

# Pulsed NMR Study on the Silica-Filled Rubber Systems

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## Synopsis

Proton spin-spin relaxation time has been measured by the pulsed NMR technique for the bound rubbers extracted from both silica-filled polyisoprene and polybutadiene composites. Two relaxation times  $T_{2s}$  (short) and  $T_{2l}$  (long) are observed for all samples. They are ascribed, respectively, to the relaxation of the tightly and loosely bound rubber components. When the silica filled polybutadiene composite is heat treated at 120°C, loosely bound rubber is preferentially formed, which leads to the increase in the total bound rubber fraction in the composite. During the heat treatment of silica-filled polyisoprene composite, a part of the loosely bound rubber phase is transformed into tightly one, and simultaneously the chain mobilities of both phases become more constrained state. These changes are accompanied by the degradation of polyisoprene molecules probably due to the strong chemical interaction of silanol group and rubber molecules. At a prolonged heat treatment, the fraction of total bound rubber in the composite decreases as a result of the degradation of the loosely bound rubber molecules.

## INTRODUCTION

The presence of fillers such as carbon black or silica in a elastomer commonly leads to marked improvement in the mechanical properties of the rubber composites. Thus, numerous studies have been reported and reviewed<sup>1-5</sup> on the reinforcement of rubber composites especially for carbon-black-filled rubber systems.

Recently, silica reinforcement has received increasing attention because of low price of silica compared to that of carbon black. Despite a great deal of research effort has been dedicated to this subject,<sup>6-9</sup> the mechanism of reinforcement for the silica-filled rubber systems has not been so clarified as to that for carbon black systems.

Pulsed NMR studies have been provided important information on the dispersion of carbon black and the higher order structure of carbon-black-filled rubber systems<sup>10-16</sup> which are essential in understanding the reinforcement of rubber composites. However, no NMR study has been reported on the higher order structure of silica-filled rubber composites and the structural changes during heating.

In this study, pulsed NMR measurements were carried out mainly on the bound rubbers extracted from rubber composites which were prepared from the precipitated silica and polyisoprene or polybutadiene. The results are discussed in terms of the thermal stability of the bound rubber structure in the silica-filled rubber systems.

## EXPERIMENTAL

### Materials

The elastomers and filler used were commercial polyisoprene (Nipole 2200), polybutadiene (Nipole 1220), and precipitated silica (Nipsil VN-3), which were kindly supplied by Nippon Zeon and Nippon Silica, respectively.

### Sample Preparation

200 mL of Rubber-benzene solution of known concentration (2 wt %) was mixed with 200 mL of silica dispersed benzene and the mixture was gently stirred by a magnetic chip for 24 h at room temperature. The silica-filled rubber composites were obtained from the mixture by freeze-dry method. In every composite, 100 parts of silica, which was dried at 100°C for 24 h under vacuum, was incorporated into 100 parts of rubber. Heat treatments of the composites were carried out at a constant temperature ranging from 50 to 150°C for different periods of time under vacuum. Bound rubber samples were prepared from both heat-treated and untreated composites by the solvent extraction method. Details of bound rubber preparations and the determination of the bound rubber fraction in the composites were described in our previous paper.<sup>14</sup>

### Measurements

Pulsed NMR measurements were performed with a JEOL pulsed NMR spectrometer (JSE-5B). The proton spin-spin relaxation time ( $T_2$ ) and the fraction of each component were determined by the solid echo sequence.<sup>17</sup> Details of the component resolution of NMR decay curves were described elsewhere.<sup>14</sup>

## RESULTS AND DISCUSSION

The higher order structure of the filled rubber systems is heterogeneous. The tightly and loosely bound rubber phases formed around the surface of carbon black have been successfully detected by NMR technique.<sup>10-16</sup> However, this method has not been applied to the silica-filled rubber systems.

