Effect of Styrene–Acrylonitrile on the Electrical Resistivity of Polycarbonate/Multiwalled Carbon Nanotube Composites

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ABSTRACT: Multiwalled carbon nanotube (MWCNT)-filled polycarbonate (PC)/styrene–acrylonitrile (SAN) blends with a wide range of blend compositions were prepared by melt mixing in a rotational rheometer, and the effect of SAN on the electrical properties of the PC/MWCNT composites was studied. The structure/electrical property relationship was investigated and explained by a combination of MWCNT localization and blend morphology. Transmission electron micrographs showed selective localization of MWCNTs in the PC phase, regardless of the blend morphology. When the SAN concentration was 10–40 wt %, which corresponded to sea-island (10–30 wt %) and cocontinuous (40 wt %) blend morphologies (PC was continuous in both structures), the electrical resistivity decreased with increases in the SAN content. The concept of an effective volume concentration of MWCNTs was used to explain this effect. When the SAN concentration was 70 wt % or higher, the electrical resistivity was very high because MWCNTs were confined in the isolated PC particles. In addition, SAN was replaced by other polymers [polystyrene, methyl methacrylate/styrene, and poly(methyl methacrylate)]; these yielded similar blend morphologies and MWCNT localization and showed the generality of the concept of effective concentration in explaining a decrease in the electrical resistivity upon the addition of a second polymer. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 3224–3232, 2011

Key words: blends; effective concentration; multiwalled carbon nanotubes; nanocomposites; polycarbonates

INTRODUCTION

Because of their excellent mechanical, thermal, optical, and electrical properties, carbon nanotubes (CNTs) have been investigated in many research fields since the landmark work of Iijima[1] was published in 1991. In particular, a number of studies have been devoted to conductive polymer composites with CNTs as the conductive filler.[2–15] Compared to traditional carbonaceous conductive fillers such as carbon black (CB), graphite, and carbon fibers, CNTs are advantageous because of their high aspect ratio, which leads to a significantly lower percolation threshold.

Electrical modification of polymer/CNT composites[4,6,7,10–15] is currently of interest because of the high cost of CNTs. Adding an immiscible polymer to the preparation of CNT-filled polymer blends has been proven to be an effective way of increasing the electrical conductivity of single polymer/CNT composites.[4,6,7,10,12] For example, poly(vinylidene fluoride) can considerably improve the electrical properties of poly(ethylene terephthalate)/multiwalled carbon nanotube (MWCNT) composites,[7] and acrylonitrile–butadiene–styrene (ABS) can reduce the electrical percolation of polyamide 6/MWCNT composites by half.[6] The success of this approach relies on selective localization of CNTs in one polymer phase of a cocontinuous structure. The concept of double percolation, originally proposed by Sumita et al.[16] for CB-filled polymer blends, has frequently been used to explain the decrease in the electrical percolation threshold. A literature survey has shown that most work on CNT-filled polymer blends involves a cocontinuous phase morphology, and very limited work[11] has been reported on sea-island structures. Wu et al.[11] reported that the conductivity of a carboxylic MWCNT-filled poly(ε-caprolactone) (PCL)/polylactide (PLA) (70/30) blend

with a sea-island structure was far higher than the conductivity of the corresponding binary PCL/MWCNT and PLA/MWCNT composites because of the selective localization of carboxylic MWCNTs in the PCL matrix and at the interface. Because many commercial polymer blends have a sea-island morphology, it is important to explore CNT-filled conductive polymer blends with a sea-island structure that have improved electrical conductivity in comparison with the corresponding binary polymer/CNT composites.

Polycarbonate (PC)/styrene–acrylonitrile (SAN) blends are well-investigated polymer blends.[17–19] The purpose of investigations is usually to provide a model study for further investigating PC/ABS blends, some of the most important polymer blends in industry, because SAN is the matrix of ABS. Göldel et al.[12] investigated MWCNT-filled PC/SAN blends with a cocontinuous structure and showed selective localization of MWCNTs in the PC phase regardless of the mixing sequence, even when MWCNTs were predispersed in SAN before blending. Significantly lowered electrical resistivity was found for PC/SAN/MWCNT composites versus the corresponding PC/MWCNT and SAN/MWCNT composites with the same MWCNT content. In this work, MWCNT-filled PC/SAN blends over the whole composition range were investigated with an emphasis on a sea-island structure with PC as the continuous phase. The goals were the determination of the structure/electrical property relationship and an understanding of the effect of SAN on the electrical resistivity of PC/SAN composites. Other MWCNT-filled PC-based polymer blends producing a sea-island structure similar to that of PC/SAN were also investigated to show the general trend of improved electrical conductivity with the addition of a second polymer.

