Excellent dispersion of MWCNTs in PEO polymer achieved through a simple and potentially cost-effective evaporation casting

Myounggu Park
Hyonny Kim
Jeffrey Youngblood
Purdue University, jpyoungb@purdue.edu
Sang Woo Han
Eric Verplogen

See next page for additional authors

Follow this and additional works at: http://docs.lib.purdue.edu/nanopub

Part of the Nanoscience and Nanotechnology Commons

Park, Myounggu; Kim, Hyonny; Youngblood, Jeffrey; Han, Sang Woo; Verplogen, Eric; and Hart, A John, "Excellent dispersion of MWCNTs in PEO polymer achieved through a simple and potentially cost-effective evaporation casting" (2011). Birck and NCN Publications. Paper 844.
http://dx.doi.org/10.1088/0957-4484/22/41/415703

This document has been made available through Purdue e-Pubs, a service of the Purdue University Libraries. Please contact epubs@purdue.edu for additional information.
Excellent dispersion of MWCNTs in PEO polymer achieved through a simple and potentially cost-effective evaporation casting

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2011 Nanotechnology 22 415703
(http://iopscience.iop.org/0957-4484/22/41/415703)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 128.46.220.170
The article was downloaded on 21/12/2011 at 18:10

Please note that terms and conditions apply.
Excellent dispersion of MWCNTs in PEO polymer achieved through a simple and potentially cost-effective evaporation casting

Myounggu Park\textsuperscript{1,6}, Hyonny Kim\textsuperscript{2}, Jeffrey P Youngblood\textsuperscript{3}, Sang Woo Han\textsuperscript{4}, Eric Verplogen\textsuperscript{5} and A John Hart\textsuperscript{4}

\textsuperscript{1} School of Aeronautics and Astronautics and Birck Nanotechnology Center, Purdue University, IN 47906, USA
\textsuperscript{2} Department of Structural Engineering, University of California, San Diego, CA 92093, USA
\textsuperscript{3} School of Materials Engineering, Purdue University, IN 47906, USA
\textsuperscript{4} Department of Mechanical Engineering, University of Michigan, Ann Arbor, MI 48109, USA
\textsuperscript{5} Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

E-mail: myounggupark@gmail.com

Received 3 July 2011, in final form 15 August 2011
Published 15 September 2011
Online at stacks.iop.org/Nano/22/415703

Abstract
A simple, reliable and potentially cost-effective composite film casting procedure is presented using the evaporation of solvent (water) from a dilute mixture of multiwalled carbon nanotubes (MWCNTs) and polyethylene oxide (PEO) polymer. It is found that the fabrication method develops excellent dispersion of MWCNTs in PEO confirmed by morphology observations, final crystallinity of polymer (amorphous) and a lower percolation threshold (closer to theoretical value) as well as higher electrical conductivity. A film thickness prediction model is derived based upon the fact that final film thickness is mainly dependent upon the dimensions of the casting mold and the loading of the MWCNTs and polymer. This simple model provides important insight that the material loss and the actual density of the base polymer are critical factors making the current casting method truly cost effective and controlling final thickness. (Some figures in this article are in colour only in the electronic version)

1. Introduction
Carbon nanotube (CNT) filled polymer composites have great potential for many applications such as strain sensors \cite{1, 2}, actuators \cite{3}, transparent electrically conductive thin films \cite{4–6}, CNT-reinforced structural composites \cite{7–12}, pH sensors \cite{13} and nanoporous membrane filters \cite{14, 15}. Most CNT–polymer composites have been produced in film form using various fabrication methods developed by previous researchers as summarized in table 1 \cite{1, 2, 4, 5, 7, 8, 13, 16, 6, 14, 15, 17–21}, except for some of the CNT–polymer composites in structural applications which are manufactured via conventional composite manufacturing processes \cite{10, 12, 22–24}. In our opinion, the pros and cons of each fabrication method will be mainly divided based upon the adequacy, capability and cost of the fabricated composite film for the desired applications. For example, some fabrication methods are found to be promising and suitable for structural application but may not be adequate for the fabrication of randomly oriented CNT composite films. Most of all, it should be noted that, despite its enormous potential, the lack of reliable, simple and cost-effective fabrication methods of CNT–polymer composite film still remains a main barrier to real world applications and commercialization. Also, overall...
Table 1. Fabrication methods of CNT–polymer composite films.