### Temperature Dependence of Spin-Spin Relaxation Time of Bound Rubber

Figure 1 shows the temperature dependence of spin-spin relaxation time ( $T_2$ ) for polyisoprene (PIR) and the bound rubber in the silica-filled polyisoprene composite (PIR-VN3). At low temperatures, the  $T_2$  for both samples is about 12  $\mu$ s and stays almost constant up to about -50°C. Above -40°C,  $T_2$  for the PIR increases sharply due to the high frequency (~10 kHz) manifestation of the glass-rubber transition of the PIR.<sup>18</sup> Above about -40°C the NMR decay curves of the bound rubber indicated the existence of two  $T_2$ 's; i.e., long  $T_2$  ( $T_{2l}$ ) and short  $T_2$  ( $T_{2s}$ ). Both  $T_{2l}$  and  $T_{2s}$  also show

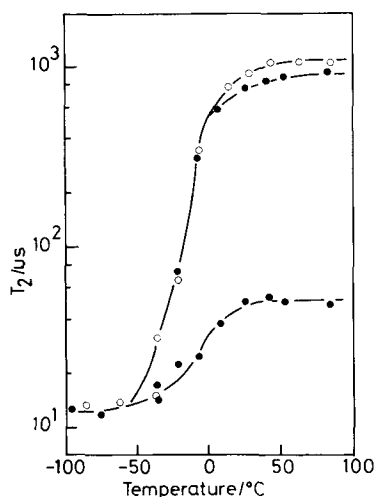


Fig. 1. Temperature dependence of  $T_2$  for PIR (○) and bound rubber in the PIR-VN3 (●).

the rapid increase around  $-10^\circ\text{C}$  due to the onset of micro-Brownian motion of the rubber component. For the bound rubber, the magnitude of  $T_{2t}$  above the transition is about  $900\ \mu\text{s}$ , which is shorter than that of  $T_2$  for the PIR. The  $T_{2t}$  component, which was not observed for the PIR, exists even above the melting temperature of the PIR.<sup>19</sup> Further, above the transition temperature the magnitude of  $T_{2t}$  is about  $45\ \mu\text{s}$  and much shorter than that of  $T_{2t}$ . From these results it is evident that the bound rubber in the PIR-VN3 have two phases with different mobilities.

Figure 2 shows the temperature dependence of  $T_2$  for polybutadiene (PBR) and bound rubber in the silica-filled polybutadiene composite (PBR-VN3). The transition temperature and the values of  $T_2$ 's above the transition are different from those observed for PIR and the bound rubber in the PIR-VN3 due to the difference in the chemical structure of the rubber. However,

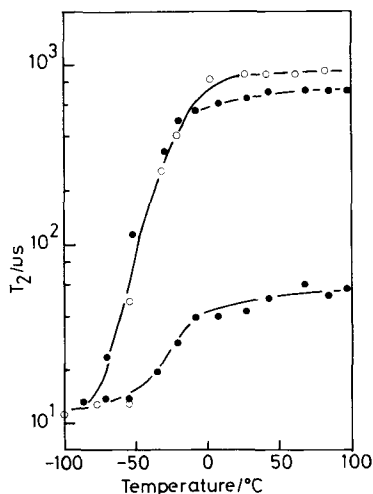


Fig. 2. Temperature dependence of  $T_2$  for PBR (○) and bound rubber in the PBR-VN3 (●).

it is clear that the bound rubber in the PBR-VN3 is also composed of two rubber phases with different mobilities. It is accepted that the bound rubber phase surrounding the carbon black consists mainly of long and short loops.<sup>12,15,16</sup> In our previous NMR study on the polyisoprene filled with a number of silicas, it was found that both  $T_{2t}$  and  $T_{2l}$  increased and the fraction of bound rubber in the composite decreased with decreasing silanol group concentration on the silica surface. The results suggested that the main active site on silica was the silanol group, and the increase in the chain mobility of the bound rubber was enhanced by the reduction of average interaction between rubber and silica.<sup>20</sup> Take those into consideration, the bound rubber in the silica-filled rubber systems is considered to be composed of tightly bound rubber component in the immediate vicinity of the filler particles and outer region of loosely bound rubber phase which are formed by the chemical interaction between silanol groups and rubber molecules. Above the transition temperature, both  $T_{2t}$  and  $T_{2l}$  are weakly dependent on the measurement temperature. Further, the changes in fraction of the two components with temperature was very small above the transition temperature (data not shown). Therefore, the NMR data for the bound rubbers of the PIR and PBR composites were obtained at 70 and 40°C, respectively.

