Behavior of load transfer in functionalized carbon nanotube/epoxy nanocomposites

Peng-Cheng Ma [a,b,*], Qing-Bin Zheng [a], Edith Mäder [c], Jang-Kyo Kim [a]

[a] Department of Mechanical Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, China
[b] The Xinjiang Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Urumqi 830011, China
[c] Leibniz-Institut für Polymerforschung Dresden e.V., Dresden 01069, Germany

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ABSTRACT

This paper presents the correlation between the functional groups, interfacial microstructure and behavior of load transfer in carbon nanotube (CNT)/epoxy nanocomposites. Nanocomposites consisting of epoxy and CNTs with/without functionalities (amino and epoxide groups) are prepared and characterized to evaluate the CNT-matrix interactions based on strain-sensitive Raman spectroscopy. The results show that nanocomposites filled with functionalized CNTs exhibit a noticeable G'-band shift in tension while those containing pristine CNTs have a marginal shift, suggesting a more efficient load transfer between the epoxy matrix and functionalized CNTs. An interesting observation is that the slope of the G'-band shifts can be either positive or negative, depending on the functional groups on CNTs and the interfacial structures created between the functionalized CNTs and polymer matrix. The mechanisms behind this observation are discussed with reference to fractography and thermo-mechanical properties of nanocomposites.

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1. Introduction

With unique mechanical and transporting properties, carbon nanotubes (CNTs) have attracted much interest for the purpose of developing polymer-based nanocomposites with excellent mechanical performance and multi-functional characteristics. The excellent properties of CNTs alone, however, do not guarantee mechanically superior products because, as in most other types of composites, the mechanical properties of nanocomposites depend not only on the properties of reinforcement, but more importantly on the degree to which an applied load is transferred from the matrix phase to the reinforcement through an interface [1–4]. Therefore, many different surface treatments and functionalization techniques have been developed with varying degrees of success to improve the interfacial adhesion of CNTs with polymer resins [5–7].

The characterization of CNT-polymer interface is a challenging task because of the technical difficulties associated with the manipulation of nano-scale objects. In the field of fiber-reinforced polymers, it is well understood that the application of a mechanical load to carbon or Kevlar fiber results in shifted wavenumbers of

Raman peaks, which are directly related to the fiber modulus. Correlating the rate of Raman shift with an applied strain leads to the evaluation of interfacial strength experienced by the stiff fibers in the composites [8]. Similar Raman shifts were also observed when CNT/polymer nanocomposites were subjected to a mechanical load [9–14]. The principle of this technique lies in the fact that when the mechanical load is transferred from polymer matrix to nanotubes, it will induce local strain to CNTs, causing a change in the C—C bond vibration which can be monitored by the Raman spectroscopy. Coupling of these Raman responses along with the mechanical deformation of matrix endows the evaluation on the interfacial interactions between the CNTs and polymer matrix. More recently, this technique was adopted to study the interfacial load transfer in graphene/polymer nanocomposites [15,16].

However, there were some discrepancies regarding experimental observations and explanation on observed Raman shift of CNT filled nanocomposites. It was reported [9] that the applied load was transferred from the matrix to pristine CNTs with a positive shift of Raman wavenumbers. Given that these CNTs were pristine ones and mostly in the form of ropes or agglomerates due to poor dispersion, it was suspected that the Raman shift obtained only reflects slippage of individual CNTs within the agglomerates [11,14], not between the CNTs and the matrix resin. For the nanocomposites containing randomly dispersed CNTs, the Raman peak of CNTs was shifted upwards under a compressive strain, whereas a slightly

* Corresponding author. The Xinjiang Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Urumqi 830011, China. Tel./fax: +86 991 3677875.
E-mail address: mapc@ms.xjb.ac.cn (P.-C. Ma).

positive shift was obtained in tension [9]. This was contrary not only to many observations in that the Raman peaks of CNTs shifted downwards when the nanocomposites were in tension [11–13,17–19], but also to the Raman response of composites containing carbon and Kevlar fibers [8]. In addition, there is a possibility that functionalized nanotubes may exhibit different behavior of load transfer under mechanical load, as different functionalities on CNTs create an interface with specific structure and properties. This issue has not been addressed in previous studies.

This paper is part of our continuous endeavor in developing novel techniques to improve the dispersion and interfacial interactions of CNTs with polymer resins [7,20–23]. A particular emphasis in this paper was placed on studying the role of functionalities on the deformation of CNTs embedded in polymer matrix using Raman spectrometry. The mechanisms behind the different behaviours of load transfer from matrix to functionalized CNTs were illustrated.

