INTERFACIAL POLYMER CRYSTALLIZATION IN POLYMER/CARBON NANOTUBE COMPOSITES

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Introduction

Crystallization plays an important role in polymer processing especially for improving interfacial interactions in the composite. There are no other nucleating agents as long and as narrow as carbon nanotubes (CNT) and particularly single-wall carbon nanotubes (SWNT). It is being increasingly recognized that a small quantity of carbon nanotube, particularly well dispersed and exfoliated SWNTs, can affect polymer orientation and crystallization[1-10]. Due to the nano-meter size dimensions of fillers, interface as well as inter-phase play a dominant role in nano-composites. Therefore clear understanding of interfacial interaction is quite important. Interfacial interactions in different nano-composites will differ depending on the surface chemistry of the nanotube (i.e. pristine tube structures, and size and chain length of functional groups). Interfacial polymer behaves differently from the bulk polymer, but it also has the ability to influence bulk nano-composite properties, as well as the physical *POLYMER-NANO* interactions[8]. Good interfacial interaction in the polymer/CNT composite will lead to an increase in load transfer between filler and matrix, improved thermo-mechanical properties, change in polymer thermal shrinkage behavior, as well as enhanced solvent resistance for the polymer[2, 11]. It is for these reasons outlined above that the work described in the paper was performed. This work includes, developing methods to promote extended-chain crystallization of linear polymers in nano-composite fibers; as well as detailed analysis of how interfacial interaction in the composite material affects polymer morphology in this zone.

Experimental

Sample Preparation - Composite Fibers

Atactic poly(vinyl alcohol) (PVA) (Lot # 636837, D_P: 18,000, and 98.4 % hydrolyzed) was dissolved in an 80:20 volume ratio of dimethyl sulfoxide (DMSO) (Cas. No. 67-68-5), and distilled water to obtain a 3 wt% solution. SWNT (Lot# P-0247, metallic impurity ~2 wt%), dispersions were obtained in DMSO (0.4 mg of SWNT/ml of DMSO) by sonicating (using a Branson 3520 bath sonicator, frequency 42 kHz, power 100 W) for 24 h at 33 °C. The mixture was continuously stirred for 72 hours with an overhead mechanical stirrer (Caframo high shear mixer, model# BDC1850) at shear speeds between 600 RPM to 700 RPM.

Gel spinning was performed using a syringe pump (Fisher Scientific Co.). The polymer solution was placed into a syringe (B-D glass syringe) and spun through a needle (Popper 18-gauge blunt tip pipeting needle). The polymer solution was maintained at ~60 °C during spinning. The air gap between needle tip and spin bath was varied between 2 to 5 mm. The solution was pumped at a linear speed of 2.5 m/min into a methanol spin bath maintained at temperatures ranging from -70 °C to 0 °C for PVA, and PVA/SWNT fiber spinning. This methanol spin-bath also acted as the first gelation bath. Fibers were subsequently drawn in a three to four stage process at various temperatures on a fiber drawing hot plate. In some cases the fibers were also drawn for a fourth stage on a hot plate at 290 °C. All gel-spun fibers were taken through several heat-drawing stages before vacuum drying for one to three days at 60 °C for testing.

Sample Preparation - Crystallization

Shear crystallization studies were carried out in dilute polymer and CNT concentrations. After crystallization for 1 h (at crystallization temperatures (T_c) of 90 and ~110 °C for polyethylene and polypropylene, respectively) a crystalline coating of polymer was observed on the nanotubes. Fibrillar crystals were removed from solution and washed repeatedly in boiling xylenes for 10 to 20 minutes at a time.

Sample Characterization

Scanning electron microscopy (SEM) was done using a LEO 1530 thermally assisted field emission microscope and a Zeiss Ultra60 SEM at operating voltages of 1-10 kV

on uncoated samples. Transmission electron microscopy (TEM) studies were carried out on Hitachi HF-2000 Field Emission Gun electron microscope (accelerating voltage 200 kV). TEM samples were prepared on Lacey carbon coated TEM grids (Electron Microscopy Sciences, Hatfield, PA, USA; Cat.# HC200-Cu). Raman spectroscopy was performed using a Holoprobe Raman microscope at an excitation wavelength of 785 nm and 1.5 MW beam power. Wide-angle X-ray scattering was done on the Rigaku Micro Max 002 X-ray generator operated at 45 kV and 0.66 mA and equipped with R-axis VI++ detector. Thermal shrinkage measurements were performed using a thermal mechanical analyzer (TMA). Tensile properties of these fibers were measured using a RSA III solids analyzer at a gauge length and crosshead speeds of 25 mm and 0.25 mm/s respectively.

