Synthesis of Polythiophene-*graft*-PMMA and Its Role as Compatibilizer for Poly(styrene-*co*-acrylonitrile)/MWCNT Nanocomposites

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ABSTRACT: A new compatibilizer, polythiophene-*graft*-poly(methyl methacrylate) (PMMA), for poly(styrene-*co*-acrylonitrile) (SAN)/multiwalled carbon nanotube (MWCNT) composite is synthesized. Fluorescence emission spectra and Raman spectra indicate that the polythiophene part of the compatibilizer strongly interacts with the surface of MWCNT, while differential scanning calorimeter (DSC) thermograms show that the PMMA graft of the compatibilizer is miscible with the SAN matrix. The use of new compatibilizer yields well-dispersed SAN/MWCNT nanocomposites with enhanced mechanical properties, whereas the simple mixture of SAN/MWCNT prepared without the addition of the compatibilizer shows an aggregation of MWCNT in SAN matrix. Particularly, SAN/MWCNT nanocomposites in the presence of the compatibilizer show dramatically improved mechanical properties even with the addition of a very small amount (0.01 wt %) of MWCNT.

Introduction

Carbon nanotubes (CNTs) have attracted enormous interest from both academia and industry, since they exhibit remarkable mechanical,[1−5] electrical,[6−9] and thermal properties.[10,11] In particular, exceptional mechanical properties of CNTs make them an ideal reinforcing material for polymer nanocomposites.[12−14] However, to fully realize the potential of CNTs as a reinforcing agent, two main issues have to be resolved: homogeneous dispersion and/or exfoliation of CNTs in a matrix polymer and good interfacial interaction between CNTs and a matrix polymer.[15−22] Generally, it is very difficult to homogeneously disperse CNTs in a matrix polymer due to their strong van der Waals attraction leading CNTs to form aggregated bundles in a matrix polymer. Moreover, as-produced CNTs are chemically inert because of the absence of functional groups on their surface, which limits efficient load transfer across the polymer−CNTs interface. Therefore, a considerable number of studies on polymer−CNT nanocomposites have focused on enhancing the compatibility between CNTs and a matrix polymer to achieve homogeneous dispersion of CNTs in a matrix polymer and efficient load transfer across the polymer−CNTs interface.

One way to enhance the compatibility between CNTs and a matrix polymer is to directly graft polymer chains onto the surface of CNTs.[18,19,21,23−28] Although this approach effectively enhances the compatibility between CNTs and a matrix polymer, it inevitably requires introduction of functional groups on the surface of CNTs through the covalent functionalization of CNTs. Most of covalent functionalization of CNTs is achieved by complicated chemical reaction processes. Furthermore, it usually destroys the π-electron system of CNTs, which results in detrimental effect on improvement in electrical and mechanical properties of the resultant polymer−CNT nanocomposites. Recently, several research groups have attempted to enhance the compatibility between CNTs and a matrix polymer via noncovalent functionalization.[15,17,22,29−32] These studies are motivated by the fact that some molecules including surfactants,[33−35] polymers,[36,37] and aromatic compounds[38−43] can be adsorbed onto the surface of CNTs via noncovalent interactions such as $\pi-\pi$ interaction, $\pi-$cation interaction, and van der Waals interaction and thus play a role of compatibilizer between CNTs and a matrix polymer. Particularly, it was demonstrated that the use of polymeric compatibilizer miscible with matrix polymer was very effective to disperse CNTs in matrix polymer by some other researchers.[21,22,44] Although the use of noncovalent functionalization has been successful for enhancement of dispersion of CNTs in polymer matrix and mechanical properties of CNT/polymer composites, the systematic strategy to design and synthesize an effective compatibilizer for a specific system has not been reported. For an effective compatibilizer, the following condition has to be satisfied: the compatibilizer favorably interacts with both the surface of CNTs and a matrix polymer.

