Hierarchical or Fibre Reinforced Nano-Composites: An opportunity to improve matrix dominated composite properties

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Abstract: We will briefly review the progress made in the development and processing of hierarchical, also called nanoenergineered or nanoreinforced, composites. Particular attention will be paid to the various methods to create hierarchical composites, i.e. reinforcing a nanocomposite further with conventional fibres or by attaching a nanoreinforcement to the surfaces of conventional reinforcing fibres and so avoiding all issues related to processing nanocomposites containing high aspect ratio nanoparticles. We will also review the properties of hierarchical composites and provide perspectives for future progress, which may require looking back at fibre wet impregnation by powder slurry processes.

1. Introduction

Although polymer nanocomposites (PNC) have received most attention in the past 20 years, a body of work on hierarchical (or "hybrid") nanotube reinforced continuous carbon fibre composites (HC) has emerged. Limitations imposed by matrix and interface dominated properties on the overall performance of conventional composites have been the driver, particularly interlaminar fracture toughness. Nano-scale reinforcement in the form of carbon nanotubes (CNTs) has been shown to provide the means to further improve state-of-the-art advanced composites. The resulting hierarchical composite (HC) materials could perform better in composite structures, and could also broaden the range of composite applications.

Various methods have been used to toughen conventional composites, but the ideal solution that affords the desired improvement in fracture toughness without drawbacks has yet to emerge. Approaches have involved introducing toughening agents into the resin, Z-pinning, stitching, 3D composite architectures, etc. [1, 2] All methods showed improvements in impact tolerance, but there have always been trade-offs usually in the form of reduced in-place properties, cost or redesign and requalification of components. Introducing nanoreinforcement into the matrix could be the most promising solution as it should lead to improvements in matrix dominated properties without affecting the overall architecture or performance of the continuous fibre HC.

2. Processing of Hierarchical Composites

There are two principal routes for producing HCs: adding the CNTs to the matrix or grafting the CNTs onto the fibre (**Figure 1**). [3] The first method primarily addresses matrix dominated properties, while the second tackles the continuous fibre-matrix interface. Both approaches

have required careful adaptation of conventional processing techniques or development of new ones to successfully introduce CNTs and exploit their exception properties.
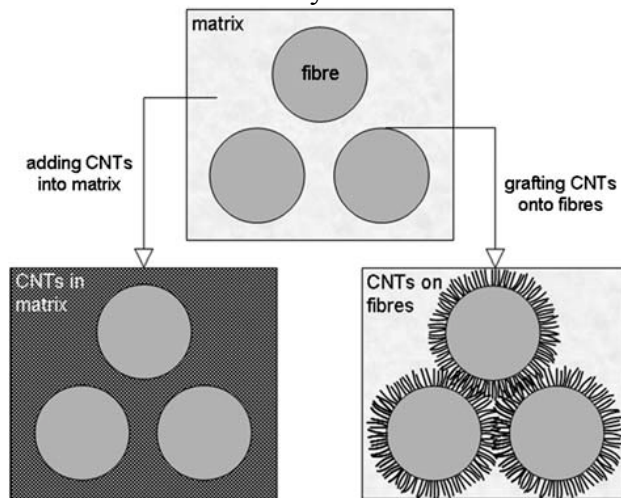

Figure 1. Schematic diagram of two potential routes for manufacturing HCs. [3]

