Facile Way To Disperse Single-Walled Carbon Nanotubes Using a Noncovalent Method and Their Reinforcing Effect in Poly(methyl methacrylate) Composites

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ABSTRACT: In this work, a noncovalent method was used to functionalize and thereby disperse single-walled carbon nanotubes (SWCNTs) in dimethylformamide with poly[methyl methacrylate-*co*-(fluorescein *O*-acrylate)] as a surfactant, and then the resultant poly(methyl methacrylate) (PMMA)-based nanocomposites were fabricated via solution casting. The dispersion level of carbon nanotubes in the solvent was investigated by means of scanning electron microscopy and atomic force microscopy. The results showed that carbon nanotubes were well wrapped by the surfactant, and small carbon nanotube bundles several nanometers or less in diameter and several micrometers in length were obtained. Both scanning electron microscopy and transmission electron microscopy confirmed the uniform dispersion of SWCNTs in the PMMA matrix. The mechanical properties of the composites were determined with a universal tension tester. The PMMA composite containing 2 wt % SWCNTs showed improved tensile properties versus neat PMMA, showing 56 and 30% enhancements of the tensile modulus and tensile stress, respectively. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3414–3419, 2009

Key words: composites; mechanical properties; stress; synthesis

INTRODUCTION

Since carbon nanotubes (CNTs) were discovered in 1991,[1] extensive research has been focused on using their remarkable characteristics (high aspect ratios, excellent mechanical strength,[2] and good electrical and thermal conductivity[3]) to fabricate various high-performance polymeric composites. However, great challenges have been encountered in preparing such materials. Both the large surface area and strong van der Waal forces[4,5] between CNTs lead to great difficulties in their uniform dispersion in a polymeric matrix. As a result, the predicted properties of CNTs usually fail to be fully reached in polymer composites.[6–8]

To exploit their pristine properties, great efforts have been made to debundle and disperse CNTs in polymeric matrices. Generally, these efforts can be summarized into two categories. One is covalent side-wall functionalization,[9–17] and the other is noncovalent wrapping of nanotubes.[18–28] For the former one, functional groups such as hydroxyl, carboxyl, and amine groups are often used to functionalize CNTs.[9,10,14] At the same time, other chemicals with high reactivity, including fluorine, nitrenes, and aryl-diazonium,[16,17] have also been employed to transform the hydrophobic surfaces of CNTs into hydrophilic ones to improve the dispersion of CNTs in the polymeric matrix. Although great progress has been achieved in fabricating mechanically strong composites, this method tends to alter, or even destroy, the nanotubes' desirable properties, such as their electronic properties and thermal conductivity. That is, it is difficult to preserve the nanotubes' pristine properties with covalent functionalization.

Noncovalent functionalization of nanotubes allows us tailor their properties, preserving almost all the original characteristics of CNTs, including the sp² nanotube structure and electronic properties, which are very significant for CNTs to be used as nanowires,[29] field-effect transistors,[30] and nanoscale electronic devices.[31] Therefore, many surfactants such as sodium dodecyl sulfate,[24,26] sodium dodecylbenzene sulfonate,[26] deoxyribonucleic acid,[19] and synthetic conjugated polymers[21,22] have been used to improve the dispersion of CNTs and enhance the electronic and thermal properties of the resulting nanocomposites. However, this method has rarely been used to improve the mechanical properties of polymer composites. Its potential in this field is not very clear because the interfacial interactions between nanotubes and polymer matrices are among the most important factors influencing the exertion of nanotubes' excellent mechanical properties. Despite this, several

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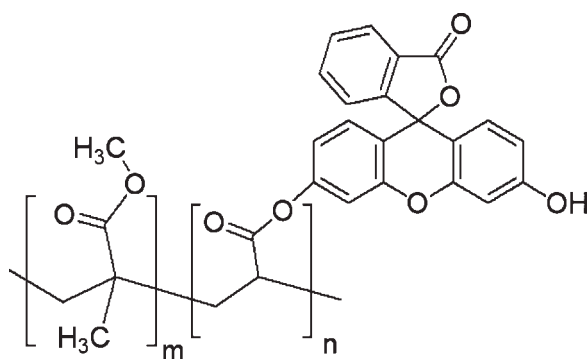
Figure 1 Chemical structure of PMMAFA.

