Macromolecules
ARTICLE

Macromolecules **2009**, *42*, 6175–6180 **6175**
DOI: 10.1021/ma802254a

Verification of Selective Adsorption of Polymer on Filler Surface in a Binary Immiscible Polymer Solution Blend Based on Nanoconfinement: Changing the Aggregate Structure and the Surface Character of Carbon Black

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Received October 13, 2008; Revised Manuscript Received June 26, 2009

ABSTRACT: The limiting cause of nanoconfinement of rubber molecules for their selective adsorption onto filler surface has been examined by changing: (1) the void size of carbon black aggregates, (2) the atomic scale roughness and chemical character of carbon black surface, and (3) the kind of filler from carbon black to silica. Nanoconfinement of rubber molecules into carbon black aggregate structure occurs at the concave (~5 nm) formed in between carbon black primary particles. Nanoconfinement is the primary mechanism, whereas chemical interaction between filler and the polymer plays a minor role in the selective adsorption. The new adsorption concept is also examined with silica nanoparticles.

Introduction

Uneven distribution of conductive filler, especially carbon black, in a binary immiscible polymer blend is one of the best ways to reduce the percolation threshold (PTC)[1] of filled polymers.[2−15] However, it is very difficult to control the location of the conductive filler in a blend. Conventionally, it has been widely accepted that polymer−polymer, filler−filler, and polymer−filler chemical interaction is the most important factor to decide the filler location. Therefore, PTC is almost automatically determined when a combination of specific polymer(s) and filler(s) is chosen.

In our previous study,[16] a novel carbon black distribution controlling method was proposed on the basis of the nanoconfinement of polymer molecules into the filler aggregates. In the study, the distribution of carbon black was successfully controlled regardless of the chemical interactions among polymers and filler. That is, selective adsorption of NBR molecules occurred onto carbon black surface in a solution of styrene butadiene rubber (SBR)/acrylonitrile butadiene rubber (NBR) 90/10 in toluene and that of SBR molecules in a solution of SBR/NBR 10/90 in chloroform. At first, the limiting cause for the nanoconfinement of the rubber molecules was hypothesized to be the size matching between R_g of the rubber molecules and the void entrance of the carbon black (Monarch 880, Cabot corporation) aggregate structure. Actually, by dynamic light scattering measurement, it was shown that the R_g of the SBR and NBR molecules in the solvent with poorer compatibility (chloroform for SBR and toluene for NBR) was suitable to be confined into the void, and the R_g of them in the solvent with better compatibility (toluene for SBR and chloroform for NBR) was too large for the confinement.[17]

However, in the case of the liquid NBR (low-molecular-weight NBR)/SBR blend in the chloroform solution system in which selective adsorption of the liquid NBR onto the carbon black surface was observed, the R_g of both rubber molecules was smaller than the void entrance of the carbon black aggregate structure.[17] This implies that the confinement of the rubber molecules into the surface roughness of the carbon black primary particles or the concave in between the primary particles might also be contributing to the selective adsorption besides the confinement into the void of aggregates as the first gateway.

In this study, we have examined the limiting cause of nanoconfinement of the rubber molecules for their selective adsorption onto the filler surface by changing the carbon black aggregate structure, the atomic scale surface roughness, and the chemical character of the filler surface. Furthermore, the possibility of applying this new concept to nanofillers other than carbon black was examined using a fumed silica.

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 SBR (Nipol 1502: $M_w = 5.0 \times 10^5$, $T_g = -52$ °C) and NBR (Nipol 1042: $M_w = 4.5 \times 10^5$, $T_g = -40$ °C) obtained from Zeon Corporation. The conductive fillers mixed with the polymers are high-structured carbon black (Monarch 880: Brunauer−Emmett−Teller (BET) nitrogen adsorption surface area = 220 m^2/g, dibutylphthalate (DBP) oil absorption value = 105 mL/100 g) and low-structured carbon black (Monarch 120: BET nitrogen adsorption surface area = 25 m^2/g, DBP oil absorption value = 70 mL/100 g) obtained from Cabot and another high-structured carbon black (Tokablack no. 5500: BET nitrogen adsorption surface area = 225m^2/g, DBP oil absorption value = 155 mL/100 g) and its graphitized carbon black (Tokablack no. 3855: BET nitrogen adsorption surface area = 90 m^2/g, DBP oil absorption value = 121 mL/100 g) obtained from Tokai Carbon. Fumed silica (CAB-O-SIL M-5: BET nitrogen adsorption surface area = 200 m^2/g) obtained from Cabot Corporation is also used to check the possibility of the application of the nanoconfinement concept for another filler. Solvents used for the solution mixing are ACS reagent grade toluene and chloroform purchased from Fisher Scientific. Both solvents can dissolve SBR and NBR.

