

Effects of Alkylation of Silicas on Interfacial Interaction and Molecular Motions Between Silicas and Rubbers

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SYNOPSIS

The interactions between rubbers and silicas were studied by means of bound rubber determination, vulcanizate swelling procedure, and tensile retraction measurement. The mobilities of rubber chain segments in mixture with silicas were investigated by thermomechanical and dynamic mechanical analyzers. The results show that when the untreated silica was incorporated into rubbers, the strong interaction of rubber with the silica apparently constrains the segmental motions of the rubber molecules, resulting in the decrease in the dynamic loss peak and the thermal expansion coefficient, and the increase in the glass transition temperature. The alkylations on silica surfaces weaken the interfacial interaction between rubbers and silicas, and the mobilities of the rubber molecules become less restricted. Furthermore, proton spin-spin relaxation time (T_2) measurements by the pulsed NMR on the insoluble bound rubber, indicate that there are two relaxing regions: an immobile (or a tight) region and a relatively free (or a loose) one. The types of the rubbers and the activities of the silica surfaces have influences on the relaxation process of the two bound rubber components. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Recently, carbon black and silica have been widely used to improve the mechanical properties of rubber composites.¹⁻³ Although a great deal of research effort has been dedicated to the filler reinforcement,^{4,5} the mechanism of the reinforcement for the filled rubber system has not been thoroughly clarified. In fact, the extent of the interaction between rubber and filler truly governs a number of the final product properties,^{6,7} and the knowledge of the interaction in a rubber-filler mixture is essential in understanding the mechanism of rubber reinforcement by active fillers.^{8,9}

To reach a better assessment of the interfacial interaction in the reinforcement process, we prepared silicas selectively modified by esterification of

the surface silanol groups with methanol or hexadecanol. The organophilic character of the corresponding silicas should be of interest due to their improved compatibility toward rubbers. For this purpose three commercial rubbers were used, a natural rubber (NR), styrene-butadiene rubber (SBR), and acrylonitrile-butadiene rubber (NBR). The corresponding filled vulcanizates were obtained. In the previous articles,¹⁰⁻¹² the effects of the alkylations of the silica surface on reinforcement of rubbers were investigated. The results showed that the extent of reinforcements in NR and SBR vulcanizates are reduced when the silicas are alkylated, especially for hexadecylates. However, in NBR vulcanizates the alkylation seems to have lower influences on the reinforcements of silicas. In this presentation, the mobilities of the interlayer between rubber and silica were studied by thermomechanical analysis (TMA), dynamic mechanical analysis (DMA), and pulsed NMR. Furthermore, quantitative estimations of the rubber-filler interaction in

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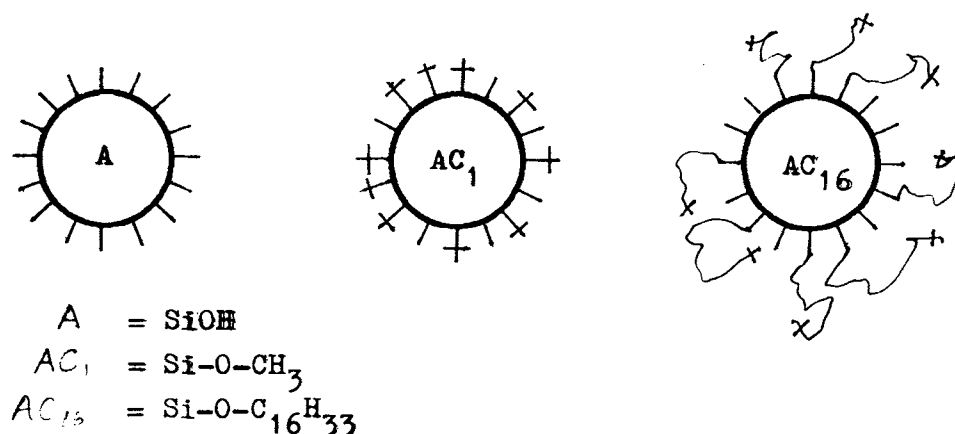


Figure 1 Illustration of the effects of alkylations on the surface structures of silicas.

the above systems were attempted through dynamic loss studies.

