Carbon 108 (2016) 381–393

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

# Multiscale metrologies for process optimization of carbon nanotube polymer composites

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ARTICLE INFO

*Article history:*
Received 16 March 2016
Received in revised form
28 June 2016
Accepted 13 July 2016
Available online 18 July 2016

ABSTRACT

Carbon nanotube (CNT) polymer nanocomposites are attractive multifunctional materials with a growing range of commercial applications. With the increasing demand for these materials, it is imperative to develop and validate methods for on-line quality control and process monitoring during production. In this work, a novel combination of characterization techniques is utilized, that facilitates the non-invasive assessment of CNT dispersion in epoxy produced by the scalable process of calendering. First, the structural parameters of these nanocomposites are evaluated across multiple length scales ($10^{-10}$ m to $10^{-3}$ m) using scanning gallium-ion microscopy, transmission electron microscopy and small-angle neutron scattering. Then, a non-contact resonant microwave cavity perturbation (RCP) technique is employed to accurately measure the AC electrical conductivity of the nanocomposites. Quantitative correlations between the conductivity and structural parameters find the RCP measurements to be sensitive to CNT mass fraction, spatial organization and, therefore, the processing parameters. These results, and the non-contact nature and speed of RCP measurements identify this technique as being ideally suited for quality control of CNT nanocomposites in a nanomanufacturing environment. When validated by the multiscale characterization suite, RCP may be broadly applicable in the production of hybrid functional materials, such as graphene, gold nanorod, and carbon black nanocomposites.

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## 1. Introduction

Carbon nanotubes (CNTs) have generated remarkable technological interest since their emergence in the 1990s, owing to their exceptional mechanical and physical properties [1,2]. In the new millennium, these high aspect ratio nanostructures are making the transition from laboratory curiosity to commercial material due to the development of synthetic techniques that are industrially scalable. Early synthesis techniques, such as arc discharge [3,4] and laser ablation [5], were batch processes with relatively low yields of CNTs. However, the emergence of chemical vapor deposition [6] (CVD) has enabled continuous, high-volume, high-rate production of nanotubes [2]. High-performance polymer nanocomposites (PNCs), which use CNTs as structural reinforcements and conductive fillers, are one of a handful of CNT-based technological applications that have reached commercial scale production [2,7–10]. CNT PNCs have found applications as light-weight, corrosion resistant, readily-processable materials for mechanical reinforcement [11,12], electro-magnetic interference shielding [13], structural health monitoring [14,15], and flame retardancy [16]. Most of these applications require that the CNTs be individually and homogenously dispersed in the polymer matrix, to maximize

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http://dx.doi.org/10.1016/j.carbon.2016.07.028
0008-6223/Published by Elsevier Ltd.

polymer-nanotube interfacial area and/or to form electrically percolating networks at lower CNT loadings [7,11,17–19].

Agglomeration in CNT-based composites is a significant problem due to the combination of van der Waals interactions and the high surface area of the CNTs [20]. In addition, commercially-available bulk CVD-grown nanotubes often have highly entangled structures [2,11,21]. These structures, resembling tumbleweeds, require extensive processing to break them down and untangle and uniformly distribute CNTs into the polymer matrix [21]. In light of this fact, several candidate methods for tailoring CNT dispersion have been investigated: ultrasonication [22,23], high-speed mixing [24], surfactant-assisted dispersion [25], melt compounding [26] and calendering [27,28]. However, many of these processing methods are not scalable to high-volume, high-throughput production processes [28].

Even when processing techniques can be scaled to an industrial level, a major obstacle to the widespread use of CNT composites is the lack of high-throughput measurement methods for metrology and continuous process optimization through *microstructural evaluation*. The need for such a measurement technique is highlighted in the 2010 WTEC Panel Report on Nanotechnology Research Directions for Societal Needs in 2020, "The next decade will see many of the early nanoscale science discoveries transition to manufacturing. The need for process metrology, quality control measurements, and associated standards is acute." [29] Such a technique should ideally probe the sample in a non-contact, non-destructive fashion and must measure a bulk property that is sensitive to the constituent properties as well as the reinforcement spatial dispersion and volume fraction. Prior to applying these techniques at the pilot or production scale, a quantitative understanding of the effects of nanocomposite morphology on the composite properties must be developed. These processing-structure-property relations are required in order to indirectly evaluate the microstructural and loading information from the measured bulk property. To support this, a suite of techniques probing the microstructure at various length scales is required, since industrially-produced CNT composites characteristically possess a hierarchical structure [30].

