A New Concept for Nanoparticle Distribution in SBR/NBR Blend Solution and Films via Molecular Confinement

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ABSTRACT: A novel mechanism of carbon black network formation in a binary immiscible rubber blend has been proposed in this paper. The network formation implies that the specific rubber molecules are selectively confined into the void of carbon black aggregate structure during their solution mixing. The selective adsorption and the feature of the conductive network formation have much potential concerning both fundamental understanding and industrial application to improve conductive polymer composites.

Introduction

In an electrically conductive filler dispersed insulating polymer system, so-called conductive polymer composites,[1–3] a sudden jump of the conductivity is observed when the concentration of the filler exceeds at a certain level, which is known as percolation threshold concentration (PTC).[4] Lowering PTC of conductive polymer composites is generally required for the material design to maintain the mechanical properties and the cost reduction.[5,6] Therefore, a large number of works have been carried out on this subject.

From the viewpoint of the filler, the most typical strategy taken is the addition of carbon black possessing higher aggregate structure.[7] Carbon black is widely used as the filler for the conductive polymer composites because of its low price, good processability, and corrosion-free surface.[8–12] The significance of the use of the carbon black with higher aggregate structure for the PTC reduction is undeniable, and according to Janzen's report,[13] the lowest PTC with carbon black having one of the highest aggregate structure is estimated to be around 5–10 vol % for a conductive rubber composite system.

From the polymer side, there are variety of strategies for the PTC reduction, including the choice of polymers whose surface tensions are far from those of fillers[3] and the use of semicrystalline polymers instead of amorphous polymers.[14–19] In recent years, there are some reports that the use of immiscible binary polymer blends successfully reduced the PTC by localizing conductive fillers at the interface or in one of the phases.[20–33]

The carbon black dispersed conductive polymer composites are usually processed by melt mixing[34] rather than solution mixing, especially when rubber is used as polymer matrix. This is due to the inconvenience to find a suitable solvent when an immiscible polymer blend is chosen for the system and the troublesome successive drying process. However, the use of solution mixing might lead to changes in physical or chemical conditions that cannot be achieved by the melt mixing method.[35] In such cases, the final structures and the physical properties of the conductive polymer composites will be strongly affected by the solvents.

The motivation for this study was to develop inexpensive, quick response sensory materials by reducing the PTC of conductive polymer composites.[36] Therefore, the carbon black with one of the highest aggregate structure (Monarch 880, Cabot Corp.) was chosen as the filler. In addition, to obtain inhomogeneous distribution of carbon black in the system, immiscible

rubber blends were chosen. A matrix with great flexibility is also preferable to obtain high sensitivity as a sensor. The immiscible rubber combinations were carefully determined to allow multiple cosolvent choices. Accordingly, SBR/NBR blends were selected as the matrix for carbon black. Normally, it would be expected that the interface or the phase in which carbon black is localized needs to be continuous to make conductive paths. Hence, the polymer blend ratios are usually chosen to be from 30/70 to 70/30 to obtain co-continuous morphology. However, during this study, a phenomenon contrary to this common sense has unexpectedly been discovered. A significantly one-sided blend, SBR/NBR = 90/10, showed better PTC reduction than that of the 70/30 case. It has also been reported that carbon black addition actually improves continuity of one-sided immiscible blends.[21] Therefore, the blend ratio, SBR/NBR = 90/10, was mainly examined.

In this study, it is discussed that the solution mixing method is quite useful to control the carbon black distribution by changing the compatibility between the polymers and the solvents. The mechanism for the inhomogeneous distribution of carbon black in the immiscible rubber blend is discussed on the basis of a molecular-confinement concept, which is assisted by the size matching between the rubber molecules and the carbon black aggregate structures.

Experimental Section

1. Mixing Procedure. Two rubbers having similar molecular weight and glass transition temperature (T_g) but different polarity are used in this study. They are styrene butadiene rubber (SBR) (Nipol 1502: $M_w = 5.0 \times 10^5$, $T_g = -52$ °C) and acrylonitrile butadiene rubber (NBR) (Nipol 1042: $M_w = 4.5 \times 10^5$, $T_g = -40$ °C) obtained from Zeon Corp. The conductive filler mixed to the polymers is carbon black (Monarch 880: Brunauer–Emmett–Teller (BET) nitrogen adsorption surface area = 220 m²/g, dibutyl phthalate (DBP) oil absorption value = 105 mL/100 g) obtained from Cabot Corp. Solvents used for the solution mixing are ACS reagent grade toluene, chloroform, and methylene chloride purchased from Fisher Scientific. Both SBR and NBR can be completely dissolved in all the solvents.