<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
<th>Final film type</th>
<th>Note</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filtering</td>
<td>SWCNTs and DMF mixture filtered through Teflon</td>
<td>SWCNT–DMF composite film</td>
<td>First macroscale strain sensing</td>
<td>[1, 2]</td>
</tr>
<tr>
<td>Filtering</td>
<td>SWCNT and SDS mixture filtered through alumina</td>
<td>Transparent and pure SWCNT film</td>
<td>Film must be transferred onto suitable substrate</td>
<td>[4, 5]</td>
</tr>
<tr>
<td>In situ polymerization</td>
<td>Functionalized MWCNTs incorporated with polymer</td>
<td>MWCNT–polymer composite film</td>
<td>Functionalized CNT used for better dispersion of CNTs</td>
<td>[7, 8]</td>
</tr>
<tr>
<td>LbL (layer by layer)</td>
<td>Dipping a charged substrate into oppositely charged SWCNT and polymer mixture</td>
<td>CNT–polymer composite film</td>
<td>Precise control of thickness possible (e.g. one monolayer at a time)</td>
<td>[13]</td>
</tr>
<tr>
<td>Spin–spray LbL</td>
<td>Laponite and PDDA solution is sprayed on substrate</td>
<td>PDDA–laponite composite film</td>
<td>Home made robotic system reduced process cycle time significantly</td>
<td>[16]</td>
</tr>
<tr>
<td>Spin coating</td>
<td>Aligned MWCNT film impregnated with polymer by spin coater</td>
<td>Aligned MWCNT–polymer composite film</td>
<td>Wettability between MWCNT and polymer is important</td>
<td>[6, 14, 15]</td>
</tr>
<tr>
<td>Centrifugation</td>
<td>SDS coated SWCNTs collected by high speed centrifugation</td>
<td>SDS coated SWCNT film</td>
<td>Self-organization due to critical SDS micelle concentration</td>
<td>[17]</td>
</tr>
<tr>
<td>Coagulation</td>
<td>Suspension of SWCNT, DMF and PMMAa dripped into distilled water</td>
<td>SWCNT–PMMA composite film</td>
<td>Immediate precipitation of PMMA due to insolubility of PMMA in DMF and water mixture</td>
<td>[18]</td>
</tr>
<tr>
<td>Evaporation</td>
<td>Water evaporated from PVA, SDS wrapped SWCNT and water mixture</td>
<td>SWCNT–PVA composite film</td>
<td>Water evaporated at 40 °C or room temperature</td>
<td>[9, 19]</td>
</tr>
<tr>
<td>Evaporation</td>
<td>Propanol evaporated from PEO, MWCNT and propanol mixture</td>
<td>MWCNT–PEO composite film</td>
<td>Propanol evaporated at room temperature</td>
<td>[20]</td>
</tr>
<tr>
<td>Evaporation</td>
<td>Water evaporated from PEO, SWCNT, and water mixture</td>
<td>SWCNT–PEO composite film</td>
<td>Water evaporated at 80 °C</td>
<td>[21]</td>
</tr>
<tr>
<td>Submersion</td>
<td>Vertically aligned MWCNT film wetted by epoxy</td>
<td>Vertically aligned MWCNT-epoxy composite film</td>
<td>Capillarity-driven wetting along the MWCNT axis</td>
<td>[11]</td>
</tr>
<tr>
<td>Infiltration</td>
<td>PDMSb is poured over vertically aligned MWCNT film</td>
<td>Vertically aligned MWCNT–PDMS composite film</td>
<td>Conformal filling of PDMS matrix into dense MWCNT network</td>
<td>[3]</td>
</tr>
</tbody>
</table>

* Single walled carbon nanotube (SWCNT). *b* N,N-dimethylformamide (DMF). *c* Note that there is no polymer matrix.
* In this method CNTs are not used but it is included for comparison purposes. * Poly(diallyldimethylammonium chloride) (PDDA).

The overarching aim of this research is to develop a simple, reliable, and cost-effective evaporation casting procedure to fabricate MWCNT–PEO composite films having microstructures of well dispersed MWCNTs within the polymer, which is the basis for the enhanced material properties including electrical and mechanical properties. The sublevel objectives are as follows:

1. determine the key evaporation casting parameters
2. characterize the films using field-emission scanning electron microscopy (FE-SEM), small angle x-ray scattering (SAXS), and direct current (DC) two-point electrical resistance measurement
3. measure the percolation threshold experimentally and compare it to the theoretically predicted value
4. develop a film thickness prediction model.

