NOTE

Surface Modification Effects of Carbon Black on Reinforced Natural Rubber

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It has been reported that the bound rubber in carbon black-rubber systems consists of two components having different segmental mobility, *i.e.*, loosely and tightly bound rubbers,^{1,2} and that the structures of these components are greatly affected by the conditions for preparing the composite³ and the nature of carbon black.⁴ We found⁵ that when oxidized carbon black is incorporated into natural rubber, the segmental mobility of both loosely and tightly bound rubbers is enhanced with increasing concentration of acid groups on the carbon black, and simultaneously the loosely bound rubber content is increased. This was explained as due to the weakening of interactions between oxidized carbon black and rubber molecules, probably caused by a decrease in hydrogen atoms (H_B) bonded to the carbon atoms at the edge of graphitic crystallites in the carbon black. It has been reported that the oxidation of carbon black induces a direct exchange of H_B for the acid group.⁶ However, functional groups such as aldehydes, alcohols, and ketones on the surface of carbon black⁷ may also be transformed into acid groups by oxidation. Therefore, an increase in acid group concentration (C_f) by oxidation may not directly correspond to a decrease in H_B content. Ohkita *et al.*⁸⁻¹⁰ reported that H_B is exchanged for the benzoyloxy group by the reaction of carbon black with benzoyl peroxide (BPO treatment), and also that the benzoyloxy group is transformed into the hydroxyl group by saponification

(BPO-SP treatment). Thus, the increase in benzoyloxy or hydroxyl groups introduced into the carbon black may correspond to the decrease in H_B . By incorporation of BPO or BPO-SP treated carbon black into natural rubber, it should be possible to obtain direct information on the previously suggested relation⁵ between the change in H_B content and the bound rubber structure. In this study, pulsed NMR measurements were carried out on bound rubber prepared from the composite of BPO or BPO-SP treated carbon black and natural rubber, and the effects of surface modification of carbon black on the bound rubber structure were examined.

EXPERIMENTAL

Samples

The carbon black and rubber used in this study were Diablack A (Mitsubishi Chemicals Co. Ltd.) and pale crepe (natural rubber), respectively. The oily matter on Diablack A was extracted with benzene for at least 50 h in a Soxhlet extractor, and the purified carbon black was dried at 100°C *in vacuo* (untreated carbon black). Benzoyl peroxide (BPO) treated and saponified (BPO-SP) carbon blacks were obtained using the procedure reported by Ohkita *et al.*¹⁰ The untreated carbon black was allowed to react with benzoyl peroxide in carbon tetrachloride for 50 h at 45°C with occasional shak-

ing. By so doing, H_B was exchanged for benzoyloxy

groups (eq 1).^{8,9} In this treatment, the secondary reaction shown in eq 2 was considered minor, since it is expected to occur only at high temperature.⁸ To remove unreacted BPO and benzoic acid produced during the reaction, the reaction mixture was washed several times with carbon tetrachloride at room temperature and then with benzene for at least 100 h in a Soxhlet extractor. The saponification of BPO treated carbon black was carried out in the following way. The BPO treated carbon black was added to a small excess of aqueous sodium hydroxide (about 0.1 mol dm⁻³) and the mixture was held at 95°C for 1 h with slow stirring. The reaction mixture was then acidified with hydrochloric acid. With this treatment, the benzoyloxy groups on the BPO treated carbon black are transformed into

phenolic hydroxyl groups (eq 3).^{9,10} The treated carbon black was washed carefully with hot distilled water and then dried at 100°C *in vacuo*. The C_f of the BPO-SP treated carbon black was determined by the base adsorption method⁵ in aqueous sodium hydroxide. The C_f of the BPO treated carbon black could not be determined by the neutralization technique, since benzoyloxy groups are saponified by sodium hydroxide. However, the number of benzoyloxy groups and the C_f are equal to that of the phenolic hydroxyl groups on the BPO-SP treated carbon black and the C_f of untreated carbon black, respectively. The oxidized carbon black, prepared by a method described elsewhere⁵

was used for comparison. Carbon gel samples were prepared from the composites of treated carbon blacks and natural rubber by the method described in our previous paper.⁵

Measurement

Pulsed NMR measurements were performed with a JEOL pulsed NMR spectrometer (JSE-5B), operating at 60 MHz. The proton spin-spin relaxation time (T_2) was determined by the solid echo sequence with a pulse width of 2 μ s and a pulse interval of 9 μ s. Solid echo signals were accumulated using a time-averaging computer. The T_2 and fraction of each component were determined by the method described in the previous paper.³

RESULTS AND DISCUSSION

Table I shows the surface area, total acid concentration (C_f) and decrement of H_B (ΔH_B) of carbon black. The surface area was determined by the B.E.T. method using nitrogen adsorption. Virtually, no change in surface area was caused by oxidation, BPO and BPO-SP treatments. Thus, the observed changes in segmental mobility and fraction of bound rubber, induced by incorporation of the treated carbon black into natural rubber, are directly related to the surface modification of carbon black as discussed below. By BPO-SP treatment, C_f increased from 0.14 to 0.29 meq g⁻¹. This increment in C_f corresponds to the ΔH_B of BPO-SP and BPO treated carbon black as described in the previous section. The oxidation of carbon black also induces an increase in C_f . In addition to the exchange of H_B for the acid group,⁶ functional groups such as aldehydes, alcohols, and ketones on the carbon black may be transformed into acid groups by oxidation.⁷ Therefore, the value of ΔH_B for oxidized carbon black may be less than 0.13 meq g⁻¹.