Prior to the mixing of all the compounds, carbon black was well dispersed in the solvent by sonication for 24 h, and the rubbers were dissolved in the solvent with stirring individually. Then, they were mixed together and sonicated for 10 h. At this point, the concentration of total rubber components in the solution was ∼5 vol %. Subsequently, the solution was cast at ambient temperature, and the obtained film was folded and pressed once by a compression molder at 100 °C and 1.0 MPa.

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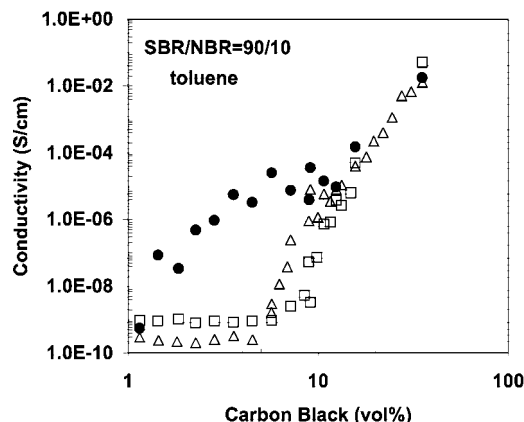
Figure 1. Influence of carbon black concentration on electrical conductivity of SBR/NBR = 90/10 (●), SBR (△), and NBR (□) composites made by the toluene solution mixing method.

2. Electrical Conductivity Measurement. Six pieces of 0.5 mm thickness, 6 mm diameter disks were cut from obtained films. The electrical resistance was measured at ambient temperature by a two-point probe technique (616 Digital Electrometer, Kiethley). Conductivity was calculated from the resistance taking the sample geometrical shape into consideration. The average conductivity of the six samples is reported.

3. Morphological Observation. A couple of droplets taken from the solution after the mixing process was cast or spin-cast onto substrates (a piece of cover glass or silicon wafer). The films were then examined by optical microscopy (OM) (BX-60, Olympus) to check the phase separation morphology. More detailed morphology was investigated by lateral force microscopy (LFM) (Explore, Thermo Microscopes). The measurement was carried out in contact mode with a spring constant of 0.032 N/m. The cantilever was fabricated from silicon nitride (Si_3N_4) and designed in a V-shape with a prove tip integrated onto the underneath of the cantilever. The length, width, and thickness of the arm are 200 μm, 18 μm, and 0.6 μm, respectively. The radius of the attached tip is about 20 nm. Imaging was carried out at a repulsive force of 1–2 nN. The deflection and torsion of the cantilever were measured with a four-segment photodetector using a laser light irradiating the backside of the free end of the cantilever, which were used respectively to obtain topographic and lateral force images.

Results and Discussion

1. Drastic PTC Reduction. The remarkable PTC reduction of carbon black dispersed SBR/NBR rubber blend composites made by the toluene solution mixing method is shown in Figure 1. By the simple substitution of the rubber components from neat SBR and NBR to their blend (SBR/NBR = 90/10), the PTC value reduced from 5.7 vol % (SBR) and 8.9 vol % (NBR) to 1.2 vol % (SBR/NBR = 90/10). The slope of the conductivity curve of the rubber blend composite gradually decreases after a small jump at the PTC (1.2 vol %), and the curve intercepts those of the composites with pure polymer matrix at the deflection point around 10 vol %. After the intersection point, all of the curves seem to behave according to the percolation theory which is described as follows:

$$\sigma = \sigma_0 (V - V_c)^t \quad (1)$$

where σ is the conductivity of the composite, σ_0 is the conductivity of the filler, V is the volume fraction of the filler, V_c is the volume fraction of the filler at PTC, and t is a constant.

Before the carbon black is added to the rubber blend (SBR/NBR = 90/10), the phase separation takes clearly sea-islands morphology as shown in Figure 2. Because of the higher interfacial tension of the NBR phase than the SBR phase, the sea-islands structure can be seen even when the SBR/NBR ratio


$50\mu m$
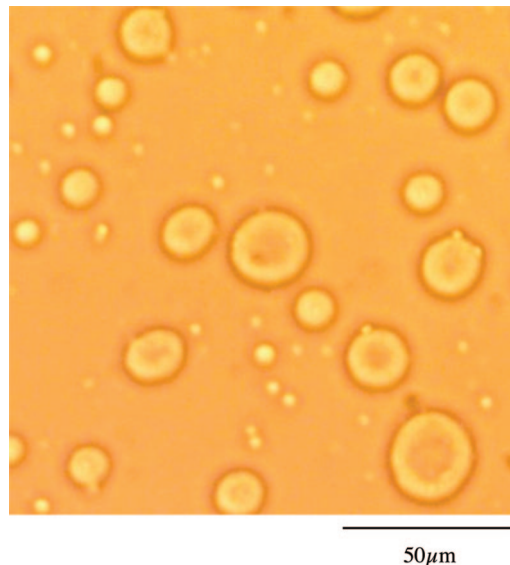
Figure 2. Optical micrograph of film morphology of spin-cast SBR/NBR = 90/10 blend after toluene solution mixing.

