Morphology and Electrical Conductivity of PS/PMMA/SMMA Blends Filled with Carbon Black

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Abstract : An alternative strategy to reduce the percolation threshold of carbon black (CB) in polymer blends was investigated using random copolymer ternary blends of polystyrene (PS), poly(methyl methacrylate) (PMMA), and a styrene-methyl methacrylate random copolymer (SMMA). The target morphology was to selectively locate CB particles in the encapsulating layer of SMMA during melt mixing. The CB used in this study is BP-2000 from Cabot and has a strong selective affinity to PS. Even when the CB was premixed with SMMA, it moves to the PS phase during the melt mixing. However, we also observed the CB particles located at the interface between SMMA and PS phases. Through this study it is found that the interaction between polymers and CB particles is critical for selectively localizing CB particles in multi-component polymer blends. Although appropriate processing condition may retard the movement of CB particles to the polymer phase with affinity, it cannot prevent it completely and locate them to the SMMA phase, which is not thermodynamically favored. To locate CB particles in an encapsulating layer of ternary polymer blends, first of all, polymers forming it should have selective affinity to CB.

Introduction

The electrical conductivity of insulating polymers can be enhanced by dispersing conductive filler such as carbon black (CB) throughout the matrix. To make the polymers conductive the filler content exceeds a certain critical value, i.e., the percolation threshold (Φ_c). However, it is a problem to reach a suitable conductivity by the addition of an amount of CB small enough to preserve the mechanical properties of the polymers and to reduce as much as possible the cost of the final composite[1].

One of the effective methods to reduce the percolation threshold is to use polymer blend technology. For most cases, CB generally has a selective affinity to particular polymers. Therefore, it is possible to locate CB to a phase with affinity when it is mixed with two immiscible polymers[2-10]. In this approach, the polymers mixed with CB should have different affinity to CB and the phase in which CB is preferably located should form a matrix. We may further reduce the percolation threshold if polymer blends with co-continuous structure are prepared. The co-continuous structure can be controlled by the factors such as blend ratio and melt viscosity[11].

In this study we investigated another method to reduce the percolation threshold of CB in polymer blends using ternary polymer blends with encapsulating structure. The target morphology was to selectively locate the CB particles in the encapsulating layer located between

matrix and dispersed phase. As a model system we chose a random copolymer blend of polystyrene (PS), poly (methyl methacrylate) (PMMA) and a styrene-methyl methacrylate random copolymer (SMMA). In the blends SMMA has the strong tendency to encapsulate minor phase due to a thermodynamic reason[12]. The location of CB particles in the blends was characterized using a transmission electron microscopy (TEM) and how the morphology affects the electrical conductivity of the blends was investigated.

Experimental

Materials

PS was obtained from Dow Chem. and SMMA and PMMA were purchased from Polysciences, Inc. The details of the polymers are summarized in Table 1. Carbon black used in this study was BP-2000 from Cabot, which is known as a highly conductive grade. It has the primary particle size of 15 nm. The polymers, which were vacuum-dried at 60°C before mixing, were melt-mixed using a home made mini-molder, operating at 210°C for 10 min. The rotor speed was fixed at 150 rpm, which corresponds to a maximum shear rate of 12 s^{-1}[13]. The mixing conditions applied for all blends were the same irrespective of mixing recipe. All blend compositions were based on the weight basis. After mixing samples were quenched in ice water. To prepare the film of 1 mm thickness for measuring electrical conductivity, the blends were hot-pressed at 210°C. Annealing was done at 210°C for 30 min under N$_2$ atmosphere to investigate the effect of annealing on

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Table 1. Polymers used in this study

Polymer	Source	M. W. (g/mol)	$|\eta^*|$ (Pa · s)[b]
PS	Dow Chemicals	200,000	2,050
PMMA	Polysciences, Inc	100,000	1,230
SMMA[a]	Polysciences, Inc	270,000	3,550

[a]70 wt % styrene unit.
[b]Measured at a shear rate of 10 s^{-1} and 210°C.

morphology and electrical conductivity.

Characterization

The morphology, especially the distribution of carbon black particles, was observed using a JEOL 2000 FXII transmission electron microscopy (TEM), operated at 100 kV. Sections of about 80 nm thickness were microtomed at room temperature with a MT-200 Ultramicrotome of RMC, Inc. The sections were stained for 15 min with the vapor of 0.5% RuO_4 in water solution, if not notified. As phenylene unit in polymers is preferentially stained under the conditions used in this study, PS appears dark, SMMA gray, and PMMA white in bright field TEM[14].