Table I. Characteristics of carbon black

Carbon black	Surface area/m ² g ⁻¹ ± 5	C_f /meq g ⁻¹ ± 0.02	ΔH_B /meq g ⁻¹
Untreated	133	0.14	0
Oxidized	121	0.27	<0.13
BPO treated	133	(0.14)	0.15
BPO-SP treated	132	0.29	0.15

Figure 1 shows the temperature dependence of T_2 for carbon gel samples (CG-U and CG-S). Here, CG-U and CG-S were prepared from the composites of natural rubber and untreated carbon black and the BPO-SP treated carbon black, respectively. Above -40°C , both samples exhibit two T_2 's, indicating the existence of long T_2 (T_{2L}) and short T_2 (T_{2C}) component, *i.e.*, loosely and tightly bound rubbers. In all the samples, a sharp increase in T_{2L} was found in the range from -40 to 20°C , where a small increase in T_{2C} was also found in the CG-S sample. The changes in T_{2L} and T_{2C} with temperature are probably due to the high frequency ($\sim 10\text{ kHz}$) manifestation of the glass-rubber transition of the samples. Above the transition temperature, the temperature dependence of T_{2L} and T_{2C} is weak and the T_{2L} and T_{2C} component fractions (f_L and f_C) in the total bound rubber remain almost constant (data not shown). All the samples showed a similar temperature dependence of T_{2C} , T_{2L} , f_C ,

Figure 1. Temperature dependence of T_2 for carbon gel samples (CG-U and CG-S): ●, CG-U prepared from the composite of untreated carbon black with natural rubber; ○, CG-S prepared from the composite of BPO-SP treated carbon black with natural rubber.

and f_L . Therefore, the values of the T_2 's and fractions (f_C and f_L) of both bound rubbers at 40°C (Table II) were used for the evaluation of the bound rubber structure. In this table, the fraction of the total bound rubber (F_{BR}), and the fractions of the $T_{2C}(F_C)$ and $T_{2L}(F_L)$ components in the filled rubber were determined by the method described in our previous paper.⁵ We found⁵ that by incorporation of oxidized carbon black with different acid group concentrations into natural rubber, F_L , F_{BR} , and the segmental mobility in the T_{2C} and T_{2L} phases increase with increasing C_f . The present study indicated that the oxidation effects of carbon black on the bound rubber content (F_{BR} , F_C , and F_L) and the segmental mobility in the T_{2C} and T_{2L} phases are not appreciable, probably due to the low value of C_f .⁵ As seen in Tables I and II, CG-S shows a F_{BR} value higher than CG-O, despite the fact that these samples have similar C_f values. This means that the increase in F_{BR} cannot be related directly to the increase in C_f . On the other hand, the samples with high values of ΔH_B had large F_{BR} values. Thus, the changes in F_{BR} are more sensitive to ΔH_B than C_f . Table II shows that the samples containing larger amounts of tightly and loosely bound rubbers have longer T_{2L} and T_{2C} . The increase in T_{2L} and T_{2C} implies an increase in segmental mobility in the T_{2L} and T_{2C} phases and suggests a decrease in the interaction between carbon black and rubber molecules. Papirer *et al.*¹¹ suggest that H_B has something to do with the chemisorption of unsaturated rubber on carbon black. If so, the chemical adsorptive activity of carbon black should decrease with increasing ΔH_B . It is generally accepted that the bound rubber phase surrounding the carbon black consists mainly of long and short loops.⁴ Thus, a reduction in the number of active points on the carbon black may cause a decrease in the number of loops. If the number of loops diminishes with increasing ΔH_B with no change in the length of

Table II. Properties of bound rubber

Carbon gel sample	Carbon black	F_{BR} ± 0.010	$T_{2C}/\mu\text{s}$ ± 1	$T_{2L}/\mu\text{s}$ ± 10	F_C ± 0.004	F_L ± 0.008
CG-U	Untreated	0.366	16	664	0.041	0.325
CG-O	Oxidized	0.379	21	681	0.040	0.339
CG-B	BPO treated	0.450	25	690	0.052	0.398
CG-S	BPO-SP treated	0.430	27	730	0.050	0.380

loops, the total bound rubber content (F_{BR}) should decrease with increasing ΔH_B , in contrast to the present results. The increase in segmental mobility and bound rubber content in the T_{2L} and T_{2C} phases, induced by the decrease in the number of active points on the carbon black, may be explained as follows. As a result of the decrease in the number of anchored points of rubber molecules, the length of the loops on the carbon black increases, leading to an increase in T_{2L} and T_{2C} , and simultaneously in both F_C and F_L . The reduction in loops contributed to the bound rubber content is compensated and/or overcome by the increase in loop length. The previous study revealed no clear change in F_C with C_f . However, CG-B and CG-S showed clear changes in F_C with ΔH_B (Tables I and II), suggesting that the chemical adsorptive activity of carbon black can be decreased more effectively by the BPO and/or BPO-SP treatment than by oxidation of the carbon black. The T_{2L} and T_{2C} of CG-B were slightly shorter than those of CG-S, despite the very small difference in F_{BR} of these samples. At present, the reason is unknown, but it is true that constraint on the segmental motion of the bound rubber in CG-B is stronger than that in CG-S. The benzyloxy group is fairly bulkier than that of other groups, and may hinder the segmental motion of the bound rubber phase.

In summary, the changes in segmental mobility and fraction of bound rubber are larger in the BPO or BPO-SP treated carbon black-natural rubber system, *i.e.*, these changes are more sensitive to the

change in the number of H_B than C_f . The decrease in the number of H_B induces an increase in segmental mobility and fractions of both bound rubber phases. The results can be explained as resulting from an increase in loop length on the carbon black owing to the decrease in the interaction between treated carbon black and natural rubber. It may be concluded that BPO or BPO-SP treated carbon black rather than oxidized carbon black is suitable for controlling the content and structure of bound rubber in a carbon black-natural rubber composite.

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