ORIGINAL ARTICLE

Distribution ratio of carbon black in polyisobutyrene/ polyisoprene rubber blends using high-resolution solid-state ^{13}C NMR

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We attempted to estimate the distribution ratio of carbon black (CB) in blends of polyisobutyrene rubber and polyisoprene rubber using high-resolution solid-state ^{13}C nuclear magnetic resonance (NMR). Our NMR analysis revealed that, in polyisobutyrene rubber/polyisoprene rubber/CB composites, CB more easily distributes in polyisoprene rubber than in polyisobutyrene rubber. We found that more than 70% of CB is distributed into the polyisoprene rubber phase. The sum of the amounts of CB in both the polyisobutyrene rubber and polyisoprene rubber phases estimated by our method using ^{13}C NMR closely corresponds with the amount of CB originally added to the compound, verifying the validity of the NMR method. Further, we observed the distribution of CB in polyisobutyrene/polyisoprene rubber blends using transmission electron microscopy and the Carbon-Black-Gel method, which can only be used for unvulcanized rubber blends, for comparison. The results obtained using these three methods show similar tendencies, which confirms the accuracy of this method of using ^{13}C NMR to determine CB distribution in rubber blends.
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INTRODUCTION

Rubber compounds are composed of several different materials to enhance their physical properties. Several types of rubber are blended and these rubber blends are used according to the performance requirements of the rubber industry. Carbon black (CB) is one of the most important materials used to reinforce rubber composites, and its distribution in blends of different types of rubber is important for improving the performance of rubber composites.[1–9] CB is known to disperse non-uniformly in rubber blends because of varying degrees of compatibility between CB and different types of rubber.[2–4,9–13] Understanding the types of rubber in which CB is distributed and the amount of CB distributed in each type is very important for improving the physical properties of rubber blend systems. Therefore, several methods have been developed to obtain information regarding CB distribution in different rubber blends; for example, transmission electron microscopy (TEM),[2–4,12–14] atomic force microscopy,[15–20] differential scanning calorimetry,[14,21,22] dynamic mechanical analysis[11,23,24] and the CB-Gel method.[25,26] Hu et al. and the authors experimented using nuclear magnetic resonance (NMR).[20,27] In our previous study,[27] using the phenomenon wherein the line widths of rubber phase signals in the NMR spectrum broaden due to the

shortening of T_2 relaxation times caused by the presence of the free electrons on the surface of CB,[20,28–31] we reported on the usefulness of high-resolution solid-state ^{13}C NMR in determining the CB distribution ratio in polyisoprene rubber (IR) and polybutadiene rubber (BR) rubber blends. These blends are generally used in tire compounds to improve the physical performance of tire tread components and sidewalls. We demonstrated that the ^{13}C NMR method may be among the most useful and robust methods for determining the distribution ratio of CB in rubber blends because of the potential for extending this method to include multiple polymer-blend systems, provided that each ^{13}C NMR resonance line is distinct. In this study, we conducted experiments with polyisobutyrene rubber (IIR) and IR rubber blends using ^{13}C NMR to verify the validity of the NMR method. The blend investigated this study is particularly important in the tire industry, as it is used for the inner liner of tires. The ratio of CB distributed between the IIR phase and the IR phase is quantified using two calibration curves that were established using the IIR/CB and IR/CB composites through analysis of the line widths of NMR peaks, respectively. In terms of practical applications, we establish the NMR method as the best available method for the evaluation of CB distribution in rubber blends.

EXPERIMENTAL PROCEDURE

Sample materials

All of the materials used in this study are commercial products. IR-2200 and Br-IIR (hereafter, IIR) were used as the types of raw rubber. CB (N220) was used as the filler. Sulfur, ZnO (zinc oxide) and stearic acid were used as curing agents and BBT (N-(benzo[d]thiazol-2-ylthio)-2-methylpropan-2-amine) was used as the accelerator. The following vulcanized rubber compounds were used throughout this study: (1) IIR with varying CB contents (0–40 parts per hundred parts of rubber (phr)); stearic acid, 2 phr; ZnO, 3 phr; sulfur, 2 phr; BBT, 1 phr; (2) IR with varying CB contents (0–70 phr); stearic acid, 2 phr; ZnO, 3 phr; sulfur, 2 phr; BBT, 1 phr; and (3) IIR/IR = 50/50 with varying CB contents (0–40 phr); stearic acid, 2 phr; ZnO, 3 phr; sulfur, 2 phr; BBT, 1 phr. The IIR/CB and IR/CB composites were prepared to establish the relationships between the ^{13}C NMR line widths and the CB contents for both IIR and IR, which were then used as calibration curves to quantify the CB contents in the two types of rubber. The IIR/IR/CB composites were prepared to characterize the CB distribution ratio in the IIR/IR rubber blends. Pure IIR and IR polymers were first preblended in a Bunbury internal mixer at 80 r.p.m. and CB was then added, followed by the addition of curative agents using a roll mill. The compound mixtures were then thermally treated at 170 °C for 10 min in a hot press for vulcanization.