The electrical resistivity of polymer composites with CB was measured using a four-probe technique. The details for measurement are well described in reference 15. An average of at least 3 measurements was used for discussion.

Results and Discussion

Morphology

From the experimental results published up to now, it is found that the affinity of CB to polymers is very dependent on the type of polymers and also on the grade of CB used. Therefore, it is important to investigate which polymer has a selective affinity to CB used in this study. Figure 1 shows TEM micrographs of 90/10 PMMA/CB and 50/50 PS/(90/10 PMMA/CB) composites. In Figure 1b, pre-mixed 90/10 PMMA/CB composite was mixed again with PS. As shown in Figure 1b, the CB particles were selectively located at the PS phase, indicating a selective affinity of the CB for PS. Since the content of styrene units in SMMA is 70 wt %, we assume the rank in the affinity to CB is PS > SMMA ≫ PMMA.
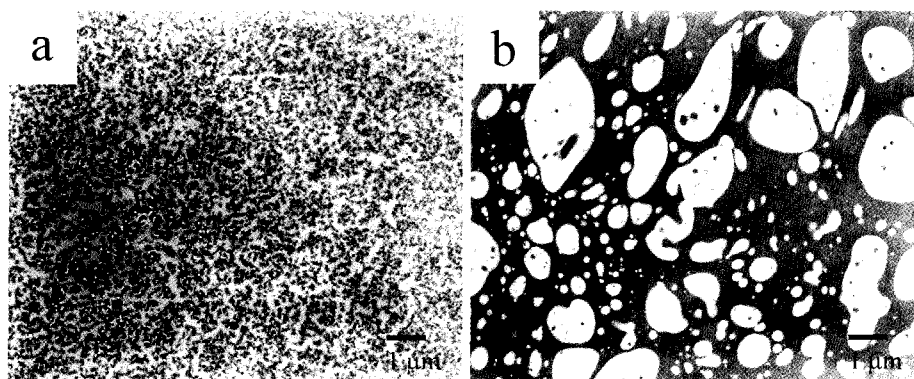

Figure 1. TEM micrographs of (a) 90/10 PMMA/CB and (b) 50/50 PS/(90 PMMA + 10 CB) composites. In Figure 1b premixed 90/10 PMMA/CB composite was mixed with PS.
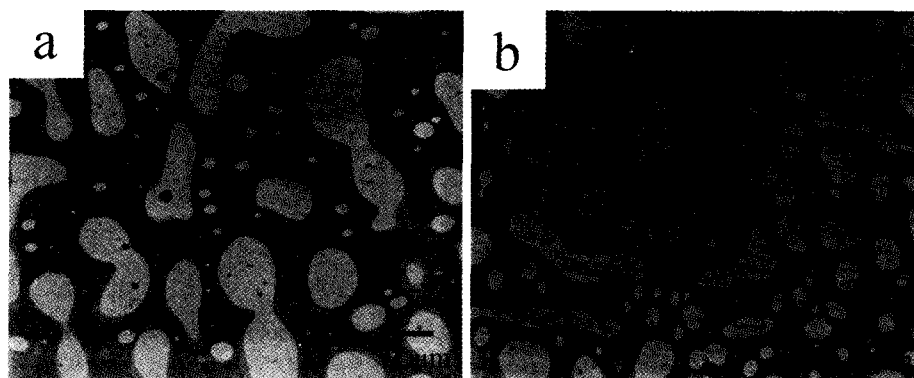

Figure 2. TEM micrographs of (a) 50/50/10 PS/PMMA/(80 SMMA+20 CB) and (b) 50/50/20 PS/PMMA/(80 SMMA+20 CB) composites. Before mixing with PS and PMMA, SMMA was premixed with 20% CB.

Table 2. Electrical resistivity of the polymer blends prepared in this study

Polymer blend	Electrical resistivity($\Omega \cdot$ cm)	Remarks
SMMA/CB		
95/5	Beyond limit	
90/10	88	
85/15	59	
80/20	7	
PS/PMMA/(80/20 SMMA/CB)		
50/50/10[a] (as-blended)	Beyond limit	Two-step mixing
50/50/10[a] (annealed[b])	250	
50/50/20[c] (as-blended)	2400	
50/50/20[c] (annealed[a])	130	
PS/PMMA/SMMA/CB		
50/50/8/1 (0.9% CB)	1710	One-step mixing
50/50/8/2 (1.8% CB)	760	

[a]The content of CB is 1.8 wt%.
[b]At 200°C for 30 min.
[c]The content of CB is 3.3 wt%.

