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Characterization of Carbon Filler Distribution Ratio in Polyisoprene/ Polybutadiene Rubber Blends by High-Resolution Solid-State ^{13}C NMR

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ABSTRACT: The distribution ratio of carbon black (CB) in a blend of polyisoprene rubber (IR) and polybutadiene rubber (BR) is characterized using high-resolution solid-state ^{13}C NMR. The relationships between the line width of the polymer's resonance lines and CB contents are estimated for both the IR/CB and BR/CB composites from the dipolar decoupling/magic angle spinning (DD/MAS) ^{13}C NMR spectra. For the IR/CB composite, the IR line width increases with the increasing CB content. A similar relationship is obtained between the BR line width and CB contents for the BR/CB composite. These relationships are used as calibration curves. On the basis of these calibration curves, the distribution ratio of CB in the IR/BR rubber blend is determined. It is found for the IR/BR/CB composite that the amount of CB in the BR phase is approximately twice as high as that of CB in the IR phase, irrespective of the CB content. The sum of the amounts of CB in both the IR and BR phases, determined from the above ^{13}C NMR experiments, mostly agree with the amount of CB originally added to the compound. This verifies the validity of the CB distribution determination method by ^{13}C NMR, as proposed in this study. A comparison with a CB-gel method, which can only be used for unvulcanized rubber blends, further confirms the results obtained from the ^{13}C NMR.

1. Introduction

The characterization of the distribution of carbon black (CB) in rubber blends is important for the improvement of the strength of the rubber materials.[1−3] It is generally accepted that CB is not uniformly dispersed in rubber blends because of the different compatibilities between the CB and each rubber component. It is considered that the compatibility between the CB and rubber is affected by various environments, i.e., unsaturation, viscosity, polarity, mixing procedure, etc.[3−5] Transmission electron microscopy (TEM)[3,4] and atomic force microscopy (AFM)[6,7] are currently used to determine the distribution ratio of CB in rubber blends. The advantages of these methods are that the CB distribution in each component of the rubber blends can be visually observed. However, the area we can observe is quite limited. The sample preprocessing is often laborious and difficult in TEM. The CB-gel method is also used to determine the distribution ratio of CB in unvulcanized blend rubbers.[8] A limitation of this method is that it cannot be used for vulcanized rubbers. Also, in this method, only polymers on the surface of the CB particles are measured.

Solid-state ^{13}C NMR is expected to be another candidate as a tool to determine the distribution ratio of CB in rubber blends.[6] Free electrons on the surface of the CB affect the spin−lattice (T_1) and spin−spin (T_2) relaxation times of the rubbers.[6,9] CB broadens the line width of the polymer signals due to the shortening of the T_2 relaxation time.[10−13] The advantages of the NMR method are (1) the entire sample can be measured, (2) no special techniques are required for sample preprocessing, (3) the sample can be nondestructively measured, and (4) both vulcanized and unvulcanized rubber can be analyzed.

Hu et al.[6] attempted to examine the distribution ratio of CB in a butyl rubber (IIR)/BR rubber blend using the high-resolution solid-state NMR line widths. They quantified the CB contents in the IIR phase of the IIR/BR rubber blend from the relationship between the CB contents and NMR line width of the IIR/CB composite.

In this paper, we attempt to quantify the distribution ratio of the CB in the IR/BR rubber blend using high-resolution solid-state ^{13}C NMR. For the IR/BR rubber blend, the fraction of CB in the IR phase and that in the BR phase are quantified using two calibration curves estimated from the IR/CB composite and BR/CB composite, respectively.

