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In-plane strength enhancement of laminated composites via aligned carbon nanotube interlaminar reinforcement

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ABSTRACT

Aerospace-grade unidirectional carbon fiber laminate interfaces are reinforced with high densities (>10 billion fibers per cm^2) of aligned carbon nanotubes (A-CNTs) that act as nano-scale stitches. Such nano-scale fiber reinforcement of the ply interfaces has been shown to increase interlaminar fracture toughness and here we show that laminate in-plane strengths are also increased. Delamination damage modes associated with pre-ultimate failure are suppressed in the in-plane loaded laminates, significantly increasing load-carrying capability: tension-bearing (bolt pull out) critical strength by 30%, open-hole compression ultimate strength by 14%, and L-section bending energy and deflection by more than 25%. No increase in interlaminar or laminate thickness is observed due to the A-CNTs, but rather the ~10 nm diameter carbon nanotubes interdigitate between carbon fibers in the adjacent laminae, *i.e.*, the observed reinforcement is not due to formation of a thicker interlayer. These increases in substructural in-plane strengths are in stark contrast to degradation that typically occurs with existing 3D reinforcement approaches such as stitching, weaving and z-pinning.

1. Introduction

One of the main limitations of advanced composite materials is their poor z-direction mechanical properties due to the unreinforced pure polymer region at ply interfaces, a known Achilles heel of advanced composites. There are several approaches to reinforce such composites in the through-thickness direction including 3D weaving, stitching, and Z-pinning [1–4]. As these approaches are based on micron-diameter fibers and their assemblies (tows), in-plane fiber movement and/or damage, fiber volume loss, and stress concentrations are produced as unavoidable artifacts during manufacturing. These act to significantly reduce the in-plane mechanical properties of the laminate, such that these technologies are not in significant use [1]. Thus, the problem of weak interfaces in composites, and concomitant issues such as damage resistance and tolerance, and their implications for over-design, are outstanding limitations in composite structural performance.

In order to avoid this reduction of the in-plane properties, carbon nanotubes (CNTs) can be used as a secondary or hybrid reinforcement that can be integrated within advanced composites [5–13]. Nanomaterials, particularly carbon nanotubes (and now graphene) in their different forms, have been extensively investigated for enhancement of modulus and toughness [14–18] due to their high surface-to-volume relative to larger reinforcements, with excellent reviews available, including a specific focus on epoxies as utilized here [6,19–29]. Less work has taken on the challenge of introducing carbon nanofibers into the interlaminar region to improve mechanical properties (usually toughness). In the limited extant work, at most modest improvements are generally noted for interlaminar toughness and shear strength (*e.g.*, [30], and see review article [31]), with in-plane properties not yet being addressed [32]. Reduction in properties are primarily attributable to the low loadings (order of 1% by volume fraction) of generally low aspect ratio randomly dispersed fibers, and most improvements are likely due to an increase in interlaminar thickness through process-zone toughening. Various nanofibers and nanofillers have been investigated with the pre-dominance of work focused on CNTs. The morphology of CNTs is typically randomly dispersed, although some attempts at structured morphology interfaces have been presented, notably aligned carbon nanofibers and nanotubes grown

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directly on microfibers (see review [11]).

Z-direction nanofibers, specifically aligned carbon nanotubes (A-CNTs), have been introduced into the interlaminar region of unidirectional composite plies in prior work (termed 'nano-stitching', see Fig. 1 [33]). The A-CNTs reinforce the interface as evidenced by steady-state fracture enhancement of 2.5–3X in Mode I and II, and importantly for the current work, do not increase the interlaminar thickness. Such toughness improvements are greater than the results reported for standard z-pinning reinforcement [1,33,34] and has the hypothesized benefit of maintaining in-plane properties due to the unobtrusive way in which the nano-scale aligned CNTs are introduced into the laminate interlaminar region. Here, we show that in-plane properties can be significantly increased, thereby giving concomitant improvement in both in-plane and out-of-plane laminate properties, in stark contrast to typical out-of-plane reinforcements (stitching, z-pinning, weaving) that degrade in-plane properties. Substructural strength tests of the type that set design limits for many practical aerospace applications, and that highlight the issue of weak interlaminar regions, include bolt-bearing (also known as tension-bearing), open hole compression (OHC) and compression after impact (CAI). Bolt-bearing and OHC failure involve mechanisms including interlaminar delamination, matrix cracking and shear, fiber microbuckling, etc [35,36]. L-shape curved laminates and other complex shapes are typical elements in aerospace structural components such as frames, co-cured webs, or angle brackets [37], and these also oftentimes fail with contributions from interlaminar modes. To explore the effectiveness of interlaminar reinforcement via A-CNTs at ply interfaces, we focus on in-plane strength evaluation including tension-bearing, OHC, and L-shape bending tests to failure.