The fabrication method presented herein is based on the evaporation of solvent from a dilute polymer solution above the melting temperature of PEO, as attempted by Chatterjee et al [21]. The advantage of a dilute polymer solution is
using flat glass plates and silicone sealant with dimensions 90 mm × 70 mm × 70 mm (L × W × H). A key aspect of this approach is that mixing is done with a dilute, low viscosity solution, to get good dispersion. The casting frame with the solution mixture is placed inside an oven (Lunaire Environment, model CE205) operating at 85 °C during water evaporation. The rate of water evaporation is increased by blowing out the oven ambient air constantly through the oven exhaust. Also, to prevent the bending of the composite film due to residual stress, a partial lid is placed on top of the casting frame. After the water is evaporated out completely, leaving a MWCNT–PEO film at the bottom, the casting frame is taken out from the oven and cooled down under room temperature ambient conditions. On the bottom surface of the casting frame, a release agent had been sprayed before casting to allow for easy peel-off of the composite film. Overall, we maintain the process temperature of 85 °C from the beginning to the end of the evaporation of water, which is relatively easy to maintain due to the low melting temperature of PEO.

2. Methods

2.1. Evaporation casting procedure

Throughout this research raw materials are used without any further treatments. The water-soluble, synthetic thermoplastic polymer, particle type PEO (molecular formula of monomer: –HO–[CH2–CH2–O]n–H–) [32–34], purchased from Sigma-Aldrich, is used as the matrix material. PVA (molecular formula of monomer: –[CH2–CH2–O]–) [32, 33] is also a water-soluble, synthetic thermoplastic polymer and is used as the control for morphology comparison with that of PEO under the same casting process (see section 4.1). The physical properties of PEO and PVA are summarized in table 2 [35]. Commercially available MWCNTs (Nano Lab) are used as conductive filler inside the PEO. The specifications of the MWCNTs are: length 1–5 μm, diameter 15 ± 5 nm, purity 95%, and bulk density 1.8 g cm−3 [36, 37]. SDS (molecular formula: C12H25NaO4S), purchased from Bioworld, is used as a surfactant [38]. It is in particle form and has a bulk density of 0.32 g cm−3 [39].

Table 2. Physical properties of PEO and PVA.

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>PEO</th>
<th>PVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>True density (g cm⁻³)</td>
<td>1.13</td>
<td>1.27–1.31</td>
</tr>
<tr>
<td>Melting point (Tm) (°C)</td>
<td>62–67</td>
<td>180–190</td>
</tr>
<tr>
<td>Glass transition temperature (Tg) (°C)</td>
<td>−50 to −57</td>
<td>75–85</td>
</tr>
<tr>
<td>Molecular weight (Mw) (Da)</td>
<td>10 × 10³ (√average)</td>
<td>8.5–12.4 × 10³</td>
</tr>
</tbody>
</table>

that it can separate and isolate polymer chains from each other completely [31]. The resulting CNT filled polymer film may have various inner and outer (surface) morphologies and properties depending on the type of CNT, functionalization, choice of polymer matrix and process parameters. In addition to these features, one of the main reasons for selecting the evaporation process is that it is relatively simple and cost effective. Note that the current evaporation method does not require specific types of CNT (e.g. MWCNT versus SWCNT), additional purification, functionalization, vertically aligned CNT film, transportation of the produced film and/or specialized automated systems (or equipment), except for minimal equipment and facilities, namely an ultrasonicator and ultrasonication (frequency 20 kHz, amplitude 15 μm) is conducted using an ultrasonicator (Misonix Sonicator 3000) for 10 min. In a separate container, the PEO is completely dissolved in de-ionized (DI) water. MWCNTs dispersed in the SDS solution and the PEO solution are mixed together. This solution mixture is subjected to ultrasonication for 30 min, and poured into a casting frame. The casting frame is built using flat glass plates and silicone sealant with dimensions 90 mm × 70 mm × 70 mm (L × W × H). A key aspect of this approach is that mixing is done with a dilute, low viscosity solution, to get good dispersion. The casting frame with the solution mixture is placed inside an oven (Lunaire Environment, model CE205) operating at 85 °C during water evaporation. The rate of water evaporation is increased by blowing out the oven ambient air constantly through the oven exhaust. Also, to prevent the bending of the composite film due to residual stress, a partial lid is placed on top of the casting frame. After the water is evaporated out completely, leaving a MWCNT–PEO film at the bottom, the casting frame is taken out from the oven and cooled down under room temperature ambient conditions. On the bottom surface of the casting frame, a release agent had been sprayed before casting to allow for easy peel-off of the composite film. Overall, we maintain the process temperature of 85 °C from the beginning to the end of the evaporation of water, which is relatively easy to maintain due to the low melting temperature of PEO.

