

Improvement in Properties of Multiwalled Carbon Nanotube/Polypropylene Nanocomposites Through Homogeneous Dispersion with the Aid of Surfactants

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ABSTRACT: The effects of different surfactants on the properties of multiwalled carbon nanotubes/polypropylene (MWCNT/PP) nanocomposites prepared by a melt mixing method have been investigated. Sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (NaDDBS) were used as a means of noncovalent functionalization of MWCNTs to help them to be dispersed uniformly into the PP matrix. The effects of these surfactant-treated MWCNTs on morphological, rheological, thermal, crystalline, mechanical, and electrical properties of MWCNT/PP composites were studied using field emission scanning electron microscopy, optical microscopy, rheometry, tensile, and electrical

conductivity tests. It was found that the surfactant-treatment and micromixing resulted in a great improvement in the state of dispersion of MWCNTs in the polymer matrix, leading to a significant enhancement of Young's modulus and tensile strength of the composites. For example, with the addition of only 2 wt % of SDS-treated and NaDDBS-treated MWCNTs, the Young's modulus of PP increased by 61.1 and 86.1%, respectively. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1117–1127, 2012

Key words: carbon nanotube; polypropylene; surfactant; conductive composite; dispersion

INTRODUCTION

Polymer nanocomposites are a new class of materials in the current century. Many nanoparticles, such as nanoclay, carbon black, metal nanoparticles, and carbon nanotubes (CNTs), have been incorporated with different polymers in order to develop materials with better barrier, electrical, thermal, or mechanical properties.^{1,2} Currently, different methods such as melt mixing, *in situ* polymerization, and solution mixing are widely used in the preparation of polymer nanocomposites.³

Since Iijima⁴ introduced CNTs in 1991, they have attracted great attention due to their unique properties.^{5–8} Because of their inherent and unique properties, CNTs become an excellent candidate for the fabrication of advanced polymer nanocomposites. Ajayan et al.⁹ reported the first polymer nanocomposite using CNTs as fillers in 1994. The number of publications in CNT/polymer nanocomposites has been increasing every year.¹⁰ However, CNTs tend

to agglomerate themselves due to their strong van der Waals interactions. Therefore, the major difficulty for the fabrication of CNT-based nanocomposites is indeed the dispersion of CNTs in a polymer matrix. Fortunately, the functionalization of CNTs seems to be an effective solution to this agglomeration problem.³ There are several approaches for the functionalization of CNTs, including defect functionalization, covalent functionalization, and noncovalent functionalization.^{3,11}

The noncovalent functionalization of CNTs is the method that improves the solubility and processability of CNTs without damaging their structure and physical properties.¹² In this method, the surfactants are used to disperse CNTs in a solvent, usually in water. The surfactants can be anionic, cationic, or nonionic.^{13,14} During the dispersion process, ultrasonication could help a surfactant in debundling of CNTs by electrostatic repulsion and by adsorption of surfactant molecules on the CNT surfaces. The main drawback of this method is that the forces between the wrapping molecules (the surfactant) and CNTs might not be strong enough to achieve high efficiency in load transfer between CNTs and a polymer matrix.³

Various polymer matrices are used for making CNT-based nanocomposites, such as thermoplastics,^{15,16} thermosetting resins,^{17,18} polymer blends,¹⁹

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liquid crystalline polymers,^{20,21} water-soluble polymers,²² conjugated polymers,²³ and so on. In this study, we have used polypropylene (PP) and multi-walled carbon nanotubes (MWCNTs) to prepare high-performance polymer nanocomposites through a melt mixing process. PP has been widely used a semicrystalline thermoplastic in many applications due to its well-known physical and mechanical properties as well as the ease of processing at a relatively low cost.

The effects of MWCNTs on the properties such as thermal, mechanical, electrical, and crystallization behaviour of CNT/PP nanocomposites have been reported widely in the literature.^{9,19–21,24} For example, Kashiwagi et al.²⁴ reported the effects of MWCNTs on the flame-retardant performance, thermal conductivity, and stability of PP. In their reports, the effect of MWCNTs on PP is more prominent in its electrical conductivity than the thermal one. In addition, various researches have been done in MWCNT/PP composites by using different mixing methods such as solution mixing, *in situ* polymerization,²⁵ and melt mixing.²⁶

Unfortunately, the improvement in properties of the MWCNT/PP nanocomposites reported is usually restricted due to the formation of MWCNT agglomeration and poor compatibility with PP. There is a number of researches available in the literature on MWCNT/PP composites, which attempted to improve the dispersion of MWCNTs and the compatibility between MWCNTs and PP by varying molecular weight of PP,²⁷ modifying MWCNTs with different methods,²⁶ introducing a posttreatment,²⁷ using an appropriate compatibilizer,²⁸ and so on.

Therefore, the aim of this study is to examine the effects of surfactant [sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (NaDDBS)]-treated MWCNTs on the morphological, rheological, mechanical, and electrical properties of MWCNT/PP composites using field emission scanning electron microscopy (FESEM), optical microscopy, thermal analysis, rheometry, tensile, and electrical conductivity tests.

EXPERIMENTAL

The matrix used in this study, PP with an average molecular weight of 190,000, was purchased from Sigma-Aldrich (USA). MWCNT (Baytubes® C 150 HP) were purchased from Bayer Material Science, Germany. According to the manufacturer's specifications, the purity, the diameter, length, number of walls, and bulk density were >95%, 5–20 nm, 1–10 μm, 3–15, and 140–230 kg/m³, respectively. The surfactants, NaDDBS and SDS, were also purchased from Sigma-Aldrich.

The sonicated MWCNTs were prepared by a bath sonicator (Cole-Parmer 8890-16) with a frequency of

TABLE I
Compounding Formulations (in Weight Percentage)

| Code | PP | MWCNT | SDS | NaDDBS |
|-------------------|-----|-------|-----|--------|
| Pure PP | 100 | – | – | – |
| PN2 | 98 | 2 | – | – |
| PN5 | 95 | 5 | – | – |
| PN10 | 90 | 10 | – | – |
| PSN2 | 96 | 2 | 2 | – |
| PSN5 | 90 | 5 | 5 | – |
| PSN10 | 80 | 10 | 10 | – |
| PNN2 | 96 | 2 | – | 2 |
| PNN5 | 90 | 5 | – | 5 |
| PNN10 | 80 | 10 | – | 10 |
| PCN2 ^a | 98 | 2 | – | – |

^a The composite with sonicated-MWCNTs.

