UNIVERSIDAD POLITÉCNICA DE MADRID

ESCUELA TÉCNICA SUPERIOR DE

INGENIEROS DE CAMINOS, CANALES Y PUERTOS

**Hybrid FRP/CNT veil hierarchical composites
with enhanced interlaminar properties and
integrated multifunctionalities**

TESIS DOCTORAL

Yunfu Ou

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Dedicated

to Luna

to my parents

and to my brother and sister

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If, one day, you ask me what is my most colorful and unforgettable stage in my life until now. “The PhD Career!” I would answer without hesitation. Those days are imbued with industriousness, expectations, learning, retrospects and great decisions, all of which are of special significance and great importance for me, leading me to the next level. 2020 has already witnessed many big events which will absolutely be remembered by the world and recorded in human history, especially COVID-19. Luckily or unluckily, I’m also going to finish my PhD career this year. Anyway, I would like to take this precious opportunity to thank the people and organizations supporting and accompanying with me in the past four years.

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RESUMEN

Los materiales compuestos poliméricos reforzados con fibras (FRP) se utilizan ampliamente en componentes estructurales debido a sus notables propiedades mecánicas y su bajo peso. Sin embargo, uno de los más importantes inconvenientes que presentan es la pérdida de prestaciones de aquellas propiedades relacionadas con la dirección de su espesor, lo que les hace especialmente sensibles a sollicitaciones con cargas fuera de plano, impactos dinámicos, etc. Los nanotubos de carbono (CNT) son materiales candidatos a compensar dicha falta de propiedades fuera del plano, aunque su integración en laminados estructurales ha sido un desafío. Uno de los principales objetivos de esta tesis es el desarrollo de estrategias de integración de estos refuerzos en compuestos laminados estructurales para mejorar su resistencia y tenacidad interlaminar. En la tesis, se han explorado dos rutas diferentes de fabricación, el moldeo por transferencia de resina asistida por vacío (VARTM) y la consolidación de materiales preimpregnados mediante compresión en caliente. El procedimiento consiste en el intercalado de los velos de nanotubos en laminados mediante un proceso sencillo y escalable industrialmente. La tenacidad a la fractura interlaminar en Modo I y Modo II, así como la resistencia a la cortadura interlaminar se han evaluado mediante los correspondientes ensayos mecánicos, permitiendo posteriormente un análisis detallado de los mecanismos de rotura y progresión del daño. Los resultados mostraron que el velo de CNT es un candidato prometedor para su intercalado en materiales compuestos laminados. Los efectos del refuerzo mediante velos de CNT dependen en gran medida de su grosor, del grado de compactación, de las arquitecturas de preformas textiles utilizadas y de las condiciones de carga. El proceso por el cual la grieta salta entre las láminas del material compuesto y los velos de CNT juega un papel predominante en los mecanismos de fractura interlaminar. El frente de la grieta se propaga alternativamente entre las interfaces del laminado y los velos, lo que activa la formación de puentes a distintas escalas mejorando significativamente la tenacidad a la fractura del laminado.

Además, los velos de CNT presentan una porosidad cercana a la de un carbono activado con unas propiedades en tracción en el rango alto de estos materiales, junto con una notable conductividad eléctrica, por lo que podrían ser utilizados como electrodos y colectores de corriente en aplicaciones de almacenamiento de energía. En esta tesis, los velos de CNT se utilizan como electrodos en

supercondensadores que se integran en laminados con el objeto de aunar, en el mismo material, capacidad de almacenamiento de energía y soporte de cargas estructurales. En la tesis, se ha desarrollado un método de fabricación simple y efectivo que consiste en la incorporación de condensadores eléctricos de doble capa (EDLC) basados en velos de CNT con un polímero electrolítico en medio. Estos dispositivos de almacenamiento de energía se intercalan entre láminas de fibras de vidrio/carbono que posteriormente se impregnan en resina mediante el método de VARTM. Se llevaron a cabo ensayos de carga y descarga del dispositivo de almacenamiento de energía durante la fase de impregnación, del curado de la resina y durante ensayos mecánicos de flexión en cuatro puntos. Los mecanismos de degradación estructural se analizaron mediante microscopía electrónica de barrido y tomografía computarizada de rayos X 3D. Durante la impregnación de resina, los dispositivos mantienen una alta estabilidad Clombiana. Sin embargo, en las primeras muestras sujetas a ensayos mecánicos, el dispositivo actúa a modo de defecto interno debido a la presencia del polímero electrolítico colectores de corriente en forma de láminas delgadas de aluminio. Las propiedades mecánicas mejoraron sensiblemente al utilizar velos de nanotubos como colectores de corriente. Además, las propiedades interlaminares de los materiales que contienen dispositivos de almacenamiento de energía mejoraron notablemente al permitir la transferencia de carga de cortadura mediante la incorporación de conectores de resina. Estos conectores se crean durante el propio proceso de infusión de resina al estar el dispositivo de almacenamiento de energía taladrado en su espesor y siguiendo una retícula regular. Este esquema de conectores de resina permite transferir cargas de forma eficiente entre dos láminas de material compuesto que contienen, entre ambas, un dispositivo de almacenamiento de energía. Se desarrolló un modelo de elementos finitos que permite diseñar dicha unión y compatibilizar la capacidad de almacenamiento de energía y la estructural, abriendo un amplio espectro de utilización de los materiales.

ABSTRACT

While FRP composites are extensively used in structural components due to their remarkable mechanical properties, a major weakness of these materials is their low through-the-thickness properties which permits the easy formation of impact-induced delamination, limiting their more widespread applications in structural engineering. CNTs carry the promise of enhancing this poor out-of-plane performance, although their integration has been challenging. One of the main objective of this thesis is the development of strategies to integrate CNTs into structural laminate composites for interlaminar toughening. Two different routes, vacuum assisted resin transfer moulding and prepreg consolidation by compression moulding, are explored to interleave different CNT fiber veils into FRP laminates in a facile and scalable way. The interlaminar fracture toughness under Mode I and Mode II loading cases are investigated and discussed comparatively, followed by a systematic analysis of failure and toughening mechanisms. Results showed that CNT veil is a promising candidate for interleaving application. The toughening effects of CNT veils depend highly on their thickness, degree of compaction, host fabric architectures as well as loading conditions etc. Interlaminar crossing plays a dominant role amongst toughening mechanisms. The crack front propagates alternately between interfaces of the laminate, triggering multi-level fiber bridging and significantly improving the fracture toughness of the laminate.

In addition, CNT fiber veils, with a porosity close to that of an activated carbon and tensile properties in the high-performance range as well as the remarkable electrical conductivity, could be ideal electrodes and current collectors for structural power application. In this thesis, CNT veils as essential part of supercapacitor were integrated into FRP composites to achieve simultaneously both load-carrying and electrochemical energy storage capabilities. A simple fabrication method was demonstrated through embedding CNT veils-based EDLC interleaves between carbon/glass fabrics, followed by resin infusion via vacuum bagging process. Coupled mechanical and electrochemical tests were carried out to realize the efficacy of the resultant structural supercapacitors under the application of mechanical forces. Possible degradation mechanisms in the samples were analysed through scanning electron microscopy and 3D X-ray computed tomography. It was found that a high coulombic efficiency and stability of EDLCs can be maintained during resin infusion. However,

further studies on coupled mechanical and electrochemical properties were hampered by the large presence of defects in the structure, most notably those arising from the presence of thick metallic current collectors, which essentially act as severe delaminations. By using CNT veils not only as active material but also as current collectors, a true multifunctional composite material was produced, which can sustain mechanical deformations without degradation of electrochemical properties. Furthermore, grid-shaped EDLC interleaves were found to be effective to improve interlaminar properties of the composite and offer a wide range of design parameters to obtain desired composite performance. A finite element model approach was employed to explore the effect of rivet structures on the lap shear behaviour of laminated materials containing EDLC devices. In parallel, experimental tests were performed to validate the proposed simulation model. The resulting model is particularly useful to design structural power composites with tailored balance between the energy/power densities and structural properties, thus opening the multifunctional spectrum.

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GLOSSARY OF TERMS AND ACRONYMS

a	Crack length
C	Compliance/Capacitance
C_{sp}	Specific capacitance
D	Diameter
I	Current
L	Length
m	Slope
E	Electric energy
E_f	Modulus of elasticity in bending
E_{real}	Real energy
F	Load
F_{max}	Maximum load
P_{real}	Real power density
t	Thickness
t_{dis}	Discharge time
w	Width
V	Voltage
δ	Displacement
σ_f	Flexural stress
ε_f	Flexural strain
ε_0	Permittivity in vacuum
ε_r	Relative permittivity
τ_{max}^{CNT}	ILSS of CNT veil/resin film specimen
τ_{max}^{BL}	ILSS of baseline
G_I	Energy release rate under Mode I
G_{IC}	Critical energy release rate under Mode I
$G_{IC,ini}$	Initiation value of G_{IC}
$G_{IC,prop}$	Propagation value of G_{IC}
G_{II}	Energy release rate under Mode II
G_{IIC}	Critical energy release rate under Mode II
T_g	Glass transition temperature
Al-CC	Aluminium current collector
ASTM	American Society for Testing and Materials

BT	Beam theory
BK	Benzeggagh-Kenane
CAG	Carbon aerogel
CC	Compliance calibration
CD	Charge-Discharge
CF	Carbon fiber/fabric
CFRP	Carbon fiber reinforced polymer
CNT(s)	Carbon nanotube(s)
SWCNT(s)	Single-wall carbon nanotube(s)
DWCNT(s)	Double-wall carbon nanotube(s)
MWCNT(s)	Multi-wall carbon nanotube(s)
CNTV	Carbon nanotube veil
CVD	Chemical vapor deposition
DCB	Double cantilever beam
EDLC(s)	Electric double-layer capacitor(s)
EMI	Electromagnetic interference
EIS	Electrochemical impedance spectroscopy
ENF	End-notched flexure
ERR	Energy release rate
FCCVD	Floating catalyst chemical vapor deposition
FEA	Finite element analysis
FIB	Focused Ion Beam
FPZ	Fracture process zone
FRP	Fiber reinforced polymer
GFRP	Glass fiber reinforced polymer
gsm	Gram per square meter
IFT	Interlaminar fracture toughness
IL	Ionic liquid
ILSS	Interlaminar shear strength

LEFM	Linear elastic fracture mechanics
LSP	Lightning strike protection
LSS	Lap shear strength
MBT	Modified beam theory
MCC	Modified compliance calibration
NDT	Nondestructive testing
PAN	Polyacrylonitrile
PBO	Poly(p-phenylene-2,6-benzobisoxazole)
PE	Polyethylene
PEK-C	polyetherketone cardo
PPTA	Poly(p-phenylene terephthalamide)
PSF	polysulfone
PVA	Polyvinyl acetate
ROI	Region of interest
RT	Room temperature
RTM	Resin Transfer Moulding
SBS	Short beam shear
SC	Supercapacitor
SPC(s)	Structural power composite(s)
SSA/S	Specific surface area
SSC	Structural supercapacitor
SEM	Scanning electron microscopy
UD	Unidirectional
UHM	Ultra-high modulus
UHMPE	Ultra-high molecular weight polyethylene
VARTM	Vacuum assisted resin transfer moulding
WIF	Wedge-insert fracture
XCT	X-ray computed tomography

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CHAPTER 1

Introduction

“Inspiration exists, but it has to find us working”

- Pablo Picasso

1.1 Delamination – a known Achilles heel of advanced composites

The past half-century has witnessed the rapid expansion of fiber reinforced polymer (FRP) composites. Their higher specific stiffness, strength and outstanding fatigue properties combined with environmental and chemical resistance make them ideal candidates for thousands of structural applications in aircraft, automobiles, civil applications, ships and offshore platform facilities, amongst others [1-4]. These high performance structural composites are based on lay-ups of stacked plies (e.g. prepregs or dry wovens) leading to extraordinary in-plane properties, dominated by fiber properties, but suffering from much poorer out-of-plane properties, which are strongly matrix-dependent. This last effect is particularly problematic and failures due to matrix cracking and ply delaminations often occur by the application of out-of-plane loads exerted during impact events [5]. Once delamination initiates and propagates inside the laminate, the integrity of the whole structure will progressively degrade and eventually result in catastrophic failure. Therefore, improving the delamination-resistance of FRP (i.e. enhancing its interlaminar fracture toughness) is of paramount importance in many applications.

1.2 Structural power composites – power the future

There is an urgent need to eliminate the fossil fuels responsible for greenhouse gas emissions. The EU, for example, has set targets to reduce greenhouse gas emissions by more than 80% by 2050 [6]. For the transport sector, these challenges have translated into rapid electrification of aircraft and vehicles as part of broader efforts to develop greener, lighter, safer and more competitive road and air transport [7]. As aircraft and vehicles become increasingly electrically powered, it is inevitable and of great importance to consider new ways to carry more electrical energy onboard [8-11]. The research on structural energy storage devices is conducted in this context, with ambition to convert

the entire automotive body or elements of the aircraft structure into an energy storage device that could work in the absence of fuel and still support the required mechanical stresses[7, 9, 11, 12]. This next generation of structural energy storage devices with superior structural and functional performances is often termed "structural power composites" (SPC) [11], and the structural supercapacitor, as one of the typical representatives, was drawn much attention in recent years.

1.3 CNT veils – a promising candidate for multifunctionalizing FRP composites

Composite performance arises from the synergistic effect of its constituent materials. This has been the motivation for incorporating nanomaterials with tensile strengths and moduli beyond current macrofiber reinforcements in order to impart these impressive properties. For example, nano-scale reinforcement using nanofillers like carbon nanotubes (CNTs) in between the plies of a fiber reinforced polymer (FRP) composite offers the opportunity to reinforce the interlaminar bonding with minimal weight penalty and effectively avoids reductions in in-plane properties. These nanocomposites exhibit remarkable structural performance and multifunctional properties by synergistically combining the characteristics of both components if proper structural and interfacial organization is achieved. Interlaminar strength is thus increased by the reinforcement in the z-direction, and crack growth is forestalled by a “pinning” mechanism that occurs between the plies [13-15].

Several approaches for integrating CNTs into FRP structural composites have been studied [16-19]. Among all these methodologies, dispersing CNTs entirely throughout the composite matrix is, to date, the most widely used route. The main problem of this approach is that the viscosity of a CNT-modified matrix increases dramatically with increasing CNT content, leading to incomplete matrix infusion [20]. Also, it is difficult to get a homogeneous dispersion of extra phases into the epoxy matrix and final laminate [21].

Assembling micro CNT to macro fiber veil [22, 23] could offer a solution for the increased viscosity and the inhomogeneous dispersion of the aforementioned route, as these veils can be easily and readily deposited in between the primary reinforcing fiber layers before infusion. Thus, the viscosity of the composite matrix is not affected. What is more, CNT fibers have an unusual yarn-like structure with an accessible surface area several orders of magnitude higher than that of a traditional fiber.