changes to 50/50. Intuitively, it seems unwise to adopt such morphology for a binary immiscible system for the purpose of the PTC reduction because carbon black should be localized in the continuous polymer phase and concentrated enough to obtain conductive networks. Therefore, in the case of the SBR/NBR = 90/10 blend system, even if all the carbon black particles are distributed into the SBR phase (sea), the carbon black is highly diluted in the dominant SBR phase, which would not achieve percolation with a small amount of carbon black. Selectively concentrating carbon black into the SBR phase would only make a small shift in the PTC, which can be estimated as only 0.6 vol % lower than that of the neat SBR's PTC. In other words, it is from 5.7 vol % of pure SBR to 5.1 vol % of the SBR/NBR = 90/10 blend. On the other hand, if all the carbon black particles are distributed into the NBR phase (islands), the NBR phase would become highly conductive even with a small amount of the carbon black due to the small amount of the NBR in the system. However, these conductive islands might be completely insulated by the SBR phase, and if so, they cannot form conductive paths. Furthermore, even if the carbon black particles are distributed at the interface of the rubber blend, obviously, it is also impossible to form conductive path due to the lack of the continuity of the interface.

In order to reveal the mechanism of the counterintuitive PTC reduction of the rubber blend composite described in this paper, careful observation of the film morphology of the composite was carried out. Figure 3 is the optical micrograph of the rubber blend composite (SBR/NBR = 90/10) including 1.43 vol % of the carbon black. The micrograph indicates that the carbon black particles are distributed into the minor polymer phase, i.e., NBR islands. In addition, these islands are fairly coagulated together by their edges. The concentration of the carbon black inside the islands is easily calculated under the assumption that the carbon black is completely distributed into the NBR phase. The concentration inside the islands is calculated to be 10.8 vol % when the average carbon black concentration of the system is 1.2 vol %. This value of 10.8 vol % has already exceeded the PTC of the neat NBR composite (8.9 vol %). Therefore, the drastic PTC reduction observed at 1.43 vol % of the carbon black concentration can be interpreted as the combination effect of the carbon black enrichment to the NBR phase and the subsequent coagulation of the islands. The LFM images also support that the carbon black is solely distributed into the NBR
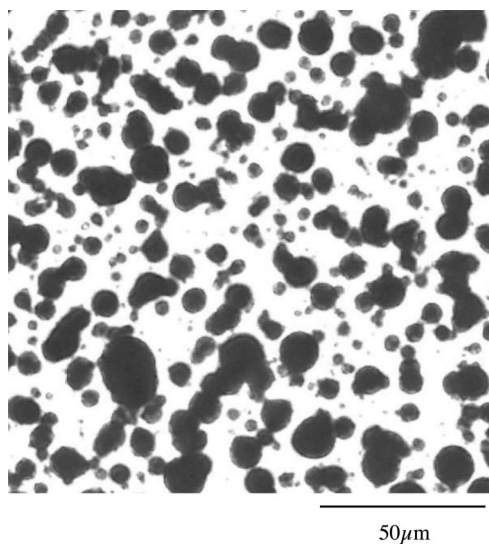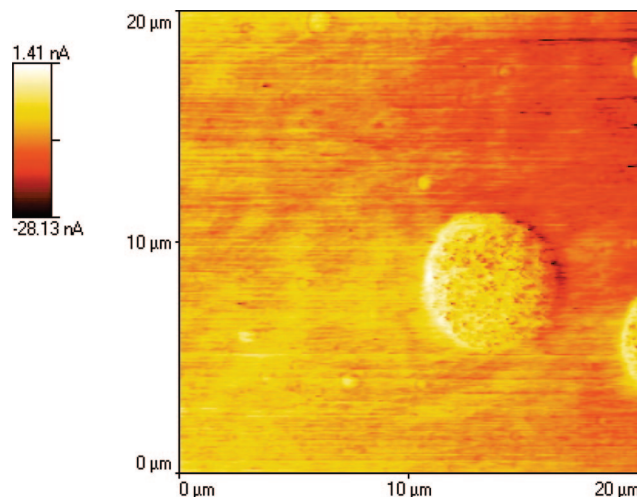
Figure 3. Optical micrograph of film morphology of cast SBR/NBR = 90/10 conductive rubber composite including 1.43 vol % of carbon black made by the toluene solution mixing method.
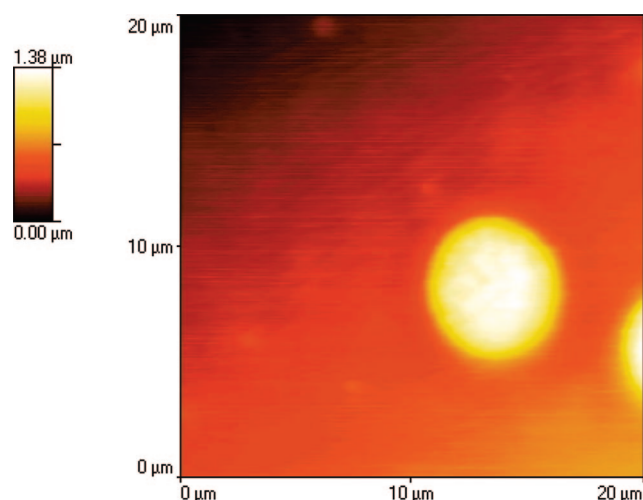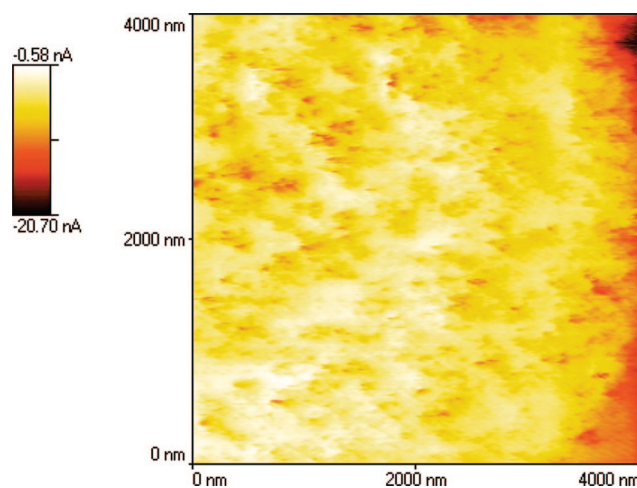