## Structural Changes of Bound Rubber during Heat Treatments

### *Treatment Time Dependence*

The composites were heat treated at 120°C for different periods of time where molecular motions of rubber segments are fully activated. Figures 3 and 4 show the fractions of total bound rubber ( $F_{BR}$ ), loosely bound rubber ( $F_l$ ) and tightly bound rubber ( $F_t$ ) in the PBR-VN3 and PIR-VN3 as a

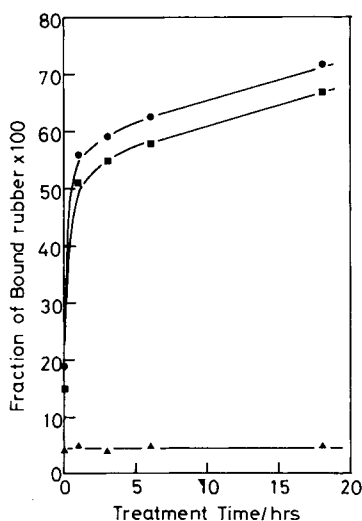


Fig. 3. Heat treatment time dependence of  $F_{BR}$  (●),  $F_l$  (■), and  $F_t$  (▲) in the PBR-VN3.

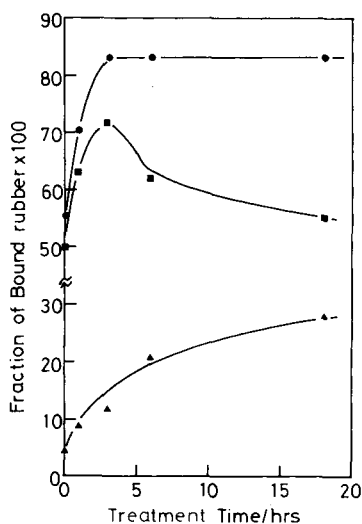


Fig. 4. Heat treatment time dependence of  $F_{BR}$  (●),  $F_l$  (■), and  $F_t$  (▲) in the PIR-VN3.

function of treatment time ( $T_h$ ). The  $F_l$  and  $F_t$  were calculated by the following equation:

$$F_{l \text{ or } t} = F_{BR} \times f_{l \text{ or } t}$$

Where  $F_{BR}$  is determined by the solvent extraction method<sup>14</sup> and  $f_l$  or  $f_t$  is the fraction of loosely or tightly bound rubber component (long or short  $T_2$  component) in the bound rubber calculated from the NMR decay curve. In the PBR-VN3 (Fig. 3), the  $F_{BR}$  as well as  $F_l$  increases abruptly up to 1 h of the treatments followed by a gradual increase with further increase in the time. On the other hand, the change in  $F_t$  with  $T_h$  is less prominent. These results indicate that the increase in  $F_{BR}$  arises from the increase in the  $F_l$ . The value of  $F_{BR}$  in the untreated PBR-VN3 ( $F_{BR}$  at  $T_h = 0$ ) is considerably lower than that for untreated PIR-VN3. Ashida et al. reported<sup>21</sup> that, in the mechanical mixing of rubbers with silica, silica tended to locate preferentially in the natural rubber phase in blends of natural rubber with polybutadiene. They suggested that this was caused by the difference in the chemical interaction of silica with rubber. The present results support their consideration.

The PIR-VN3 shows a quite different structural changes during the treatments compared with those for the former. The  $F_{BR}$  increases sharply up to 3 h of treatments followed by saturation. Although the  $F_l$  also increases up to 3 h, the value begins to decrease after 3 h of the treatments. The  $F_t$  continues to increase over the range of time. These indicate that after 3 h of the treatments, the loosely bound rubber component transforms partially into tightly rubber phase. Dannenberg<sup>3</sup> reported that heat treatments of silica-filled SBR exhibited the beneficial effects on the mechanical properties. However, the details of the mechanism for the improvements were not discussed. During heat treatments, the interaction between filler and

rubber may change, further, thermal degradation of rubber molecules may occur. In order to elucidate the origin of the structural changes during the treatments, the changes in molecular weight of rubbers, concentration of unoccupied silanol groups on the silica surface, and the mobilities of bound rubbers were investigated as a function of  $T_h$ . Usually bound rubber is insoluble to the good solvent of rubber due to strong interaction between filler and rubber. Thus, the molecular weight was determined for the free rubber which was extracted from the composites by viscosity measurements at 30°C. To calculate the molecular weight ( $M_\eta$ ), the following equations were used.