EXPERIMENTAL

Materials

The rubbers used in this study were NR, SBR, and NBR, whose compositions were as follows. A commercial SBR-1502 contained 23.6 wt % styrene. A commercial NBR (Krynac 34.50) had an acrylonitrile content of 34 wt %. The silica used was Aerosil-130 (coded as A), the approximate particle diameter, surface area, and silanol coverage of which are 160 Å, 130 m²/g, and 4 SiOH/nm², respectively.

Methylation of Silica Surfaces

Twenty grams of silica, previously heated in an oven at 110°C for 24 h, was suspended in 400 mL of CH₃OH and the solution was stirred at a specific temperature for a specific time. Then the treated sample was centrifuged and dried, first at room temperature in an oven and then the temperature was raised to 150°C for 6 h.

Hexadecylation of Silica Surfaces

Thirty grams of predried silica was added to 300 g of hexadecanol, and stirred at 200°C for a specific time. Finally, the solution was extracted with CHCl₃/toluene to remove the unreacted hexadecanol. The treated silicas were dried in air at 110°C.

Measurements of Grafting Ratio

The percentage of grafting (R_g) was calculated as follows,

$$R_g = c \cdot N / (a \cdot n \cdot s) \quad (\text{CH/nm}^2) \quad (1)$$

where c is the weight percentage of carbon in sample, N is Avogadro's number, a is the atom weight of carbon, n is the number of atoms in the alkyl, and s is the specific surface area of silica (nm²/g).

In this work, the percentage of grafting is 2.89 CH₃ groups/nm² (i.e., 70% coverage) for methylated silica (coded as AC₁), and 1.34 C₁₆H₃₃ groups/nm² (i.e., 50% coverage) for hexadecylated silica (coded as AC₁₆). Schematic illustrations of surface structures of the three silica fillers are shown in Figure 1.

Sample Preparation

Silicas and rubbers were mixed at 50 rpm in a Brabender mixer. After the rubber was premixed at 140°C for 2 min, silica filler (50 phr) was incorporated into the rubber, and the mixing was continued until an equilibrium torque value was attained.

Some of the master batches prepared above were compounded with dicumyl peroxide (1.0 phr) on a cool two-roll mill; specimens were press vulcanized in a mold at 110°C.

Bound Rubber Determination

Bound rubber content was determined in unvulcanized compounds (0.5 g) in toluene (100 mL) at room temperature for 7 days; the solvent was refreshed after every 24 h. The silica gel (bound rubber plus

silica) was separated and suspended in acetone and dried.

Vulcanizate Swelling Procedure

Vulcanizates samples (0.5 g, 1.9 mm thick) were swollen in 50 mL toluene at room temperature for 7 days. These swelling conditions were sufficient to reach equilibrium. The swollen vulcanizates were weighed immediately after swelling and after drying overnight at 80°C. From the swelling data, values of the volume fraction of rubber in the equilibrium swollen vulcanizate (V_r) were calculated by using eq. (2)¹³:

$$V_r = \frac{1}{1 + \frac{d_r}{d_s} \left(\frac{1 - f_{\text{sol}}}{1 - f_{\text{sol}} - f_{\text{fil}}} \right) \left(\frac{W_s}{W_0} - 1 \right)} \quad (2)$$

where f_{fil} and f_{sol} are the weight fractions of filler and of soluble polymer, respectively; d_r and d_s are the densities of the rubber and of the solvent, respectively; and W_0 and W_s are the corresponding dry weight and swollen weight of the sample.

Determination of Molecular Weight Between Crosslinks

Tensile retraction measurements¹³ were used to determine the effective molecular weight between crosslinks of vulcanized rubbers. A 47-mm internal diameter, 50-mm external diameter ring, cut out of a 6-mm thick compression-molded sheet, was elongated at crosshead speed of 50 mm/min to a desired maximum extension of 25, 50, and 100%, respectively. Then this sample was immediately retracted at the same rate until the stress reached zero. The effective molecular weight between crosslinks (M_c) can be obtained by extrapolating from M_c versus λ_{max} , using eqs. (3) and (4),

$$\frac{\sigma}{2(\lambda - \lambda^{-2})} = C_1 + \frac{C_2}{\lambda} \quad (3)$$

$$M_c = \frac{dRT}{C_1} \quad (4)$$

where σ is the stress based on the undeformed dimensions, C_1 and C_2 are empirical constants, M_c is the molecular weight between crosslinks at a given strain, d is the density of the sample, R and T are the gas constant and absolute temperature, respectively, and λ is the extension ratio.