2.1. Resin transfer and infusion methods

Conventional composite production methods such as resin transfer moulding (RTM) or resin film infusion (RFI) have provided the most convenient routes to making HCs. Both of these methods are commonly employed in industry because they allow great flexibility in choosing the shape and size of the part that is to be manufactured. However, the addition of CNTs had been known to cause tremendous increases in viscosity [4], a phenomenon associated with the low rheological percolation threshold, impeding the flow of the matrix and leading to only partial impregnation of the continuous fibres. [5] Additionally, agglomeration and the formation of a percolating network had been shown to cause filtering in all resin transfer methods, resulting in an inhomogeneous matrix (**Figure 2**). [6, 7] The limitations imposed by the impregnation techniques have thus made it impossible to manufacture good quality HCs with CNT loadings higher than 1% by weight of the PNC matrix.
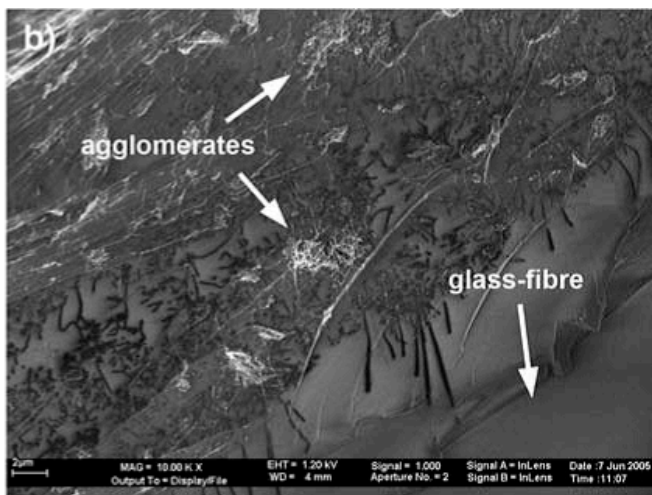

Figure 2. Agglomerates in sample containing 0.3% CNTs by weight of matrix. A resin rich region can also be observed next to the main reinforcing fibres. [8]

2.2. Prepregging methods

A different route involves impregnating the continuous fibres with the CNT loaded matrix using prepregging techniques. [9-11] One approach involves pulling fibres through a PNC melt and winding them onto a drum to obtain HCs. The maximum amount of

nanoreinforcement employed thus far has been 1.5% by volume of matrix. Fibre volume fractions of 50-65% can be achieved with evidence of good CNT dispersion in the resin. The state of the art in producing HCs through a prepregging route is represented in [10, 12, 13]. the manufactured laminates had a fibre volume fraction of 65% and excellent dispersions of CNTs when introducing 5% nanotubes by weight of matrix (**Figure 3**).
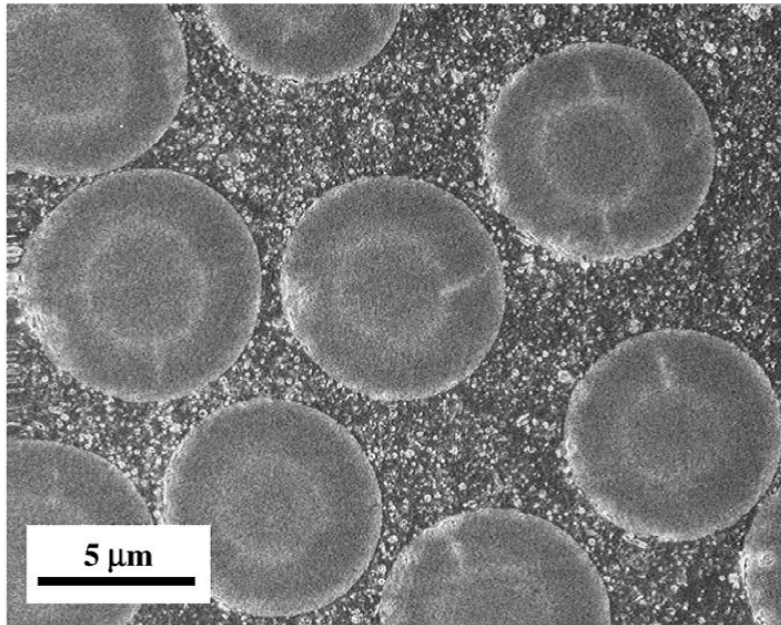

