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A Study on the Effect of Multi-scale Reinforcement – Functionalized Multi-walled Carbon Nanotubes and Basalt Fibers Reinforced Epoxy Laminates

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ABSTRACT

Cross-ply laminates reinforced with basalt fibers and functionalized multi-walled carbon nanotubes (MWCNTs) were fabricated from unidirectional epoxy prepregs. MWCNTs with varied surface conditions were prepared by oxidization or esterification, and then dispersed into a DGEBA epoxy system. The dispersion of the MWCNTs in the epoxy was improved by surface modification, resulting in improved composite mechanical properties as well. Significant increases in elastic modulus and strength were observed for epoxies with functionalized MWCNTs, especially for esterified species. When MWCNT-filled epoxies were used as matrices for basalt fiber/epoxy laminates, the reinforcement effects of MWCNTs on the composite elastic modulus exceeded expectation and were independent of surface functionalization.

Keywords : A. Carbon nanotubes; A. Nano composites; A. Laminate; B. Mechanical properties; C. Elastic properties.

INTRODUCTION :

In the present study, multi-walled carbon nanotubes were grafted with epoxy-compatible surface modifiers [1] before being dispersed directly into the epoxide. The resultant nanotube-filled epoxies were used as matrices in composite laminates reinforced with continuous basalt fibers, selected for the unique thermal, mechanical, and chemical characteristics. The morphology and mechanical behaviors of the nanotube reinforced

epoxies (NEs) were analyzed and related to those of NE/basalt laminates, or hierarchically reinforced nanocomposites

EXPERIMENT :

Chemical Modification of MWCNTs :

MWCNTs (5 grams, 5 - 15 μm in length and 20 - 60 nm in diameter) were dispersed in 500 ml of concentrated 3:1 $\text{H}_2\text{SO}_4/70\% \text{HNO}_3$ following the procedure used by Liu et al.[2] Moderate oxidation while maintaining a high MWCNT aspect ratio was achieved by 30 minutes sonication and 30 minutes stirring at room temperature. After the acid treatment and exhaustive washes with deionized water, HCl was added to the acid mixture to facilitate the termination of CNT surface defects with carboxylic acid groups, rather than carboxylate. The solution was again extensively washed with deionized water until the pH value of the decantate became the same as deionized water. The acid-treated MWCNTs (denoted as o-CNTs) were collected on a 0.45 μm cellulose acetate membrane by vacuum filtration and were dried in a vacuum oven at 80°C for 24 hours.

Some of the o-CNTs were esterified through a procedure similar to the one reported by Chen et al. [3] The esterification was carried out by mixing milled o-CNTs and PGE in a DMF solution with TPP as the catalyst. The mixtures were refluxed in an oil bath heated to 150°C under inert gas (N_2) atmosphere for 36 hours. These esterified nanotubes with phenyl and *beta*-hydroxyl functionalities on the surface were denoted as the PGE-CNTs. After the treatment, the nanotubes were thoroughly washed with anhydrous ethanol, collected with the PTFE membrane, and dried in a vacuum oven at 80°C for 24 hours.

Composite Preparation :

Nano-epoxy coupons (NE coupons) :

The raw-CNTs, o-CNTs, and PGE-CNTs were milled and dispersed in THF using a bath sonication for 10 min. The epoxy was mixed with THF (1:1 by volume) in a dual-axis high-speed shear mixer (Keyence HY501). The two mixtures were blended for another 10 minutes and degassed for 5 minutes in the mixer. The resultant suspension was denoted as nanotube-filled epoxy (NE). Afterwards, THF was evaporated at 80°C in a vacuum chamber for 48 hours. Finally, the curing agent and the accelerator were added to the NE at 4.21 phr and 1.05 phr respectively. The epoxy system was then mixed and degassed again in the mixer prior to casting. The off-stoichiometry epoxy composition was optimized for filament winding/hot press processes and was used throughout this work. The blend was cast into an aluminum mold pretreated with epoxy mold release to produce the NE specimens. The curing cycle was 1 hour at 120°C and post curing at 160°C for three hours. NE specimens were prepared at 0.25, 0.5, and 1.5 vol% MWCNT loadings. (See reference 28 for the estimation of vol%. The percentage of CNTs refers to the fraction of CNT in epoxy resin throughout this work unless otherwise stated.) Five beam-shaped NE coupons were cut and polished from each specimen for tensile test. Following the procedure described above, control samples from pure epoxy resin were also prepared and tested for comparison.

Multi-scale reinforced laminates (MSRs) :

The NEs were also used to fabricate the MSR specimens. Unidirectional prepreg was made on a lab-scale drum-winding machine, where basalt fibers (Rov 68-680/10/Int/Ext., BASALTEX) were pulled through a resin bath before being wound onto a spinning drum at preset rates. The resin bath contained NE (0vol%, 0.5vol% or 1.5vol% MWCNT loading), the curative and the initiator, which were prepared beforehand using the same mixing and degas procedure mentioned above except that THF was used as diluent at this stage. The unidirectional prepreg was cut from the drum and heated at 60°C for 20 min. Four plies of prepreg were cut and stacked in a (0/90/90/0) sequence. Lamination was performed using a hot press at 120°C and 100 psi (~0.69 MPa) pressure for 1 hour, followed by a post-cure at 160°C for 3 hours. Finally, laminated MSR samples were cut into five tensile coupons (2.54 cm x 20.32 cm x 0.05 cm) with 3.81 cm tabs glued to both ends of each coupon.