EXPERIMENTAL

Materials

The MWCNTs used in this work were supplied by Tsinghua University (Beijing, China). The purity was greater than 95 wt %. The diameter of the MWCNTs ranged from 3 to 20 nm with a statistically average diameter of 10 nm, and the length was several micrometers. PC (FN2500A) with a density of 1.20 g/cm^3 and a melt flow index of 8.0 g/10 min was kindly provided by Idemitsu (Tokyo, Japan). SAN with a density of 1.06 g/cm^3, a melt flow index of 44.2 g/10 min, and an acrylonitrile concentration of 24 wt % and poly(methyl methacrylate) [PMMA; weight-average molecular weight (M_w) = 1.1 × 10^5 g/mol, weight-average molecular weight/number-average molecular weight (M_w/M_n) = 1.6] were provided by Mitsubishi Corp. (Tokyo, Japan). Polystyrene (PS;

M_w = 2.8 × 10^5 g/mol, M_w/M_n = 5.0) was provided by Formosa Plastic Group (Taipei, China). Methyl methacrylate/styrene (MS) with a methyl methacrylate to styrene mass ratio of 64/36 was purchased from Lanzhou Petrochemical Co (Lanzhou, China).

Sample preparation

PC, SAN (or PS, MS, or PMMA), and MWCNTs were prepared by melt mixing in a rotational rheometer (RH-200A rheometer, Harbin Hapro Electrical Technology Co., Ltd., Harbin, China) to obtain PC/SAN/MWCNT (or PC/PS/MWCNT, PC/MS/MWCNT, or PC/PMMA/MWCNT) composites. The processing temperature was 250°C, the rotational rate was 60 rpm, and the mixing time was 10 min. PC and SAN (or PS, MS, or PMMA) were dried in vacuum ovens at 120°C for 8 h and at 100°C for 4 h, respectively, before use. All percentages are weight percentages unless otherwise specified.

Measurement of the electrical resistivity

Details for the measurement of the volume resistivity can be found in a previous article.[14] Briefly, samples with higher electrical resistivity (>10^8 Ω cm) were measured by the ZC-36 resistivity test (Shanghai Cany Precision Instrument, Shanghai, China). For more conductive samples (<10^8 Ω cm), the electrical resistivity was measured with a four-point test fixture. Data from four measurements were averaged.

Characterization

The surfaces of the samples were cryofractured in liquid nitrogen and then etched with a 10 wt % NaOH aqueous solution at room temperature for 4 h to remove the PC phase. After they were rinsed with deionized water and dried, the etched surfaces were observed by field emission scanning electron microscopy (FESEM) with a JEOL model (Tokyo, Japan) JSM-7401 apparatus with an operating voltage of 1.0 kV to investigate the phase morphology of the samples.

Transmission electron microscopy (TEM) was carried out on a Hitachi H-800 (Tokyo, Japan) electron microscope at 200 kV to examine the localization of MWCNTs. Ultrathin sections were made with a glass knife on an ultratome (EM UC6, Leica, Solms, Germany).