TEM observation

A HITACHI H-7100 transmission electron microscope (HITACHI, Ltd., Tokyo, Japan) was used at an acceleration voltage of 100 kV. The specimen was cut using a cryo-microtome to a thickness of 50–100 nm and then transferred onto a 300-mesh copper grid fixed on a TEM holder. Photoshop and Image J were used as the image processing software.

Solid-state ^{13}C NMR determinations

All of the dipolar-decoupling/magic-angle-spinning (DD/MAS) ^{13}C NMR determinations were conducted using a Bruker Avance 400 spectrometer (Bruker BioSpin, Fällanden, Switzerland) at a ^{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 π/2 pulse width and the pulse delay were 4.35 μs and 6 s, respectively. We used ^1H dipolar decoupling at 58.5 kHz for the detection of free induction decay throughout this study. The ^1H-^{13}C dipolar couplings in the rubber blend systems were weak, the line widths in the DD/MAS experiments were constant with ^1H dipolar decoupling of field strength greater than 3 kHz, and the acquisition time was 68 ms. Adamantine was used to adjust the magnet shimming to 3 Hz. The samples were packed at the center of a zirconia rotor with 1/4 effective inner volume to enable easier shimming and to suppress the influence of temperature gradients. All measurements were performed at 298 K. The ^{13}C chemical shifts were described 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

In unvulcanized rubber, a polymer gel surrounds CB and is physically bonded to it. This polymer gel is called CB gel and is insoluble in toluene; therefore, when unvulcanized rubber is immersed in toluene, the CB gel is separated from the free polymer. Unvulcanized IIR/IR rubber blends with varying CB contents (10–40 phr) were cut into small pieces weighing approximately 0.5 g and placed in a 150-mesh size stainless cage, which was immersed in 300 ml of toluene for 48 h at room temperature. The insoluble portion was then dried for 4 h at room temperature followed by 4 h at 333 K in a vacuum. Once dried, this insoluble polymer was analyzed using pyrolysis gas chromatography. The ratio of polymer indicates the distribution ratio of CB.[25]

RESULTS AND DISCUSSION

TEM imaging

We observed the distribution of CB in IIR/IR rubber blends using TEM for comparison with the NMR method. Figure 1a shows the TEM image of the IIR/IR = 50/50 rubber blend with a CB content of 10 phr. IIR is shown in light gray, IR is shown in dark gray and CB is shown as black spots. Figure 1b shows the same images after being processed with the image processing system. The white area is IIR, the black area is IR and the gray spots are CB. From Figure 1b, the distribution ratio of CB can be calculated. Likewise, Figure 2 shows the IIR/IR = 50/50 rubber blend with a CB content of 30 phr. The results are indicated in Table 1. We found that the CB content is greater in the IR phase than in the IIR phase. In general, it is difficult to distinguish the blend polymer morphology using TEM when the CB content is high. In fact, when CB is included, the IR area increases as the CB content increases, which confirms the difficulty in accurately calculating the distribution ratio of CB in each rubber phase. Nevertheless, we can see that CB is more easily dispersed into the IR phase.

NMR spectra of IIR, IR and an IIR/IR rubber blend

To determine the CB distribution ratio in the IIR/IR rubber blends, it was necessary to ensure that the ^{13}C NMR resonance lines of IIR and IR were completely separated. Figure 3a–c show the NMR spectra of IIR, IR and the IIR/IR rubber blend, respectively. The three peaks assigned to IIR[32] can be observed in Figure 3a and the five peaks assigned to IR[32] can be observed in Figure 3b. For the IIR/IR rubber blend, the eight peaks of both types of rubber are completely distinct (Figure 3c).