The free space between bundles in the CNT is then able to be taken up by non-cross-linked resins via capillary force [24]. The neighboring plies can thus be tightly “bridged” by CNT-toughened epoxy resin, significantly enhancing the interlaminar properties of FRPs.

In addition, since CNTs possess exceptional mechanical properties as well as excellent electrical conductivity and piezoresistivity, they can be utilized not only to toughening the weak interlaminar layer (resin rich region) of FRP, but also to enable FRP structures with multifunctionalities, i.e. damaging sensing, energy storage etc.

1.4 Objective and structure of the thesis

This thesis deals with the development of strategies to integrate macroscopic CNT fiber veils into structural laminate composites. The aim is to improve the mechanical properties, especially the interlaminar properties, of traditional fiber-reinforced polymer composites, while providing them with new functions derived from the unique yarn-like structure of CNT fibers and the low dimensionality of their constituents.

Following a general introduction of the research motivation in Chapter 1, Chapter 2 reviews typical failure mechanisms of FRP composites, with the focus on delamination failure. Different interlaminar toughening methods were also reviewed, with more attention being given to interleaving methods with nanofiber veils. The CNT and its assemblies are then briefly introduced, focusing more on their structures as well as mechanical and electrical properties, followed by a detailed review of using CNT and its assemblies for interlaminar toughening and structure power application.

The materials and methods used for fabrication of FRP composites laminates and assembling of structural supercapacitor are described in Chapter 3, as well as the details of characterization techniques used to analyze the properties of produced interlaminar-toughened laminates and structural SCs.

Chapter 4 focuses on the improvement of interlaminar properties of FRP composites by interleaving CNT veils, and meanwhile tries to understand the interlaminar toughening mechanisms of CNT veils in different fabric architectures (unidirectional or woven) and loading cases (i.e. Mode I or Mode II). Different strategies to integrate macroscopic CNT fiber veils into structural laminate composites

were developed and optimized in order to achieve “full resin infiltration”. A joint work with Tortech Nano-Fibers was performed in order to develop and industrialize proposed methods for CNT implementation in structural laminate composites as well as systematically investigate the thickness effect of CNT interleaves on interlaminar properties of woven CFRP composite laminate.

Chapter 5 introduces the fabrication and characterization of structural SC based on all-solid thin sandwich structures of CNT fiber veils and PE membrane. Two generations of Structural SCs developed in our lab were detailed, followed by a successful demonstration of their possible application. A simulation tool was developed and experimentally validated to investigate the possible influence of the rivet structure on the shear properties of resultant laminate, providing a novel methodology to design structural power composites with tailored balance of structural and multifunctional functions.

Finally, the main conclusions of the research work and possible future directions are summarized in Chapter 6.

CHAPTER 2

Literature review

“Whoever is careless with the truth in small matters cannot be trusted in important matters”

-Albert Einstein

2.1 Brief introduction of FRP and its failure mechanisms

Fiber reinforced polymer (FRP) is a composite material made of a polymer matrix reinforced with fibers (see **Figure 2-1**). The fibers are usually glass, carbon, aramid, or basalt, which serve as reinforcement agent and vary in fabric architectures such as woven, stitched and braided. The polymer is either thermoset (i.e. vinyl ester resin) or thermoplastic (i.e. polypropylene), which works as “glue”, holding the fibers together to transfer loads from broken fibers to non-damaged fibers and avoid bulging.

Fig. 2-1 the main constituents of FRP

FRP composites usually consist of several layers with different directions. Their failure mechanisms can be divided into 2 categories: intralaminar failure and interlaminar failure (see **Figure 2-2**). The intralaminar failure exists within a ply, which includes fiber rupture, the debonding between fiber

and matrix, fiber pull-out and also matrix rupture. The typical interlaminar failure is delamination, which occurs at the interface between adjacent layers. It may develop during manufacturing due to non-optimum curing or the introduction of foreign bodies. It may also result from impact damage, or from the three dimensional interlaminar stresses that develop at stress-free edges of discontinuities [25]. Compared with intralaminar failures, delamination is more harmful and destructive; once it happens, the stiffness of FRP will significantly degrade, and often cause catastrophic failure. So, it is very urgent and important to enhance the interlaminar properties of FRP in large-scale engineering practice.

Fig. 2-2 Schematics of failure mechanisms of FRP

2.2 General toughening mechanisms and techniques

From the fracture mechanics point of view, the fracture process can be considered as a mutual competition between intrinsic damage processes that happen ahead of the crack tip to promote its propagation, and extrinsic crack-tip-shielding mechanisms that act generally behind the tip of a crack to inhibit this. Toughening mechanisms thus can be categorized into two types: intrinsic and extrinsic as schematically shown in **Figure 2-3** [26]. Intrinsic toughening mechanisms are the dissipative processes, associated with making these processes more difficult and primarily related to the enlargement of plastic zone, as such they will exert influence on both the initiation and propagation of cracks. Examples of intrinsic toughening include plasticity, void growth, micro-cracking, phase changes and crazing [27]. With extrinsic toughening, the inherent fracture resistance of the composite material remains unchanged. Instead, extrinsic mechanisms such as crack bridging act principally behind the crack tip, or more precisely, on the wake of the crack to shield the local

stresses and strains actually experienced at the crack. Examples of extrinsic toughening mechanisms include processes as crack bridging by unbroken fibers or a ductile phase in composites, the frictional interlocking of grains during intergranular fracture in monolithic ceramics and the presence of collagen fibrils spanning microcracks in bone [28]. It is worth noting that extrinsic toughening mechanisms, unlike intrinsic ones, are only effective in resisting crack growth (that is, crack propagation stage), and their effect is dependent on critical length of crack processing zone.

Fig. 2-3 Schematic illustrating both intrinsic and extrinsic aspects of toughening mechanisms associated with crack extension [26].

On the basis of aforementioned toughening mechanism, a number of methods to prevent delamination have been developed over the years, which can be generally divided into three different categories: matrix toughening, improvement of fabric architecture and interleaving. [25, 29-36]

2.2.1 Matrix toughening

Thermosetting polymers, for example epoxy resins, are principally identified as strong and rigid but brittle materials. Although their strength and rigidity are needed for various engineering applications, the brittle nature blocks their wider usage. Therefore, toughening of these materials has become a necessity to ensure their feasibility and applicability in practical applications. The addition of a second phase (either rigid or soft) can be a solution [37].

Rubber, for instance, has been successfully utilized as one of the soft toughening materials. Different rubbers present different toughening mechanisms. For phase separated rubber, the presence of a

rubbery phase can absorb energy during their deformation upon loading. While by incorporating preformed rubber particles, a multiplicity of stress concentration points is introduced, promoting multiple crazing, which leads to more energy dissipation due to the production of more new surfaces [38]. Even though obvious toughening effects have been achieved by modifying epoxy matrices with rubbers, there are some associated problems: decrease of the glass transition temperature (T_g), degradation of yield strength, Young's modulus as well as the thermal and environmental stability, and so forth [39]. Furthermore, the toughening effect of rubbers were affected by the crosslink density of epoxy resin, and the majority of the successful cases were reported for epoxy systems with relatively low crosslink density [40]. For aerospace-grade epoxy systems which normally have high level of crosslink density, alternative toughening agents are required.

Thermoplastics with relatively high T_g could be an alternative to rubber for toughening the epoxy resins.[41-43]. Since late 1980s, various thermoplastics have been integrated into epoxy systems as toughening agent, including polyphenylene oxide (PPO) [40], polyether sulfone (PES) [44], polyether imide (PEI) [45], polyphenylene ether (PPE) [46], polysulfone (PSF) [47], and polyethylene terephthalate (PET) [48], etc. Possible toughening mechanisms in these systems includes plastic deformation, crack pinning and bridging, crack deflection, shear banding, etc. [40]. Several literature reviews on the topic of thermoplastic toughened epoxy resins are also available [40, 49].

The addition of more rigid particles, such as glass beads [50], silica [51, 52], graphene [53] etc. has been reported to improve the stiffness and toughness of the epoxy resin. The main toughening mechanisms cover crack pinning, crack deflection, matrix plastic deformation along interfacial regions, and/or debonding [54, 55]. Spanoudakis and Young [49], for example, introduced glass particles into the epoxy resin. They found that the crack propagation behaviour is strongly dependent on the volume fraction and size of the particles. Moreover, the adhesive strength between particle and matrix affects both the crack propagation and the appearance of the fracture surface. Zhang et al. [52] successfully fabricated SiO_2 /epoxy nanocomposites via a special sol-gel technique, in which silica nanoparticles with an average diameter of 25 nm were almost perfectly dispersed in the epoxy matrix. The static/dynamic modulus and fracture toughness of the composites were improved with increasing silica content up to 14 vol.%. Significant improvements were achieved for both stiffness and toughness when the interparticle distance was smaller than the nanoparticle diameter.

2.2.2 Improvement of fabric architecture

In order to enhance the through-the-thickness properties of the laminate composites, various woven or three dimensional (3-D) fabrics have been introduced. Unlike unidirectional (UD) laminates which contain parallel fiber tows within each ply, fiber tows of woven fabrics are interlacing between each other in warp and weft direction in a certain order (see **Figure 2-4** [56]). Normally, the interlaminar fracture toughness (IFT) of woven FRP composites is higher than that of UD composites [57, 58]. One reason is that crack propagation can be deflected because of the existence of weft yarns, the other can be ascribed to the roughness of woven fabrics which generates the plastic zone between fiber tows at crack tip front [59-61]. However, it should be pointed out that in-plane properties of woven FRP are degraded compared with that of UD laminates as their weaving structure disrupts the fiber continuity.

Fig. 2-4 Schematic diagrams of representative 2-D woven fabric [56]

The mode I interlaminar fracture behavior of woven aramid-fiber/epoxy resin laminates has been investigated as a function of the fabric weave and the fabric surface texture adopted in the construction of the laminates [59]. The rising R-curves (resistance to fracture versus crack extension) were obtained for all the materials investigated, which can be attributed to the presence of fiber bridging during crack propagation. The critical energy release rate under mode I (G_{IC}) depended on both the fabric weave and the surface texture. The largest values of G_{IC} were acquired for those

laminates in which the surface of the fabrics contains a high density of fiber ends. Among the weave variations studied, larger values of G_{IC} were obtained for those FRP laminates holding the coarser plain fabric weaves [62].

In addition, the existence of reinforcing fiber in the through-thickness direction could carry load and therefore improve out-of-plane properties. Different strategies involving 3D weaving (**Figure 2-5a** [63]), Z-pinning (**Figure 2-5b** [36]) and stitching (**Figure 2-5c** [64]) have been employed to this end.

Fig. 2-5 (a) different 3-D weaving architectures [63]; (b) Schematic of the UAZ® process which is the most common method used to manufacture z-pinned laminates [36]; (c) Schematic of a non-crimp fabric (NCF) with Tricot stitching [64].

Falconnet et al. [65] reported that knitted fabric composite laminates possess exceptional interlaminar fracture toughness (IFT). The origin of the high IFT values, which are superior to UD even woven fabric composites, lies in the complex fabric architecture. The 3-D loop structure induces various energy dissipation mechanisms, which do not occur in other laminate composites. Toughening mechanisms such as yarn bridging and breakage, crack branching and friction were identified using scanning electron microscopy (SEM). Kim et al. [66] tried to characterize delamination behavior of the composite laminates made of several weft-knitted fabrics. The results showed that the G_{IC} values for the knitted composites were approximately 10 or 20 times higher than that of uniweave composites, and influenced by fiber volume fraction of the composites and the tightness factor of the knitted preforms. For the stitched composites, Dransfield et al. [67] have given

an overall review. They reported that stitching can significantly improve some mechanical properties such as the delamination resistance and the compression-after-impact (CAI) strength of the CFRP composite laminates. However, it may result in the degradation of other properties due to the breakage of in-plane fibers and/or the creation of resin pockets. Although 3-D composites showed much higher interlaminar fracture toughness than the 2-D composites, there is an unavoidable, and often significant, reduction of the in-plane mechanical properties due to lamina fiber damage, stress concentration, loss of in-plane volume fraction as well as crimping and misalignment of the load-bearing fibers by insertion of the z-binder yarns during weaving [68]. For example, it is often found that the in-plane tension, compression and flexural properties of the 3-D composite are 10-40% lower than the 2-D composite with the same in-plane fiber content [69].

2.2.3 Interleaving Techniques

The concept of interleaved composites was firstly patented in 1986 by American company Cyanamid [70]. Through incorporating a thin flexible layer in between composite layers, the damage tolerance of the composites can be improved. Generally, interleaf materials can be classified into three types: particle, film, fiber veils. A schematic of placing interleaf on composite prepreg is shown in **Figure 2-6** [71]. The aim is to introduce another phase at the interlaminar region.

Fig. 2-6 Methods of interleaving in composite laminates: (a) Particle Interleaving; (b) film interleaving and (c) fiber veil interleaving.

In terms of particle interleaving methods, a full commercial product (T800H/3900-2), which possesses heterogeneous interlayer including fine thermoplastic particles, has already been applied in the primary structures of Boeing 777 [72, 73]. In general, several steps were needed: thermoplastic pellets produced by various techniques are firstly dried and pulverized into fine powders, which was then sieved into particulates of diameter no larger than 10 μm [74]. These fine powders are later sprinkled uniformly over a prepreg with an optimized areal weight and pressed so that the particles

attach or embed into the prepreg. The modified prepreg is then cut, laminated and cured using the standard manufacturing process. The toughening mechanisms of particle interleaved laminates have been extensively investigated, which are similar to matrix toughening detailed in **Section 2.2.1** and include crack pinning, crack-path deflection, particle bridging, crack-shielding and reduction of stress concentration due to debonding and micro-cracking [43]. A comprehensive experimental investigation with regard to the effect of particle size, loading and adhesion on modulus, strength and toughness of the resin system has been conducted by Fu et al. [75]. The results indicated that the strength and toughness of a polymeric composites can be improved by appropriate inclusion of materials and geometrical parameters (i.e. size and volume fraction of the particles) as well as size distribution.

The film interleaving presents many options that are not possible with particle interleaving. This includes the blend of different polymers with different functionalities. The films include epoxies or thermoplastic of various thickness. The same matrix resin was used as toughening interleaves to ensure compatibility and ease of processing. The increased resin region relieved the plastic zone restrains and therefore improved the fracture toughness of composites laminates [76]. Singh and Partridge [77] for example, used similar matrix resins as interleaf materials with a thickness of 50 and 200 μm , respectively. G_{IC} was increased from 213 J/m^2 (non-interleaf) to 310 J/m^2 (50 μm interleaf) and 369 J/m^2 (200 μm interleaf). One of the successful development of film interleaving is the Toho UT500/111 prepregs interleaved with Ethylene-based ionomer film. This kind of film has high ductility and good adhesion to epoxy resin. It is reported that interlaminar fracture toughness increased significantly by inserting thin ionomer film but the additional increase with the increase of the ionomer thickness was marginal [78]. Introducing a lay of high-toughness resin between prepreg lays was proven to increase IFT in both modes I and II, but also increase composite thickness and weight [25, 79]. Gillespie and Smiley [80, 81] demonstrated that the fracture behavior of interleaved composites can be characterized by the radius of the plastic deformation zone at the crack front. When the radius is bigger than the interlayer thickness, the plastic area extends beyond its boundaries and cracks appear in the bonded interfaces between interlayer and fibers, rather than those within interlayer, which are typically stronger. Some of the thermoplastic particles and film interleaving have demonstrated the enhancement of interlaminar fracture toughness and reduction in delamination growth rates, but the thickness of interleaf is substantially high (about 20 to 50%

of the ply thickness), which has resulted in an obvious increase of laminate thickness, even decreasing in-plane stiffness and strength in excess of 20% [82].