42 kHz. One hundred milliliters of deionized water containing 1 g of raw MWCNTs were sonicated for 2 h at room temperature. Then, the aqueous mixture was dried in a vacuum oven at 60°C for 48 h. The surfactant-treated MWCNTs were prepared by a suspension method as follows. One hundred milliliters of aqueous solution containing 1 g of surfactant were sonicated with 1 g of raw MWCNTs for 2 h at room temperature by using the same bath sonicator with the frequency of 42 kHz. Therefore, the ratio between MWCNTs and surfactant was 1 : 1 in weight in the prepared suspension. Then, the suspension was dried in a vacuum oven at 60°C for 48 h.

Before mixing, PP and all types of MWCNTs (i.e., raw, sonicated and surfactant-treated MWCNTs), were dried at 60°C for 12 h in a vacuum oven. A twin-screwed microcompounder (Haake Minilab II) was used to prepare MWCNT/PP composites with different compositions, and the amount of material fed for each composite sample was about 6 g. A rotational speed of 30 rpm was used at a mixing temperature of 180°C for 15 min. The sample codes and compounding formulations for the nanocomposites prepared in this work are listed in Table I. PCN2 with the sonicated MWCNTs was prepared for comparison to study the effects of sonication on the properties of the MWCNTs added in the PP. The compounded samples were molded at 200°C with 600 bars for 10 s into different shapes by using a mini-injection machine (Haake MiniJet).

A thermal gravimetric analyzer (TGA 2950, TA Instruments) was used to confirm the ratio between MWCNTs and surfactants. The thermogravimetric analysis (TGA) tests were carried out under dry nitrogen over a temperature range of 25–600°C at a heating rate of 10°C/min.

Transmission electron microscopic (TEM) analysis was performed on a JEM-2010F (Jeol Co., Japan) electron microscope. For analysis, the MWCNT samples were prepared by sonicating about 1 mg of the

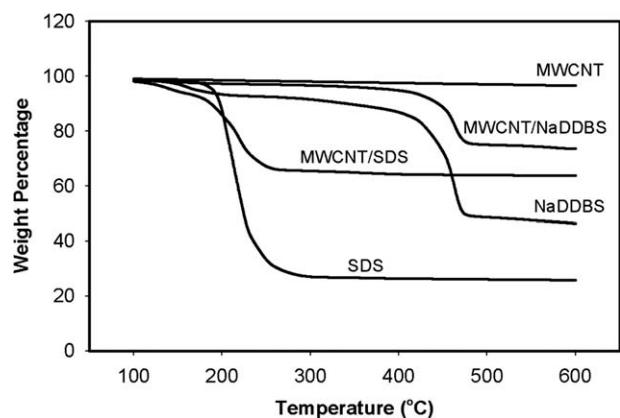


Figure 1 The TGA thermographs of SDS, NaDDBS, MWCNT, SDS-treated MWCNTs and NaDDBS-treated MWCNTs.

MWCNTs powder in 10 mL of ethanol for 15 min at room temperature using a bath sonicator (Cole-Parmer 8890-16) with a frequency of 42 kHz. A few drops of the resulting suspension were deposited on a TEM grid (200 mesh).

Melt rheological measurements were performed on a rotational rheometer (Anton Paar—Physica MCR301) for the molded samples ($\Phi 25$ mm \times 1 mm). The experiments were carried out in a frequency sweep mode at 5% constant strain using a parallel plate geometry with a diameter of 25 mm at 200°C under dry nitrogen.

An inverted optical microscope (Olympus GX51) attached with 3CCD camera (Sony DSP Exwave HAD) was used to characterize the dispersion of the different types of MWCNTs in the PP matrix. The thin films with 1 μ m thickness of the samples were fabricated by a laboratory scale hot press at 200°C and 10 bars for 5 min.

Surface morphology of the tensile fractured samples was observed by FESEM, after silver coating. The analysis was done using a JEOL JSM-5800 SEM.

Differential scanning calorimetric (DSC) measurements were carried out using a thermal analyzer (TA DSC Q20) in a temperature range of 25–200°C, at a ramping temperature of 10°C/min under dry nitrogen. The first cooling and heating thermograms of DSC were used for the analysis. The crystallinity of sample (χ_c) was determined with the following equation²⁹:

$$\chi_c = \frac{\Delta H_f}{\Delta H_f^0 w_t} \quad (1)$$

where ΔH_f is the heat of fusion of the sample, ΔH_f^0 is the theoretical specific melting heat of 100% crystalline isotactic PP, which was taken as 209 J/g,^{30,31} and w_t is the weight fraction of PP.

Tensile tests were carried out on the dumbbell-shaped samples with the dimension of 90 mm \times

5 mm \times 1.6 mm by an Instron universal testing machine (Instron 5569) at room temperature with an extension speed of 5 mm/min and an initial gauge length of 35 mm. For each composite, four measurements were repeated within an experimental error of $\pm 2\%$.

Electrical conductivity measurements (voltage-current) were carried out at room temperature using a probe station of four-pointed fixture (CASCADE—REL 4800) combined with a precision LCR meter (HP Agilent—4284A). The applied voltage was varied from 0.01 to 1.00 V with an increment of 10 mV/s.

RESULTS AND DISCUSSION

The ratio between surfactant and MWCNTs

TGA was used to determine the ratio between the surfactant and the multiwalled carbon nanotubes (MWCNTs) before the composites were fabricated. Figure 1 shows the thermographs of SDS, NaDDBS, MWCNT, MWCNT/SDS, and MWCNT/NaDDBS. From this figure, MWCNT showed no or little decomposition over the temperature range, while the surfactants, SDS and NaDDBS, showed the dramatical loss above 300 and 480°C, respectively. Therefore, we consider that the weight loss in the surfactant-treated MWCNTs (i.e., MWCNT/SDS and MWCNT/NaDDBS) was due to the decomposition of the surfactants during the experiments.

Table II lists the weight loss in percentage for all the samples at 600°C. From this table, the weight loss of SDS-treated MWCNT is 36.6%, which is about the half of that of pure SDS (73.1%). Similarly, the weight loss of NaDDBS-treated MWCNT is 26.5%, which is about the half of that of pure NaDDBS (53.1%). From these results, it could be concluded that the weight ratios between the surfactants and MWCNTs were 1 : 1.

