Studies on the Structure and Formation Mechanism of Carbon Gel in the Carbon Black Filled Polyisoprene Rubber Composite

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SYNOPSIS

The structure and formation mechanism of carbon gel in carbon black filled polyisoprene composites were studied by the pulsed NMR technique. The composites were prepared from a wide range of molecular weights by a solution blend. The carbon gels were extracted from the composites by a solvent-extraction method. The content of carbon gel was not governed by the molecular weight of rubber but was controlled by the viscosity of rubber solutions which were used for the blend. Three rubber phases, having different spin–spin relaxation times, were detected in all the carbon gels. The increase of carbon gel content in the composites was mainly from the increase of highly mobile rubber phase, and the gel became soft with the development of this phase. On the other hand, the content and structure of glassy rubber phases were not affected by the size of the carbon gel, and they showed almost a constant value despite the large change in the carbon gel content. A part of the highly mobile rubber phase in the gels could be removed by solvent extraction at high temperature. These results suggest that the formation of carbon gel is primarily governed by two factors: One is the well-known rubber–carbon black interaction, and the other is a physical crosslink between the carbon gel and unbound rubber molecules during blend. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The incorporation of carbon black into elastomers develops the so-called bound rubber around carbon blacks, and such structural developments are believed to enhance the physical and mechanical properties of carbon black/rubber composites. Thus, numerous studies have been reported and reviewed on the carbon black/rubber interaction and its effect on reinforcement. It is generally accepted that the carbon black filled rubber system is composed of two rubber phases: One is the so-called bound rubber (carbon gel) in which rubber molecules are adsorbed on the carbon black surface, and the other is a free rubber (nonbound rubber) which is soluble in common organic solvents. The amount of carbon gel is

affected by many factors such as chemical structure[1] and the molecular weight of rubber,[2-4] the surface area of the carbon black,[5] and the technique for the dispersion of carbon black in the rubber.[3,6] Although these results have been explained by a chemical or physical interaction between rubber molecules and carbon black, complete understanding is still lacking.

Pulsed NMR studies have revealed that carbon gel has a multicomponent phase whose structure depends on the extent of interaction between carbon black and rubber.[3,7-10] Thus, it is expected that structural analyses of carbon gel prepared under various conditions would give us useful information on the formation mechanism of carbon gel.

In this study, structural analyses were carried out by the pulsed NMR method for carbon gels prepared from polyisoprene with various molecular weights and carbon black by a solution blend. The mixing method was considered to minimize chemical re-

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Table I Molecular Weights and Polydispersities of the Samples

Sample No.	M_w	M_n	M_w/M_n
1	1,280,000	670,000	1.91
2	1,045,000	377,000	2.77
3	717,000	286,000	2.50
4	554,000	167,000	3.31
5	489,000	159,000	3.07

action during mixing such as degradation and recombination of rubber molecules. The structure of carbon gel was analyzed as a function of the molecular weight of polyisoprene, and the results are discussed in terms of a formation mechanism of carbon gel in the carbon black filled polyisoprene system.

EXPERIMENTAL

Samples

Materials used were polyisoprene rubber (Nippol2200, M_w = 1,280,000, Nippon Zeon Co.) and ISAF-grade carbon black having a surface area of 111 m²/g determined by N_2 gas adsorption and a Stokes' diameter of 85 nm. Rubber samples with various molecular weights were prepared by the mastication of as-received polyisoprene at 55°C and 60 rpm for various periods of time. The molecular weights and polydispersities of the samples are listed in Table I.