Recently, electrospun thermoplastic nanofibers were used to improve the IFT of composite and achieved great success [4, 21, 83-89]. This nanofibrous interlaminar toughening strategy is, in principal, the same as film interleaving method, but integrates nanofibrous veils with substantially high surface area rather than the continuous polymeric films. This relatively new concept was first introduced by Kim and Reneker [84]. Dzenis et al. [90], Zucchelli et al. [91] and Palazzetti et al. [92] thoroughly reviewed the available literatures that have followed the development of this novel idea and demonstrated capabilities and prospect of electrospun nanofiber veils as interleaf materials for interlaminar toughening of composite materials. It is clear from the available studies that nanofiber veil interleaving toughening method is considered a promising strategy to toughen composite laminates under both in-plane and out-of-plane loading conditions [93]. But it should be pointed out that the polymer choice of electrospun nanofiber for toughening composites should be made deliberately in compliance with the polymer matrix chemistry and cure conditions [91, 94, 95], because the thermal stability, wettability, and nanofiber interfacial compatibility with the resin system will exert influence on the interlaminar toughening performance.

Several experiments focused on utilizing electrospun nanofibers which can be dissolved in the resin such as polyetherketone cardo (PEK-C) [87], polysulfone (PSF) [96] or phenoxy-based nanofibers [97]. The reported improvements in IFT would be ascribed to a phase separation of the dissolved nanofibers which leads to tough particulate phases, as illustrated in **Figure 2-7** [96]. Several polymer types which can retain their nanofibrous structure in the final composite, such as polyacrylonitrile (PAN) [98], polyimide (PI) [99], and Nylon 6.6 [100, 101] etc. The advantages of keeping the nanofibrous structure are that the physical and mechanical properties of nanofibers can be retained and that there is no increase in viscosity of the matrix resin due to dissolution of the nanofibers.

Fig. 2-7 Schematic representation of PSF nanofibrous membrane toughened carbon fiber/epoxy prepreg: (a) nanofibrous membrane deposited unidirectional prepreg, (b) dissolution of PSF nanofibers and (c) aligned spheres generated from dissolved PSF nanofibers by reaction-induced phase separation.[96]

2.3 Carbon nanotube and its assemblies

2.3.1 Brief introduction of CNT

CNTs are best portrayed as seamless cylindrical hollow fibers, comprised of a single sheet of pure graphite (a hexagonal lattice of carbon, resembling a chain link fence). Based on the number of graphitic layers, CNTs are classified as single-wall (SWCNT), double-wall (DWCNT) or multi-wall (MWCNT) (**Figure 2-8a** [102]). SWCNT consists of a single sheet of graphene with diameter of order of 1 nm [103]. MWCNT consists of an array of such cylinders formed concentrically and separated by 0.35 nm and can have diameters from 2 to 100 nm [104]. Recent improvement in nanotube synthesis have led to CNTs with length up to 650 μm [105] and CNTs with aspect ratios of $10 - 10^7$ are routinely produced [106].

CNTs owe their strength and stiffness to their strong C-C bonds and their hexagonal array in the tube [107]. The experimental strength of individual CNTs is considerably superior to that of the other fibers as displayed in **Figure 2-8b** [106]. The value of specific strength of CNTs far exceeds the strongest fiber in the graph (PBO fiber). The comparison gives an indication of the potential of using CNTs to make new high-performance fibers and in other applications like nano-reinforcing in structural laminate.

Fig. 2-8 (a) Schematics of different CNT types [102] and (b) a comparison of the tensile properties of nanotubes with those of current high-performance fibers [106].

Besides exceptional mechanical properties, Individual CNTs can bear excellent electrical and thermal conductivity. The electrical properties of SWCNTs depend on their molecular structure and

can be related to their chiral indices (n, m) [108, 109]. Specifically, all armchair tubes are metallic and only a fraction of the zig-zag tubes fulling the condition of $(2n + m) / 3 = \text{integer}$ are metallic. The remaining tubes with zig-zag type as well as all of the chiral type are semiconducting. It should be pointed out that the electrical properties of CNTs depend not only on the chiral angle of their layers but also on their separation [110]. For instance, the electrical conductivity of a multilayered nanotube is also influenced by the electron hopping between graphene sheets. Thus, although the electrical conductivity of individual metallic SWCNTs has been reported to be $\sim 10^8$ S/m [111], it is only $\sim 10^6$ S/m for individual MWCNTs [112]. In addition, the thermal properties of CNTs are able to surpass copper, with the thermal conductivity of SWCNTs and MCWNTs approaching 3500 and 3000W/(m·K), respectively [113, 114].

2.3.2 Production of CNT assemblies

It is highly desirable to assemble CNTs into macroscopic and engineered structures with controlled morphologies and properties [115]. To date, many methods have been developed to assemble CNTs into macroscopic fiber veils, which may be divided into three families, together resulting in 5 different types of CNT assemblies as shown in **figure 2-9**. The first family uses liquids to create suspensions or solutions of short and mass-produced CNTs. CNT-solvent solutions then can be filtered to fabricate random planar ‘buckypaper’ [116] (**figure 2-9a**), or spun into coagulating fluids to produce single fibers, and later processed into a mat [117] (**figure 2-9b**). The second family involves processing vertically aligned CNTs grown from substrates by chemical vapor deposition (CVD). These CNT ‘forests’ may be drawn into aligned 2-dimensional mats [118] (**figure 2-9c**) or by flattening via the so-called ‘domino pushing’ process [119] (**figure 2-9d**). The final family uses direct-spun carbon nanotube aerogels, produced via the ‘Windle process’ [120] (**figure 2-9e**). Direct-spun fibers are produced by the spinning of aerogel layers onto a rotating mandrel, with or without solvent condensation, produces direct-spun mats. This method was introduced by Li et al. [120] in 2004 and has received much attention since it has been scaled up at real industrial production.

Fig. 2-9 Various methods for producing CNT mats: (a) Buckypaper from filtration [116]; (b) Wet spinning from solution [117]; (c) Fiber spun from CNT forest [118]; (d) “Domino pushing” of CNT forest [119] and (e) Direct-spinning via the “Windle Process” [120]

2.3.3 Structure and properties of CNT assemblies

In CVD direct-spinning process (‘Windle process’), the dilution in the gas phase of the very long CNTs reduces their entanglements, thus enabling the drawing of the in-form fiber and alignment of the building blocks [121]. The rate at which the aerogel is drawn is a fundamental parameter controlling the final configuration of the fiber (random or oriented), and the dilution of the aerogel through either slowing down the precursor feed rate or speeding up the hydrogen carrier gas flow rate enables much faster fiber drawing rates (**Figure 2-10** [122]).

Fig. 2-10 (a) Schematic illustration of the direct-spinning process of CNT fiber showing the effect of aerogel dilution on the maximum drawing rate and the configuration of the final fibers; (b) and (c) are SEM images of randomly-oriented and highly-aligned CNT fibers obtained from different drawing rates.

Structures

Direct-spun fiber veils/mats exhibit three distinct hierarchies of microstructure, as illustrated in **Figure 2-11**: the carbon nanotube, nanotube bundle, and the interlinked bundle network [123].

Fig. 2-11 (a) The hierarchical microstructure of direct-spun CNT mat [123].

Their nanostructures are complex with each CNT veils consisting of CNT bundles, which are an assembly of individual CNTs interacting via van der Waals forces [115]. The individual CNTs have different morphologies (length, diameter, wall number, and chirality). Finally, there is a wide range of contamination compounds in the material structures such as the residual catalyst and other carbon structures like side products. These impurities can be reduced by optimizing the synthesis process or purification treatments [124].

Mechanical properties

Figure 2-12 [125] summarizes the specific tensile strength and modulus of CNT fibers synthesized by different methods and compares them with other common structural materials. The specific tensile strength and elastic modulus of as-synthesized CNT fibers are roughly at around 1.5 GPa/SG and 70 GPa/SG, respectively, which have already outperformed that of steel and Al alloys, as well as PET, meta-aramid (Nomex), and glass fibers. Several CNT fibers are reaching 2 GPa/SG in specific tensile strength and 100-150 GPa/SG in specific tensile modulus, almost at the level of medium-strength commercial carbon fibers (T300), liquid crystalline aromatic polyester (Vectran) and para-aramid (Kevlar).

CNT fiber veils obtained from CVD direct-spinning process usually have outstanding mechanical properties in the axial direction [115]. Their tensile strength strongly depends on the interactions between CNTs and CNT bundles, which are correlated with the catalyst and carbonaceous impurities, CNT morphologies, packing density of the CNT bundles, and CNT alignment. Those parameters can be controlled by optimizing the synthesis process to reduce catalyst and carbonaceous impurities [126], increasing the degree of CNT alignment [121] and producing long, thinwalled nanotubes with smaller diameters featuring larger specific surface areas [127].

Fig. 2-12 Specific tensile strength versus specific Young's modulus of CNT fibers compared with commercial high-performance materials [125]

Electrical properties

The theoretical and experimental research on CNT fiber assemblies predict that proper control of the morphology of these macroscopic assemblies of CNTs should produce the material of excellent electrical conductivity comparable to the conductivity of individual nanotubes [128, 129]. Electric conductivity of the CNT products spun from the floating catalyst method strongly depends on the contact areas between CNTs and CNT morphologies (length, diameter, wall number, chirality, and impurities). It can be improved by increasing the CNT length while reducing nanotube diameter, impurities, and wall number through a synthesis process or post-treatments. Furthermore, the CNT products fabricated by the floating catalyst process show an electrostructural effect in a liquid medium due to the rearrangement of the hierarchical structure of individual CNTs as well as CNT bundles [130]. Their change in electrical conductivity with temperature and water vapor may offer information with respect to the nature of the CNTs, such as purity and metallic/semiconducting ratio [131, 132]. To date, the best electric conductivity of CNT fibers spun from floating catalyst reported in literatures is 2.24×10^6 S/m [133].

2.4 Using CNT and its assemblies for toughening FRP composites

2.4.1 Integration routes: From filler to other more complex structures

Over the past decades, huge efforts have been made on the improvement of interlaminar fracture toughness in fiber/epoxy composites through nanoparticle reinforcement, as summarized in **Table 2-1**. These works mainly vary with respect to the filler integration method, fabrication method adopted, composite system, mass fraction of nano-fillers, fiber geometry and configuration. Generally, the major CNT integration techniques can be classified and broken down into: (i) mixing in bulk resin [134-138] (**Figure 2-13a**), (ii) in-situ CNT growth (i.e. CNT sizing) [15, 139, 140] (**Figure 2-13b**), (iii) physical transfer of the CNT particles (i.e. spray coating) [141-146] and (iv) CNT interleaving technique [88, 89, 147, 148] (**Figure 2-13c**).

Fig. 2-13 Schematic of different CNT integration techniques: (a) dispersing CNTs entirely throughout the composite matrix; (b) deposition of CNTs directly on to the carbon fiber surface and (c) CNT interleaving technique.

The first method often leads to large improvements in matrix properties at low volume fractions, but reaching saturation around 5 wt.%, after which mechanical enhancements become less significant. Such limitation on the CNT volume fraction is predominantly attributed to the increasing difficulty in dispersing individual CNTs above volume fractions greater than $\sim 1\%$ [149]. Consequently, interest has shifted towards the growth of CNTs directly on the carbon fibers (CFs) by means of chemical vapour deposition (CVD) processes [150].

Tab. 2-1 Property improvement in hierarchical nanofiller/polymer composites

<i>Filler integration method</i>	<i>System Nanofiller/fiber/matrix</i>	<i>Fabrication method</i>	<i>Mass fraction/ Area density</i>	<i>CNT geometry</i>	<i>Mechanical improvement</i>	<i>Ref.</i>
<i>Mixing in bulk resin</i>	<i>D&MWCNTs/woven glass/epoxy</i>	<i>RTM</i>	<i>0.3 wt. %</i>	<i>MWCNT: D =15 nm L=50 μm; DWCNT:D=3 nm L=10 μm</i>	<i>No improvement</i>	<i>[136]</i>
	<i>MWCNTs/UD-carbon/epoxy</i>	<i>Autoclave</i>	<i>1 wt. %</i>	<i>D=10-15 nm L> 500 nm</i>	<i>60% Mode I 75% Mode II</i>	<i>[137]</i>
	<i>S&MWCNTs(-NH₂)/UD-carbon/epoxy</i>	<i>Autoclave</i>	<i>0.5 wt. %</i>	<i>D = 9.5 nm</i>	<i>75% at initiation and 83% in propagation (Mode I)</i>	<i>[138]</i>
	<i>MWCNTs(-COOH)/UD-carbon/epoxy</i>	<i>VARTM</i>	<i>0.5, 1 and 1.5 wt. %</i>	<i>D=20-30 nm L=10-30 μm</i>	<i>25%, 20% 17 % at 0.5, 1, 1.5 wt. % (Mode I)</i>	<i>[134]</i>
	<i>DWCNTs(-NH₂)/woven carbon/epoxy</i>	<i>VARTM</i>	<i>0.1 wt. %</i>	<i>D=4-7 nm L=1-5 μm</i>	<i>-23% Mode I</i>	<i>[135]</i>
<i>In-situ CNT growth</i>	<i>MWCNTs/woven carbon /epoxy</i>	<i>Hand lay-up</i>	<i>-</i>	<i>-</i>	<i>50% Mode I</i>	<i>[139]</i>
	<i>MWCNTs/woven carbon /epoxy</i>	<i>VARTM</i>	<i>2.24 wt. %</i>	<i>L=10-300 μm</i>	<i>83% Mode I (Initiation)</i>	<i>[140]</i>
	<i>MWCNTs/woven alumina /epoxy</i>	<i>Hand lay-up</i>	<i>-</i>	<i>D=14 nm L=20-30 μm</i>	<i>76% Mode I</i>	<i>[15]</i>
<i>Spray coating</i>	<i>MWCNTs(-COOH)/UD-carbon/epoxy</i>	<i>VARTM</i>	<i>0.6 wt. %</i>	<i>D=20-40nm L < 5μm</i>	<i>24% Mode I</i>	<i>[144]</i>
	<i>Plasma-modified CNT/UD-glass/epoxy</i>	<i>Hot press</i>	<i>1.2 g/m²</i>	<i>-</i>	<i>46% Mode I</i>	<i>[143]</i>
	<i>SWCNTs/woven carbon/epoxy</i>	<i>VARTM</i>	<i>0.01 wt. %</i>	<i>D=1-1.4 nm</i>	<i>6% Mode I</i>	<i>[146]</i>
	<i>CNTs/woven carbon/epoxy</i>	<i>Hand lay-up Vacuum moulding</i>	<i>0.047 wt. %</i>	<i>-</i>	<i>50% Mode I</i>	<i>[142]</i>

	<i>MWCNTs(-COOH)/UD-carbon/epoxy</i>	<i>Hot press</i>	<i>0.5 wt.%</i>	<i>D=8-15 nm L=10-50 μm</i>	<i>17% Mode I</i>	<i>[145]</i>
	<i>CNT veil/UD-carbon/epoxy</i>	<i>Autoclave</i>	<i>0.5-2 g/m²</i>	<i>L=1-10 μm</i>	<i>No improvement in Mode I; >50 % Mode II</i>	<i>[147]</i>
	<i>CNT veil (-NH₂)/UD-carbon/epoxy</i>	<i>Hand lay-up</i>	<i>0.2 g/m²</i>	<i>D=10 nm L=300 μm</i>	<i>13 % Mode I</i>	<i>[148]</i>
<i>Interleaving</i>	<i>Electrospun SPS fibers/UD-glass/epoxy</i>	<i>VARTM</i>	<i>12-22 g/m²</i>	<i>D=2.1 μm</i>	<i>90% Mode I 100 % Mode II</i>	<i>[88]</i>
	<i>Electrospun PA6.9 fibers/woven glass/epoxy</i>	<i>Hot press</i>	<i>3 g/m² 18 g/m²</i>	<i>D=245 nm</i>	<i>50% for 3 g/m² 62% for 18 g/m² (Mode I)</i>	<i>[89]</i>

Note: D is diameter of out-layer of CNT or electrospun fiber and d stands for that of inner-layer and L corresponds to the length; AR and CF mean aspect ratio and carbon fiber respectively, and UD- is the abbreviation of unidirectional; -COOH and -NH₂ mean that the CNTs were functionalized.

