Composites Science and Technology 72 (2012) 446–452

Contents lists available at SciVerse ScienceDirect

Composites Science and Technology

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

Augmented fatigue performance and constant life diagrams of hierarchical carbon fiber/nanofiber epoxy composites

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ARTICLE INFO

Article history:
Received 8 March 2011
Received in revised form 14 June 2011
Accepted 3 December 2011
Available online 9 December 2011

Keywords:
A. Carbon nanotubes
A. Laminate
A. Polymer–matrix composites (PMCs)
B. Fatigue
B. Mechanical properties

ABSTRACT

We report the results of an extensive multi-stress ratio experimental study on the axial fatigue behavior of an all-carbon hierarchical composite laminate, in which carbon nanofibers (CNFs) are utilized alongside traditional micron-sized carbon fibers. Primary carbon fibers were arranged in matrix-dominated biax ±45° lay-ups in order to establish matrix and matrix/fiber interaction based performance. CNFs were matrix dispersed by three-roll calender milling. Results indicate that the CNF-reinforced composites collectively possess improved fatigue and static properties over their unmodified counterparts. Large mean lifetime improvements of 150–670% were observed in fully compressive, tensile and tensile dominated loadings. Enhancements are attributed to the high interface density and damage shielding effect of the CNFs within the matrix. Further improvements are believed to occur when the nanofibers arrest and redistribute small scale, slowly propagating matrix cracks at low applied stresses. These results highlight the ability of a nanometer-sized reinforcing phase to actively participate and enhance matrix properties while moving toward a cost effective alternative to current material solutions.

1. Introduction

The introduction of new aircraft, bridges and near 10 MW wind turbines containing fiber-reinforced plastics (FRPs) has dictated refining of the traditional design drivers and engineering of these materials. In fatigue intensive wind energy applications for example, a common characteristic in the higher capacity turbine models is the development of larger blades with more swept area. Escalating mass due to the larger blade designs has heightened the significance of both static and dynamic design constraints based on gravitational loads. These considerations along with the mechanical attractiveness and decreasing price have enticed the transition from glass to carbon in both blade and spar designs. Nijssen [1], using results from the European OPTIMAT program [2], and Samborsky et al. [3] in the US Department of Energy (DOE)/Montana State University (MSU) fatigue database [4] have shown major fatigue improvements over all glass composites by using carbon/glass fiber hybrid laminates. Moreover, Joosse et al. [5] reported the possibility of reducing blade costs by 4–5% by replacing glass with carbon due to material reductions imparted by using stiffer fibers. The ultimate goal is simple: to produce larger, lighter and stiffer structures capable of withstanding long-term and sustained cyclic loads while making them viable economic alternatives to traditional solutions. To this regard, creating a hierarchical structure through the use of a nano-reinforced matrix phase in conventional carbon fiber laminates could provide added mechanical robustness and the heightened resistance to cyclic loading essential to these structures.

Nano-scale reinforcement of an epoxy system with 1 wt.% dispersed carbon nanofibers (CNFs) was previously shown by our group [6] to improve fatigue life by nearly an order of magnitude at low applied stress amplitudes. Grimmer and Dharan [7,8] explored the hierarchical effect in multiwall carbon nanotube (MWCNT)/glass fiber/epoxy composites. Results from a single, fully tensile R-value (R is defined as the ratio of minimum to maximum stress in a fatigue cycle; $R = S_{min}/S_{max}$) showed a fatigue life improvement of 150% at low applied stress amplitudes in the MWCNT-reinforced laminates. Fatigue life enhancements of these systems are typically more prominent at low cyclic loads. It is hypothesized that the nanometer-scale reinforcing elements more effectively accept and redistribute strain energy at low applied stresses through the preservation of the fiber/matrix interface. In addition, the existence of agglomerated nanotubes or fibers can create stress-concentrating sites that negate enhancements at higher loads. The negative influence of agglomeration is reduced at lower stress amplitudes due to a decrease in stress intensity surrounding the nested filaments. Yavari et al. [9] also reported tensile and bending fatigue life improvements in glass fiber/epoxy composites via matrix dispersed nanotubes and graphene platelets. Enhancements in both modes of testing were observed over the full range of applied loads, however, more dramatic increases were

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doi:10.1016/j.compscitech.2011.12.006

detected in bending. The authors suggest, based on ultrasound scans of the coupons, that the disparity between testing modes lies with the graphitic fillers functioning mainly to suppress delamination and buckling of the primary fiber/matrix interface on the compression side during bending.

Fundamental materials research commonly emphasizes the study of quasi-static strength and stiffness properties over long-term fatigue and creep performance. Furthermore, typical studies usually focus on fiber-dominated (e.g., [0] or [0/90]) or quasi-isotropic [0/±45/90] architectures. In-plane monotonic properties of hierarchical composites with fiber-dominated glass [7,10] and carbon [11,12] primary fiber architectures are not significantly affected by matrix reinforcement. Improvements to matrix-dominated properties such as delamination [13,14] and interlaminar shear [10,15] have been reported via matrix-dispersed nanofillers. Relatively few fatigue studies though have been published based on matrix-dominated laminates containing only angle-ply primary fibers. Although fewer applications exist for these fiber patterns (e.g., areoshell skin in wind rotor blades), performance comparisons over a wide range of dynamic loading conditions remain essential for the evaluation and subsequent prediction of fatigue life for these materials. This is especially true of fiber composites whose behavior in tension and compression are often inconsistent due to their anisotropic nature and matrix property dependence. Generation of a constant life diagram (CLD) is a simple and effective technique to convey modeled constant amplitude load and life data over multiple *R*-values for later use in more practical spectrum loading predictions and materials design based on assigning fatigue damage.