2.2. Characterization of MWCNT–PEO composite films

FE-SEM. Outer (surface) and inner (cross-sectional) morphologies of cast MWCNT–PEO composite film are observed using an FE-SEM (FEI NOVA nanoSEM). To reveal the inner morphology, MWCNT–PEO composite samples are freeze-fragmented after dipping them into liquid N₂ for 5 min.

SAXS. Ex situ SAXS analysis of MWCNT–PEO composite film and pure PEO film using the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, Cornell High Energy Synchrotron Source (CHESS) at Cornell University, and NanoStar (x-ray source: Cu Kα) at the X-Ray Microanalysis Laboratory (XMAL) at the University of Michigan is performed to evaluate the crystallinity of PEO, the alignment of MWCNTs in the PEO matrix, and the as-grown MWCNT film. The details of the SAXS experimental setup from CHESS are described in [40].

DC two-point electrical resistance measurements. DC two-point electrical resistance measurements of MWCNT–PEO composite films are conducted using a precision multimeter (Keithley 2000) to measure electrical conductivity and to experimentally determine the electrical percolation threshold. Composite film strips with different loadings of MWCNTS in weight fraction (wt%) are prepared as shown in figure 1(a); these strips shown in figure 1(a) are lower wt% ones. The dimensions of the strips are 50 mm × 4.0 mm × 1.4 mm (L × W × T). The DC two-point electrical resistance measurement...
setup is schematically depicted in figure 1(b). Although the two-point measurement method includes the resistance of lead wires and contacts, it is known that this added resistance can be neglected when the measured resistance is greater than a few Ohms [41]. To make a secure contact with the lead wires to the cross-section of the sample, each lead wire was heated (50°C) and, then, gently pressed onto the sample surface until it embedded into the cross-sectional area. In general, the four-point probe method is a more suitable measurement scheme than the two-point probe method to characterize the thin films because the length of a thin film is much larger than the thickness. However, in the current research, the thickness of the composite strip (1.4 mm) is large enough to result in secured cross-sectional electrical contact, and thus the two-point measurement setup is adopted. The four-point electrical measurement setup is also going to be developed for better accuracy.

2.3. Film thickness prediction model

The simple relationship between the thickness of the MWCNT–polymer composite films and the manufacturing parameters is derived based upon the fact that final film thickness is mainly dependent upon the dimensions of the casting frame and the loading of the MWCNTs and polymer.

3. Results

3.1. Morphology of fabricated MWCNT–PEO film

Fabricated free standing MWCNT–PEO composite films produced by the evaporation casting method are shown in figure 2. The composite film, fabricated with the casting frame lid in place, was free of residual stress, showing no warping (figure 2(a)) while the film without the lid shows a curved shape due to residual stress from non-uniform drying (see figure 2(b)). Typical morphologies of the MWCNT–PEO composite films are shown in figures 3 (outer morphology) and 4 (inner morphology). The thickness of the fabricated composite film is uniform and the MWCNTs are well dispersed inside the PEO matrix. Also, the cross-sectional morphology (figure 4(b)) shows no distinctive sign of MWCNT aggregation. It is shown from the previous research [30, 34, 42, 43] that the morphology is closely related to the crystal nucleation and growth within the polymer in the presence of MWCNTs. For example, for semicrystalline polymers such as PEO [30, 43], there is phase separation between crystalline and amorphous regions, and MWCNTs were found to be confined in the amorphous region [43] (one of the main causes of MWCNT
aggregation). Thus phase separation might have negative effects on the dispersion of MWCNTs inside the matrix. Since FE-SEM observations alone are not enough to evaluate crystallinity, additional characterization techniques were used (see following sections).

3.2. Ex situ SAXS results of MWCNT–PEO composite films

Ex situ SAXS is mainly conducted to determine the crystallinity of PEO [40, 44] and the alignment of MWCNTs in the PEO matrix [45, 46]. The 2D SAXS images of pure PEO film and MWCNT–PEO composite film, having 1.44 vol% of MWCNT, are shown in figures 5(a) and (b) respectively. Only the pure PEO specimen (figure 5(a)) shows a signature of crystalline (lamellar) structure (diffraction ring) while the PEO/MWCNT composite specimens do not (figure 5(b)). The scattering intensity, $I(q)$, is plotted in figure 6(a) (pure PEO) and 6(b) (MWCNT–PEO composite film) as a function of scattering vector $q$, which is given by equation (1) as

$$q = \frac{4\pi \sin \theta}{\lambda}$$  \hspace{1cm} (1)

where $\lambda$ is the wavelength of the x-ray (0.1371 nm) and $\theta$ is half of the diffraction angle of the peak.

