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Controlled nanostructure and high loading of single-walled carbon nanotubes reinforced polycarbonate composite

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Abstract
This paper presents an effective technique to fabricate thermoplastic nanocomposites with high loading of well-dispersed single-walled carbon nanotubes (SWNTs). SWNT membranes were made from a multi-step dispersion and filtration method, and then impregnated with polycarbonate solution to make thermoplastic nanocomposites. High loading of nanotubes was achieved by controlling the viscosity of polycarbonate solution. SEM and AFM characterization results revealed the controlled nanostructure in the resultant nanocomposites. Dynamic mechanical property tests indicated that the storage modulus of the resulting nanocomposites at 20 wt% nanotubes loading was improved by a factor of 3.4 compared with neat polycarbonate material. These results suggest the developed approach is an effective way to fabricate thermoplastic nanocomposites with good dispersion and high SWNT loading.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Carbon nanotubes (CNTs) are one of the strongest and stiffest materials, having exceptional tensile strength and modulus but a low density [1, 2]. CNTs also possess superior thermal and electrical properties [2]. Lightweight multifunctional nanocomposites can be produced with outstanding strength, stiffness and electric conductivity by effectively incorporating CNTs into matrix materials. However, effective utilization of nanotubes in composites applications is dependent on the ability to disperse nanotubes uniformly throughout the matrix. Nanocomposites produced by conventional methods, such as direct mixing, melt blending or solution casting, usually fail to yield significant improvements in composite performance because these methods cannot solve several manufacturing problems, including non-uniform CNTs dispersion, inadequate tube loading and lack of nanotube alignment.

Polycarbonate (PC) is a high molecular-weight, amorphous engineering thermoplastic that demonstrates exceptionally high impact strength over a wide temperature range. PC is characterized by an excellent combination of toughness, heat resistance, flame resistance and dimensional stability, making PC advantageous for producing high performance CNTs/PC nanocomposites. Researchers have fabricated CNTs/PC nanocomposites via melt processing and solution casting [3–6]. However, PC's high melting temperature and viscosity makes fabricating high-quality CNTs/PC composites through injection or extrusion molding difficult. The concomitant viscosity problem with increasing tube loading also presents a challenge in both melting processing and solution casting, especially for fabricating high-loading nanotubes composites. We have demonstrated a resin-infiltration technique for fabricating high-loading epoxy composites [7]. Now we extend this technique to the nanotubes reinforced thermoplastic composites. This paper reports a method of fabricating

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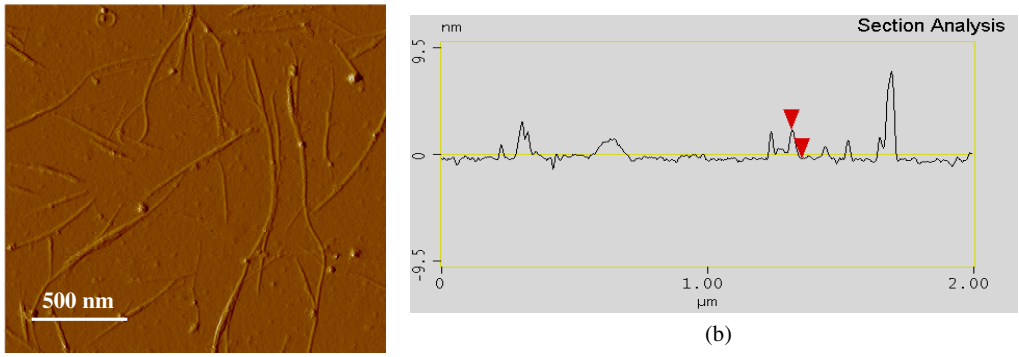


(a) (b)

Figure 1. (a) AFM image of dispersed nanotubes in aqueous suspension. (b) Diameter measurement through section analysis.

CNTs/PC nanocomposites with controlled nanostructure and high loading by using preformed nanotube membrane materials.

