

A POWDER BASED PROCESSING ROUTE TO PRODUCE NANO AND HIERARCHICAL COMPOSITES WITH HIGH NANOFILLER LOADINGS

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Abstract

A route to manufacture hierarchical composites (HCs) based on wet powder impregnation was adapted to accommodate thermosetting matrices. The resulting carbon fibre prepreps contained as much as 13.6 vol% carbon nanotubes (CNTs) in the matrix and were consolidated into laminates with 50 to 55% fibre volume fraction and 6.1% CNTs by total volume. Microscopic characterisation revealed that matrix homogeneity and laminate microstructure were affected by the powder particle size and degree of tow overlap during drum winding. The interlaminar shear strength was strongly affected by the quality of the material, requiring optimization of the processing parameters to improve the laminate quality.

1. Introduction

Although carbon fibre composites have provided a lighter and stiffer alternative to metals in load bearing structures, their poor matrix dominated properties still complicate or restrict their structural use. Structural failure almost always initiates as delamination and/or compressive failure due to the inferior interlaminar fracture toughness and longitudinal compression strength 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, Z-pinning, stitching and 3D composite architectures. All of these approaches have shown improvements in damage tolerance, but there have always been trade-offs usually in the form of reduced in-place properties, cost or redesign and requalification of components. [2] Incorporating thermoplastic particles in epoxy resins has been a particularly popular and successful toughening method, with commercially available third generation prepreps attaining an interlaminar fracture toughness of around 300 J/m² [3]. The drawbacks of thermoplastic toughening are reduced compression and fatigue performance and increased sensitivity to processing [2], with the local distribution of thermoplastic particles heavily disturbed in structures such as skin-stringer elements. [4]

The addition of nanoreinforcement to continuous fibre composites has been shown to have virtually no effect on the fibre dominated properties of composite laminates, such as tensile, compressive and flexural moduli and tensile strength. [5-11] On the other hand, all matrix dominated properties have been enhanced by the addition of CNTs to the matrix: compression and flexure strength by as much as 15% and 18% [10], interlaminar shear strength by 27% [11] and Mode I and Mode II interlaminar fracture toughness by 100% and 28%, respectively [12]. The particularly impressive Mode I enhancement of 100% was in a relatively brittle system with a baseline G_{IC} of 86 J/m^2 , for which short fibre theory predicts significant toughening by debonding, pull-out, and fibre fracture. [13] By placing an aligned CNT forest in the interlaminar region of a laminate before consolidation the ILSS, Mode I and Mode II fracture toughnesses can even be improved by 69%, 150% and 200%, respectively. [14, 15] This approach not only requires large, highly aligned CNT forests that do not act on the intralaminar space, but it is not yet clear whether the toughening is due to the CNTs or the resin rich layer in the interlaminar region. With regards to absolute values, even for unidirectional (UD) HCs with thick CNT and resin rich interlayers the Mode I interlaminar fracture toughness values are only as high as $500\text{-}550 \text{ J/m}^2$ [3, 15], although typically in the $170\text{-}200 \text{ J/m}^2$ range for HCs manufactured using more conventional processes [16, 17] and as high as 650 J/m^2 when using low T_g matrices [9].

Attempts to produce HCs by reinforcing the matrix with CNTs have been plagued by processing difficulties caused by the increased matrix viscosity and nanotube infiltration. Some groups [18-20] have tried manufacturing HCs by conventional methods such as resin transfer moulding (RTM) and resin film infusion (RFI), but using matrices containing more than 1 wt% CNTs resulted in CNT agglomeration and partial impregnation of the continuous fibres. Chen adapted the drum winding technique directly from prepreg manufacturing and produced good quality HCs containing 1.5% CNTs by volume of matrix [21]; however, this method is limited to low CNT concentration as increasing the CNT loading would render the impregnation bath too viscous for successful impregnation. Yokozeki has demonstrated the capability to produce good quality HCs in terms of homogeneity, CNT dispersion and distribution as well as mechanical and multifunctional properties using a wet impregnation route. [12, 16, 22]

This work is primarily concerned with developing a processing route that allows the manufacturing of HCs with higher CNT loadings than previously reported, as well as highlighting 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 12 wt%, but has not been explored due to limitations in processing and manufacturing. [23] The processing route explored in this paper is based on a wet powder impregnation method [24] and designed to surmount issues such as insufficient impregnation, fibre damage or lack of potential for scalability encountered with other methods such as film stacking, melt pultrusion and dry impregnation.