attempts have been made to fabricate reinforced polymer composites with the aforementioned method.[18,20,25,32–34] For example, Chen et al.[18] fabricated a series of Parmax composites reinforced by noncovalently functionalized single-walled carbon nanotubes (SWCNTs), and remarkable enhancements in both the mechanical and electronic properties of the composites were achieved; Zhang et al.[33] also reported that the addition of SWCNTs treated with poly(vinyl pyrrolidone) and sodium dodecyl sulfate obviously improved the tensile strength and modulus of the poly(vinyl alcohol) matrix.

Poly(methyl methacrylate) (PMMA) is one of the most important commercialized polymeric materials and is widely used in architectural and optical fields. Up to now, there has been a lot of research focused on the fabrication of PMMA/CNT composites.[14,25,35–37] It has been found that the storage modulus of a PMMA matrix at room temperature is doubled by the addition of CNTs.[14] Clayton et al.[35] prepared PMMA/CNT nanomaterials via *in situ* bulk polymerization, and transparent PMMA/CNT composites with increased dielectric constants were obtained. However, to the best of our knowledge, no research work concerning the fabrication of high-performance PMMA composites containing noncovalent functionalized CNTs has been reported.

As a surfactant, poly[methyl methacrylate-*co*-(fluorescein *O*-acrylate)] (PMMAFA) has a chemical structure similar to that of PMMA (Fig. 1). It is thought that the aromatic rings in the side chains of PMMAFA could produce affinities with SWCNTs via strong π–π interactions and that the main chain of PMMAFA could increase the compatibility with the PMMA matrix. Therefore, such an amphiphilic copolymer could increase both the dispersion of CNTs and the interfacial interaction between the nanotubes and PMMA matrix. Inspired by this assumption, we fabricated PMMA composites reinforced by PMMAFA-wrapped SWCNTs via solution casting. The mechanical properties of the resultant composites and morphologies of SWCNTs dispersed in the PMMA matrix were inves-

tigated with a universal tension tester and scanning electron microscopy (SEM), respectively.

EXPERIMENTAL

Materials

PMMA with a weight-average molecular weight of 360,000 g/mol, PMMAFA, dimethylformamide (DMF), and hydrochloric acid were all purchased from Sigma–Aldrich (Singapore) and used directly without any purification. SWCNTs with a purity higher than 95% were purchased from the Chengdu Institute of Organic Chemistry of the Chinese Academy of Sciences. These SWCNTs, produced by catalytic chemical vapor deposition, had diameters of about 1–2 nm and lengths of about 5–10 μm. Before use, the pristine SWCNTs (p-SWCNTs) were purified with the following steps: they were heated at 380°C for 4 h in air, and this was followed by refluxing in the concentrated hydrochloric acid for 24 h. The obtained SWCNTs were washed with water several times and then were dried in a vacuum oven at 70°C to obtain a constant weight.

Fabrication of the PMMA composites

The procedure to disperse SWCNTs in DMF was as follows: 20 mg of SWCNTs was sonicated in 10 mL of DMF for 5 min with a high-power cup-horn ultrasonic processor (60 W; Vibra-Cell, Sonics, USA), and then 15 mg of PMMAFA was added before the solution was shaken vigorously. After that, the solution was sonicated further for another 30 min, and this was followed by 4 h in an ultrasonicator bath (S30H Elmasonic, Elma). The resulting suspension was centrifuged at 14,000 rpm for 50 min to remove the large particles, and the weight of dry sediments was about 5 mg. A black and stable solution containing 1.5 mg/mL SWCNTs was obtained.

