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Characterization of carbon nanotube dispersion and filler network formation in melted polyol for nanocomposite materials

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ABSTRACT

Different grades of carbon nanotubes (CNTs) were dispersed in poly(tetramethylene ether glycol) (PTMEG) without any solvent in the presence of a block copolymer dispersing agent by ultrasonication at a temperature well above the melting point of the PTMEG. The state of CNT dispersion at different length scales was evaluated by using optical microscopy, UV–Vis spectroscopy, rheological measurements, differential scanning calorimetry, thermogravimetric analysis and sedimentation tests. Optical microscopy can be used to characterize the state of dispersion and CNT network formation on a micrometer scale, whereas UV–Vis provides useful information about the dispersion of individual CNTs at nanoscale. Furthermore, the strength and quality of the network formed can be assessed using different modes of rheological measurements. Dispersion at nanoscale also affects the crystallization behavior of PTMEG, while network formation strongly influences suspension thermal stability and sedimentation behavior. The results obtained using different methods indicate equivalence between UV–Vis spectroscopy, rotational rheometry and PTMEG crystallization behavior for probing the CNT state of dispersion at nanoscale, while an analogy in detection of CNT network formation and strength is observed between oscillatory rheometry, thermogravimetric analysis and sedimentation tests.

1. Introduction

Carbon nanotubes (CNTs) have attracted significant attention in recent years due to their high aspect ratio and remarkable mechanical, thermal and electrical properties, rendering them as an ideal filler for advanced polymer composites and gels [1,2]. However, due to strong interparticle interactions, individual CNTs tend to form micrometer-size bundles which entangle and condense into larger agglomerates with inferior properties [3,4]. Difficulties in uniformly dispersing CNTs have resulted in sub-par material properties as compared with what could theoretically be achieved for well-dispersed systems [3]. In other words, the material properties of CNT nanocomposites are controlled by the state of CNT dispersion in the polymer matrix and nanotube/polymer interfacial interactions [5]. Researchers are still facing challenges to achieve homogeneous dispersion of CNTs at single-nanotube level and to enhance the CNT/polymer interfacial interactions [5,6].

Numerous methods such as high pressure homogenization [7], ball milling and [8] ultrasonication, [9] as well as covalent and noncovalent surface functionalization and using ionic liquids [10] are currently being developed to mitigate these problems. However, the more fundamental question of how dispersion at different length scale affects network formation and the ensuing composite properties remains a challenge. Individually dispersed CNTs affect the system crystallization behavior and enhance the mechanical properties of CNT/polymer nanocomposites [5,11]. Other properties such as electrical and thermal conductivity are strongly sensitive to the formation of a percolated network [1,12].

Moreover, while the formation of a heterogeneous aggregated network can increase the electrical conductivity, the mechanical and electrical properties may not follow the same trend with increasing filler concentration [13]. Therefore, it is still a challenge to simultaneously optimize all physical properties of the nanocomposite system [13]. Thus, a comprehensive evaluation of the state of CNT dispersion at different length scales, i.e., aggregates, bundles and individual nanotubes, as well as network formation and its strength/quality would be mostly beneficial.

Different methods have been used to evaluate the CNT dispersion both qualitatively and quantitatively. UV–Vis spectroscopy measures the absorbance of light at specific wavelengths [14]. Since individual nanotubes more actively absorb light in the UV wavelength region, well-dispersed samples show strong absorbance in the UV region [15], thus, the intensity of UV absorbance can be considered to probe quantitatively the state of CNT dispersion at the individual carbon nanotube scale or *nanoscale dispersion*. Optical microscopy, commonly used to observe CNT dispersion and network formation at the microscale, can provide useful information about the aggregate size and *microscale*

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dispersion quality [2,16]. However, this method is qualitative and usually covers a small area of the sample which may not be representative for the whole system.

It is generally accepted that rheological analysis of CNT suspensions can provide insight into their microstructure and can be correlated with system property enhancement [17]. The rheological properties of polymer/CNT suspensions are strongly affected by the CNT volume fraction, the nanotube aspect ratio, polymer–CNT interactions and the state of CNT dispersion and network formation [18,19]. The presence of uniformly distributed CNT aggregates and well-dispersed individual CNTs and bundles must be considered in the definition of "good mixing" for CNT suspensions [18]. However, the occurrence of different microstructures at different length scales may result in contradictory interpretation of the data for CNT–polymer nanocomposites [20].

The objectives of this work are to evaluate the state of CNT dispersion at different length scales and to provide quantitative measures of dispersion and filler network quality. Moreover, to the best of our knowledge, this is the first comprehensive and systematic study on the direct dispersion of CNT in melted semi-crystalline media using ultrasonication without the aid of solvents.

2. Materials and methods

2.1. Materials

The polyol matrix used in this study is a polytetramethylene ether glycol (PTMEG, $M_n = 950–1050$ g/mol). A high molecular weight block copolymer with pigment affinic groups soluble in dicarboxylic acid ester (30%), and amine value of 11 mg KOH/g (DIN 58176) was used as dispersing agent (DA). The dispersing agent consists of both lyophobic and lyophilic blocks in which the lyophobic part adsorbs onto the surface of CNTs, while the lyophilic part is swollen by the PTMEG media, preventing CNT aggregation through steric stabilization [21].

