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Functionally graded carbon nanofiber/phenolic nanocomposites and their mechanical properties

Ehsan Bafekrpour [a,b,*], Chunhui Yang [c], Maurizio Natali [d], Bronwyn Fox [a]

[a] Institute for Frontier Materials, Deakin University, Locked Bag 20000, Geelong, Victoria 3220, Australia
[b] Department of Materials Engineering, Monash University, Clayton, Victoria 3800, Australia
[c] School of Computing, Engineering and Mathematics, University of Western Sydney, Locked Bay 1797, Penrith, NSW 2751, Australia
[d] University of Perugia, Strada di Pentima 4, 05100 Terni, Italy

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ABSTRACT

For the first time, functionally graded carbon nanofiber/phenolic nanocomposites were designed and fabricated. The effect of compositional gradients on the flexural properties of functionally graded carbon nanofiber/phenolic composite beams was evaluated. Samples with four compositional gradients as well as a non-graded nanocomposite with the same total carbon nanofiber content and geometry were fabricated using a combination of powder stacking and compression molding techniques. Analytical and finite element models were both performed to investigate the effects of compositional gradients, boundary conditions, and external loadings on flexural properties of nanocomposite beams. Close agreement was observed between analytical solutions, finite element analyses and experiment. The morphology of the fracture surfaces was examined using a scanning electron microscope. The results showed that the flexural properties of carbon nanofiber/phenolic nanocomposites can be greatly improved by controlling the carbon nanofiber content across the thickness of the samples.

1. Introduction

Phenolic resins demonstrate low flammability and smoke properties, excellent resistance to degradation under extreme thermal operating conditions, as well as low density and thermal conductivity. All of these properties make it a safe and cost-effective material of choice in industries such as automotive and aerospace [1–3]. There has been considerable interest in phenolic resins for the thermal protection system in aerospace industry [4]. Its excellent ablative resistance has made it a promising material for reentry vehicles and rocket motor nozzle materials [5]. However, mechanical performance of theses phenolic structures has been a concern as they must withstand high pressures, and phenolic often suffers from low mechanical properties [6].

Many researchers have focused on improvement of mechanical properties by introducing nanofillers into the phenolic matrix [7–10]. Carbon nanofibers (CNFs) have been specifically suited for this purpose due to their high surface area, excellent mechanical stiffness and strength, and relatively low cost [11–13]. However, only a limited enhancement in mechanical properties has been achieved in spite of CNF elastic modulus of about 400 GPa [14–16]. In order to solve the above problem, numerous works with focus on processing and nanofiller factors that influence the mechanical properties have been reported. Extensive research has been conducted to investigate the effect of functionalization [17–19], dispersion [20,21], aspect ratio [22], acid treatment [23], heat treatment [24], plasma treatment [25] purification [26], and orientation [27,28] of CNFs as well as fabrication processes such as extrusion processing [29], spin casting [30], solution casting [31,32], in situ processing [7], and melt spinning [33] on the overall resulting properties of the polymer nanocomposites. However, there is still a very limited improvement in the mechanical enhancement in polymeric matrices as a result of the addition of such nanofillers [34]. Therefore, an optimization in design of nanofiller-reinforced nanocomposites is required due to the limited reinforcing effects and fully take advantage of the existing mechanical properties.

Functionally graded materials (FGMs) with gradient microstructures have been shown to have excellent and controllable material properties. Nanofiller-reinforced FGMs have recently received growing attention as forthcoming advanced materials with novel properties and functions. We have recently reported the fabrication of functionally-graded synthetic graphite/phenolic composites with a significant improvement in thermo-mechanical and viscoelastic properties [35,36]. We also showed that the tem-

* Corresponding author at: Department of Materials Engineering, Monash University, Clayton, Victoria 3800, Australia. Tel.: +61 3 990 50393; fax: +61 3 522 71103.

E-mail addresses: ehsan.bafekrpour@monash.edu, e.bafekrpour@gmail.com (E. Bafekrpour).

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perature gradient field and transient time of functionally-graded composites are highly influenced by the compositional gradients [37–39]. Zheng et al. [40] fabricated Sialon–Si3N4 graded composite ceramic tool materials and investigated the optimal structural parameters and sintering parameters for mechanical properties. However, a systematic study on influence of compositional gradient on mechanical behavior of functionally graded carbon nanofiber/phenolic nanocomposite beams has not been reported in the literature, and further studies of such advanced nanocomposites are thus required.

In the present study, functionally graded carbon nanofiber/phenolic nanocomposites were designed, fabricated, and the effect of compositional gradients across the thickness of the beam samples on flexural properties were investigated experimentally and analytically. An analytical model was developed for further investigation of flexural behavior of non-graded nanocomposite (NGN) and functionally graded nanocomposite (FGN) beam samples with different compositional gradients under three boundary conditions and subjected to both concentrated and distributed loadings. The analytical solutions and governing equations were derived based on the first-order shear deformation theory. An extended rule of mixture was employed to evaluate the Young's modulus and shear modulus of nanocomposites by introducing the reinforcing efficiency of CNF within the phenolic matrix. The reinforcement efficiency was calculated by comparing the Young's modulus obtained from the experiment with that from the rule of mixture in this study. The analytical results were compared with the experimental and FE model data for deflection and flexural modulus of different gradient patterns and the difference sources were discussed. The fracture surface of samples and toughness evolution with CNF content were also investigated.