For the fabrication of the PMMA composites, 1.5 g of PMMA was completely dissolved in 10 mL of DMF. Then, 10 mL of the SWCNT solution was added before the mixture was sonicated in an ultrasonicator bath for 15 min. After that, the solution was poured into a mold. The mold was heated at 100°C in a vacuum oven for 3 h to remove the solvent, and a black sheet of 50 mm × 50 mm was obtained. Before mechanical property testing, the large sheet was cut into a rectangle with dimensions of 50 mm × 5 mm and heated in the oven at 80°C for another 3 h. The samples fabricated with these procedures were designated PMMA0, PMMA1, PMMA2, and p-PMMA2. The number represents the concentration of SWCNTs in the composite. For example, PMMA1 represents a sample with an SWCNT concentration of 1 wt %. In addition, p-PMMA2 represents a sample with a

p-SWCNT concentration of 2 wt % without any surfactant.

Measurements

SEM measurements were carried out on a JEOL (Japan) JSM-6700F field-emission scanning electron microscope. Samples of the composites were etched by reactive ion etching with argon as the reactive gas to expose SWCNTs on the surfaces of the composites. The etching was performed with a March PX-500 cleaning system at 40 W with a 10-sccm volumetric flow rate for 160 s. An atomic force microscopy (AFM) image was obtained with a Shimazdu SPM 9500 J2 atomic force microscope. The SWCNT sample was spread on freshly cleaved mica via spin casting from a DMF solution. The scan was always at a constant rate of 1.5 Hz, and the scan size was 5.5 μm × 5.5 μm. The optical images of the distribution of SWCNTs in the PMMA matrix were observed and recorded with a digital camera (Axiovert 200M, Zeiss). Transmission electron microscopy (TEM) micrographs were obtained with a JEOL 100CX with an acceleration voltage of 100 kV. The tensile testing was carried out on a universal tester (model 5543, Instron). A 10-N load cell was used to test the samples in uniaxial tension. The gauge length was 20 mm, and the crosshead speed was 2 mm/min. To ensure data accuracy and repeatability, at least five samples were tested under each condition.

RESULTS AND DISCUSSION

Usually, pristine CNTs tend to severely bundle because of strong van der Waals forces; this leads to their poor dispersion in the polymeric matrix, and the predicted properties are not reached. Therefore, how to debundle and disperse nanotubes in the polymeric matrix is critical in achieving high-performance composites. Although the covalent modification of CNTs allows us to obtain high-strength polymeric composites successfully, this method always weakens the excellent electronic and thermal conductivity of nanotubes. The noncovalent method can help us to preserve nearly all of their original characteristics, but how to improve the dispersion of nanotubes in the polymeric matrix is a great challenge. Figure 2 shows SEM images of p-SWCNTs and SWCNTs treated with PMMAFA. Obviously, the p-SWCNTs were in the form of tight networks of entangled, randomly oriented groups [Fig. 2(a)]. However, after being ultrasonicated and wrapped with PMMAFA, SWCNTs in the form of disentangled, straightened small bundles were obtained. Generally, there are three kinds of mechanisms to explain the load transfer from the polymeric matrix to the rigid nanotubes,[38] including van der Waals forces, physical
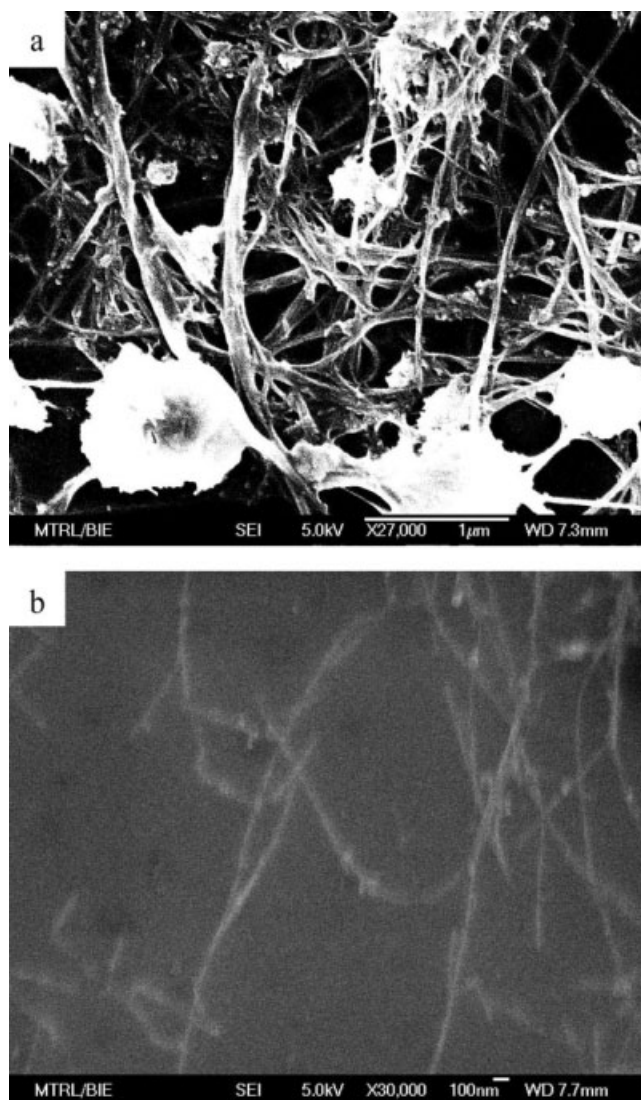