Figure 4. Topographical image of SBR/NBR = 90/10 conductive rubber composite including 1.43 vol % of carbon black made by the toluene solution mixing method.

Figure 5. LFM image of SBR/NBR = 90/10 conductive rubber composite including 1.43 vol % of carbon black made by the toluene solution mixing method.

Figure 6. LFM image (inside dropwise phase shown in Figure 5) of SBR/NBR = 90/10 conductive rubber composite including 1.43 vol % of carbon black made by the toluene solution mixing method.

phase, and there is no trace of the carbon black in the SBR phase (Figures 4–6).

In addition, the coagulation mechanism of the NBR islands including the carbon black needs to be explained. First of all, even if all of the carbon black is distributed to the NBR phase, the volume ratio of the separated phases will not significantly change before and after the carbon black addition. The change of the volume ratio is only few percent, to be exact, that is from SBR/NBR = 90/10 to SBR/(NBR with carbon black) = 88.7/11.3. Such a slight volume change should not affect the continuity of the NBR phase. Therefore, the coagulation of the islands should have other reasons. According to the "viscoelastic phase separation" concept, when the mobility of the components inside minor phase is lower than that of the dominant phase, it is known that these islands tend to coagulate together and form a transition gel network without the size growth of the individual island.[37] The gel network is quite stable for a long time without any chemical cross-linking. Consequently, in this study, it would be understood that the lower mobility, namely, the higher viscosity of the carbon black-containing NBR island phase than that of the SBR phase, caused the formation of the conductive network.

Another important thing needs to be discussed here is the driving force for the selective distribution of carbon black to the NBR phase. Conventionally, the chemical interaction between filler and polymer is assumed to be the most important factor to settle the distribution of the filler to the particular phase. Because of the nature of the higher polarity of the NBR and the chemically active graphite crystalline edges on the carbon black surface, the NBR might be a better candidate for the selective adsorption onto the carbon black surface. However, because the carbon black surface has both hydrophilic and hydrophobic sites, the SBR would also be a candidate for the selective adsorption. In the next section, we will see the occurrence of selective distribution of the carbon black to the SBR phase.

2. Solvent Effect. Figure 7 illustrates the conductivity curves of the conductive rubber composites made by the chloroform solution mixing method. The difference between this result and the previous one (Figure 1) is the rubber blend ratio and the type of the solvent. In addition, Figures 8 and 9 compare the conductivity curves of the composite blends in different solvents. The results indicate that an opposite trend of the conductivity is obtained when the solvent used for the mixing process is changed from chloroform to toluene. When toluene is chosen for the mixing process, the significant PTC reduction appears
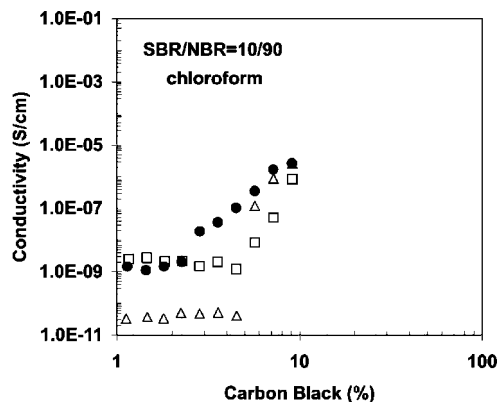
Figure 7. Influence of carbon black concentration on electrical conductivity of SBR/NBR = 10/90 (●), SBR (△), and NBR (□) composites made by the chloroform solution mixing method.
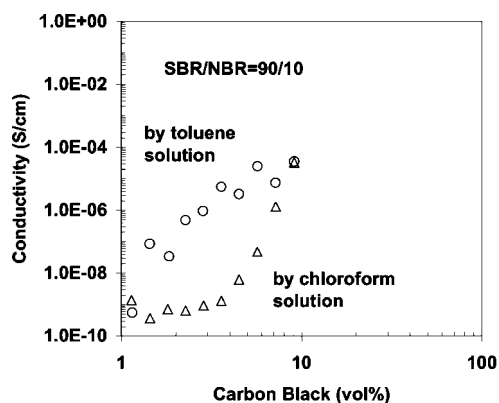