2. Experimental Section

Sample Preparation. All materials used in this study, IR, BR, CB (N220), and curatives, are commercial products. Three kinds of samples were prepared; i.e., the IR/CB composites, BR/CB composites, and IR/BR/CB composites. The respective blend contents are shown in Tables 1−3. The IR/CB composites were prepared in order to estimate the relationship between the ^{13}C NMR line width and CB contents, which was used as a calibration curve to quantify the CB contents in the IR. Similarly, the BR/CB composites were prepared to quantify the CB contents in the BR. The IR/BR/CB composites were prepared to characterize the CB distribution ratio in the IR/BR rubber blend. Pure polymers of IR and BR were first preblended in a Bumbury internal mixer at 80 rpm, then the CB was added. These were followed by the addition of the curatives using a roll mill. The compound mixtures were then thermally treated at 170 °C for 10 min in a hot press for vulcanization.

Solid-State ^{13}C NMR Measurements. All the DD/MAS ^{13}C NMR measurements were carried out using a Bruker Avance 400 spectrometer at the ^{13}C resonance frequency of 100.6 MHz. A double resonance probe with a 7 mm MAS probehead was used. The MAS spinning speed was 5 kHz (±1 Hz). The ^{13}C $\pi/2$ pulse width and the pulse delay were 4.35 μs and 6 s, respectively. We

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Table 1. Formulation of Polyisoprene Rubber (IR) with Different Carbon Black (CB) Contents in phr[a]

sample no.	1	2	3	4	5	6	7	8
IR	100	100	100	100	100	100	100	100
N220 CB	0	10	20	30	40	50	60	70
stearic acid	2	2	2	2	2	2	2	2
ZnO	3	3	3	3	3	3	3	3
sulfur	2	2	2	2	2	2	2	2
BBT[b]	1	1	1	1	1	1	1	1

[a] Parts by weight for hundred parts of rubber. [b] *N*-(benzo[d]thiazol-2-ylthio)-2-methylpropan-2-amine.

Table 2. Formulation of Polybutadiene Rubber (BR) with Different CB Contents in phr[a]

sample no.	1	2	3	4	5	6	7	8
BR	100	100	100	100	100	100	100	100
N220 CB	0	10	20	30	40	50	60	70
stearic acid	2	2	2	2	2	2	2	2
ZnO	3	3	3	3	3	3	3	3
sulfur	2	2	2	2	2	2	2	2
BBT[b]	1	1	1	1	1	1	1	1

[a] Parts by weight for hundred parts of rubber. [b] *N*-(benzo[d]thiazol-2-ylthio)-2-methylpropan-2-amine.

Table 3. Formulation of IR/BR Rubber Blend with Different CB Contents in phr[a]

sample no.	1	2	3	4	5	6
IR	50	50	50	50	50	50
BR	50	50	50	50	50	50
N220 CB	0	10	20	30	40	50
stearic acid	2	2	2	2	2	2
ZnO	3	3	3	3	3	3
sulfur	2	2	2	2	2	2
BBT[b]	1	1	1	1	1	1

[a] Parts by weight for hundred parts of rubber. [b] *N*-(benzo[d]thiazol-2-ylthio)-2-methylpropan-2-amine.

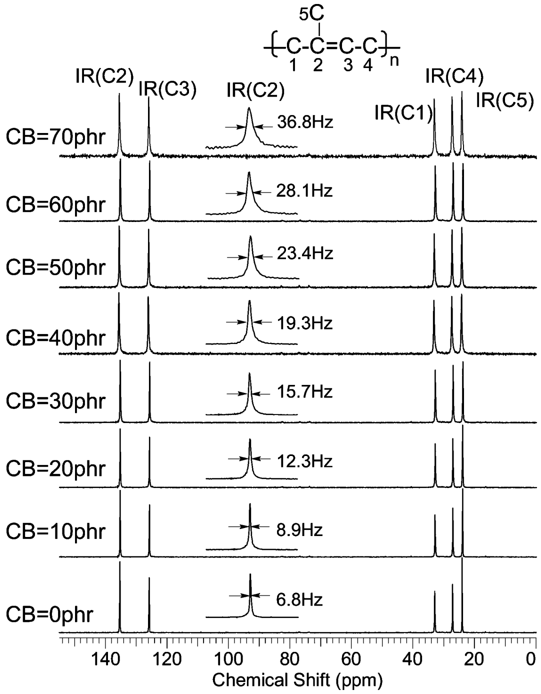

Figure 1. DD/MAS ^{13}C NMR spectra of vulcanized IR with different CB contents. Expanded spectra are also shown for the C2 carbon.