Calibration of CB content in IIR and IR using ^{13}C NMR

In our previous study,[27] we described the changes in the ^{13}C NMR line widths of IR with CB contents varying between 0 and 70 phr. The line
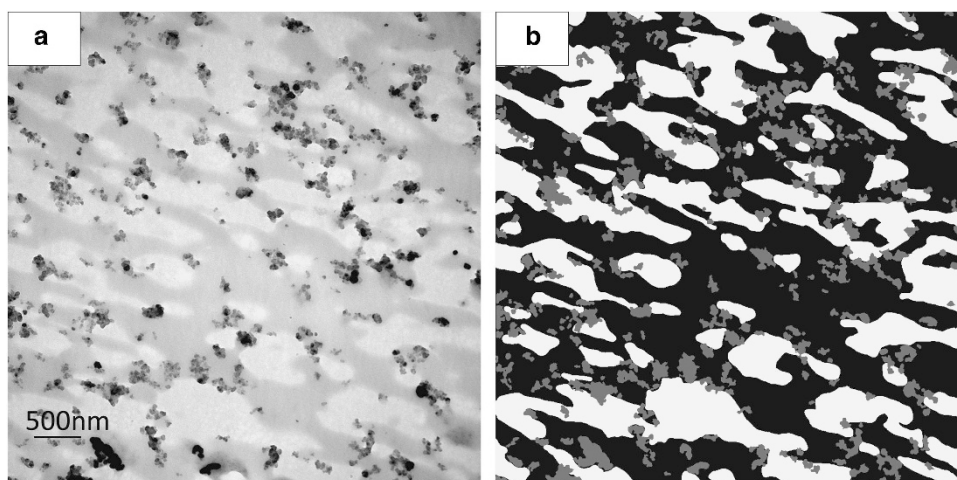

Figure 1 TEM image of the IIR/IR = 50/50 rubber blend with a CB content of 10 phr. TEM image (**a**) and processed image of IIR/IR/CB (**b**).
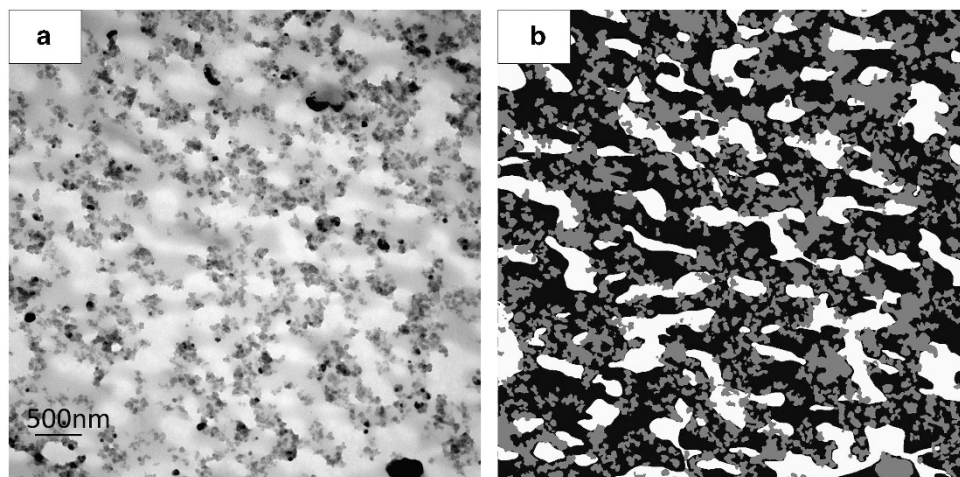
Figure 2 TEM image of the IIR/IR = 50/50 rubber blend with a CB content of 30 phr. TEM image (**a**) and processed image of IIR/IR/CB (**b**).

Table 1 CB distribution ratio in the vulcanized IIR/IR rubber blends determined using the TEM method

Overall CB content of compound (phr)	Ratio of IIR/IR in original compound IIR:IR	Area ratio of the (white+gray within white) and (black+gray within black) areas (IIR+CB):(IR+CB)	Distribution ratio of CB (%) IIR:IR
10	50:50	(37+2):(51+10)	17:83
30	50:50	(21+3):(47+29)	9:91