Figure 8. Influence of carbon black concentration on electrical conductivity of SBR/NBR = 90/10 composites made by the toluene or chloroform solution mixing method.

Figure 9. Influence of carbon black concentration on electrical conductivity of SBR/NBR = 10/90 composites made by the toluene or chloroform solution mixing method.
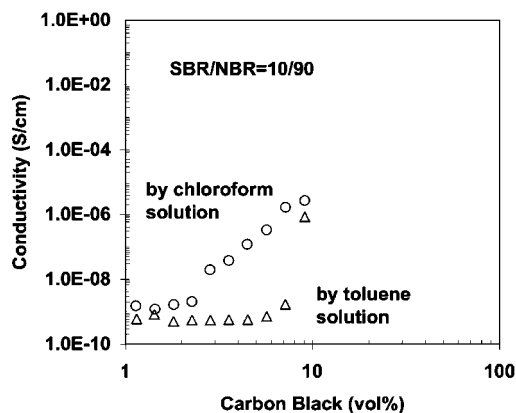

Figure 10. Swelling tendency of SBR/NBR = 50/50 blend solution in different types of solvent.
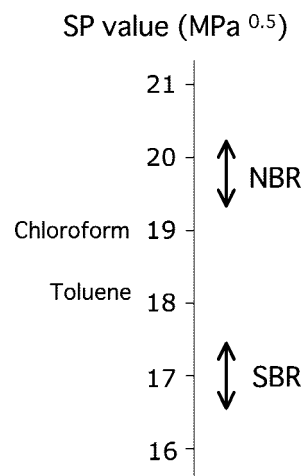
Figure 11. Hildebrand solubility parameters of SBR, NBR, toluene, and chloroform.

when the composite is made of the blend with the SBR/NBR = 90/10 ratio. Simply changing the rubber blend ratio from SBR/NBR = 90/10 to SBR/NBR = 10/90, the PTC reduction clearly disappears. On the other hand, when chloroform was chosen for the solvent, the conductivity curves show an opposite trend to the toluene solution. Namely, there is PTC reduction only when the ratio is SBR/NBR = 10/90.

To explain these phenomena, it should be pointed out the very important role of the radius of gyration (R_g) of the rubber molecules in the solvents. SBR exhibits better compatibility with toluene than NBR. However, it is opposite in chloroform. The compatibility can be easily compared by the visual observation
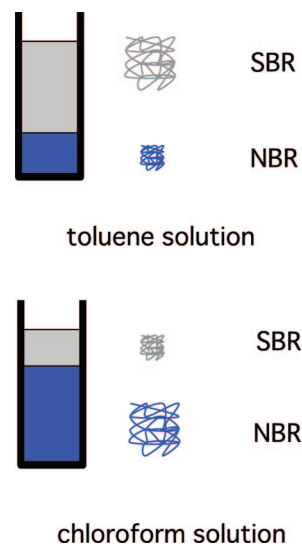
shown in Figure 10. In the toluene solution including 5.0 vol % of polymers which consists of the same amount of SBR and NBR, the volume ratio of the separated phase is SBR/NBR = 70/30. On the other hand, in the chloroform solution case, the ratio is SBR/NBR = 30/70. This fact intuitively implies that the R_g of SBR in toluene is larger than that of NBR and vice versa in chloroform, which is in good agreement with the Hildebrand solubility parameters among the rubbers and the solvents as shown in Figure 11. On the basis of the information, the following molecular confinement concept is proposed to explain the PTC reduction phenomena observed.