Results and Discussion

Poly(vinyl alcohol)/SWNT Composite Fibers[11]

PVA and PVA/SWNT (99/1) fibers were processed by gel-spinning. With 1 wt% loading of SWNT the modulus and tensile strength increased by 49% and 63% respectively (Table 1). PVA and PVA/SWNT fibers show an increase in average toughness from 40 to 58 J/g, and this is higher than the toughness of commercially produced high-performance polymeric fibers Kevlar® (25-30 J/g) and Zylon® (46 J/g). Based on rule-of-mixtures for uniaxial composites [12, 13] the effective stress contribution of the SWNT in the composite fiber is ~110 GPa. This value suggests excellent reinforcement of the PVA by SWNT at low weight concentrations, and exceptional load transfer between the SWNT and PVA matrix.

Table 1. Mechanical properties of PVA and PVA/SWNT (99/1) fibers [14].

Samples	Tensile Modulus (GPa)	Tensile Strength (GPa)	Elongation-to-break (%)	Toughness (J/g)
PVA	47	1.6	5.9	40
PVA/SWNT (99/1)	70	2.6	5.6	58

When treated in DMSO at 60 °C, the PVA fiber is completely fibrillated, while PVA/SWNT fibers are mostly intact. This implies that PVA/SWNT fiber has higher solvent stability as compared to the PVA fiber. Wet shrinkage data for fibers treated in water shows that SWNT significantly increases the hydrolytic stability of the PVA fiber. The average shrinkage values for PVA and PVA/SWNT fibers in boiling water are 46% and 14%

respectively. PVA/SWNT fibers show a 70% improvement in the shrinkage properties over PVA fibers (Fig.1). Best values for PVA/SWNT fibers in boiling water show only a 5% overall shrinkage (Fig.1).
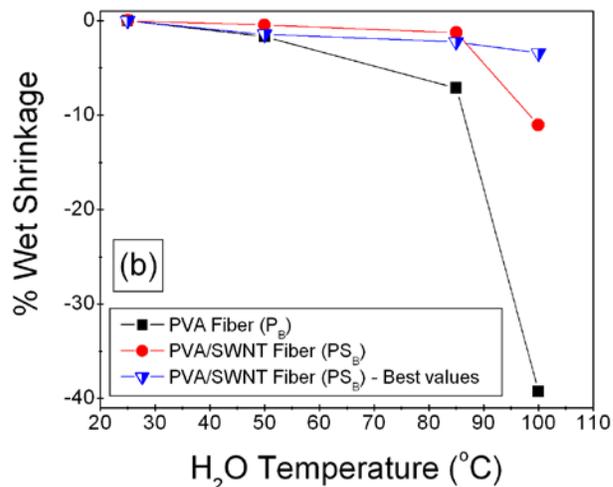

Fig. 1 Wet shrinkage in PVA and PVA/SWNT (99/1) fibers kept for 30 minutes in water at various temperatures.

Treatment of PVA/SWNT fibers in boiling DMSO also led to fibrillation of the fiber, and by comparison the complete dissolution of the PVA fiber. HR-TEM observations of these fibrillated regions show the presence of exfoliated SWNT in the PVA fiber, and thick PVA crystalline coating on the SWNT. HR-TEM also shows that the PVA lattice fringes are clearly visible in these well-crystallized interfacial regions. The PVA lattice is found to exist along the length of the SWNT. This extended-chain PVA crystallization at the PVA-SWNT interface may be one factor influencing the large increase in mechanical properties for the composite as compared to the neat fiber.

In an effort to understand how the presence of CNT in the composite influences the polymer microstructure, ongoing work to study interfacial crystallization in polymer/CNT dispersions (i.e. SWNT, few-wall and multi-wall carbon nanotubes) have been studied, and some results are discussed in the next section.