RESULTS AND DISCUSSION

Blend morphology of the PC/SAN/MWCNT composites

To investigate the structure/electrical property relationship, the blend morphology of 1 wt % MWNCT-filled PC/SAN blends with different amounts of
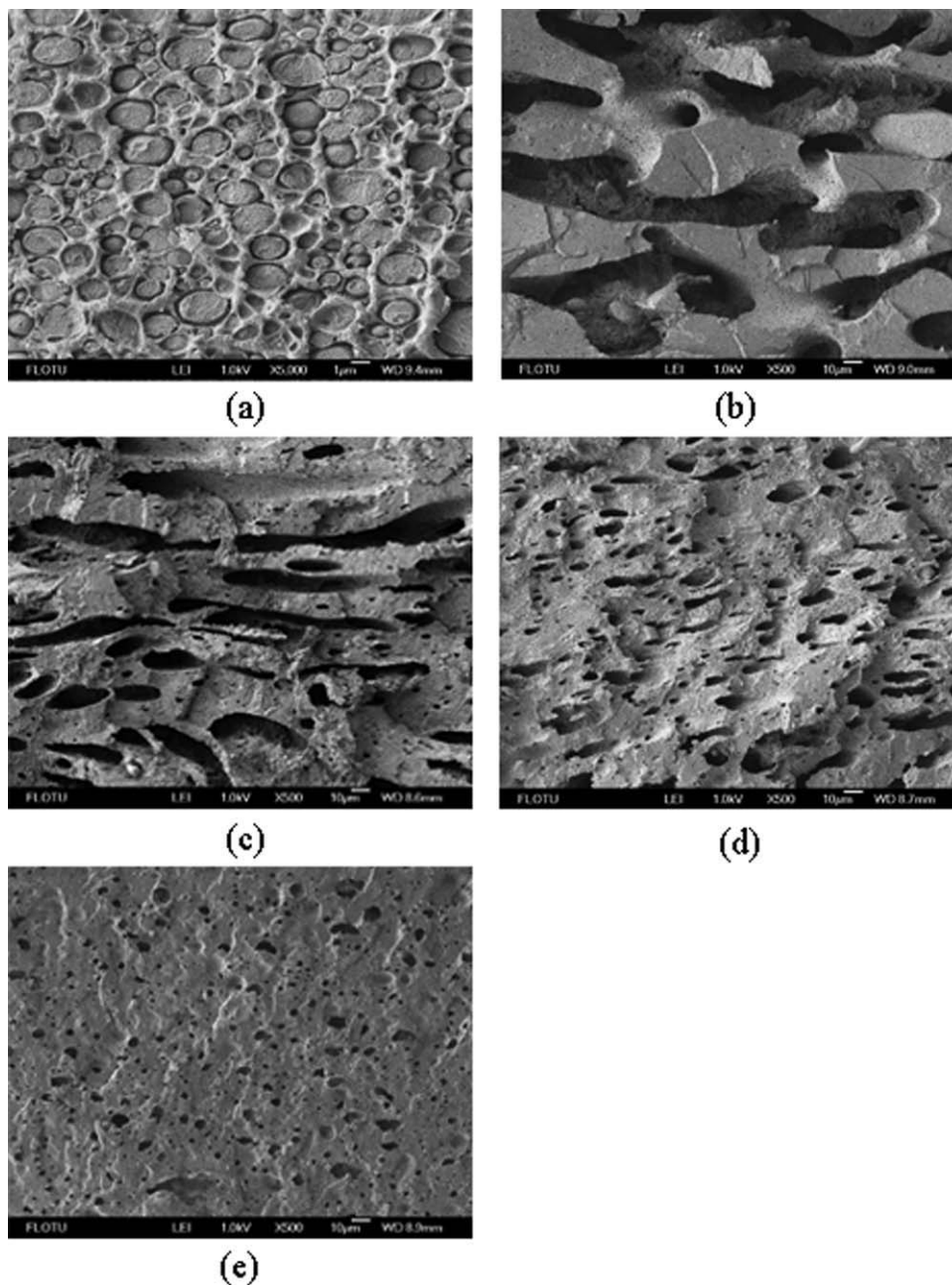
Figure 1 FESEM micrographs showing the morphology of PC/SAN/MWCNT composites with increases in the SAN content: (a) 30, (b) 40, (c) 50, (d) 60, and (e) 70 wt % SAN. The fractured surfaces of samples b–e were exposed to an aqueous solution of 10 wt % NaOH at room temperature for 4 h to remove the PC phase, but the surface of sample a was not. The MWCNT concentration was fixed at 1 wt %.

SAN (from 30 to 70 wt %) was investigated by FESEM, and the micrographs of the cryofractured surfaces are shown in Figure 1. The PC phase was removed from the samples shown in Figure 1(b–e) via etching with a 10 wt % NaOH aqueous solution for better observation, whereas it was not removed from the sample shown in Figure 1(a) because the sample would have been destroyed if the continuous phase of the sea-island structure had been removed. Clearly, when the SAN concentration was 30 wt % [Fig. 1(a)], a typical sea-island morphology was

formed with PC as the continuous phase and SAN as the dispersed phase. The particle size was 0.5–3 μm. When the SAN concentration was increased to 40 wt % [Fig. 1(b)], the sample had a cocontinuous phase structure. With 50 and 60 wt % SAN [Fig. 1(c,d)], mixed structures were observed. Although it was mainly constructed with a cocontinuous structure, an inverse sea-island structure with PC as the dispersed phase and SAN as the continuous phase was also observed; this was indicated by small, black holes with a diameter of approximately 1 μm
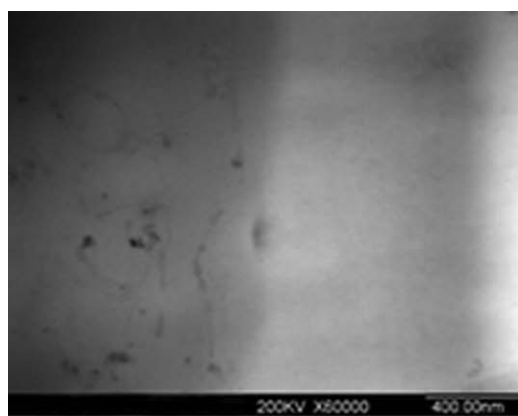
(a)
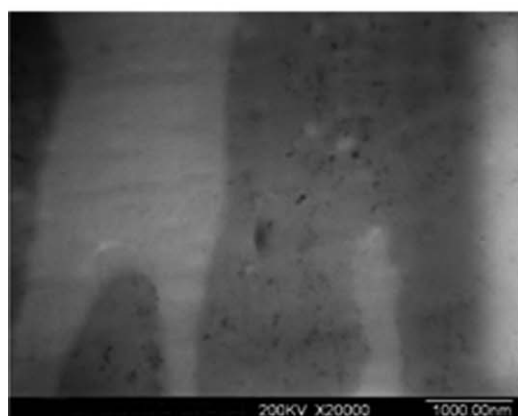
(b)
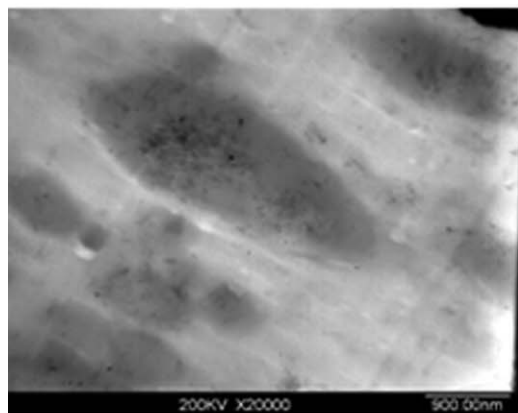
(c)

