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The effect of bulk-resin CNT-enrichment on damage and plasticity in shear-loaded laminated composites

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ABSTRACT

One way to improve multi functionality of epoxy-based laminated composites is to dope the resin with carbon nanotubes. Many investigators have focused on the elastic and fracture behavior of such nano-modified polymers under tensile loading. Yet, in real structural applications, laminated composites can exhibit plasticity and progressive damage initiated mainly by shear loading. We investigated the damage and plasticity induced by the addition of carbon nanotubes to the matrix of a glass fiber/epoxy composite system. We characterized both the modified epoxy resin and the associated modified laminates using classical mesoscale analysis. We used dynamic mechanical analysis, scanning electron microscopy, atomic force microscopy and classical mechanical testing to characterize samples with different concentrations of nanofillers. Since the samples were prepared using the solvent evaporation technique, we also studied the influence of this process. We found that in addition to the global increase in elastic regime properties, the addition of carbon nanotubes also accelerates the damage process in both the bulk resin and its associated glass–fiber composite.

1. Introduction

Traditionally, fiber reinforced polymers (FRPs) are used in structural applications due to their excellent mechanical behavior. Some applications also require that FRPs have outstanding electrical or thermal properties if they are intended to replace metallic materials with such properties. An example is the requirement of low electrical resistivity for electrical tomography based structural health monitoring [1] or the requirement of lightning protection in materials used to construct airplanes [2]. Glass fiber laminated composites are usually a poor conductor and these multifunctional properties must be introduced to the material. One promising option is through nano-enrichment. The addition of CNTs and other types of nanofillers to traditional composite materials has created a new type of composite referred to as multiscale or hierarchical composites. They are made of constituents embedded on the same matrix but whose dimensions are on completely different scales. Comprehensive reviews on multiscale and hierarchical composites were published by [3,4].

However, the introduction of CNTs in the matrix increases the complexity of the damage mechanisms observed in laminated composites. Here, we studied the damage and plasticity properties of CNT-enriched glass–fiber/epoxy laminated samples. First, we studied the behavior of the bulk matrix by preparing and testing CNT-doped epoxy resin samples. Then, we used the vacuum infusion technique to impregnate glass–fiber plies into multiscale glass–fiber reinforced polymer (GFRP) samples. $[\pm 45]_{2s}$ angle-ply specimens were then tested under loading/unloading tensile conditions to investigate the response of a single ply under shear loading. Indeed, very few investigations have been conducted on the shear response of CNT-doped laminates; those available focused on their elastic and ultimate strength behaviors [5]. We followed the framework of classical mesoscale damage mechanics based on the works of Ladevèze and co-workers [6]. This modeling approach has been demonstrated to be robust and popular in laminate design.

We describe in Section 2 the materials, preparation procedures and characterization techniques. In Section 3, we provide comprehensive experimental observations on both the bulk resin and related laminates. It appears that although CNT-enrichment clearly improves the initial elastic stiffness of a composite system, it can also accelerate the damage process. We discuss this observation in terms of Dynamic Mechanical Analysis (DMA), mechanical testing, morphological analysis (including scanning electron microscopy (SEM) and Atomic Force Microscopy (AFM)).

2. Materials and methods

2.1. Description of raw constituents

We prepared carbon nanotube-doped epoxy samples and carbon nanotube-doped glass–fiber reinforced polymer (GFRP)

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laminates using the following commercially available raw materials. –COOH functionalized MWCNTs are provided by CheapTubes and produced by catalyzed chemical vapor deposition. Per the supplier's specifications, the purity was greater than 95 wt.% and the residual ash was less than 1.5 wt.%. The raw powder contained 2.56 wt.% of –COOH groups.

The specified dimensions (outer diameter from 8 to 15 nm; inner diameter from 3 to 5 nm; length from 10 to 50 μm) were confirmed by transmission electron microscopy (TEM) observations. EPOLAM 2063, provided by AXSON Technologies is a blend of cycloaliphatic (CA) epoxy resin and a diglycidyl ether of bisphenol-A (DGEBA) resin. We mixed it with a compatible hardener, (anhydride 1,2,3,6-tetrahydromethyl-3, 6-methanophtalique), in equal parts by volume. According to the supplier's specifications, the tensile strength and the Young's modulus of this epoxy are 57 MPa and 3.1 GPa, respectively, at 23 °C. The glass transition temperature is expected to range from 180 °C to 200 °C depending on the curing cycle. Finally, for the laminated composites we used plain woven E-glass fiber cloth provided by HEXCEL (HEXTS92145) (surface weight: 220 g/m^2). The warp, considered as the main reinforcement direction, consists of bundles of 400 filaments (approximate diameter of the single filament: 9 μm); the weft is made of 200 filaments (approximate diameter of the single filament: 7 μm). Both warp and weft are present at 6 bundles per centimeter.

2.2. Sample preparation

2.2.1. Preparation of bulk resin samples

Three different material configurations designated as M1, M2 and M3 were investigated. The processing of these samples is illustrated in Fig. 1.

Material M1 (Fig. 1a) was made from neat epoxy resin. Firstly, the epoxy resin was heated to 80 °C to lower the viscosity. Then, the hardener was added and blended using a magnetic stirrer for 15 min at 80 °C. The ratio of resin to hardener was 5:5.35 (by weight) as prescribed by the supplier.