A rubber–benzene solution, 150 mL, of known rubber content (1–3 g) was mixed with 100 mL of carbon black dispersed in benzene, and the mixture was gently stirred by a magnetic chip at 35°C for 30 min. For all mixing, the rate of stirring was kept nearly constant. The carbon black filled composites were obtained from the mixed solution by a freeze-dry method. The composites were composed of 50 parts of carbon black and 100 parts of rubber. The carbon gel samples were obtained from the composites by a solvent-extraction method. The composites were cut into small pieces and then packed in a wire mesh case, which was immersed in a large amount of toluene and stirred for 72 h at room temperature. Details of the carbon gel preparation were described in our earlier article.[7]

Measurements

The viscosity of rubber solution (η) used for mixing was evaluated from the specific viscosity by the following equation:

$$\eta = \eta_{red} = \eta_{sp}/C$$

where η_{red} and η_{sp} are the reduced and specific viscosities of the rubber solutions, respectively, and C is the polymer concentration (g/100 mL). The η_{sp} was measured by a capillary viscometer at 35°C. The content of carbon gel (gram of insoluble rubber per gram of carbon black in the carbon gel, G_t) was determined by percentages of weight loss measured by a thermal gravimetric analyzer (TG/DTA220, Seiko Instruments). Pulsed NMR measurements were performed with a JEOL pulsed NMR spectrometer (FSE 60). The free-induction decay was determined by the solid echo method operating at 60 MHz and 30°C. The proton spin–spin relaxation time (T_2) and the fraction of each component were determined by fitting the solid echo signals to a Weibull function. The content of each component (gram of rubber per gram of carbon black) was calculated by the following equation:

Content of each component (g/g)

$$= \text{fraction of each component} \times G_t$$

Details of the NMR measurements are described in our earlier article.[7]

RESULTS AND DISCUSSION

Carbon Gel Content

Figure 1 shows the relation between carbon gel content (G_t) and polymer concentration for two different
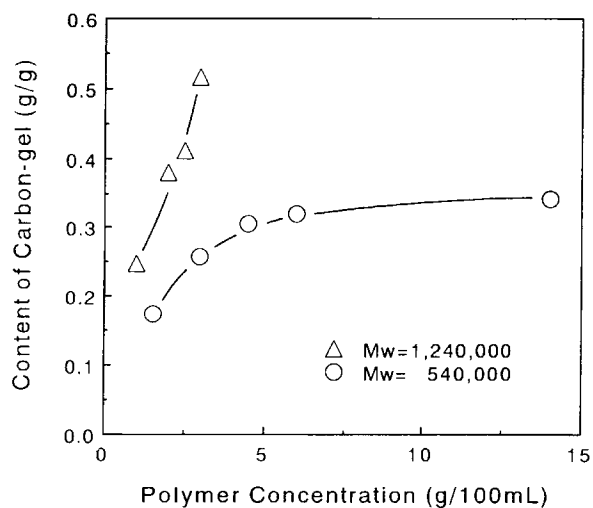

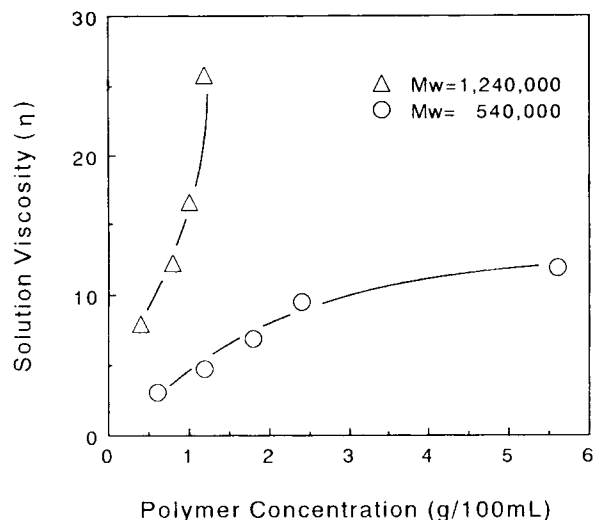**Figure 1** Polymer concentration dependence on carbon gel content.