Figure 2 TEM pictures showing the localization of MWCNTs in the PC phase with the addition of (a) 30, (b) 60, or (c) 70 wt % SAN. The white phase corresponds to SAN, whereas the gray phase represents PC.

in the white SAN matrix. When the SAN concentration was as high as 70 wt % [Fig. 1(e)], the blend morphology changed into the inverse sea-island structure, and PC was the dispersed phase. We can speculate that the same type of phase morphology

would have been observed if the SAN concentration had been higher than 70 wt % (e.g., 80 or 90 wt %).

Localization of MWCNTs in the PC/SAN/MWCNT composites

The localization of MWCNTs was investigated with TEM. Figure 2 shows micrographs of 1 wt % MWCNT-filled PC/SAN blends containing 30, 60, or 70 wt % SAN; these correspond to sea-island, cocontinuous, and inverse sea-island structures, respectively. Two types of regions (white and gray) are clearly shown. The white regions are the SAN phase, and the gray regions are the PC phase.[12] MWCNTs are seen as black lines or speckles. Black MWCNTs were not distributed homogeneously within the two polymers but were selectively localized in the gray PC phase, regardless of the blend morphology.

In general, the localization of a conductive filler depends on many factors, such as the affinity of the conductive filler to each polymer, the interfacial tension, the mixing sequence, the mixing time, and the viscosity of the two polymers, and it can be predicted thermodynamically by the wetting coefficient.[16] In the work of Göldel et al.,[12] the wetting coefficient for PC/SAN/MWCNT was calculated and was used to predict the localization of MWCNTs in the PC phase. Our observation was in agreement with the thermodynamic prediction.

Electrical resistivity of the PC/SAN/MWCNT composites

Figure 3 shows the effect of different amounts of SAN (0–100 wt %) on the electrical resistivity of PC/MWCNT composites with two MWCNT loadings (0.5 and 1 wt %). When the MWCNT loading was 0.5 wt %, the PC/MWCNT composite was an insulant with a very high electrical resistivity (log
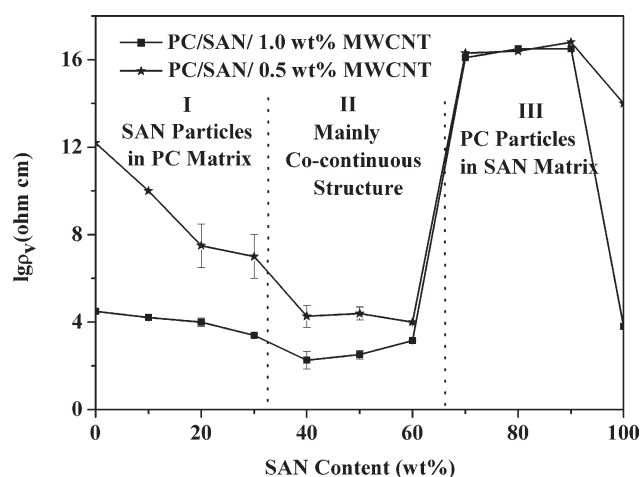