TMA Measurements

Specimens, $6.5 \times 8.5 \times 3.0$ mm, cut from the compression-molded sheets were tested on a Perkin-Elmer TMS-2 thermomechanical analyzer with rising rate of 10°C/min from -150° to 180°C.

DMA Measurements

A Perkin-Elmer DMA-7 was used to measure the dynamic loss of the filled vulcanizates ($6.2 \times 5.0 \times 30.0$ mm) cut from the compression-molded sheets over the temperature range -120° to 20°C with the heat rate of 2°C/min and a vibration frequency of 3.3 Hz.

Pulsed NMR Measurements

Two grams silica filler was mixed with 200 mL rubber-toluene solution of 2 wt % concentration and the mixture was gently stirred by a magnetic chip for 24 h at room temperature. The silica gel (bound rubber plus silica) was separated from the mixture and suspended in acetone to exchange toluene with the more volatile solvent, then filtered. The silica gel was dried at 120°C *in vacuo* for 16 h.

Pulsed NMR measurements were performed on a Bruker pulsed NMR spectrometer (SXP4-100), operating at 90 MHz. In this study, the width of the 90° pulse and the pulse interval were adjusted to be 0.2 and 10 μ s, respectively.

RESULTS AND DISCUSSION

Interfacial Interactions

Table I shows the experimental values of bound rubber content (B_{tol}), volume fraction of swollen rubber (V_r), and molecular weight between crosslinks (M_c) of rubbers filled with untreated silica (A), methylated silica (AC₁) and hexadecylated silica (AC₁₆), respectively. From the data of B_{tol} , it is obvious that the alkylations result in a decrease of the amount of the bound rubber. Generally, bound rubber is caused by many factors, such as physical and/or chemical adsorption, hydrogen bonding, and entanglement of molecules, etc. For the untreated silica filled system, the bound rubber content is governed by physical and/or chemical adsorption. Thus when the silica surface was alkylated, the interaction between the rubber and silica surface was weakened by reduction of the concentration of active sites on the silica surface, showing a decrease in B_{tol} . It is interesting to note that when AC₁₆ filled NBR was

Table I Values of Bound Rubber Content, Volume Fraction of Swelling, and Effective Molecular Weight Between Crosslinks of Rubbers Filled with Untreated and Treated Silicas (50 phr)

Sample	B_{tol} (%)	V_r	M_r ($\text{g mol}^{-1} \times 10^{-3}$)
NR	—	0.18	2.18
NR + A	54.5	0.19	0.92
NR + AC ₁	49.0	0.18	1.66
NR + AC ₁₆	Gel	0.13	8.28
SBR	—	0.20	1.75
SBR + A	48.1	0.25	0.37
SBR + AC ₁	47.3	0.23	0.74
SBR + AC ₁₆	Gel	0.16	3.31
NBR	—	0.31	1.58
NBR + A	50.3	0.34	0.69
NBR + AC ₁	45.9	0.29	0.74
NBR + AC ₁₆	0	0.28	1.29

dissolved in toluene, the AC₁₆ filler was easily extracted from the NBR matrix, and its B_{tol} was zero. But the AC₁₆ filled NR or SBR system always forms a gel in toluene, which is mainly attributed to entanglement between the hexadecyl group and NR (or SBR) owing to good compatibility. The AC₁₆ with bound rubber was difficult to extract from the rubber matrix. Therefore, it is difficult to obtain the accurate values of B_{tol} for AC₁₆ filled NR or SBR.

The data of V_r in Table I were also used for estimating the influence of silica surface modifications on swelling behavior of the filled vulcanized rubbers in toluene environments. For a given rubber, it is evident that the addition of untreated silica increases V_r , then V_r decreases gradually with the increasing length of alkyl groups on the silica surfaces. This seems to depend on the silanol coverage of silica. The alkyl chains on the modified silicas reduce the possibility of forming physical and/or chemical adsorption and hydrogen bonding between silanol group of silica and rubber matrix, thus, resulting in a decrease of V_r .

