



# Thermosetting hierarchical composites with high carbon nanotube loadings: En route to high performance



Tomi M. Herceg<sup>a, b, c</sup>, M. Shukur Zainol Abidin<sup>c, d</sup>, Emile S. Greenhalgh<sup>c</sup>, Milo S.P. Shaffer<sup>b</sup>, Alexander Bismarck<sup>a, e, \*</sup>

<sup>a</sup> Polymer & Composite Engineering (PaCE) Group, Department of Chemical Engineering, Imperial College London, London SW7 2AZ, United Kingdom

<sup>b</sup> Departments of Chemistry and Materials, Imperial College London, London SW7 2AZ, United Kingdom

<sup>c</sup> The Composites Centre, Department of Aeronautics, Imperial College London, SW7 2AZ, United Kingdom

<sup>d</sup> School of Aerospace Engineering, Universiti Sains Malaysia, Malaysia

<sup>e</sup> Polymer & Composite Engineering (PaCE) Group, Institute for Materials Chemistry and Research, Faculty of Chemistry, University of Vienna, Währingerstr. 42, Vienna A-1090, Austria

## ARTICLE INFO

### Article history:

Received 9 September 2015

Received in revised form

8 February 2016

Accepted 9 February 2016

Available online 12 February 2016

### Keywords:

Carbon nanotubes

Hybrid composites

Fracture toughness

Fractography

Powder processing

## ABSTRACT

A wet powder impregnation route to manufacture carbon fibre reinforced thermoplastic composites was adapted to accommodate thermosetting matrices reinforced with high fractions (20 wt%/13.6 vol%) of multiwalled carbon nanotubes (CNTs). The produced carbon fibre prepregs were consolidated into laminates with fibre volume fractions of 50–58% and up to 6.1 vol% CNTs. Microscopic imaging confirmed successful consolidation at intermediate CNT loadings, but some voidage at the highest CNT loading due to the highly viscoelastic uncured matrix. Nonetheless, through-thickness electrical conductivity and Mode I interlaminar fracture toughness were enhanced by as much as 152% and 24% to unprecedented values of  $\sigma = 53 \text{ S m}^{-1}$  and  $G_{IC} = 840 \text{ J m}^{-2}$ , respectively. Fractographic characterisation indicated that crack deflection was the mechanism responsible for the improved fracture toughness. The material properties were shown to be strongly dependent on the microstructure of the matrix.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Although carbon fibre composites are a lighter and stiffer alternative to metals in load bearing structures, their poor matrix dominated properties still complicate or restrict their use in structural applications. Structural failure almost always initiates as matrix micro-cracking or delamination due to the inferior interlaminar shear strength and fracture toughness of composite laminates relative to their in-plane properties, such as tensile strength and stiffness [1]. Some of the approaches employed to improve out-of-plane properties have involved introducing toughening agents into the resin [2], Z-pinning [3], stitching [4] and 3D composite architectures [5]. All of these methods have produced improvements in damage tolerance, but there have always been trade-offs

usually in the form of reduced in-plane properties, cost, redesign and requalification of components [6]. Incorporating thermoplastic particles in epoxy resins has been a particularly popular and successful toughening method: laminates manufactured using commercially available third generation prepregs possess a Mode I interlaminar fracture toughness of around  $400\text{--}500 \text{ J m}^{-2}$  [7,8]. The drawbacks of thermoplastic toughening are reduced compression and fatigue performance, and increased sensitivity to processing [6], with the local distribution of toughening particles heavily affecting the mesostructure in structures such as skin-stringer elements [9].