Figure 3 Electrical resistivity of the PC/MWCNT composites as a function of the SAN content.
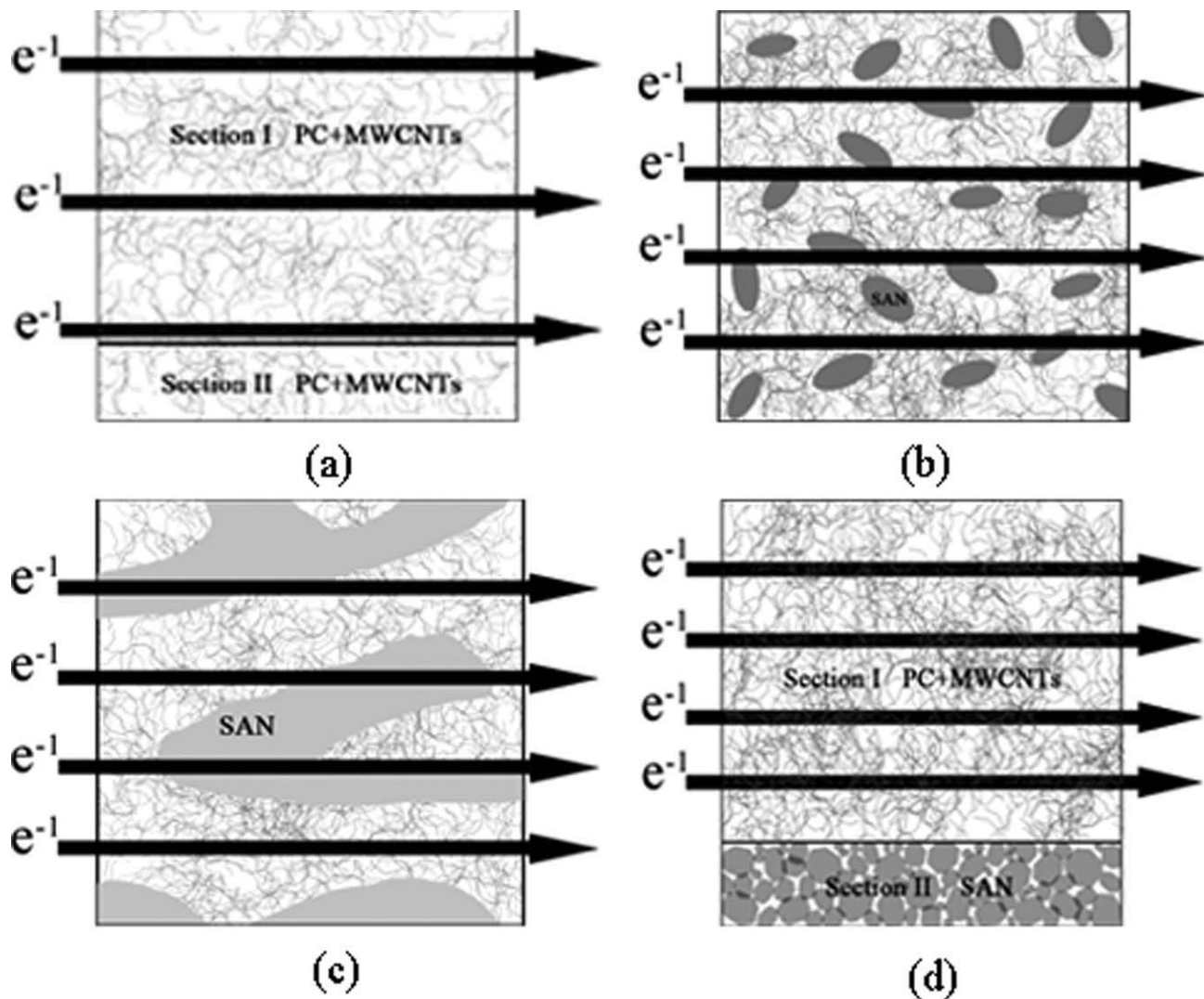
Figure 4 Illustration of the influence of SAN on the resistivity of the PC/MWCNT composites: (a) a PC/MWCNT composite without SAN, (b) a PC/MWCNT/SAN composite with a sea-island blend morphology, (c) a PC/MWCNT/SAN composite with a cocontinuous blend morphology, and (d) a PC/MWCNT/SAN composite with PC as the continuous phase (imaginary state).

volume electrical resistivity (ρ_v) = 12.4). The electrical resistivity decreased sharply with the addition of SAN up to 40 wt % (expressed as the mass ratio of SAN to the whole composite). A decrease of 8 orders of magnitude was observed, and the composite containing 40 wt % SAN was conductive. When the amount of SAN was increased further to 50 and 60 wt %, the electrical resistivity changed only slightly. However, the electrical resistivity increased suddenly by 12 orders of magnitude when the SAN concentration increased to 70 wt %, and the composite became an insulant again. With further increases in the SAN content (80 and 90 wt %), the electrical resistivity remained high. When the MWCNT loading was 1 wt %, the PC/MWCNT composite was conductive with a log ρ_v value of 4.5. The electrical resistivity decreased gradually and mildly with an increase in the SAN concentration up to 40 wt %, at which a

decrease of 2 orders of magnitude was observed. It then increased slightly with further increases in the SAN concentration (50 and 60 wt %). When the SAN concentration was 70–90 wt %, the electrical resistivity was very high, and the materials were insulants.