Tensile retraction measurements were used to determine the effective molecular weight between crosslinks of vulcanized rubbers. In addition, it can give information of the interaction between rubber and filler. The data for M_r in Table I show that M_r is reduced by adding the untreated silica, and then increases gradually with the increasing length of alkyl chains on the silicas for a given vulcanized rubber system at the same vulcanization condition. Apparently, M_r is related to the interaction between rubber and filler. The alkylations on silicas reduce this in-

teraction, thus decreasing the number of the effective crosslinks, that is, an increase in M_r of the vulcanized rubbers. Here, the effects of entanglements on the interaction of silicas with vulcanized rubber were ignored because the entanglements are lost upon straining of vulcanized rubbers.

It is interesting that there is a significant increase in M_r of NR or SBR by adding AC₁₆ compared with that of the other systems. It is mainly because that the hexadecyl on the AC₁₆ plays a plasticizer role for rubber vulcanization. The order of the compatibility of AC₁₆ with rubbers is NR > SBR > NBR, so their effective molecular weights also show the same order.

Thermomechanical Properties

Table II shows the experimental values of thermal expansion coefficients and glass transition temperatures (T_g) of vulcanized rubbers filled with silicas. It can be seen that the thermal expansion coefficients of the filled rubbers are decreased by adding the untreated silica, then are increased with the length of carbon chains on silica whether at below or above their respective T_g . Only the variations of the thermal expansion coefficients of the rubbery region are greater than those of the glassy region. On the other hand, their T_g shifts to higher temperature by adding the untreated silica, and then to lower a one when the silicas were alkylated.

The thermomechanical properties of filled vulcanizates are affected by many factors, such as the

Table II Values of Thermal Expansion Coefficients and Glass Transition Temperature of Vulcanizates Filled with Untreated and Treated Silicas (50 phr) Measured by TMA

Sample	T_g (°C)	α_1 ($\text{K}^{-1} \times 10^{-4}$)	α_2 ($\text{K}^{-1} \times 10^{-4}$)
NR	-67.5	0.81	2.27
NR + A	-65.0	0.54	1.83
NR + AC ₁	-66.0	0.61	1.96
NR + AC ₁₆	-67.0	0.79	2.23
SBR	-53.0	2.34	5.56
SBR + A	-51.0	1.73	3.86
SBR + AC ₁	-52.0	1.84	4.55
SBR + AC ₁₆	-54.0	1.96	5.21
NBR	-29.0	0.86	2.06
NBR + A	-28.0	0.68	1.61
NBR + AC ₁	-28.0	0.68	1.72
NBR + AC ₁₆	-28.0	0.73	1.76

α_1 , thermal expansion coefficient below T_g ; α_2 , thermal expansion coefficient above T_g .

molecular structure of rubber; the shape, size, and content of filler; and the interaction between the rubber and filler. In the same rubber, filler, and their compositions, the interfacial interaction is undoubtedly one of the most important factors. The addition of silica constrains the molecular motions of the rubbers, therefore increasing their T_g and reducing their thermal expansion coefficients. When the silica surface was alkylated, the weakened interaction between the silica surface and the rubber leads to the increase in the thermal expansion coefficient and decrease in T_g .

Dynamic Mechanical Properties

To clarify the TMA results above, we used DMA to investigate the dynamic loss of the vulcanizates. Figure 2 shows the dynamic loss of pure NR and filled NR. The addition of the untreated silica greatly reduces the $\tan \delta$ of the NR matrix. After alkylating, the $\tan \delta$ gradually increases with the length of carbon chain on the silica surface, but it is still lower than that of pure NR due to the reduction of the effective volume fraction by the incorporation of fillers. On the other hand, the T_g of NR is improved significantly by adding the untreated silica, then re-