RESULTS AND DISCUSSIONS :

Properties of the Nanotube Reinforced Epoxies (NEs) :

The tensile modulus and fracture strength of the NE specimens are illustrated in Fig. 1 (each point represents the average of 5 test values). Linear increases in composite tensile modulus with respect to nanotube volume fractions were observed for all three systems. Although the composites with raw-CNTs and o-CNTs exhibited similar increases in modulus, the tensile strength of the NEs with raw-CNTs decreased, an indication of CNT agglomerations and poor CNT/epoxy interface stress transfer. The linearity of strength data for both o-CNT and PGE-CNT was present for low CNT loadings and failed to hold at 1.5vol%. Notably, PGE-CNT composites with 1.5vol% CNTs exhibited modulus and strength increments of ~30% and ~ 60% respectively. With judiciously functionalized nano-fillers [4], PGE-CNT reinforced epoxy presented the highest reinforcement efficiency of the samples tested.

Properties of the Multi-scale Reinforced Composite Laminates (MSRs) :

SEM images of fracture surfaces revealed that the inclusion of 0.5vol% MWCNTs in NE enhanced fiber-matrix adhesion and increased surface irregularity. (Fig.2) The incorporation of MWCNTs resulted in fracture surfaces with a more “ductile” appearance compared to the clean debonded surface characteristic of the control sample. For samples reinforced with raw-CNTs, debonded regions were observed on basalt fiber surfaces, indicating the CNT-rich region and CNT-free regions in the raw-CNT filled NE (Fig.2b). In contrast, basalt fibers were covered with an interfacial NE layer without any debonded region for both o-CNT and PGE-CNT reinforced MSRs in all the fracture surfaces observed (Fig. 2c, d).

The results of tensile tests for the multi-scale composites laminates are reported in Fig. 3. Increases in the elastic modulus of approximately 10% were achieved for the laminates with o-CNT or PGE-CNT modified epoxy at 0.225vol% overall nanotube volume fraction (CNTs account for 0.5vol% of the NE, and the volume fraction of the NE in the MSR is 45vol%). The o-CNT and PGE-CNT reinforced laminates exhibited similar linear increases in elastic modulus relative to CNT loading, irrespective of the chemical modification. In contrast, no

proportional strength increment was observed at 1.5vol% CNT loading for both species, a result of the sensitivity of tensile strength to CNT dispersion. In addition, the tensile strength of the o-CNTs reinforced laminates was consistently greater than those with PGE-CNTs. This finding was attributed to superior fiber-matrix stress transfer that resulted from the high CNT loading layer at the interface.[4, 5]

CONCLUSIONS :

Appropriate choice of surface groups led to uniform dispersion and covalent integration of MWCNTs into a DGEBA epoxy system. Tensile tests of the bulk NEs revealed increases in both elastic modulus and strength, albeit lower than theoretical predictions due to natural CNT waviness and agglomeration. Direct incorporation of functionalized MWCNTs into epoxy/basalt composite laminates improved the elastic properties of the composites, particularly in the fiber direction, and this increase was expected based on the matrix properties obtained from NE specimens.

Figure 1. a. Experimental tensile stress vs. CNT volume fraction plotted with theoretical predictions. b. Experimental tensile strength at break vs. CNT volume fraction.

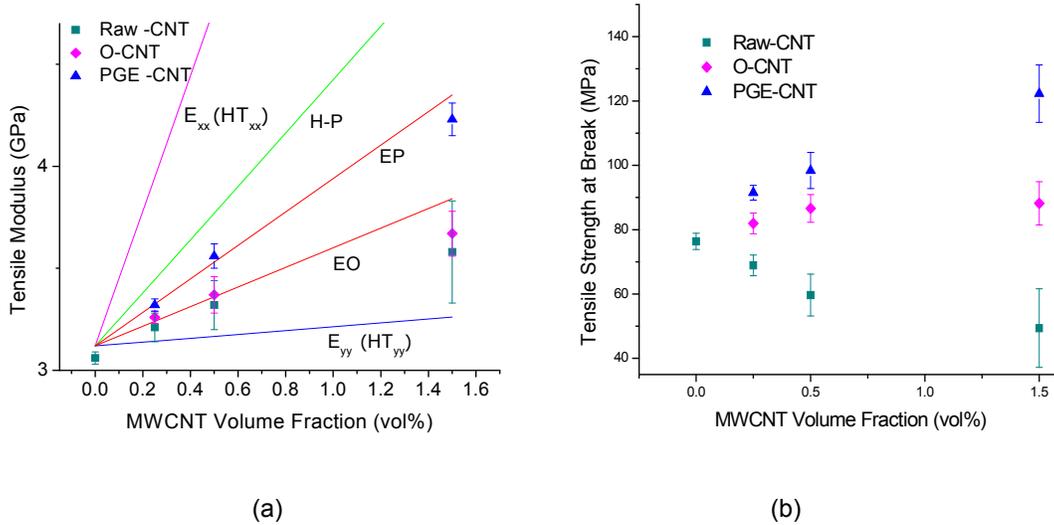


Figure 2. SEM images of basalt fiber fracture surface of MSRs with 0.5 vol % CNT inclusions.