Comparing the two curves of different MWCNT loadings, we have found that they have some common features and can be divided into three regions (Fig. 3), although the electrical resistivity values at the starting points are very different. In region I, the electrical resistivity decreases with an increase in the SAN concentration; in region II, the electrical resistivity changes slightly; and in region III, the electrical resistivity is very high. This can be explained by the blend morphology in combination with the localization of MWCNTs. In region III, the blends have a sea-island morphology with PC as the dispersed phase. MWCNTs are confined in the PC particles,
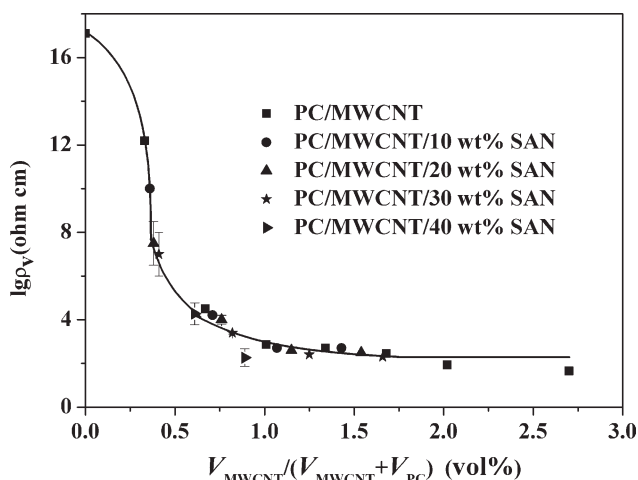
Figure 5 Electrical resistivity/MWCNT concentration curve for PC/MWCNT composites and electrical resistivity/effective volume concentration data points for PC/SAN/MWCNT composites.

and the conductive path of MWCNTs cannot be formed. As a result, the electrical resistivity is very high. In region I, PC is the continuous phase of the sea-island structure. The mechanism for the decrease in electrical resistivity upon the addition of SAN is illustrated in Figure 4. Figure 4(a) represents a PC/MWCNT composite and can be divided into two sections: I and II. After the addition of SAN [Fig. 4(b)], an imaginary state can be drawn, as shown in Figure 4(d), in which section II is occupied by SAN; the volume fraction of MWCNTs in section I increases because all the MWCNTs are localized in section I. Therefore, MWCNTs connect with one another with a higher probability, and this results in a decrease in the electrical resistivity. At the beginning of region II, the blend (40 wt % SAN) has a cocontinuous structure. It can be seen as the extreme case of region I. The lowest electrical resistivity is found as a result of a maximized MWCNT concentration in section I [Fig. 4(c)]. As the SAN concentration increases further to 50 and 60 wt %, some MWCNTs are confined

in the PC particles because of the presence of the inverse sea-island structure; the electrical resistivity does not decrease further.

Effective volume concentration of MWCNTs

In our previous work[13] dealing with electrically inert particle such as calcium carbonate ($CaCO_3$)-filled polymer/MWCNT composites, the concept of the effective volume concentration was used to quantitatively evaluate the effect of $CaCO_3$ on the electrical resistivity of the composites. Here, the same concept is adopted to show the effect of SAN (10–40 wt %) on the electrical resistivity of PC/MWCNT composites because of the similarity of the two cases: MWCNTs do not enter $CaCO_3$ or SAN. Thus, the effective volume concentration is defined as the volume of MWCNTs (V_{MWCNTs}) to the sum of V_{MWCNTs} and the volume of PC (V_{PC}) as follows:

$$V_{MWCNTs}/(V_{MWCNTs} + V_{PC}) \times 100\% \qquad (1)$$

The effective volume concentration of MWCNTs according to the data presented in Figure 3 at SAN concentrations of 10–40 wt % were calculated, and the electrical resistivity/effective volume concentration data sets are shown in Figure 5; the solid line is the electrical resistivity/MWCNT concentration curve for PC/MWCNT composites without SAN. The data points for PC/SAN/MWCNT composites are all around the curve and prove that the concept of the effective volume concentration can be used to explain the decrease in the electrical resistivity with the addition of SAN up to 40 wt %, at which PC is continuous in either a sea-island or cocontinuous structure. Deviation is inevitable because the conditions for using the concept of the effective volume concentration are ideal. In practice, a small amount of MWCNTs may reach the interface or even the SAN phase, and the dispersion state of MWCNTs in the PC phase may well be different from that in PC/MWCNT composites. It is known that different

TABLE I
γ Values for MWCNTs, PC, PS, MS, and PMMA

Polymer	γ at 20°C (mN/m)	$-d\gamma/dT$ (mN/mK)	χ^P	γ at 250°C (mN/m)	γ^d at 250°C (mN/m)	γ^P at 250°C (mN/m)
MWCNTs[a]	45.3	—	0.59	45.3	18.4	26.9
PC[b]	42.9	0.06	0.246	29.1	21.94	7.16
PS[b]	40.7	0.072	0.168	24.14	20.08	4.06
MS[c]	40.5	0.074	0.24	23.57	17.90	5.67
PMMA[b]	41.1	0.076	0.281	23.62	16.98	6.64

γ = surface tension, and $\gamma = \gamma^d + \gamma^P$; χ^P = polarity, and $\chi^P = \gamma^P/\gamma$; T = temperature; d = dispersion component; P = polar component.
[a] The data were taken from Nuriel et al.[24]
[b] The data were taken from Wu.[23]
[c] The data were taken from Baudouin et al.[22]