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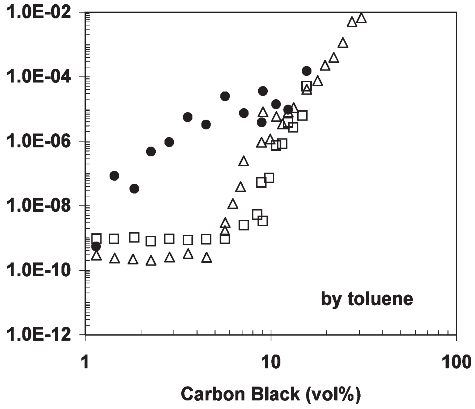

Figure 1. Influence of high-structured carbon black (Monarch 880) concentration on electrical conductivity of SBR/NBR = 90/10 (●), SBR (△), and NBR (□) composites made by toluene solution mixing method.

Prior to the mixing of all compounds, carbon black or silica was well dispersed in the solvent by sonication for 24 h, and the rubbers were dissolved in the solvent with individual stirring. Then, they were mixed together, and sonication was applied for 10 h. The concentration of total rubber components in the solution was approximately 5 vol %. Afterward, the solution was cast at ambient temperature, the solvent was dried, and the obtained film was folded and pressed once by a compression molder at 100 °C and 1.0 MPa.

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

3. Fourier Transform Infrared Spectroscopy. Fourier transform infrared (FT-IR) spectra were obtained on a Bomem Michelson MB 110 FT-IR spectrophotometer that was equipped with a deuterated triglycine sulfate (DTGS) detector. Samples were cast onto KBr plate and dried in a vacuum oven at room temperature for 24 h. The spectrometer was continuously purged with nitrogen gas to minimize water vapor and atmospheric carbon dioxide. The spectra were recorded with the coaddition of 16 scans at a resolution of 4 cm^{-1}.

4. Morphological Observation. A couple of droplets of rubber blend solutions including fumed silica obtained by the mixing process were spin-cast onto substrates (a piece of cover glass). The films were then examined by optical microscopy (OM) (BX-60, Olympus) to check the phase separation morphology.

Results and Discussion

1. Low-Structured Carbon Black. A remarkable PTC reduction of the carbon-black-dispersed SBR/NBR rubber blend composite cast from a toluene solution is shown in Figure 1. On the basis of the selective distribution mechanism of carbon black in a binary immiscible rubber blend via nanoconfinement of the rubber molecules into the carbon black aggregate structure previously proposed,[16] the remarkable PTC reduction of the rubber blend composite can be interpreted as follows. Because the composite is prepared by toluene solution, the R_g of SBR is larger than that of NBR by the difference of the polymer compatibility with the solvent. From the dynamic light scattering measurement, it has already been found that the apparent hydrodynamic radius of the SBR is about 150 nm and that of the NBR is about 5 nm in the dilute toluene solution.[17] It is possible that this large radius may have been observed by the molecular aggregation rather than the radius of a single molecule. The size of the primary carbon black particle used was 25 nm according to the data provided by the manufacturer. Therefore, the entrance size of the void of the carbon black aggregates should be close to this value. Therefore, the majority of the SBR molecules is considered to be excluded from the void of the carbon black aggregates, and only the NBR molecules can be confined there. Once some of the NBR molecules are confined in the void, the additional NBR molecules can easily accumulate on the carbon black surface, depending on the concentration of the NBR solution, and then all carbon black particles covered with the NBR molecules will migrate into the remaining NBR phase. Because the carbon black covered with NBR is the minor phase, it forms islands. During the next drying process, the increased viscosity of the islands causes coagulation of the islands. Finally, the carbon-black-concentrated NBR phase becomes the conductive network in the composite. If the entrance size of the void of the carbon black aggregates is the limiting cause for the selective adsorption of the rubbers, then another carbon black having larger entrance size of the void must allow confinement of some SBR molecules and reduce the dominant adsorption of the NBR molecules. Monarch 120 is a suitable carbon black to examine this hypothesis because of a larger primary particle size, thus having larger void structures.