Figure 3. HC with good dispersion of 5 wt% cup-stacked CNTs (white dots) in the matrix surrounding carbon fibres. [10]
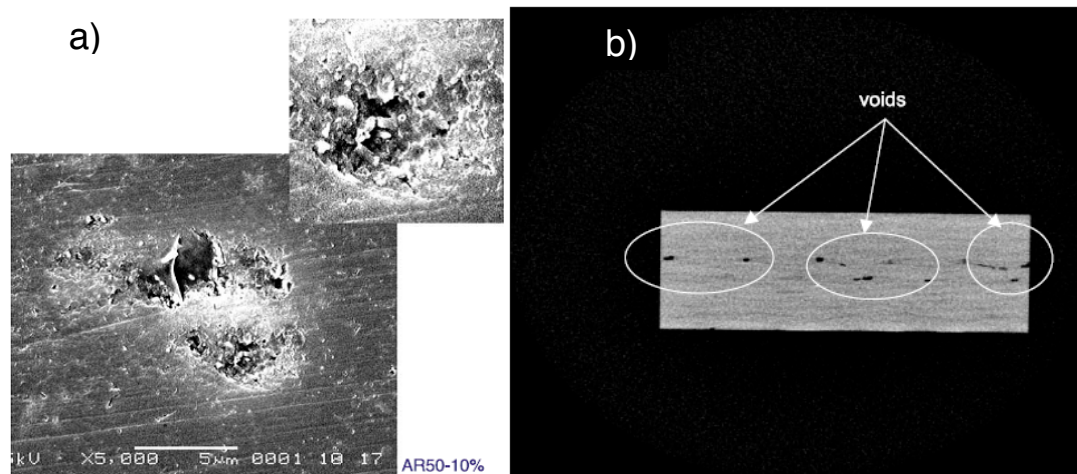

Figure 4. HCs containing 10 wt% CSCNT with a) agglomerations and b) voids.

HCs containing 10 wt% CNTs in the matrix were also produced by the same method, although unsuccessfully. [14] The laminates were inhomogeneous, containing both nanotube agglomerates and voids (**Figure 4**) that most likely resulted from the nanoreinforced matrix resisting flow during consolidation.

2.3. Nanoreinforcement restricted to the interlaminar region

Yet another approach explored has involved introducing the nanoreinforcement in the interlaminar zone only. The CNTs were either dispersed in a solvent and sprayed onto fibre mats [15, 16], applied to prepregs with rollers [17] or mixed with epoxy and used as a glue to

bond plies together. [18] With these relatively simple methods, the loading of CNTs in the interlayer has only been reported as high as 1%.

More complex approaches have involved growing aligned CNT forests onto a substrate followed by sandwiching them between tacky prepregs. After autoclaving, a nanotube rich epoxy interlayer was formed. [19] The same idea was also adapted to growing CNTs onto weaves which could then be placed around the midply of a laminate. [20]
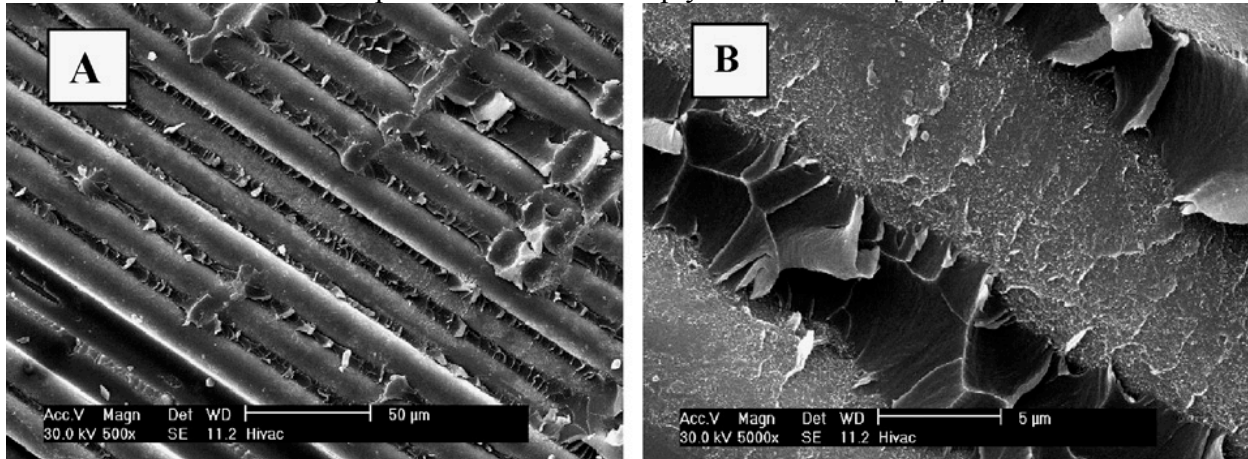

Figure 5. CNT reinforced matrix in interply region of a SBS sample. [16]

3. *Mechanical properties of Hierarchical Composites*

As discussed previously, attempts to improve fracture toughness by adding thermoplastics or Z-pins had typically resulted in poor constituent properties when compared to the non-toughened material. Therefore, along with considering whether nano-reinforcing the matrix enhances interlaminar fracture toughness, it is also critical to consider how matrix dominated in-plane properties are affected. Compression stiffness and strength are of particular interest for composite structures as they determine buckling performance and structural compression strength, respectively.