2. Experiments

Single-walled carbon nanotubes (SWNTs) were used in this study, which were P-grade SWNT products with a residual metal content of 3–12 wt%, produced by Carbon Nanotechnologies Inc. The SWNTs were first made into buckypapers, which are thin films of preformed nanotube networks [8]. Aqueous suspensions were prepared by mixing the SWNTs with suitable surfactant [9, 10] and distilled water under ultrasonic power 85 W m^{-2} for about 60 min. These nanotube suspensions, which can remain stable for more than two months, were pumped through a nylon filter membrane. After filtration, the SWNT membrane or buckypaper was peeled from the filter membrane. Finally, the buckypaper was thoroughly washed with isopropanol to remove the adsorbed surfactant, resulting in a thin membrane with 10–25 μm thickness.

PC solution was prepared by dissolving PC granules in chloroform (Fisher Scientific Inc. A.C.S. grade) at room temperature through intense stirring. After the solution was stirred for several hours (the stirring time is dependent on the PC concentration), the PC particles were completely dissolved in the chloroform, resulting in a clear solution. Before buckypaper impregnation, the permeability of PC solution through the buckypaper in the thickness direction (z direction) was measured to predict the PC solution infiltration time. Distilled water was used as a testing fluid. Distilled water flowed through the buckypaper in the thickness direction under 14.7 psi vacuum pressure. Four parameters—flow rate, vacuum pressure, buckypaper thickness and surface area—were recorded to calculate the buckypaper's z-direction permeability. The PC infiltration was performed under the same conditions of the permeability tests, except substituting PC solution for distilled water. PC used in the research was LEXAN 103–112, purchased from GE Plastics Inc. After infiltration, the impregnated buckypaper was air dried for 12 h and subsequently annealed in a vacuum oven for 10 h to remove any residual solvent. A stack of layered PC-impregnated buckypaper (6 layers) was hot-pressed into nanocomposite films at 580 °F for 10 min and then cooled down to room temperature (Hot press: Carver Laboratory Equipment, Hydraulic Unit Model # 3925, Carver Inc.). Hot-pressing was conducted in air, and the thickness of the resultant composite was about 0.7 mm, while both length and width were 50.8 mm.

The nanostructures of buckypaper and SWNTs/PC nanocomposites were characterized with the scanning electron microscope (SEM, JSM-7401F) and the atomic force microscope (AFM, Multimode SPM, Nanoscope IIIa, Veeco Inc.). The mechanical properties of the nanocomposites were measured with a dynamic mechanical analyser (DMA2980, TA Instrument Inc.) using the tensile (film) mode with 5 °C min^{-1} ramp rate and 1 Hz single frequency. The temperature range was from 25 to 300 °C.

3. Result and discussions

3.1. SWNT dispersion

The dispersion quality of SWNTs in the suspension was examined by the AFM. A small drop of suspension was spread on a silicon wafer for AFM examination. Figure 1(a) shows the AFM image of the dispersed nanotubes. Diameter measurements of SWNTs from AFM were based on height profiles through section analysis, as shown in figure 1(b). SWNTs length was quantified by the commercial imaging processing software, SIMAGIS. This software package has the capability of automatically analysing multiple AFM images to measure length information of SWNTs and their ropes [11]. Figure 2(a) reveals the results of the measured diameters. Diameters of nanotube ropes were mostly less than 6 nm, while a small fraction fell in the range of 6–14 nm. The average diameter of SWNTs and ropes was about 5.6 nm. Figure 2(b) shows the length measurement results, indicating that small ropes were an average of 547 nm long.

As shown in figure 3(a), the buckypaper has a certain strength, and it is flexible enough to facilitate handling in the experiments [12]. Figure 3(b) shows an SEM image of a buckypaper sample, indicating that the nanotube network consists of continuous individual SWNTs or ropes self-assembled by van der Waals force. Figure 4 shows the SIMAGIS analysis results of the rope size measurements, which were based on the horizontal profiles. In the buckypaper, the average diameter of all the SWNT ropes was 13.5 nm. The

