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Effect of carbon nanofiber z-threads on mode-I delamination toughness of carbon fiber reinforced plastic laminates

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ABSTRACT

Delamination is a major drawback of carbon fiber reinforced plastics (CFRPs). Studies have reported that carbon nanofibers (CNFs) can improve the delamination toughness of various FRPs. However, lack of CNF alignment control caused substantial uncertainty in the improvements. In this study, a novel CNFs z-threaded CFRP (ZT-CFRP), which utilized z-aligned CNFs as long-range reinforcement threading through the packed carbon fiber bed, was manufactured. The mode-I delamination toughness (G_{IC}) of the ZT-CFRPs was tested against both control CFRPs and unaligned CNF-modified CFRPs (UA-CFRPs). Through statistical comparison against control CFRPs, UA-CFRPs exhibited a relative change in mean G_{IC} and coefficient of variation of +13.99% and +116.35%, respectively, whereas the ZT-CFRPs of equivalent CNF concentration exhibited a relative change in mean G_{IC} and coefficient of variation of +28.93% and −12.33%, respectively. Accordingly, the CNF z-threads were found to play a positive role in toughening CFRPs, as supported by delamination experiments and microscopy analysis.

1. Introduction

1.1. Background and previous works

Given recent advances in composite manufacturing techniques, carbon fiber reinforced plastics (CFRPs) have become commonplace in a wide variety of engineering applications due to their high modulus-to-weight and strength-to-weight ratios. These traits make CFRPs particularly desirable to industries in which weight-savings is paramount, such as the aerospace and automotive industries. However, unlike traditional metals, CFRPs are anisotropic (i.e., the material properties are directionally-dependent). While CFRPs exhibit desirable material properties in the direction of carbon fiber reinforcement, they are severely limited in the through-thickness direction (i.e., z-direction), which lacks a reinforcing fiber network. Furthermore, CFRPs' z-directional mechanical strength is substantially weakened by the carbon fiber-resin matrix interface and the distinctly different mechanical properties between the rigid carbon fiber and relatively softer resin matrix. As CFRPs are typically used as laminated structures, the absence of effective z-directional reinforcement results in an inability to resist delamination when subjected to large out-of-plane mechanical loads.

Various methods have been studied to counteract delamination issues, however, the most common methods involve either fiber stitching [1–3] or nanoparticle reinforcements [4–13], which can be subdivided into interleaving and direct matrix dispersion approaches. Fiber stitching is costly and difficult for complex and large CFRP part manufacturing, thus its applications are constrained by part-size, complexity, and budget. Moreover, the stitching needles can break and interrupt the carbon fiber reinforcement, thereby reducing the CFRP's compressive strength in the x-y plane, particularly under hygrothermal conditions [3]. Therefore, the improvements in interlaminar fracture toughness provided by fiber stitching are offset by the reduction in other critical material properties. Recently, nanoparticle reinforcements have also been used to provide significant increases in interlaminar fracture toughness. However, many of the reported results suffered from substantial increases in uncertainty [4–6,11,12].

An increasingly prevalent research approach in the field of nanoparticle reinforcement is the insertion of nano-reinforced resin layers (i.e., nanoparticle enhanced interlayers or interleaves) along the mid-plane of a FRP laminate, which enhances interlaminar strengths [4–7]. Lee et al. [4] achieved mode-I delamination toughness (G_{IC}) increases of over 30% using a CNT-laden

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nanowoven carbon tissue (NWCT) interlayer. However, the coefficient of variation (i.e., CV, which is standard deviation divided by the mean) of the CNT-NWCT was nearly ninefold larger than the control CFRP. Arai et al. [5] increased G_{IC} by approximately 50% using a CNF interlayer, yet their G_{IC} plots illustrate that the samples with the CNF interlayer exhibited significantly larger standard deviations than the control sample. Garcia et al. [6] grew a dense z-aligned CNT forest on a silicon substrate, transferred the CNT forest to a prepreg, and then joined two carbon fiber prepreg layers to form a through-thickness aligned CNT forest interlayer (i.e., interleaf); this method provided G_{IC} improvement of approximately 50% and 150% for AS4/8552 and IM7/977-3 commercial prepregs, respectively, along the CNT forest interlayer as compared to the baseline CFRP laminates. Although CNTs and CNFs in nanoparticle-reinforced interlayers have yielded positive results, the increase in thickness, weight, and complexity makes interleaf implementation between every interlaminar plane of a FRP laminate less practical for lightweight composite designs and manufacturing consistency. However, it should be noted that selective interleaving, as elaborated in [6,7], may still provide a potential method of circumventing these inherent shortcomings by strategically reinforcing critical locations rather than the entire structure.