Figure 2 Polymer concentration dependence on solution viscosity.

molecular weight samples $(M_w = 1,240,000$ and $540,000)$. In this case, the concentration corresponds to that for the polymer solution used for mixing with carbon black dispersed benzene. For both series, the G_t increases with polymer concentration. The results can be explained qualitatively by eq. (1), which is applicable to well-known isothermal solution adsorption[2]:

$$x = k_1 C^{1/n} \qquad (1)$$

where x is a mass of adsorption per unit weight of adsorbent, which corresponds to G_t, C is the concentration of the solution, and k_1 and n are constants. At a given concentration, the G_t for the high molecular weight sample is larger than for the low molecular weight one. In polymer solution, the solution viscosity at a constant polymer concentration increases with molecular weight. Thus, molecular weight effects must be taken into consideration. The concentration, C, in eq. (1) can be correlated with molecular weight by eqs. (2) and (3):

$$\lim_{c \to 0} \eta_{sp}/C = [\eta] = KM^\alpha \qquad (2)$$

$$\eta_{sp}/C = [\eta] + \chi \cdot C \qquad (3)$$

where η_{sp} is specific viscosity; $[\eta]$, the limiting viscosity number; M, molecular weight; K and α, constants; and χ, the Flory–Huggins coefficient. Equations (2) and (3) indicate that the viscosity of the polymer solution (η) increases with polymer concentration; further, the η at a given concentration

increases with molecular weight. These were confirmed experimentally as shown in Figure 2. From these results, it is expected that the G_t is directly related to η. In Figure 3, the G_t is plotted against η. The polymer solutions were prepared by using two different molecular weights, and η was adjusted by controlling the polymer concentration in the polymer solution. It is evident that G_t is simply related to η and is independent of the molecular weight of rubber.

There are extensive works on the molecular weight effects of rubber on the content of carbon gel. These studies have demonstrated the principal effects of molecular weight, i.e., increase in the content with molecular weight[3] and a preferential adsorption of high molecular weight materials on the carbon black.[4,11] In this study, the G_t was also studied as a function of molecular weight of rubber. Figure 4 shows the relation between the molecular weight of rubber (M_w) and G_t. The composites were prepared from mixtures of carbon black dispersed benzene and polymer solutions with constant polymer concentration of 1.2 g/100 mL. In accordance with the published data,[2-4] G_t increases with molecular weight under the same polymer concentration. However, it should be noted that with increasing M_w the viscosity of the polymer solution also increases. Thus, the apparent increase of G_t with molecular weight is due to the increase of viscosity of the polymer solution.

Structure of Carbon Gel

As shown in the previous section, G_t was simply related to the viscosity of polymer solution. Thus, the
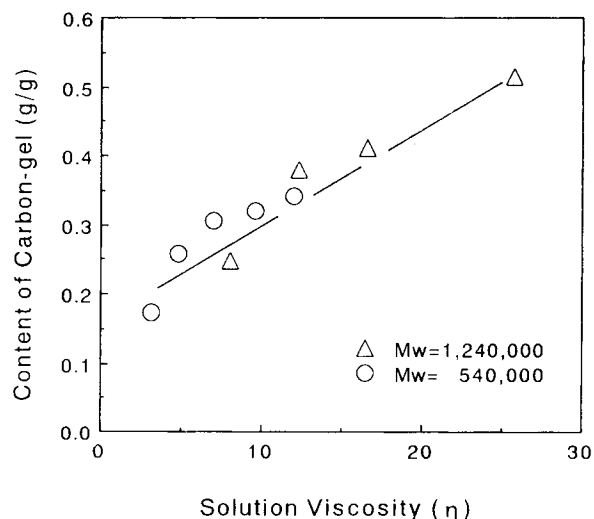