Abbreviations: CB, carbon black; IIR, polyisobutyrene rubber; IR, polyisoprene rubber; TEM, trans–mission electron microscopy.
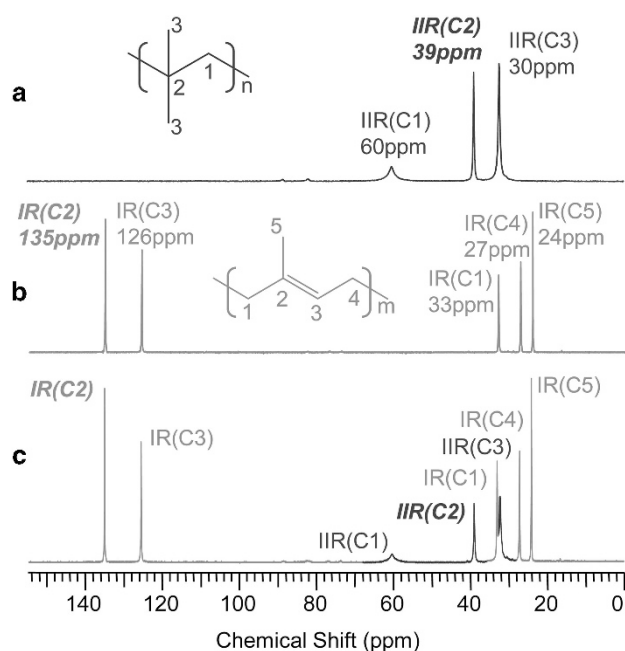

Figure 3 DD/MAS ^{13}C NMR spectra of IIR (**a**), IR (**b**) and a 50/50 IIR/IR rubber blend (**c**). A full color version of this figure is available at *Polymer Journal* online.

Figure 4 DD/MAS ^{13}C NMR spectra of vulcanized IIR with varying CB contents. Expanded spectra are also shown for C2 carbon. A full color version of this figure is available at *Polymer Journal* online.

widths of IR(C2) increased as CB contents increase and a clear relationship could be observed. We also found similar relationships for the line widths of the other four peaks of the IR. In this study, we investigate the relationship between the ^{13}C NMR line widths of the
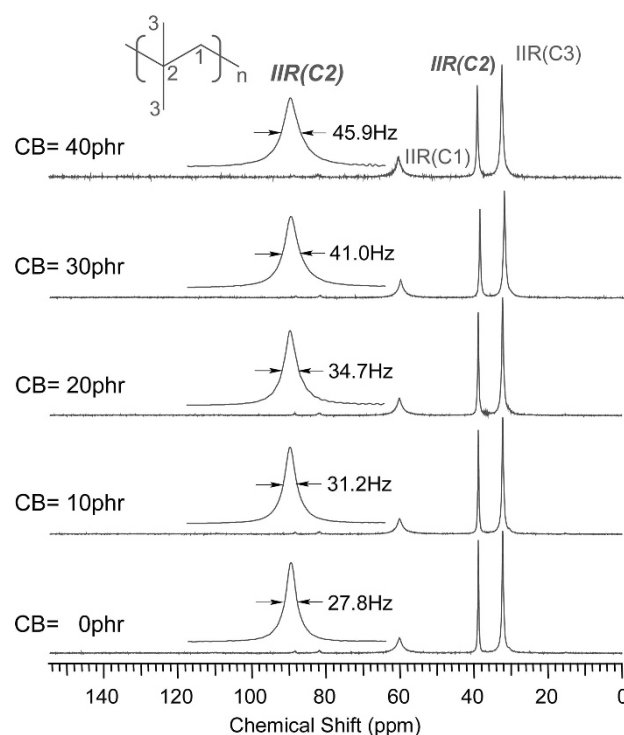
IIR peaks and CB contents of 0–40 phr to determine the CB distribution ratio in IIR/IR rubber blends. Figure 4 shows the DD/MAS ^{13}C NMR spectra of vulcanized IIR with varying CB contents (0–40 phr). The line widths increase with increasing CB content. The changes in the line widths of IIR(C2) and IR(C2) with varying CB contents are shown in Figure 5. The data of IR(C2) are obtained from Kotani *et al*.[27] A clear relationship is apparent for both IIR(C2) and IR (C2). These relationships can be used for calibration to determine the CB distribution ratio in the IIR/IR rubber blends. Note that a similar relationship is also observed in the resonance line of IIR(C3). However, as the resonance line of IIR(C1) has low sensitivity and a broad peak width, it is not referred to in this study.