$$\text{PIR}^{22}: (\eta) = 2.00 \times 10^{-4} M_\eta^{0.728}$$

$$\text{PBR}^{23}: (\eta) = 3.05 \times 10^{-4} M_\eta^{0.725}$$

In Figure 5, the  $M_\eta$  of pure rubber (PIR and PBR) and the free rubbers extracted from the PIR-VN3 and PBR-VN3 are plotted against  $T_h$ . Almost no change in  $M_\eta$  with  $T_h$  is observed for pure rubbers and the free rubber extracted from the PBR-VN3. In contrast, the free rubber extracted from the PIR-VN3 shows a sharp decrease in  $M_\eta$  at the initial stage of the treatments. Further, ESR study<sup>24</sup> showed that the bound rubber which was extracted from the heat-treated PIR-VN3 involved large amount of free radicals, which were less in the heat treated PBR-VN3 and pure rubbers. In this study, silica was incorporated into rubber by the solution mixing method to minimize the mechanical degradation of rubber molecules during the mixing. These results demonstrate, first, that the thermal degradation of rubber molecules is negligible under the conditions used in this study, and, second, that partial degradation of PIR molecules occurs during the heat treatments only when silica is incorporated into PIR. In the present

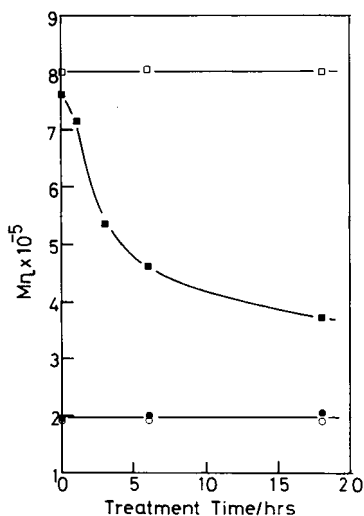


Fig. 5. Changes in  $M_\eta$  with heat treatment time for PIR ( $\square$ ), PBR ( $\circ$ ), and free rubbers extracted from the PIR-VN3 ( $\blacksquare$ ) and PBR-VN3 ( $\bullet$ ).

study, details of the interaction and degradation mechanisms were not investigated. However, it is evident that the PIR molecules react with silanol groups during the treatments, and simultaneously a part of the PIR chains is degraded into small molecules by this reaction. Kawaguchi et al.<sup>25</sup> studied the adsorption of polybutadiene onto silica surface by infrared spectroscopy. They concluded that the large frequency shift of the silanol groups was caused by interaction between the double bonds in polybutadiene and the surface silanol groups. It is also suggested<sup>21</sup> that the interaction for polyisoprene is stronger than that for polybutadiene.

The amount of adsorbed water ( $W$ ) for the PIR-VN3 and PBR-VN3 determined at 25°C and at relative humidity of 95% is plotted against  $T_h$  in Figure 6. For the PBR-VN3, the  $W$  decreases sharply at the initial stage of the treatments followed by the gradual decrease. The decreases in the  $W$  correspond to the decreases in the number of unoccupied silanol groups in the composite. As shown in Figure 2, the  $F_l$  as well as  $F_{BR}$  of the PBR-VN3 increases abruptly and then gradually with increasing treatment time. These results indicate that the increase in  $F_{BR}$  of the PBR-VN3 during the treatments arises from the enhancement of the interaction between free rubber in the composite and silanol groups. The  $W$  for the PIR-VN3 also decreases sharply at the initial stage of the treatments; further, the  $W$  continues to decrease slowly where the  $F_{BR}$  is attained to almost constant value (see Fig. 3). As described previously, the loosely bound rubber in the composite transforms into tightly bound rubber during the treatments, and this process is accompanied by the partial degradation of the rubber molecules. The degraded molecules in the loosely bound rubber phase may contact with unoccupied silanol groups, which leads to the slow decrease in the  $W$  at prolonged treatments.

Figure 7 shows the heat treatment time dependence of  $T_{2l}$  and  $T_{2t}$  for the

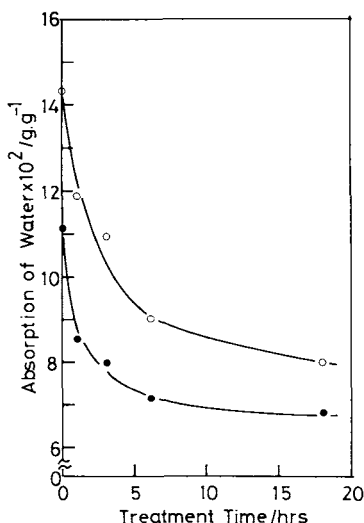


Fig. 6. Absorption of water ( $W$ ) onto PIR-VN3 (●) and PBR-VN3 (○) plotted against heat treatment time.

