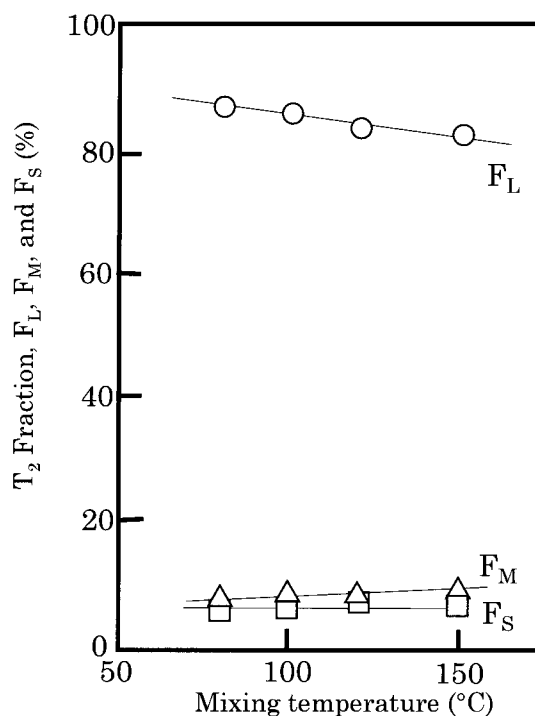

Figure 8 Mixing-temperature dependence on the component fraction of T_2 of the composites.
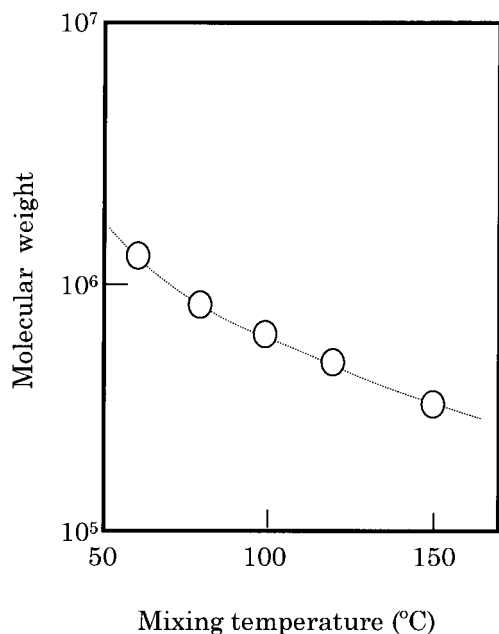
Figure 9 Changes in MW of free rubber in the composites with the mixing temperature.

Figure 10 Heat treatment temperature dependence on the molecular weight relation (MW/MW$_0$).

free rubber in the composite. The segmental mobility of free rubber is usually higher than that of the highly mobile phase in the bound rubber. Thus, the T_{2L} for free rubber is larger than that for bound rubber. However, the difference is not large enough to observe separately. So the T_{2L} data obtained in this study was an averaged value. Therefore, with the increasing of the fraction of bound rubber, the T_{2L} decreased. However, this consideration is not applicable to the T_{2L} data above 120°C, since the fraction of bound rubber keeps constant above 120°C.

In Figure 9 the number averaged molecular weight (MW) of PEA extracted from the composites is plotted against mixing temperature. The MW decreased with increasing mixing temperature. This result suggests that the thermal degradation and/or shearing breakdown of rubber molecules must be taken into consideration during mixing.

Figure 10 shows the molecular weight retention (MW/MW$_0$) of PEA as a function of heat treatment temperature in air. The retention decreased rapidly above 100°C. This means that thermal degradation of PEA molecules becomes significant above 100°C.

Figure 11 shows the molecular weight retention of free rubber in the composite as a function of mixing energy calculated from torque curve at a mixing temperature of 120°C. Although the re-
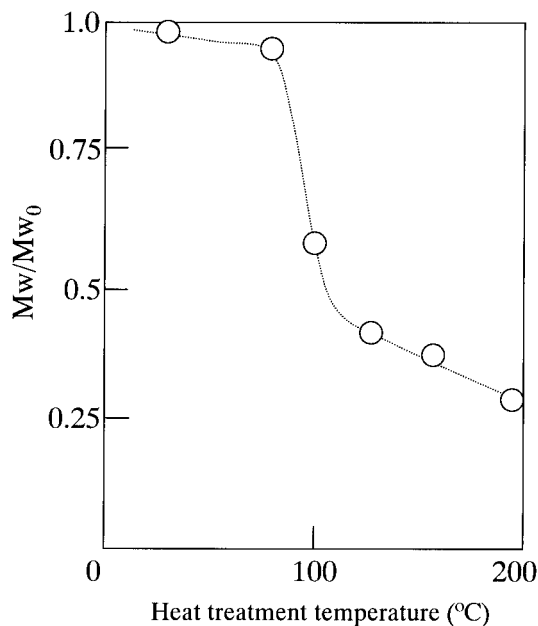
tention drops abruptly in the small energy region, the change of retention with the energy is very small above 1,000 MJ/m^3. This means that most of the breakdown of PEA molecules by mechanical mixing terminates around WIT. From these results it can be presumed that the bound rubber
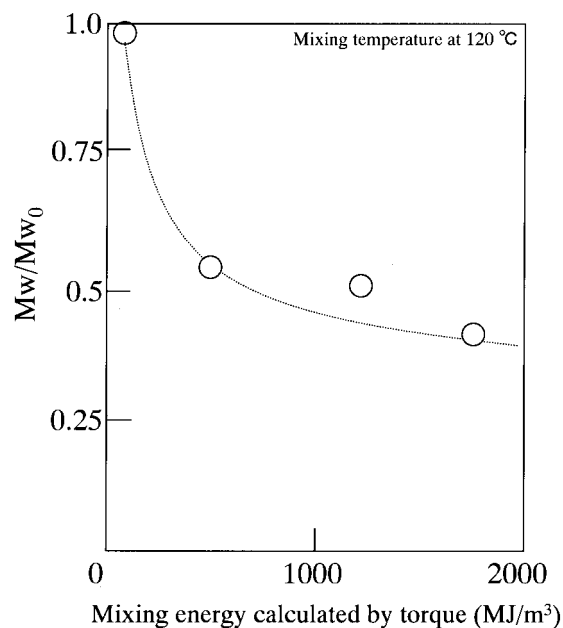