In this study, we report an effective compatibilizer to homogeneously disperse multiwalled carbon nanotube (MWCNT) in poly(styrene-*co*-acrylonitrile) (SAN). For this purpose, a compatibilizer is designed to have a strong interaction with both the surface of MWCNT and the SAN matrix through noncovalent interactions. To satisfy this condition, a new compatibilizer composed of polythiophene backbone and PMMA grafts is synthesized, where the polythiophene backbone of the compatibilizer strongly interacts with the surface of MWCNT via $\pi-\pi$ interaction as reported in our previous study[42] and PMMA grafts of the compatibilizer interact with the SAN matrix since PMMA is miscible with SAN. The effect of this new compatibilizer on dispersion of MWCNT and mechanical properties of SAN/MWCNT nanocomposites is examined as a function of MWCNT content.

Experimental Section

Materials. All reagents were purchased from Sigma-Aldrich otherwise noted. 3-Thiopheneethanol (99%), triethylamine (99%), 2-isobutyryl bromide (99%), iron chloride ($FeCl_3$) (97%), 3-hexylthiophene (99+%), copper(I) bromide (CuBr) (99.999%), copper(I) chloride (CuCl) (99.995%), and *N*,*N*,*N*′,*N*′′,*N*′′-pentamethyldi-

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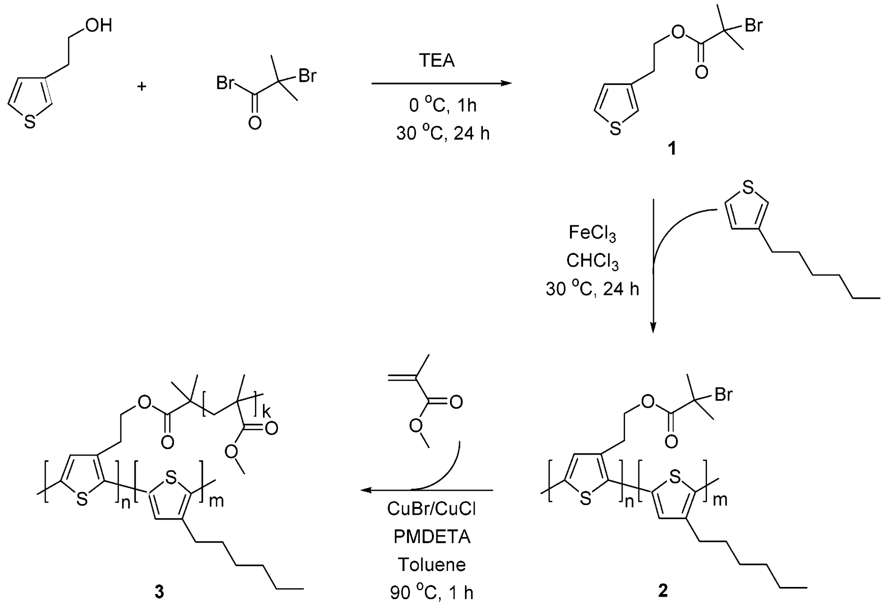

Figure 1. Overall synthesis route of the compatibilizer (**3**).

ethylenetriamine (PMDETA) (99%) were used as received. Methylene chloride, chloroform, and toluene used as solvent were purchased from Daejung Chemicals & Metals and dried by distillation over CaH_2. Methyl methacrylate (MMA) (99%) was washed with 5% NaOH aqueous solution and subsequently distilled water to remove hydroquinone. Then, MMA was dried by distillation over CaH_2. MWCNT with a diameter range of 25−70 nm and SAN with 24 wt % acrylonitrile (AN) content were supplied from Jeio Co. and LG Chem Co., respectively, and were used as received.

Synthesis of 2-Bromo-2-methylpropionic Acid 2-Thiophene-3-ylethyl Ester (BMPT) (1). A three-neck round-bottom flask was charged with 3-thiopheneethanol (4 mL, 0.036 mol), triethylamine (5.5 mL, 0.040 mol), and 40 mL of methylene chloride under a nitrogen atmosphere. The flask was cooled in an ice bath to 0 °C. Then, 2-bromoisobutyryl bromide (5.3 mL, 0.043 mol) dissolved in 10 mL of methylene chloride was slowly added into the reaction flask drop by drop under a nitrogen atmosphere. After complete addition, the reaction mixture was stirred at 30 °C for 24 h. The reaction mixture was filtered to remove white precipitate of triethylamine hydrochloride. Then, the filtrate was diluted with 300 mL of diethyl ether and washed sequentially with 1% HCl, 5% Na_2CO_3, and distilled water. The crude product in diethyl ether layer was condensed by evaporation of diethyl ether, and the residue was purified by a silica column chromatography using a mixed solvent of ethyl acetate and *n*-hexane (5:95/v:v) as an eluting solvent. The yield was 8.9 g (0.032 mol, 89%). Elemental analysis: calcd C 43.3, H 4.7, O 11.5, S 11.6; found C 43.5, H 4.7, O 11.6, S 11.9.

