Carbon 125 (2017) 63–75

Contents lists available at ScienceDirect

Carbon

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

Enhanced durability of carbon nanotube grafted hierarchical ceramic microfiber-reinforced epoxy composites

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ARTICLE INFO

Article history:
Received 9 May 2017
Received in revised form
11 August 2017
Accepted 2 September 2017
Available online 6 September 2017

ABSTRACT

Carbon nanotube (CNT) hierarchical composites are increasingly identified as next-generation aerospace materials, so it is vital to evaluate their long-term structural performance under aging environments. In this work, the durability of hierarchical CNT grafted aluminoborosilicate microfiber-epoxy composites (CNT composites) are compared against aluminoborosilicate composites (baseline composites), before and after immersion in water at 25 °C (hydro) and 60 °C (hydrothermal), for extended durations (90 d and 180 d). The addition of CNTs is found to reduce water diffusivities by approximately 1.5 times. The mechanical properties (bending strength and modulus) and the damage sensing capabilities (DC conductivity) of the CNT composites remain intact regardless of exposure conditions. The baseline composites show significant loss of strength (44%) after only 15 d of hydrothermal aging. This loss of mechanical strength is attributed to fiber-polymer interfacial debonding caused by accumulation of water at elevated temperatures. *In situ* acoustic and DC electrical measurements of hydrothermally aged CNT composites identify extensive stress-relieving micro-cracking and crack deflections that are absent in the aged baseline composites. SEM images of the failed composite cross-sections highlight secondary matrix toughening mechanisms in the form of CNT pullouts and fractures that enhance the service life of composites.

1. Introduction

Fiber reinforced plastics (FRPs) are used extensively in aerospace, automotive, and energy applications due to their high stiffness and strength-to-weight ratios, as well as their ability to be manufactured into complex shapes [1–4]. Traditionally, FRPs are anisotropic materials that are strong in the fiber plane with relatively weak interlaminar regions that are susceptible to failure when subjected to non-tensile loading conditions such as shear or compression [5,6]. Composite engineers have addressed the inadequacies in the interlaminar region by using three-dimensional fiber architectures such as weaving, stitching, braiding or z-pinning, which add fiber yarn reinforcements between adjacent fiber layers to improve structural properties under shear and compressive loading. However, these fiber additions lead to a significant decrease in the composite strength due to the geometric defects introduced by fiber crimping, fracture and distortion, while increasing the potential for weak, resin-rich regions [7,8]. The optimization of mechanical properties continues to require specialized composite designs and remains a primary area of focus for this field. Common aerospace-grade epoxy matrices are non-conductive and exhibit poor functionality toward electrostatic discharges, electromagnetic interference and lightning strike protection. Hence, secondary challenges for aerospace applications are mitigation of static discharge and the use of non-destructive techniques for sensing hidden damage within a composite

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http://dx.doi.org/10.1016/j.carbon.2017.09.006
0008-6223/Published by Elsevier Ltd.

structure.

Highly conductive, mechanically superior nanofillers such as CNTs can address deficiencies in mechanical (non-tensile) and electrical properties of aerospace composites [9–12]. Even at low volume fractions, the CNT networks stiffen the polymer matrix and prevent rapid crack growth through secondary energy dissipation mechanisms such as CNT pullouts and CNT fractures, that can enhance the service life of nanotube enabled composites [13]. CNTs are impregnated into fiber composites using two principal methods: matrix dispersion and fiber attachment. Matrix dispersion involves directly dispersing CNTs in the resin followed by resin infusion into fiber layers, whereas fiber attachment consists of directly adhering the CNTs onto fiber layers prior to resin infusion. Literature studies indicate that the increase in mechanical performance of a nanocomposite is a strong function of resin/nanofiller interfacial properties for a given CNT aspect ratio and dispersion [14–17]. As FRPs manufactured by matrix dispersion often encounter CNT agglomeration with no significant improvement in mechanical properties [18–20], the current study focuses on FRPs manufactured by directly adhering CNTs to fiber surfaces.

Multi-walled carbon nanotubes (MWCNTs) are grown on top of the alumina microfiber surface *via* a chemical vapor deposition (CVD) process that results in a dense “mohawk” CNT forest extending from the fibers. The resulting “fuzzy” fiber textile layers are then stacked and infused with a thermoset resin using commercial resin transfer manufacturing techniques. Improvements in both interlaminar and intralaminar properties are observed in these hybrid systems, where the radially arranged CNTs wick the polymer resin *via* capillary action to form strong interfacial bonds between the resin and the nanotubes [21,22]. In addition, CVD growth of the CNTs increases the spacing between individual fibers and increases the area of the tow cross-section. This results in a lower volume fraction of resin pockets between fiber tows and textile layers with CNTs bridging the inter- and intra-ply regions within the composite [23]. Even at a low CNT volume fraction (approximately 1% by volume), the electrical conductivity of composites can be improved by up to 6 orders of magnitude [24].