Effect of surfactants on MWCNTs

Figure 2 shows the TEM images of the raw MWCNTs, SDS-treated MWCNTs, and NaDDBS-treated multiwalled carbon nanotubes (MWCNTs) used in this work. The existence of highly entangled

TABLE II
The Percentage Weight Losses of SDS, NaDDBS, SDS-Treated MWCNTs, and NaDDBS-Treated MWCNTs at 600°C

| Sample | Weight loss (%) |
|------------|-----------------|
| CNT | 0.2 |
| SDS | 73.1 |
| CNT/SDS | 36.6 |
| NaDDBS | 53.1 |
| CNT/NaDDBS | 26.5 |

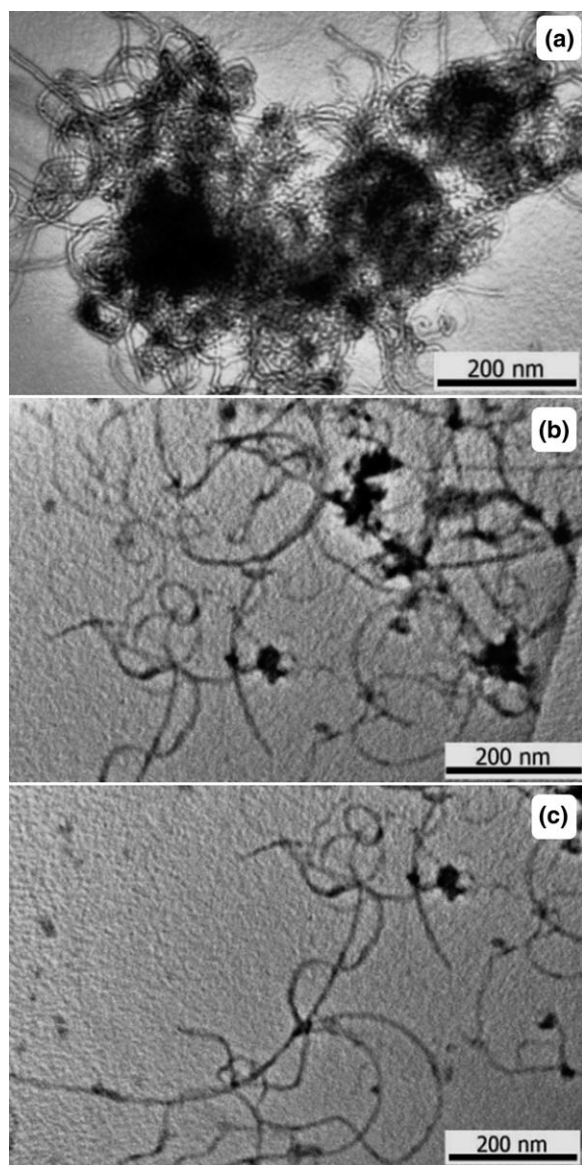


Figure 2 TEM micrographs of (a) raw MWCNTs, (b) SDS-treated MWCNTs, and (c) NaDDBS-treated MWCNTs.

network-like structure of MWCNTs is well evident from the micrograph. In Figure 2(a), raw MWCNTs were found as bundles, while the surfactant-treated MWCNTs were individually separated as shown in Figure 2(b,c) for SDS-treated MWCNTs and NaDDBS-treated MWCNTs respectively. This is because the surfactants were adsorbed on the surfaces of nanotubes during the dispersion procedure where the sonication might also help the surfactants to debundle nanotubes.³²

Rheological properties of MWCNT/PP composites

Figure 3(A) represents the complex viscosity (η^*) of the pure PP and multiwalled carbon nanotubes/polypropylene (MWCNT/PP) composites as a function of angular frequency (ω). From this figure, the

pure PP showed nearly a Newtonian behavior, while the composites exhibited non-Newtonian and shear thinning one over a frequency range studied. This non-Newtonian behavior was more pronounced for the composites with higher loading of MWCNTs. The complex viscosity increased with increasing MWCNT content, which was more prominent at lower frequencies. Kim et al.³³ reported the similar observation and considered that the increase in the complex viscosity with increasing MWCNT content in the polymer composites was attributed to the increase in the interactions between CNTs and the matrix polymer. Thus, the higher viscosity and shear thinning behavior of the MWCNT/PP composites reflect the stronger interfacial interaction between

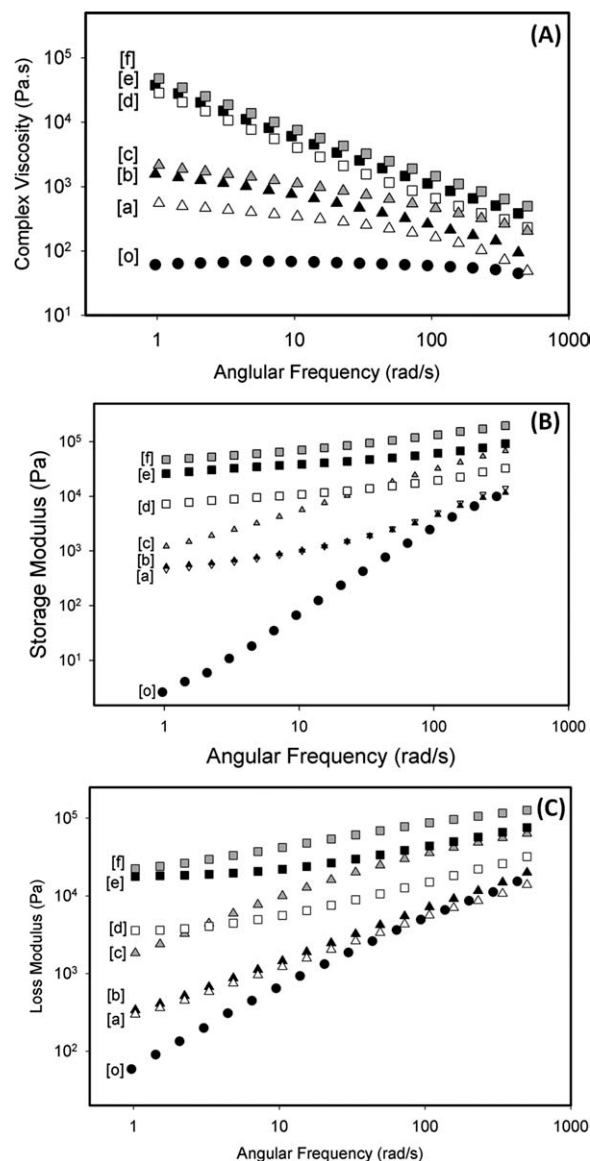


Figure 3 Rheological properties of pure PP, PN, PSN, and PNN composites: (A) complex viscosity, (B) storage modulus, and (C) loss modulus—where (o) pure PP, (a) PN5, (b) PSN5, (c) PNN5, (d) PN10, (e) PSN10, and (f) PNN10.