Copolymerization of BMPT (1) and 3-Hexylthiophene. $FeCl_3$ (2.3 g, 0.014 mol) was placed in a three-neck round-bottom flask, and the flask was purged with nitrogen gas. Then, 20 mL of chloroform was added to the flask, and a solution of **1** (1 g, 0.0036 mol) and 3-hexylthiophene (0.65 mL, 0.0036 mol) in 5 mL of chloroform was added to the reaction flask under a nitrogen atmosphere. After complete addition, the reaction mixture was stirred at 30 °C for 24 h. The reaction mixture was precipitated into 800 mL of methanol, and the copolymer of BMPT and 3-hexylthiophene as the product (P(BMPT-*co*-HT)) (**2**) was collected by filtration and subsequent washing with methanol. Then, the residual monomers were removed by Soxhlet extraction with methanol for 72 h, and the product was dried at 30 °C under vacuum. The yield was 0.67 g (42%).

Atom Transfer Radical Polymerization of MMA Using P(BMPT-*co*-HT) (2) as a Macroinitiator. A three-neck round-bottom flask was charged with CuBr (10 mg, 0.075 mmol) and CuCl (1.4 mg, 0.015 mmol), and the flask was degassed and backfilled with argon gas repeatedly three times. Toluene (10 mL) degassed by three freeze-and-thaw cycles was added to the flask, followed by addition of 0.8 mL of MMA (7.5 mmol) to the flask. A mixture of **2** (30 mg) and degassed toluene (5 mL) was added to the flask. Finally, PMDETA (0.03 mL, 0.15 mmol) was added to the flask. After three freeze-and-thaw cycles, the reaction mixture was allowed to stir at 90 °C for 1 h. The reaction mixture was diluted with 50 mL of chloroform to dissolve polymer. The mixture was then passed through a column of Al_2O_3 to remove copper. The resulting polymer solution was concentrated, and then the concentrated solution was precipitated into 1 L of *n*-hexane. The P(BMPT-*co*-HT)-*g*-PMMA (**3**) was collected by vacuum filtration and subsequent washing with *n*-hexane, followed by drying at 30 °C under vacuum. The conversion was 0.1 g (13%).

Preparation of SAN/3/MWCNT Nanocomposite Films. All of SAN/**3**/MWCNT nanocomposites with different loadings of MWCNT were prepared by solution blending. A typical procedure of SAN/**3**/MWCNT nanocomposite containing 0.05 wt % MWCNT is as follows: A dispersion of 1 mg of **3** and 1 mg of MWCNT in 20 mL of chloroform was sonicated for 1 h. Then, the dispersed solution was added to a solution containing 2 g of SAN in 20 mL of chloroform. The mixture was sonicated for an additional 10 min and precipitated in excess methanol. The precipitate was collected by filtration and washed subsequently with methanol. The filter cake (SAN/**3**/MWCNT nanocomposite) was dried at 30 °C under vacuum for 24 h. Films of SAN/**3**/MWCNT were prepared by solution casting: A solution of SAN/**3**/MWCNT in chloroform was poured onto a glass plate, and then a doctor blade was used to prepare a solution film. Then, the solvent was slowly evaporated at room temperature for 6 h, and the film was thoroughly dried under high vacuum at 30 °C for 24 h.

Measurements. The $\pi-\pi$ interaction between MWCNT and polythiophene of **3** is identified by comparing the fluorescence emission spectra and Raman spectra of **3** with those of SAN/**3**/MWCNT nanocomposite. For measurement of fluorescence emission spectra, 0.3 mg of **3** and 30 mg of SAN/**3**/MWCNT with 1 wt % MWCNT were dissolved in 20 mL of chloroform, respectively, and then their fluorescence emission spectra were obtained from a fluorescence spectrometer (RF 5301, Shimadzu). Raman measurements were carried out on the powder samples using a Jobin Yvon (T64000) with Ar laser at excitation wavelength of 514 nm.