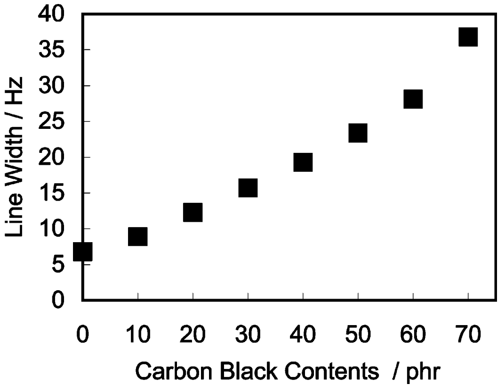

Figure 2. DD/MAS ^{13}C NMR line widths of vulcanized IR with different CB contents.

used the ^{1}H dipolar decoupling of 58.5 kHz during the detection of the free induction decay throughout this study. The ^{1}H−^{13}C dipolar couplings in the rubber blend systems were found to be weak, and the line widths in the DD/MAS experiments were unchanged with ^{1}H dipolar decoupling with a field strength above 3 kHz. The acquisition time was 68 ms. The line widths were of particular importance in this study. Therefore, we carefully adjusted the magnet shimming using adamantine to 3 Hz. The samples were packed into the center of the zirconia rotor with a $^1/_4$ effective inner volume, which makes the shimming easier. This also suppresses the effect of temperature gradients. The measurements were carried out at 298 K throughout this study. The ^{13}C chemical shifts were expressed as values relative to adamantine using the ^{13}C resonance line at 29.5 ppm for $-CH_2$ as the external reference.

CB-Gel Method. The CB-gel was prepared by extracting free rubber from the unvulcanized rubber blend of the IR/BR with different CB contents (10−50 parts per hundred parts of rubber (phr)). The unvulcanized rubber was cut into small pieces of approximately 0.5 g. The pieces were placed in a cage with a mesh size of 150 and immersed in 300 mL of toluene for 48 h at room temperature. The insoluble portion is then dried for 4 h at room temperature followed by drying for 4 h at 333 K under vacuum. This dried insoluble portion is called the CB-gel. Polymer compositions of the CB-gels were analyzed using a pyrolysis gas chromatograph (PGC). The pyrolysis temperature was 863 K, and the column temperature was from 343 to 453 K.

3. Results and Discussion

Calibration of CB in IR. In order to determine the CB distribution ratio in the IR/BR rubber blend, the relationship between the ^{13}C NMR line widths of the IR peaks and CB contents was investigated. Figure 1 shows the DD/MAS ^{13}C NMR spectra of the vulcanized IR with different CB contents (0−70 phr). Five peaks, assigned to *cis*-1,4-polyisoprene,[14] are observed; IR(C1) $-\underline{C}H_2-C(CH_3)=CH-CH_2-$ at 33 ppm, IR(C2) $-CH_2-\underline{C}(CH_3)=CH-CH_2-$ at 135 ppm, IR(C3) $-CH_2-C(CH_3)=\underline{C}H-CH_2-$ at 126 ppm, IR(C4) $-CH_2-C(CH_3)=CH-\underline{C}H_2-$ at 27 ppm, and IR(C5) $-CH_2-C(\underline{C}H_3)=CH-CH_2-$ at 24 ppm. It was found that the line widths increase with the increasing CB contents as shown for IR(C2) in the inset of Figure 1. In order to quantify the relationship, the change in the line width of IR(C2) with different CB contents is shown in Figure 2. The obvious relationship can be seen between the line width of IR(C2) and the CB contents. Note that similar relationships are observed for the other four resonance lines of the IR. From the calibration curve in Figure 2, the CB contents in the IR can be quantified from the line width of IR(C2).