Figure 11 Mixing energy dependence on the molecular weight retension (MW/MW$_0$).
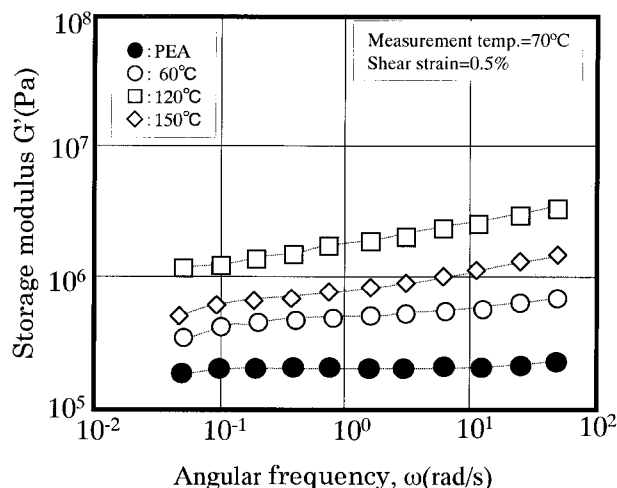
Figure 12   Storage modulus (G') of PEA and composites as a function of angular frequency (ω).

formation was derived from both filler–gel formation by physisorption of rubber molecules on the silica and rubber–gel formation by the chain scission and recombination of PEA molecules during the mixing. We could not determine the fraction of rubber gel in the bound rubber, but it is reasonable to speculate from Figures 4 and 10 that above 100°C the fraction of rubber gel should increase abruptly. In the NMR sense, the T_2 value of rubber gel is almost similar to that of pure rubber. Thus the increase of T_{2L} for the composite with mixing temperature above 120°C might arise from the increase of the fraction of rubber gel.

Shown in Figure 12 is the shear storage modulus (G') measured at 70°C and induced 0.5% shear strain as a function of angular frequency (ω) for pure PEA and silica-filled compounds prepared at 60, 120, and 150°C. For pure PEA, the G' shows the rubberlike plateau zone, as the G' is almost constant within the range of ω studied. The G' for the silica-filled composite prepared at 60°C increased with ω, but the change was small. At a given ω, the G' increased with increasing mixing temperature up to 120°C, where the G' showed the largest angular frequency dependency. Above 120°C of mixing temperature, the G' rapidly decreased at a given ω. It is generally recognized that, in the frequency region where the rubberlike plateau zone appears, the increase of G' with ω is due to the increase of network structure in the system.[21,22] As shown in Figure 5, the size of agglomerates became smaller with mixing temperatures up to 120°C, which en-

hanced the development of network structure and simultaneously improved G' at a given ω due to the homogeneous dispersion of silica. When the mixing temperature exceeded 120°C, a part of the network structure might be broken by the chain scission, which reduced the G' at a given ω as well as the small change of G' with ω.

CONCLUSIONS

A study was carried out on the mixing temperature dependence on structure development in composites from fumed silica and polyethylacrylate rubber (PEA).

High-resolution solid-state NMR results revealed that there was no chemical bonding between silanol groups on the silica and PEA molecules. Nevertheless, a bound-rubber structure appeared in the composites. The content and structure of bound rubber were greatly affected by the mixing temperature of silica and PEA. With increasing mixing temperature, the size of agglomerates formed by silica particles decreased; further, the molecular weight retention of free rubber in the composites also decreased. The bound rubber is likely to be composed of filler gel and rubber gel. The filler gel was primarily formed by a physisorption of rubber molecules on the silica that was controlled by the dispersibility of silica. On the other hand, the rubber gel was formed by a recombination of degraded molecules. With an increase of the mixing temperature from 60 to 120°C, the dispersibility of silica in the rubber was greatly improved; however, the change in the molecular weight retention of free rubber was not so prominent. Above 120°C, the molecular weight change was remarkable, but the dispersibility didn't change so much. These combined changes induced the mixing temperature dependence of structure and the content of bound rubber in the silica-filled PEA rubber composites.

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