TABLE II
Wetting Coefficients of the Composites and Localization of the MWCNTs in the Composites According to Predictions by Sumita's Model and Observations by TEM

Composite	Wetting coefficient	Sumita's model	TEM
PC/PS/MWCNT	8.67	PC	PC
PC/MS/MWCNT	3.62	PC	PC
PC/PMMA/MWCNT	1.19	PC	PC

dispersion states of MWCNTs result in different electrical resistivity values.[13,20,21] The data in Figure 3 at SAN concentrations of 50 and 60 wt % are not

included in Figure 5 because the electrical resistivity did not decrease further on account of the presence of an inverse sea-island structure with PC as the dispersed phase, although the effective volume concentration of MWCNTs increased.

In fact, Sumita et al.[16] showed the validity of the effective volume concentration in their work on CB-filled high-density polyethylene/polypropylene blends in which CB was exclusively localized in the high-density polyethylene phase. However, their work was limited to a cocontinuous blend morphology. The electrical conductivity did not change at a polypropylene concentration of 20 or
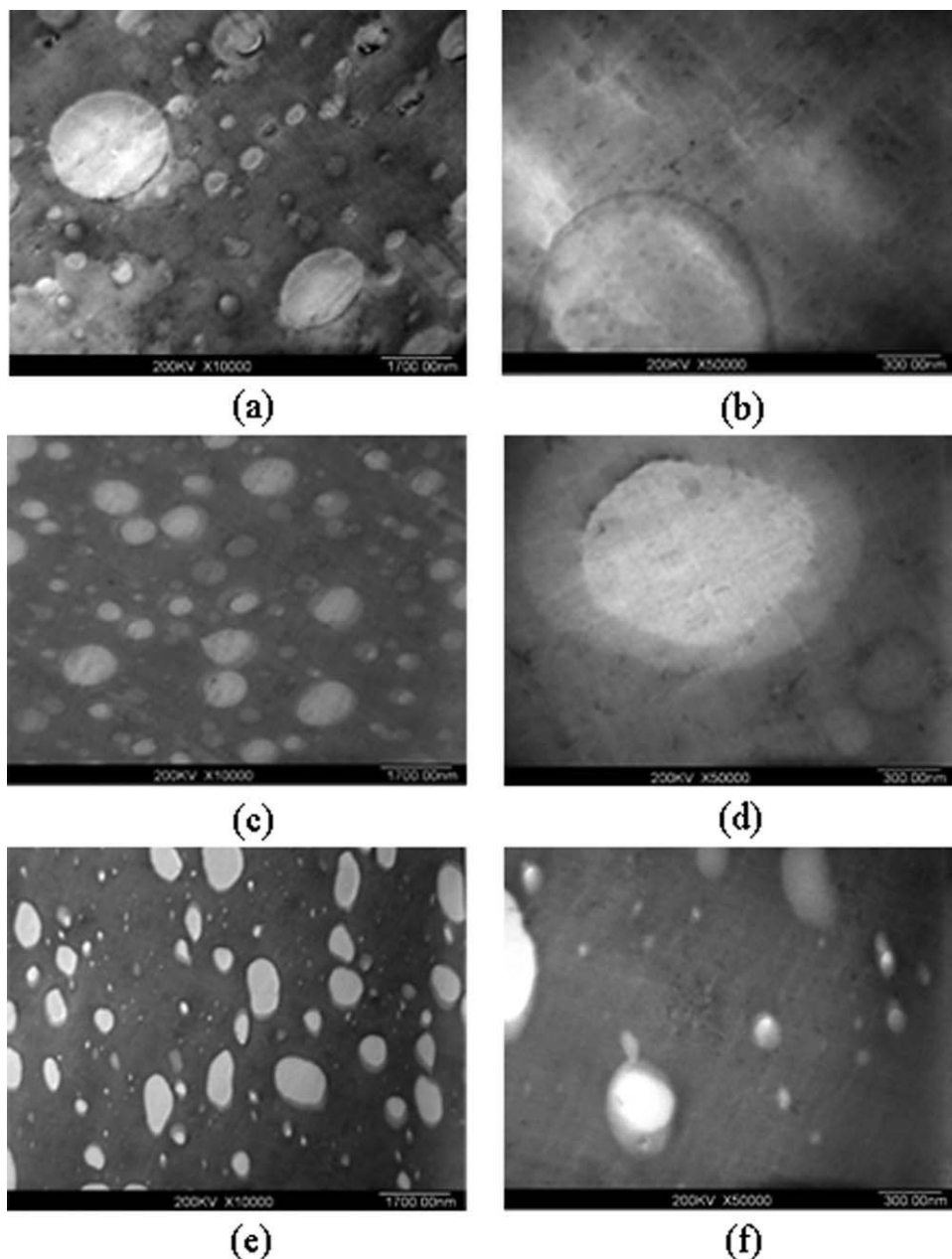