3.1. Fracture toughness of Hierarchical Composites

It has become apparent that the addition of nanotubes and nanofibres enhances Mode I and Mode II fracture toughness of composites [3]; understanding the mechanisms which explain this behaviour is perhaps the more interesting question. It should first be noted that great care must be taken to truly disambiguate toughening due to nano-reinforcement from other toughening effects. A number of studies [17, 19, 21, 22] have claimed toughening due to introduction of CNTs in the interlaminar region at the midply of a laminate, when in doing so a resin rich layer was also created (**Figure 6**). The toughness enhancement reported for such samples must be considered carefully in light of previous work showing that the presence of a 200 μm resin rich layer in the crack path enhanced the Mode I fracture toughness by almost 100%. [23]
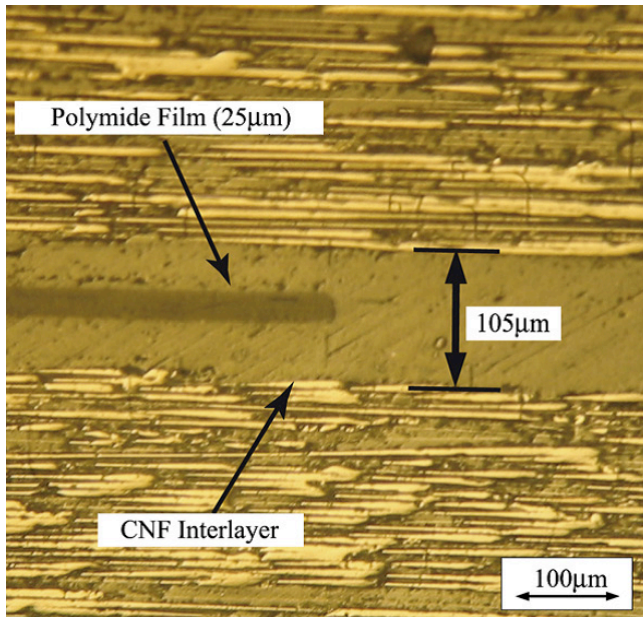
Figure 6. Thick resin layer in the interplay region resulting from the localised application of nanofibres. [17]

For carbon and glass fibre composites, cracks predominantly advance either along the fibre-matrix interface or by cleaving the matrix. [24] Mechanisms that improve the fracture toughness of bulk PNCs such as pullout, de-sheathing, bridging and fibre fracture also apply to crack growth through the matrix of an HC. In most investigations of HC fracture toughness, extensive crack deflection that dramatically increased the surface area in the crack plane was observed from microscopy of the fractured surfaces (**Figure 7**-9).
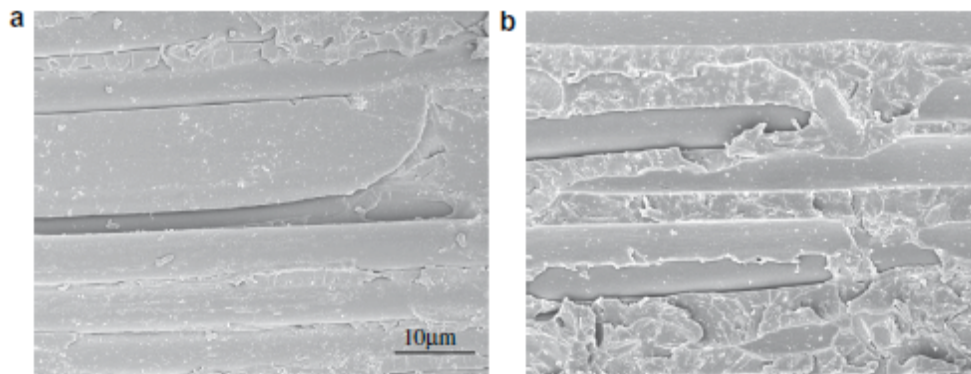

Figure 7. Mode I fracture surfaces of HCs containing a) 0 wt% CNTs and b) 5 wt% CNTs in bulk matrix. [13]