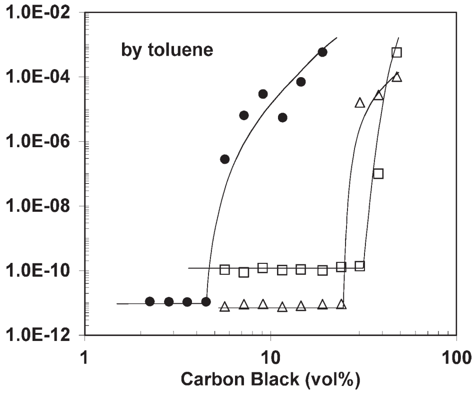

Figure 2. Influence of low-structured carbon black (Monarch 120) concentration on electrical conductivity of SBR/NBR = 90/10 (●), SBR (△), and NBR (□) composites made by toluene solution mixing method.

The conductivity curves of the rubber blend composite (SBR/NBR 90/10) and the neat rubber composites including the lower-aggregate-structured carbon black (Monarch 120) are shown in Figure 2. The PTCs of the neat SBR and NBR composites with lower-structured carbon black (Monarch 120) are 24.0 and 30.2 vol %, respectively, whereas those with finer carbon black (Monarch 880) are 5.7 and 8.9 vol %, respectively. The decrease of the PTCs is expected because the carbon black aggregate structure is more complex and the primary particle size is decreased. However, the drastic PTC reduction of the rubber blend composite is still observed here. It is further lowered to 4.5 vol %, and the trend seems as if those curves of the finer carbon black composites are just shifted to the higher carbon black concentration region. When it is hypothesized that all carbon black particles are distributed to the NBR phase in the blend, the carbon black concentration in the NBR phase can easily be estimated. The concentration is 31.5 vol % in the NBR phase at the PTC (average concentration is 4.5 vol %) of the rubber blend composite, and this value is fairly consistent with the PTC (equivalent to 30.2 vol %) of the neat NBR composite. This implies that all carbon black particles have already been

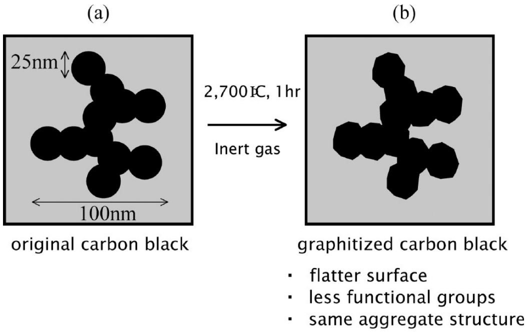

Figure 3. Schematic images of original carbon black (Tokablack no. 5500) and its graphitized carbon black (Tokablack no. 3855).

completely distributed to the NBR phase at the PTC of the rubber blend composite. That is, even the entrance of the void of the carbon black aggregate structure is widened, and the overwhelmingly dominant confinement of the NBR molecules into the void cannot be obstructed by the SBR molecules. Therefore, the exact match between the entrance size and R_g does not seem to be the limiting condition for the selective confinement ahead of the selective distribution of the carbon black particles to the NBR phase. Rather, the R_g of the confined molecules can be smaller than the entrance size of the aggregate structures.

2. Graphitized Carbon Black. A carbon black treated at high temperature, a so-called graphitized carbon black, possesses smoother surface and lower concentration of surface functional groups compared with the untreated carbon black precursor. Therefore, the comparative study of the original carbon black and the graphitized carbon black provides us with a unique opportunity to examine the role of enthalpic parameter and entropic parameter. If the enthalpic parameter is more important, as has been emphasized in the adhesion study in the past, then the PCT should be higher for the graphitized carbon black because of the poor adsorption of the polymer on the surface. If the entropic parameter is more important, as is the emphasis given in the current study, then the PCT should decrease because of the increased adsorption of the polymer onto the surface.