The pure PEO curve shows a local maximum (see the arrow in figure 6(a)) at $q = 0.24$ nm$^{-1}$. The length of periodicity, $d$, is calculated to be 26.2 nm using equation (2) [47, 48]

$$d = \frac{\lambda}{2 \sin \theta}.$$  \hspace{1cm} (2)
Figure 6. Intensity ($I$) versus scattering vector ($q$). (a) Pure PEO film, (b) MWCNT: 1.44 vol%.

Figure 7. Typical SAXS pattern of vertically aligned MWCNT forests grown to millimeter heights on a Si substrate using a modified chemical vapor deposition (CVD). (a) Butterfly shaped SAXS pattern. (b) As-grown MWCNT film.

The $d$ value is similar to the ones reported by other researchers [44, 49, 50]. Note that pure PEO is a semicrystalline polymer and the length of periodicity, $d$, varies depending on the amount of amorphous phase [44].

For the PEO–MWCNT composite specimen, the local maximum observed in the pure PEO film disappeared (figure 6(b)), which indicates that the lamellar structure of PEO was not formed. Also from the SAXS pattern (figure 5(b)) it is confirmed that there is no indication of the alignment of MWCNTs (i.e. the butterfly, ‘∞’, shape in figure 7(a)) found in the typical SAXS pattern of vertically aligned MWCNTs grown on a Si substrate by atmospheric pressure thermal chemical vapor deposition (CVD) (figure 7(b)) (for details see [51]) and vertically aligned MWCNT film–VRM 34 composite film fabricated by mechanical densification and polymer wetting in figure 8 (for details see [46]). These results show that the current fabrication method can produce an amorphous PEO matrix and this can be the basis of achieving a good dispersion of MWCNTs [52].

3.3. Percolation threshold of MWCNT–PEO composite film

The electrical percolation threshold can be identified as a certain volume fraction of conductive filler inducing a dramatic jump of electrical conductivity of the composite [53–61]. This sudden increase of electrical conductivity is the main characteristic of the composite material reaching the percolation threshold ($\Phi_c$). The measured electrical conductivity as a function of the volume fraction of MWCNTs is plotted in figure 9; the weight fraction was converted into the volume fraction using the densities of MWCNTs and PEO. The electrical conductivity measurements at each volume fraction were made two or three times to check the reproducibility of electrical resistance values. However, the number of measurements was not enough to show error bars (statistically not meaningful) and thus we did not include them. The percolation threshold is observed to be between 0.14 and 0.28 vol% (0.5 and 1.0 wt%) of MWCNTs as indicated by the solid line in figure 9.

The most commonly adopted model to predict the percolation threshold is based upon the excluded volume concept [62, 63] and it has been successfully applied to explain the percolation threshold change of various microscale objects–polymer composites [64, 65]. In the 3D case
for random orientation of conductive fillers inside polymer, the percolation threshold, \( \Phi_c \), can be calculated by the equation given by Balberg assuming that MWCNTs are thin cylinders (capped hemispherical cylinders) [64–66]

\[
\Phi_c = 1 - \exp \left( -\frac{1.4V_{cyl}}{\langle V_e \rangle_{cyl}} \right)
\] (3)

where \( V_{cyl} \) is the volume of a capped hemispherical cylinder and \( \langle V_e \rangle_{cyl} \) is the average excluded volume of a capped hemispherical cylinder.

The experimentally determined percolation threshold range is found to be close to the model prediction (table 3) when the length 5 \( \mu \)m and diameter 10 nm are chosen for the MWCNT cylinder per specification of the MWCNT used, despite the fact that the MWCNTs are not straight but in general exhibit curved geometry. This result supports the view that the MWCNTs in the PEO matrix are randomly oriented.

### 3.4. Thickness prediction model for MWCNT–polymer composite film

In modeling of film thickness prediction, it is assumed that a non-porous MWCNT–polymer composite film is formed. In general, thermoplastic polymer polymerized from a molten state contains voids similar to cured thermoset polymer, depending on the various parameters such as temperature, time and rate. Thus no void assumption is ideal; this non-porous assumption is often adopted to calculate the volume fraction of constituent elements in fiber-reinforced composites.

The casting mold is depicted in figure 10. The total volume, \( V_{mp} \), of the MWCNT–polymer composite film is calculated from the geometry of the casting mold and the film thickness as

\[
V_{mp} = abh
\] (4)

where \( a \) is the length of the casting mold, \( b \) is the width of the casting mold and \( h \) is the thickness of the film.