The crack deflection mechanism occurred regardless of processing route or fracture mode and, generally, increases fracture toughness because in addition to the energy required to drive the crack through the length of the material, more energy is required to create additional surface area. [25] The deflection can be so extensive that the crack is deviated from the interface to propagating almost entirely through the bulk matrix (**Figure 8**); this phenomenon can be advantageous for composite toughening depending on the relative fracture toughnesses of the matrix and fibre-matrix interface.
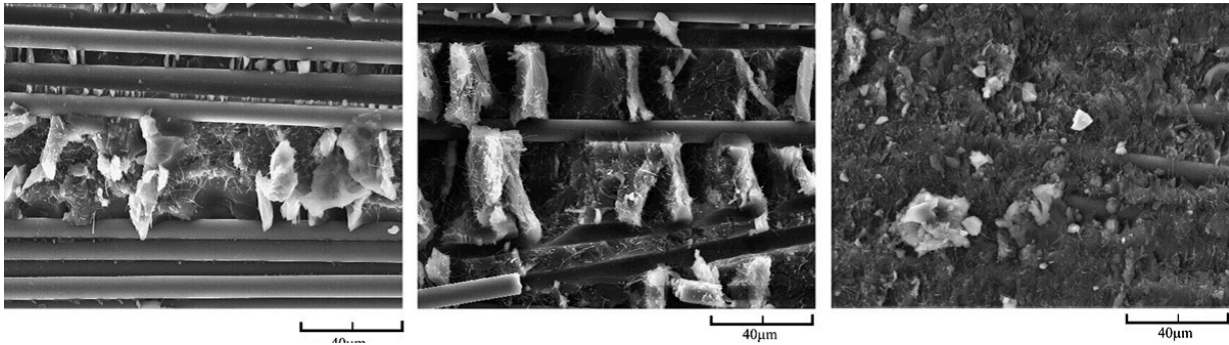
Figure 8. Crack branching at fracture surface in Mode II tested laminates with CNT reinforced interplay region. [17]

Mechanisms such as fibre bridging and crack branching that involve the continuous fibres and the plies should also be considered. Fibre can severely increase the apparent fracture toughness of a material due to fibres carrying load directly across the fracture plane. Reduction in fibre bridging with the addition of CNTs in the interply region was observed in some studies [19, 21]. This could have been a result of either the matrix being stiffened through the addition of CNTs and thus not allowing fibres to nest during consolidation, or due to the strong adhesion between the continuous fibres and the nanoreinforced resin reducing the number of fibres de-bonding from the matrix and bridging across the fracture plane. [26]

In addition to fibre bridging, interlaminar cracking (**Figure 9**), a precursor for crack branching, was also observed [26]. Furthermore, CNT agglomerates, microvoids and mircrocracks in the matrix component of their HCs due to unsuitable processing, could form a path of least resistance for the crack, and, if present in ply interfaces adjacent to the fracture plane, could lead to interlaminar cracking and subsequent crack branching. [7] These observations suggest that the processing and production should perhaps be carefully controlled to ensure homogeneity in the matrix and the absence of defects to allow for the measurement of the true material fracture toughness.
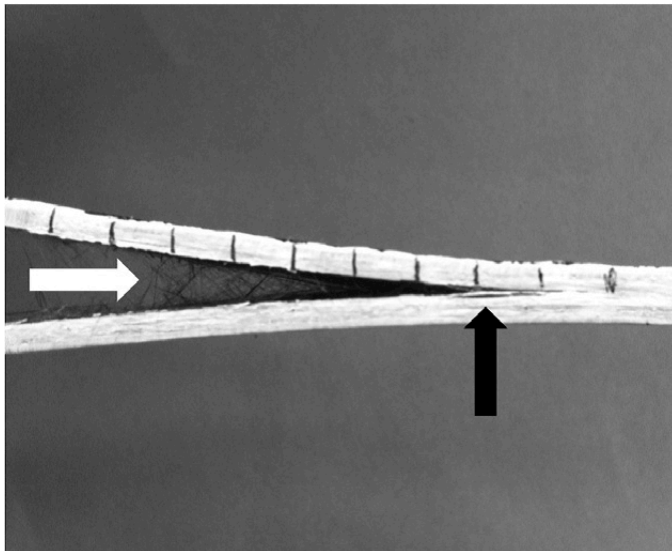