The thermal treatment of carbon black is usually carried out at a very high temperature about 2700 °C under inert the atmosphere. Figure 3a,b shows the schematic images of untreated carbon black and graphitized carbon black, respectively. They have similar primary particle sizes but different atomic scale surface character. Because of the difficulty of the very high magnification observation, the detailed structure of the carbon black primary particles is still controversial. However, most researchers agree that the primary particles of carbon black consist of a large number of small graphite crystallites that lie on top of one another at the surface.[18-21] The exposed crystallite edges make the surface quite active both physically and chemically. Once normal carbon black is heat-treated, many functional groups are destroyed, and the small graphite crystallites form larger ones. Consequently, the surface becomes more nonpolar and flatter than non-heat-treated carbon black. The reduction of the small roughness in the graphitized carbon black is reflected on the BET nitrogen adsorption specific surface area. The surface area of the graphitized carbon black (Tokablack no. 3855) used in this study is 90 m^2/g, and that of the original carbon black (Tokablack no. 5500) is 225 m^2/g. Here it is important to point out that the difference in the nitrogen adsorption values does not mean the difference in the primary particle size in this specific case. In general, small primary particle carbon black (16 nm, Monarch 880) has a larger specific surface area (220 m^2/g) than that (25 m^2/g) of the larger one (75 nm, Monarch 120). However, both the original carbon black and the graphitized carbon black have similar primary particle size (25 nm). This seeming contradiction is explained as follows. Considering the atomic scale surface roughness that is around the cross sectional area of a nitrogen molecule (0.162 nm^2), carbon black and graphitized carbon black have much different character. The difference can be expressed by using fractal theory. Avnir and Pfeifer[22,23] proposed that the required molecular volume to cover the surface with a monolayer is given by

$$V_{\text{mono}} \approx S\sigma^{-D/2} \tag{1}$$

where S is the Hausdorf measure of the surface, σ is the effective cross sectional area of the adsorbate, and D is the surface fractal dimension. When the surface is perfectly smooth, D = 2 and S is the surface area, and the value increases with the degree of surface irregularity up to 3. On the other hand, V_{mono} is also obtained by the BET equation for low pressure isotherm[24]

$$V_{\text{mono}} = \frac{V\left(1 - \frac{p}{p_0}\right)[1 + (c-1)\frac{p}{p_0}]}{c\frac{p}{p_0}} \tag{2}$$

where p is the pressure, p_0 is the vapor saturation pressure of the adsorbate, c is the adsorption strength, and V is the volume of adsorbed gas. Therefore, it is possible to determine the surface fractal dimension of various fillers from the slope of the log(V_{mono}) versus log(σ) plot by changing the type of adsorbate, for example $\sigma(\text{Ar}) = 0.138$ nm^2, $\sigma(\text{N}_2) = 0.162$ nm^2, σ(ethane) = 0.269 nm^2, σ(propane) = 0.359 nm^2, and σ(butane) = 0.406 nm^2. Using this method, Xu et al.[25] reported the value $D = 2.0 \pm 0.1$ for a series of graphitized carbon black made from different grades of carbon black, and Zerda et al.[26] reported the value $D = 2.2 \pm 0.1$ for a series of different grades of carbon black. These results imply that carbon black and graphitized carbon black can be distinguished by the atomic scale surface irregularity, and the difference affects the molecular volume to cover the surface with a monolayer adsorbate. In other words, even their primary particle size is similar; untreated carbon black can adsorb more adsorbate than graphitized carbon black. Therefore, the large difference of the BET nitrogen adsorption specific surface area between the graphitized carbon black (90 m^2/g, Tokablack no. 3855) and the original carbon black (225 m^2/g, Tokablack no. 5500) indicates the significant difference of the atomic scale surface irregularity of the primary particles.

Both Figures 4 and 5 illustrate the remarkable PTC reduction of the rubber blend (SBR/NBR 90/10) composites including untreated and graphitized carbon black, respectively. Both results imply the selective distribution of the fillers to the NBR phase and the consequent formation of the electrically conductive path, as previously explained. If the size matching between the atomic scale surface roughness of the carbon black primary particles and R_g of the rubber molecules in the toluene solution is the limiting cause for the selective confinement, then the use of the graphitized carbon black should suppress the selective adsorption of the NBR molecules. In addition, because of the few functional groups on the graphitized carbon black surface, the chemical interaction between the surface and the NBR molecules cannot be taken into account for the attractive force. Despite these