Figure 2 shows the TEM micrographs of PS/PMMA/ SMMA ternary blends filled with CB. Before mixing, SMMA was premixed with CB of 20 wt %; the CB content is higher than the percolation threshold in SMMA matrix, as listed in Table 2. The results from Figure 2 may be summarized as follows:

a) Even though CB particles are added to SMMA phase and thus increase the melt viscosity of SMMA, the SMMA still forms an encapsulating layer, indicating that the CB does not affect the encapsulating structure of the PS/PMMA/SMMA blends with CB. It is noteworthy that the relative melt viscosity is critical for the morphology evolution of binary and ternary polymer blends, especially at the early stage of mixing[16,17].

b) During melt mixing the CB particles moves from premixed SMMA phase to PS phase having larger selective affinity to CB, even though the difference in selective affinity between PS and SMMA is expected to be small. This indicates that the surface characteristic of CB and thus its relative interaction with polymers are critical in determining where CB locates in the multiphase blend systems.

c) We can also observe the CB particles located at the interface between SMMA and PS phases during mixing. They are considered to be trapped during movement from SMMA phase to PS phase. The particles trapped may open us a possibility to selectively locate them at the interface, independently of the thermodynamic situation, if we carefully choose the mixing conditions such as mixing time and temperature and shear rate. Recently, Jerome et al. studied the effect of mixing condition on the selective localization of CB particles in polymer blends and reported that it is possible to locate them at interface
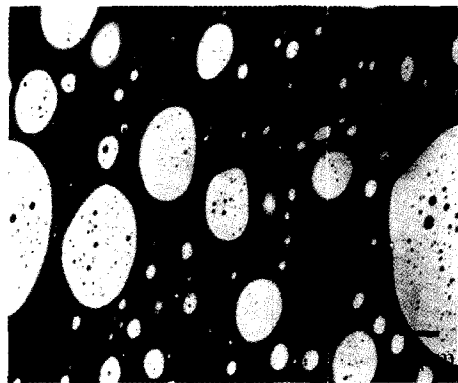
Figure 3. TEM micrograph of 50/50/10 PS/PMMA/(80 SMMA + 20 CB) composite, annealed at 210°C for 30 min.

under the very narrow mixing condition[8,10]. However, they also pointed out the surface characteristic of CB particles is most important for the purpose, as expected from our result.

Even though encapsulating layer of SMMA contributes to reduce the interfacial tension between matrix and dispersed phase and thus to decrease the size of dispersed phase, it cannot prevent static coalescence upon annealing[12]. However, solid particles accumulated at the interface between matrix and encapsulating layer might change the coarsening behavior of random copolymer ternary blends. Figure 3 shows the annealing effect on the morphology of 50/50/10 PS/PMMA/(80 SMMA+20 CB) blends. Compared with the micrograph of Figure 2a, the shape of the dispersed phases is changed from irregular one to ellipsoid during annealing. The Waddel diameter of dispersed domains do not increased after annealing, indicating that the growth of the size of dispersed phase is significantly depressed compared with PS/PMMA/SMMA blends unfilled with CB[12]. It might be understood in terms of the increase in the melt viscosity of matrix phase and the hardening of interface by solid CB particles. The hindered coalescence by CB particles located at interface has reported for PE/PS/CB composite[8].