CB distribution ratio in IIR/IR rubber blends determined using the ^{13}C NMR method

As shown in the previous section, two calibration curves were obtained based on measurements of single rubber compound of IIR+CB and IR +CB for the quantification of the content of CB in both IIR and IR. Figure 6 shows the DD/MAS ^{13}C NMR spectra of the vulcanized IIR/ IR = 50/50 rubber blends with varying CB contents (0–40 phr) to determine the distribution ratio of CB. The line widths of both IIR and IR increase in correlation to the overall CB contents. In the IIR/ IR = 50/50 rubber blend, the IIR ratio of all rubber is 50%. The CB content in the IIR phase of the IIR/IR = 50/50 rubber blend is half of the IIR phase CB value calculated from the calibration curve for the IIR/CB composite. Results are listed in the third column of Table 2. Likewise, the CB content in the IR phase of the IIR/IR = 50/50 rubber blend is half of the IR phase CB value calculated from the calibration curve for the IR/CB composite. Results are listed in the fourth column of Table 2. The CB content is greater in the IR phase than it is in the IIR phase, irrespective of the total CB content. The fifth column shows the distribution ratio of CB in the two phases. We found that more
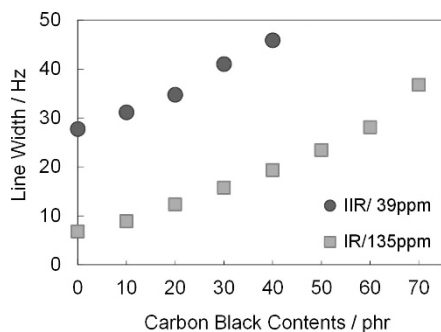

Figure 5 DD/MAS ^{13}C NMR line widths of vulcanized IIR and vulcanized IR[27] with varying CB contents. A full color version of this figure is available at *Polymer Journal* online.

than 70% of the CB content is distributed into the IR phase of the present sample (IIR/IR = 50/50 rubber blends with CB content = 10–40 phr). The CB distribution ratio in the IR slightly increases with the increase in the CB content up to 30 phr, but decreases when the CB content reaches 40 phr. It is possible that, when the CB content is less than 30 phr, it is easier for CB to enter into the IR phase. However, when the CB content increases to 40 phr, it becomes harder for CB to enter into the IR phase because CB is already abundant in this phase. The second column of Table 2 indicates the sum of the CB contents in both rubber phases. These data closely correspond with the amount of CB originally added to the compound. This close agreement demonstrates the accuracy of the method of using ^{13}C NMR to determine the distribution of CB.

Characterization of CB distribution ratio using the CB-Gel method

To further confirm the validity of the NMR method, we compared its results with those of the CB-Gel method. The weight percentages of polymer in the CB gel of the unvulcanized IIR/IR rubber blends analyzed using pyrolysis gas chromatography[25] indicate the CB
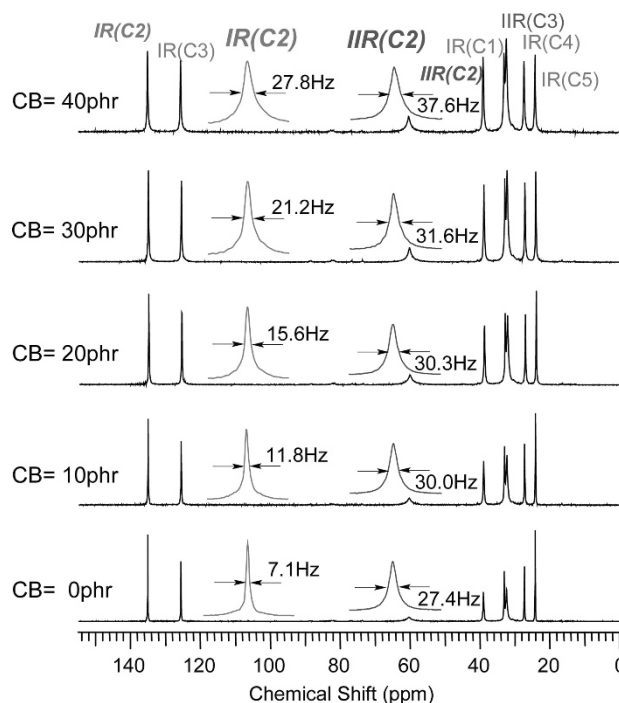

Figure 6 DD/MAS ^{13}C NMR spectra of vulcanized IIR/IR rubber blends with varying CB contents. Expanded spectra are also shown for the IIR(C2) and IR(C2) carbons. A full color version of this figure is available at *Polymer Journal* online.