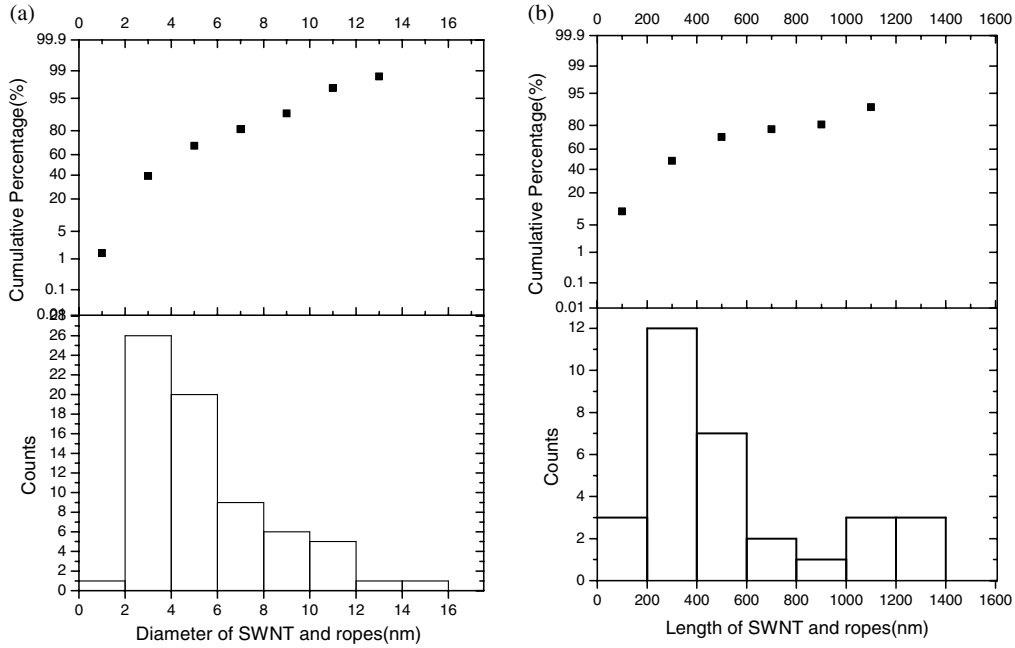


Figure 2. (a) Diameter distribution of nanotube ropes. (b) Length distribution of nanotube ropes.

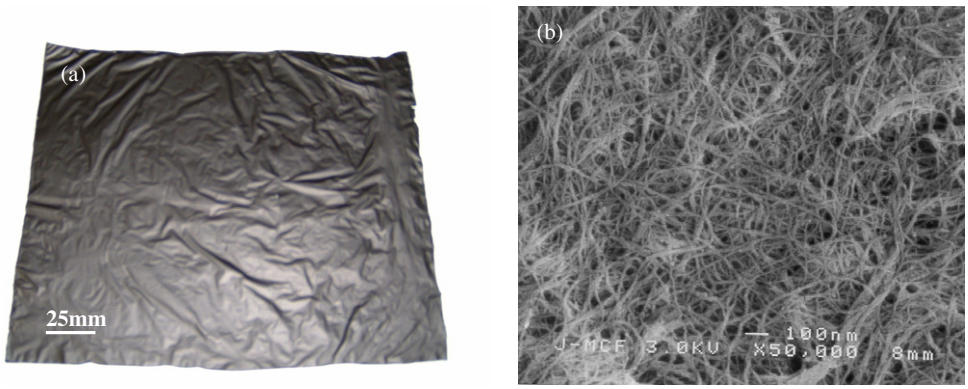


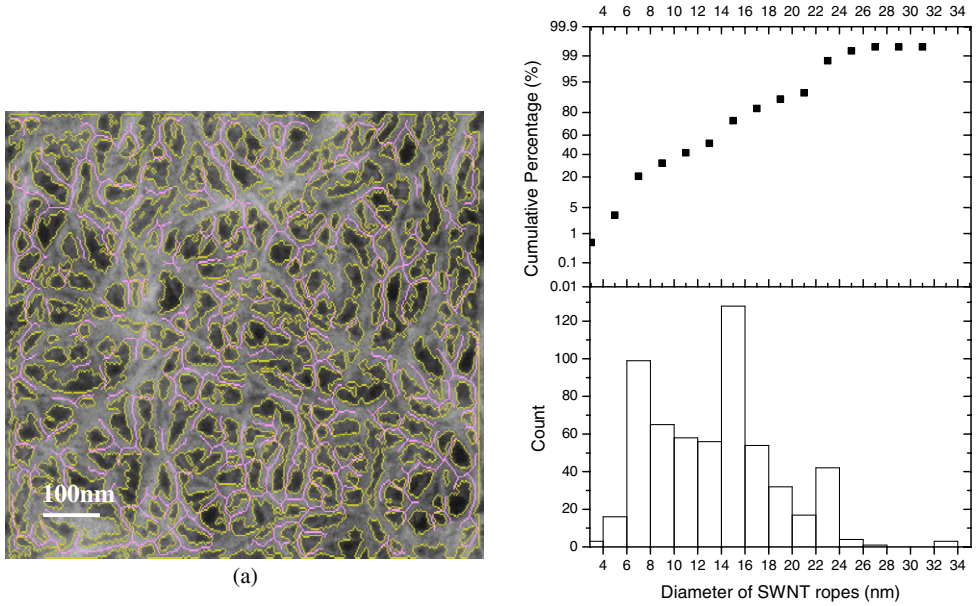
Figure 3. SWNT buckypaper: (a) buckypaper sample; (b) SEM image of random buckypaper.