Another common nanoparticle reinforcement approach is to uniformly disperse nanoparticles in the matrix material throughout the FRP. This direct matrix dispersion approach is fundamentally different from the interleaving approach because its purpose is to homogeneously improve the matrix's mechanical properties and also enhance the FRP's interlaminar toughness, which is typically considered a matrix-sensitive property. However, many challenges exist in the dispersion process and the processes used to incorporate the nano-resin into the FRP system. Despite the challenges, CNTs and CNFs have been reported to enhance the interlaminar strength of glass fiber reinforced plastics (GFRPs) via uniform dispersion in the matrix material without adding any interleaves between GFRP laminae. A generic approach is to infuse the nano-resin into a preform of dry fibers via Liquid Composite Molding (LCM) processes. Sadeghian et al. [8] successfully infused 1 wt% CNF-modified polyester into GFRP laminates to improve interlaminar fracture toughness by approximately 100%. In their study, a CNF/polyester matrix was infused into the preform of random glass fiber mats using Vacuum Assisted Resin Transfer Molding (VARTM). This study also elaborated on nanoparticle filtration issues, which occurred as the CNF/polyester mixture flowed through the glass fiber preform. As the CNF length (approximately 50–500 μm) is much larger than the pore size within the glass fiber bed (glass fiber diameter ~20 μm, so the pore size is of the same order of magnitude), certain unaligned CNFs could be filtered by the glass fiber bed and gradually clog the flow channel, resulting in uneven CNF concentration and a visible color gradient in the GFRP. Fan et al. [9] infused MWCNT-modified epoxy into a preform of woven glass fiber mats via two different types of VARTM processes. The best improvement in the interlaminar shear strength (ILSS) was 33%, which was found in the 2 wt% MWCNT-modified GFRP sample manufactured with injection and double vacuum assisted resin transfer molding (IDVARTM). The IDVARTM utilized a step-wisely controlled atmosphere to (i) reduce the atmosphere and permit more nano-resin being injected into the flow distribution medium layer under the vacuum bag and above the glass fiber preform and (ii) subsequently increase the atmosphere to compact the nano-resin filled flow distribution medium layer thus squeeze the nano-resin into the glass fiber preform that is under strong vacuum. Although IDVARTM can handle higher MWCNT concentration than traditional VARTM, IDVARTM was not able to create the preferable MWCNT alignment that traditional VARTM produced and IDVARTM provided a lesser increase in ILSS at 0.5 wt% MWCNT concentration as well. The micrographs provided within their study indicated that the short CNTs (compared with the gap between two adjacent glass fibers in the pictures) had slightly preferred alignment along the flow direction while under a traditional VARTM process but not under IDVARTM. Accordingly, Fan et al. concluded that the slightly preferred MWCNT alignment contributed to the ILSS improvement in addition to MWCNT concentration.

Together, the accumulated literature suggests that lack of control over CNT/CNF alignment and filtration could induce inconsistent composite quality. Furthermore, since carbon fibers (diameter ~5 μm) are much smaller than glass fibers (diameter ~20 μm), the narrower gap between adjacent carbon fibers creates severe challenges in terms of CNF or CNT alignment and filtration control; these issues are compounded for CNF applications (compared with CNT applications), as CNFs are much longer (approximately 50–200 μm) and thicker (diameter ~50 to 150 nm) than CNTs (length ~5 to 20 μm; diameter ~1 to 20 nm). As such, no significantly successful studies regarding the infusion of CNF-modified resin in CFRPs have ever been reported.

To avoid the aforementioned challenges, electrophoretic deposition of water-dispersed short CNTs (preferred length of 2–6 μm, shortened from original length of 10–20 μm by nitric acid treatment) on woven carbon fabric, which was then dried and then stacked into a preform and infused with resin via VARTM process, has been studied [10] and produced an interlaminar shear strength increase of approximately 30%. However, handling the deposited CNTs on dry carbon fiber fabric could be cumbersome. Wicks et al. [11] provided an alternative by growing CNTs in-situ on alumina fibers to create novel "fuzzy fiber reinforced plastics" or FFRPs, which yielded a 76% increase in mean G_{IC} and an approximately twofold increase in the relative error (i.e., error/mean). Another FFRPs study by Wicks et al. [12] illustrated the differences that CNT length and epoxy grade (aerospace grade and marine grade) played in regards to G_{IC}. For the aerospace epoxy, short CNTs actually reduced the G_{IC} by 50%, whereas the long CNTs increased the mean G_{IC} by 32%, while also increasing the relative error by nearly 20% w.r.t. control. For the marine epoxy, short CNTs and long CNTs increased the G_{IC} by 89% and 100%, respectively. However, short CNTs and long CNTs also increased the relative error by 12% and 78%, respectively. Due to the exposure to high temperatures and/or metal catalysts, this process is not compatible with carbon fabrics. Moreover, the uncertainty in the improvements may be a concern. As such, the FFRPs method still needs future improvements to make it more robust.

1.2. Research rationale

This paper takes a notably different approach than the literature with respect to the nano-reinforcing strategy, manufacturing process, and the attempt to gain an understanding of the roles of CNF alignment in CFRPs. Based on insights from the aforementioned nano-resin VARTM literature [8], it is clear that CNFs can potentially benefit z-directional strengths. However, multiple studies have suggested [8,9] that poor CNF alignment control and the aforementioned filtering effect could be responsible for reducing the effectiveness of the CNF reinforcement or even, in some cases, weakening the composites. Although the works by Garcia et al. [6] and Wicks et al. [11,12] illustrated that both vertically-aligned CNTs in the interlayer and radially-aligned CNTs deposited on individual alumina fibers can improve interlaminar fracture toughness, none of the studies made a comparison against laminates with randomly distributed CNTs of the same ingredients. As such, none of these previous works provided any direct proof that improving CNF alignment and filtering issue could make the CFRP composite, of same ingredients, stronger. Nevertheless, it is reasonable to assume that one could maximize CNFs' potential to