



# Significance of interfacial interaction and agglomerates on electrical properties of polymer-carbon nanotube nanocomposites



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## ABSTRACT

The ability to control the dispersion state of carbon nanotubes (CNTs) in polymer matrices is closely related to the electrical tunability of polymer-CNT nanocomposites. In this study, the effect of polymer-CNT interactions at the molecular level on the extent of CNT dispersion and consequent electrical properties of the developed nanocomposites are investigated. Two polymer models with dissimilar affinities towards CNTs are studied: polyamide-6 (PA6) having high, and polystyrene (PS) having low affinity towards CNTs. Experiments demonstrate that enhanced polymer-filler interactions in PA6-CNT system lead to improved CNT dispersion at the nanoscopic level. However, PS-CNT system, having higher number density of micro-agglomerates, has approximately ten times lower percolation threshold (0.3 wt% versus 2.9 wt%) and significantly enhanced electrical properties. High affinity of PA6 towards CNTs is proposed to adversely influence electrical properties via encapsulation of CNTs by PA6 through possible wrapping and interfacial crystallization of polymer chains. On the other hand, enhanced electrical properties in PS-CNT nanocomposites are attributed to higher number density of micro-agglomerates, contributing to secondary internal electric field.

## 1. Introduction

Carbon nanotubes (CNTs), due to their unique properties, have drawn great appeal as an ideal conductive filler in development of electroactive polymer nanocomposites [1,2]. Moreover, tunable level of conductive network of CNTs in the polymer matrix entitles the polymer-CNT nanocomposites to be employed in a broad spectrum of applications requiring different conductivities. This includes, but is not limited to, charge storage, antistatic dissipation, electrostatic discharge (ESD) protection and electromagnetic interference (EMI) shielding [3,4].

The effectiveness of producing electrically conductive polymer-CNT nanocomposites significantly depends on the ability to disperse CNTs inside the polymer matrix [5–7]. Dispersion state of filler is governed by many factors such as structure of filler, rheological properties of polymer matrix, polymer-filler compatibility, and mixing technique [8–10]. Accordingly, many studies have been focused on modification of the mentioned parameters to obtain better dispersion and electrical properties [11–13]. Li et al. [7] carried out an analytical-experimental study on critical factors determining the percolation threshold and electrical conductivity of polymer-CNT nanocomposites. Employing the analytical model, the authors found out that minimum percolation threshold occurs when there are no CNT agglomerates and local

concentration of individual CNTs is uniform throughout the sample. However, their experiments showed no apparent percolating behavior in the samples for which the best dispersion state of CNTs was obtained. They ascribed this to reduction in CNTs aspect ratio, caused by the specific procedure used for preparing the samples.

On the other hand, few studies have explored the significance of CNT agglomerates on the level of conductive network and electrical properties [14–18]. The general procedure includes obtaining a well-dispersed mixture through proper mixing process, and then CNTs were stimulated to re-agglomerate (e.g. thermally or shear-induced secondary agglomeration) during processing steps. The resulting agglomerated nanocomposites percolated more readily compared to the homogenized one, leading to much higher electrical conductivity. The enhancement in electrical conductivity was ascribed to improved inter-particle connections, due to the so-called secondary agglomeration, which in turn facilitate the formation of continuous conductive network. In other attempts [19–23], inspired by volume-exclusion effect of crystals, amorphous polymers were replaced by semi-crystalline polymers as the matrix phase to enhance conductive network. The idea is that CNTs are expelled from the crystalline phase and thus the actual concentration of CNTs populated in the amorphous phase becomes much higher than the nominal loading. Although higher electrical conductivity has

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been reported when a semi-crystalline polymer was employed, a few studies observed better network formation in amorphous polymers [24,25]. Such distinct observations in the literature on the effect of dispersion state and crystallinity on electrical properties originate from the engagement of other parameters, such as interfacial interaction, disregarded.

In the current study, our goal is to investigate how the type of interfacial interaction between polymer and CNT influences the dispersion state of CNTs and electrical properties of the resulting nanocomposites. Two homopolymers, amorphous polystyrene (PS) and semi-crystalline polyamide-6 (PA6) with dissimilar affinities towards CNT, were employed to obtain distinct dispersion states of CNTs within the polymer matrices. Based on molecular dynamic simulation results, PS has a very low affinity towards CNTs, while PA6 chains highly interact with CNTs [26,27]. Nanocomposites of these polymers at different CNT concentrations were melt blended in a miniature mixer under identical processing conditions. The states of dispersion, at both nanoscopic and microscopic scales, were examined through transmission electron microscopy (TEM) and light transmission microscopy (LM), and quantified via image processing. The two studied nanocomposite systems showed very distinct electrical properties, i.e. electrical conductivity, current-voltage characteristic, EMI shielding and imaginary permittivity. Correlating the dispersion state of CNTs to electrical properties, this study gives new insight on the role of polymer-CNT interfacial interaction, as well as CNT agglomerates on the quality of conductive network formation, and consequent electrical properties of the developed nanocomposites. These findings provide an in-depth understanding from polymer-filler interactions, the interpretation of resulting electrical properties data, and a platform for engineering nanocomposite structures for an application of interest.