In order to test the hypothesis that growing CNTs on CF bundle or tow would enhance the properties of polymeric carbon composites, Kepple et al. [139] functionalized woven CF in situ with CNTs. Results revealed that CNTs as-grown on the woven CF substantially improve the fracture toughness of the resulting composite on the order of 50%, accompanied by no loss in structural stiffness of the final composite structure. However the high growth temperature, which is typically associated with CNT growth (600 –1200 °C), results in the mechanical degradation of CFs and removing of the polymer sizing [151]. The mechanical degradation of the CFs in the CVD synthesis method can be attributed to the introduction of fiber flaws by surface oxidation and thermal degradation [152].

It is worth mentioning that Wicks et al. [15] grew radially-aligned CNTs in situ on the surface of fibers in a woven alumina cloth as shown in **Figure 2-14**, providing prominent three-dimensional reinforcement. It was shown that aligned CNTs bridge the plies, improving the already tough system by 76% in steady state (more than 1.5 kJ/m² increase in mode I fracture). But this method is limited by growing fuzzy fibers on alumina woven fabric whereas most of the industries commonly use carbon fiber woven cloth. Also, this method may not be easily scalable as production of fuzzy fiber plies is a challenge for larger parts.

Fig. 2-14 Schematics of fuzzy-fiber-reinforced plastic (a) Radially-aligned CNTs grown on alumina fiber cloth. (b) CNT intralaminar and interlaminar reinforcement.

Steiner et al. [153] claimed that it is possible to preserve carbon fiber strength and stiffness by tensioning CFs during CVD growth at temperatures in excess of 700 °C. They also demonstrated that fiber strength and stiffness can be preserved via performing CVD below the fiber's strength-loss threshold temperature (~550 °C for the HTR40 fibers and closer to ~600 °C for AS4 fibers). However, processing CFs in the form of a weave or tow is more applicable in most industrial applications, whereas aforementioned method is limited to the use of single CFs due to the complicated steps, which would be hard to realize large-scale industrial production.

Godara et al. [138] successfully manufactured CNT/CF/epoxy prepreg using high-shear calendaring equipment and Drumwinder technique (**Figure 2-15**), then an autoclave was employed to produce laminate. It was found that addition of CNTs has shown a significant reduction in the coefficient of thermal expansion (CTE) for TMWCNT and DWCNT systems, presumably by restricting the mobility of the polymer network and inducing microstructural rigidity. A noticeable improvement was also observed in the crack initiation and propagation energy of the CNT-toughened composites. However, there are many critical issues that need to be optimized (like the stability of dispersions, viscosity control and optimization of surface modifications) to transfer excellent intrinsic properties of CNTs to three phase composites.

Fig. 2-15 Prepreg production setup: (a) Drumwinder equipment and (b) prepreg on the drum.[138]

A novel and practical technique for dispersion of multi-walled carbon nanotubes (MWCNTs) onto woven CFRP prepreg is reported by Sunil and Dikshit [16] as demonstrated in **Figure 2-16**, and it was proved to be worked well in facilitating further percolation of CNTs into a few top layers of fibers within the tows.

Fig. 2-16 Method of CNT dispersion and transfer onto CFRP preregs: (a) Spraying of MWCNT in a solvent, (b) evaporation and drying of solvent, (c) transfer of MWCNT layer to prepreg with inverted substrate, and (d) an uniform layer of MWCNT transferred to prepreg.[16]

Wang et al. [154] attempted to integrate CNT thin film (buckypaper) into CF prepreg composites via autoclave process. A resin flow model in autoclave processing for BP/CF interply hybrid composite fabrication was proposed as displayed in **Figure 2-17**. Although dramatic improvements in both in-plane and through-thickness electrical conductivities were achieved with this method, a degradation in mechanical performance was also observed. It was found that when CNT content exceeded 10 wt.%, resin flow was significantly inhibited, and BP acted as a barrier to the through-thickness flow due to its low permeability and bubbles in CF layers were not able to be expelled, leading to a high

void content.

Fig. 2-17 Resin flow model in autoclave processing: (a) initial hybrid structure layup, (b) resin flow along through-thickness direction into dry BP, and (c) resin bleeding out from the sides of the CF prepreg layer after full impregnation of the BP.[154]

Even though so many efforts have been contributed to explore CNT-integration methods, most of them are either time-consuming with limited scale-up potential due to a complicated manufacturing protocol or costly as RTM or autoclave methods need to be used to create a void-free laminate. It is noteworthy that Latko et al. [155] employed a melt-blown technique to manufacture a non-woven veil with 5 wt.% of multi-walled carbon nanotubes. This method is commonly utilized as fast, low cost method and can easily be up-scaled for the processing of thermoplastic nanocomposites with CNTs. In turn, the final CNT doped veil product is a desired structure which can be utilized as an interlayer in reinforced multifunctional composites. Due to their stickiness and flexibility they are perfect nanocarriers of CNTs for the resin infusion process applied in laminate fabrication.

Recently, much attention has been paid to the use of thin veils of carbon nanotubes (CNT) as interleaves in laminated composites [147, 148, 156-158]. These veils can be intercalated between the primary reinforcing fiber layers before infusion, so there is no need to disperse them into the resin. Therefore, there are no disadvantages such as increased viscosity from dispersing nanofillers in resin and uneven distribution or segregation from filtration of nanofillers [159, 160]. Compared with electrospun thermoplastic interleaves, CNT fiber veils have order-of-magnitude higher surface area and fracture energy [125]. They are also thermally and chemically stable, and are already produced industrially [125, 161], thus making them a promising interleaf material for widespread implementation in structural composites. CNT veils can be made extremely thin (<50 nm), and with sufficiently high longitudinal Young's modulus to preserve interlaminar rigidity, if properly integrated.

Although the use of CNT fiber veils offers many potential benefits compared to traditional toughening methods, the research on composites enhanced with CNT fiber veils is limited and often contradictory. Hong Xu et al. [162] proposed a novel method for developing continuous CNT film interleaved carbon fiber composites to enhance the interlaminar properties of laminated composites. In this method, CNT film fabricated by floating catalyst chemical vapor deposition method is directly deposited on unidirectional CF at the exit of the furnace. Then the CNT-coated fabric was infused with epoxy resin, which was dissolved in acetone with a solid content of 30 wt.%. After acetone evaporation, several plies of the infused fabrics were stacked ply-by-ply and then cured via a hot-press molding method. It has been found that the flexural strength and interlaminar shear strength increased initially with increasing CNT film content, and then decreased, which is due to the insufficient wetting of resin in the thick CNT films. In this approach, controlling the thickness of the CNT film is important because a thicker CNT film results in lower interlaminar shear strength and lower flexural strength. Nistal et al. [148] interleaved an ethylenediamine-functionalised multilayer CNT web (0.2 g/m^2) between CF plies, and reported a 13% enhancement in the Mode I IFT. Di Leonardo et al. [157] introduced pristine and functionalized carbon nanotube (CNT) webs at the interlaminar region of two different thin-ply CFRP systems (NTPT 402 prepreg, and TeXtreme/SE84LV). Experimental results showed that the Mode I IFT for the NTPT 402 system was substantially lower while there was no reduction in the steady state value of the Mode I IFT when SE84LV resin was used.

2.4.2 Critical factors of CNT reinforcement for interlaminar toughening

CNT loading

Considering CNTs bear excellent mechanical performance compared with traditional fibers, it is rationally expected that mechanical properties of these CNT-reinforced composites increase with increasing CNT loading. But it is not true. When mixing CNTs into resin, the high surface area of CNTs generates potent intrinsic van der Waals forces between individual CNTs, causing tubes to agglomerate and band together in bundles [163, 164]. As the CNTs concentration increases, this phenomenon proves to be more pronounced [163]. The resultant agglomerates act as defect sites rather than reinforcements in polymer nanocomposites, leading to degradation in overall mechanical properties. An optimum loading level is therefore preferred for CNTs in nanocomposites. This was

proved by the research work of Borowski et al. [134]. Their experimental results showed a 25%, 20%, and 17% increase in the maximum IFT of the CFRP composites with the addition of 0.5, 1.0, and 1.5 wt% CNTs, which indicates there is optimum percentage between 0 and 0.5 wt%. When interleaving CNT assemblies (mat/film/veil) into FRP system, there is no agglomeration issue since the position of individual CNT is almost fixed. However, the CNT loading (the thickness of CNT assemblies) can influence the resin infiltration states of laminates since the time for resin infiltration is limited for standard composites manufacturing processes. In addition, the delamination behavior may also change with increasing the thickness of CNT-toughened interlayer, which influences the final toughening effects [16]. Nguyen et al. [147] introduced aligned CNT sheet into unidirectional CFRP system. Mode II interlaminar fracture toughness was found to be significantly improved (~70%), while Mode I fracture toughness slightly decreased. This reduction was attributed to partial impregnation of epoxy into the thick CNT film and the sheet forming an interlaminar layer which acts as a barrier for micro-scale fiber bridging. Joshi and Dixit [16] found that the highest interlaminar strength was exhibited by samples containing 1.32 g/m² CNT, which corresponded to the enhancement of 26% in G_{IC} , while the sample with CNT loading of 3.62 g/m² corresponded to a reduction of 20% as compared to the neat samples.

CNT Type

The addition of CNTs into epoxy leads to toughness improvements in the range of 20%-50% depending on the type of CNTs and functionalization employed on the CNTs [165-168]. Florian et al. [165] systematically studied the influence of different types of CVD-grown CNTs (single-, double-, multi-wall and functionalized CNTs) on the mechanical properties of epoxy-based nanocomposites. The relatively large improvement in ultimate strength by SWCNTs compared to the other nanofillers was observed, which can be attributed to the high specific mechanical properties and the highest aspect ratio of the SWCNTs. In addition, combined with the high specific surface area, SWCNT do not have inactive internal layers, they bear the highest potential to improve the strength of materials. While adding small amounts of MWCNT does not significantly affect the ultimate strength of the epoxy resin. This can be easily interpreted by considering the concentric structure of MWCNTs. Owing to the absence of stress transfer to internal layers, only outermost layers of MWCNTs contribute to the mechanical reinforcement. The bridging traction between

MWCNTs and matrix is just as weak as van der Waals forces between internal layers of MWCNTs. The reinforcement potential of the CNTs can only be achieved when an effective load transfer from the surrounding epoxy matrix into the CNT and reverse is possible. Thus a nice impregnation with the matrix, combined with a strong interfacial adhesion must be ensured. However, the larger the provided interface, the more serious the dispersion conditions, thus aggravating the impregnation. Alternatives could be CNTs bearing a smaller specific surface area, which can realize a better dispersibility. An even better resolution should be utilizing functionalised SWCNTs, realising an appropriate dispersion and matrix adhesion. Florian et al. [165] also found that a functionalisation with amino-groups improved the dispersibility in all cases and stabilised the CNT-suspension, thus, reducing the reagglomeration. This effect was attributed to an assimilated polarity of the surface and to a possible reaction between the introduced amino-groups and the epoxy resin, thus, integrating the CNTs into the epoxy-network structure.

Alignment

The orientation of CNT fiber requires equal attention in interlaminar toughening of laminate composites. This mainly because nano-bridging, the main toughening mechanism of nanocomposite, is dependent on a good load transfer from matrix to the nanofibers [89], while nanofiber orientation affects such load transfer. Palazzetti et al. [100] have revealed that random nanofibers were more preferable than oriented ones under Mode I loading whereas aligned nanofibers seemed to be more suitable than random ones under Mode II loading. Better Mode I interlaminar performance of random nanofibers can be ascribed to their higher porosity compared with aligned ones and a better adhesion between adjacent fabric plies is expected. Daelemans et al. [85] also found there a strong effect of nanofiber orientation on toughening mechanism during Mode II crack propagation. The critical energy release rate under Mode II (G_{IIC}) of nanofiber interleaved laminates increased by ~50%, 75%, and ~100% when three nanofibrous veil morphologies with a distinct orientation of the nanofibers (parallel, transverse, and random to the crack growth direction, respectively) are used as compared to virgin laminate without nanofibers. According to fractographic analysis, the nanofiber interleaved laminate showed two distinct failure modes consisting of intralaminar failure similar to the virgin laminates (Type A), and, interlaminar failure at points where the crack passes from one side of the interlayer to the other (Type B), as described in **Figure 2-18**. The different fracture

behaviors were attributed to nanofiber bridging zones, which develop predominantly in Type A failure regions for parallel interleaved laminates and mostly in Type B failure regions for transverse interleaved laminates. Laminates with randomly oriented interleaves could develop nanofiber bridging zones in both failure regions and thus exhibited the highest enhancement in interlaminar fracture toughness. In this case, the toughening effectiveness of randomly oriented nanofiber veils should be highly favorable for practical applications because of uncertain crack growth direction in practice as well as ease of manufacturing and processing.

Fig. 2-18 Two different failure morphologies of nanofiber interleaved laminates.[85]

2.4.3 Interlaminar toughening mechanisms with nanofiber veils

FRP composites interleaved with nanofiber veils possess multilevel hierarchy. **Figure 2-19**, for example, illustrates the hierarchical structure of a woven carbon fabric/CNT veils/epoxy composite laminates with different levels. Some reports suggested the existence of different toughening mechanisms at different length scale [86]. In order to advance the research and design highly damage-resistant composites, it is extremely crucial to get a thorough understanding of toughening mechanisms at each level.