diameter distribution of SWNT ropes seems to shift slightly to the right as compared to that of the SWNT ropes in the aqueous suspension measured by AFM sectional analysis. This difference seems to be from the measurement method by SIMAGIS, since this software measures the diameters according to the horizontal profiles. In spite of this change, almost 80% of SWNT ropes showed small diameters less than 16 nm, indicating that the buckypaper provides an effective way to produce well-dispersed SWNTs in the bulk samples.

3.2. PC solution infiltration

Currently it is difficult to fabricate well-dispersed, high-loading thermoplastic nanocomposites through a conventional melting process due to high viscosity. This paper has presented a method involving buckypaper impregnation (solution process) to overcome the manufacturing difficulties of the melting process. The buckypaper impregnation method, or solution process, provides the capability to realize the high-loading composite with controlled nanostructure. The buckypaper pore size was measured through the absorption of nitrogen gas by porosimetry (TriStar 3000, Micromeritics Instrument Corporation). The test results indicated the pore diameters of buckypaper range from 2 to 311 nm, and about 80% are above 50 nm. Since the porous structures of the buckypaper are at nanoscale, the comparability between buckypaper pore size and the dimension of the polycarbonate molecules must be checked. The polycarbonate resin used in this study had a weight-average molar mass (M_W) of about 36 000 g mol^{-1} or about 140 repeat units in each PC molecule. Figure 5 shows the molecular structure of PC repeat unit using molecular dynamic (MD) simulation. The MD simulation was carried out with Materials Studio using the COMPASS force field by considering one molecule in a near-infinite dilution limit [13]. The size of PC molecule was acquired at the simulation of 200 ps, indicating that a single polycarbonate chain is close to the dimension of 9.7 nm × 8.6 nm × 0.9 nm, which is small enough to penetrate the buckypaper pores.

For an in-plane wetting of buckypapers, the driving force primarily comes from surface tension. Due to nanoscale pore



(a) (b)

Figure 4. (a) Smart identifying SWNT ropes of buckypaper SEM image in SIMAGIS software. (b) Rope diameter distribution of the buckypaper.

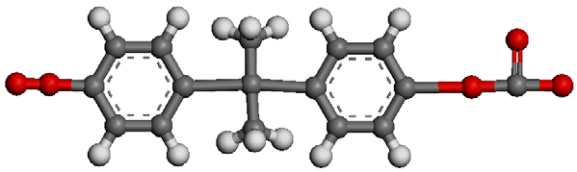


Figure 5. Molecular structure of polycarbonate repeat unit.

size, the in-plane permeability of the buckypapers is very small, and therefore impregnating buckypaper through in-plane wetting is extremely difficult [14]. Therefore, a through-thickness infiltration system was designed to impregnate polycarbonate solution into the buckypapers. Through thickness (z direction) flow behaviour of the buckypaper can be modelled with one-dimensional Darcy's law. The z-direction permeability K_z (saturated permeability) was calculated using the following equation derived from Darcy's law [12]:

$$K_z = \frac{Q\eta L}{AP} \tag{1}$$

where Q is the flow rate; η is the viscosity of fluid; L is the thickness of buckypaper; P is the vacuum pressure across buckypaper; A is the surface area of buckypaper.

The results of z-direction permeability test on the resulting buckypaper show the average value of buckypapers' z-direction permeability was about 2×10^{-19} m^2 [12]. On the other hand, infiltration flow rate is the ratio of flow volume to infiltration time, as shown in equation (2):

$$Q = \frac{\Delta V}{\Delta t} = \frac{A\Delta L}{\Delta t} \tag{2}$$

where Q is the flow rate; L is the thickness of buckypaper; A is the surface area of buckypaper; ΔL is the flow distance in the infiltration time of Δt; Δt is the infiltration time; ΔV is the flow volume in the infiltration time of Δt.