Figure 2 SEM images of (a) p-SWCNTs and (b) wrapped SWCNTs.

intertwists, and covalent and noncovalent bonds (e.g., hydrogen bonding) between the matrix and CNTs. In improving the dispersion and maximizing the load transfer from the polymeric matrix to the CNTs and thereby strengthening the polymeric matrix, the length of the CNTs is one of the crucial factors. If the nanotubes are too long, it will be hard to disperse them in the matrix uniformly. However, if the nanotubes become too short, their maximum loading level will be compromised. On the basis of the results from Dalton et al.[39] and Mcintosh et al.,[40] CNTs with a length of several micrometers are crucial. From Figure 2(b), it was easy for us to notice that the length of SWCNTs obtained by our method ranged from 0.3 to 2 μm, and the ones with lengths of 1–2 μm were dominant. Compared with the results reported in the literature, our results are similar to those of former studies in which the CNTs
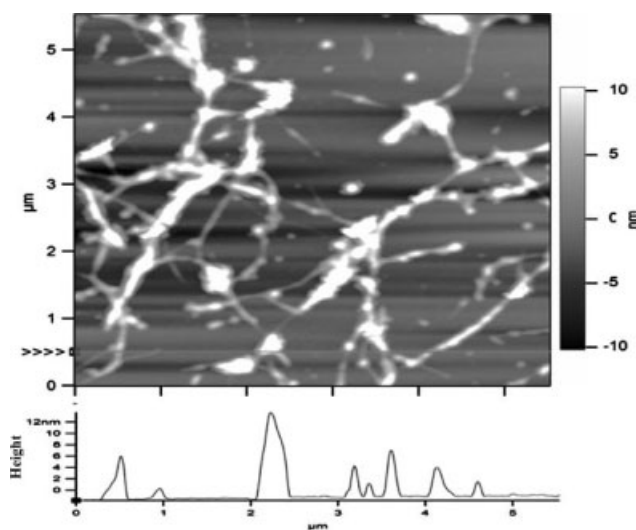
Figure 3 AFM image of wrapped SWCNTs.

were functionalized by a noncovalent method.[18,19] Apparently, the well-dispersed SWCNTs were suitable for fabricating high-performance nanocomposites.

To reveal the dispersion of treated SWCNTs further, an AFM image is shown in Figure 3. The surfactants wrapped on the SWCNTs can be clearly seen, and they correspond to the sharp light pots attached to their side walls. Their diameters ranged from 2 nm to several nanometers (obtained from the AFM height analysis), and their length was several micrometers; this matched the initial geometry of the CNTs when they were added to the polymer matrix. At the same time, the network structures formed by wrapped SWCNTs could obviously be seen, as also reported in the literature.[19,41] Maybe the network structures could contribute to the reinforcement of the PMMA matrix because the load transfer from the polymeric matrix to the rigid CNTs plays an important role in strengthening the CNT composites. The network structures prevent the slippage of SWCNTs in the matrix. As a result, they can bear more loads instead of just being pulled out from the matrix when force is applied to the composites.