Material M2 (Fig. 1b) was our nano-doped material. Firstly, we dispersed MWCNTs into ethanol by sonication (Sonicator: CPX500 Cole-Parmer Instruments, frequency: 20 kHz) for 2 h in an ice bath. Then, we added the MWCNTs–ethanol solution to the epoxy (preheated to 80 °C); this mixture was stirred continuously using a magnetic stirrer for 2 h with the temperature maintained just above 80 °C until all the ethanol evaporated. Afterwards, the mixture was sonicated and stirred at the same time using a magnetic stirrer for 30 min at 80 °C. Finally, the required amount of hardener was added and the solution was thoroughly stirred for 15 min. We prepared M2 with three different MWCNT contents: 0.05 wt.%, 0.5 wt.% and 1.0 wt.% with respect to the total weight of the resin and hardener. We named the corresponding materials M2-0.05, M2-0.5 and M2-1.0.

Material M3 (Fig. 1c) was made by repeating exactly the same steps used to make material M2, except that the MWCNTs were not introduced. The purpose of material M3 was to distinguish the effect of the addition of MWCNTs from the effect of processing. All bulk resin samples were prepared by molding the epoxy resin in a 80 °C preheated steel mold. The mold was kept at 80 °C for 6 h followed by a postcuring cycle of 6 h at 180 °C to ensure the complete curing of the samples (the extent of curing was checked by differential scanning calorimetry using a Netzsch DSC 204 F1 calorimeter; the results – not reported here – demonstrated complete crosslinking).

2.2.2. Preparation of laminated samples

Three laminated materials, called C1, C2-0.05 and C2-0.5, were prepared using the vacuum infusion technique.

An E-glass fiber cloth was cut into 300 × 300 mm plies and then stacked together to form $[\pm 45]_{2s}$ angle-ply laminates. The vacuum infusion was performed using the Infuplex system commercialized by Diatex (Fig. 2). Preheated resin at 80 °C flowed from an open container toward the inside of the vacuum-tight mold (also preheated to 80 °C), impregnating the fabric stack within. The plate was submitted to 1 bar of vacuum pressure at 80 °C for 6 h to ensure initial curing. Then, a post-curing cycle at 180 °C lasting 4 h

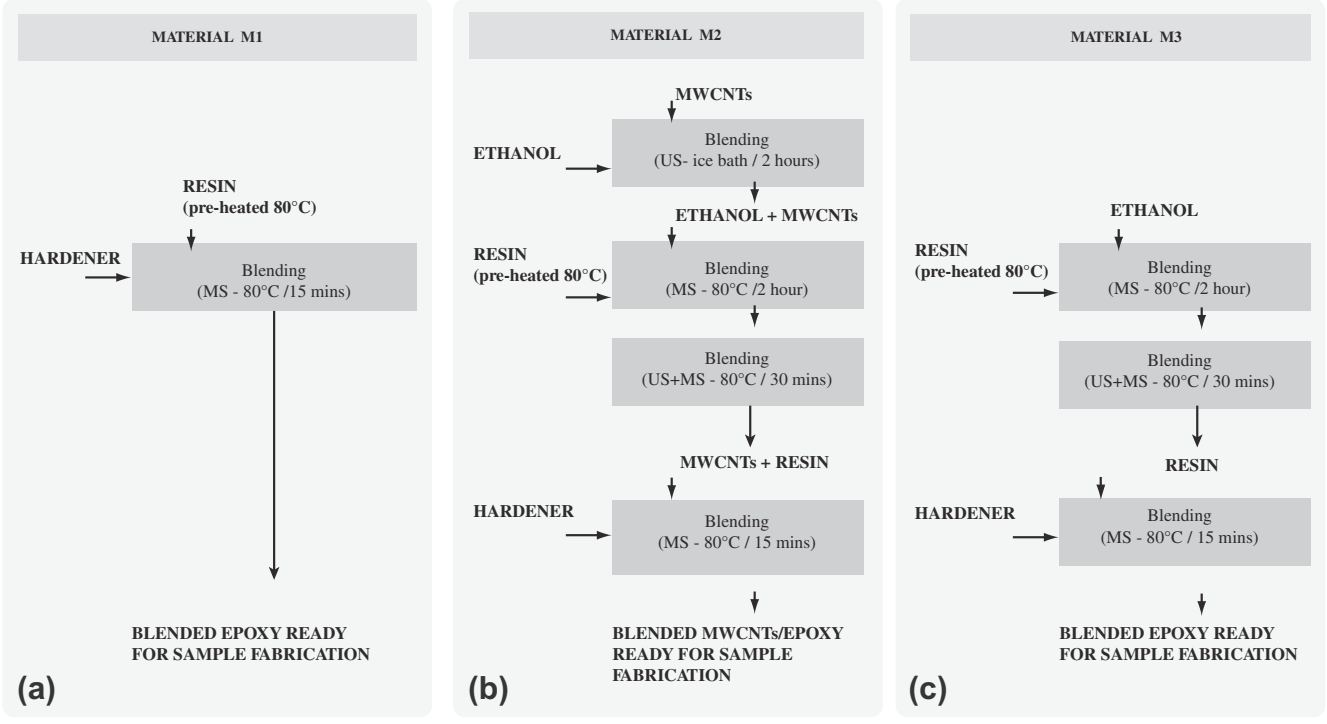

Fig. 1. Processing flow chart for the three material configurations, M1, M2 and M3 (MS: magnetic stirring, US: ultra-sonication).