Carbon nanotubes (CNTs) and carbon nanofibres (CNFs) can stiffen, strengthen and toughen thermosetting matrices [10] while also enhancing thermal and electrical conductivities [11,12]. Thus, they have been incorporated as a third component into conventional carbon fibre composites, resulting in truly multifunctional hierarchical composites (HCs) [13]. The incorporation of nano-reinforcements into continuous fibre composites has been shown to have little effect on the fibre dominated properties of composite laminates [14–20]. Nonetheless, matrix dominated properties have

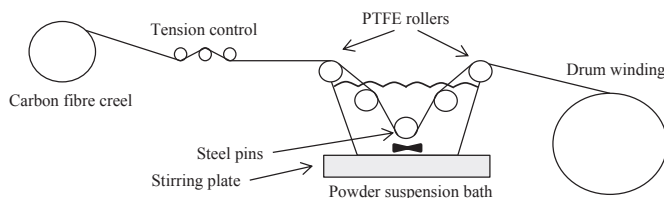
\* Corresponding author. Polymer & Composite Engineering (PaCE) Group, Department of Chemical Engineering, Imperial College London, London SW7 2AZ, United Kingdom.

E-mail addresses: [a.bismarck@imperial.ac.uk](mailto:a.bismarck@imperial.ac.uk), [alexander.bismarck@univie.ac.at](mailto:alexander.bismarck@univie.ac.at) (A. Bismarck).

been enhanced by the addition of CNTs to the matrix: compression and flexural strength increased by as much as 15% and 18% [19], interlaminar shear strength by 27% [20] and Mode I and Mode II interlaminar fracture toughness by 100% and 28%, respectively [21]. The particularly impressive enhancement of the fracture toughness by 100% was observed for composites with a relatively brittle matrix with Mode I strain energy release rate ( $G_{IC}$ ) of  $86 \text{ J m}^{-2}$ . By placing an aligned CNT forest in the interlaminar region of a laminate before consolidation, the ILSS, Mode I and Mode II fracture toughness can even be improved by 69%, 150% and 200%, respectively [22–24]. This approach not only requires large, highly aligned CNT forests that do not reinforce the inter-fibre space but may be confounded, in some cases, by the toughening due to a thicker resin rich layer in the interlaminar region [25]. With regards to absolute values, even for unidirectional (UD) HCs with thick CNT and resin rich interlayers, the Mode I interlaminar fracture toughness values were only as high as  $500\text{--}550 \text{ J m}^{-2}$  [7,23], although typically in the  $170\text{--}200 \text{ J m}^{-2}$  range for HCs manufactured using more conventional processes [26,27] and as high as  $650 \text{ J m}^{-2}$  when using low  $T_g$  matrices [18].

Attempts to produce HCs by reinforcing the matrix with CNTs have been plagued by processing difficulties caused by the increased matrix viscosity due to the presence of anisotropic nanofillers [28] and nanotube self-filtration [29]. HCs manufactured using conventional methods such as resin transfer moulding (RTM) and resin film infusion (RFI), resulted in CNT agglomeration and gradients [30–32] when aiming to incorporate more than 1 wt% CNTs. Similarly, good quality HCs containing 1.5 vol% CNTs in the matrix were manufactured by melt impregnating continuous fibres with a nanoreinforced matrix [33]. Thus far, the HCs with the highest CNT/CNF loadings (10 wt% in the matrix) were manufactured by “wet coating” to impregnate carbon fibre tows with a nanoreinforced epoxy matrix; the filler, in this case, consisted of “cup-stacked” CNFs with an aspect ratio of only ten [34].

Following on from the approaches described above, the aim of this work was to adapt a powder based impregnation method from thermoplastic composite manufacturing [37] to produce thermosetting HCs with high CNT loadings, and highlight the benefits of the approach. Previous studies have demonstrated that the mechanical and multifunctional properties of HCs can be enhanced by increasing the CNT loading in the matrix, a trend that could continue for loadings higher than 10 wt%, but has not been explored due to limitations in processing and manufacturing [35]. The processing route explored in this paper is based on a wet powder impregnation method [36] and designed to surmount issues such as insufficient impregnation, high matrix viscosity, fibre damage or lack of potential for scalability encountered with other methods such as film stacking, melt pultrusion and dry powder impregnation [37].



**Fig. 1.** Schematic of the wet powder impregnation drum winding line used to produce HC thermosetting composite preregs.