Figure 3 Solution viscosity dependence on carbon gel content.
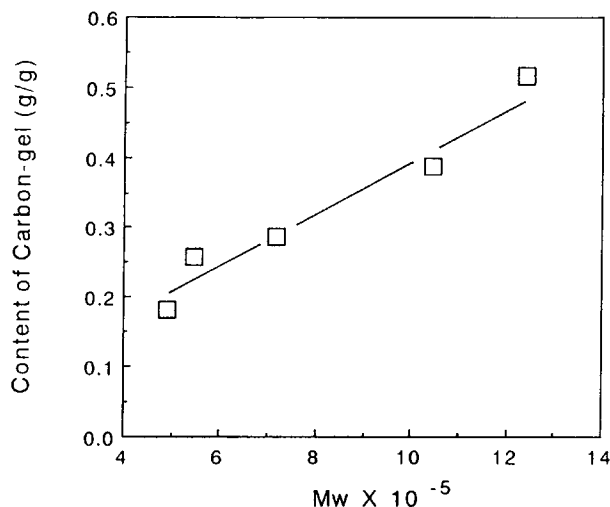
Figure 4 Molecular weight dependence on carbon gel content.

composites with different G_t were prepared from a wide range of molecular weight and of polymer concentrations in the solutions, and the structure of carbon gel was investigated as a function of G_t. In Figure 5, spin–spin relaxation time (T_2) and the absolute content of each T_2 component are plotted against G_t. All the carbon gels studied exhibited three kinds of spin–spin relaxation times depending on the mobility of rubber segments, i.e., short T_2 (T_{2s}), intermediate T_2 (T_{2m}), and long T_2 (T_{2l}). The absolute content of each T_2 component (G_s, G_m, G_l) was calculated from the NMR spectrum and G_t. According to the carbon gel model suggested by O'Brien et al.,[9] the lower mobile phase (T_{2s}, ~ 20 μs) consists of rubber segments near the active sites on carbon black. The mobility of this phase is highly restricted by anchoring rubber segments at the adsorption point. The highly mobile phase (T_{2l}, 500–600 μs) is composed of the long loop and tail of long chains. However, the mobility of this phase is not so high compared with nonbound polyisoprene (1130 μs). The intermediate phase shows a relatively short T_2 (T_{2m}, 40–80 μs), suggesting highly restricted motions of rubber segments at the boundary of the T_{2s} phase. As seen in the figure, both T_{2l} and G_l increase with G_t. On the other hand, T_2 and the content of lower mobile phase (T_{2s}, T_{2m}, G_s, and G_m) are almost independent of G_t. These results suggest an important aspect for the formation mechanism of carbon gel. If the carbon gel formation could be attributed to multisegment adsorption of polymer molecules,[11,12] the G_s and G_m as well as G_l should increase with G_t, different from the present results. The fact that the increase of G_t is attributable to the development of

a highly mobile phase (T_{2l} phase) implies that the formation mechanism of the highly mobile phase in the carbon gel is different from that of rubber phases for which mobility is highly restricted.

As discussed, the G_t is simply related to the viscosity of polymer solution. In this work, an almost constant stirring rate was utilized for the solution blend. Thus, the increase of solution viscosity corresponds to the increase of shear viscosity during mixing. With increasing shear viscosity, the interchain interactions between rubber molecules in the solutions and in the carbon gels might be enhanced by physical (entanglements) and chemical (chain scissions followed by recombinations) factors. As seen in Figure 5, the increase of G_t arises from the increase of G_l, which is accompanied by the increase of segmental mobility of the phase. This strongly suggests that the interaction between carbon black and rubber molecules in the highly mobile phase
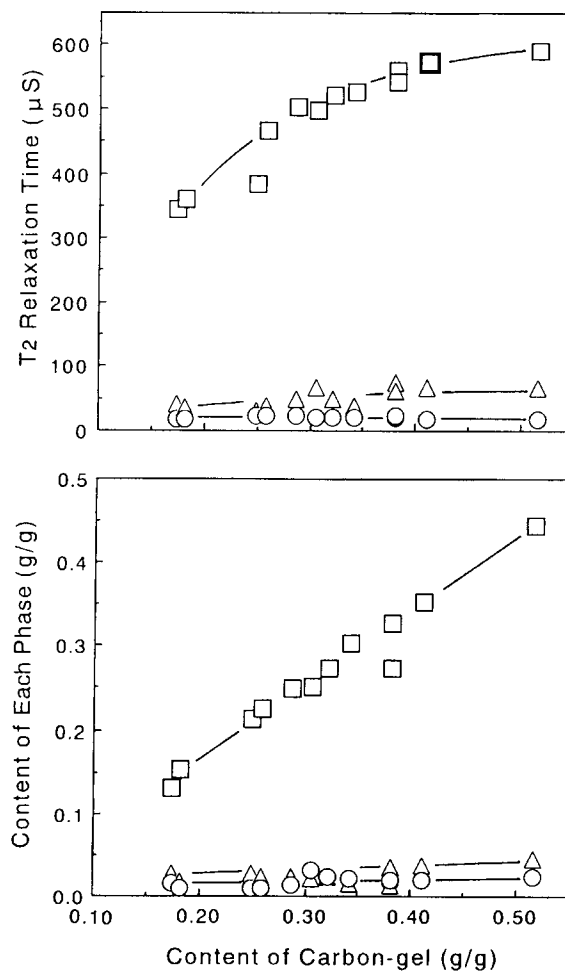

