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Viscoplastic characterization and modeling of hybrid carbon fiber/carbon nanotubes reinforced composites

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ABSTRACT

This investigation illuminates the effect of surface grown carbon nanotubes (CNTs) on the viscoplastic behavior of fiber reinforced plastics (FRPs). The study demonstrates the feasibility of growing CNTs on conventional woven carbon fibers without degrading the fibers structural properties. The subsequent hierarchal reinforcement was utilized to fabricate laminated FRPs. The viscoplastic behaviors of the hybrid composites were investigated through series of stress relaxation and creep tests at different thermomechanical environments. The results of the experimental tests were utilized to both construct and validate a phenomenological viscoplastic constitutive model of the hybrid FRPs. The experiments and the model predictions established that surface grown CNTs could enhance the composite resistance to viscoplastic deformation.

1. Introduction

Structural fiber reinforced plastic (FRP) composites including those reinforced with high performance fibers (e.g., glass, carbon, aramid or their combinations) are evolving as viable alternatives to metals for structural applications due to their elevated specific strengths and stiffness [1]. However, emerging applications of FRPs entail the exposure to elevated thermomechanical environments, which precludes their life cycles and durability, making it crucial to investigate their time/temperature dependent deformation. As embodiments of temporal thermomechanical behaviors of FRPs, creep and stress relaxation are of particular importance as they affect the strength and durability of structures made of FRPs. The deformations or changes in the material properties driven or amplified by exposure to prolonged times and/or elevated temperatures are referred to as viscoplastic deformations. Polymer matrix composites are prone to progressive deformation under constant loads (creep) and bare lesser loads under constant displacement (stress relaxation) in longer time durations. These time-dependent deformations should be accounted for in the design of FRPs structures as they could jeopardize the load bearing capacity and might induce structural instabilities.

The main source for the viscoplastic deformations in FRPs is the polymeric matrix where the constituent chains tend to slide against each other and straighten. Although the addition of carbon fibers enhances the mechanical properties of the polymers considerably - including the resistance to viscoplastic deformation - other issues arise when these microscale fibers are incorporated. Straightening of the fibers from their possible initial waviness and more notably the slippage mechanisms between the fibers and matrix are major contributors to the viscoplastic deformations in FRPs.

The insufficient resistance of FRPs to viscoplastic deformations can be mitigated by the addition of nanofillers to the polymeric matrix. Nanofillers were utilized to modify the viscoplastic behavior of polymer matrix composites [2]. The presence of nanofillers could compensate for the viscous properties of polymers up to an extent; however, it brings about other changes such as reducing the ductility and altering the electrical/thermal properties of the composite. The amount of change depends on the volume fraction of the nanofillers, their morphology and ultimately their adhesion to the matrix. In the case of nanofillers with high intrinsic Van der Waals forces (such as carbon nanotubes; CNTs), the lack of proper dispersion becomes detrimental if the volume fraction exceeds a certain metric called the percolation threshold. The percolation threshold is considered to be the minimum volume fraction at which a filler can uniformly be dispersed in a matrix properly to form a 3D connected network throughout the matrix without agglomeration. Most research to-date focus on using CNTs

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as reinforcements in a polymeric matrix by shear mixing and perhaps subsequent alignment of single- or multi-walled CNTs in the matrix [3–5]. Alignment and dispersion are crucial factors that are challenging to control experimentally using oft-repeated mixing methods. Carbon nanotubes embedded in a polymeric matrix form aggregates that are not only poorly adhered to the matrix, but also concentrate stresses; compromising the contribution of the CNTs as reinforcement. Sonication [6] and calendaring [7] have been employed to resolve this problem, but are not effective beyond ~3.0% CNT volume fraction due to the formation of aggregates [8]. The extreme difficulty in uniformly dispersing CNTs in polymer matrices arises from the large surface area of CNTs [9]. Dispersion and extrusion techniques have been reported in the literature for producing CNTs composites [10]. However, in both techniques, producing uniform and well-dispersed CNTs reinforced composite is difficult because of the small amount of solid 'powder' (carbon) compared with the large amount of liquid polymer (matrix) in early mixing stages. This often leads to phase separation due to the strong van der Waals forces between CNTs compared with that between CNTs and polymer [4].

Several protocols were applied to enhance the fiber/matrix interface and, thus, hinder the slippage mechanism between the fibers and the matrix encountered in viscoplastic deformations. The chemical treatment approach utilizes acidic reagents (e.g. chlorosulfuric acid, nitric acid, etc …) to attach functional groups such as carboxyl, ether or hydroxyl to the fiber to improve the load transfer and adhesion between the fiber and the matrix. It was demonstrated that the chemical treatment improves the wettability and the surface roughness of the fibers, which in return, increase the tensile strength, and the interlaminar shear strength of the composite [11]. However, the chemical treatments could induce excessive erosion to the fiber leading to a reduced composite strength.

