

# The effect of solvent choice on the mechanical properties of carbon nanotube–polymer composites

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## Abstract

The effect of solvent choice on the mechanical properties of polymer nanotube composites has been investigated. Composites of double-walled nanotubes in polyvinyl alcohol were fabricated using water, DMSO and NMP as solvents. Various amounts of solvent remained trapped in both polymer and composite films even after drying as measured thermogravimetrically. In general, the glass transition temperature decreased as solvent content increased. However, deviations from this behavior suggested the presence of trapped NMP at the polymer–nanotube interface. Both static and dynamic mechanical measurements showed increases in mechanical properties on the addition of nanotubes for water and DMSO-based composites. However, for NMP-based composites, the mechanical properties were reduced compared to the polymer at room temperature. However, the NMP-based composites became significantly stiffer than their polymer counterparts at elevated temperatures suggested thermally assisted NMP desorption from the interface. Unlike the calorimetric measurements, dynamic mechanical measurements of the glass transition temperature showed no significant anomalies, again suggesting desorption of NMP from the interface at higher temperature. This work shows that solvent choice can have a dramatic effect on the mechanical properties of polymer–nanotube composites.

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## 1. Introduction

Due to their superior mechanical properties, carbon nanotubes (CNT) have long been mooted as the ultimate reinforcing filler in polymer-based composites. However, the effective utilization of the mechanical properties of nanotube composites depends on the quality of their dispersion and the level of polymer–nanotube interfacial bonding [1,2]. A common technique for producing polymer–nanotube composites has been solution processing (for a comprehensive review of this field see [1]). In this technique, nanotubes and polymer are mixed in a common solvent. Nanotube dispersion relies on the interaction of the nanotubes with the polymer dispersant [3]. In general, solvent choice is motivated by the requirement that the

polymer dispersant should be soluble in the solvent. Polyvinylalcohol (PVA) has been extensively used as a matrix for nanocomposites because of its solubility in a range of solvents including water [4–8]. In addition, PVA is known to be a good dispersant of nanotubes [3,5–7]. In most of the CNT–PVA studies, water has been used as solvent [4–6,8–10]. However, in recent times, alternative solvents such as dimethylsulfoxide (DMSO) have been gaining popularity for fabrication of solution-based composites [11,12].

However, PVA is soluble in a wide range of solvents such as DMSO, *N*-methyl-2-pyrrolidone (NMP) and ethylene glycol [12–15]. The solvent choice can have significant effects on the morphology of the resultant solution cast polymer films. For example, the polymer crystallinity can vary greatly depending on whether the solvent used is a good or bad solvent for PVA [13]. Such solvent related effects are likely to have significant impact on the mechanical properties of solution processed polymer–nanotube

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films. In addition, it has recently been shown that carbon nanotubes can be dispersed in certain solvents without the need for polymer dispersants [16–19]. One of the most effective solvents studied was NMP [16,18,20]. This is significant as NMP is also a solvent for PVA. Thus, one would expect that PVA–CNT formation in NMP would result in efficient nanotube dispersion resulting in very good quality composites.

The aim of the present study was to understand the effect of solvent choice on the mechanical properties of solution processed CNT–polymer composites. This subject is poorly understood with the only study having been carried out on epoxy–nanotube composites [21]. Three different solvents with different solubility parameters for PVA were used for fabrication and characterization of DWNT–PVA composites. The resultant composites were found to have mechanical properties that depended significantly on solvent choice.