Figure 9. Fibre bridging (white arrow) and interlaminar cracking (black arrow) in specimen tested in Mode I. [26]

3.2. Compression Properties of Hierarchical Composites

Traditionally, composite compression mechanics fit in frameworks of either the Rosen or Argon models [24], but have been recently clarified experimentally [27]. The matrix

contributes to failure by microcracking due to shear while the fibres exhibit both shear-driven compressive failure and kinkband formation due to bending failure. As such, nanoreinforced matrices should enhance the compression strength of HCs because they are both stiffer and have higher shear strengths [28] than un-reinforced epoxies.

Compression performance was generally enhanced when introducing CNTs, with the only exception being a result of inadequate processing. [29] Even if an HC does not contain sufficient CNTs to enhance compression modulus, a significant (39% [30]) improvement in compression strength can be achieved. The improvement was attributed to the increased load carrying capacity in the interfibre space due to the presence of CNTs. Moreover, the quality of the nanomaterial dispersion has been shown as instrumental in attaining an improvement in compression strength. For low CNT loadings, employing block copolymers [30] or functionalising CNTs [31] can be sufficient to control the quality of CNT dispersions and achieve improved HC compression strength.

Fibre	Nanofiller	Loading in matrix	Max improvement		Ref.
			Stiffness	Strength	
UD CF	MWCNT	0.5 wt%	3%	-7.6%	[29]
CF weave	MWCNT	0.5 wt%	0%	39%	[30]
CF weave	CSCNT	10 wt%	6.7%	14%	[14]
UD CF	CSCNT	10 wt%	5%	10%	[10]
CF weave	CNF	1 wt%	n/a	12.7%	[31]

Table 1. Compressive properties of HCs.

As higher CNT volume fractions are introduced into HCs, the optimal CNT volume fraction at which compression strength is maximised is not the maximum CNT volume fraction if the manufacturing route is not suitable for dispersing high CNT loadings and agglomerates form. [30] The compression strength improvements of HCs containing 10% CNTs by weight of matrix, the highest reported loadings [10, 14], were modest; the authors identified not only agglomerations and adjacent areas of non-homogeneous CNT distributions (**Figure 10**) even in the best cases, but also voids, all of which were attributed to the difficulty of the processing.
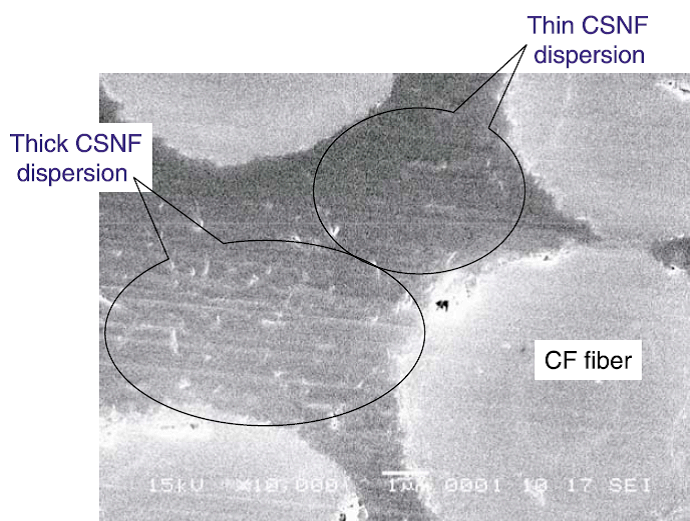

Figure 10. Non-homogeneous CSCNT dispersion in HCs. [14]

At the laminate scale, fractographic evidence revealed a mechanistic change in fracture upon the introduction of carbon nanofibres. [31] In the baseline laminate (**Figure 11**), fracture