MWCNTs and the PP matrix as well as better dispersion of MWCNTs in the composites. Therefore, in our case, with the aid of the surfactants, NaDDBS or SDS, there was a better dispersion of MWCNTs in the PP matrix compared to the raw MWCNTs. The π - π interaction between the benzene ring of NaDDBS with the MWCNTs contributed to the better compatibility between the NaDDBS-treated MWCNTs and PP.³⁴ Therefore, it can be concluded that the NaDDBS-treated MWCNTs had a better compatibility as well as a better dispersion as compared to the SDS-treated MWCNTs and the raw MWCNTs.

In general, at the same loading of MWCNTs, the composites with surfactant-treated MWCNTs have higher viscosity than that of the composite with raw MWCNTs. The higher viscosity of the composites with surfactant-treated MWCNTs is considered to be mainly attributed to (1) the better compatibility between the surfactant-treated MWCNTs and PP and (2) the better dispersion of the surfactant-treated MWCNTs in the PP matrix. For example, it would be reasonably considered that the well-dispersed nanotubes are able to form loose network-like clusters in the PP matrix, which may restrain polymer chains to flow and then increase melt viscosity. At the same time, these loose network-like clusters of MWCNTs contribute to a higher electrical conductivity.

The storage modulus (G') and loss modulus (G'') versus angular frequency for the pure PP, MWCNT/PP, SDS-treated MWCNT/PP, and NaDDBS-treated MWCNT/PP composites at 200°C are shown in Figure 3(B,C). The G' and G'' of the composites dramatically increased with increasing angular frequency and the MWCNTs loading compared to that of the pure PP. These results indicate that there was a transition from a liquid-like behavior to a solid-like behavior with increasing the MWCNT loading. As the rheological measurements observed at lower frequencies represent the longer relaxation times of PP, the differences among these composites are more dominant at low frequencies, indicating that the rheological properties of PP had been differently modified by the addition of the different types of MWCNTs. The storage modulus, G' , at lower frequencies becomes almost independent of frequency as the MWCNT loading increases as shown in Figure 3(B). This phenomenon is attributed to a dynamic network of MWCNTs, which could delay the large-scaled motion of the PP molecules.³⁵ At 10 wt % MWCNT loading, the composites with surfactant-treated MWCNTs (PSN10 and PNN 10) showed the higher storage moduli at the lower frequencies compared to the composite with raw MWCNTs (PN10). Du et al.³⁶ reported that better dispersion and less alignment of CNTs resulted in more restric-

tion on the mobility of polymer chains at the same loading of CNTs in the polymer composites. Besides, the properties of MWCNTs, such as the size, aspect ratio, and interfacial properties, all influence the rheological properties of the nanocomposites. In our study, the frequency-independent storage moduli of the composites with surfactant-treated MWCNTs could be related with the better dispersion of MWCNTs in the PP matrix.

Finally, the pure PP showed the nearly terminal flow behavior while the others showed the nonterminal ones. It was observed that the composites containing the surfactant-treated MWCNTs showed the higher complex viscosity, storage, and loss moduli than the composites with the same loading of raw MWCNTs. This result suggests that the surfactant-treated MWCNTs would have a better dispersion in the polymer matrix.³⁷ Moreover, NaDDBS-treated MWCNTs contributed to the higher viscosity and storage modulus of the composites than SDS-treated MWCNTs at the same loading of MWCNTs. This is because NaDDBS-treated MWCNTs had better interfacial interaction via π - π interaction than SDS-treated MWCNTs. As a result, the stronger interaction between NaDDBS and MWCNTs greatly reduced the agglomeration of MWCNTs.

Dispersion state of different multiwalled CNTs in PP

Figure 4 shows the optical micrographs of PN2, PSN2, and PNN2 thin films with 1 μm thickness. From Figure 4(a), there are some black dots, which are bigger than the size of 10 μm , showing that the raw MWCNTs still tend to agglomerate in the PP matrix. But, for PSN2, the size of the black dots obviously becomes smaller when compared with that of raw MWCNTs as shown in Figure 4(b). Although there are still some small black dots and spots observed, the image of PNN2 in Figure 4(c) is much clearer than the rest (PN2 and PSN2), indicating a better dispersion of CNTs. This shows that because of NaDDBS, most of the MWCNTs were dispersed uniformly in the PP matrix, and, as a result, the image is more apparent.

The SEM photographs of the cross-sectional fracture of the MWCNT/PP composites are shown in Figure 5. From Figure 5(a), the larger agglomerations of raw MWCNTs are shown in the circle indicators, while the individual raw MWCNTs dispersed in the PP matrix are highlighted in the circle-headed arrows. From this figure, it is significantly observed that the dispersion of raw MWCNTs was poor in the PP matrix, and the MWCNTs tended to form aggregates in the PP matrix. Because of the agglomeration problem of raw MWCNTs, the overall performance of the composites filled with raw