The miscibility between SAN and PMMA graft of **3** was determined by comparing the glass transition temperatures of SAN, **3**, and SAN/**3**/MWCNT using a Perkin-Elmer DSC 7 differential scanning calorimeter. First, the samples were heated from 0 to

180 °C at a rate of 20 °C/min, kept for 3 min at the final temperature to remove the thermal history, and then quenched to 0 °C. Finally, the samples were reheated at the heating rate of 20 °C/min. The data from the second run were used for discussion.

The fracture surfaces of SAN/MWCNT and SAN/**3**/MWCNT films were observed for analysis of dispersion of MWCNT using a Jeol JSM-6330F field emission−scanning electron microscopy (FE-SEM), operated at an accelerating voltage of 5 kV.

The tensile properties of SAN, SAN/MWCNT, and SAN/**3**/ MWCNT films were measured with a universal testing machine (Instron-5543) with a 1 kN load cell at a constant cross-head speed of 3 mm/min. At least three specimens were tested for each sample, and the tensile properties are reported on average.

Results and Discussion

Figure 1 shows the synthesis route of P(BMPT-*co*-HT)-*g*-PMMA. The chemical structures of BMPT (**1**), P(BMPT-*co*-HT) (**2**), and P(BMPT-*co*-HT)-*g*-PMMA (**3**) are identified by ^{1}H NMR (Avance DPX-300, Bruker), as shown in Figure 2. The molecular weight (M_n) of **2** and its distribution (M_w/M_n) as measured by gel permeation chromatography were 2.6 × 10^4 g/mol and 4.17, respectively. Analysis of ^{1}H NMR spectra of **2** (Figure 2B) reveals that the molar ratio (m/n in Figure 2B) of **1** to 3-hexylthiophene units in the copolymer **2** is 3, indicating that one ATRP initiating site (**1**) exists every four monomeric units in the copolymer **2**. Examination of the ^{1}H NMR spectrum of **3** (Figure 2C) also reveals that the average degree of polymerization of PMMA graft chains was about 30. Here, it should be mentioned that an irreversible termination reaction may take place during ATRP of MMA. To avoid this irreversible termination reaction, a small amount of CuCl was added as a catalyst during reaction (see Experimental Section). It is well-known that the addition of deactivator such as CuCl and $CuBr_2$ prevents the irreversible termination reaction during ATRP.[45]

A specific interaction between MWCNT and polythiophene part of **3** is a prerequisite to accomplish the aim of this study. First, the $\pi-\pi$ interaction between them is verified by the fluorescence spectroscopy. Figure 3 shows the fluorescence emission spectra of **3** and SAN/**3**/MWCNT in chloroform when the dilute sample solutions are irradiated at 420 nm, corresponding to the excitation wavelengths of **3**. As can be seen in Figure 3, the strong fluorescence of **3** is quenched in SAN/**3**/ MWCNT. This quenching mainly arises from an efficient energy transfer between MWCNT and polythiophene of **3** via $\pi-\pi$ interaction.[46,47] Thus, the fluorescence emission spectra provide a clear evidence for the existence of significant $\pi-\pi$ interaction between MWCNT and polythiophene part of **3** in chloroform. Furthermore, the $\pi-\pi$ interaction between MWCNT and polythiophene part of **3** in solid state is also verified by Raman spectroscopy. It is well-known that the strong attachment of polymer onto the surface of CNTs leads the absorption wavenumber of tangential G-band of MWCNT to shift toward higher wavenumber due to an increase in the elastic constant of the harmonic oscillator of the polymer-coated CNTs.[48] Figure 4 shows the Raman spectra of MWCNT, SAN/MWCNT, and SAN/**3**/MWCNT, where SAN/MWCNT is prepared by solution mixing of SAN and MWCNT without the addition of the compatibilizer (**3**). The peaks at around 1340 and 1570 cm^{-1} correspond to the disorder-induced D-band and the tangential G-band of MWCNT, respectively. As can be seen in Figure 4, the tangential G-band of MWCNT in SAN/**3**/MWCNT slightly shifts to higher wavenumber (~3 cm^{-1}) as compared to that of pristine MWCNT, whereas the tangential G-band of MWCNT in SAN/MWCNT remains unchanged, which suggests that the upper shift in the tangential G-band of MWCNT is attributed to the strong $\pi-\pi$ interaction between MWCNT and polythiophene part of **3**.