Substituting equation (2) into equation (1) results in equation (3) to determine PC infiltration time:

$$\Delta t = \frac{\eta L \Delta L}{K_z P} \tag{3}$$

where η is the viscosity of PC solution; L is the thickness of buckypaper film; P is the vacuum pressure across buckypaper. ΔL is the flow distance in the infiltration time of Δt; K_z is the z-direction permeability.

Integrating equation (3) yields the formulation of the infiltration time:

$$t = \int_0^L \frac{\eta L}{K_z P}\,\mathrm{d}l = \frac{1}{2}\frac{\eta L^2}{K_z P} \tag{4}$$

where η is the viscosity of PC solution; L is the thickness of buckypaper film; P is the vacuum pressure across buckypaper; K_z is the z-direction permeability.

Based on equation (4), infiltration time can be estimated, as shown in figure 6. In the experiments, the infiltration time was measured by a stopwatch from the switching-on of the pressure till observation of the solution coming out of the buckypaper bottom. Infiltration time can be controlled via PC solution viscosity, as shown in figure 6(a). Furthermore, it was observed that higher solution viscosity yielded higher PC concentration, thus resulting in lower SWNT loading in the final nanocomposites, as shown in figure 6(b). In other words, desired infiltration time and final nanotubes loading of the nanocomposites can be achieved with tailored viscosity of PC solution. For instance, using a viscosity of about 10 cp would allow a short infiltration time and the final nanotubes loading of around 50% in the materials. Hence, this simple technique is effective in achieving high, controlled SWNT concentration and good tube dispersion.

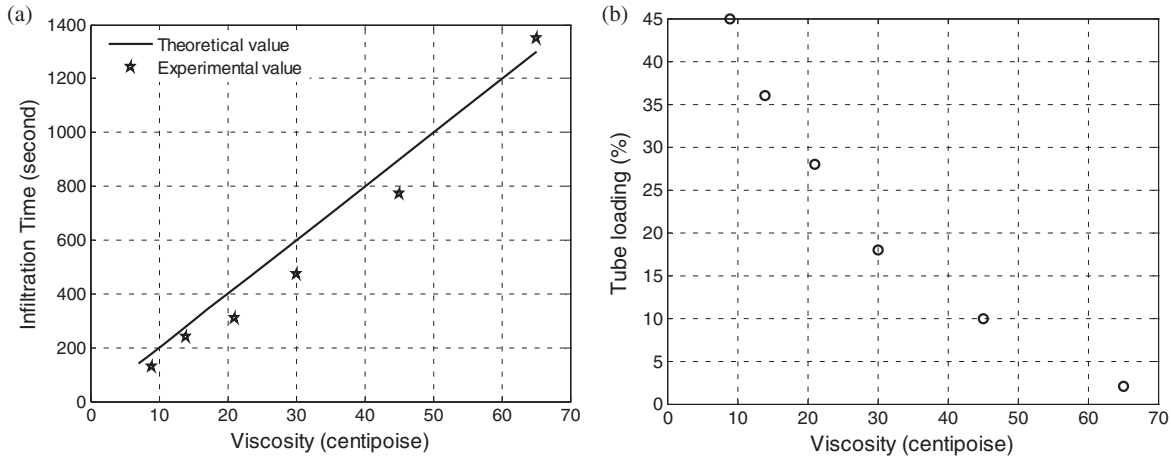


Figure 6. Effect of viscosity on the buckypaper impregnation: (a) infiltration time versus viscosity; (b) tube loading versus viscosity.