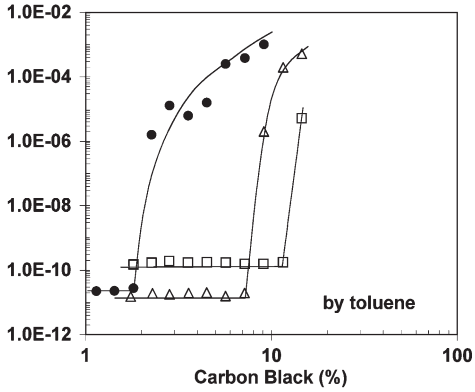

Figure 4. Influence of original carbon black (Tokablack no. 5500) concentration on the electrical conductivity of SBR/NBR 90/10 (●), SBR (△), and NBR (□) composites made by toluene solution mixing method.

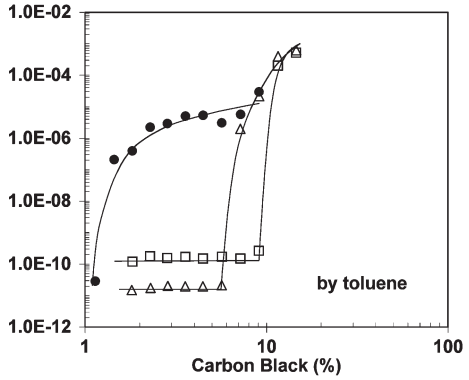

Figure 5. Influence of graphitized carbon black (Tokablack no. 3855) concentration on electrical conductivity of SBR/NBR 90/10 (●), SBR (△), and NBR (□) composites made by toluene solution mixing method.

negative factors for the selective adsorption, the result indicates that the NBR molecules still seem to be attracted to the graphitized carbon black in the toluene solution. Ban et al. reported electron micrographs of benzene-extracted unvulcanized SBR/carbon black compounds, and the remaining rubber is dominantly observed at the concaves of the primary particles.[27] This tendency is also observed when they used graphitized carbon black as a filler, and they concluded that there is no uniform layer of surface-bound rubber. Although their experimental condition is different from ours, it is possible to say that the surface roughness does not affect the attraction between rubber molecules and the surface of the primary particles in a solution mixing. Therefore, the limiting factor of the confinement must be the size matching between the size of the concaves, which is formed in between primary particles, and the R_g of the rubber molecules in a solution. According to our previous report concerning SBR/(low-molecular-weight NBR) and PS/NBR blends, the critical R_g must be around 5 nm. This size is larger than the atomic scale roughness discussed here and smaller than the void size of carbon black aggregate structure. In addition, the chemical interaction between the fillers and the polymers also seems to play a rather unimportant role for the selective adsorption. To confirm this idea, one of the extreme cases is chosen below. The nanoconfinement effect takes place when the R_g is approximately half the size of the nanospace. Of course, this number is not precise. The trend starts slowly. Therefore, the critical R_g of 5 nm for the void size of 20−30 nm may be justified. In summary, despite using graphitized carbon black, which shows a lower number of surface species and lower surface area (BET nitrogen adsorption surface area = 90 m^2/g, DBP oil absorption value = 121 mL/100 g against the original carbon black with BET nitrogen adsorption surface area = 225 m^2/g, DBP oil absorption value = 155 mL/100 g), the graphitized carbon black shows lower PCT value. This fact strongly suggests that in addition to the traditionally accepted enthalpic adsorption mechanism, there seems to be an additional and, in this case, dominant mechanism based on entropic factors.

Figure 6. Photograph illustrating uneven distribution of fumed silica (CAB-O-SIL M-5) to the bottom NBR phase of SBR/NBR 90/10 blend in toluene solution.

3. Selective Distribution of Silica. Figures 6 and 7 show the controlled distribution of fumed silica particles in SBR/NBR rubber blend solutions. In the case of the blend ratio SBR/NBR 90/10, to localize the fumed silica particles to the NBR phase, toluene must be a suitable solvent when the nanoconfinement concept is considered. The result clearly shows the perfect distribution of the fumed silica particles to the bottom NBR phase (Figure 6). To confirm the perfectly uneven distribution of the silica particles to the NBR phase, FT-IR measurement has been carried out. The spectra shown in Figure 10 illustrate the fact that the characteristic peaks of silica are only identified with those of NBR in the spectrum obtained from clouded bottom minor phase. Alternatively, for the SBR/NBR = 10/90 blend, chloroform must be the suitable solvent to distribute the silica particles to the SBR phase, and the result also shows selective distribution of the silica particles to the upper SBR phase (Figure 7). Furthermore, the optical micrographs shown in Figures 8 and 9 also indicate that the silica particles are only included in the minor phase representing NBR and SBR, respectively. Therefore, even such a case using a polar filler that has a good compatibility with only NBR, to arrange the selective distribution of the filler to the relatively nonpolar SBR phase can be accomplished by changing the R_g of the polymers