As far as the nanocomposites are concerned, the evaluation of the dispersion of nanoparticles in the matrix is the most important thing. A visual image is a rude but easy and widely used way to characterize the dispersion of CNTs in the polymer matrix.[32,42] Figure 4 shows optical images of p-PMMA2 and PMMA2 samples. In p-PMMA2 [Fig. 4(a)], the SWCNTs were poorly dispersed, and large agglomerations were easily seen. However, in PMMA2 [Fig. 4(b)], the SWCNTs were uniformly dispersed, and no SWCNT clusters were visible at the micrometer scale. This might indicate that an effective steric

obstruction of the aggregation and improved compatibility with the matrix were obtained when the surfactant was added to SWCNTs.

Besides the characterization on a macroscopic scale, the dispersion of CNTs on a microscopic scale is more important. Figure 5 shows an SEM image of the PMMA2 surface after its treatment with plasma. In this SEM image [Fig. 5(a)], the mesh structure formed by SWCNTs in the PMMA matrix is obvious. A similar structure is shown in Figure 3. In a general sense, this network is beneficial for strengthening the polymeric matrix. On the basis of Figure 5(b), a lot of polymers attached to the surface of SWCNTs can be seen. In comparison with Figure 3, not only did more polymers cling to SWCNTs, but they also spread on the SWCNT walls more homogeneously. This was possibly due to the fact that some of the PMMA chains twisted together PMMAFA also
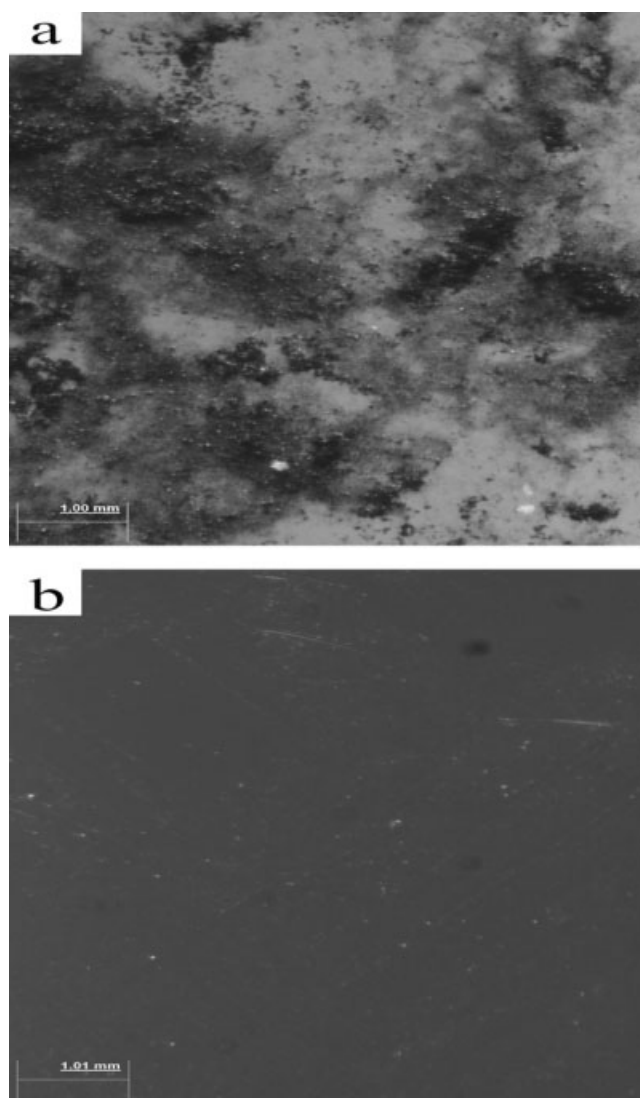