Calibration of CB in BR. A similar relationship is also found for the BR/CB composite. Figure 3 shows the DD/MAS ^{13}C NMR spectra of the vulcanized BR with different CB contents (0−70 phr). Two peaks, assigned to *cis*-1,4-polybutadiene,[14] are observed; BR(C1) $-\underline{C}H_2-CH=CH-\underline{C}H_2-$ at 28 ppm and BR(C2) $-CH_2-\underline{C}H=\underline{C}H-CH_2-$ at 130 ppm. It was found that the line widths increase with the increasing CB contents, as with the IR/CB composite. The change in the line width of BR-

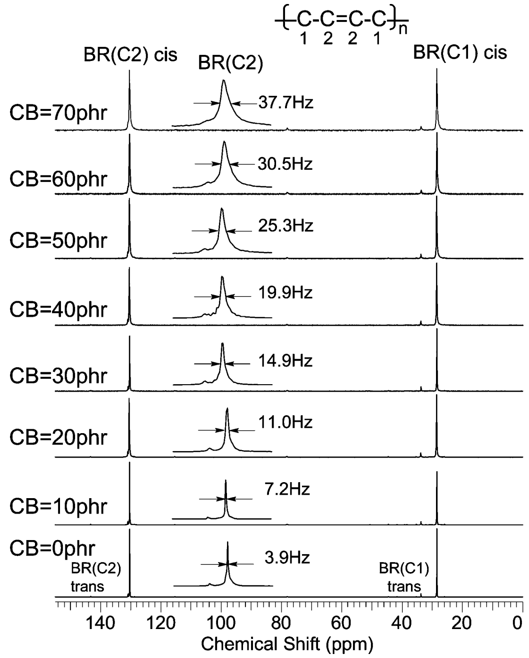

Figure 3. DD/MAS ^{13}C NMR spectra of vulcanized BR with different CB contents. Expanded spectra are also shown for the C2 carbon.

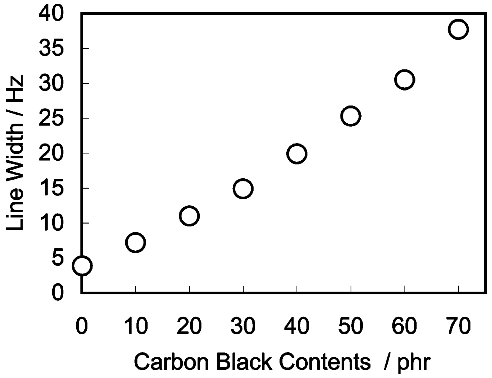

Figure 4. DD/MAS ^{13}C NMR line widths of vulcanized BR with different CB contents.

(C2) with different CB contents is shown in Figure 4. A similar relationship is also observed for the resonance line of BR(C1). Therefore, it is possible to quantify the CB contents in the BR for rubber blends containing CB, using the calibration curve in Figure 4.

CB Distribution Ratio in IR/BR Rubber Blend. As already described, two calibration curves are obtained for the quantification of the CB contents in both the IR and BR, respectively. We are now ready to determine the CB distribution ratio in the IR/BR rubber blends. Figure 5 shows the DD/MAS ^{13}C NMR spectra of the vulcanized IR/BR rubber blend with different CB contents (0−50 phr). The details of the blend compositions are shown in Table 3. Seven peaks are separately observed. Five peaks are assigned to the IR and two peaks are assigned to the BR as already described. Figure 6 shows the change in the line widths of the IR(C2) at 135 ppm and the BR(C2) at 130 ppm for the different CB contents. The CB contents in the IR phase of the IR/BR rubber blend are quantified from the line width of IR(C2) in Figure 6 using the calibration curve for the IR/CB composite in Figure 2. Likewise, the CB contents in the BR phase are quantified from the line width of BR(C2) using the calibration curve in Figure 4.