Fig. 2-19 The hierarchical structure of CF/epoxy composites interleaved with CNT veils.

Nanotoughened epoxy

A nanotoughened epoxy, provides insights on the interaction between the nanofibers and the epoxy resin. Similar to regular FRP, the properties of such a nanotoughened epoxy will mainly depend on the mechanical properties of the nanofibers and epoxy matrix as well as the adhesion between them.

Figure 2-20 [165] schematically presents possible processes and mechanisms, explaining the deformation and failure of CNTs when bridging a crack. The initial situation of the CNT in an ideal case (**Figure 2-20a**) is a completely impregnated and isolated CNT embedded in the matrix, but how it develops (like **Figure 2-20 b-e**) depends on the interfacial adhesion and the mechanical properties of the CNTs. In case of a weak interfacial bonding, simple pull-out of the CNT from the matrix occurs (**Figure 2-20b**), which is the most commonly observed. In contrast, a very strong bonding between CNT and matrix will result in a complete rupture of the CNT (**Figure 2-20c**) or to fracture of the outer layer and a telescopic pull-out (which is also called sword-sheath pull-out) of the inner tube(s) (**Figure 2-20d**). A spatial bonding of the reactive groups at the interface enables a partial debonding of the interface, but allows a crack bridging (**Figure 2-20e**), which suppresses a further crack opening. However, increasing stresses would finally lead to a failure of the CNT, according to **Figure 2-20c** and **d**.

Fig. 2-20 Schematic description of possible fracture mechanisms of CNTs. [165]

Daelemans et al. [86] proposed similar toughening mechanisms (**Figure 2-21 a-d**) when investigating the FRP composites interleaved with electrospun nanofibers. The proposed mechanism of nanofiber bridging was also confirmed by scanning electron microscopy (SEM) analysis on the fracture surface of broken single edge notched bending (SENB) specimens (**Figure 2-21e and f**).

Fig. 2-21 Schematic of an embedded nanofiber interacting with the crack front (a), which can lead to (b) straining without debonding, (c) straining with partial debonding from the epoxy, or (d) complete debonding (e) SEM pictures of fracture surface of PCL nanotoughened epoxy exhibiting strong adhesion between epoxy and PCL nanofibers as the PCL nanofibers are strained without debonding from the epoxy. (f) weak adhesion between epoxy and PA6 nanofibers proven by the smooth surface of the PA6 nanofibers and imprints left in the epoxy.[86]

The fracture surfaces of nanocomposites provide first information about fracture mechanisms and the influence of particle modification on the fracture behaviour. **Figure 2-22** [165] shows SEM

images of fracture surfaces of the neat epoxy resin (a) and a representative nanocomposite containing 0.1 wt% DWCNT–NH₂ (b). The imaged fracture surfaces were taken from similar areas of the failed specimens. The general toughening effect of nanoparticles reflects itself in a significantly larger roughness of the fracture surface of the sample containing CNTs.

Fig. 2-22 SEM images of fracture surfaces: (a) the epoxy and (b) a DWCNT–NH₂/epoxy composite.[165]

It has been well discussed in the literature that the enhancement in the toughness of CNT-toughened epoxy is through the pull-out mechanism [168, 169]. However, other mechanisms such as bridging and void growth after pull-out have also been reported in the literature [170]. Hsieh et al. [171] investigated the contribution of three different mechanisms (i.e. pull-out, de-bonding and void growth) to the fracture toughness of CNT-toughened composites. By calculating the fracture energy of the above mentioned mechanisms, it was shown that the contribution of the void growth after de-bonding is meagre and hence can be neglected. From the above discussed theoretical and experimental results, it is clear that pull-out and bridging of CNTs from the matrix contribute majorly to the toughening improvement in polymer matrices.

Interfacial properties and crack propagation in Nano-toughened interlayer

The interlaminar region in laminated composites is considered to be a weak part of the laminate, as it bears a resin-rich layer and is exposed to stress concentration due to a mismatch in elastic properties of neighbouring plies. The IFT is usually a controlling design parameter since damage on the structural level of composites is mainly governed by delamination between plies resulting from cracks in the interlaminar region. Through interleaving the laminate with CNT veils, the interlaminar region will comprise no longer solely of brittle epoxy resin, but rather of a composite layer of CNT toughened epoxy.

In this interlaminar level, the loading condition may exert significant influence on the toughening effects of CNT veils. Under Mode I loading conditions, crack growth subjects the CNTs to normal forces. When the CNT-matrix adhesion is weak, large-scale peeling of CNTs from matrix would happen. Therefore, the adhesion between CNTs and epoxy resin becomes very crucial under Mode I delamination growth. Weak interfacial strength leads to low-energy uptake by the CNTs and thus poor toughening performance. Under Mode II, adhesion between CNT and epoxy resin would be of relatively less importance, because the shear adhesion strength of all CNTs is relatively high due to their high surface area to volume ratio. As a result, high improvements in G_{IIC} may be obtained. The crack propagation behavior within the interlaminar region may also influence the toughening mechanisms. Daelemans et al. [85, 86] systematically studied the delamination behaviors of electrospun nanofiber interleaved FRP composites under different loading conditions. They reported that delaminations in virgin composites progress almost exclusively at the fiber-epoxy interface. The energy required for such interfacial failure depends on the adhesion between fibers and matrix resin and forms the major contribution to the interlaminar fracture toughness of virgin laminates. The delaminations in nanofiber interleaved composites show the same fiber-epoxy interfacial failure, but they additionally show regular crossings of the interlaminar region, as shown in **Figure 2-23**.

Fig. 2-23 Schematic view of the delamination path in virgin and interleaved composite laminates under Mode I (a) and Mode II (b) loadings.[86]

Noting that more interlaminar crossings are observed under Mode II loading than under Mode I loading. Generally, to improve the fracture toughness on the interlaminar level, the nanocomposite interlayer characteristics (fracture toughness, nanofiber properties, adhesion) and the interaction between the delamination path (interlaminar crossings, microcrack formation) are of crucial importance and should be deliberated to design damage-resistant composite materials.

Fiber bridging

The resistance to fracture in several types of materials, such as wood, composites increases with crack growth before reaching a steady plateau and/or failure. Such a behavior, characterized conventionally by a rising resistance curve (R-curve), is ascribed to the development of toughening mechanisms during the crack propagation [172]. A substantive factor involved in the crack growth resistance concerns the influence of the fibers. Generally, delamination cracks have trajectories dominated by the matrix. However, some interaction with the fibers is inevitable due to instabilities of crack path and imperfection of fiber alignments [173]. These interactions with fibers have the desirable effect of suppressing delamination, which causes the nominal delamination resistance to increase as the crack extends [174]. However, such interactions also cause the delamination resistance to depend on specimen geometry, loading mixity, etc. [175]. Spearing and Evans [176] found that interlaminar fracture resistances obtained from DCB tests are sensitive to fiber bridging. Comparatively weak pullout tractions result in resistances many times the fracture resistance for crack growth initiation. The shape of the resistance curve is influenced by the stiffness of the arms of the specimen relative to the bridging forces.

2.5 Using CNT and its assemblies for structural power application

The development of FRP composites has focused on their structural performance since the initial introduction into transport applications, with properties such as delamination resistance and compression strength being of great importance. However there has been a move to exploit polymer composites in multifunctional roles in recent years [177]. A very significant and promising advancement in this area is the development of truly multifunctional components, which can simultaneously confer structural and non-structural functionality in laminate composites, such as

energy storage FRP composites. These stiff, strong and lightweight continuous fiber reinforced composite laminates with the capability of energy storage are normally termed as “structural power composites” (SPCs) [11].

There are various devices commonly used for electrical energy storage, including capacitors, supercapacitors, batteries, and fuel cells. The Ragone plot in **Figure 2-24** introduces the most common way of comparing different energy storage devices in terms of their energy and power densities [178]. As demonstrated, batteries possess high energy density but modest power density due to the relatively slow kinetics of the redox processes involved. Traditional capacitors offer limited energy density but high power density as only electrons are transported during charge/discharge. Supercapacitors provide a compromise and can evidently bridge the gap between batteries and capacitors in terms of both power and energy densities. Furthermore, supercapacitors have longer cycle life than batteries because the chemical phase changes in the electrodes of a supercapacitor are much less than that in a battery during continuous charging/discharging [179]. These key attributes make supercapacitors more attractive and versatile as high powered energy storages and it is desirable to integrate supercapacitors with structural composites.

Fig. 2-24 Ragone plot representing the power and energy densities of SC and other electrochemical systems [178].

2.5.1 A brief introduction of EDLC

Electric double layer capacitor (EDLC), also known as supercapacitor, is the electric energy storage

system based on charge–discharge process in an electric double layer on porous electrodes. **Figure 2-25** [180] shows the operation mechanism of EDLC. Initially, the anions and cations are distributed randomly in the electrolytes. When an external voltage is applied to the electrodes, the anions will move towards the positive polarized electrode surface, while cations will be attracted to the negative side, leading to a charge process. Eventually, an EDL is formed between electrode and electrolyte interface. In contrast, by removing the external voltage and adding a load resistance simultaneously, ions will drift back to the equilibrium position, which corresponds to the discharging process.

Fig. 2-25 Charging and discharging processes for a EDLC [180].

The energy density of EDLC can be expressed as follows:

$$E = \frac{CV^2}{2} \quad (2-1)$$

where E is electric energy stored in the EDLC, C is capacitance, and V is applied voltage.

The above formula suggests that the electrochemical window of the electrolyte is a key factor in energy storage, since the total stored energy varies as the square of applied voltage. Therefore, EDLC with a non-aqueous electrolyte has essentially a higher energy density than the aqueous type EDLC because non-aqueous electrolytes have wider electrochemical windows (≈ 3 V) compared with aqueous electrolytes (≈ 1 V) [181].

Optimization of the electrode material is also crucial, since at a given maximum voltage the total stored energy is proportional to the capacitance. In general, it is believed that there is a proportional correlation between specific surface area (SSA) and the specific capacitance of activated carbons based on the following equation [182].

$$C_{sp} = \int \frac{\epsilon_0 \epsilon_r}{t} dS \quad (2-2)$$

where C_{sp} is specific capacitance, ϵ_0 is permittivity in vacuum, ϵ_r is relative permittivity of the double layer, t is thickness of the double layer and S is specific surface area.

A larger SSA leads to a larger gravimetric capacitance and hence a higher energy storage density. An analysis of the capacitance-SSA relationship for various carbon-based electrodes from the literature is provided in **Figure 2-26** [183]. As can be seen there, the average gravimetric capacitance of EDLCs increases quasi-linearly with increasing the SSA of the carbon electrodes, in line with the **Equation (2-2)**.

Fig. 2-26 Average gravimetric capacitance of carbon-based materials reported in the literature [183].

2.5.2 Towards structural supercapacitors (SSCs)

The key to successfully make a SSC relies on the synergistic action of its structural and functional units which results in marginal degradation of the corresponding mechanical and functional performances, and with perceptible enhancement in overall system behavior [184]. To date, two basic architectures have been explored to manufacture SPCs achieving simultaneously both load-carrying and electrochemical energy storage capabilities [9, 11, 185].

In one architecture, the focus is chiefly on the synthesization of a structural polymer electrolyte [186, 187], which serves as the matrix of the composite structures by thoroughly impregnating the electrodes as well as the separator, allowing ionic motion meanwhile providing with sufficient interfacial and mechanical strength. One of the most representative architectures was schematically shown in **Figure 2-27** [9]. It demonstrates a structural supercapacitor composite made of carbon

fabrics as electrodes, sandwiching a glass fabric separator and embedded in an ion conducting matrix. However, this ground-breaking design faced the challenge of increasing the intrinsically low specific surface area ($\sim 0.2 \text{ m}^2/\text{g}$), which leads to a very small specific capacitance ($\sim 0.06 \text{ F/g}$), several orders of magnitude below values for conventional carbon materials in supercapacitor electrodes.

Fig. 2-27 A novel architecture of SSC with carbon fabrics as structural electrodes [9].

In order to increase the SSA of CF, Qian et al. [188] studied a variety of CF modification methods, including chemical activation by KOH, CNT sizing and CNT-grafting. As shown in **Figure 2-28a** and **b**, after chemical activation, most of the crenulations were etched away and the fiber surface became noticeably rougher, as a result of the porosity development during the activation process. **Figure 2-28c** and **d** are the SEM images of CNT-sized and grafted CFs, a uniform coating of CNTs was achieved. **Figure 2-28e** compares the specific surface area and capacitance of CFs after different modifications, in the most promising cases (CNT-grafting), up to a hundred-fold improvement in electrical storage capacity was achieved.

Fig. 2-28 SEM images of (a) as-received, (b) KOH activated, (c) CNT-sized and (d) CNT-grafted CFs; (e) Comparison of specific surface area and capacitance of CF after different modifications [188].

The growth of a highly porous carbon aerogel (CAG) network around the CF fabrics is another promising way. Qian et al. explored the multifunctional performance of CAG-modified CF fabric electrodes (see **Figure 2-29a**) [185]. The results revealed that CAG-modification not only improved the SSA of CF fabrics (as high as $163.1 \pm 1.8 \text{ m}^2/\text{g}$), but also reinforced the polymer matrix surrounding the primary fibers, leading to dramatic improvements in the in-plane shear properties (see **Figure 2-29b**).

Fig. 2-29 (a) The fracture surfaces of CAG-modified carbon fabric composite and (b) Comparison of in-plane shear properties of structural supercapacitor with and without CAG modification [185].

Deka et al. [189, 190] tried to CuO nanowires and ZnO nanotubes on CF fabrics as shown in **Figure 2-30**. The SSA of corresponding metal oxides modified CF was enhanced up to 133-165 m²/g, corresponding to a specific capacitance range of 6.75-18.82 F/g, which is comparable to that of conventional non-structural SCs. It is worth noting that the tensile and in-plane shear strength of structural SCs were improved after addition of nanostructured metal oxide.

Fig. 2-30 SEM images of woven carbon fabric grown with (a) CuO nanowires [189] and (b) ZnO nanotubes[190].

Another challenge when employing this architecture is balancing the needs between ionic conductive behavior and mechanical performance when using polymeric electrolytes. **Figure 2-31** [191] clearly demonstrates a trade-off between ionic conductivity and Young's modulus for structural electrolytes. The Young's modulus of electrolyte generally increases with increasing degree of crosslinking or other arrangement of the polymer chains that lower their mobility. In contrast, ionic conductivity in polymeric electrolytes decreases with diminishing the mobility of polymer chain. This could explain why ionic conductive (non-structural) electrolytes are usually liquids whereas structural (non-conducting) polymer matrices are mostly rigid thermoplastics or thermosets [186]. Whether adding inorganic salts to the polymer system [192], or combining an ionic liquid with a polymeric matrix [193], existing methods to produce structural polymer electrolytes are still challenging to implement [187].