## 2. Experimental

### 2.1. Composite preparation

The employed materials included polystyrene (PS, EA 3130 grade, AmSty LLC), Polyamide-6 (PA6, Zytel 7301 grade, Dupont Co.), and Multi-walled CNTs (NC7000™ Nanocyl S.A., Sambreville, Belgium). The properties of materials are listed in Table S1 and S2 of supporting information. The polymers and CNTs were dried in vacuum oven (Fischer Scientific Isotemp 281A) at 80 °C and  $-20$  inHg for about 2 h prior to conducting the experiments. PS-CNT and PA6-CNT nanocomposites with different CNT loadings were then generated by melt mixing of the constituents with an Alberta Asymmetric Miniature Melt-mixer (APAM) [28]. The pure polymers were first masticated within the mixing cup for 3 min, and then CNTs were inserted into the melt mixer and mixed for an extra 15 min. The melt mixing process was performed at 240 °C and 240 rpm. Long mixing time was employed to assure that the nanocomposite morphology in the chamber was stabilized. Afterwards, the samples were compression molded into rectangular cavities ( $10.2 \times 22.9 \times 1.8$  mm<sup>3</sup>) at 240 °C under 35 MPa for 5 min using a Carver compression molder (Carver Inc., Wabash, IN). These samples were employed for morphological and electrical characterizations.

In order to evaluate the affinity of CNTs to the polymer matrices, a blend of PA6/PS/CNT was prepared by following a two-step procedure. First, the polymers with a volumetric ratio of PA6/PS 10/90 were melt blended in the APAM at 240 °C and 240 rpm for 15 min. Afterwards, CNT in the amount of 1.0 wt% was added to the batch and the mixing process continued at the same conditions for additional 15 min. Low volumetric ratio of PA6/PS was considered to assure higher affinity of CNTs to the PA6 phase.

### 2.2. Rheology

Viscosity of the polymers at the processing conditions was obtained

from complex viscosity data by applying Cox-Merz rule [29] along with Carreau-Yasuda fitting model [30]. Frequency sweep test was performed at 240 °C under nitrogen atmosphere over angular frequency range of 0.01–100 rad s<sup>-1</sup> in the parallel plate (25 mm) configuration of an Anton Paar modular compact rheometer (MCR 302 WESP).

### 2.3. Morphological characterization

The state of CNT dispersion in the polymer matrices was investigated at two different scales, i.e. microdispersion and nanodispersion. The microdispersion state of CNTs within the polymer matrices was analyzed using light transmission microscopy (LM) on thin sections (2 μm thickness) of the compression-molded samples. The samples were cut with a Leica EM UC6 (Leica Biosystems®, Germany) ultramicrotome at room temperature. An Olympus BX60 optical microscope (Olympus Corporation, Japan) equipped with an Olympus DP80 camera was used to capture images with dimensions of  $1000 \times 1400$  μm<sup>2</sup> from different cut sections. The obtained images were quantified using the ImageJ software.

For microdispersion state evaluation, particle size distribution and number density of agglomerates per area, with equivalent circle diameter  $> 5$  μm (area  $> 19.6$  μm<sup>2</sup>), were acquired for 15 cuts, ca. 21 mm<sup>2</sup>. The 5 μm follows the British Standard ISO 18553:2002 method for the assessment of degree of dispersion in polyolefin products filled with pigment or carbon black. Size distribution of the agglomerates was calculated based on their relative area. The relative agglomerate area is defined as the area of a group of agglomerates classified in a specific size range over total area of agglomerates in LM images.

Moreover, the relative transparency of the samples was quantified by dividing the transparency of the sample cut over the transparency of the glass slide/cover glass assembly. This technique detects the agglomerates with sizes equal to or slightly larger than the wavelength of visible light, ca. 400–700 nm, but smaller than visually recognizable agglomerates. Forty different agglomerate-free areas per sample were randomly selected to find the mean and standard deviation values. Further information on employing LM to evaluate microdispersion state of nanofillers within nanocomposites is presented elsewhere [31].

Nanodispersion state of CNTs was evaluated using transmission electron microscopy (TEM). Ultrathin sections ( $\sim 100$  nm) of the samples were cut using an ultramicrotome EM UC6/FC6 setup with an ultrasonic diamond knife at room temperature. The sections were floated off water, and thereafter transferred on carbon-film TEM copper grids. TEM characterization was carried out on a Tecnai TF20 G2 FEG-TEM (FEI, Hillsboro, Oregon, USA) at 200 kV acceleration voltage with a standard single-tilt holder.

### 2.4. Electrical properties measurement

Two conductivity meters were employed to measure the DC electrical conductivity of the generated materials under applied voltage of 90 V. For the nanocomposites with an electrical conductivity higher than  $10^{-4}$  S cm<sup>-1</sup>, the measurements were conducted according to the ASTM 257–75 standards using a Loresta GP resistivity meter (MCP-T610 model, Mitsubishi Chemical Co., Japan) connected with a 4-pin ESP probe. For electrical conductivities  $< 10^{-4}$  S cm<sup>-1</sup>, the measurements were performed with a Keithley 6517A electrometer connected to a Keithley 8009 test fixture (Keithley instruments, USA). This setup was also utilized to obtain current-voltage characteristic of the nanocomposites by performing voltage sweep test in the range of 1–80 V.

EMI shielding measurements over the X-band frequency range (8.2–12.4 GHz) were performed using an E5071C network analyzer (ENA series 300 KHz – 20 GHz). The samples were sandwiched between two waveguides of the network analyzer, which sent a signal down the waveguide incident to the sample. The scattering parameters (S-parameters) of each sample were recorded and used to measure EMI

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