The CB contents determined by the above procedures are listed in the third and fourth columns of Table 4. It was found that the CB contents in the BR phase are richer than those in the IR phase. The second column of Table 4 shows the summation of the CB contents in the IR and BR phases in the third and fourth columns, respectively. The total amounts of CB in the IR and BR phases are in excellent agreement with the amount of CB originally added to the compounds (compare the second and first columns of Table 4). This excellent agreement shows the validity of the CB distribution determination method by ^{13}C NMR, as proposed in this study. The fifth column of Table 4 shows the distribution ratio of CB in both phases. The ratio of the CB contents in the two phases is in the range of IR/BR = 1:2.3−1.8 for the present sample (IR/BR = 50/50 and CB content = 10−50 phr). The CB distribution ratio

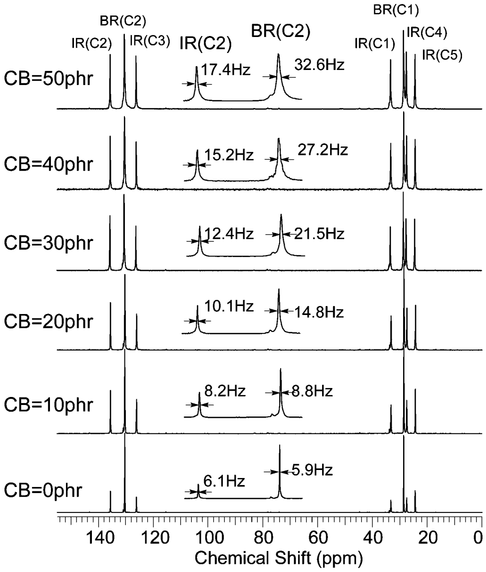

Figure 5. DD/MAS ^{13}C NMR spectra of vulcanized IR/BR with different CB contents. Expanded spectra are also shown for the IR-(C2) and BR(C2) carbons.

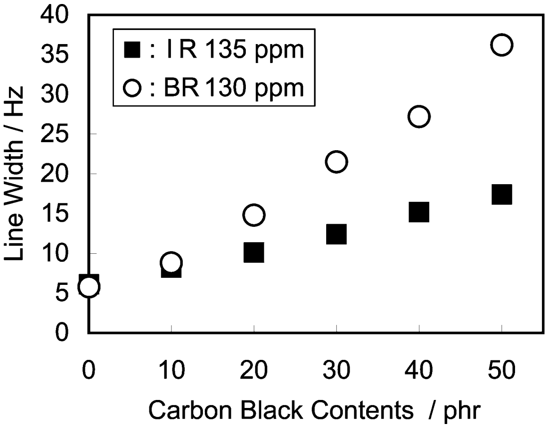

Figure 6. DD/MAS ^{13}C NMR line widths of vulcanized IR/BR with different CB contents.

Table 4. CB Distribution Ratio in the "Vulcanized" IR/BR Rubber Blend by the ^{13}C NMR Method

		amount of CB		
CB contents of the whole compound (phr)	total amount of CB in IR + in BR (phr)	in IR (phr) (135 ppm)	in BR (phr) (130 ppm)	distribution ratio of CB IR/BR
10	10.5	3.2	7.3	1:2.3
20	20.3	6.2	14.1	1:2.3
30	31.7	10.6	21.1	1:2.0
40	41.5	14.1	27.4	1:1.9
50	49.6	17.6	32.0	1:1.8

Table 5. CB Distribution Ratio in the "Unvulcanized" IR/BR Rubber Blend by the CB-Gel Method

CB contents of the whole compound (phr)	weight percent of polymer in CB-gel IR/BR	distribution ratio of CB IR/BR
10	37/63	1:1.7
20	41/59	1:1.5
30	42/58	1:1.4
40	41/59	1:1.5
50	40/60	1:1.5

in the BR phase is approximately twice as high as that in the IR phase and slightly decreases with the increase in the CB contents.