Fig. 2-31 An analysis of the relationship between Young's Modulus and ionic conductivity for various electrolytes [191].

In the other architecture, the structural and ionic conduction functions of the matrix are separated through the use of two different phases separated physically in the SSC and introduced at different stages of the manufacturing process, as schematically shown in **Figure 2-32**.

Fig. 2-32 a new SSC architecture through embedding thin-film devices inside structural reinformant layers, thus the functional electrolyte is separated from structural matrix by insulating layers

Due to the fact that the thin-film devices and their substrates become totally embedded into the FPR laminates, the thin-film structures also benefit from this integration and become thus more resilient to deterioration or damage from external environments (loadings and corrosion etc.) than what the thin-film devices and their substrates are able to withstand if deployed into the physical environment all by themselves.

Actually, this approach has been widely used to make structural cells. For example, Pereira et al. [184] published a pioneer work in this area, in which thin film lithium energy cells were integrated

into CFRP composites. They reported that embedded energy cells did not show much deviation from the charge/discharge performance of baseline under a tensile loading up to 450 MPa, about 50% of the ultimate tensile strength of CFRP. Similar embedded technology was employed in Kim's work [194], in which a thin film amorphous silicon solar cell and a thin film solid state lithium-ion battery were electrically connected to a printed circuit board (PCB), then co-cured with the composite laminate to form an energy harvesting/storage composite laminate.

Very recently, this route has also been used in SSCs with more integration of energy-storing and structural elements. Sun et al. [195], for instance, incorporated a thin interleaf of carbon fiber/solid electrolyte supercapacitor inside Kevlar fabric/epoxy preregs (see **Figure 2-33**). The resultant structural power composites demonstrated electrode-normalized value of specific capacitance, energy density and power density of 3.79 F/cm^3 , $3.37 \times 10^{-4} \text{ Wh/cm}^3$ and 0.04 W/cm^3 , respectively, as well as laminate flexural strength and flexural modulus of 192 MPa and 9.3 GPa, respectively.

Fig. 2-33 Manufacturing process of the Kevlar fabric/carbon fabric-based SC/epoxy hybrid composite [195].

Though the above research efforts have demonstrated the effectiveness in achieving both energy storage and load-carrying capabilities of hybrid composites by imbedding energy storage devices. There still exist potential risks of delamination. For instance, inspection of multiple commercial brands of Li-ion pouch cells has uncovered no evidence of physical or chemical bonding between the active bi-cell core and pouch packaging [196]. This implies poor load transfer between the core and the external packaging through frictional shear and normal compression. Thus in this type of structural battery design, cells would be restricted to the positions where favorable deformation modes like out-of-plane compression or planar tension are dominated, which greatly limits the degree of freedom for structural designs. In addition, the thin EDLC interleaved into the composite

can also act as an internal defect/delamination. This is mainly because that, on the one hand, the separator in the EDLC layer is very soft, and its resistance to the opening/sliding between adjacent layers is extremely small. On the other hand, aluminum foils and insulating layers are commonly used as current collectors and protective layers, which are usually poorly-bonded with the polymeric composite layers and can also be potential delamination sources. As SSC manufacturing and performance advance, it is pertinent to focus on improving our understanding of interlaminar properties in these complex multi-material systems, and to develop strategies that maximise properties in multi-parameter space and enable design across the envelope of multifunctional properties.

2.5.3 CNT fiber veils as the tough electrodes/current collectors in embedded energy storage system

The basic function of electrodes in energy storage devices is to transfer the current produced by the device with minimal losses, therefore the electrical conductivity is one of the most critical parameter for choosing electrode. However, in the quest for “high strength, high toughness and high stiffness” and lightweight SPC for multifunctional applications, the electrodes must also be light, compatible and mechanically durable. Furthermore, if the electrode has a high porosity/surface area, it can also take part in energy storage at its interface with an electrolyte via direct intercalation of ions, or by mean of hosting another phase that can undergo a redox reaction, which can significantly increase the capacitive performance of electrodes [197].

Activated carbons (ACs) with surfaces areas as high as 2000 m²/g and specific capacitances in the range of 100-150 F/g are commonly found in commercial electrochemical double layer capacitors (EDLCs). However, ACs are hardly shaped to tough free-standing electrodes due to their powder nature and poor mechanical properties, therefore they are not perfect choice of structural electrode for SSC. Carbon fibers (CFs), due to their outstanding mechanical properties, have been suggested as electrode candidates for SSC. A challenges in these systems is the intrinsically low surface area of CF, which leads to a very small specific capacitance. Even after physical/chemical surface activation or modification by CNT or GAG, the specific area of modified CFs is still orders of magnitude lower than that of activated carbons, as discussed in **Section 2.5.2**.

In general, the requirements for producing multifunctional structural electrodes for structural power

composites can be summarized as: high electrical conductivity for effectively charge transfer, electrochemical stability, high surface areas and mechanical robustness. It is thus not surprising that CNTs have been extensively used in this field, as they seem to match these requirements perfectly. The reported specific surface area of pure CNTs is in between 120 and 500 m²/g with the specific capacitance ranging from 2 F/g to 200 F/g [198-200]. Using single-walled carbon nanotubes (SWNTs) as the electrode materials, a specific capacitance, power density and energy density up to 180 F/g, 20 kW/kg and 7 Wh/kg, respectively, have been reported [201, 202]. More importantly, many of the reported EDLCs based on pure CNTs demonstrated high-rate capabilities and cyclic stabilities, together with rectangular cyclic voltammograms and symmetric triangular galvanostatic charge–discharge profiles, indicating high performance for charge storage [203]. As for mechanical and electrical properties, more details can be found in **Section 2.3**.

It is worth noting that the axial properties of individual CNTs can be efficiently exploited on a macroscopic length-scale by assembling these building blocks into CNT fibers. Normalized by their low density (1-2g/cc), CNT fibers have tensile properties in the high performance range [115, 204, 205], electrical conductivity similar to steel [133] and a large specific surface. As such, they seem to be a perfect electrode candidate for SSC application, even serving as current collectors for replacing conventional metallic ones.

Using CNT fiber veils as electrodes opens a new clue for addressing the fundamental challenge of producing a matrix that is both stiff and with high ionic conductivity. Typically, this is achieved by making a fine-tuned mixture of a structural matrix with a lithium salt, which upon curing segregates into a bicontinuous structure of stiff matrix with channels for ion transport [206]. In addition, the intrinsically high surface area of CNT veils also facilitates adhesion of pseudocapacitive materials. In general, those nanofiber veils acts as a scaffold to support a nanostructured MO_x with high gravimetric power/energy density. If the CNT veil has high electrical conductivity, such architecture can minimize overall electrical resistance by shortening the charge diffusion length across the inorganic phase and acting effectively as a built-in current collector. More importantly, ultrathin CNT veil electrodes enables to make relatively thin EDLC interleaves and makes it possible to generate hole-patterns in the EDLC part to promote the interconnection of CF plies by epoxy revits, which is hardly realized when using thick CF electrodes. This method is not only simple, but also enables the design and fabrication of composites with different balance of mechanical and

electrochemical properties.

It should be pointed out that although the excellent mechanical and electrochemical properties of CNT assemblies indicate their potentially large contribution to the field of multifunctional energy storage, still there is a lack of reports on structural SCs based on this material and a lack of studies unveiling feasibility of producing large-area CNT fiber electrodes with reproducible performance for employment in multifunctional SPC systems.

2.6 Summary

While FRP composites are widely utilized in structural components due to their favorable mechanical properties, delamination between reinforcing plies remains a major problem, weakening the composite structure and limiting more widespread applications of FRPs. A number of methods to prevent delamination have been reviewed in this thesis, which mainly include matrix toughening via the addition of a second phase (either rigid or soft), laminate stitching, 3D woven, Z-pinning, particle/film/fiber veil interleaving etc. Among them, interleaving nanofiber assemblies (electrospun thermoplastic fiber veils or CNT fiber veils) is particularly competitive and promising. Firstly, these veils can be easily and readily deposited in between the primary reinforcing fiber layers before infusion, thus avoiding the well-known challenges related to increased viscosity when using nanocarbons as fillers. Additionally, their nanoscale diameters enable the production of ultra-thin interleaves, which can be utilized to improve the interlaminar fracture toughness with minimal thickness/weight penalty and effectively avoids reductions in in-plane properties.

Previous studies demonstrated the potential of reinforcing the interlaminar region with different kinds of CNT veils/mats (as-spun, functionalized or densified), but remain inconclusive and of limited generality because some fundamental aspects of CNT veil/mat toughening remain unclear. Often overlook, for example, is the degree of resin infiltration into the CNT veils. It is hard to control and difficult to evaluate, but resin infiltration is expected to depend on resin properties as well as on veil morphology, thickness and surface chemistry (functionalization). Overall, a systematic interlaminar test campaign and a thorough understanding of the fracture and toughening mechanism is clearly needed in order to link the structure of CNT fiber veils to their effects on interlaminar

fracture toughness.

Multifunctionalization of FRP composites, especially by supplementing energy storage capabilities, is a promising approach to realize lightweight structural energy storage devices for future transportation tools. The drive to produce materials for those devices that can withstand extreme loading conditions possibly encountered during their service period calls for mechanically robust electrodes and current collectors. The assembly of CNTs into macroscopic architectures has led to a new type of mesoporous graphitic materials with an exceptional combination of high surface area, electrical conductivity and toughness. For example, CNT fiber veils fabricated via CVD direct-spinning process, with a porosity close to that of an activated carbon and tensile properties in the high-performance range as well as the electrical conductivity similar to metals, could be ideal electrode and current collectors for SPC application.

CHAPTER 3

Materials and methods

“It matters if you just don’t give up”

- Stephen Hawking

In this chapter, materials and methods used in this thesis were detailed. Since there are two different topics (interlaminar toughening and structural supercapacitors (SCs)), specific materials and methods related to each topic were described separately, followed by a brief introduction of other advanced characterization equipments employed in this thesis.

It should be mentioned that fabrication and electrochemical characterization of Structural SCs were performed together with Dr. Evgeny Senokos and Dr. Moumita Rana in different development stages.

3.1 Materials for interlaminar toughening

3.1.1 CNT veils, carbon fabrics and preregs

Macroscopic veils of CNT fibers were synthesized by the direct spinning process, whereby a CNT web (aerogel) is directly drawn from the gas-phase during growth of CNTs by FC-CVD [120].

Generally, three different CNT veils were used in this thesis as listed in **Table 3-1**.

Tab. 3-1 Comparison of different CNT veils used for interlaminar toughening of FRP.

Types	Temperature (°C)	iron catalyst	promoter	carbon source	Diameter (nm)	Area density (g/m ²)	Tensile strength (N/Tex)	Young’s Modulus (GPa)	Providers
<i>CNTV1</i> (Section 4.1)	1250	Ferrocene (1.5%)	Thiophene (0.8%)	Butanol (97.7%)	3-9	0.8	0.07	2	Imdea (lab-scale)
<i>CNTV2</i> (Section 4.2)	1200	Ferrocene	Thiophene	Methane	-	0.5/1.0/1.5	0.18	11	Tortech (industrial-scale)
<i>CNTV3</i> (Section 4.3)	1300	Ferrocene (1.2%)	Thiophene (1.2%)	Toluene (97.6%)	3-9	0.8	0.30	15	Imdea (lab-scale)

The CNTs veils used in **Section 4.1** (*CNTV1*) were synthesized using ferrocene as iron catalyst, thiophene and butanol as sulfur catalyst promoter and carbon source, respectively, in hydrogen atmosphere at 1250 °C with precursor feed rate of 5 mL h⁻¹ and a winding rate of 5 m min⁻¹. These conditions produce long, highly graphitic CNTs with 3-5 layers [207] and a low degree of alignment in the aerogel [121]. The diameters of CNTs range from 3-9 nm [207]. As shown in **Figure 3-1a**, the CNT fibers were continuously drawn out at the exit of the furnace and directly deposited onto the surface of a piece of dry carbon fabric (G0926 Hexcel woven fabric with a weave style of 5H satin and 370g/m² of areal weight as well as 0.38mm of ply thickness (see **Figure 3-1b**)) which was wrapped on a winder of D = 10 mm diameter. Winding time of CNT fibers was set as 0.5 h, which gave an areal density of 0.8 g/m², resulting in a thickness of 30 micron of CNT veil after infusion. In its as-made state the same veil was fluffy and would have a thickness of more than 3 mm. This thickness was chosen for two reasons: a) the final interleaf is thin relative to a CF ply, but sufficiently thick to study possible cohesive failure through it, and b) the thickness is similar to that found in commercial veils produced by companies that have scaled up this FC-CVD process.

Fig. 3-1 (a) Schematic of direct spinning of CNT fibers from the gas phase by CVD; (b) Dry carbon fabric with a weave style of 5H satin. CNT fiber veils were directly grown on the surface of carbon fabric forming a fluffy/cotton-like structure

CNT veils used in **Section 4.2** (*CNTV2*) were synthesized using iron catalyst, sulfur as promotor and methane as carbon source, respectively, in a hydrogen atmosphere above 1200 °C. They were directly deposited onto the surface of carbon fabrics, similar with aforementioned method in our lab.

Figure 3-2 a and **b** showed the surfaces of 5H satin fabric before and after CNT veil deposition. CNT veils were finally densified because the veils in the fluffy state can not be handled easily during laminate manufacturing. It should be pointed out that the veils were densified mechanically instead of exposure to ethanol spray since the latter was proved to be harmful for interlaminar toughening, as detailed in **Section 4.1**. **Figure 3-2 c** demonstrated a high porosity of CNT veil structure after suffering mechanical densification.

Fig. 3-2 G0926 Hexcel woven fabric with a weave style of 5H satin: (a) before and (b) after CNT veil deposition; (c) a high resolution image of CNT veils under SEM.

The CNT veils for **Section 4.3 (CNTV3)** utilizing ferrocene (1.2%) as iron catalyst, thiophene (1.2%) and Toluene (97.6%) as sulfur catalyst promoter and carbon source, respectively. The reaction was carried out in the hydrogen atmosphere at 1300 °C with precursor feed rate of 3.7 mL h⁻¹ and a winding rate of 20 m min⁻¹. The CNT fibers were continuously drawn out at the exit of the furnace and directly deposited onto the surface of a piece of unidirectional carbon fiber prepreg (unidirectional UD HexPly® AS4/8552 prepreg with 34% resin content and 194g/m² areal weight, as shown in **Figure 3-3b**), which was wrapped on a rotating drum (D = 10 mm). CNT fiber winding was carried out following the carbon fiber direction with a deposition time of 20 min, which gave an areal density of 0.8 g/m². A high-resolution micrograph of the as-produced CNT fiber veil is

presented in **Figure 3-3c** showing an ultrahigh porosity.