The total volume, \( V_{tot} \), of the MWCNT–polymer composite film also can be calculated as

\[
V_{tot} = \frac{m_c}{\rho_c} + \frac{m_p}{\rho_p} + \frac{m_s}{\rho_s}
\] (5)

where \( m_c \) and \( \rho_c \) are the mass and density of the MWCNTs, \( m_p \) and \( \rho_p \) are the mass and density of the polymer, and \( m_s \) and \( \rho_s \) are the mass and density of the SDS.

By setting equations (4) and (5) equal to each other, the thickness of the MWCNT–polymer composite can be calculated as

\[
h = \frac{1}{ab} \left( \frac{m_c - m_{cl}}{\rho_c} + \frac{m_p - m_{pl}}{\rho_p} + \frac{m_s - m_{sl}}{\rho_s} \right)
\] (6)

Ideally the final film thickness can be predicted using equation (6); however, it was found that the values predicted by equation (6) are much higher than those of the actual measured film thicknesses due to material loss during processing (e.g. mixture solution left on the mixing beakers and vertical walls of mold). Thus equation (6) can be modified as

\[
h = \frac{1}{ab} \left( \frac{m_c - m_{cl}}{\rho_c} + \frac{m_p - m_{pl}}{\rho_p} + \frac{m_s - m_{sl}}{\rho_s} \right)
\] (7)

where \( m_{cl}, m_{pl}, \) and \( m_{sl} \) are the loss of the MWCNT, the polymer, and the SDS, respectively.

The total loss, \( m_{tot} \), of raw material can be obtained by subtracting the final mass of the film from the total mass of the input materials. Then we assume that the major loss is only from the polymer \( (m_{tot} \approx m_{pol}) \) due to the relatively small amount of MWCNT content. Equation (7) can then be written as

\[
h \approx \frac{1}{ab} \left( \frac{m_c}{\rho_c} + \frac{m_p - m_{pol}}{\rho_p} + \frac{m_s}{\rho_s} \right)
\] (8)

The bulk densities of MWCNT (\( \rho_c \)) and SDS (\( \rho_s \)) used are 1.8 g cm\(^{-3}\) and 0.32 g cm\(^{-3}\) respectively. As for the density of PEO (\( \rho_p \)), three different densities are reported in [67]: bulk density (0.384 g cm\(^{-3}\)), tap density (0.449 g cm\(^{-3}\)), and true density (1.32 g cm\(^{-3}\)). Also note that the true density of PEO for the current research (provided by the vendor) is 1.13 g cm\(^{-3}\). However, the best prediction was obtained when the experimentally measured density of the pure PEO film (0.5 g cm\(^{-3}\)) fabricated by the current method was used.
Figure 11. MWCNT–PVA composite film. (a) Outer (surface) morphology. (b) Inner (cross-sectional) morphology.

Table 4. Amount of raw materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass of PEO (g)</th>
<th>Mass of MWCNTs (g)</th>
<th>SDS (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>4</td>
<td>0.004</td>
<td>0.2</td>
</tr>
<tr>
<td>C</td>
<td>3</td>
<td>0.0025</td>
<td></td>
</tr>
</tbody>
</table>

Table 5. Final film thickness–model prediction and measured values.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Model prediction (mm)</th>
<th>Measured average thickness (mm)</th>
<th>% error</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.29</td>
<td>0.27</td>
<td>+7.4</td>
</tr>
<tr>
<td>B</td>
<td>0.29</td>
<td>0.29</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>0.37</td>
<td>0.35</td>
<td>+5.7</td>
</tr>
</tbody>
</table>

Considering the relatively short fabrication time used in our approach (less than 6 h depending on experimental conditions) it can be assumed that the mixture of PEO and SDS encapsulated MWCNTs in 85 °C water remains stable during the evaporation process.

To quantify the effect of evaporation temperature on the final inner morphology of composite films (MWCNT–PEO versus MWCNT–PVA), simple electrical resistivity measurements of these two samples was conducted and are summarized in table 6. The MWCNT–PVA composite film shows much higher electrical resistivity than the MWCNT–PEO composite film, which indicates that process temperature above the melting temperature of PEO is beneficial for the dispersion of MWCNTs, as measured by the lower resistivity. Note that MWCNT–PVA composite film was fabricated using the same casting process and then freeze-fractured to observe the inner morphology. The outer and inner morphologies are shown in figures 11(a) and (b) respectively. The current processing temperature is within the crystallization temperature range of PVA but above the melting temperature ($T_m$) of PEO (see table 2). The severe aggregation of MWCNTs is observed in the MWCNT–PVA composite (figure 11(b)) but not observed in the MWCNT–PEO composite (figure 4(b)).