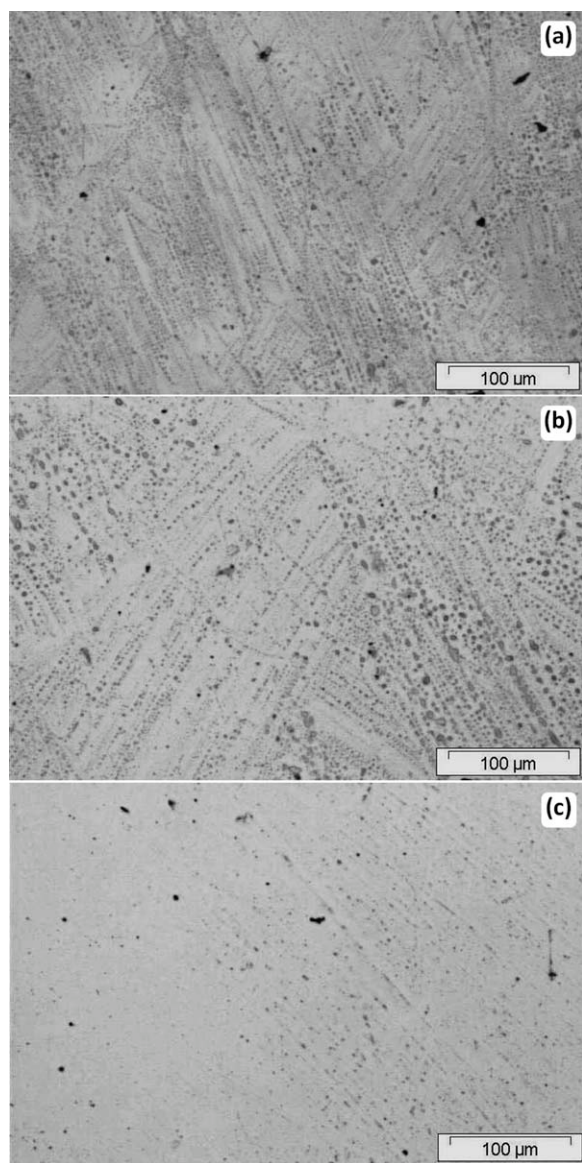


Figure 4 Optical micrographs of composite thin films: (a) PN2, (b) PSN2, and (c) PNN2.

MWCNTs tends to be poor. This is because these agglomerates of raw MWCNTs reduced the interfacial area between MWCNTs and the polymer matrix and interrupted the formation of network structure, which would affect efficient transfer of excellent properties of MWCNTs to the polymer matrix as further explained in the following section.

On the other hand, the composites filled with the surfactant-treated MWCNTs showed the better dispersion in the PP matrix when compared with the composite containing the same amount of raw MWCNTs. As shown in Figure 5(b,c), the bright dots and some lines indicate that the ends of the broken surfactant-treated MWCNTs were dispersed in the PP matrix. This is because the surfactant molecules could serve as a link between the MWCNTs and PP matrix, providing hydrophobic interactions

that can enhance the contact at the interface.³⁸ Thus, as a consequence of this uniform dispersion of surfactant-treated MWCNTs, the composites with these types of MWCNTs have better mechanical performance than those with raw MWCNTs. Besides, it was interestingly observed from Figure 5(d–f) that the diameters of surfactant-treated MWCNTs are larger than those of raw MWCNTs. Generally, the thicker MWCNTs can be explained by two aspects:

1. Because of the surface modification of MWCNTs by surfactant molecules, there could be a better compatibility between the polymer matrix and the MWCNTs, so that those MWCNTs were coated with the polymer molecules during the fabrication process and these polymer molecules were not removed during mixing and injection.^{20,39} This phenomenon was also reported even in the polymer composites with raw MWCNTs.⁴⁰
2. Because of the excessive interfacial adhesion between the surfactant molecules and the MWCNTs, it is difficult to remove the surfactant molecules from the MWCNTs after surfactant treatment.³⁴ Therefore, MWCNTs were coated with the surfactant molecules during the modification process, and these surfactant molecules were not removed during the mixing and injection-molding process.

In our case, MWCNTs could be coated with the surfactant molecules during the surfactant-treatment process. Then, these surfactant-treated MWCNTs were coated again with the polymer molecules during mixing due to the better compatibility between them. Finally, these coated polymer molecules were not removed after a tensile test. As a result, it could be observed the significant increase in the diameters of the surfactant-treated MWCNTs as shown in Figure 5(e,f).

Effects of different multiwalled CNTs on the crystallization of PP

To study the effect of different types of MWCNTs on PP crystallization in the composites, DSC measurements were carried out. In Table III, the crystallization temperature (T_c), melting temperature (T_m), heat of fusion (ΔH_f), and crystallinity (χ_c) obtained from DSC studies are summarized.

The DSC melting endotherms [Fig. 6(a)] showed that PP had a main melting peak at 151.3°C with an additional shoulder peak at 148.6°C, corresponding to the melting behaviors of the α -form and β -form crystals, respectively.⁴¹ However, for the MWCNT/PP nanocomposites, the shoulder peak decreased in the presence of MWCNT, which was more obvious