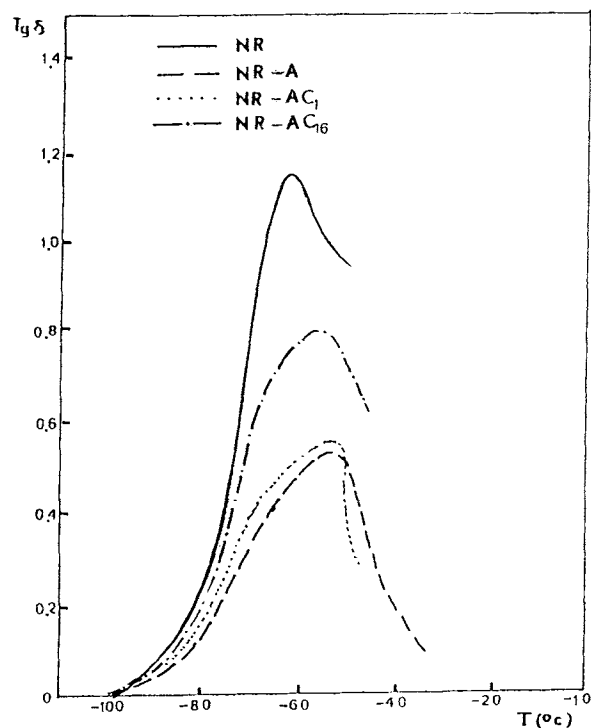


Figure 2 Dynamic loss vs. temperature for NR and filled NR.

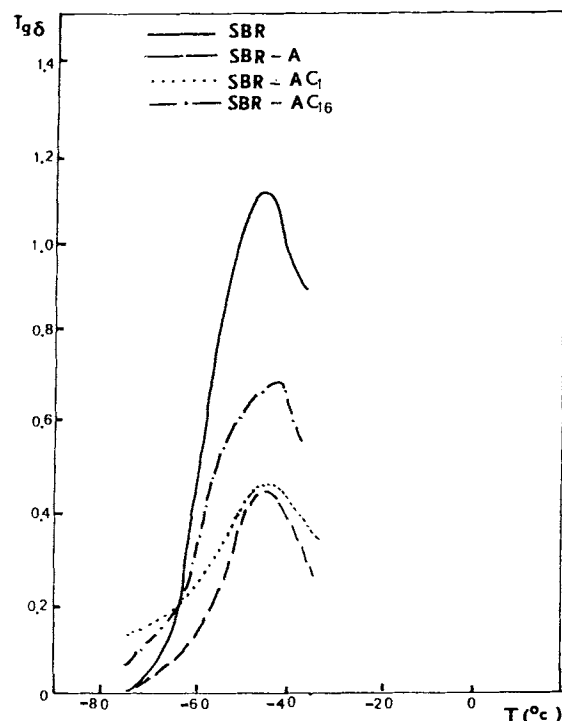


Figure 3 Dynamic loss vs. temperature for SBR and filled SBR.

duced with increasing the length of the carbon chain on the silica.

From the molecular motion point of view, we can see that when the untreated silica was mixed into the rubber matrix, some of rubber was absorbed preferentially and formed bound rubber, which greatly constrains the molecular motions of rubber, resulting in the increase in T_g and decrease in $\tan \delta$. When the silica was modified by alkylates, the reduction of the surface energy weakened the interaction between filler and rubber and relatively decreased the constrain on rubber molecules. Therefore, the T_g shifts to a lower temperature and $\tan \delta$ increases. This effect is more apparent when increasing the length of the carbon chain on the silica.

Figure 3 shows the dynamic loss of pure SBR and filled SBR. The changes of T_g and $\tan \delta$ of the filled SBR are similar to those of the filled NR system. But the change of T_g in the former system is smaller than in the latter, owing to the relatively weaker interfacial interaction in filled SBR compared to that in filled NR.

Figure 4 shows the dynamic loss of pure NBR and filled NBR. It is noteworthy that the T_g of the filled NBR systems seems independent of the length of the carbon chain alkylated on the silica surfaces in the TMA and DMA measurements. This can be

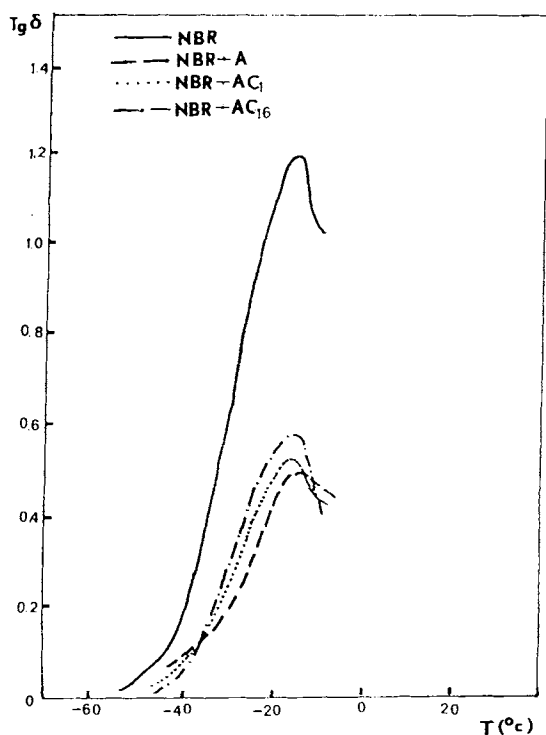


Figure 4 Dynamic loss vs. temperature for NBR and filled NBR.