2. Experimental

Fabrication of the laminates, including A-CNT synthesis and introduction to the laminate interfaces are first presented. This is followed by a discussion of the strength testing employed herein: bolt bearing ("filled-hole tension" or "tension bearing"), open hole compression (OHC), and L-shape bend configurations.

2.1. Aligned-CNT synthesis and laminate fabrication

A-CNTs, sometimes termed forests or vertically aligned CNTs (VACNTs), were grown in a tube furnace (Lindberg/Blue M) by chemical vapor deposition (CVD) at atmospheric pressure following procedures previously documented [38]. Si wafer pieces (30 cm × 40 cm) coated with catalyst (1/10 nm of Fe/Al_2O_3) by e-beam evaporation were placed in the quartz tube (44 mm inner diameter) reactor and pretreated at 650 °C for 7 min at reducing atmosphere (H_2/He) to condition the catalyst. A reactant mixture ($H_2/He/C_2H_4$) is introduced for 30 s to produce ~20 μm high A-CNTs. In order to facilitate the transfer of the forest, a reduction cycle is applied, reducing the attachment between the CNTs and the Si substrate. Further details of the process can be found elsewhere [39]. The A-CNT forests are found to have an areal density of ~1 vol% corresponding to 10^9–10^{10} CNTs per cm^2, with each CNT comprised of 3–5 walls and having an outer diameter of ~8 nm, giving an inter-CNT spacing of ~80 nm. The A-CNT forests are nominally 20 μm in length with non-trivial variability (~±10 μm) in height with extremes of 3 μm and 30 μm noted.

The A-CNT forests were introduced to the interlaminar region by manually transferring them to the surface of the composite prepreg plies. A unidirectional aerospace-grade carbon fiber and epoxy prepreg tape (Hexcel AS4/8552) was used. The prepreg material is designed to give 63.5% carbon fiber by volume and a nominal cured ply thickness of 0.130 mm in the cured laminate. The Si wafers were positioned with the CNT side in contact with the prepreg surface and moderate vacuum and heat (~1 bar and ~60 °C) was applied on each individual prepreg ply by using a vacuum bag and heating blanket assembly. Once the A-CNTs had attached to the tacky prepreg surface of a ply, the Si wafers were manually released from the attached CNT forests and the lay-up of the next ply continued until the lay-up was completed. Effectiveness of the transfer process was between ~75 and 90% of ply surface area. A standard 16-ply $[(0/90/\pm45)_2]_s$ quasi-isotropic laminate with 15 A-CNT reinforced interfaces is created. The laminates were assembled with the appropriate cure materials and cured in an autoclave following the industry process specifications (6 bar of total pressure at 1.5 °C/min to 180 °C, hold for 2 h, cool at 3 °C/min to 60 °C and vent pressure, let cool to room temperature). Baseline and A-CNT specimens were cured in the same laminate. Once the laminates (210 × 300 mm^2 in-plane dimensions) were cured, specimen edges were cut to size and prepared for the different tests. Specimen dimensions and test specifics are provided below. All of the specimens, baseline and A-CNT reinforced, had measured thickness within 1 standard deviation of the nominal 2.080 mm laminate thickness.

2.2. Laminate strength testing

Specimen configurations and testing details are described for

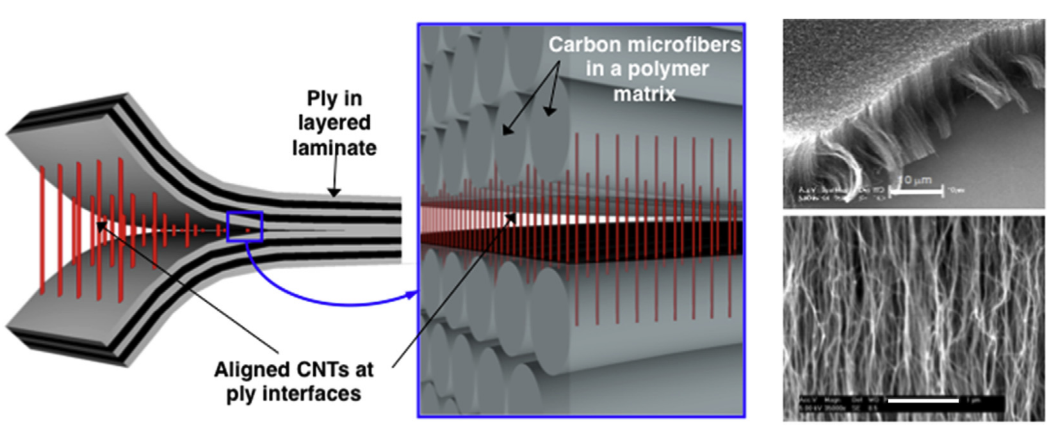

Figure 1. 'Nanostitching' concept where aligned carbon nanotubes (A-CNTs) bridge ply interfaces in laminated composites: (*left*) concept illustration of A-CNTs at a laminate interface, and (*right*) scanning electron micrographs of representative A-CNT forests showing CNT alignment.