We focus on the size matching between the R_g of the rubber molecules and the void entrance of the carbon black aggregates. Most carbon black particles have persistent structure, so-called "aggregate structure". The aggregate structure, which has a grape-bunch-like shape and cannot be destroyed during the mixing process, is formed by the fused primary particles. The voids of the carbon black aggregates discussed in this paper correspond to the spaces surrounded by the primary particles. We hypothesize that the size matching between the R_g of the rubber molecules and the void size of the carbon black aggregates is the key factor for the selective adsorption of the particular rubber molecules on the carbon black surface. In Figure 12, if we chose toluene as a solvent for the solution mixing of the SBR/NBR = 90/10 blend with carbon black, the
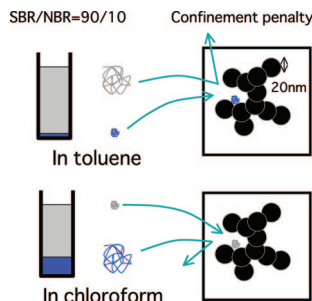
Figure 12. Selective adsorption mechanism of rubber molecules based on molecular confinement concept.

R_g of NBR is assumed to be small enough to be confined into the voids of the carbon black aggregates because the compatibility of NBR to toluene is rather poor. The entrance size is determined to be about 20–30 nm from its TEM micrograph. Meanwhile, the compatibility of SBR with toluene is good, which makes the R_g to be too large for the confinement. Therefore, the NBR molecules can be selectively adsorbed on the carbon black surface. Eventually, after some accumulation of the NBR molecules on the carbon black surface, the carbon black particles will be covered with NBR molecules, and then the particles will migrate into the NBR phase. In fact, we can macroscopically observe the phase separation of the black viscous phase and the upper clear phase after the solution was allowed to stand for a week. Furthermore, proton nuclear magnetic resonance spectroscopy (^{1}H NMR) cannot detect SBR in the bottom black phase. On the other hand, when the solvent is switched to chloroform, the R_g of SBR is considered to be suitable for the confinement in the void of the carbon black aggregate structure. In such a case, the carbon black particles will be covered with SBR, and then the SBR-covered aggregates will be selectively transferred to the SBR phase. However, under this SBR dominant (SBR/NBR = 90/10) condition, the carbon black inside the SBR phase is too dilute to cause a drastic PTC reduction. This inefficiency has already been explained in the drastic PTC reduction section. In the same manner, we can use this concept to explain the phenomenon observed for the other blend ratio (SBR/NBR = 10/90). For such a system, the PTC reduction should be observed only when chloroform is chosen for the solvent. As expected, it is indeed the case. Thus, the concept considering the molecular confinement of the rubbers into the void of the carbon black aggregate structure seems applicable to interpret the contrary conductivity improvement depending on the chosen solvents.

3. Blend Ratio. When the SBR/NBR blend ratio is systematically changed to 90/10, 80/20, and 70/30, the PTC is also systematically changed (Figure 13). On the basis of the fact that the PTC is 8.9 vol % for the conductive rubber composite consisting of the neat NBR and carbon black, and assuming that all carbon black particles are distributed into the NBR phase of the SBR/NBR rubber blends and the conductive phase is always continuous, it is possible to estimate the PTC of the blends in proportion to the blend ratio. Table 1 is the comparison between the calculated carbon black concentration of the blend when the NBR phase exceeds the PTC and the values of the actual PTC observed from the experiments. The fairly consistent result implies that even if the blend ratio is changed, the selective adsorption of the NBR molecules on the carbon black surface occurs, and the subsequent migration of those surface-modified carbon black particles into the NBR phase also happens in the same manner.

4. Destruction of the Conductive Network. Figure 14 shows the change of the conductivity curves of the blends processed under different compression molding conditions. The film was
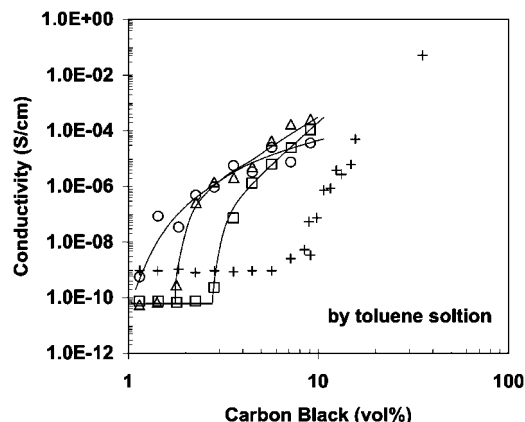
Figure 13. Influence of carbon black concentration on electrical conductivity of various SBR/NBR blend (90/10 (○), 80/20 (△), 70/30 (□), 0/100 (+)) composites made by the toluene solution mixing method.