Three commercially available multi-walled carbon nanotubes (CNTs), provided by Parker Hannifin Corporation, named CNT-A, CNT-B and CNT-C were used. All CNTs were produced by catalytic vapor deposition but have different bulk densities. The supplier reported characteristics of CNTs are summarized in Table 1.

2.2. Dispersion of CNT in polyol

Suspensions of different CNTs in PTMEG have been prepared by dispersing 10 mg (~0.06 vol.%) of carbon nanotubes in 10 g of polyol and 30 mg of dispersing agent (DA) using a tip sonicator (Sonics CP750, 165 W) in the pulse mode (5 s sonication followed by 3 s pause) for 20 min at 50–55 °C. A control sample without carbon nanotubes was processed similarly.

2.3. Characterization techniques

Scanning electron microscopy (SEM) images of the as-received CNT samples were acquired using a JEOL JSM-6510LV instrument with an operating voltage of 30 kV. The dispersion of nanotubes in polyol was observed using an Olympus BX51 Optical Microscope. Small Angle X-ray Scattering (SAXS) measurements were done at the beamline D1 of Cornell High Energy Synchrotron Source CHESS. The sample-to-detector distance and the scattering vector, q, were calibrated using a silver behenate (AgBe) standard with a characteristic (001) peak position at $q = 1.076\ \text{nm}^{-1}$. The beam energy was 10.6 keV with different sample-to-detector distance of 0.645, 1.121, 1.836, or 1.854 m. X-ray detector was a Med Optics CCD camera with a pixel size of $46.9 \times 46.9\ \text{mm}^2$ and 1024×1024 pixels where the detector was protected from the intense scattering in the incident plane by a 2 mm diameter tantalum rod. The X-ray wavelength was $\lambda = 0.1155$ nm. The scattering vector q is defined as $q = 4\pi \sin(\Psi/2)/\lambda$, where Ψ is the scattering angle. Typical exposure times for SAXS patterns were collected for 1 s. The X-ray images were processed using POLAR software (Stonybrook Technology and Applied Research, Inc.).

Table 1
Characteristics of used carbon nanotubes.

Nanotube sample	Outer mean diameter (nm)	Length (μm)	Purity (wt.%)	Bulk density (kg/m^3)
CNT-A	~9.5	~1.5	>90	48.10 ± 0.42
CNT-B	~13	>1	>95	141.29 ± 1.76
CNT-C	~13	>1	>95	78.31 ± 1.68

Dynamic rheological properties were measured using a Thermo Scientific Haake Mars III rheometer at 30 °C. Experiments were carried out in both oscillatory and rotational shear modes using parallel plate geometry with a diameter of 35 mm and gap of 1 mm. Frequency sweeps from 100 to 0.01 Hz were applied at the stress of 0.1 Pa which lies in the linear viscoelastic region. Shear rate sweeps from 10 to 0.01 s^{-1}in the rotational shear mode were also performed. The specimens were placed between the preheated plates and were allowed to equilibrate for approximately 4 min prior to each run, which was found to be satisfactory for measurement reproducibility. Moreover, the maximum error in the rheological tests based on at least 3 measurements on each sample is less than 15%, confirming the reproducibility of the measurements.

The UV and visible light absorptions of the dispersions were obtained using a UV–Vis spectrophotometer (Hitachi U-2800) operating in the range of 200–800 nm. The samples were diluted 20 times using tetrahydrofuran (similar solubility parameters with PTMEG [22]) in order to obtain a detectable transmission during the measurements. The crystallization and melting behavior of the samples were investigated using a TA Instruments Q100 DSC. In the first cycle, samples were heated from −50 °C to 50 °C (above melting point of PTMEG) and held for 2 min and then cooled down back to −50 °C with a rate of 10 °C/min. The second cycle was applied similarly as the first one and was used to evaluate crystallization and melting behavior. Thermogravimetric analysis (TGA) was performed with a TA Instruments Q500 at a heating rate of 10 °C/min under nitrogen atmosphere. Sedimentation tests were performed by monitoring the suspensions stored at 60 °C.

3. Results and discussion

3.1. CNT characterization

SEM images of the as-received powders are shown in Fig. 1, in which micron size agglomerates even bigger than 100 μm can be observed. For the CNT-B and CNT-C samples, an apparent condensed agglomerate structure, in agreement with their higher bulk densities can be noticed, while a highly porous structure is observed for the CNT-A. It has been reported that CNT agglomerates with lower bulk density need lesser deformation stress and energy for dispersion [23].

Small Angle X-ray Scattering (SAXS) can provide morphological insight into both nanoscopic properties such as average CNT diameter and ensemble properties such as CNT orientation [24]. Fig. 2 shows scattering intensities as a function of the scattering vector q for different CNTs.

The CNT-B sample shows a distinct peak at ~0.37 nm^{-1}, while CNT-C and CNT-A samples show broadened shoulders (revealed through a change in the slope of intensity) at ~0.42 and 0.90 nm^{-1}, respectively. These results can be used to calculate CNT diameter according to [24] (Eq. 1):

$$d = 2\pi/q_{max} \tag{1}$$

where, q_{max} is the corresponding scattering vector for the peak or shoulder intensity as shown in Fig. 2. Accordingly, the average diameters are