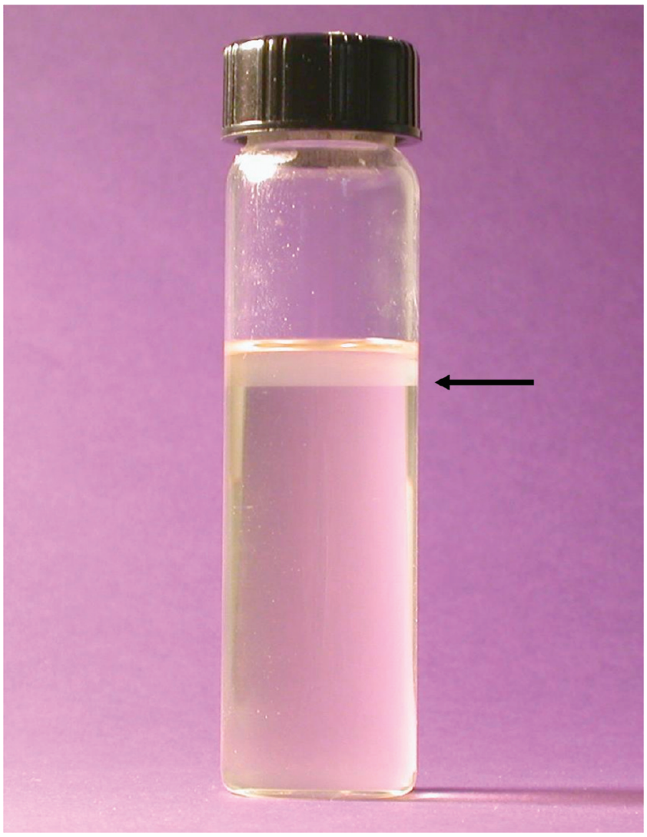

Figure 7. Photograph illustrating uneven distribution of fumed silica (CAB-O-SIL M-5) to the upper SBR phase of SBR/NBR 10/90 blend in chloroform solution.

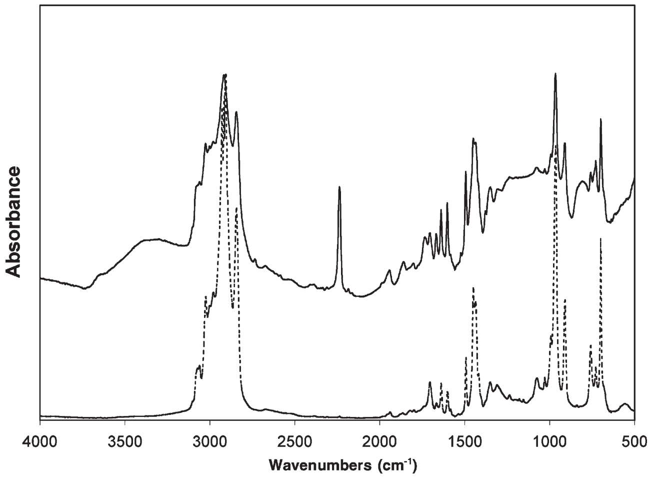

Figure 8. FT-IR spectra illustrating uneven distribution of fumed silica (CAB-O-SIL M-5) to the bottom NBR phase of SBR/NBR 90/10 blend composite. (----, upper clear phase; —, bottom cloud phase).