Table 1. Observed PTC of Various SBR/NBR Compositions and Calculated PTC under the Assumption That All Carbon Black Is Distributed to the NBR Phase

SBR/NBR	90/10	80/20	70/30	0/100
observed PTC (vol %)	1.2	1.8	2.8	8.9
calculated PTC (vol %)	0.9	1.8	2.7	
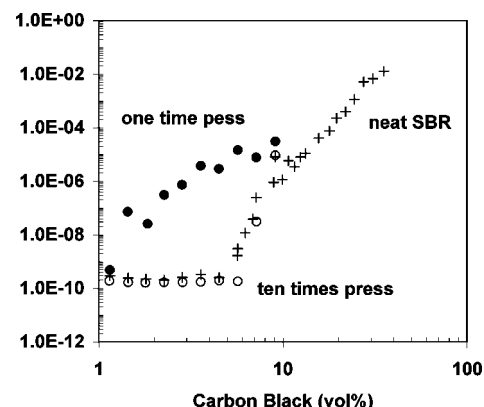
Figure 14. Influence of carbon black concentration on electrical conductivity of SBR/NBR = 90/10 composites made by the toluene solution mixing method with different molding process.

initially cast from a solvent, but the film was repeatedly compression molded to change the carbon black distribution. The PTC reduction of the SBR/NBR = 90/10 is clearly suppressed by the enhanced severity of the molding process. This result implies that the continuous NBR phase formed during the casting process is destroyed by the repetitious deformation applied to the sample during the molding process. The conductive network formation can be explained by the viscoelastic phase separation as it has been mentioned in section 1. The driving force for the viscoelastic phase separation observed here is the large difference of the viscosity between the phase-separated rubbers in the solution. The increase of the viscosity of the NBR phase can be explained by two factors. One is the hydrodynamic effect caused by the uneven distribution of the carbon black to the NBR phase. The other is the insufficiency of the solvent in the NBR phase by its lower compatibility with toluene than that of SBR. During the solvent evaporation, both factors synergistically cause the viscosity increase of the NBR phase, and then islands coagulate without the individual size growth. Here, the higher mobility of the diluted SBR phase also helps the sequence to occur smoothly. At last, when the solvent completely evaporates, the viscosity of the SBR phase also

increases and the network morphology is fixed. If the conductive network is destroyed by repetitious deformation at this point, it seems difficult to reconstruct the network because the viscosity of the SBR phase has also increased quite high. Then, the broken network structure will be preserved. Of course, the viscosity difference caused by the hydrodynamic effect of the carbon black might still proceeds the network formation of the NBR phase, but it will take a long time. Therefore, the PTC reduction of the composite after the repetitious deformation applied by the molding process is suppressed.

5. Advantages of the Solution Mixing. From the viewpoint of the controlled selective adsorption of one of the rubber molecules, solution mixing is superior to melt mixing. Wu et al. pointed out that the flexibility of molecular chains is more important than the chemical interactions between polymer and carbon black for a selective adsorption of polymer molecules onto the carbon black surface. As they mentioned, if the high flexibility of molecular chains is related to their low glass transition temperature (T_g), it would be difficult to selectively adsorb one of the polymer when T_gs of the two components in a blend are close to each other. It is the situation in our case. The T_gs of SBR (-52 °C) and NBR (-40 °C) are quite close to each other. Furthermore, the T_g of NBR, in which we want to localize the carbon black, is higher than that of SBR. In any case, it is difficult to obtain the structure observed in this study by using conventional melt mixing processes. For the selective adsorption mechanism based on the molecular confinement concept proposed above, it is important to consider not only the flexibility of the molecular chains but also the size. The selective adsorption causes the selective localization of carbon black in a solution blend. Therefore, the solution mixing seems to be a more flexible method than melt mixing from the viewpoint of filler distribution control.

6. PTC Shifts of Homopolymer Composites. It has been generally accepted that polymer–polymer, filler−filler, and polymer−filler chemical interactions are the most important factors to decide PTC of conductive polymer composite systems. In other words, a PTC is almost automatically settled into a thermodynamically stable state when a specific polymer(s) and filler(s) combination is chosen and mixed well. Therefore, it is very difficult to change a PTC in a specific system without chemical modification of filler or polymer. However, as demonstrated in this paper, we could change the PTC of the SBR/NBR conductive rubber composites by changing the solvent for the solution mixing, and the selective adsorption mechanism is explained by the proposed molecular confinement concept. If the application of this concept were to be successful, PTC of conductive polymer composites should be able to be predicted and controlled according to the proposed mechanism even when homopolymers are used in the system, because the state of the coagulation of the carbon black particles can be controlled by changing the adsorption tendency of the polymer to the surface of the carbon black.