Figure 4 shows the TEM micrographs of 50/50/8/2 PS/ PMMA/SMMA/CB composites, prepared using one-step mixing. As shown in Figure 4a, when the microtomed specimen is stained with the vapor of RuO_4, it is difficult to differentiate where CB particles locate. Figure 4b is the TEM micrograph of unstained specimen. Since the PMMA phase appears lighter than the PS in the micrograph due to electron beam thinning of the PMMA[18], we can differentiate which phase corresponds to which polymer. As shown in Figure 4b the CB particles are selectively located at the PS phase. Contrarily to the micrograph of the sample prepared by two-step mixing (Figure 2a), we can not see any CB particles at the interface. This result indicates that mixing sequence is important in order to
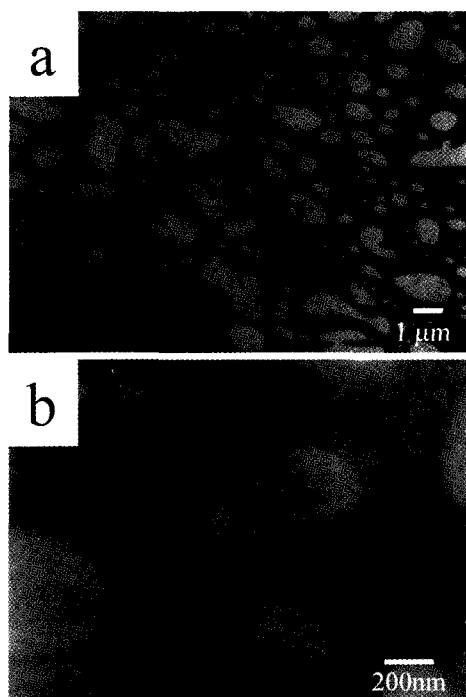
Figure 4. TEM micrographs of 50/50/8/2 PS/PMMA/SMMA/ CB composites, prepared using a one-step mixing. Figure 4b is the TEM micrograph of unstained specimen.

selectively locate the CB particles at interface; two-step mixing is desirable for the purpose.

Electrical resistivity

Table 2 lists the electrical resistivity of PS/PMMA/ SMMA ternary blends filled with CB. The data is very limited and thus only feasible for qualitative discussion. The results shown in Table 2 are summarized as follows:

a) As expected, the electrical resistivity of SMMA significantly decreases by several decades with adding CB. At 20 wt % CB loading the value reached to 7.0 $\Omega \cdot$ cm, indicating that the composite is highly conductive and contains the CB beyond the percolation threshold. This is consistent with the published data for other styrenic polymers, which have the percolation threshold in the range of 10-20 wt %.

b) The electrical resistivity of 50/50/10 PS/PMMA/(80/ 20 SMMA/CB) composite, which has the 1.8 wt % CB, is beyond the measurement limit of our instrument, whereas that of 50/50/20 composite with 3.3 wt % CB have the electrical conductivity of $2.4 \times 10^3 \ \Omega \cdot$ cm. The value is between those of 95/5 and 90/10 SMMA/CB composites.

c) The blend prepared by one-step mixing has lower electrical resistivity rather than that prepared by two-step mixing. This is interesting because two-step mixing is effective in selectively localize CB particles at interface. Only when the amount of CB particles, which are located

at the interface between SMMA and PS, is higher than the percolation threshold and also the final morphology is co-continuous, we can expect significantly reduced percolation threshold. As shown in Figure 2a, the morphology of the composite prepared by two-step mixing is not co-continuous. It is possible to prepare composites with co-continuous structure by varying the blend composition under the same mixing conditions.

d) Annealing at melt significantly decreases the electrical resistivity of polymer composites investigated in this study. During annealing the shape of dispersed phase is changed to ellipsoid, even though the size is not increased. The morphology change will help to form a network of CB particles in polymer matrix and thus to decrease electrical resistivity.

Summarizing the results mentioned above, the encapsulating layer of SMMA does not play an important role except for decreasing the content of matrix phase and thus reducing relative fraction of CB in ternary polymer blends. However, it should be noted that the bare interface of immiscible polymer blends is very weak and thus resultant blends will have poor mechanical properties. On the other hand, the encapsulating layer of SMMA increases the interfacial adhesion between PS and PMMA[19].

Conclusions

The experimental results reported in this study emphasize that the surface characteristics of CB plays a critical role in selectively localizing them to a preferred position, an interface between matrix and dispersed phase in binary polymer blends or an encapsulating later in ternary polymer blends. Even though SMMA has 70 wt % styrene units and thus has similar solubility parameter to PS, the migration of CB particles from SMMA phase to PS phase can be not prevented completely, indicating that the thermodynamic factor is foremost important in selectively localizing the CB particles. Therefore, in order to locate CB particles in an encapsulating layer of ternary polymer blends and thus reduce the percolation threshold, the encapsulating layer should have a selective affinity to CB. This will be possible if we modify the surface characteristic of CB for the purpose.

Acknowledgement

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