initiated via delamination near the mid ply (highlighted areas in **Figure 11**a) most likely due to splitting in the plies perpendicular to the loading direction, ultimately inducing translaminar fracture and failure. The ply splitting is a direct result of matrix microcracking at the fibre-matrix interface. The nanoreinforced laminate failed more akin to a unidirectional composite (**Figure 11**). Failure seems to have initiated via in or out-of-plane kink band formation, followed by post-failure delamination. This mechanistic change suggests that the addition of CNTs functions primarily by enhancing the matrix shear strength, which in turn inhibits microcracking and delamination, improving HC compression strength.
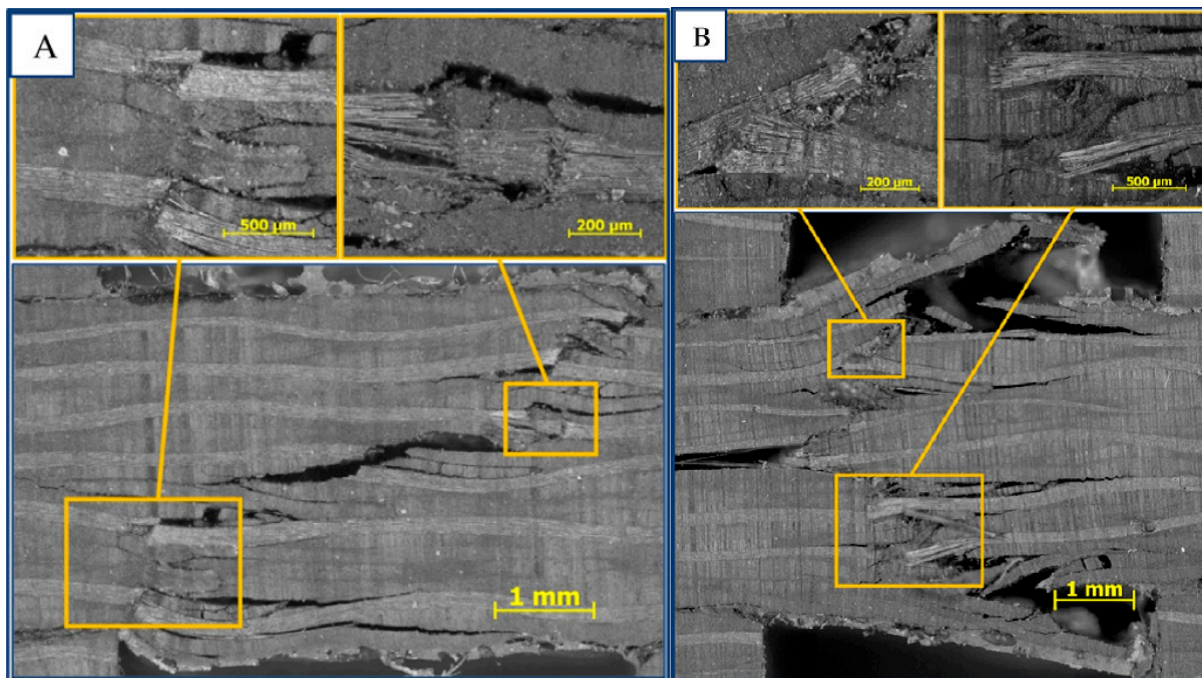

Figure 11. Different failure modes of a) conventional and b) HC woven composites under uniaxial compressive loading. [31]

4. Summary and outlook

A number of methods based on both conventional composite processing technologies and novel techniques have been utilised to produce good quality HCs, but with relatively low CNTs loadings. The conventional resin transfer methods were hampered by the high viscosities of the PNC so that only materials with 1% CNTs by weight of matrix could be processed. Similarly, drum winding was only completely successful for low loadings of 5 wt%, probably also due to viscosity of the fibre impregnation bath. Processing techniques in which only one ply interface is nanoreinforced are expensive, have no effect on the intralaminar region and potentially misrepresent the material fracture toughness.

Although HCs manufactured to date contain only modest CNTs loadings, enhancement of both fracture toughness and compression strength have been achieved. Fractographic examinations revealed that crack deflection is the mechanism that would contribute most to enhanced fracture toughness, while the shear strength of the matrix is critical to improving compression strength. Processing permitting, these mechanisms should be effective even at higher loadings and provide further performance enhancement.

Progress in this area may require looking back at wet impregnation by powder slurry processes. This technique was first proposed in 1995 as an effective method for making thermoplastic based continuous fibre composites [32, 33]; it is versatile as the continuous fibre volume fractions can be controlled by the concentration of powder in the impregnation bath or the speed and tension used for pulling the fibres. More recently, it has seen a

resurgence as it is thought capable of accommodating any matrix as long as it is in powdered form. [34]

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