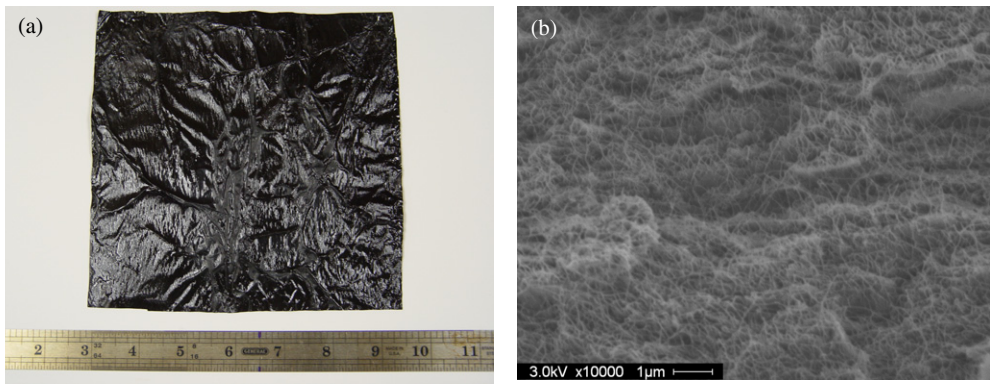


Figure 7. Impregnated buckypaper: (a) macroscopic image of impregnated buckypaper; (b) SEM image of a cross section for the impregnated buckypaper.

Figure 7(a) shows a 6.5″ × 6.5″ dried PC-impregnated buckypaper. The buckypaper surface was thoroughly wetted by polycarbonate. Figure 7(b) shows an SEM image of the cross section of the impregnated buckypaper, which indicates even impregnation throughout and intercalation with nanotubes. Nanotube ropes were homogeneously spread over the polycarbonate, and continuous intercalation networks formed in the resultant composite. Aggregations of nanotubes were not observed. The formative tube networks in the nanocomposite were almost the same as those in the previous impregnated buckypaper and original buckypaper. This indicated that the impregnation of polycarbonate solution through buckypaper yielded controlled nanostructure in the nanocomposite. Since nanocomposite with various nanotube loading can be achieved by adjusting the viscosity of polycarbonate solution, this impregnation technique appears to be an effective way to achieve thermoplastic composites with high-loading of nanotubes.

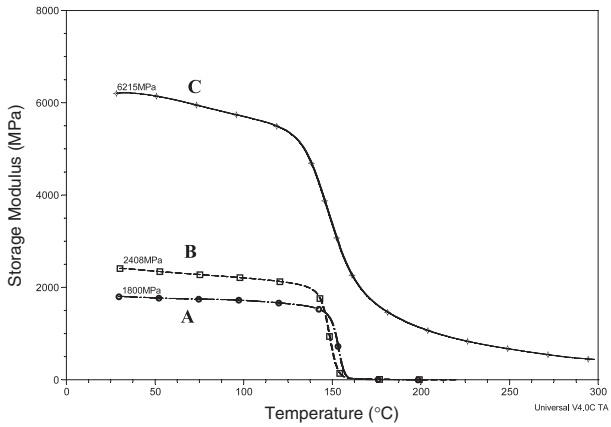


Figure 8. Dynamic mechanical analysis of SWNT reinforced polycarbonate composites: (A) pristine PC, (B) 2 wt% SWNTs/PC composite, (C) 20 wt% SWNT-buckypaper/PC composite.

3.3. Nanostructure and properties of SWNT-buckypaper/PC nanocomposites

The SWNT-buckypaper/PC nanocomposite used for mechanical characterization was fabricated by hot-pressing six layers of PC-impregnated buckypaper in a thickness-controlled flat mold. DMA tests were performed in single-frequency, temperature-ramping mode. Storage modulus indicates the amount of energy stored in the composite as elastic energy, which is highly influenced by the reinforcement mechanical properties, geometric characteristics, reinforcement loading and interfacial bonding between reinforcement and the matrix.