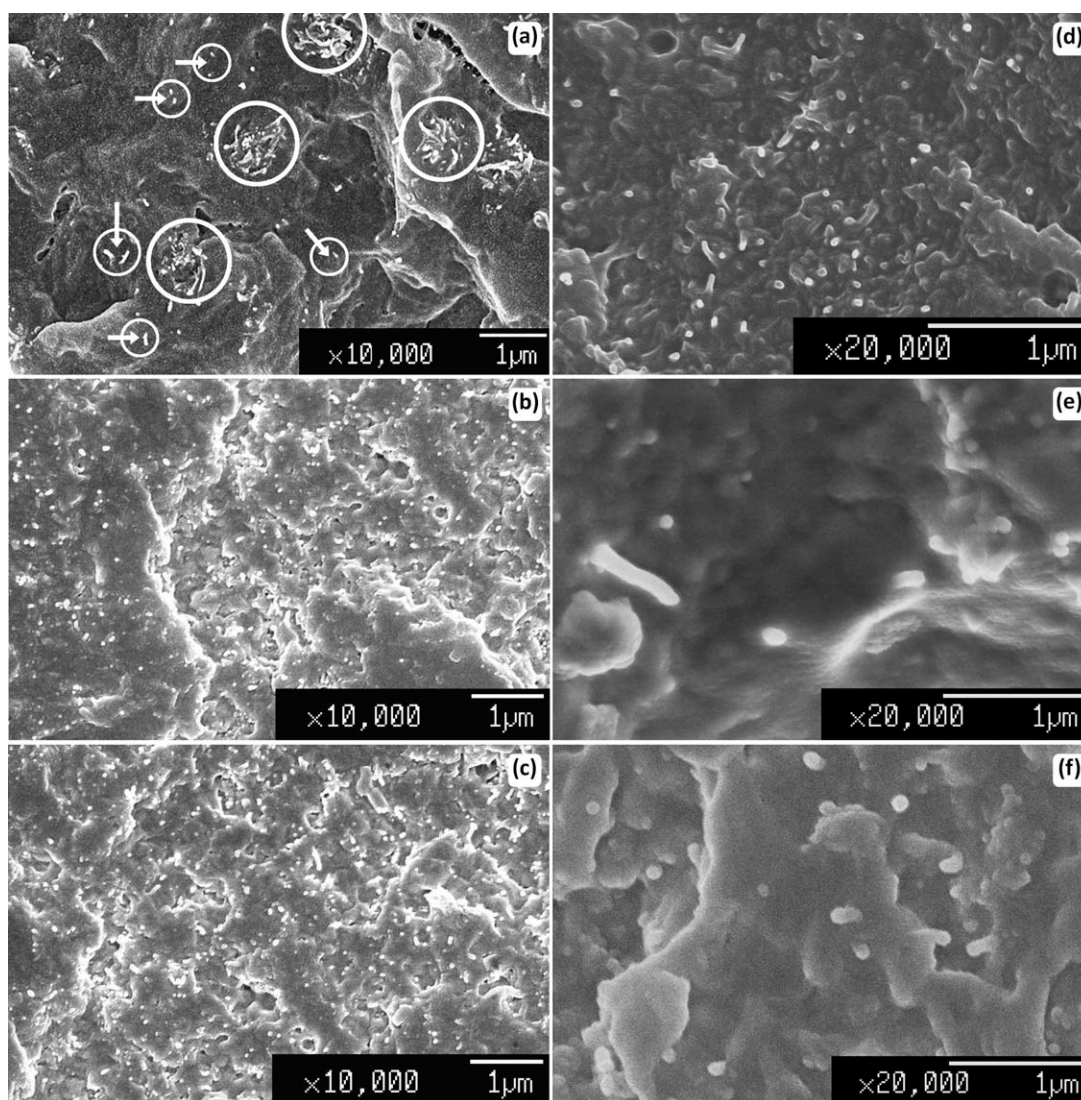


Figure 5 FESEM micrographs of tensile fracture samples of composites at 10k magnification: (a) PN10, (b) PSN10, and (c) PNN10.

when the content of MWCNTs in the MWCNT/PP nanocomposites was higher. These results showed that the presence of MWCNTs promoted the crystallization of PP for the formation of α -crystals, but they had a less effect on that of the β -form. Zheng et al.² observed the similar effects of clay on polymorphism of PP in the clay/PP nanocomposites. They reported that clay had an insufficient effect on the crystallization rate of the β -form crystal. Our composites also followed their finding that no shoulder peaks were observed for the composites incorporated with MWCNTs and only the α -phase crystallites existed. The melting peak temperature of PP was affected by the incorporation of MWCNTs. The melting temperature of PP tended to increase with an addition of MWCNTs due to their nucleating effect on PP.⁴² It is observed that the melting temperature of PP shifted higher by 4.5°C for PN10, 5.1°C for PSN10, and 6.2°C for PNN10.

From Figure 6(b), it can be seen that the pure PP showed only a crystallization peak temperature at about 112.4°C. The PP crystallization temperature

TABLE III
DSC Properties of the Composites Prepared in This Study

| Sample | T_c (°C) | T_m (°C) | ΔH_f (J/g) | χ_c (%) |
|---------|------------|------------|--------------------|--------------|
| Pure PP | 112.4 | 148.5 | 80.5 | 38.52 |
| PN2 | 115.5 | 154.4 | 74.8 | 36.52 |
| PN5 | 117.7 | 155.3 | 72.2 | 36.36 |
| PN10 | 121.5 | 156.0 | 68.1 | 36.20 |
| PSN2 | 116.3 | 155.2 | 76.12 | 37.94 |
| PSN5 | 118.2 | 156.0 | 69.15 | 36.76 |
| PSN10 | 122.2 | 156.4 | 60.26 | 36.04 |
| PNN2 | 118.7 | 155.5 | 76.46 | 38.11 |
| PNN5 | 120.8 | 156.4 | 71.27 | 37.89 |
| PNN10 | 124.1 | 157.5 | 60.93 | 36.44 |
| PCN2 | 115.9 | 154.8 | 75.1 | 36.67 |

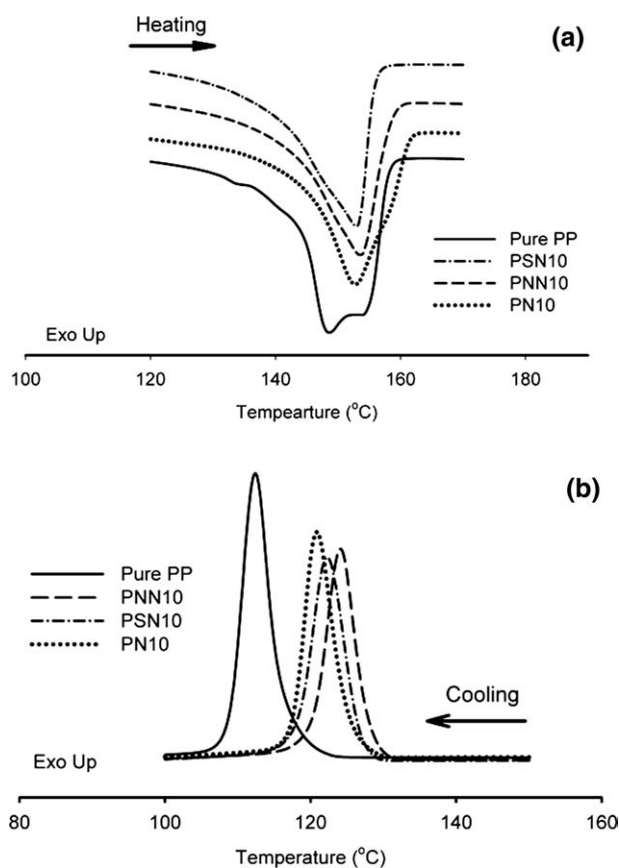


Figure 6 DSC thermograms for pure PP, PN10, PSN10, and PNN10 at the rate of 10°C/min in dry nitrogen gas: (a) melting and (b) crystallization.

shifted to the higher temperature side while incorporated with MWCNTs. These results indicate that the nanotube may act as a nucleating agent, which promotes the crystallization process of PP during a cooling process. It was also observed that the crystallization temperature increased with increasing the MWCNT content in the composites. Seo et al.⁴⁰ reported that the addition of MWCNTs enhanced the nucleation of PP during a crystallization process. Bao et al.⁴¹ also reported that the addition of MWCNTs into PP resulted in an improved heterogeneous nucleation effect. When the MWCNT loading increases in the PP matrix, more heterogeneous nucleation sites are available, and hence more polymer chains are induced to crystallize, which causes the crystallization peak to shift toward the higher temperature. Therefore, the incorporation of the MWCNTs effectively enhanced the crystallization temperature of the PP matrix through heterogeneous nucleation.