Figure 4 Optical images of different composites: (a) p-PMMA2 and (b) PMMA2.
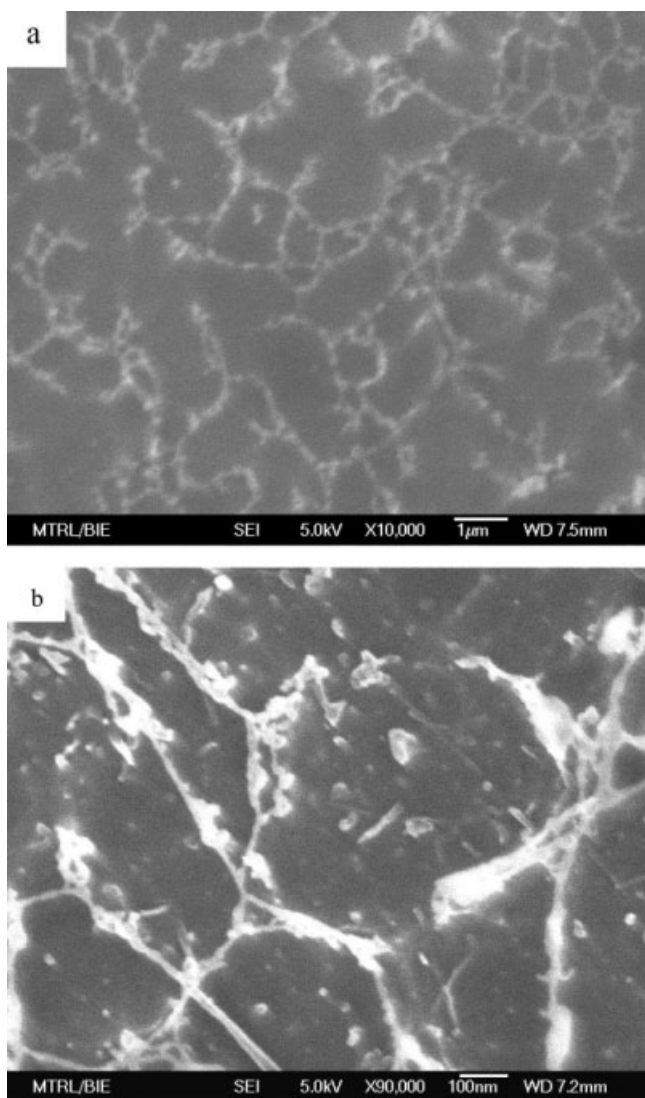
Figure 5 SEM images of the surface of PMMA2 after it was treated with plasma: (a) ×10,000 and (b) ×90,000.

Figure 6 TEM image of SWCNTs dispersed in the PMMA matrix.

increased when modified CNTs were added. The tensile stress of PMMA0 was 49 MPa. It was increased to 58 MPa for PMMA1 (an increment of 17.6%) and 65 MPa for PMMA2 (an increment of 30%). The tensile modulus was increased from 1580 MPa for PMMA0 to 1910 MPa for PMMA1 (increased 20%) and 2460 MPa for PMMA2 (increased 56%). However, comparing the tensile properties of PMMA0 and PMMA2 with those of p-PMMA2, we found that the tensile stress of p-PMMA2 was almost the same as that of PMMA0 (only an increment of 6%) and much lower than that of PMMA2 (a reduction of 20%). Tensile properties of CNT/polymer composites are mostly dependent on the dispersion of CNTs and the surface adhesion between the CNTs and polymer. On the basis of our results for the mechanical properties, it can

attached to the surface of SWCNTs synchronously, and this resulted in the better compatibility of SWCNTs with the PMMA matrix.

Figure 6 presents a TEM image of wrapped SWCNTs dispersed in the PMMA matrix. This TEM microphotograph shows that the diameter of the SWCNTs lay between 5 and 10 nm, and this was similar to the results from the height analysis of AFM in Figure 3 and confirmed the good dispersion of SWCNTs in the polymeric matrix again.