Characterization of CB Distribution Ratio Using CB-Gel Method. The validity of our characterization method for the CB distribution contents is proven by the agreement of the values in the first and second columns of Table 4. In this section, we compared the CB distribution ratio obtained by our method (Table 4) and that by the CB-gel method. The CB distribution ratios calculated from the polymer gel ratio on the surface of the CB particles, obtained by PGC,[8] are shown in the second column of Table 5. It was found that the weight percent of CB in the BR is higher than that in the IR. PGC shows only the weight percent of IR and BR in the CB-gel. Therefore, there are no data on the summation of the CB contents in both phases. However, the distribution ratio of CB shown in the third column of Table 5 can be compared for that obtained from the ^{13}C NMR method in the fifth column of Table 4. The distribution ratios of CB in the CB-gel, IR/BR = 1:1.7−1.4, roughly agree with those of the ^{13}C NMR method. Also, the results from both the ^{13}C NMR method and the CB-gel method have similar tendencies; the CB distribution ratio in the BR phase slightly decreases with the increase in the CB contents. More specifically, the obtained values are somewhat different between the two methods. Two possibilities can be considered for the origin of this slight inconsistency. First, the samples for the ^{13}C NMR measurements and CB-gel measurements are vulcanized and unvulcanized, respectively. It would be possible that the redistribution of CB occurs during the vulcanization process. Second, for the CB-gel experiments, most of the rubbers are removed during the sample preparation process and only the rubbers on the CB surfaces are measured. It has not yet been verified whether or not the rubber distribution on the CB surfaces quantitatively corresponds to the distribution of CB in the entire sample, although the CB-gel method has often been used for the estimation of the distribution ratio of CB in unvulcanized rubber blends. Unfortunately, the CB-gel method can be applied to only unvulcanized rubbers. However, the NMR method can be applied to both the unvulcanized and vulcanized rubbers. The ^{13}C NMR experiments using the unvulcanized rubbers are now in progress in our group in order to gain more insight about this issue. We are also planning experiments for other rubber blend and polymer blend systems to quantify the CB contents in these systems and to understand the robustness and the limit of this method.

4. Conclusions

The distribution ratio of CB in the IR/BR rubber blend samples were characterized using high-resolution solid-state ^{13}C NMR. Clear relationships between the line widths of the dipolar decoupling/magic angle spinning (DD/MAS) ^{13}C NMR spectra and CB contents were found. The CB contents in the IR and BR phases of the IR/BR rubber blend can be quantified from the calibration curves obtained from the IR single polymer mixed with CB and the BR single polymer mixed with CB. It was found that the distribution ratio of CB in the IR/BR rubber blend with different CB contents (10−50 phr) is approximately IR/BR = 1:2 and that the ratio of CB in the BR phase slightly decreased with an increase in the CB contents. The summation of the CB contents in both the IR and BR phases in the IR/BR blend, determined from the ^{13}C NMR spectra, are in excellent agreement with the amounts of CB originally added to the compound. Moreover, the results from the ^{13}C NMR method roughly agree with those from the CB-gel method. These agreements confirm the validity of the ^{13}C NMR method as proposed in this study. We think that this CB distribution determination method by ^{13}C NMR can be extended for multiple polymer blend systems, as long as the ^{13}C NMR resonance lines are separated. We are now starting ^{13}C NMR experiments for the quantification of the CB distribution ratios in rubber blends consisting of three polymers.

The most crucial aspect of the ^{13}C NMR method is that the entire sample can be nondestructively measured, irrespective of whether or not it is vulcanized. The ^{13}C NMR method in this study will become one of the most useful and robust methods to determine the distribution ratio of CB in rubber blends.

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