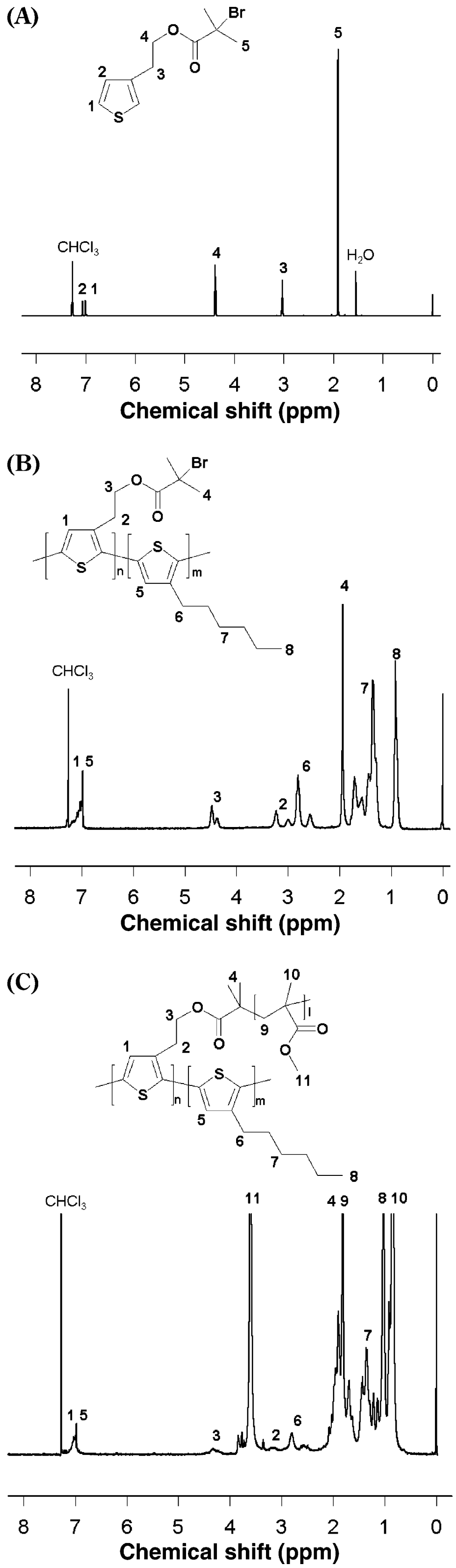

Figure 2. Chemical structure and ^{1}H NMR spectra of BMPT (A), P(BMPT-*co*-HT) (B), and P(BMPT-*co*-HT)-*g*-PMMA (C).

The miscibility between SAN matrix and PMMA graft of **3** is another important prerequisite in this study because it can realize homogeneous dispersion of MWCNT in SAN matrix and good interfacial adhesion between MWCNT and SAN matrix. To verify the miscibility between SAN and PMMA, the glass transition temperatures (T_g) of **3**, SAN, and SAN/**3**/

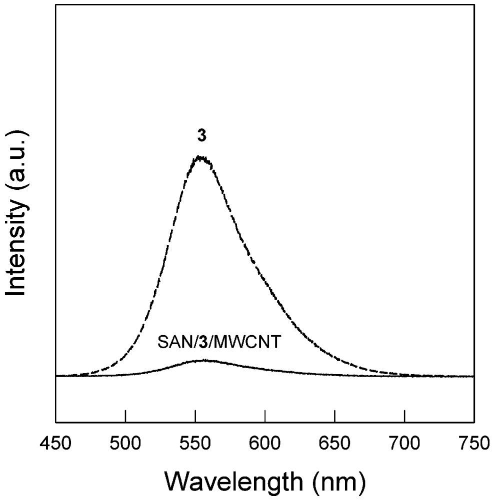

Figure 3. Fluorescence emission spectra of the compatibilizer (**3**) and SAN/**3**/MWCNT in chloroform when the samples are irradiated at 420 nm.