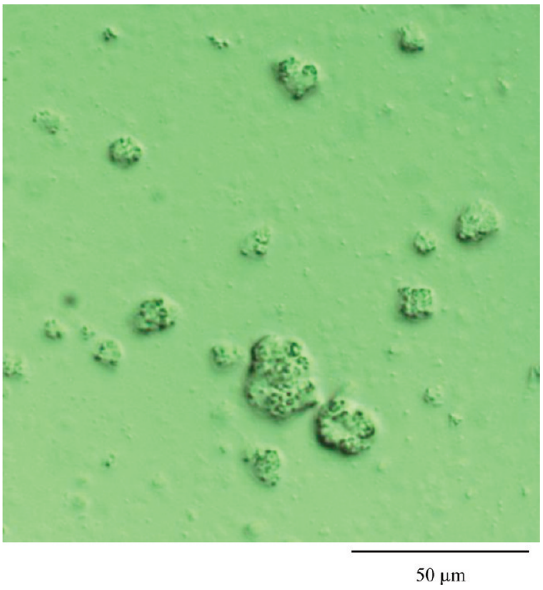

Figure 9. Optical micrograph illustrating uneven distribution of fumed silica (CAB-O-SIL M-5) to the NBR phase of SBR/NBR 90/10 blend composite via toluene solution.

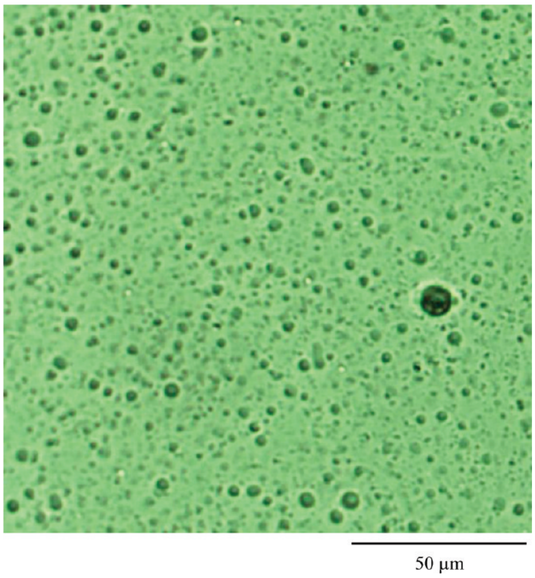

Figure 10. Optical micrograph illustrating uneven distribution of fumed silica (CAB-O-SIL M-5) to the SBR phase of SBR/NBR 10/90 blend composite via chloroform solution.

in a solvent. Consequently, the geometrical factor between the polymers and the filler seems to be more important than the chemical interactions in these solution systems. The further importance of the results obtained with silica is that the selective adsorption of a polymer via nanoconfinement is not limited to carbon black particles alone but is also applicable to other particles with very different surface functionality and topography. The significance of this high-surface-area silica experiment is that we did not change the surface chemical structure of the substrate or the solvent. If the solvent is changed, even if the surface structure is kept the same, then the adsorption characteristic changes. However, when both are kept constant, yet still drastic adsorption characteristic changes are observed, the use of the enthalpic parameter as the major cause of adsorption for the case studied here needs to be re-examined. We reached the same conclusion of the increased importance of the entropic parameter for adsorption when the void size approaches the hydrodynamic size (or aggregate size) of the molecule through the graphitized carbon black as well as the high-surface-area silica.

Conclusions

Even when the entrance of the void of the carbon black aggregate structure is wide enough to induce both rubber molecules confinement in a SBR/NBR blend toluene solution, the selective distribution of the carbon black particles to the NBR phase is still dominant. This result implies that the exact match of the entrance size of the void and R_g is not a requirement for the selective confinement of the rubber molecules. Rather, the critical R_g can be slightly smaller than the entrance dimension.

From the result of the graphitized carbon black addition, it was demonstrated that atomic scale surface roughness is not the limiting cause for the nanoconfinement, either, and the chemical interaction between the polymers and the fillers also seems to play rather unimportant role. Therefore, considering this result with the critical R_g (~5 nm), which was previously measured in the SBR/(low-molecular-weight NBR) chloroform solution, the concave in between carbon black primary particles must be the location for the competitive confinement of the rubber molecules.

The successful control of silica distribution to both the SBR and NBR phases just by changing the type of the solvent strongly suggests that the R_g of the rubber molecules is more important to decide the filler location than the chemical interaction between filler and polymer. Moreover, the proposed concept for selective adsorption via nanoconfinement might be more generally applicable to many nanoparticles than just carbon black.

Acknowledgment. We gratefully acknowledge the partial financial support of Yokohama Rubber Co.

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