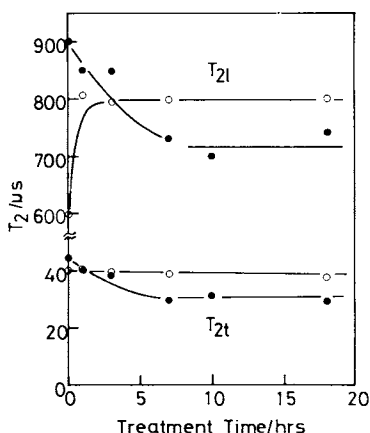


Fig. 7. Heat treatment time dependence of  $T_{2l}$  and  $T_{2t}$  for the bound rubbers in the PIR-VN3 (●) and PBR-VN3 (○).

bound rubbers in the PIR-VN3 and PBR-VN3. For the bound rubber in the PBR-VN3, the  $T_{2l}$  increases abruptly at the beginning of the treatment; however,  $T_{2t}$  shows an almost constant value over the range of the  $T_h$ . At the initial stage of the treatment, the content of loosely bound rubber increases sharply with the expense of free rubber (see Fig. 2). These results suggest that the mobility of the loosely bound rubber formed during the treatments is higher than that of preformed one. For the bound rubber in the PIR-VN3, both  $T_{2l}$  and  $T_{2t}$  decrease up to 7 h and approach the constant values at prolonged treatments. The results indicate that the bound rubber structure changes into more constrained one during the treatments. The limiting values of  $T_{2t}$  and  $T_{2l}$  obtained in this study are still longer than those for carbon gel samples,<sup>14,15</sup> which suggests that the limiting bound rubber structure is not so compact as to that of carbon gel. At the initial stage of the treatments, the loosely bound rubber is formed with the expense of free rubber in the composite, similar to the PBR-VN3, and, simultaneously, partial degradation occurs in the bound rubber phase, which enhances the increase in the interaction between filler and the bound rubber.

#### *Treatment Temperature Dependence*

As shown in the previous section, the structural changes of bound rubber in the PIR-VN3 are accompanied by the degradation due to the chemical interaction between silanol group and polyisoprene. It is thus expected that the changes for the PIR-VN3 are closely related to the heat treatment temperature. In Figure 8, molecular weight ( $M_\eta$ ) of the PIR and free rubber in the PIR-VN3 is plotted against treatment temperature. The treatment was carried out at a constant temperature for 18 h under vacuum. The PIR shows no change in the  $M_\eta$  even after the treatment at 150°C, whereas the  $M_\eta$  for the free rubber begins to decrease around 70°C. The  $F_{BR}$ ,  $F_l$ , and  $F_t$  of the PIR-VN3 are plotted against treatment temperature in Figure 9. The  $F_{BR}$  begins to increase below the temperature where molecular degradation is not observed (see Fig. 7). Around 100°C, the  $F_{BR}$  shows a max-



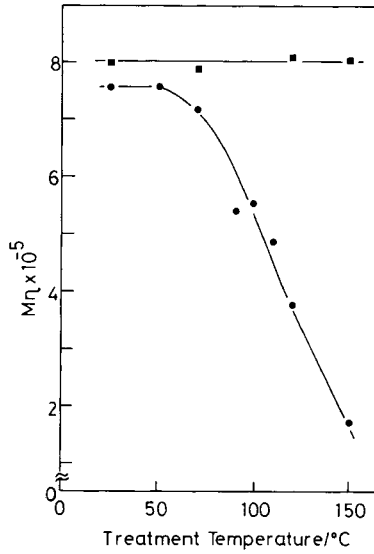


Fig. 8. Changes in  $M_n$  with heat treatment temperature for PIR (■) and free rubber extracted from the PIR-VN3 (●).

imum value and then begins to decrease with further increase in the temperature. The changes in  $F_l$  with temperature is quite similar to those for the  $F_{BR}$ . The  $F_l$  increases slowly up to 100°C, and the increase continues even above the temperature where the  $F_{BR}$  and  $F_l$  decrease. The  $T_{2i}$  and  $T_{2l}$  of the bound rubber in the PIR-VN3 are plotted against the treatment temperature in Figure 10. The  $T_{2l}$  shows the decrease around 70°C where

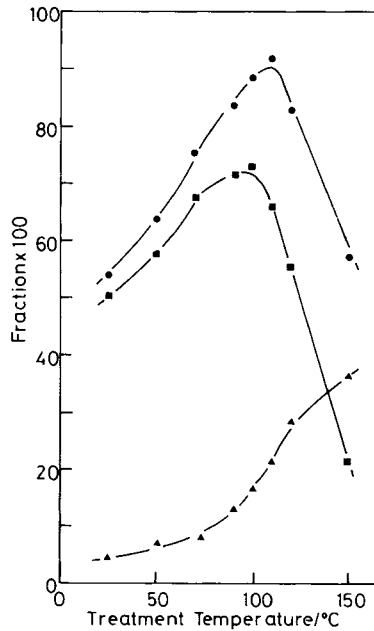


Fig. 9. Heat treatment temperature dependence of  $F_{BR}$  (●),  $F_l$  (■), and  $F_f$  (▲) in the PIR-VN3.