2. Experimental

2.1. Materials

As with conventional prepregging processes, the required materials were matrix and carbon fibre. The process by which the nanoreinforced matrix, i.e. nanocomposite, was produced

involves shear mixing epoxy resin, curing agent and CNTs (NC 7000, Nanocyl) in an extruder followed by powdering of the extrudate in a cryogenic ball mill. For this initial study, nanocomposites with CNT concentrations of 5.9 and 13.6 vol% were selected in addition to the neat resin, which was processed in the same fashion as the nanocomposites. The selected epoxy resin and curing agent were EPIKOTE 1001 and dicyandiamide (DICY), both generously provided by Hexcel. This resin and hardener in conjunction with the CNTs are solid at room temperature and were thus a good model system for developing a novel prepregging method.

Epoxy sized Hexcel AS4C-GP fibres in 12k tows was chosen as the carbon fibre and also generously supplied by Hexcel. The epoxy sizing not only improves compatibility with the epoxy based matrix, but also aids handling and reduces the amount of fibre damage as tows pass through the impregnation line.

2.2. Prepregging

HCs were manufactured using an adapted wet powder impregnation route (Figure 1). The impregnation slurry consisted of nanocomposites powder suspended in deionised water with the aid of Triton X-100 surfactant (Sigma Aldrich, UK). The proportions of the slurry components were initially taken as those used in [24], but required adjustment to produce prepregs with ~55% fibre volume fraction (v_f) consistently.

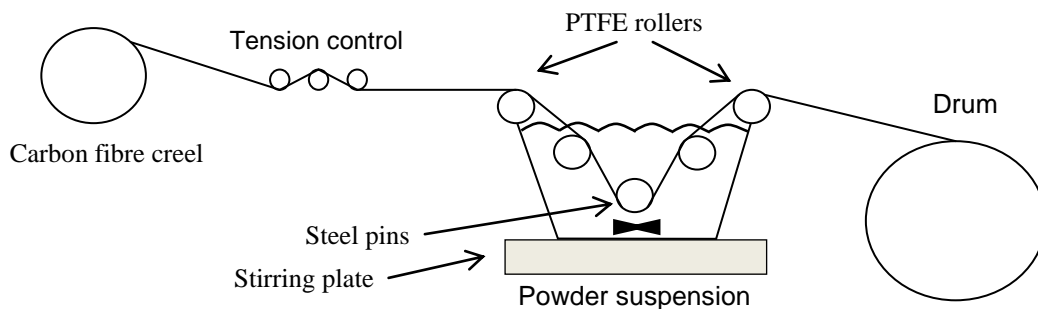


Figure 1. Schematic of the wet powder impregnation drum winding line used to produce prepreg.

The carbon fibre was pulled through the impregnation bath with a tension of 10 N and speed of 6-7 rpm. The drum winder was run for 30-35 revolutions before the tow leading onto the drum was cut, the prepreg was removed by cutting it across the length of the drum and it was unrolled from the drum onto a sheet of PTFE film to dry. The prepregs were dried at ambient conditions as well as under vacuum. The volume fractions of the plies were estimated from the weight of the plies, the amount of fibre in the plies and the densities of the fibre and matrix. Removing the prepreg from the relatively small diameter winding drum induces out of plane waviness, which was removed by hot pressing each ply at 100°C and 1 ton of pressure.

Laminates were 18 ply stacks with those prepregs closest to 55% v_f in the middle and those with lower v_f at the extremities to allow for some matrix bleed. Stacked plies were debulked for 10-15 minutes in a vacuum table (Vacform Composites, UK) throughout the lay-up process. The number of plies was selected in order to obtain a laminate approximately 3 mm thick. The middle plies were offset $+3^\circ/-3^\circ$ to prevent fibre nesting and separated by 25 μm thick PTFE film (Aerovac Umeco, UK) inserted 60 mm into the laminate to form a starter

crack for the fracture toughness measurements. Curing was done as with the NCs, but always including a dwell to allow melt relaxation.

