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Mode I and Mode II fracture energy of MWCNT reinforced nanofibrilmats interleaved carbon/epoxy laminates

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ABSTRACT

Laboratory scale carbon/epoxy laminates were interleaved with electrospun Nylon 66 nanofibrilmat reinforced with multi wall carbon nanotubes (MWCNTs). The effect of the MWCNTs on the fracture energy was evaluated under Mode I and Mode II loading. It is shown that while nanofibrilmat interleaving resulted in a 3 times increase of the Mode I fracture energy compared to the non-interleaved laminates and the MWCNT reinforced nanofibrilmat interleaving resulted in a 4 times increase. Evaluation of the Mode II fracture energy indicated a 40% increase as a result of nanofibrilmats interleaving, while MWCNT reinforced nanofibrilmat interleaving resulted in a 60% increase. Mechanisms for the fracture energy increase of the MWCNT reinforced nanofibrilmats are suggested based on the test data and fractographic study of post-test specimen surfaces.

1. Introduction

Composite materials are increasingly important structural materials for aeronautical and space engineering, naval and road vehicles, civil engineering, sporting goods and other consumer products. This is due to their specific mechanical properties, innovative design possibilities, and advanced low cost fabrication methods. However, composite structures may be subjected to a variety of low velocity impact events during service that can generate barely visible surface damage, but extensive internal damage. This can have significant effects on subsequent performance, eventually leading to decreased structural reliability [1]. Numerous studies have been dedicated to improving impact resistance of composite structures, which requires understanding of composite failure mechanism under impact loading [2–7]. A low velocity impact laminate failure sequence consists typically of four major failure modes [8]: (i) matrix mode, in which cracking occurs at various angles to the fibers due to tension, compression or shear, (ii) delamination mode produced by interlaminar stresses that occurs only after the generation of a matrix crack, (iii) fiber failure in tension and in compression (fiber buckling), and (iv) penetration, once an impacting object completely perforates the structure. The first two modes arise essentially from a combined in plane mixed mode interlaminar fracture. Hence, improved composite material impact resistance may result from improving the fracture energy or delamination resistance under the two in-plane modes of fracture. Resistance to delamination growth can be expressed in terms of critical strain energy release rate (SERR), which has components corresponding to the basic delamination Modes I and II [9]. One of the most common methods for improving the fracture energy is interleaving, where a discrete interlayer (thermoset or thermoplastic) is added between the laminated plies. The fracture energy improvement mechanism by interleaving has been studied intensively in the past [10,11], and various theoretical mechanisms have been suggested [12,13], but the phenomena are not yet well understood. Previous work of Singh and Partridge [14] demonstrated the potential of self-same carbon epoxy composites interleaving on mixed mode Interlaminar Fracture Toughness (IFT). It was revealed that while Mode I fracture toughness can be improved by 70%, Mode II can be improved by 200%. The increase was attributed to relief of plastic constraint at the crack tip. Recently, Hojo et al. [15] studied the influence of a self-same epoxy interleaf on Mode I and Mode II IFT of carbon fiber (CF)/epoxy composites. Their study revealed that the Mode II interlaminar toughness of the interleaved laminates was approximately twice that of the base laminates. Furthermore, the authors claim that the self-same interplay thickness is a key-factor for toughness improvement. Recently, Yasaee et al. [16] reported on a 200% improvement of Mode II interfacial toughening by different interply strips such as: thermoplastic films, chopped aramid fibers and thermoset adhesive films. Kuwata and

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Hogg [17] investigated the Mode II interlaminar toughness by interleaving with non-woven polyester/carbon and polyamide veils, reporting a 150% Mode II interlaminar toughness improvement. Other types enhanced interfacial fracture energy of different structures can be found, such as in carbon fiber aluminum foam sandwich with short aramid fibers, where the interfacial toughening was increased by over 80% [18]. In attempts to improve delamination resistance by interleaving, an efficient novel interlayer preparation method known as Electrospinning (ES) has been used in the last decade [19,20] The ES method enables fabrication of fibrous polymer sheets and nanofibrilmats, with characteristic fiber diameters ranging from μm down to a few nm, in a one-step process [21]. It was found that ES based nanofibrilmats exhibit superior mechanical and thermomechanical properties relative to bulk materials or micron scale fibers [22–24]. One of the most important benefits of the ES process is the ability to create nano-composites by integrating carbon nanotubes (CNTs) into the nanofibrilmats [25,26]. This is considered a promising although highly challenging application of CNTs [27]. Nanocomposites have a significant energy absorption potential due to the unique CNT properties (i.e. high aspect ratio, very large CNT/matrix interface area and superior mechanical properties) [28]. This potential has triggered several studies; Seyhan et al. [29] studied the influence of 0.1 wt.% MWCNTs modified carbon/epoxy matrix on Mode I and Mode II fracture toughness. It was found that while Mode II fracture toughness was improved by a negligible factor of 8%, Mode I was not improved at all. The authors attributed the results to the poor MWCNT dispersion in the matrix. Tsantzalis et al. study [30] dealt with the use of Carbon nanofibers (CNF) and Zirconate Titanate dopants for the epoxy matrix of CFRP. While the presence of CNF led to 100% increase of Mode I fracture toughness, the Zirconate Titanate particles led to a decrease of the fracture toughness due to their brittle character. The authors claimed that the fracture energy improvement was a result of unidirectional carbon fibers bridging and pull-out phenomena. Kostopoulos et al. [31] further investigated the influence of CNF and Zirconate Titanate particles addition to epoxy matrix of CFRP under Mode II loading. It was discovered that each filler addition led to a fracture toughness increase as a result of different mechanisms; CNF contribute as a result of fiber bridging and pull-out phenomena, while the PZTs contributed by blunting and bifurcating the crack. The combination of both fillers leads to the best fracture resistance properties.