Fig. 3-3 (a) Schematic of direct spinning of CNT fibers from the gas phase by FFCVD; (b) unidirectional carbon AS4/8552 prepreg with fluffy CNT veils deposited on the surface and (c) high resolution SEM picture of as-produced CNT fiber veil

3.1.2 Resin and auxiliary materials

Greenflow 75 (Composite Envisions LLC) was used as distribution medium (or resin flow medium), which is designed to efficiently distribute resin under vacuum. Polyester EconoStitch (88 g m^{-2}) layers were used as peel-ply materials. DERA KANE 8084 was chosen as matrix which is an elastomer-modified bisphenol-A epoxy vinyl ester resin for structural applications and provided by Ashland Inc. Both the MEKP hardener and Cobalt octoate catalyst were available from Plastiform S.A. By using a recommended concentration of precursors (resin: hardener: catalyst = 100:1.0:0.2), the gel time is around 60 min, which was judged enough to manufacture the laminate by resin infusion (VARTM).

3.2 Methods for interlaminar toughening

3.2.1 Laminate preparation

Vacuum assisted resin transfer molding (VARTM)

An optimized VARTM method was employed to make the CF/CNT veils/epoxy hierarchical

laminate, as shown in **Figure 3-4 and 3-5**. The main objective of this technology is to fully impregnate the fabric as a result of the resin propagation between fibers and fiber bundles, while reducing as much as possible the voids entrapped and the dry spots. The impregnation driving force comes from the pressure differential between the inlet and outlet gates and the resistance to resin flow is controlled by the permeability of the porous fiber bed and the rheological properties of the fluid. Two layers of distribution media were placed onto the upper and bottom surfaces to promote the out-of-plane resin flow, to guarantee complete wet-out of the preform and to eliminate dry spots and voids. It should be pointed out that this method ensures good impregnation in those regions of laminate affected by the presence of the teflon film (25 μm) insertion used for crack initiation in fracture coupons. The length of distribution medium was designed to be 30 mm shorter than that of fabric in order to slow down the speed of flow front before it reaches the outlet and leave enough time to complete infiltration of z-direction. Peel plies were purposely inserted into the interfaces between distribution medium and carbon fabrics for the easiness of removing the redundant parts after curing. Before starting infusion, resin was degassed for 10 minutes in a vacuum chamber under a vacuum degree of -0.88 bar. After completing the infusion process, the inlet and outlet of the system were closed off and cured at room temperature (RT) for 24 hours, followed by a post curing step at 60 °C for 2 hours. Note that CNT-interleaved composites and baseline (without CNT) were manufactured in a same batch in order to minimize the influence of other uncontrollable factors on the testing results.

Fig. 3-4 Schematic of VARTM

Fig. 3-5 Preparation of fiber preform: (a) before and (b) after vacuum on and (c) lay-up of preform.

Prepreg consolidation by Compression moulding

2 panels of 20 plies unidirectional carbon fiber prepreg (280 mm × 280 mm) following the $[0^\circ]_{20}$ lay-up with a nominal thickness of 3.65 mm were consolidated by using compression moulding (see **Figure 3-6**). In both of the two panels, the mid-plane ply (11th in the lay-up) was covered with fluffy as-produced CNT veils (see **Figure 3-3b**). Such method was designed to allow extra resin bleeding from prepreg layers to impregnate the dry CNT interleaf. In order to guarantee a good resin impregnation of the CNT veils, the 10th prepreg ply of one panel was stuck with a thin 8552 resin film layer (25 μ m), facing with the CNT veils on the 11th ply. A 25 μ m-thick teflon film was inserted at the mid-plane as a crack starter in the mode I fracture tests. An additional panel was prepared by interleaving only with the 8552 resin film in order to ascertain its effect without CNT veil reinforcement. Hot-plate press machine (LabPro 400, Fontijne Presses) was then used to consolidate laminate panel from pre-impregnated sheets of fiber-reinforced composites by simultaneous application of pressure (up to 7 bar) and heat (up to 180 °C) according to the recommendations of the prepreg supplier for an autoclave cure cycle.

Fig. 3-6 (a) schematic of hot press method; (b) and (c) lay-ups of prepreg in which 2 different interleaves were integrated

3.2.2 Specimen preparation

The standard double cantilever beam (DCB) specimens used in **Section 4.1** were cut from aforementioned well-prepared laminates utilizing a water-refrigerated milling machine. The lateral side of each specimen was then sprayed with white primer paint and the 60 mm after the pre-crack marked in 1 mm increments to track crack growth throughout the test. The configuration and size of the standard specimen can be seen in **Figure 3-7**.

Fig. 3-7 Schematic configuration of the DCB specimen and a group of real specimens.

It is worth noting that End-Notched Flexure (ENF) specimens used in **Section 4.2** and **Section 4.3** were directly extracted from previously tested DCB specimens as shown in **Figure 3-8**, which is quite material-saving and creates a more real pre-crack with a small tip radius for ENF test. Short beam shear (SBS) specimens were then precisely cut from ENF specimens utilizing a diamond-wire cut machine.

Fig. 3-8 a new conception for preparation of mode II sample.

3.2.3 Mechanical characterization for interlaminar properties

Interlaminar fracture toughness was measured by using DCB and 3-point ENF specimens for mode I and II crack propagation, respectively. Three-point bending tests on SBS specimens were also employed to evaluate the interlaminar shear strength (ILSS). **Figure 3-9** summarizes the test configurations and corresponding dimensions of the DCB, ENF and SBS specimens.

Fig. 3-9 Configurations of specimens for (a) Mode I, (b) Mode II and (c) short beam shear (SBS) tests. Dimensions are in mm.

DCB tests

The DCB tests were carried out in accordance with ASTM Standard D5528-01 [208], which specifies either hinges or end blocks for load introduction. Measurements were conducted in a screw-

driven testing machine (Instron 3384) at cross-head speed of 1 mm/min. Force was recorded by utilizing a 500 N load cell and the DCB arm opening displacement using the cross-head movement. Crack growth was visually observed every millimeter and listed in an experimental sheet. Time was also recorded in order to correlate the crack growth with the force and displacement. In order to assure the crack propagation, specimens were pre-loaded to create a ~5 mm pre-crack. After unloading, the specimen was loaded again until another 50 mm propagation had been reached.

There are several data reduction methods can be employed to calculate the Mode I fracture toughness (G_{IC}) involving Area method, Beam Theory (BT) method, Modified Beam Theory (MBT) method, Compliance Calibration (CC) method and Modified Compliance Calibration (MCC) method[208, 209]. In our work, MBT method was chosen because it yields the most conservative results [208]. Traditional BT method without correction overestimates the Mode I fracture toughness value because of the imperfect beam built-in during the DCB test, which allows the rotation at the crack tip. This overestimation can be balanced by pretending the DCB specimen has a slightly longer initial delamination so the crack total length is replaced by $(a + |\Delta|)$, the strain energy release rate (G_I) can be obtained by the following equation:

$$G_I = \frac{3*F*\delta}{2*w*(a+|\Delta|)} \quad (3-1)$$

where F is the load; δ is the load point displacement; w is the sample width, and a is the crack length from the load point. The coefficient Δ could be determined by plotting the cube root of the compliance (displacement divided by force) against the crack length.

Data points from DCB experiments were used to construct a delamination resistance curve (R -curve), which is the graph of strain energy release rate (G) versus crack length (a). From the R -curve, two types of critical G values can be calculated, the initiation ($G_{IC,ini}$) and propagation ($G_{IC,prop}$) values. $G_{IC,ini}$ is the energy dissipated when the crack starts to propagate, which might vary for each specimen as the value strongly depends on the crack tip condition [210] and location of the edge of the film [211]. $G_{IC,prop}$ is the value where the G value achieve a constant state and the crack propagates in a self-similar way independent on the crack length. The G value of interest for this experiment was $G_{IC,prop}$, because it is more realistic in practice for determining the likelihood of the crack to continue to propagate.

ENF Tests

For Mode II ENF specimens, an initial crack was firstly generated by subjecting the specimen first to Mode I crack propagation. Then the whole testing was guided by ASTM D7905[212]. Specifically, 3-point bending tests were carried out on Instron 3384 with a 10 kN load cell, under stroke control of 0.05 mm/min. Data reduction of the fracture toughness, G_{IIC} , of the ENF specimens is based on the compliance calibration method, as given by equation below:

$$G_{II} = \frac{3ma_0^2F^2}{2w} \quad (3-2)$$

where m is the slope of the $C - a^3$ calculated from the specimen compliance and the cube of the crack length. The initial crack length a_0 was set as 30 mm. At the onset of fracture, the force corresponded with the peak load $F = F_c$ and mode-II energy release rate to the interlaminar fracture toughness $G_{II} = G_{IIC}$.

SBS Tests

The interlaminar shear strength (ILSS) of the manufactured laminates was evaluated by means of the short beam shear (SBS) test based on the ASTM standard D2344 [154]. Prismatic specimens of 3.65 mm thick, 7.2 mm wide and 22 mm long were cut from the unidirectional laminate with the fibers following this latter dimension, and were loaded in three-point bending with a support span of 14.6 mm at a constant cross-head speed of 1.0 mm/min. ILSS was determined by:

$$ILSS = \frac{3}{4} \frac{F_{max}}{wt} \quad (3-3)$$

where F_{max} is the maximum load, and w and t are the width and thickness of the specimen, respectively.

3.3 Materials for manufacturing structural SCs

CNT veils were supplied by Tortechnanofibers. They were produced by winding multiple individual CNT fiber filaments onto a spool. Synthesis conditions were adjusted to produce few-layer multiwalled CNTs. Typical dimensions of the nonwoven CNT fiber fabrics were 8 x 19 cm², corresponding to an aerial density of ~ 1.6 mg/cm². Aluminum foil (25 μm thickness and 99% purity) received from Goodfellow was used as a current collector. The polymer matrix used consists of

DERAKANE 8084 elastomer-modified bisphenol-A epoxy vinyl ester (Ashland Inc.), MEKP hardener and cobalt octoate catalyst, which is suitable for vacuum bag infusion processes and very convenient for fabrication of the multifunctional composites. Three different fabrics (carbon and glass) were used for mechanical reinforcement of structural SCs in different development stages as shown in **Figure 3-10**.

Fig. 3-10 (a) 5H satin woven carbon fabric of 370g/m²; (b) Plain woven glass fabric of 220g/m² and (c) Plain woven glass fabric of 195 g/m²

3.4 Methods for manufacturing and characterizing structural SCs

3.4.1 Assembly of self-standing all-solid electric double layer capacitors (EDLCs)

EDLC layer assembly was generated based on a method reported earlier [213]. Briefly, the polymer-ionic liquid membrane was prepared by dissolving PVDF-co-HFP and PYR14TFSI (4:6) in acetone and casting it at room temperature on a flat surface using doctor blade. Similarly, a PVA membrane was prepared by dissolving PVA into a mixture of water and ethanol (1:1) at 95 °C and casting it at room temperature. The thickness of the polymer electrolyte and PVA membranes were optimised at 60 and 15 μm , respectively. The membranes were dried at room temperature. To assemble the EDLC, the polymer electrolyte-ionic liquid membrane was sandwiched between two free-standing CNT layers, followed by two protective PVA membranes. The layers were consolidated by applying a force of 2 tons for 10 minutes, followed by lamination using a commercial lamination machine. Hole patterns were produced by cutting EDLC layers with a ZING 16/24 laser cutting machine (Epilog Laser).

3.4.2 Fabrication of structural power composite with embedded all-solid EDLCs

The structural power composites were fabricated by vacuum assisted resin infusion using CF or GF fabrics and a thermosetting resin. A thin self-standing EDLC based on CNT fibers and PE membrane interleaf was placed between fabric layers prior to infusion of epoxy resin. The epoxy matrix consisted of MEKP hardener, cobalt octoate catalyst and DERA KANE 8084 elastomer-modified bisphenol-A epoxy vinyl resin, which were mixed at the recommended ratio of 100:1.5:0.3. The infusion process involves sealing the fabric lay-up with a plastic bag and applying vacuum to infuse the fluid through the fabric as porous media. Upon opening an inlet port connected to the resin pot the resin flows through the laminate driven only by the pressure gradient between inlet and outlet. Infusion was carried out using two layers of distribution media which ensures appropriate through-the-thickness flow from both sides of the interleaf to avoid void generation. To avoid direct contact between EDLC interleaf and carbon fabrics double-sided adhesives tape was attached to both sides of the EDLC interleaf. This was not necessary for GFRP system. The full curing process takes 48 hours at room temperature, with the matrix reaching its gel point after 30 – 60 minutes.

3.4.3 Electrochemical and mechanical testing

Electrochemical test

Electrochemical characterization involved performing galvanostatic Charge-Discharge (CD), and electrochemical impedance spectroscopy (EIS), using a Biologic potentiostat (SP200). The capacitance (C_{sp}) of devices was calculated from the slope (m) of the discharge profile:

$$C_{sp} = I/m \quad (3-4)$$

Where I is the applied current. Real energy (E_{real}) and real power density (P_{real}) values were calculated by integrating the discharge profile of the full devices using the following equations:

$$E_{real} = I \int V dt \quad (3-5)$$

$$P_{real} = \frac{E_{real}}{t_{dis}} \quad (3-6)$$

Where V is the voltage and t_{dis} is the discharge time.

Three-point bending test

The 3-point bending test provides values for the flexural stress σ_f , flexural strain ε_f , modulus of elasticity in bending E_f and the flexural stress–strain response of the material. The main advantage of a three-point flexural test is the ease of the specimen preparation and testing.

In this thesis, 3-point bending tests were performed on rectangular cross-section beams using a universal electromechanical testing frame (INSTRON 3384), according to ASTM D790 standard [214]. For rectangular cross section, flexural stress σ_f , flexural strain ε_f and the modulus of elasticity in bending E_f be calculated as follows:

$$\sigma_f = \frac{3FL}{2bt^2} \quad (3-7)$$

$$\varepsilon_f = \frac{6Dt}{L^2} \quad (3-8)$$

$$E_f = \frac{L^3m}{4bt^3} \quad (3-9)$$

Where F is the total applied force measured with the load cell, L is length of support span, b is width of the beam, t is thickness of the beam, D is deflection of the center of the beam and m is the slope of the initial straight-line portion of the load deflection curve.

Four-point bending test

The major difference between 4-point and 3-point bending modes is the location of the maximum bending moment and maximum axial fiber stress. In 4-point bending, the maximum axial fiber stress is uniformly distributed between the loading noses. In 3-point bending the maximum axial fiber stress is located immediately under the loading nose.

In this thesis, four-point bending test of structural composites was also carried out on rectangular cross-section beams with a universal electromechanical testing machine (INSTRON 3384) by using a displacement rate of 1 mm/min. The tests were performed according to ASTM D6272 standard [215]. The beam dimensions were 250.0 mm x 40.0 mm x 2.9 mm, for the sample length, width and thickness, respectively. The load span and the support span were set at 100 mm and 200 mm, respectively. The flexural stress σ_f was calculated for every point on the load-deflection curve using the following equation:

$$\sigma_f = \frac{3FL}{4bt^2} \quad (3-10)$$

The flexural strain (ε_f) can be calculated as follows:

$$\varepsilon_f = \frac{4.36Dt}{L^2} \quad (3-11)$$

3.5 Other characterization techniques

3.5.1 Optical microscopy

Optical micrographs were obtained in reflection mode with an optical microscope (OLYMPUS BX51) equipped with a camera (OLYMPUS ColorView), and were acquired employing the built-in system (analySIS auto), together with options of black&white or colour mode. Each series of the samples were captured at constant focus and light intensity in order to make them more comparable. Here, the optical microscope was used to fast visualize the distribution of CNT veils in the cross section of the composite laminates as well as to determine the thicknesses of specific layers.