However, at the same loading of 10 wt % MWCNTs, the composites with SDS and NaDDBS surfactants (i.e., PPSN10 and PNN10, respectively) exhibited no significant effect on the crystallization temperature compared to the composite without any

surfactant (i.e., PN10). Sahoo et al.²² also reported that at the same MWCNT loading, the presence of surfactant would not show any significant effect on the crystallization behavior of PP in the MWCNT/PP nanocomposites. There is a similar observation in the literature on the MWCNT composites with nylon 6 as the matrix.²⁸ From those results, it is concluded that the presence of the surfactants did not virtually affect the crystallization behavior of PP, whereas the incorporation of MWCNTs into PP was responsible for the changes in the crystallization of PP. Moreover, it was found that both melting and crystallization peaks in the nanocomposites were narrower than those in PP. This is due to the higher thermal conductivity of the MWCNTs in the composites.⁴² The higher thermal conductivity of the MWCNTs when compared with that of the PP matrix is responsible for the sharper and narrower crystallization and melting peaks, as heat could be more uniformly distributed in the samples containing the MWCNTs.

The heat of fusion (ΔH_f) slightly decreased with increasing the loading of MWCNTs in the composites. The heat of fusion is proportional to the amount of crystallinity in the sample. The crystallinities of all the composites are lower than that of pure PP. This is because the addition of MWCNTs enhanced crystallization temperature of the composites compared to pure PP, but reduced the molecular mobility of PP simultaneously. Consequently, the crystallinity of PP in the composites reduced slightly with the increase in the loading of MWCNTs in the PP matrix. Therefore, the degree of crystallization of all the composites decreased when compared with pure PP.

Mechanical properties of PP incorporated with different multiwalled CNTs

Figure 7 shows the tensile properties for MWCNT/PP composites, SDS-treated MWCNT/PP composites, and NaDDBS-treated MWCNT/PP composites. The presence of MWCNTs improved the mechanical properties of the PP matrix. Generally, the improvement in the mechanical properties of MWCNT/polymer composites could be attributed to either their enhanced crystallinity or the interaction of MWCNTs with the polymer matrix or both. But, in our case, the degrees of crystallization of the MWCNT/PP composites are lower than that of pure PP as discussed previously. Therefore, the enhanced mechanical properties of the composites in this study are only due to the better dispersion of MWCNT with the PP matrix.

From Figure 7(a), the Young's modulus of the pure PP increased from 800 to 1050 MPa for PN2, 1124 MPa for PCN2, 1280 MPa for PSN2, and 1481

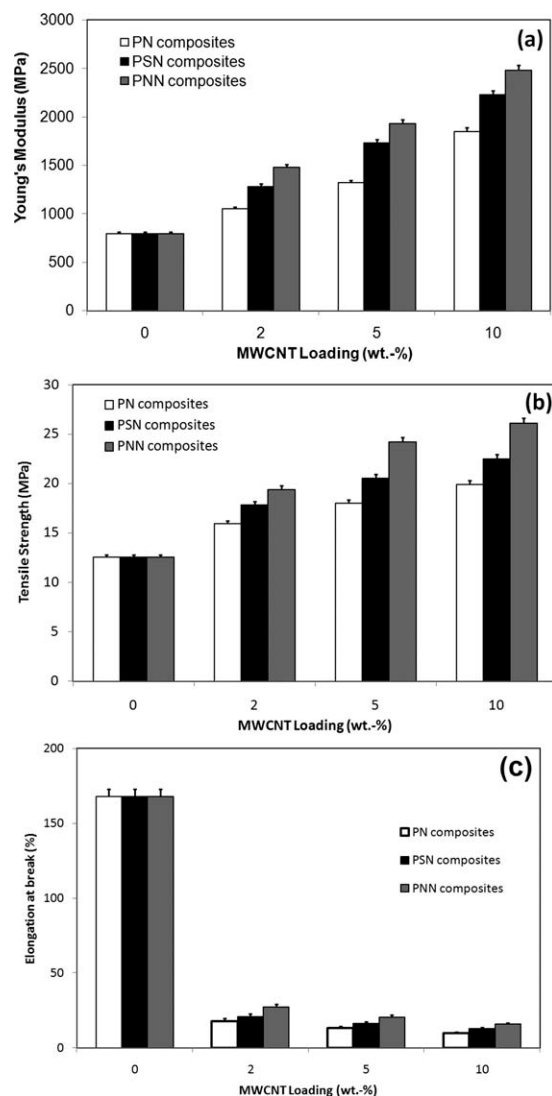


Figure 7 Mechanical properties of PN, PSN, and PNN composites at different MWCNT loading.

MPa for PNN2, respectively, only at 2 wt % of MWCNT loading. The Young's modulus increased with loading of MWCNTs for all composites. This is because, while being incorporated with fillers, the mobility of the polymer chains is limited. The restriction in chain mobility increases with the increase in the loading of fillers. This reduced mobility of polymer chains makes the composites more rigid, and, as a result, the composites have higher moduli than the unfilled PP. Compared to PN2 con-

taining the pristine MWCNTs, PCN2 with the sonicated MWCNTs showed the higher tensile modulus due to the better dispersion of the sonicated MWCNTs. Moreover, the tensile moduli of the composites with surfactant-treated MWCNTs are higher than those with raw MWCNTs with or without sonication. The weight fractions of the surfactant present in the composites make the filler loadings of those composites higher which make the matrix molecules more restricted, and, therefore, the composites with the surfactant-treated MWCNTs have higher moduli than those with raw MWCNTs.