4. Discussion

4.1. Key process parameters for improved dispersion of MWCNTs in PEO polymer

It is well known that hotter water can dissolve PEO faster and more effectively than warm water. However, to avoid the precipitation of PEO above 93 ± 3 °C [33], the processing temperature was restricted to be under this value. PEO with low molecular weight of less than 3400 is less hydrophilic compared to higher molecular weight PEO [42] and also tends to aggregate easily and sink faster due to a lack of viscosity. Thus higher molecular weight PEO ($10 \times 10^5$) is chosen as the matrix to make a stable and uniform CNT polymer solution.

It is shown that SDS encapsulated CNTs can be stable for approximately three months at room temperature [42] and stable for approximately 24 h at 70 °C [68]. Therefore, shorter process time is critical for high temperature evaporation to avoid non-uniform volume fraction through the film thickness.

4.2. Outer and inner morphologies of composite films

A comparison of morphologies of composite films between the current research and previous reports using evaporation procedures is given in table 7 [20, 21, 69, 70]. Direct observations of outer (surface) and inner (cross-sectional) morphology of fabricated MWCNT–PEO samples using FE-SEM is one of the important characterization procedures to verify that the current fabrication procedure is capable of producing a composite film having well dispersed MWCNTs inside the PEO matrix. Overall, reported outer (surface) morphologies indicate that MWCNTs are well dispersed. However inner (cross-sectional) morphologies are not included in the previous reports, and thus meaningful evaluation of process temperature versus final morphologies cannot be generated.
### Table 6. Electrical resistivity of the pristine polymer and MWCNT–polymer composites

<table>
<thead>
<tr>
<th>Composite film</th>
<th>Resistivity (Ω cm)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT–PEO</td>
<td>2–7</td>
<td>MWCNT; 6.3 vol% (10 wt%)</td>
</tr>
<tr>
<td>MWCNT–PVA</td>
<td>7.6 × 10⁻³–5 × 10⁻⁴</td>
<td>MWCNT; 7.2 vol% (10 wt%)</td>
</tr>
</tbody>
</table>

### Table 7. Morphologies of CNT–PEO composites.

<table>
<thead>
<tr>
<th>No</th>
<th>PEO molecular weight (Da)</th>
<th>CNT type and amount</th>
<th>Solvent</th>
<th>Temperature and time</th>
<th>Key findings regarding morphologies</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10 × 10⁵</td>
<td>MWCNT (10 wt%)</td>
<td>Water</td>
<td>85 °C, 6 h</td>
<td>MWCNTs are observed to be evenly distributed (figures 7 and 8)</td>
<td>Current research</td>
</tr>
<tr>
<td>2</td>
<td>60 × 10⁴</td>
<td>MWCNT (10 wt%)</td>
<td>Propanol</td>
<td>RT</td>
<td>MWCNTs are observed to be evenly distributed (figure 3(a) in [20])</td>
<td>[20]</td>
</tr>
<tr>
<td>3</td>
<td>10 × 10⁴</td>
<td>SWCNT (10 wt%)</td>
<td>Water</td>
<td>80 °C, 24 h</td>
<td>Morphology of the composite is not included in this report</td>
<td>[21]</td>
</tr>
<tr>
<td>4</td>
<td>60 × 10⁴</td>
<td>MWCNT (1 wt%)</td>
<td>Water</td>
<td>60 °C, 48 h</td>
<td>MWCNTs are observed to be evenly distributed (figure 3(b) in [69])</td>
<td>[69]</td>
</tr>
<tr>
<td>5</td>
<td>30 × 10⁴</td>
<td>MWCNT (0.4, 2 wt%)</td>
<td>Water</td>
<td>60 °C, 48 h</td>
<td>MWCNTs (0.4 wt%) are observed to be evenly distributed (figure 8(a) in [70])</td>
<td>[70]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>MWCNTs (2.0 wt%) are observed to have aggregation (figure 8(b) in [70])</td>
<td></td>
</tr>
</tbody>
</table>