Figure 5 T_2 and content of each phase at 30°C as a function of carbon gel content: ($\square$) T_{2l} phase; ($\triangle$) T_{2m} phase; ($\bigcirc$) T_{2s} phase.

decreases with increasing G_l. As will be shown in the next section, the G_l was greatly reduced by solvent extraction at high temperatures. From these results, it is reasonable to speculate that a part of the highly mobile phase is formed by physical entanglement between long loops developed on carbon black and unbound rubber.

Solvent Extraction of Carbon Gel

Some of the rubber molecules in carbon gel can be removed by solvent extraction. Further, the extent is dependent on the conditions for extraction and on the degree of interaction between rubber and carbon black.[13] Thus, solvent extraction was carried out to evaluate the distribution of the interaction. The carbon gels were prepared from high molecular weight material (M_w = 1,280,000) by solution blending. The concentration of polymer solution used for the blend was 0.8 g/100 mL. The solvent extraction was carried out for 12 h at a constant temperature ranging from 25 to 113°C using toluene. The G_t of extended carbon gel is plotted against extraction temperature in Figure 6. Figure 7 shows the extraction temperature dependence on T_2 and content of each phase for extracted carbon gel. Two interesting facts can be seen in these figures: The first is that the content of the highly mobile phase (G_l) decreases with increasing extraction temperature which is accompanied by a decrease in the chain mobility of this phase. The second is that the content and segmental mobility of highly restricted phases (G_s, G_m, T_{2s}, T_{2m}) are not affected even by high-temperature
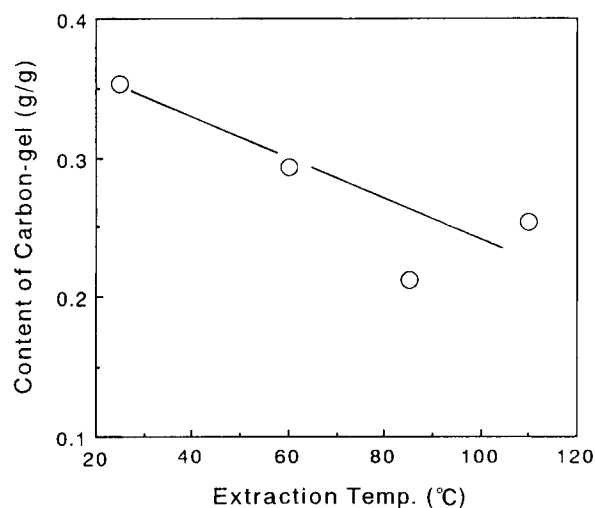