Shear Crystallization Studies in Polymer/Carbon Nanotube Dispersions

At very low concentrations, SWNT exfoliation was observed in xylenes as evidence by van Hove transition in the UV-Vis spectra (Fig.2). However, within minutes of being removed from the sonication bath, SWNTs were found to re-aggregate in the xylene dispersion. For these crystallization studies, achieving a fully exfoliated system

even at a very dilute concentration in these solvents is a challenge. In this work, fibrillar crystallization experiments were carried out using freshly sonicated CNT dispersions to avoid the problem of nanotube re-aggregation prior to polymer crystallization.
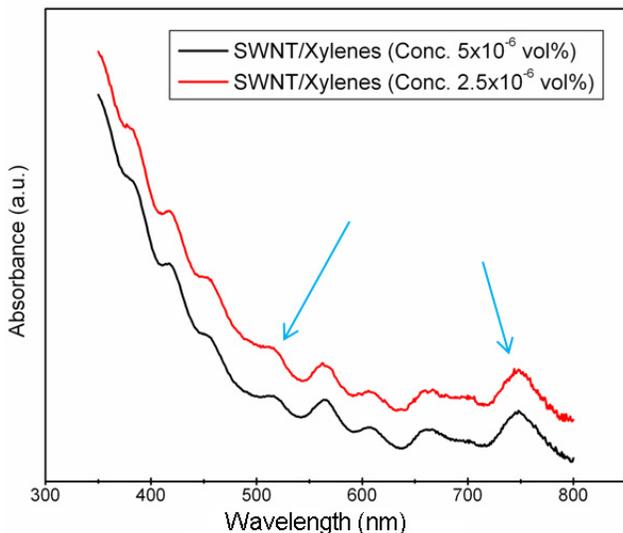

Fig. 2 UV-Vis spectra for low concentrations of single-walled carbon nanotubes (SWNT) dispersed in xylenes showing van Hove transitions (arrows).

During crystallization, polymer molecules experience confinement of conformation and orientation for two reasons, (i) surface interaction with the nanoubes, and (ii) limited spacing/separation distance between tubes. To estimate surface interaction between the polymer and nanotubes an arc length model (Fig.3) is use to compare area available for polymer interaction based on nanotube size. For same angular measurements the arc length of nanotubes with various diameters changes significantly (Table 2). An angle of ~70° was chosen to allow for one polymer molecule (i.e. ~0.6 nm cylindrical diameter of fully extended polymer chain) to interact with an individual SWNT. As shown in Table 1, as tube diameter increases more polymer chains can be accommodated at the surface of a nanotube (e.g. for CNF > MWNT > FWNT > SWNT → 100 chains > 30 chains > 5 to 10 chains > 1 chain). For this reason, polymer confinement is less restrictive for large diameter tubes. Therefore nucleation/growth direction can vary, whereas small diameter tubes are more directionally (i.e. along the nanotube axis) restrictive.
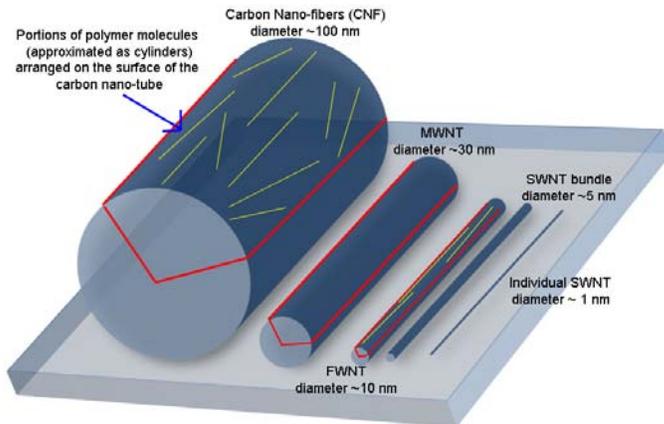

Fig. 3 Schematic showing the size (diameter) variation on carbon nanotubes and the corresponding arc length (for angular measurement of ~70°), indicating differences in contact area for polymer-tube interaction.

Table 2. Listing of Arc Length Measurements for Various Carbon Nanotubes of Different Diameters.

CNT Type	Diameter/ Bundle Size (nm)	Arc Length (for 70° measurement) (nm)
SWNT (individual)	1	0.6 (individual polymer chain)
SWNT (bundles)	~5	~3
FWNT (few-wall)	~10	~6
MWNT (multi-wall)	~30	~18
CNF (nano-fiber)	~100	~61

In addition to the surface confinement, space between tubes is also limited. The separation distance, s between tubes is calculated using Equation 1, where V_f is the volume fraction of polymer in the fibrillar crystal and d_t is the diameter if the nanotube[15].

$$V_{f(polymer)} = 1 - \frac{\pi d_t^2}{2\sqrt{3}(d_t + s)^2}$$ (1)

Table 3 lists the calculated separation distances for the various CNTs used. V_f of 0.8 to 0.9 is used because it is representative of the amount of polymer present in these fibrillar crystals studied here.