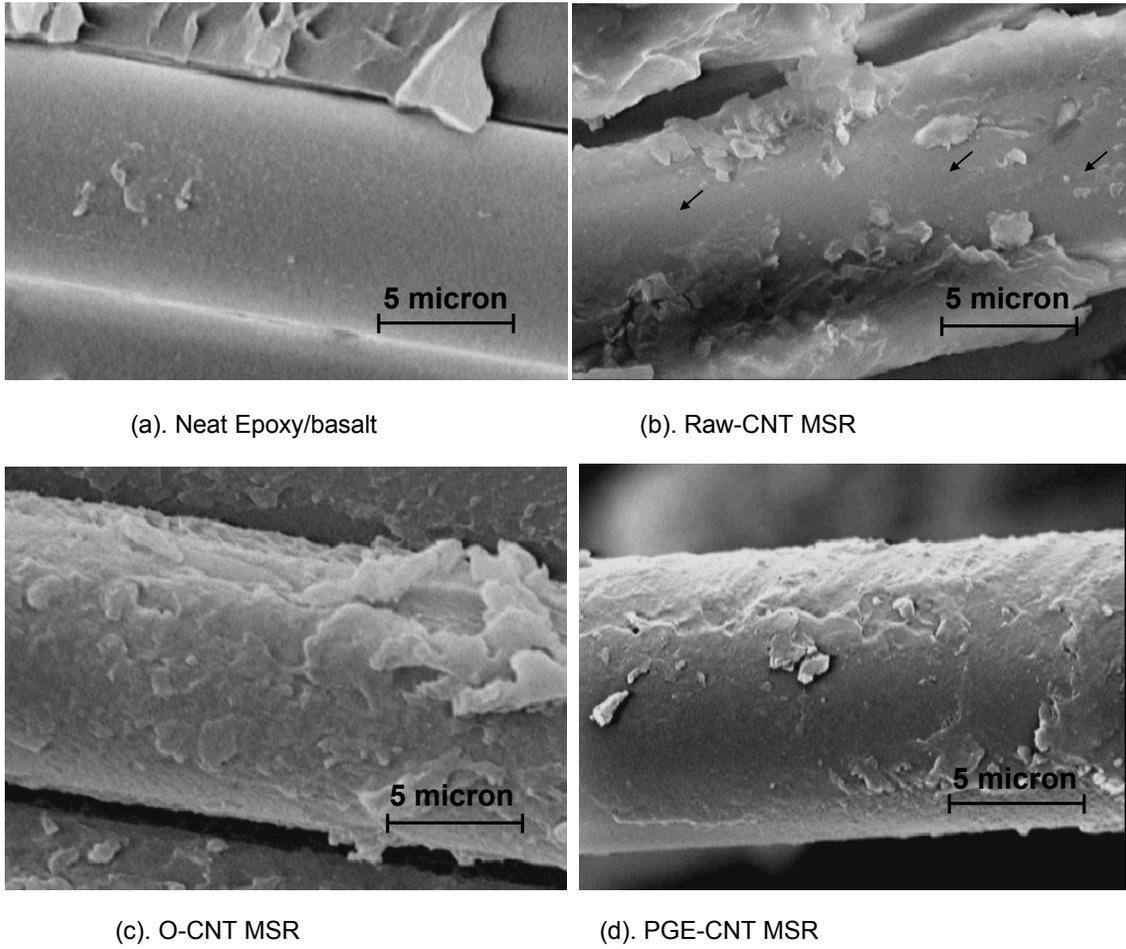
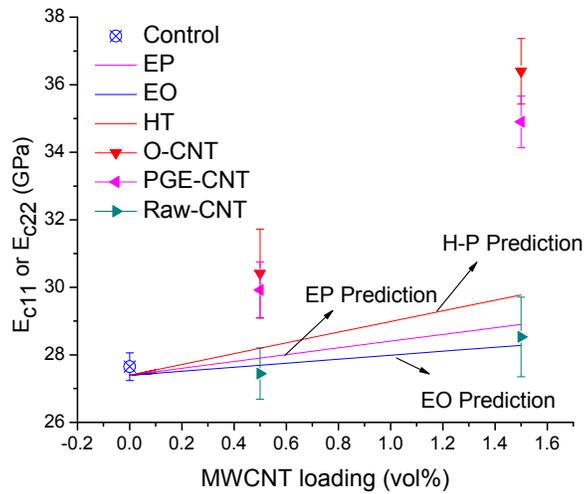


Figure 3. E_{c11} vs. CNT volume loading: measured values and predicted curve.



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