### Table 8. Crystallinity of CNT–PEO composites.

<table>
<thead>
<tr>
<th>No</th>
<th>Method</th>
<th>Key findings regarding crystallinity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SAXS</td>
<td>No signature of lamellar structure in composite film of MWCNT 10 wt%</td>
<td>Current research</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Signature of lamellar structure in pristine PEO film</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Length of periodicity (d) of pristine PEO film: 26.2 nm</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Average orientation of MWCNTs within PEO: random distribution</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Raman spectroscopy</td>
<td>Degree of individual MWCNT is measured within PEO polymer</td>
<td>[20]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Good crystallization of MWCNTs: I_D/I_G = ~ 0.25</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>WAXS⁹, DSC⁸</td>
<td>Degree of crystallinity decreases as the content of SWCNT increases</td>
<td>[21]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WAXS: crystallinity is 85% for pure PEO and 60% for 0.2 wt% of SWCNT</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>DSC: crystallinity is 95% for pure PEO and 70% for 0.2 wt% of SWCNT</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>DSC, Polarized light microscopy</td>
<td>DSC: degree of crystallinity of pure PEO is 50.1%</td>
<td>[69]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DSC: degree of crystallinity of sample with 5 wt% of MWCNT is 46.26%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Polarized light microscopy: spherulite density decreases and texture disrupted as the amount of MWCNT increases by more than 2 wt%</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>DSC</td>
<td>Considerable decrease in the rate of crystallization without much effect from addition of MWCNTs on the overall crystallinity</td>
<td>[70]</td>
</tr>
</tbody>
</table>

### 4.3. Crystallinity of MWCNT–PEO composites

The analysis of the crystallinity of CNT–PEO composite films from the previous reports using evaporation procedures is summarized in table 8 [20, 21, 69, 70]; numbers in the first column of table 8 correspond to those in table 7. The final PEO phase of the MWCNT–PEO composite is found to be amorphous in the present research by SAXS analysis and this is in agreement with the known tendency, especially for high temperature evaporation cases (e.g. no 3 in table 8): as the content of MWCNT increases, the crystallinity of PEO decreases. There is no significant change in the degree of crystallinity in other cases (nos 4 and 5 in table 8). Apparently the high temperature process induced the amorphous phase of PEO.

### 4.4. Percolation threshold

The percolation threshold of the MWCNT–PEO composite films fabricated by the current process is compared with other CNT–PEO composite films fabricated by evaporation methods (see table 9 [20, 21, 69, 70]). The numbers in the first column of table 9 correspond to those in tables 7 and 8. Considering the type and dimension of CNTs used in each case, the
percolation threshold values of the current research are within a reasonable range, with SWCNT–PEO having the lowest value. Note that conductivity of the composite film near the percolation threshold of the current method is $\sim 10^{-3} \, \text{S cm}^{-1}$, the highest among reported values. This can be a beneficial feature for, e.g., macroscale strain sensor applications because of the relative ease of detecting conductivity change near the percolation threshold induced by strain [71].

4.5. Insight from the thickness prediction model

A simple calculation using the thickness prediction model derived in section 3.4 shows that the present evaporation method is capable of producing consistent predictable film thickness. The model provides insight into how material loss and knowledge of the final pure PEO film density are important for predicting the final film thickness. For the current method to be truly cost effective, the material loss during processing should be as low as possible. The limitations of this model are: the no void assumption, loss of SDS and MWCNTs and the effect of the residual SDS are neglected, and two important parameters, material loss, $m_{\text{loss}}$, and density of pure PEO film, $\rho_{\text{PEO}}$, are heavily dependent upon processing. Thus it may not be practical to use this model but it is presented here for processing and thickness control insight.

5. Conclusions

In the present research, we have developed an MWCNT–PEO composite film fabrication process based upon an evaporation casting method. In this process, evaporation of the solvent (water) is performed above the melting temperature of the polymer (PEO) until a solid MWCNT–PEO film is formed. Higher molecular weight, shorter evaporation time, and the residual SDS during the high temperature film forming process. As for future work, the generalization of the current method should be further investigated to provide answers to the naturally arising questions such as ‘does this method apply to the polymer systems with higher melting temperatures?’; this is also important from a commercialization point of view.

### Acknowledgments

This research was supported by Purdue Research Foundation. Also, this research was supported partly by MIT’s Nano-Engineered Composite Structures Consortium. The authors appreciate the support from our sponsors. It is gratefully acknowledged that this research was conducted partly using two synchrotron sources: the National Synchrotron Light Source at the Brookhaven National Laboratory, which is supported by the US Department of Energy, Office of Science and Office of Basic Energy Sciences (contract no DE-AC02-98CH10886), and the Cornell High Energy Synchrotron Source, which is supported by the National Science Foundation and the National Institutes of Health under grant no DMR-0225180. The authors further acknowledge the helpful contribution of Mr Justin Nieuisma in the Department of Astronomy at the University of Michigan by proofreading this paper.

### References


[16] Merrill M H and Sun C T 2009 Fast, simple and efficient assembly of nanolayered materials and devices Nanotechnology 20 075606


[41] Keithley inc. 2004 I–V measurements of nanoscale wire and tubes with the model 4200-SCS and Zyvex S100 nanomanipulator Application Note Series No 2418


12