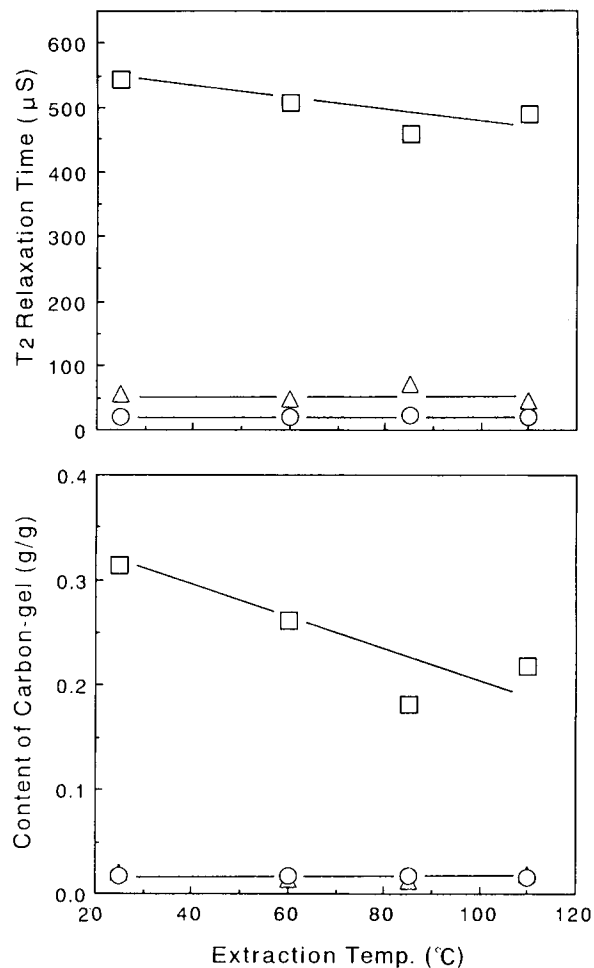**Figure 7** T_2 and content of each phase at 30°C as a function of extraction temperature; symbols as in Figure 5.

Figure 6 Extraction temperature dependence on carbon gel content.

extraction. Thus, the change in G_t with extraction temperature arises from the change in G_l.

In this study, solution blending was utilized for the preparation of rubber composites from which carbon gels were obtained. Our previous work[3] revealed that solution blending caused no noticeable change in the molecular weight of rubber during mixing. Thus, it is unlikely to expect chain scission or chemical crosslinking of rubber molecules during solution blends. A possible explanation for the decrease of G_l is the removal of physically entangled rubber molecules which are not adsorbed directly on carbon black. The results shown in Figure 7 indicate that rubber molecules in the less mobile phases have a strong interaction with carbon black, and they cannot be removed from the carbon gel even under severe extraction conditions. If a single rubber chain forms a loop or a cilia on the carbon black, the segmental mobility of the chain is expected to have a

distribution, from a highly restricted motion near the active sites on carbon black to a liquidlike motion near the top of the loop or the end of the cilia. In this study, the distribution corresponds to the appearance of three kinds of spin–spin relaxation times and their absolute values. The interaction between carbon black and such molecules might be too strong to eliminate them from a carbon black surface even under severe solvent extraction conditions. Rubber molecules in the solution (unbound rubber) can form an entanglement with a loop during solution blending. The segmental mobility of such entangled molecules is supposed to be considerably higher than the loop or cilia. By eliminating such molecules, the averaged segmental mobility of the highly mobile phase is reduced, which is reflected in the decrease of T_{2l}.

CONCLUSION

For the carbon black filled polyisoprene systems prepared by solution blending, the following conclusions were obtained:

1. The content of carbon gel is not directly dependent on the molecular weight of rubber, but is a function of viscosity of the rubber solution used for the blend.
2. The increase of carbon gel content arises mainly from the increase of highly mobile rubber phase, and the gel becomes soft with the development of this phase.
3. However, this phase can be partly removed by solvent extraction at high temperatures.
4. The content and mobility of the glassy rubber phase are not affected by the size of the carbon gel (content of carbon gel in the composite).
5. As the formation mechanism of carbon gel, a physical crosslink between the carbon gel and unbound rubber molecules is considered likely in addition to the well-known rubber–carbon black interaction.

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