2. Experimental

2.1. Materials and nanocomposite fabrication

The CNTs used in this study were basically the same as those employed previously [21,22]. They were multi-walled CNTs and synthesized by a chemical vapor deposition method (supplied by Iljin Nanotech, Korea). CNTs containing two different functionalities, i.e., amino and epoxide groups, were prepared, aiming at creating a specifically interfacial structure, a surface formed by a common boundary of reinforcing CNTs and epoxy matrix that is in contact with and maintains the bond in between for load transfer. For the functionalization of CNTs, the pristine CNTs (P-CNT) were first subjected to UV/O_3 treatment in a chamber (Jelight 144AX-220 UV/Ozone Cleaning System) to oxidize and create oxygenated groups (mainly carboxylic groups) on the surface [20,24]. The attachment of amino groups on CNTs (NH$_2$-CNT) was realized by direct coupling between the carboxylic groups on CNTs and the ethylene diamine (EDA, Aldrich) with the assistance of dicyclohexylcarbodiimide (DCC, Aldrich) and dimethylamino-pyridine (DMAP, Aldrich) as catalysts [22]. The silane functionalization of CNTs (Si-CNT) was accomplished by converting the carboxylic groups to hydroxyl ones on CNTs using lithium aluminum hydride (LiAlH$_4$, Aldrich) followed by silanization in a glycidoxypropyltrimethoxysilane (GPTMS, Aldrich) solution [21]. Fig. 1 shows the schematics of reactions taking place during the functionalization.

The nanocomposites containing different CNTs with a fixed weight content of 0.25% were made from diglycidyl ether of bisphenol A (DGEBA, Epon 828, Shell Chemical) as an epoxy monomer and m-phenylenediamine (m-PDA, Sigma–Aldrich) as a curing agent. For the fabrication of CNT/epoxy nanocomposites, the pristine or functionalized CNTs were dispersed in ethanol for 1 h before adding the monomer epoxy, and the mixture was ultrasonicated in a water bath for 1 h each at 60 °C and 80 °C, respectively. The mixture was then outgassed at 80 °C to eliminate the entrapped air and the remaining solvent. The m-PDA hardener was added into the mixture in the ratio of 14.5/100 by weight. The mixture was moulded into a flat plate and cured at 80 °C for 2 h, followed by post cure at 150 °C for additional 2 h.

2.2. Characterization

The functional groups attached on CNTs were quantitatively analyzed using a thermogravimetric analyzer (TGA, Unix/TGA7 by Perkin Elmer). Specimens were heated from ambient to 800 °C at a heating rate of 10 °C/min under air flow. Field emission transmission electron microscope (TEM, 2010F, JEOL) with an energy dispersion X-ray analyzer (EDX) was used to characterize the surface morphology and chemical composition of CNTs before and after functionalization.

The Raman spectra of CNTs and CNT/epoxy nanocomposites were obtained using a micro-Raman system (RM 3000, Renishaw). The excitation source was a He–Ne laser with a wavelength of 633 nm and the spectra data were collected in the backscattering mode. For the deformation of nanocomposites, the cured nanocomposite plates were cut into rectangular specimens with dimensions 50 mm long × 3 mm wide × 1 mm thick, which were loaded in a microtensometer consisting of a specially-made load cell in conjunction with a micrometer. A 50× lens was used to focus the laser on the specimen surface with a 2–3 μm diameter laser spot, and the laser beam was polarized using a polarizer along the direction of mechanical load to maximize the signals from CNTs parallel to this direction. To minimize stress relaxation of nanocomposites and heating effect of laser, 5 scans with 10% of full power (2 mw) were optimized for each Raman spectrum collection (time is about 60 s). The nanocomposite specimens were deformed step-by-step at intervals of about 0.1% strain by rotating the micrometer, and the strain was estimated by dividing the change in gauge length by the original length of the specimen. The Raman spectra were collected from the exactly same spot of the specimen at different strains to detect the in-situ deformation of CNTs in the nanocomposites. All selected bands were fitted and deconvoluted using a combination of Gaussian and Lorentzian functions to identify the peak position.

The fractured surface of nanocomposites was examined using a scanning electron microscope (SEM, JSM-6700F, JEOL). The mechanical properties of nanocomposites were measured on a dynamic mechanical analyzer (DMA-7, Perkin Elmer). Rectangular samples with dimensions 20 mm long × 3 mm wide × 1 mm thick were tested in three point bending from 30 °C to 170 °C at a heating rate of 10 °C/min and a frequency of 1.0 Hz in an argon atmosphere.
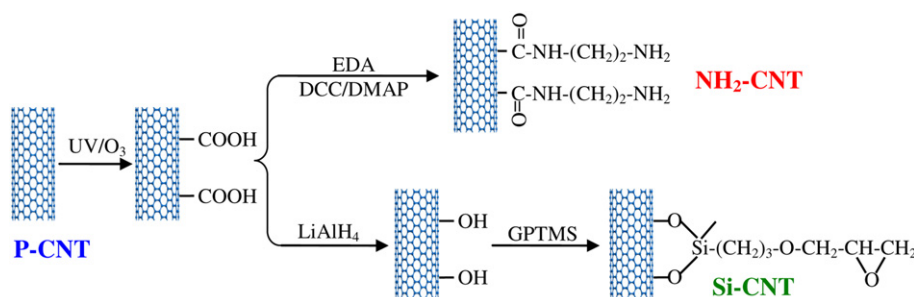

Fig. 1. Schematics of reactions for CNT functionalization.