## 2. Experimental

### 2.1. Sample preparation

The double-walled nanotubes (DWNTs) used here were grown by CVD with a nominal purity of 90% and purchased from Nanocyl ([www.nanocyl.be](http://www.nanocyl.be); Nanocyl<sup>®</sup>-2100). They had a mean diameter of 3.5 nm with lengths between 1 and 10  $\mu\text{m}$ . Due to their large diameter, they have very low density of  $\sim 750 \text{ kg/m}^3$ . These particular nanotubes contain small amounts (<10%) metal oxide impurity. Polyvinyl alcohol was purchased from Aldrich (Aldrich: product code P-8136). The water used was deionized in-house while the NMP and DMSO solvents were spectroscopic grade (Aldrich). Solutions of PVA were prepared using water, DMSO and NMP as solvents, by sonication in a low power sonic bath (Ney Ultrasonik) for 4 h. Each solution was divided in two and 0.25 wt% DWNTs added to one of the portions to give a composite dispersion. Each composite dispersion was sonicated for 10 min using a high-power ultrasonic tip processor (model GEX600, 120 W, 60 kHz), followed by 2 h in a sonic bath and again for 10 min under the sonic tip. These dispersions were then left undisturbed for 24 h to allow any large nanotube aggregates or impurities to sediment out. Indeed, for each solvent, miniscule amounts of sediment (compared to the volume of nanotubes added to each solution) could be observed after settling, suggesting that a very small fraction of the nanotube material had fallen out of solution. This sediment was then removed by decantation to another vial. Polymer only solutions and the CNT–polymer dispersions were then drop cast into (40 mm  $\times$  40 mm  $\times$  10 mm) Teflon trays. Films were then formed by drying in a vacuum oven at 60  $^\circ\text{C}$ . Two sets of freestanding films were obtained for each solvent–polymer and solvent–polymer–CNT combination: (**1d**) with 1 day drying time at 60  $^\circ\text{C}$  under vacuum and a second set (**5d**) with 5 days drying under vacuum at the same temperature. After drying, the films were stored

for approximately 2 days in ambient conditions. This resulted in a small amount of water uptake by the polymer. The composite films had mass fractions of slightly <0.25 wt%. Taking the densities of PVA and DWNT to be 1300 and 750  $\text{kg/m}^3$ , this results in volume fractions of  $V_f \sim 0.4 \text{ vol}\%$ .

A sample labeling scheme has been employed. This scheme is in three parts: The first part of the sample name can be “**1d**” or “**5d**” depending on whether the drying time was 1 day (**1d**) or 5 days (**5d**), the second part denotes the solvent, while the third part could be “**p**” or “**c**” depending on whether the sample was polymer or composite, respectively. Thus “**1dDMSOp**” denotes a polymer sample dried for 1 day, made using DMSO as solvent.

### 2.2. Characterization techniques

Thermogravimetric analysis (TGA) measurements were carried out for all the samples using a Perkin–Elmer Pyris 1 TGA with a temperature scan rate of 10  $^\circ\text{C}/\text{min}$ . In general, TGA is used to monitor sample oxidation. However, in this case, it is used to ascertain the level of solvent entrapment in the samples after drying. To assess the morphological properties of the samples, differential scanning calorimetry (DSC) was performed using a Perkin–Elmer Diamond DSC. Three heat runs were recorded for each sample by repeatedly heating from 0 to 230  $^\circ\text{C}$  at 40  $^\circ\text{C}/\text{min}$ . Between each heating scan, a cooling run from 230 to 0  $^\circ\text{C}$  at 40  $^\circ\text{C}/\text{min}$  was also monitored. In each case, after the first heat run, the temperature was held at 230  $^\circ\text{C}$  for 3 min in an attempt to evaporate the trapped solvent. Dynamic mechanical thermal analysis (DMTA) tests were performed on Perkin–Elmer Diamond DMA. Uniform strips of dimension 2.5 mm  $\times$  3 mm  $\times$   $\sim 0.05 \text{ mm}$ , cut by means of a die cutter were used. Film thicknesses were measured using a digital micrometer. These experiments were run at temperature range from  $-30$  to 170  $^\circ\text{C}$  with a frequency of 1 Hz. Tensile testing (TT) measurements were carried out using the same instrument as used for DMTA. Each reading for TT is the average of three individual measurements.

## 3. Results and discussion

### 3.1. TGA analysis

Thermogravimetric analysis curves are plotted as derivative TGA curves ( $-dM/dT$ ) in Fig. 1. In this format, the mass loss due to oxidization/evaporation of a given species appears as a peak. In the curves representing both polymer and composite samples, peaks in the region of 350 to 500  $^\circ\text{C}$  were observed. These are due to decomposition of PVA through elimination of water and pyrolysis [22,23] while no peak was observed for CNT oxidation because of the extremely small quantities of CNT in the samples. The peaks observed at approximately 190, 175 and 100  $^\circ\text{C}$  in Fig. 1a, b and c, respectively, are due to the evap-

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