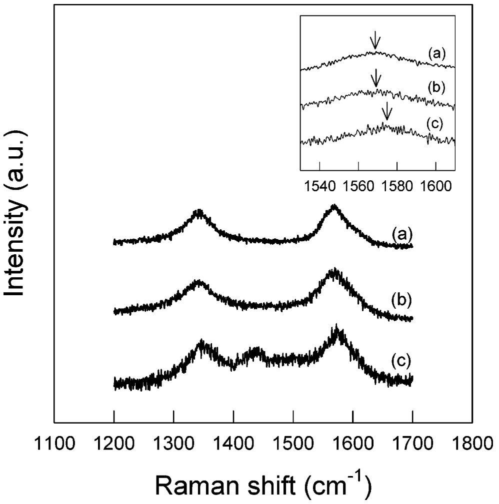

Figure 4. Raman spectra of the MWCNT (a), SAN/MWCNT (b), and SAN/**3**/MWCNT (c). In SAN composites, the amount of MWCNT is fixed at 10 wt %.

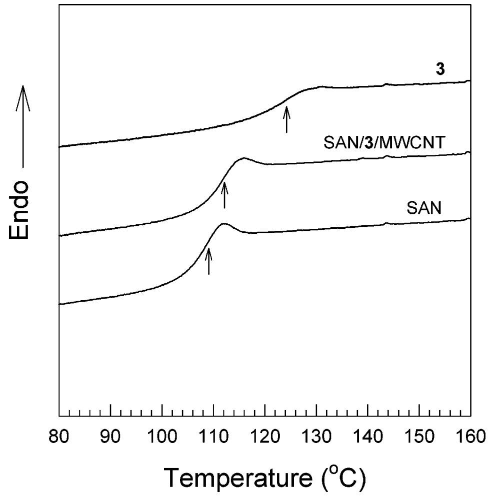

Figure 5. DSC thermograms of compatibilizer (**3**), SAN, and SAN/**3**/MWCNT with 1 wt % MWCNT.

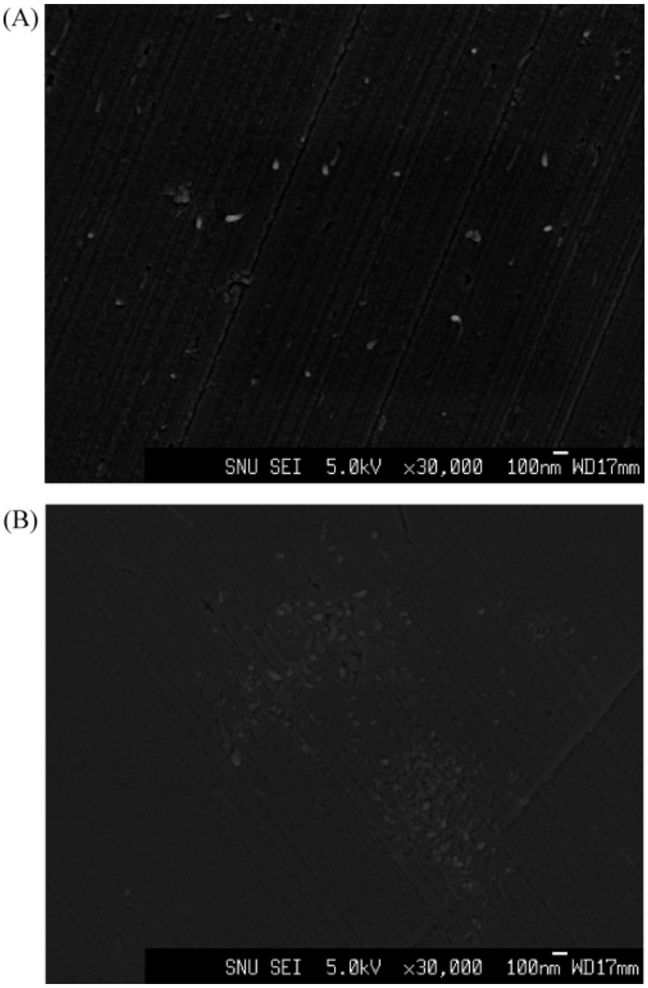

Figure 6. FE-SEM images of the fracture surface of SAN/**3**/MWCNT (A) and SAN/MWCNT (B). The amount of MWCNT in SAN/**3**/MWCNT and SAN/MWCNT is 1 and 0.05 wt %, respectively. The white spots indicate MWCNTs.