Arai et al. [32] investigated both Mode I and Mode II fracture toughness improvement of carbon-nanofiber/epoxy interleaving. It was reported that a significant fracture toughness improvement was achieved; 50% and 200–300% for Mode I and Mode II, respectively. White et al. [33] studied the influence of Epoxy/Polyamide/MWCNT interlayers. The results indicated a 2.5 times Mode II fracture toughness increase compared to an Epoxy/Polyamide interlayer.

The work presented here is based on the authors' continuing study [25] that demonstrated a major improvement of carbon/epoxy laminate Mode I IFT by interleaving with electrospun Nylon 66 nanofibrilmats. In the study herein, further improvement is exhibited by MWCNT reinforcement of an electrospun nanofibrilmat. Both Mode I and Mode II fracture energies, G_{IC} and G_{IIC}, of carbon/epoxy laminates were evaluated. The results indicate the potential of this pioneer MWCNT reinforced electrospun Nylon 66 nanofibrilmat for improving G_{IC} and G_{IIC}.

2. Experimental procedure

2.1. Polymer solution preparation and MWCNT dispersion process

Two solutions were used: (i) 20 wt.% ARKEMA® Nylon 66 pellets were dissolved in a 70/30 wt.% mixture of Trifluoroethanol (TFE) and Formic Acid (FA), and 5 wt.% TRITON X-100 was added as a surfactant. (ii) The above solution plus 20 wt.% MWCNT Nylon 66 master batch, ARKEMA GRAPHINSTRENGTH® CM7-20 pellets, in a suitable quantity to produce a 5 wt.% MWCNT reinforced Nylon 66 solution. (Characteristics of the MWCNT's are; (i) 5–15, mean number of walls, (ii) 10–15 nm, mean outer diameter. (iii) 0.1–10 μm, length).

The latter solution was prepared based on mechanical dispersion of MWCNTs by high shear mixing [34] with surfactant addition. This combination of methods has been shown to reduce formation of MWCNT aggregates [35,36]. The solutions were mixed at room temperature for 1 h. A LABEC® HOG-020 shear mixing apparatus was used to homogenize the latter solution, operating at 8000 rpm for 10 min.

2.2. The electrospinning process

The ES system consists of an 18 cm diameter drum rotating at 120 rpm, used as a collector, and a solution injector. A 40 kV power source generates an electric field between the drum and the injector and directs the solution jet to cover the rotating drum. To achieve an optimum uniformity of the nanofibrilmat thickness, a mechanism for sliding the injector uniformly across the drum width was installed. The flow rate for both solutions was 1.2–1.4 ml/h. The nanofibrilmats were collected over a two hour process. The resulting nanofibrilmat area was approximately 100 × 500 mm, 70–100 μm in thickness, and of areal density 10–12 g/m^2.

2.3. The nanofibrilmats

Two types of nanofibrilmats were evaluated: *neat electrospun fibers (ES)* and *electrospun fiber with 5wt% MWCNT*. The thicknesses of the fiber mats were measured using a digital micrometer. A widthwise strip of the nanofibrilmat was cut into 10 × 10 mm specimens and the dimensions were measured for each specimen. The specimens were weighed using a XT220A PRECISA analytical balance. The areal density measurement was averaged from the individual results. SEM observations of the ES nanofibrilmats show a randomly distributed nanofibrilmat structure with sub-micron fiber diameter, as shown in Fig. 1. TEM observation of the *ES + 5%MWCNT* nanofibrilmats demonstrated two typical features: aligned MWCNT in the nanofiber length direction (Fig. 2a), and tangled agglomerates of a few MWCNTs perforating the Nylon 66 nanofiber layer (Fig. 2b).

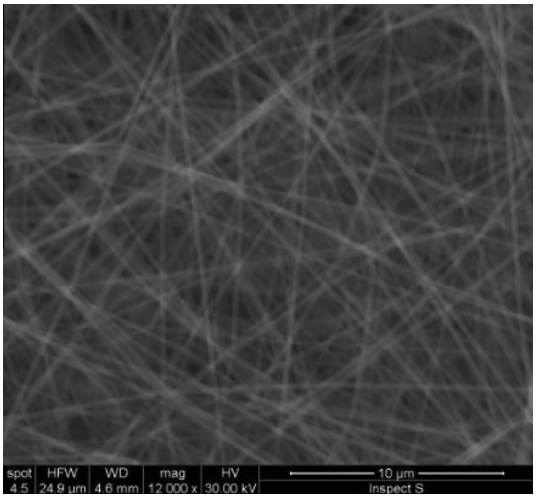

Fig. 1. SEM image of an ES nanofibrilmat.