It is observed from Figure 7(b) that with the addition of 2 wt % MWCNTs, the tensile strength showed a 27% increase for PN2, 33% increase for PCN2, 42% for PSN2, and 55% for PNN2, respectively. The tensile strength increased from 12.5 MPa for the pure PP to 19.9 MPa for PN10, 22.5 MPa for PSN10, and 26.1 MPa for PNN10, respectively. It is found that the tensile strengths of the composites with surfactant-treated MWCNTs are higher than those of the composites with raw MWCNTs with or without sonication. The uniform dispersion of surfactant-treated MWCNTs in the PSN composites and the PNN composites contributed to the reinforcing mechanism in those composites. However, for the PN composites with raw MWCNTs, the MWCNTs were agglomerated due to the strong van der Waals forces among them. This agglomeration of MWCNTs was verified from the SEM images in Figure 5. The big agglomerations were obviously present in the PN composites while the PCN2, the PSN composites and PNN composites, showed no or little agglomerations. The aggregations of raw MWCNTs reduce the total surface area of the nanotubes, which interrupts the stress transfer from the polymer matrix to nanofillers.⁴³ Moreover, the PNN composites showed a higher tensile strength than the PSN composites. This phenomenon can be explained by two aspects: (1) the interactions among the components in the composite and (2) the dispersion state of MWCNTs with different surfactants. NaDDBS has a stronger interaction with MWCNT surface and a better ability to disperse MWCNTs compared to SDS due to its headgroup and longer alkyl chain.³⁴ As a result, the overall mechanical performance of the PNN composites could be significantly improved.

TABLE IV
Electrical Conductivities of Pure PP, PN, PSN, and PNN Composites

| Sample code | Pure PP | PN5 | PN10 | PSN5 | PSN10 | PNN5 | PNN10 |
|---------------------|---------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| Vol % MWCNT | 0 | 3.8 | 7.6 | 3.8 | 7.6 | 3.8 | 7.6 |
| Conductivity (S/cm) | 1×10^{-16} | 4.5×10^{-7} | 2.1×10^{-6} | 2.4×10^{-6} | 6.7×10^{-4} | 2.6×10^{-6} | 6.9×10^{-4} |

The densities of PP and MWCNTs were taken as 0.9 and 1.2 g/cm³, respectively.

Figure 7(c) shows the elongation at break for MWCNT/PP composites, SDS-treated MWCNT/PP composites, and NaDDBS-treated MWCNT/PP composites. From Figure 7(c), it is observed that the elongation at break for the pure PP decreased from 168 to 18% for PN2, 21% for PSN2, and 27% for PNN2, respectively, only at 2 wt % of MWCNT loading. Notably, the elongation at break dropped very much for all composite samples after the addition of MWCNTs into the PP matrix. These results indicate that the MWCNT/PP composites are harder but more brittle than PP. This is because the MWCNTs could act as defects in the composites, which reduced the homogeneity and continuity of the matrix PP. Compared to the PN composites, PSN and PNN composites have the slightly higher values of elongation at break. This is because the elongation at break of MWCNT/PP composites strongly depends on the dispersion state of MWCNTs in the PP matrix and the compatibility between MWCNTs and PP chains.²⁰ For the PNN composites, for example, the better dispersion of MWCNTs and the better compatibility between the NaDDBS-treated MWCNTs and PP chains resulted in the highest elongation at break among all the composites studied at the same MWCNT loading.

Electrical conductivities of MWCNT/PP composites enhanced by different types of surfactants

As carbon nanotubes (CNT) exhibit the high aspect ratio and high conductivity, they can be the excellent candidate for the fabrication of conductive composites. The electrical conductivity of the multiwalled CNTs/polypropylene (MWCNT/PP) composites as a function of MWCNT loading is shown in Table IV. The electrical conductivity of pure PP is 10^{-16} S/cm.⁴⁴ The composite with 5 wt % raw MWCNTs showed the electrical conductivity of 4.5×10^{-7} S/cm. The conductivity of the composites increased with increasing MWCNT content and the electrical conductivity of the composite with 10 wt % raw MWCNTs was increased to 2.09×10^{-6} S/cm. At low contents, conducting fillers were dispersed as isolated clusters within the polymeric matrix. Above the percolation threshold, individual fillers tended to link together to form conductive networks. This led to significant increase in electrical conductivity of the composite.

The uniform dispersion of surfactant-treated MWCNTs in the composites resulted in the higher electrical conductivity than the composites with raw MWCNTs. The electrical conductivity of 2.4×10^{-6} S/cm at 5 wt % of MWCNTs and that of 6.7×10^{-4} S/cm at 10 wt % MWCNT, respectively, were achieved in the presence of SDS in the composites. Therefore, it is obviously found that the incorpora-

tion of a surfactant with MWCNTs played an important role in the homogeneous dispersion of MWCNTs in a polymer matrix so as to allow conductive networks to be formed more easily. For the composites filled with NaDDBS-treated MWCNTs, the electrical conductivity at 5 and 10 wt % of MWCNTs were 2.6×10^{-6} and 6.9×10^{-4} S/cm, respectively. From these results, it is found that the electrical conductivities of NaDDBS-MWCNT/PP composites do not differ from SDS-MWCNT/PP composites at the same loading of MWCNTs. Thus, it can be concluded that the surfactant molecules could not contribute directly to the electrical properties of the composites although they could help MWCNTs to disperse in the PP matrix.

CONCLUSIONS

In this work, we have studied the properties of PP composites filled with different types of MWCNTs. The morphological, rheological, thermal, crystalline, mechanical, and electrical properties of PP nanocomposites with raw MWCNTs, SDS-treated MWCNTs, and NaDDBS-treated MWCNTs have been examined carefully. The effects of two surfactants, SDS and NaDDBS, on the properties of MWCNT/PP composites have been reported. The surfactant-treated MWCNTs resulted in the improvement in their state of dispersion in the polymer matrix and largely enhanced the mechanical and electrical properties of the composites. Overall, NaDDBS showed the stronger effects on PP than SDS. It is confirmed that the dispersion of the MWCNTs in PP and the interfacial interactions among MWCNTs, surfactant and PP matrix are the key factors that determine the overall performance of a MWCNT/polymer composite.

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