The results are shown in Figure 15. The PTC of the conductive rubber composites consisting of the neat NBR and carbon black shifts from 8.9 to 3.6 vol % when the solvent is changed from toluene to methylene chloride. The relationship of the Hildebrand solubility parameters among the rubber and the solvents is shown in Figure 16. When the NBR is dissolved in methylene chloride, the R_g of the molecules is much larger than the void entrance of the carbon black aggregates because of the high compatibility between the NBR and methylene chloride. Therefore, most of the NBR molecules should be excluded from the void of the carbon black aggregate structure. This means that carbon black particles cannot interact with the NBR molecules as much, and then the phase separation between NBR and carbon black will occur. Accordingly, the excluded
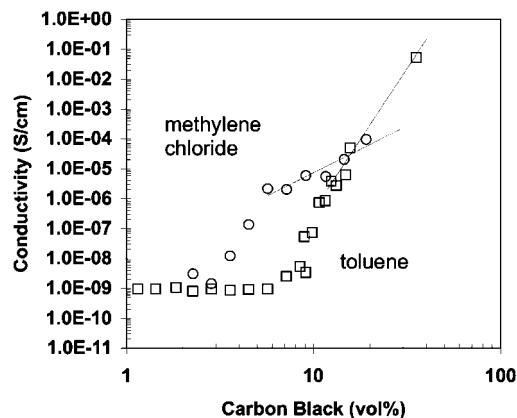
Figure 15. Influence of carbon black concentration on electrical conductivity of SBR/NBR = 90/10 composites made by the toluene and methylene chloride solution mixing method.
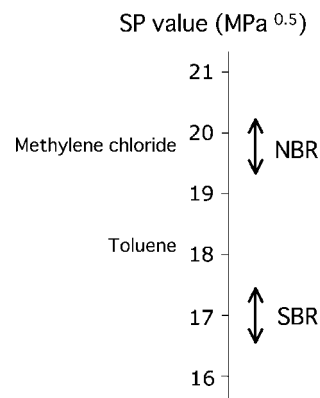
Figure 16. Hildebrand solubility parameters of SBR, NBR, toluene, and methylene chloride.

carbon black particles from the NBR phase can easily form conductive paths; therefore, the PTC will decrease. On the other hand, in the case of toluene solution, the R_g of the NBR molecules is small enough to be confined into the void of the carbon black aggregates because of the fairly poor compatibility with the solvent. In this case, most of the carbon black aggregates can be covered well by NBR molecules. Thus, the individually insulated carbon black particles hardly form the conductive paths rather than the previous case. Accordingly, the PTC will increase. In addition, the difference of the slopes of the conductivity curves after PTC also indicates the difference of the conductive network structure. Balberg reported that the steepness of the slope, the value of t in eq 1, becomes smaller when the carbon black aggregate structure changed higher.[7] In our study, the t value of the toluene solution case is similar to the type of carbon black with higher aggregate structure and that of the methylene chloride case corresponds to the case as if the carbon black aggregate structure is lowered. This trend corresponds to the change of the network formation tendency of carbon black in different solvent as explained above. Consequently, in our study, the degree of network formation can be controlled by changing the compatibility between the polymer and solvent, although the same carbon black is added to the homopolymer systems.

7. Novelty of the Selective Adsorption Mechanism Using the Molecular Confinement Concept. The molecular confinement concept is applied by paying attention to the size matching between the polymer molecules and the void entrance size of the carbon black aggregate structure. Even if there are active sites on the filler surface that interacts with the polymers,

polymer adsorption would not occur as long as polymer chains could not enter the voids of the aggregates. To emphasize this condition, solution mixing is purposely chosen in this study to emphasize the R_g difference of the polymers. All of the results shown above indicate that both the SBR and the NBR could be selectively adsorbed onto the carbon black surface by suitable choice of solvent. Conventionally, the enthalpic interactions among polymers and fillers are considered the most important factor for the selective adsorption. Therefore, because of the nature of the high polarity of the NBR and the chemically active graphite crystalline edges on the carbon black surface, the NBR molecules should be the candidates for the selective adsorption onto the carbon black surface. However, we could successfully distribute the carbon black particles into both the NBR and the SBR phase by changing the compatibility between the rubbers and the solvents. This result implies that the size matching is a more important factor for the selective adsorption in the presence of a solvent than enthalpic factors.

Conclusions

The remarkable PTC reductions were observed in the carbon black dispersed SBR/NBR system, with the solution mixing method, in the cases of the SBR/NBR = 90/10 with toluene and the SBR/NBR = 10/90 with chloroform. These results can be interpreted as the combination of the selective distribution of the carbon black to the minor rubber phase and the subsequent coagulation of the phase. The selective distribution of the carbon black can be explained by the selective adsorption of a polymer. This selective adsorption mechanism is explained via molecular confinement concept. On the other hand, the coagulation of the phase is explained by the viscoelastic phase separation caused by the viscosity difference between the phases. The conductive network is destroyed by the repetitious deformation applied to the sample during the cumulative molding process, and it does not reconstruct. The molecular confinement concept also successfully explains the shift of the PTC observed for the composites consisting of neat NBR and carbon black. Regardless of the degree of the chemical interactions between the polymers and the carbon black, which is considered as the most important factor to settle the carbon black distribution, we could succeed in selectively distributing the carbon black particles into both the SBR and NBR phase by changing the compatibility between the rubbers and the solvents.

References and Notes

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