Figure 6 TEM micrographs of PC/polymer/MWCNT composites: (a,b) PC/PS/MWCNT (79/20/1), (c,d) PC/MS/MWCNT (79/20/1), and (e,f) PC/PMMA/MWCNT (79/20/1).
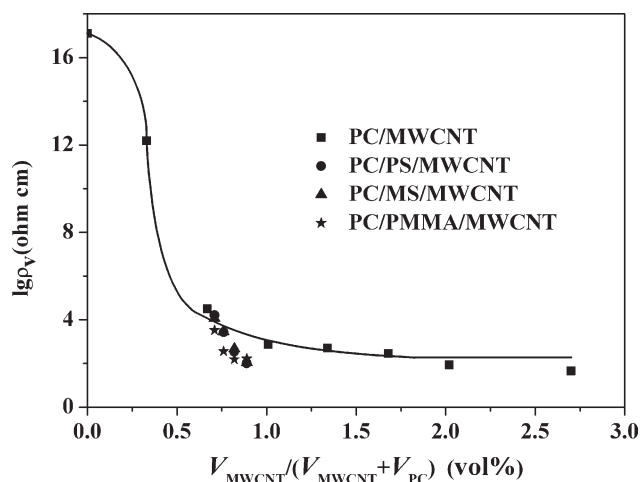
Figure 7 Electrical resistivity/MWCNT concentration curve for PC/MWCNT composites and electrical resistivity/effective volume concentration data points for PC/PS/MWCNT, PC/MS/MWCNT, and PC/PMMA/MWCNT composites.

even 40 wt %, probably because of the high percolation threshold of CB, which resulted in weak sensitivity of the conductivity to changes in the effective volume concentration of CB.

Other PC-based polymer blends/MWCNT composites

To further verify the concept of the effective volume concentration, SAN was replaced by PS, MS, and PMMA to obtain PC/PS/MWCNT, PC/MS/MWCNT, and PC/PMMA/MWCNT composites with a sea-island phase morphology, and the localization of MWCNTs and the electrical resistivity values of the composites were examined.

Sumita's model[16] was used to predict the distribution of MWCNTs in the aforementioned composites. The surface tensions of the polymers are listed in Table I. The surface tension of MS (γ_{MS}) was calculated with an arithmetic mean value adapted to random copolymers:[22]

$$\gamma_{MS} = \chi_{PMMA}\gamma_{PMMA} + \chi_{PS}\gamma_{PS} \qquad (2)$$

where χ_{PMMA} and χ_{PS} are the molar fractions and γ_{PMMA} and γ_{PS} are the surface tensions of PMMA and PS,[23] respectively.

The wetting coefficients of the composites are listed in Table II and predict that MWCNTs in the composites will localize in the PC phase in all three cases.

Figure 6 shows TEM photographs of the three kinds of PC-based composites; the PC phase was stained with RuO$_4$ and appears as a dark region, whereas the white particles correspond to PS, MS,

and PMMA. For the PS and MS system, the white particles appear to be a little black, and this may be due to the long staining time [Fig. 6(a,c)]; it can still be determined that MWCNTs selectively localized in the PC phase, whereas the PS or MS phase was free of MWCNTs [Fig. 6(b,d)]. For the PC/PMMA/MWCNT composite, the PMMA phase was bright and free of MWCNTs, and MWCNTs were observed exclusively in the PC phase [Fig. 6(e,f)]. In all three cases, the localization of MWCNTs was in agreement with the prediction from Sumita's model.

The resistivity values of the PC/PS/MWCNT, PC/MS/MWCNT, and PC/PMMA/MWCNT composites containing 1 wt % MWCNT and different amounts of PS (or MS or PMMA) ranging from 10 to 40 wt % are plotted as a function of the effective volume concentrations of MWCNTs in Figure 7; the PC/MWCNT curve is also shown for comparison. Some of the data points are around the curve, whereas others show relatively large deviations. As pointed out earlier, deviation is inevitable because the conditions for using the concept of the effective volume concentration cannot always be perfectly met. Anyway, the electrical resistivity showed a decreasing tendency with the addition of the second polymer increasing, and this was in agreement with the prediction using the concept of the effective volume concentration.

CONCLUSIONS

The incorporation of SAN up to a concentration of 40 wt % can reduce the electrical resistivity of PC/MWCNT composites. The more SAN is added, the more obvious the effect is. This phenomenon can be explained by the increase in the effective volume concentration of MWCNTs resulting from selective localization of MWCNTs in the PC phase. The concept of the effective volume concentration is valid for both sea-island and cocontinuous phase morphologies in which PC is continuous. Other polymers such as PS can be used instead of SAN to produce similar electrical resistivity as long as MWCNTs are exclusively localized in the PC phase. This work shows that the method of using an immiscible polymer to modify the electrical conductivity of polymer/CNT composites can be generalized to a sea-island blend morphology instead of being limited to a cocontinuous structure.

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