In this research, we utilize a combination of imaging and scattering techniques for evaluating the multiscale structure of CNT-epoxy nanocomposites with varying CNT concentrations and dispersion states manufactured using an industrially-relevant calendering process (three-roll mill) [28,31]. Various dispersion morphologies are achieved by varying the size of the smallest gap in the three-roll mill. We use novel scanning gallium-ion microscopy (SGIM) to characterize the CNT spatial arrangement at large length scales ($\approx$100 μm) with resolutions down to 100 nm. We then employ a combination of transmission electron microscopy (TEM) and reciprocal-space small-angle and ultra-small-angle neutron scattering (SANS and USANS, respectively) to examine morphological features in the 0.1 nm to 10 μm range. This microstructural information is analyzed to obtain metrics to quantitatively evaluate the differences in CNT spatial arrangement at relevant measurement length scales.

While microscopy and scattering techniques provide a quantitative description of the nanocomposite morphology these techniques can be time consuming and can require extensive specimen preparation. There is a critical need to develop techniques capable of real-time monitoring of nanocomposite structure during the manufacturing process. Previous studies demonstrate that the electrical conductivity (alternating current (AC) and direct current (DC)) of CNT composites are strongly dependent on the spatial dispersion and mass fraction of CNTs, displaying order-of-magnitude variation as a function of CNT dispersion and concentration [7,17,32,33]. Resonant cavity perturbation (RCP) is a well-established, non-contact and non-destructive technique used to characterize the effective dielectric properties of materials at microwave frequencies [34]. We have recently demonstrated advances to this technique, which have increased its accuracy by approximately an order of magnitude for the measured properties [35]. Further, we have applied RCP to measure the effective dielectric properties of CNT materials in roll-to-roll manufacturing [36]. The sensitivity of the electrical conductivity to CNT dispersion and loading, and the ability of RCP to measure these properties accurately and in a non-contact fashion, make this technique well-suited for quality control of industrial CNT-polymer composites.

In this work we use a multi-walled carbon nanotube/epoxy nanocomposite as a model system to establish a quantitative link between the as-produced morphology, quantified using dispersion metrics obtained from established imaging and scattering characterization methods, and the effective-medium bulk electrical properties measured using RCP. By establishing this fundamental processing-structure-property relationship we can understand the sensitivity of the RCP measurements to variation in the state of dispersion. The methodology established through combining these characterization techniques with RCP measurements may be used to both optimize processing conditions as well as to provide the necessary process control feedback data to ensure desired dispersion in an industrial setting using non-contact measurements. We believe that this methodology is broadly applicable to the quality control and process optimization of many other industrially-produced, functional, nanocomposite materials reinforced with conductive materials such as graphene, nanographite flakes, carbon black, and metallic nanowires.

## 2. Experimental

### 2.1. Materials

The model nanocomposite system used for this study consists of commercially-available, CVD-grown, multi-walled carbon nanotubes (MWCNT) (CM 95; Hanwa Nanotech, Korea [37]) and a low-viscosity epoxy resin system frequently used in the manufacture of composite materials. The epoxy resin system consists of a bisphenol-F epichlorohydrin epoxy monomer (EPON 862; Hexion, USA [37]) cured with an aromatic diamine curing agent (EPIKURE Curing Agent W; Hexion, USA [37]). The as-received carbon nanotubes have a highly-entangled morphology and are typically agglomerated as particles ranging from 20 μm to 200 μm in diameter (Fig. 1a). Due to the complex structure of the agglomerates, it is difficult to accurately measure the initial individual nanotube lengths ($\approx$10 μm). The average CNT diameter is found to be (14.3 $\pm$ 2.5) nm from TEM imaging (Fig. 1d) (Unless noted otherwise, uncertainties are quoted as $\pm$ 1 standard deviation derived from multiple measurements).

### 2.2. Nanocomposite processing

To produce nanocomposites with varying states of filler spatial organization for characterization, we used a calendering technique that has been identified as a scalable method for CNT dispersion. This method involves passing a mixture of CNTs and matrix through horizontal, parallel cylinders, each rotating in opposite directions at different angular velocities [27,28,31]. When passing through the small gap between the velocity-mismatched cylinders, the CNT-epoxy mixture is homogenized by a uniform shear force (Fig. 1b). The mixture forms a thin film over the adjacent cylinders and is collected using a scraper blade.

In order to produce nanocomposites with varying concentrations and morphologies, samples were prepared with different