Table 3. Calculated Separation Distance, s between Carbon Nanotubes of Various Diameters.

CNT Type	Diameter/ Bundle Size	Separation Distance, s (nm) – V_f (polymer) ~0.8 to 0.9
SWNT	3 to 5	0.9 to 1.5 nm
FWNT	~10	2.5 to 3 nm
MWNT	~30	8 to 9 nm
CNF	~100	27 to 31 nm

During crystallization, polyethylene molecules are compacted when crystal growth is nucleated by the carbon nanotubes (Fig.4). D-spacing was measured for the major crystallographic peaks using wide-angle X-ray diffraction (WAXD). Contraction of chain packing is most pronounced for samples containing SWNT. Similar contraction of the d-spacing was also observed from WAXD for samples using polypropylene.
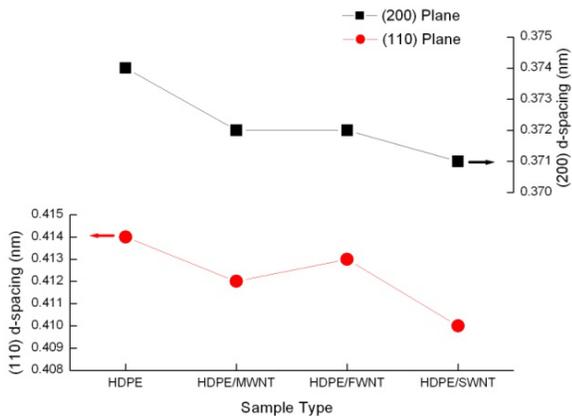

Fig. 4   WAXD data showing the change in d-spacing for the major reflections (110) and (200) of polyethylene crystallized in the presence of various diameter nanotubes.

For both, polyethylene/SWNT and polypropylene/SWNT fibers formed during shear crystallization, removal of bulk polymer was done by solvent washing in xylenes. This process allows for the analysis of the interfacially crystallized polymer. WAXD studies of the washed samples revealed oriented polymer at the interface (Fig.5). Under the shear crystallization conditions used, orientation of the polymer was only observed for samples containing SWNT. For polyethylene samples shish structure remained intact on SWNT and was mostly unaffected by boiling in xylenes. Average lamellar thickness of polyethylene was ~40 nm.
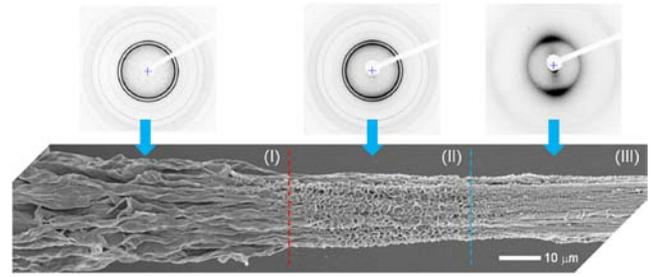

Fig. 5   SEM of a polyethylene fibrillar crystal showing, (I) pristine crystal, (II) after washing in hot xylenes, and (III) after repeated washing in boiling xylenes. Each region (I, II, and III) is accompanied by corresponding wide-angle X-ray pattern showing that polyethylene at the interface (region III) is oriented onto the nanotube.

Conclusion

In addition to reinforcing polymer composites using CNT to improve mechanical properties, the morphology of these fibers were also studied to determine polymer-CNT interfacial interaction. Additionally, shear crystallization of various polymers in the presence of CNT show that the polymers are able to form a crystalline coating on CNT in the presence of shear flow. CNT are able to template crystallization, and orientation along the fibrillar crystal direction for the polymer. Crystallization confined by the CNT becomes more pronounced as CNT diameter decreases due to less surface interaction and smaller separation distances between tubes. The largest polymer chain packing contraction observed for samples contain single-walled carbon nanotubes. Further optimization of these crystallization experiments are currently underway to achieved the goal of extended-chain polymer crystallization on CNT.

Understanding the nature of polymer-CNT interaction will lead to a more efficient use of CNT in composites as well as better processing methods, which may in turn contribute to lower cost of these materials, more widespread use, improvement in properties of composite fibers, as well as the production of functional polymer/CNT composite fibers tailored for specific applications.

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