2.3. Physical characterisation

The densities of three sections approximately 60mm x 20mm from each laminate were measured using a pycnometer (Accupyc 330, Micromeritics). The fibre, matrix and void volume fractions were determined according to ASTM D3171, using a sulphuric acid and hydrogen peroxide mixture to digest the resin.

Laminate sections were embedded in an Epoxicure resin and cured at room temperature for 24 hours. The mounted sections were first ground on a Motopol 12 polishing machine at 150 rpm, 20 N of pressure per sample and for 2-3 minutes using each of P320, P800 and P2500 grit sandpapers. Polishing was done in a similar fashion for 4-6 minutes using microfiber cloths and diamond suspensions of 6, 3 and 1 µm. All polishing equipment was purchased from Buehler. The distribution of matrix and fibre in the HC as well as the presence of voids were investigated using an optical microscope (BX41M, Olympus) in bright field illumination mode.

2.4. Interlaminar shear strength

Interlaminar shear strength (ILSS) of the composite laminate was measured using the short beam shear (SBS) test in accordance to ASTM D 2344. The test was conducted with a span of 12 mm at a crosshead speed of 1 mm/min. Equation 1 was used to calculate the ILSS (F^{sbs}), where P_m was the maximum load observed during the test, b and h were the measured specimen width and thickness, respectively.

$$F^{sbs} = 0.75 \frac{P_m}{bh} \quad (1)$$

3. Results and discussion

3.1. Laminate composition and microstructure

The fibre and void volume fractions of the laminates are summarized in Table 1. The v_f of the laminates were surprisingly close to the target value of 55% considering the novelty of the manufacturing procedure. The void fractions in the baseline laminate and the one containing 2vol% CNTs are encouragingly low and are evidence that the material was indeed sufficiently consolidated. The higher void content of the HC with the higher CNT loading suggests that the large amount of CNTs in the matrix drastically increased its viscosity, leading to less successful consolidation.

CNT volume fraction in matrix (%)	CNT volume fraction in composite (%)	V_f (%)	Void volume fraction (%)
0	0	55.±0.6	0.6±0.2
5.9	2.7	58.8±0.7	0
13.6	6.1	49.7±0.9	2.7±1.7

Table 1. Fibre and void volume fractions as measured by acid digestion of laminates with varying CNT loadings.

Based on the calculated volume fractions it was also determined that the overall CNT volume fractions in the HCs were 2.7 and 6.1%. The highest reported CNT loading in an HC was 12% by weight of matrix [22]; the HC with the highest CNT loading manufactured through the process presented here contains 75% more CNTs.

Optical microscopy of polished cross sections confirmed that the HCs containing 6.1 vol% CNTs were indeed riddled with microscopic voids (black regions in Figure 2a). In contrast, the baseline composite had only few, isolated voids (Figure 2b). Additionally, the optical micrographs also provided information about the fibre and matrix dispersion. The high viscosity of the nanocomposite matrix has clearly impeded flow and caused segregation of matrix and fibres during the consolidation, as evidenced by the grey resin rich regions in Figure 2a. The resin rich regions within the HC laminate could also be associated with the powder clusters on the surface of the individual prepregs. The resistance of the nanocomposite matrix to flow would also prevent filling any gaps between or within plies, giving rise to the observed voids. On the contrary, the relatively low viscosity of the neat epoxy resin has allowed for the consolidation of a laminate with a homogeneous fibre and matrix dispersion (Figure 2b).