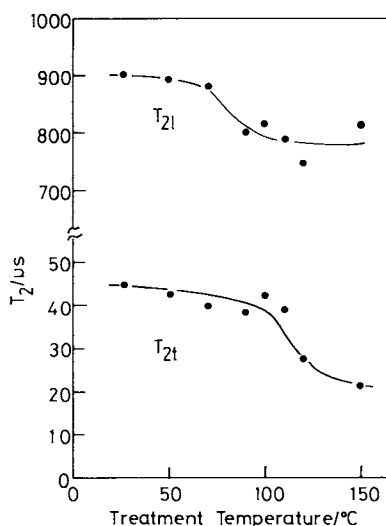


Fig. 10. Heat treatment temperature dependence of  $T_{2i}$  and  $T_{2t}$  for the bound rubbers in the PIR-VN3.

the  $M_n$  begins to decrease. On the other hand, the decrease in  $T_{2t}$  is observed around 120°C where the  $F_{BR}$  and  $F_l$  begin to decrease. From these results the structural changes of PIR-VN3 during the treatments are considered by dividing into three temperature regions. Stage I (up to 70°C): this temperature region is low enough to suppress the molecular degradation and high enough for the free rubber to get contact with the free silanol group due to the increased chain mobility, which induces the increase in the loosely bound rubber content in the composite. Stage II (70–120°C): at this stage the increase in the  $F_l$  as well as  $F_{BR}$  and the molecular degradation are prominent. Further, the chain mobility in the loosely bound rubber phase changes into more restricted state. A part of the free rubber in the composite transforms into loosely bound rubbers, and simultaneously the tightness of loosely bound rubber phase increases due to the increase in the interaction. The degraded molecules of loosely bound rubber may reform the bound rubber, but the mobility is more restricted state than that of preformed one. During this process, large part of the free silanol groups may be expended. Stage III (120°C~): At this stage the rubber molecules which can react with the free silanol groups are limited due to a lesser amount of active site on the silica surface. The large decrease in  $F_l$  as well as  $F_{BR}$  and the sharp increase in the  $F_t$  accompanied by the suppression of the molecular motions of the tightly bound rubber phase suggest that the rubbers in the vicinity of the filler particle react with free silanol groups. Both loosely and tightly bound rubbers are partially degraded during this stage. The loosely bound rubber transforms into tightly bound rubber and free rubber; however, the free rubber cannot reform the bound rubber, which induces the decrease in the  $F_l$ . The tightly bound rubber also changes into more tight state, similar to loosely bound rubber, which leads to the decrease in the chain mobility of this phase.

The results described in the previous section may be related to the combination of stages II and III mentioned above.

## CONCLUSION

Incorporation of precipitated silica into polyisoprene or polybutadiene produces a bound rubber as a result of the interactions between silica and rubber segments. The bound rubber is composed of two phases with different mobilities, i.e., loosely and tightly bound rubbers, similar to carbon black-filled-rubber systems. When the filled polybutadiene composite is heat treated at 120°C, loosely bound rubber is formed preferentially, which leads to the increase in the total bound rubber fraction in the composites. Silica-filled polyisoprene composite shows a quite different structural changes during the heat treatments compared with those for the former. At the initial stage of the treatments, the loosely bound rubber is formed with the expense of nonbonded rubber in the composite. At the second stage, loosely bound rubber component transforms partially into tightly bound rubber phase. Up to this stage, the chain mobilities of the two phase become more restricted state due to the increased interaction between filler and rubber molecules. The changes are accompanied by the partial degradation of polyisoprene molecules caused by the chemical reaction of silanol group on the silica surface and the rubber. At the final stage, degraded loosely bound rubber changes into free rubber due to the lesser amount of the free silanol group, which leads to the decrease in the fraction of total bound rubber in the composite. All the changes described for polyisoprene composite become more prominent with increasing treatment temperature and time.

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Received December 5, 1984

Accepted January 24, 1985