explained by the fact that the carbon chains on silicas have poor compatibility with NBR; the fillers, whether they are modified or not, only act as rigid particles filled in the NBR matrix.¹²

The detailed values are shown in Table III.

Quantitative Estimate of Thickness of Interlayer

In the present work, dynamic mechanical studies were used for quantitative estimate of the extent of rubber–filler interaction by comparing the $\tan \delta$ of the filled and unfilled systems. If dynamic loss in filled and unfilled rubbers has common origins, an equation derived by Nielsen¹⁴ is,

$$\tan \delta_c / \tan \delta_r = 1 - \phi_f \quad (5)$$

where ϕ_f is the volume fraction of the filler and $\tan \delta_c / \tan \delta_r$ (the subscripts c and r refer to the compounded and pure rubber, respectively) are relative loss of filled rubbers. The equation is valid only for an agglomerate-free composite, based on rigid solid particles, and excluding interactions (e.g. adhesion) at the polymer–filler interface.¹⁵

The dynamic loss performance is particularly interesting around the T_g . Because the matrix phase will not, in general, deform filler particles, the energy

losses are mainly due to the rubber that acts as the dissipative medium. The fillers and the relative dynamic loss should be related simply to the rubber volume fraction, as indicated in Eq. (2). If there is significant physicochemical (dispersion force) or specific (e.g. acid–base) interaction between rubber and filler, this will tend to immobilize a layer of rubber around each solid particle. Assuming the dispersed silica to be a rigid sphere, the immobilized rubber layer will contribute to the effective filler volume fraction in the compound. As a result of such rubber–filler interaction, Eq. (2) then can be rewritten, with the introduction of a correction parameter B , as shown by Iisaka and Shibayama,¹⁶

$$\tan \delta_c / \tan \delta_r = 1 - B\phi_f, \quad (6)$$

which is applicable particularly to the region around T_g . The correction parameter B , which represents the extent of rubber–filler interaction, is related to the effective thickness of the matrix–filler interphase through^{8,17}

$$B = (1 + \Delta R/R)^3 \quad (7)$$

where R is the radius of dispersed fillers and ΔR is the apparent thickness of the immobilized rubber layer.

Table III gives the values of B and ΔR in Eq. (4). It is seen that the correction parameter and apparent thickness of the immobilized rubber layer are gradually decreased with increased length of the carbon chain on the silica. This shows that the extent of rubber–filler interaction and the thickness of the

Table III Data of Dynamic Mechanical Analysis for Vulcanizates Filled with Untreated and Treated Silicas (50 phr)

Sample	T_g (°C)	$\tan \delta$	B	ΔR (Å)
NR	-61.0	1.15	—	—
NR + A	-50.0	0.33	4.07	52.2
NR + AC ₁	-52.0	0.38	3.82	49.4
NR + AC ₁₆	-56.0	0.57	2.88	37.8
SBR	-45.0	1.10	—	—
SBR + A	-43.0	0.44	3.35	39.7
SBR + AC ₁	-43.0	0.46	3.25	38.5
SBR + AC ₁₆	-44.0	0.78	1.63	14.1
NBR	-16.0	1.18	—	—
NBR + A	-15.0	0.49	3.16	37.4
NBR + AC ₁	-15.0	0.52	3.02	35.8
NBR + AC ₁₆	-15.0	0.58	2.75	32.1

interlayer are also decreased. Although in our view their significance is primarily relative, the ΔR values appear to be in good agreement with that of the immobilized rubber layer (45 Å) reported in the literature.¹⁸

The results of this study, although emphasizing the importance of interfacial interaction to the development of composite properties, are not intended to overstress that point. Contributions from a variety of other factors should not be neglected in a comprehensive approach to the question of property development in filled rubber compounds. The fineness of dispersion attained in the filled compound, interparticle friction, and an ensuing compositional heterogeneity in the vicinity of the particles should be included.