Aerospace applications of nanoengineered composites rely on their shear strength and toughness (joints and wing spans, landing gear trailing arms), electrical conductivity (de-icing, EMI shielding) and thermal properties (engine exhausts and nozzles), where these materials are expected to perform for long operating periods at varying temperature, strain, and humidity conditions [25–29]. Optimizing the microstructure of the CNT network and the interfacial interactions to tailor the composite for these important applications requires novel approaches for manufacturing and design. One area lacking data for hybrid FRPs is durability. This information is critical to avoid a material system with poor service lifetimes. The established methodologies for characterizing FRP aging are exposure to “hot and wet” conditions followed by mechanical testing and Highly Accelerated Lifetime Testing (HALT), which provides a pass/fail condition, but only has a limited capacity to predict product reliability [30,31]. This work utilizes accelerated aging protocols and *in situ* experimental measurements to identify and track the evolution of failure mechanisms in these advanced composites.

Several routes have been identified through which composites degrade under hydrothermal conditions. At short exposure times or low temperatures, plasticization of the matrix and swelling induced interfacial stresses lead to reduced mechanical performance. These effects however, may be reversed upon drying [32–34]. At longer exposures or high temperatures, resin and fiber degradation, and void formation, cause irreversible reduction in the mechanical performance through a combination of failure modes that include fiber damage, matrix cracking or interface debonding [35–42]. The presence of MWCNTs in composites has the potential to affect composite durability by modifying water absorption, resin cure chemistry and interfacial bonding characteristics. The conclusions of the majority of early studies on dispersed CNT systems differ depending on the CNT functionalization, CNT volume fractions, dispersion methodology and the CNT/polymer interactions. Some of the prominent studies on durability of these systems are summarized in Refs. [43–47].

While there are several studies on the long-term effects of water and temperature on resin chemistry and mechanical property changes in dispersed CNT-epoxy and CNT-FRP systems [43–47], there are no studies on the durability of hierarchical composites, where the CNTs are directly attached to fiber surfaces. The current study focuses on measuring the aging characteristics (water diffusivity, polymer plasticization and hydrolysis reactions) of the nanoscale CNT reinforcement of the polymer in a model aluminoborosilicate fiber composite system. The aluminoborosilicate fibers used here are heat treated and suitable for high-temperature refractory applications. It has been previously shown that the CVD growth process degrades commercial fiber materials such as glass or carbon [48], thereby making them unsuitable for studying the properties of grafted CNT fiber-composites. Though there have been recent advancements in depositing carbon nanotubes onto individual carbon fiber tows, obtaining a complete 3-D CNT coverage on fiber-mats using the CVD process is still a challenge [49]. Both these requirements are well satisfied in the case of aluminoborosilicate fibers, which can withstand the harsh growth conditions encountered during the CVD process and support 3-D CNT growth [26]. These fibers have been previously used to understand several aspects of the hierarchical CNT composites including manufacture and processing ([23,50]), physical properties ([21,24,25,28]), and resin infusion. Hence, despite having lower mechanical properties than commercially relevant fibers (glass and carbon), this aluminoborosilicate fiber system is useful for investigating the aging characteristics of the hierarchical CNT composites.

Various physical and chemical characterization techniques were employed to study the aging characteristics of the CNT composites. The effect of CNTs on water absorption and solvent diffusivity into the resin, was studied by gravimetric water uptake measurements. Combining mechanical strength measurements with *in situ* acoustic and electrical measurements, the changes in damage propagation were studied as a function of mechanical strain and successfully correlated against SEM images of failed surfaces. Finally, the primary cause of strength failure in hydrothermally aged alumina fiber specimens was determined using SEM, Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR), and differential scanning calorimetry (DSC). Our results demonstrate that the presence of radially grown CNTs helps mitigate interfacial failures in fiber reinforced composites under accelerated aging environments and, furthermore, provides a significant increase in the component lifetime.

2. Materials and methods

2.1. Composite manufacture

The laminates used in the study consist of plain weave aluminoborosilicate fiber mats (approximately 55% by mass, with or without CNTs) (ultra temp 391 fibers, Cotronics Corporation, NJ, areal density of 371 g/m^2) that are infiltrated with an aerospace epoxy resin (RTM6, Hexcel Corporation) using a Vacuum Assisted Resin Infusion (VARI) process [25]. The as-received fibers were treated with a non-hygroscopic coating/sizing by the manufacturer. MWCNTs (approximately 2% by mass) were deposited on fiber