In this comparative study we report the most extensive published fatigue dataset for any hierarchical fiber laminate configuration to date. In it, we have generated constant amplitude fatigue data from both neat and CNF matrix-reinforced carbon fiber biax ±45° laminates at a variety of dynamic loading conditions totaling 110 separate fatigue tests. Data were subsequently fit to a power law model then represented and contrasted on a five *R*-value, stress based CLD.

2. Experimental

2.1. Materials and laminate manufacture

GANF is a commercial grade helical-ribbon carbon nanofiber produced by Grupo Antolín Ingeniería, Burgos, Spain. Fiber morphology appears similar to the more common stacked-cup structure but is comprised of a continuous graphitic ribbon of approximately five graphene layers helically rolled about the fiber axis. Vera-Agullo et al. [16] provided TEM evidence of the continuous graphitic nature and gave a comprehensive characterization of the sample. The CNFs were dispersed in a low viscosity commercial grade diglycidyl ether of bisphenol A/F (DGEBA/DGEBF) epoxy resin (Resoltech 1800, Resoltech, Eguilles, France) to exact a final concentration of 1 wt.% in the matrix, not the entire laminate. Dispersions were processed by a three-roll calendering operation. The diamine hardener, 1,2-diaminocyclohexane, was added and mixed to the dispersion then degassed at approximately −1 bar for 30 min. The resin and curing agent were combined at a weight ratio of 100:17.

A total of ten laminates (30 × 30 cm) were produced via the vacuum assisted resin transfer molding (VARTM) technique. A filtration effect has on occasion been reported when manufacturing laminates by VARTM – especially at filler concentrations above 1 wt.% [13,17]. Low viscosity resin and proper use of distribution media has been shown to greatly reduce the effect [13]. The high-strength carbon primary fibers were PAN-based and arranged in a 200 g/m^2 areal weight (A_w) unidirectional fabric supplied by Hexcel Inc. Each ply was carefully positioned and laid out as a $[\pm 45]_6$ configuration on a tempered glass mold coated with mold release. After the ply stacking procedure was complete, release fabric and resin distribution media concluded the layup. Mastic sealant and vacuum film created an airtight envelope around the laminate, through which vacuum was pulled and resin was infused during manufacture. Laminates were initially cured under vacuum at 40 °C for 12 h. After removal of the vacuum film and resin distribution media, the composites underwent additional curing for 15 h at 60 °C and a post cure of 6 h at 110 °C.

Fiber volume fraction, V_f, for each panel was determined in accordance with ASTM D 3171 using $V_f = A_w \times N/\rho_f \times h$, where A_w is fabric areal weight, N is number of plies, ρ_f is fiber density and h is laminate thickness. Table 1 summarizes the measurements. Fiber content was observed to be fairly consistent across the panels. Coupons were CNC machined from the panels using diamond coated tooling and water lubrication and randomly distributed throughout the test programs (see data matrix).

2.2. Test methods

Two rectangular coupon geometries were used throughout the test programs. Dimensions were chosen based on their successful application in prior work by Nijssen [1] and Samborsky et al. [3]. Coupons used in static tensile and fully tensile fatigue testing were 150 × 25 × ~2.5 mm. Tests that included a compressive component were performed with shorter specimens to prevent buckling (no anti-buckling guide was utilized). These coupons had dimensions of 127 × 25 × ~2.5 mm. The resulting distance between grips were 40 mm and 13 mm, respectively. No bonded tabs were used due to the relatively low stiffness imparted by the lack of 0° primary fiber-reinforcement. Failures consistently occurred within the gauge section, both in static and fatigue testing. The issue of grip related failure in very stiff hybrid and all-carbon laminates remains an open-ended problem [18].

All testing was conducted using an Instron 8516 100 kN servo-hydraulic machine with wedge grips. Static testing was conducted in displacement control mode. The ASTM recommended displacement rates were converted to strain rates and related to the shorter gage lengths, hence displacement rates are specified below the ASTM-rates but strain rates were in the end very similar to the standard. As a result, all static tests were conducted at a displacement rate of 0.4 mm/min. Corresponding initial strain rates were 0.01 and 0.03 min^{-1} for tensile and compressive tests, respectively. It is noteworthy to mention that tensile strength was shown by Samborsky et al. [3] to differ by only 2% when varying the displacement rate from 0.02 mm/s to 13 mm/s in a hybrid carbon/glass laminate. In tensile tests, deformation was measured with a clip on type extensometer over a gage length of 25 mm and modulus values were calculated between 0.001 and 0.003 absolute strain. Constant amplitude, sinusoidal waveform fatigue tests were run in load control mode at five *R*-values (10, −2, −1, −0.5, 0.1), see

Table 1
Average thickness and V_f for each panel (standard deviation in parentheses).

Material	Panel name	Thickness (mm)	Fiber content, V_f (%)
Neat matrix, $[\pm 45]_6$	0-A	2.43 (0.02)	54.8 (0.6)
	0-B	2.46 (0.03)	54.3 (0.7)
	0-C	2.41 (0.03)	55.2 (0.7)
	0-D	2.42 (0.03)	55.1 (0.6)
	0-E	2.39 (0.03)	55.7 (0.7)
1.0 wt.% CNF, $[\pm 45]_6$	1-A	2.48 (0.04)	53.9 (1.0)
	1-B	2.46 (0.05)	54.2 (1.1)
	1-C	2.41 (0.02)	55.3 (0.4)
	1-D	2.40 (0.05)	55.5 (1.2)
	1-E	2.38 (0.02)	55.9 (0.5)