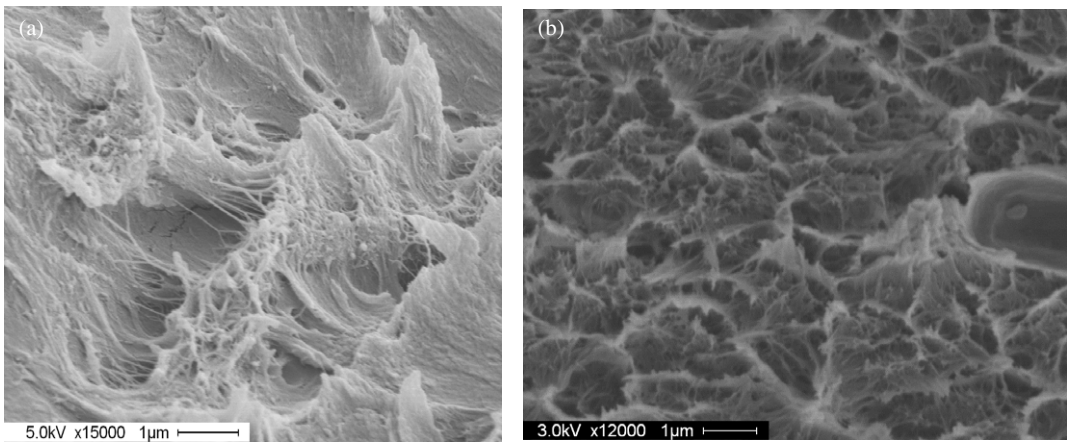


Figure 9. SEM images of SWNTs/PC composite fracture surfaces: (a) 2 wt% SWNTs loading casting sample; (b) 20 wt% SWNT loading buckypaper composite sample.

Table 1. Modulus of CNTs/PC composites.

Approaches	Tubes loading by weight (%)	Storage modulus (GPa)	Referred literature
Buckypaper impregnation	SWNT: 20	6.2	This study
Melting mixing	MWNT: 1.5–15	∼1.0	[15]
Solution casting	SWNT: 0.05–0.25	1.6–2.1	[3]
	Functionalized SWNT: 0.5–2	2.35–2.52	[16]
	MWNT: 5–20	1.1–2.42	[17, 18]

Figure 8 shows the storage modulus of a pristine polycarbonate is 1.8 GPa. Comparatively, the modulus of 2 wt% SWNT reinforced polycarbonate (produced by solution casting method) increased to 2.4 GPa, a factor of 1.3 increment, and the modulus of 20 wt% SWNT-buckypaper reinforced polycarbonate jumped to 6.2 GPa, a factor of 3.4 increment. Obviously, the controlled nanostructure and high loading contributed to the improved mechanical performance in the thermoplastic nanocomposites. Table 1 lists the storage modulus of CNTs reinforced polycarbonate composites prepared from conventional methods in the reported literature. It can be seen that the buckypaper/PC solution infiltration method achieved a higher mechanical property.

The fracture surfaces of the SWNT-buckypaper/PC composites with 20 wt% tube loading were characterized with SEM, as shown in figure 9. The dimpled morphology in the fracture surface indicates that considerable level of localized plastic deformation occurred to prevent formation or coalescence of microvoids, which can potentially lead to crack propagation. This type of dimple fracture suggests that mechanical properties of SWNT-buckypaper/PC composites were enhanced due to the well-dispersed SWNT network.

Theoretical modulus of PC/SWNTs composite was estimated by the Cox–Krench model [11]. Computation results showed that the elastic modulus of nanocomposites was 3.7 GPa for 2 wt% tube loading and 64.25 GPa for 20 wt% loading. These theoretical values are much higher than the experimental measurements. Theoretical calculation may overestimate the modulus by using individual nanotube modulus rather than bundle modulus, which have a much lower modulus [19]. It is very difficult to achieve the individual tube dispersion in the experiments. Another possible major reason of this mismatch may arise from the weak interfacial bonding, a consequence of the smooth and chemically inactive surface of SWNTs. The weak interfacial bonding significantly reduced the efficiency of the load transfer and resulted in low modulus in the experiments. In addition, the low experimental values could also stem from the short SWNT lengths, which were 547 nm on average [20]. Therefore, even though this paper has demonstrated an effective method to fabricate high-loading thermoplastics nanocomposites with controlled nanostructure, much more efforts, such as nanotube functionalization, are needed in order to realize the full potentials of carbon nanotubes in the composite applications.

4. Conclusions

An effective approach was presented to acquire good dispersion and high loading of nanotubes in the fabrication of SWNTs/PC composites, which is very difficult using conventional manufacturing techniques. A controlled nanostructure of SWNTs/PC composite can be achieved through impregnating preformed SWNT networks or buckypaper with PC solution. This method can also be extended to other suitable thermoplastic resins for high nanotube loading nanocomposites. The comparison between experimental value and theoretical prediction indicates that functionalization is necessary to improve load transfer efficiency. In addition, this method also makes it feasible to fabricate aligned nanocomposites if buckypaper is composed of aligned nanotubes.

Acknowledgments

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