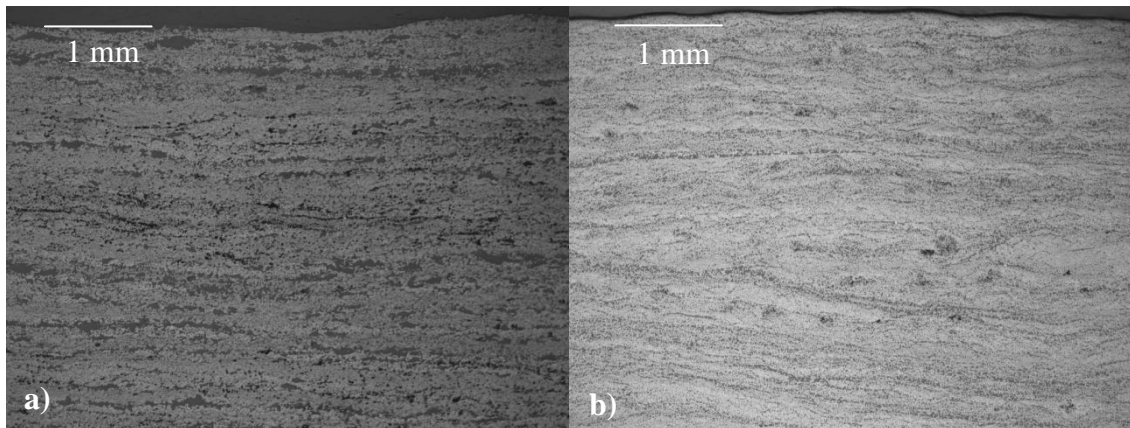


Figure 2. Optical micrographs of polished a) HC with 5.5vol% CNTs and b) baseline composite sections showing voids and fibre/matrix dispersion.

3.2. Interlaminar shear strength

The introduction of CNTs was expected to improve the ILSS of the composites, as with all matrix dominates properties. The HC containing 2.7vol% CNTs had a larger ILSS than the baseline material, while the HC with more CNTs had a similar ILSS to the baseline material (Figure 3). The mechanism causing the ILSS improvement with the addition of CNTs is not entirely understood, but it is believed that stiffening the matrix reduces the mismatch between fibre and matrix stiffness, allowing larger stresses to develop at the fibre-matrix interface without compromising fibre-matrix compatibility. [25] Laminates tested in the SBS configuration are particularly sensitive to voids due to the stress state in the interlaminar region; the HCs with the higher CNT loading are affected by the high void content, reflected in the reduced ILSS performance relative to the HCs with the lower CNT content. Although the fibre-matrix interface can be significantly strengthened (150%) by growing CNTs onto the fibres to directly reinforce the interface [26, 27], the extent of the improvement observed in this work (10%) is similar to that reported elsewhere [9, 11, 18]. The relative improvement is modest, but the maximum ILSS value achieved (91 MPa) is on par with that of commercial

high performance UD composites [28] even though strengthening the fibre-matrix interface was not explicitly targeted via this processing method.

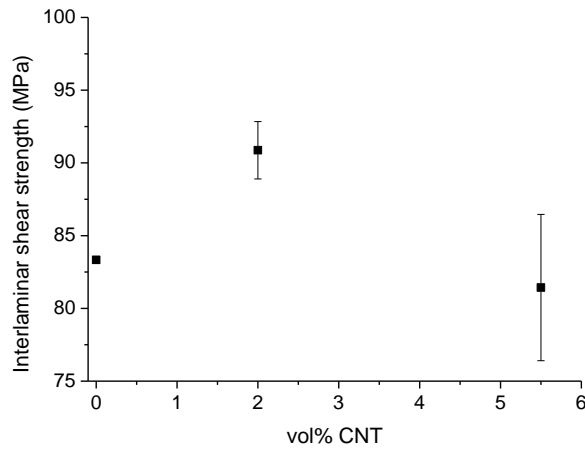


Figure 3. Interlaminar shear strength of composites as measured by SBS method.

4. Conclusions

A processing route based on wet powder impregnation was developed to manufacture HCs with higher CNT loadings than any previously reported. Impregnation of carbon fibre tows with epoxy resin containing up to 13.6vol% CNTs was successful, yielding unidirectional prepregs. Prepreg sheets were consolidated by vacuum assisted compression moulding into laminates with 50-55% fibre volume fractions and CNT contents of 2.7 and 6.1vol%. The high viscosity of the nano reinforced matrix impeded flow during consolidation, causing inhomogeneous CNT dispersion in the matrix as well as up to 4.5vol% voids in the HC with the higher CNT loading. An interlaminar shear strength of 91 MPa was achieved, and optimisation of the prepregging method should yield better quality laminates with attractive mechanical and multifunctional properties.

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