MWCNT are measured by a differential scanning calorimeter (DSC), and their T_g's are compared in Figure 5. As can be seen in Figure 5, a single T_g of SAN/**3**/MWCNT is observed at 114 °C instead of two T_g's of the SAN and **3**, indicating that PMMA graft of **3** is miscible with SAN matrix. From the results of fluorescence emission spectra, Raman spectra, and DSC thermograms, it is concluded that the compatibilizer (**3**) synthesized in this study can strongly interact with MWCNT via the $\pi-\pi$ interaction and is also miscible with SAN matrix, suggesting that **3** synthesized in this study can play a role of an effective compatibilizer for SAN/MWCNT nanocomposites.

Figure 6 compares FE-SEM images of the fracture surfaces of SAN/**3**/MWCNT and SAN/MWCNT films. The sample films for FE-SEM observation are ultramicrotomed with a diamond knife to produce the smooth fracture surface, as shown in Figure 6. The FE-SEM image of SAN/**3**/MWCNT shows the homogeneous dispersion and/or exfoliation of individually separated MWCNT in SAN matrix where bright spots indicate MWCNT, as shown in Figure 6A, whereas SAN/MCWNT shows a severe aggregation of MWCNT in the SAN matrix, as shown in Figure 6B.

The stress–strain curves of SAN and SAN/**3**/MWCNT films with different MWCNT content are shown in Figure 7A, and their mechanical properties are listed in Table 1. Both Young's modulus and tensile strength of the SAN matrix are dramatically improved without sacrifice of the elongation at break when MWCNT is incorporated in SAN matrix in the presence of the compatibilizer, as can be seen in Figure 7A. The most striking feature shown in Figure 7A is that the addition of only 0.01 wt % MWCNT to neat SAN leads to an increase in both

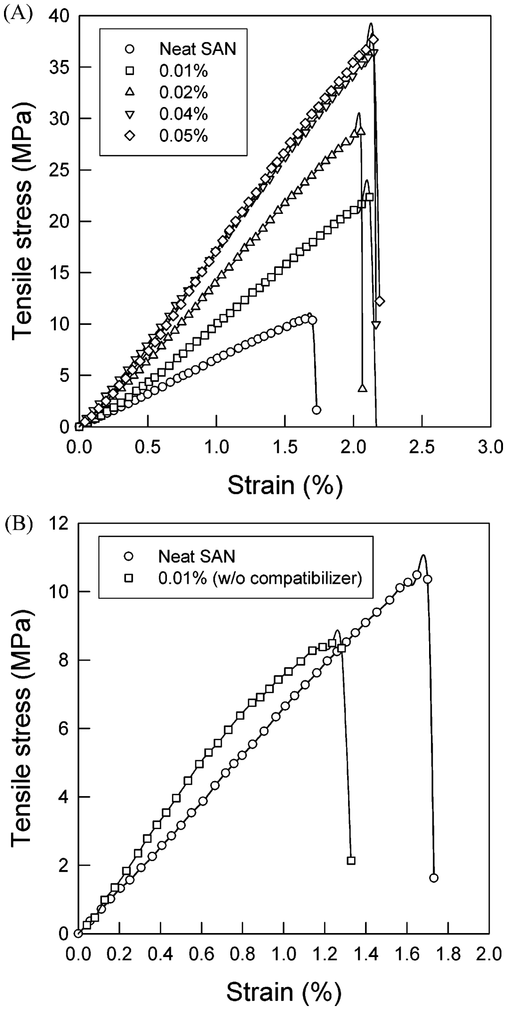

Figure 7. Stress−strain curves for the neat SAN and SAN/**3**/MWCNT with various MWCNT contents (A) and the neat SAN and the SAN/MWCNT with 0.01 wt % MWCNT (B).