Table 2 CB distribution ratio in the vulcanized IIR/IR rubber blends determined using the ^{13}C NMR method

Overall CB content of compound (phr)	Total amount of CB in IIR+IR (phr)	Amount of CB		Distribution ratio of CB (%) IIR:IR
		in IIR(phr) (39 ppm)	in IR(phr) (135 ppm)	
10	13.6	3.5	10.1	26:74
20	19.5	3.9	15.6	20:80
30	27.8	5.6	22.2	20:80
40	41.0	12.4	28.6	30:70

Abbreviations: CB, carbon black; IIR, polyisobutylene rubber; IR, polyisoprene rubber; NMR, nuclear magnetic resonance.
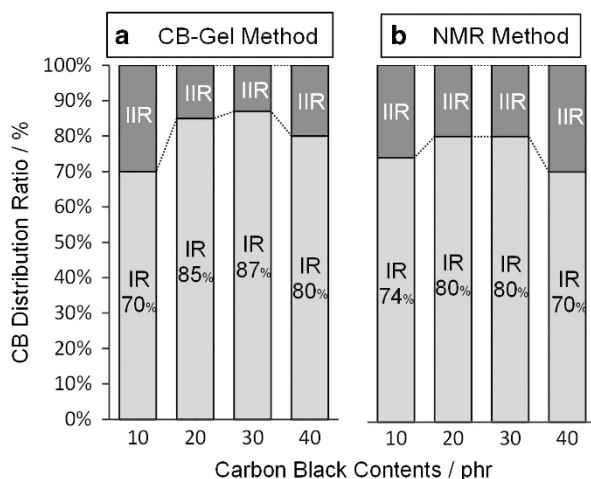
Figure 7 CB distribution ratio with varying CB contents in 'un'vulcanized IIR/IR rubber blends determined using the CB-Gel method (**a**) and in vulcanized IIR/IR rubber blends determined using the ^{13}C NMR method (**b**). A full color version of this figure is available at *Polymer Journal* online.

distribution ratio, which are shown in Figure 7a. More than 70% of the CB content is found to be distributed in the IR phase than it is in the IIR phase. The CB distribution ratio in the IR phase slightly increases with the increase in the CB content up to 30 phr, but decreases when the CB content reaches 40 phr. Figure 7b shows the CB distribution ratio in vulcanized IIR/IR rubber blends as listed in the fifth column of Table 2. Thus, the results obtained using the CB-Gel method and those obtained using the NMR method show very similar tendencies. The specific values obtained through these two methods are somewhat different. Nonetheless, it is important to note that the CB-Gel method only measures the polymer on the surface of the CB particles, and only in unvulcanized rubber.

CONCLUSIONS

We have found a clear relationship between the line widths of the DD/ MAS ^{13}C NMR spectra of various rubber blends and their CB contents. We succeeded in determining the distribution ratio of CB in the IIR/IR rubber blend samples using high-resolution solid-state ^{13}C NMR, as we had done with IR/BR rubber blends in our previous study. The CB contents in the IIR and IR phases of the IIR/IR rubber blends can be quantified using the calibration curves obtained from the single IIR and IR polymers mixed with CB. In the sample IIR/ IR = 50/50 rubber blends with CB contents of 10–40 phr, we found that more than 70% of CB is distributed into the IR phase and that the sum of the CB contents in both rubber phases closely corresponds with the amount of CB originally added to the compounds. In the IIR/ IR rubber blend systems, the results from the ^{13}C NMR method and the CB-Gel method show similar tendencies. The TEM images of the IIR/IR rubber blends with CB = 10 and CB = 30 phr indicate that CB more easily distributes into the IR phase than into the IIR phase. The close agreement between these three methods confirms the accuracy of the ^{13}C NMR method.

In our previous study, we confirmed that CB more easily distributes into BR than into IR and, in this paper, we have confirmed that CB more easily distributes into IR than into IIR. In conclusion, using the NMR method, we could predict that CB is most easily distributed in rubber in order from BR > IR > IIR. Generally, it is said that CB is mostly distributed in BR due to the large number of unsaturated

bonds. Our results also show this. Thus, this verifies the accuracy and validity of the NMR method, and also indicates that the NMR method can be applied to multiple rubber blends as long as the NMR resonance lines are separated. We are now conducting ^{13}C NMR experiments to measure CB distribution in BR/IIR rubber blends and in IR/BR/IIR rubber blends to clarify the order of the ease of CB distribution.

It is very important from the perspective of the tire industry to establish a quick and efficient method for determining CB distribution in rubber, as this distribution has enormous impact on the properties and performance of tires. Using the NMR method, an entire sample can be measured without being destroyed in the process, irrespective of its CB content. Further, this method can be applied to multiple rubber blends provided that the ^{13}C NMR resonance lines are distinct. Hence, the NMR method is to be the best available method for determining CB distribution in rubber materials.

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