2. Experimental procedure

2.1. Functionally graded nanocomposite beam design

Two sets of specimens with the same thickness of 5 mm and total CNF content of 5.5 wt% CNF were designed and fabricated: (a) single layered samples with a uniform mass fraction of CNF across the thickness, which was termed a non-graded nanocomposite (NGN) (b) multilayered samples with the mass fraction of CNF varying in different layers, which was termed as functionally graded nanocomposites (FGNs). FGNs were designed to consist of eight layers with the same thickness including two layers with 0 wt% CNF, two layers with 2 wt% CNF, two layers with 4 wt% CNF, and two layers with 16 wt% CNF. Four different FGNs were achieved by changing the order of these layers. FGN-1 was designed to have 16 wt% CNF layers on the top and bottom surfaces of the beam, and then the CNF mass fraction decreased toward the center. FGN-2 had 0 wt% CNF layers on the top and bottom surfaces and 16 wt% CNF layers at the center. The CNF mass fraction increased from 0 wt% at the bottom side to 16 wt% at the top side of the FGN-3 beam. FGN-4 had a reverse compositional change compared to FGN-3. More details of sample designs can be found in our previous publications [35,37].

2.2. Materials and sample fabrication

Graphitized carbon nanofibers with diameters of about 1.5 μm, 99% purity and density of 1.75 g/cm^3 supplied by Nanostructured & Amorphous Materials, Inc., were used as nano-scale reinforcing constituents. A phenolic thermosetting resin with ~9% hexamethylenetetramine obtained from Hexion Specialty Chemicals Pty Ltd was used as the matrix material. Four different stepwise functionally graded nanocomposites as well as non-graded nanocomposites with the same geometry and total nanofiller content were designed and prepared. Samples were prepared in several steps. Firstly, creation amount of phenolic resin and CNF were exactly weighed depending on the CNF mass fraction. Then, the powder mixtures of CNF and phenolic resin with a certain mass fraction were ball milled for 3 min (8000M, Mixer/Mill, Maker, Spex, USA) to ensure homogeneous dispersion of CNF within the phenolic resin. All samples were fabricated using compression molding and powder stacking technique. A die with a rectangular cut-out of dimension 200 × 200 mm^2 and depth of 50 mm and a punch were designed. The corners of the die and punch were provided with a fillet of radius of approximately 10 mm to avoid stress concentration and cracking. Four ejector pins were designed at the bottom of the die. Standard tolerance was left between the die and punch. Premixed composite powders of certain CNF contents were settled in a die of a hot press in a desired sequence using a stacker device. The graded stacks of composite powders were heated up to 130 °C for 10 min and subsequently hot pressed at 180 °C and 4 tonne force for 10 min and finally cooled down. These parameters were chosen after a series of experiments for the production of defect free samples. Samples were then post cured at 180 °C for 2 h to achieve completely cured samples.

2.3. Tensile test

The Young's modulus of phenolic and its nanocomposites containing 2, 4, and 16 wt% CNF were measured for FE analysis and analytical solutions. They were obtained from the tensile test according to ISO 527-3 using a 30 kN Instron tensile tester with a video camera for recording displacement. All tests were conducted at a crosshead speed of 1 mm/min at room temperature. The tensile test samples were 50 × 10 × 1.5 mm^3. Three measurements were taken for each individual nanocomposite layer.

2.4. Flexural test

The three-point bending test was performed on phenolic, FGNs, and NGN samples using a computer controlled LLOYD LR30K testing machine The tests were conducted according to the ISO 178 at the crosshead speed of 1 mm/min. The beam specimen dimensions were 100 mm × 10 mm × 5 mm. The span length was 80 mm and the diameter of cylindrical supports was 5 mm. FE and analytical predictions of deflection and flexural modulus of phenolic, FGNs, and NGN were verified by studying the load–deflection behavior of the samples. At least three identical samples were used for each sample condition to ensure the reproducibility in load–deflection results.

2.5. Scanning electron microscopy (SEM)

The distribution of CNFs within the phenolic matrix and layer interfaces were investigated with a scanning electron microscope (SEM Supra 55VP) at an accelerating voltage of 5 kV and a working distance of 7 mm.

2.6. Optical microscopy

Optical microscopy was used to investigate the cross section of different configurations of FGNs using Olympus SZX12 digital camera coupled with an Olympus DP70X long distance optical microscope. Samples were cast in 30 mm diameter metallographic mounts, ground using three different grit silicon carbide papers on a Struers polishing and then polished on a MD-Mol, MD-Nap and MD-Chem surface with the abrasive types of DP-Susp, p 3 μm, DP-Susp, p 1 μm and OP-S, 0.04 μm, respectively.