Mobilities of Bound Rubbers

The bound rubber phase surrounding the silica consists mainly of long and short loops.¹⁹⁻²¹ Two relaxation times of short T_2 (T_{2t}) and long T_2 (T_{2l}) are observed for all samples as shown in Table IV. This implies that the bound rubber is composed of two regions of molecular mobility, a tight region, which is presumably the area immediately surrounding the silica, and a loose region, where the rubber segmental motions are free in comparison to the tight region, but constrained in comparison to the motions in the pure rubber.

For the silica-filled NR system, it was found that both T_{2t} and T_{2l} increase and the component ratio of tightly bound to loosely bound decreases with increasing the length of the carbon chain on the silica. This suggests that the main active site on silica was the silanol group; and the reduction of content of silanol groups caused by alkylating on the silica surfaces leads to the reduction of the average interaction between rubber and silica, then improving the chain mobility of the bound rubber. Moreover, the long carbon chain improves the compatibility between silica and NR, which increases the loosely bound rubber component, and reduces the possibility of the chemical interaction at the interface. Therefore, the ratio of tight to loose components decreases gradually.

For the silica-filled SBR system, the chain mobilities of the tightly bound rubber become relatively easier by the reduction of the chemical interaction between SBR and filler with the increasing length of the carbon chain on the silica, showing the increase in T_{2t} . It is noted that, unlike the filled NR system, the T_{2l} in the filled SBR system decreases. This can be explained by the fact that the lower

Table IV Spin-Spin Relaxation Times and Components Ratio of Bound Rubbers

Sample	T_{2t} (μ s)	T_{2l} (μ s)	M_{2t}/M_{2l}
NR + A	56.5	13.8	5.29
NR + AC ₁	69.0	14.9	2.99
NR + AC ₁₆	146.0	25.7	0.47
SBR + A	227.1	20.3	0.05
SBR + AC ₁	189.1	22.4	0.18
SBR + AC ₁₆	146.7	30.9	0.45
NBR + A	75.5	13.8	1.24
NBR + AC ₁	49.5	13.9	4.26
NBR + AC ₁₆	101.2	20.6	0.89

compatibility of the carbon chain on the silica with SBR rather than with NR makes the content of phenol in the loosely bound rubber phase higher than that in the tightly bound rubber phase. Then the molecular motions in the loose region are more constrained compared to those in the filled NR system, especially in the AC₁₆ filled system. It is the compatibility that causes the loosely bound rubber component to apparently decrease with the increasing length of the carbon chain on the silica, resulting in the improvement in the component ratio of tight to loose phases.

The silica-filled NBR system has similar order in the relaxation behavior to the silica-filled SBR system, apart from a sharp change in T_{2t} and M_{2t}/M_{2l} in the AC₁₆ filled system.

For the AC₁₆-filled NBR system, the poor compatibility and hence the weak chemical interaction between AC₁₆ and NBR improves the mobility in both the tight and loose regions, and causes the relative reduction in the tightly bound rubber component and the relative increase in the loosely bound rubber component, that is, the increase in M_{2t}/M_{2l} .

CONCLUSION

The incorporations of silica into NR, SBR, and NBR remarkably constrain the mobility of rubber molecules caused by the interfacial interaction between rubber and silica, therefore reducing the dynamic loss and the thermal expansion coefficient and shifting the T_g to a higher temperature.

When the silica surface was methylated, especially hexadecylated, the interfacial interaction was weakened due to the reduction of the concentration of active sites on the silica surface, showing the decrease in B_{tot} and V_r , and the increase in M_r .

And the molecular mobilities of rubbers become less restricted accordingly, owing to the alkylations.

The thickness of the interlayer, which affects the extent of the interaction between silica and rubber, decreases gradually when increasing the length of the alkylated carbon chain on silica.

The pulsed NMR results show that a bound rubber is produced by the addition of silicas as a result of the interaction between silica and rubber segments. Within the bound rubber there are two regions of molecular mobility: a tight region, which is presumably the area immediately surrounding the silica, and a loose region, where the rubber segmental motions are relatively free in comparison to that in the tight one.

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