Table 1. Mechanical Properties of SAN and SAN/MWCNT Nanocomposite Films

samples	Young's modulus (MPa)	tensile strength (MPa)	elongation at break (%)
neat SAN	598 ± 75	10.3 ± 1.1	1.7 ± 0.2
0.01%	1203 ± 48	22.2 ± 1.4	2.2 ± 0.3
0.02%	1574 ± 35	27.8 ± 2.0	2.1 ± 0.1
0.04%	183 ± 66	36.5 ± 3.7	2.2 ± 0.5
0.05%	1890 ± 130	35.8 ± 3.1	2.2 ± 0.1
0.01%[a]	835 ± 23	7.4 ± 1.1	1.2 ± 0.1

[a] SAN/MWCNT composite is prepared without the addition of the compatibilizer.

Young's modulus and tensile strength of SAN by two times (see Table 1). When the tensile properties of SAN/MWCNT without the compatibilizer are compared with those of neat SAN, it is revealed that the SAN/MWCNT shows the tradeoff behavior in tensile properties, as shown in Figure 7B. In other words, Young's modulus of SAN/MWCNT is increased compared to that of neat SAN, whereas their tensile strength and elongation at break are lower than neat SAN. This tradeoff in tensile properties of SAN/MWCNT may be attributed to the poor dispersion of MWCNT in SAN matrix, as identified by FE-SEM image (Figure 6B).

Figure 8 shows the FE-SEM image of crack of SAN/**3**/MWCNT film, when the sample film for FE-SEM observation is slightly elongated with a universal tester to produce micro-cracks in the film. It is clearly observed that some MWCNTs connect the crack, indicating good interfacial adhesion between SAN and MWCNT. Hence, it is believed that the improved mechanical properties of SAN/**3**/MWCNT shown in Figure 7A and Table 1 are attributed to the homogeneous dispersion of MWCNT in SAN matrix as well as good interfacial adhesion between SAN and MWCNT, when MWCNT is modified by the compatibilizer. Wang et al.[21] also reported that SAN was reinforced by the incorporation of PMMA-grafted MWCNT prepared by covalent functionalization of MWCNT. Unlike their approach, we successfully reinforce SAN with MWCNT functionalized via the noncovalent approach.

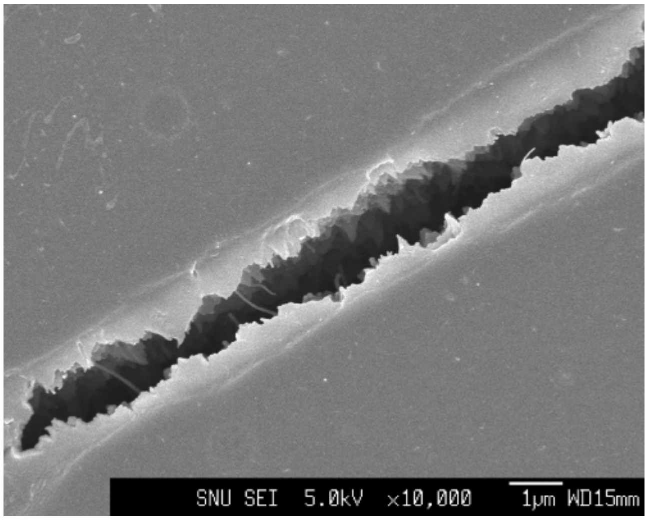

Figure 8. FE-SEM image of crack of SAN/**3**/MWCNT with 3 wt % MWCNT.

Conclusion

A new compatibilizer that can effectively disperse MWCNT in SAN matrix was synthesized. The fluorescence emission spectra and Raman spectra identify a significant $\pi-\pi$ interaction between MWCNT and polythiophene of the compatibilizer, and DSC thermograms also substantiate the miscibility between SAN matrix and PMMA graft of the compatibilizer. The addition of only 0.01 wt % of MWCNT in SAN matrix in the presence of the compatibilizer leads to a dramatic increase in both Young's modulus and tensile strength of SAN matrix without sacrifice of elongation at break. The improved mechanical properties of SAN/**3**/MWCNT are attributed to both the homogeneous dispersion of MWCNT in SAN matrix and good interfacial adhesion between SAN and MWCNT functionalized with the compatibilizer.

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