An alternative approach to impede the slippage mechanism between the fibers and the matrix can be achieved via the creation of well-attached, small-scale physical obstacles on the fibers surface (i.e., whiskerization). Whiskerization can resolve the dispersibility and agglomeration issues discussed earlier as no physical mixing is needed. The whiskers could be high aspect ratio crystalline silicon carbide, silicon nitride or CNTs grown on the surface of the fibers. The growth of high aspect ratio nanotubes on the fiber surface induces less stress concentration in the fiber since they induce stiffness gradient from the fiber to the matrix [12]. The growth of 1D carbon nanostructures (multi and single wall carbon nanotubes) and ZnO nanorods on commercially available carbon fibers has been demonstrated via different studies [13–15]. Carbon nanotubes were grown on carbon yarns and carbon fabrics surface using the catalytic chemical vapor deposition (CCVD) with different catalysts such as nickel, cobalt and iron at high temperatures (600 °C–1000 °C). Zhang et al. [16] have grown high density multiwall carbon nanotubes (MWCNTs) using the CCVD process at high temperatures 700–800 °C on the surface of sized and un-sized carbon fibers. The results showed a 40% decrease in the tensile strength of the sized carbon fibers when exposed to 700 °C growth environment. Identical results were observed for the un-sized fibers but at temperatures higher than 800 °C which contrasts the important role played by the fibers sizing. Since the carbon fibers and the grown 1D nanowhiskers are of different size and nature, the term "hybrid nanocomposite" is used throughout the remaining text to address the whiskerized carbon FRPs. Several studies showed that both in plane and out of plane properties of carbon nanofiller modified carbon fiber and glass fiber polymer composites are considerably higher than pristine composites [5,17–28].

The time-temperature dependent behavior of conventional FRPs has been studied utilizing different constitutive models that were originally designed for polymers [29–33]. Creep tests require prolonged testing time as the rate of change can be very slow (in some cases several years). Hence, different accelerated methods have been developed to predict the long-term creep behavior of polymeric materials using data from tests at elevated temperatures with considerably shorter durations. The time–temperature superposition (TTSP), Findley's model [34], Schapery's model [35] and polymer modified thermal activation energy theory [36] are some of the widely utilized accelerated creep testing schemes. Viscoelasticity of FRPs has been studied utilizing standard short-time creep tests at different temperatures to predict their long-term creep behavior [31,37]. Like many other mechanical properties, the creep compliance and the stress relaxation modulus (as two influential material parameters for viscoelasticity) are much weaker along the transverse direction to the fiber orientation [38]. This heightens the importance of studying the flexural creep properties in orthotropic or transversely isotropic FRPs where the axial direction is designated as the fiber direction, which exhibits the least deformation, imposed by time or temperature variations.

The goal of this study is to delineate the effects of growing CNTs on the surface of carbon fibers on the viscoplastic behavior of FRPs. In particular, the creep and the load relaxation behaviors of hybrid FRPs based on hybrid carbon fiber/CNTs reinforcements are examined under different thermomechanical environments. To quantify the change in the viscoplastic behavior, we examined the changes in the parameters of a phenomenological viscoplastic model developed by T. Gates for FRPs [39].

2. Materials, processing and experimental techniques

2.1. Samples preparation

PAN-based woven carbon fibers with 3 k bundles, Thornel® T650 (Cytec, Inc.), were utilized as the reinforcement in this study. The sizing on the fibers was removed by placing the as -received sized fibers in a tube furnace at 550 °C for 30 min under inert environment (nitrogen). The de-sized fibers are afterward employed in a three-layer polymer matrix composite to further investigate the effect of the sizing removal on the mechanical properties of the composite. Carbon nanotubes were grown utilizing the graphitic structure by design (GSD) method, detailed elsewhere [15,40–43].

The GSD method requires a thin layer of Ni to be applied on the fibers as a catalyst for the CNTs growth. The Ni layer (2 nm) was deposited on the de-sized carbon fibers utilizing a magnetron sputtering system (ATC Orion from AJA International). The carbon yarns were placed, separately, inside a quartz tube furnace. Three mass flow controllers were required for the three input gases: an inert gas (UHP N_2), a hydrocarbon (C_2H_4), and Ultra High Purity H_2. The synthesis processes comprised three steps: (i) a reduction step, at 550 °C under N_2/H_2 environment, was carried out for 2 h under atmospheric pressure to break the nickel film into nanoscale sized particles and to remove any nickel oxides, (ii) flushing of the system with nitrogen to remove the reduction byproducts and, (iii) the introduction of the "deposition mixture," which consisted of $N_2/H_2/C_2H_4$ while maintaining the temperature at 550 °C. The growth time was set to 30 min.

Per our previous investigations [44], the uniform growth of CNTs might not be the best topology to improve the fiber matrix interface; very dense growth could prevent the matrix from infiltrating through to reach the base carbon fibers; leading to poor matrix/fiber adhesion. Hence, to overcome this hurdle, a patterned CNT growth is more favorable and can be achieved by enforcing interspacing in the catalytic nickel film. A perforated mesh template was clamped to the carbon fiber fabrics during the sputtering of nickel.