It is well known that CNTs have excellent mechanical properties such as high strength and modulus. A small amount of CNTs uniformly dispersed in the polymeric matrix can increase its mechanical properties significantly. Figure 7 shows representative stress–strain curves for PMMA0, p-PMMA2, PMMA1, and PMMA2. Their tensile stress, tensile modulus, and elongation at break are summarized in Table I. The tensile modulus and stress of PMMA composites
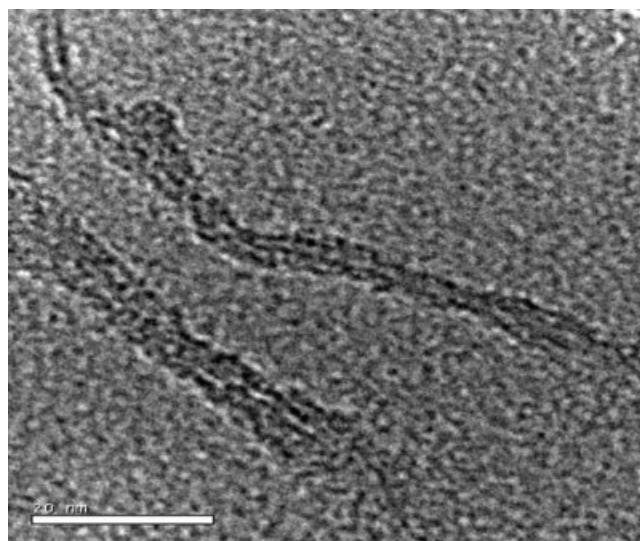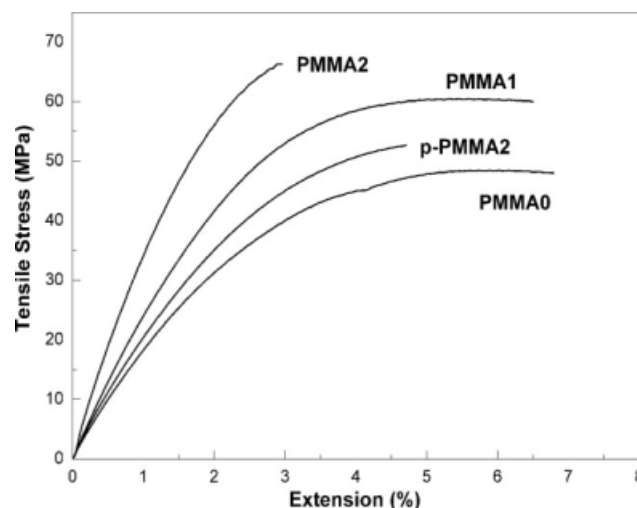

Figure 7 Typical stress–strain curves for PMMA0, p-PMMA2, PMMA1, and PMMA2.

TABLE I
Tensile Properties of PMMA0, p-PMMA2, PMMA1, and PMMA2

Sample name	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation (%)
PMMA0	1580 ± 90	49 ± 2	6.2 ± 0.4
p-PMMA2	1680 ± 110	54 ± 3	4.7 ± 0.2
PMMA1	1910 ± 60	58 ± 3	5.5 ± 0.5
PMMA2	2460 ± 170	65 ± 4	3.1 ± 0.4

The data in parentheses are the relative errors.

be concluded that PMMAFA was a good surfactant for dispersing CNTs in the PMMA matrix and increased the adhesive force between them. These in turn promoted load transfer from the PMMA matrix to the rigid CNTs and thus enhanced the strength of the composite.

CONCLUSIONS

In this study, PMMAFA, whose chemical structure is similar to that of PMMA, was employed as a surfactant to disperse and functionalize SWCNTs by a non-covalent method, and then the resulting PMMA composites were fabricated. On the basis of the results from SEM and AFM, the SWCNTs were well wrapped by PMMAFA and uniformly dispersed in DMF just by sonication. The diameter of SWCNTs dispersed in DMF ranged from 2 nm to several nanometers, and their length was several micrometers. The networks formed by well-dispersed SWCNTs were observed in the PMMA matrix. They were helpful in strengthening the composites further. The addition of functionalized SWCNTs improved the tensile properties of the PMMA matrix significantly. When the content of SWCNTs was increased up to 2.0 wt %, the composite exhibited a tensile modulus of 2460 MPa (56% higher than that of neat PMMA) and a tensile strength of 65 MPa (30% higher than that of neat PMMA). All the results demonstrated that PMMAFA is a good surfactant for dispersing SWCNTs and then fabricating high-strength PMMA-based composites. The noncovalent functionalization of CNTs was proved to be an effective way of strengthening the mechanical properties of CNT composites.

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