## 2. Experimental

### 2.1. Prepregging line design

Our drum winding line (Fig. 1) has four components that serve to feed the carbon fibre tow, control the fibre tension, impregnate the individual fibres with resin, pull and wind the prepreg. The first two units form a closed circuit tension control system (Izumi International) that provides carbon fibres (Hex tow<sup>®</sup> AS4C-GP, 12k filaments, Hexcel) from a creel with a maximum tension of 10 N. The epoxy sizing on the fibres not only improves compatibility with the epoxy resin matrix, but also aids handling and reduces the amount of fibre damage when the fibres pass through the impregnation line. With sufficient spreading, up to four fibre tows can be run concurrently to provide a wider impregnated tow if desired.

The third unit is an in-house designed and fabricated wet powder impregnation bath. It can hold up to 500 mL of powder slurry and is fitted with two polytetrafluoroethylene (PTFE) rollers where the fibres enter and exit, and three steel pins inside the bath, all designed and placed to spread the fibre tow. The solid component of the slurry was an uncured, ground, nanoreinforced bisphenol A based thermoset resin (EPIKOTE<sup>™</sup> 1001, Hexion) nanocomposite (NC) containing the latent curing agent dicyan diamide (Dyhard<sup>®</sup> 100S, AlzChem AG) and Nanocyl<sup>™</sup> NC 7000 CNTs prepared as described in Ref. [38]. The particle size distribution of the powder used in the impregnation bath determines the degree of impregnation: if the particle size ( $d_{50}$ ) is below  $5 \mu\text{m}$  the particles will pass through the fibre tow, yielding a dry prepreg; if the particle size exceeds  $25 \mu\text{m}$ , the powder will sediment on to the surface of the tow, leaving the middle dry, resulting in a non-homogeneous prepreg [37]. The effect of the powder particle size on impregnation is discussed in Section 3.1. The fibre volume fraction ( $v_f$ ) of the preregs is determined by the powder content in the bath and the fibre residence time. The NC powder was prevented from aggregating or settling by magnetic stirring. The impregnation bath was chilled to  $5 \text{ }^\circ\text{C}$  using a cooling jacket to prevent fusion of the powder particles, which was necessary because the uncured epoxy has a relatively low  $T_g$  ( $25 \text{ }^\circ\text{C}$ ).

The fourth unit consists of an in-house built filament winder fitted with a 115 mm diameter drum. The tow take-up and transverse speeds can be controlled independently. Any slurry dripping during winding was collected in a tray placed under the drum and returned to the impregnation bath.

### 2.2. Prepregging procedure

The impregnation slurry contained a surfactant (Triton<sup>™</sup> X100, Sigma Aldrich) dissolved in deionized water by magnetic stirring to prevent powder aggregation. Once completely dissolved, the NC powder (neat resin, resin containing 5.9 and 13.6 vol% (9.1 and 20 wt%) CNTs) was slowly added to the surfactant solution while stirring. The slurry in the impregnation bath at the beginning of the drum winding process (henceforth referred to as “starter bath”) had a volume of 350 mL and contained 10 wt% NC powder and 0.06 wt% surfactant. In parallel, another more concentrated slurry (“top-up bath”) containing 15 wt% NC powder and 0.06 wt% surfactant was prepared. The starter bath was supplemented with 25 ml of more concentrated slurry from the top-up bath before each run, and 25 ml were added every 5 min during each run to replenish the powder depleted by the impregnation process. The carbon fibre roving was pulled through the impregnation bath with a tension of 10 N and wound at a speed of 6–7 rpm (equal to  $2.2\text{--}2.5 \text{ m min}^{-1}$ ) with a transverse speed of  $2 \text{ mm s}^{-1}$ . The drum winder was run for 30–35 revolutions before the impregnated tow

Download English Version:

<https://daneshyari.com/en/article/819958>

Download Persian Version:

<https://daneshyari.com/article/819958>

[Daneshyari.com](https://daneshyari.com)