3.5.2 Ultrasonic C-scan

The ultrasonic C-scan is perhaps one of the most commonly used Nondestructive Testing (NDT) methods. In this technique, the surface of an immersed sample is scanned, and a projection of the reflected and/or transmitted ultrasound is collected and analyzed. Therefore, it is a volumetric inspection method. The transmission C-scan gives an integrated view of the damage zone, while the reflection C-scan offers the details on the depth distribution of the damage zone. Typical frequencies are 1-10 MHz (low MHz range) for composite materials. Lowering the frequency gives rise to poor spatial resolution as depth profiling is directly related to the ultrasonic wavelength. Increasing the frequency leads to excessive attenuation of the ultrasonic signal in FRPs due to high damping properties of the polymer matrix and scattering at fiber bundles and porosities [216].

In this thesis, C-scan (Tecnitest Triton 1500 USPC-3100 ultrasonic) was performed to determine the quality of the panel after manufacturing and to localize the possible defects.

3.5.3 Scanning electron microscopy

Scanning electron microscope (SEM) enables to achieve considerably higher resolution of the specimens, as compared to the optical microscope, utilizing a beam of electrons to form an image instead of light. The SEM maps scattered secondary electrons from the atoms of the sample, and

thereby constructs an image which provides information about the surface morphology. Back-scattered electrons and X-rays occurring after interaction of the electron beam with the sample contain additional information about elemental composition of the material. Here, SEM was employed to determine the morphology of CNT fibers, PE membrane and their composites as well as the fracture surfaces of the laminates. The scanning surfaces of the specimens in some cases were coated with a thin layer of conductive sputtering gold (Au). They were then tested on a dual beam FIB-FEGSEM microscope (Helios NanoLab 600i FEI) using an accelerating voltage of 5-20 kV, depending on the scanning regions of interests.

3.5.4 Raman spectroscopy

The Raman spectroscopy is a non-destructive vibrational technique which is utilized to qualitatively or quantitatively analyze molecular composition of the materials. Raman signal from a sample, also known as Raman scattering, occurs due to inelastic interaction of the single wavelength laser beam with the material that causes changes in polarizability of the sample's molecules in electric field. Every Raman signal corresponds to a specific vibrational frequency of a molecule bond, and it is highly sensitive to the orientation of the bonds. This makes Raman spectroscopy a very powerful method for characterization of carbon nanomaterials and, particularly, CNTs.

In this work, Raman analysis (Renishaw PLC) was performed to fast distinguish the constituents on the fracture surfaces as well as to assess the impregnation level of the resin inside the CNT veils. An excitation wavelength of 532 nm from a tunable YAG laser was focused on the sample using laser power in the range of 1-5 mW so as to avoid sample heating.

3.5.5 X-ray computed tomography (XCT)

XCT is a method using X-rays to create cross-sections of a physical object that can be used to regenerate a virtual model without destroying the original object. This technique relies on the differences between X-ray absorption coefficients of different sample phases. The computer-assisted reconstruction method allows to convert the X-ray radiographies taken from various viewing angles into a 3D images of analyzed samples.

In this thesis, XCT was utilized to analyze the morphology of structural power composites,

distribution of epoxy resin and quantitative contribution of voids to the total volume of the sample. Prismatic samples were extracted from the center of each of specimens by using a diamond wire. For the first generation of Structural SC, X-ray tomography was performed at the TOMCAT beamline of the Swiss Light Source (Paul Scherrer Institute, Villigen) using a monochromatic X-ray beam energy of 18 keV. X-ray images were acquired with the detector at 40 mm distance from the sample to allow for phase contrast effect. Four consecutive volumes were acquired and stitched together after reconstruction. The image reconstructions were made using phase retrieval algorithm based on Paganin approach. The internal microstructure of the second generation of Structural SC was studied at Imdea Materials institute using a Nanotom 160NF (GF-Phoenix). Tomograms were collected at 75 kV and 110 μ A using a molibdenum target. For each tomogram, 1900 radiographs (averaging 8 consecutive radiograph and skipping 1 for the next projection) were acquired with an exposure time of 500ms. The tomograms were then reconstructed using an algorithm based on the filtered back-projection procedure for Feldkamp cone beam geometry. The measurements were performed and analyzed with the help of Dr. J. J. Torres, Dr. F. Sket and Dr J. García from IMDEA Materials.

CHAPTER 4

Toughening of laminated composites by CNT veil interleaves

“Do not, for one repulse, give up the purpose that you resolved to effect”

- William Shakespeare

In this chapter, CNT veils were interleaved into the FRP laminate composites for improving their inherently weak interlaminar properties. Different strategies were developed and optimized in order to achieve “full resin infiltration”. **Section 4.1** reported a facile and scalable infusion protocol for manufacturing woven laminates containing lab-scale CNT veil interleaves. A combination of optical imaging and a Raman spectroscopy was firstly used to provide a new rapid tool to unambiguously determine the crack propagation path by simple visual inspection of fracture surface. In **Section 4.2**, a joint work with *Tortech Nano-Fibers* was performed in order to develop and industrialize previously proposed methods for CNT implementation in structural laminate composites as well as systematically investigate the thickness effect of CNT veil interleaves on interlaminar properties of woven CFRP laminates. **Section 4.3** further explored the interlaminar toughening mechanisms of CNT veils in unidirectional CFRP laminates as well as the CNT integration techniques in prepreg system.

4.1 Woven laminates containing lab-scale CNT veil interleaves

In this section, a new strategy to integrate CNT veils into woven carbon fiber fabrics/epoxy laminates with improved interlaminar properties is being developed. The veils are directly affixed to the surface of carbon fabric at the point of veil fabrication and do not require any previous treatment. Composite specimens for mode-I delamination tests are produced under optimized Vacuum Assisted Resin Transfer Molding (VARTM). The results show that the degree of compaction of the starting CNT fiber veil is the dominant factor with respect to the critical strain energy release rate in mode-I delamination (G_{IC}). Taking advantage of the strong resonant Raman scattering signal from the CNTs synthesized in this work, the crack propagation path could be facilely and quickly determined which can be used as a fractography method to describe the observed G_{IC} values.

4.1.1 Optimization of laminate manufacturing

Even though the VARTM method is a very mature method in the area of laminate manufacturing, there still exist a lot of factors that need to be well-controlled to make high quality composites. For instance, the number of distribution medium layers used (layers used to efficiently distribute resin under vacuum driven impregnation), infusion time, resin-degassing time and curing time etc. Distribution medium bears high permeability and thus enables rapidly and evenly distribute resin laterally across the part, especially in the through-the-thickness direction of the laminate. However, the surface would usually be very rough when using it due to its intrinsic roughness. In the first panel manufactured by using this technique, only one piece of distribution medium was laid on the upper surface of the preform, and was proved not to be enough to deliver composite laminates free of voids and defects (**Figure 4-1**).

Fig. 4-1 resultant laminate with only one layer of distribution media.

Infusion time also exerts a profound influence on the quality of laminate. Switching off the vacuum outlet too early will finally lead to obvious thickness variation along the direction of resin flow. **Figure 4-2a** and **b** show the C-scan image and cross-sectional image of CNT-toughened laminate in which non-degassed resin was used. Apparently, there are many macro voids inside, most of which were possibly induced during resin-mixing process. While resin-degassing is strongly suggested before infusion, it should be kept in mind that there is an intrinsic trade-off between degassing time and infusion time because the reaction started when the precursors were mixed together. The best policy is to choose a suitable mix proportion of precursors, realizing a relatively long gel time without mechanical penalty when fully cured, which allows an efficient primary degassing.

Certainly, demolding time is also very important. As you can see in **Figure 4-2 c**, the first panel was taken out of the mold after 24 hours of curing at room temperature, as suggested by the provider. Micro-cracks can be clearly observed in the outer layer, which were likely to be produced by the peeling forces when removing of the peel plies. It indicated that resin after 24 hours was not fully cured. Fortunately, this phenomenon disappeared if panels were demoulded after 48 hours.

Fig. 4-2 (a) C-scan image and (b) Cross-sectional image of CNT-toughened laminate made from resin without degassing, both of which prove that there are many voids inside. (c) Higher magnification cross-sectional image of resultant laminate with different curing time.

Drawing a lesson from previous try and error, an optimized VARTM protocol was proposed, in which appropriate fabrication parameters were selected as listed in **Table 3-1**.

Tab. 4-1 Optimized fabrication parameters for VARTM

Distribution medium	Degassin g time	mix proportion of precursors	Infusion time	Demolding time (curing at RT)
2 layers	10 minute	resin: hardener: catalyst = 100:1.0:0.2 (60 min gel time)	Around 20 min (Stop when resin reservoir around inlet was consumed)	48 h

Figure 4-3a shows an example of a final CF/CNT veils/epoxy hybrid composite produced using the aforementioned optimized method. Visual inspection proved that there exist no obvious

defects/voids on its surface. C-Scan picture (**Figure 4-3b**) combined with cross-sectional micrographs (**Figure 4-3c** and **d**) further confirmed almost void-free laminate production. Optical microscopy (**Fig. 4-3d**) also shows that the CNT veil maintains its shape after infusion and is fully integrated in the composite. It follows the contour of the CF fabric leaving no gap between the two plies, which is a prerequisite to reinforce the interface between the two laminae. SEM characterization of the interleaf region (after laminate fracture), as shown in the example in **Fig. 4-3e**, confirmed that the veils are successfully infiltrated by the matrix.

The interleaf thickness determined from optical micrographs is around 30 μm and corresponds to a volume fraction of approximately 1%. It was controlled by adjusting the time the CNT fiber was wound on the spool. At its exit from the CVD reactor, the deposition of the CNT produces a very low density veil ($< 0.02 \text{ g/cc}$) reminiscent of the CNT aerogel morphology. For reference, in its as-made state, the same veil would have a thickness of more than 3 mm. Densification of CNT fibers driven by capillary forces induced by exposure to volatile solvents such as ethanol and acetone is known to increase longitudinal tensile properties [217, 218] and can improve adhesion to surfaces. Understanding the role of such densification is not only important to establish clear veil structure-interlaminar property relations, but also because commercial larger scale CNT veils are available already in densified format. In order to gain a first insight into the role of densification, two types of composites were produced. In one laminate, fluffy as-produced CNT veils were used, while in another, the CNT veils were densified at the point of spinning by exposure to ethanol spray.

Fig. 4-3 Characterization of laminates with CNT veils. (a) Surface examination showing optimal surface finish; (b) C-scan picture and (c,d) optical micrographs confirming that there are no appreciable voids in the composite (e) SEM image of CNT veils at the fracture surface.

4.1.2 Mode I interlaminar fracture toughness

Pristine and CNT veil-interleaved woven composites were produced with the 5H Satin weave fabrics as described and tested as discussed above. Though the load-extension curves of the DCB specimens made with the woven composites always display stick-slip crack propagation behavior, as shown in **Figure 4-4a**, the experimental data can still be utilized to generate crack resistance curves (R-curves) [219]. There is a small scatter of the G_{IC} values in the resulting R-curves (see **Figure 4-4b**) related to the local variation of toughness on account of the interlaminar resin pockets and the wavy nature of the woven fabric, but each of the groups has clearly distinctive values.

There is moderate carbon fiber bridging in the pure woven laminates, resulting in a relatively flat R-curve, which is in line with other similar systems [89]. For the control samples without CNT veils, the difference between $G_{IC,ini}$ and $G_{IC,prop}$ is marginal, especially when compared with the differences observed in unidirectional fiber reinforced composites [89, 220]. Incorporation of the low-density, as-produced CNT veils, produces a sharp rise in the R-curve, with the propagation value of fracture toughness ($G_{IC, prop}$) increasing up to ~50% compared with the initiation value ($G_{IC, ini}$) due to a

hierarchical bridging toughening mechanism (see **Section 4.1.3**). Remarkably, the average values of $G_{IC, prop}$ for as-produced CNT samples are 60% higher compared with the corresponding value of the baseline material. In contrast, the densified veils produced a 28.4% decrease of $G_{IC, prop}$. The CNT layer in this latter case functioned essentially as a defect that weakened the interlaminar region and did not produce any carbon fiber-bridging, thus effectively reducing the fracture toughness of resulting laminate.

Fig. 4-4 Representative Load-extension curves (a) and R-curves (b) of specimens with and without CNT veils; (c) comparison of Mode I interlaminar fracture toughness for CNT-interleaved composites (as-produced and pre-densified CNT veils) and baseline (without CNT veils).

4.1.3 Toughening mechanisms

Fractography

The fracture surfaces of tested specimens were examined by electron microscopy and Raman spectroscopy. SEM micrographs of the reference specimen (**Figure 4-5a**) show a clean matrix fracture surface with no fiber-bridging, in line with its flat R-curve shape. These are typical features of low toughness mode I fracture surfaces. The fracture surface is totally different (see **Figure 4-5b**) for the composite with as-produced CNT veils. Overall, the fracture surface is now quite rough, which is beneficial for energy dissipation and therefore as a toughening mechanism. Closer inspection shows that there are two levels of fiber bridging operating at different length scales: firstly, the presence of broken carbon fibers evidences carbon fiber bridging and pull-out, and the presence of substantial of pull-out CNTs indicates strong matrix level CNT bridging. These combined mechanisms lead to the observed rising of the R-curve.

In comparison, the fracture surface of laminates interleaved with densified CNT veils (**Figure 4-5c**)

shows peeling of the CNT interleaf layer. No carbon fiber was easily detected at fracture surface, which indicates that the densified CNT layer guided the crack and hindered the formation of carbon fiber bridging. This is in agreement with the flat R-curve obtained also for these specimens, and hence, the fracture energy obtained in this case can be endorsed to the intrinsic fracture energy of the CNT layer in the absence of other superior scale toughening mechanisms.

Fig. 4-5 Comparison of fracture surfaces: (a) Control sample without CNT veils; (b) sample interleaved with as-produced CNT veils and (c) sample containing pre-densified CNT veils.

Crack propagation

Toughening effect, to a considerable degree, depends on crack behavior. Several surface analysis technologies were used in order to get a deeper insight into the crack initiation and propagation behaviors as well as the corresponding toughening mechanisms. The starting point of this analysis is the observation that the fracture surfaces of the two types of samples with CNT interleaves exhibit clear differences by simple visual inspection. The tougher one, with the low-density interleaf, consists of a complex pattern of “patches” of three different, well-defined colour tone (shiny-S, grey-G and dark black-B). Examples of these regions are marked in the fracture surfaces of **Figure 4-6**. A further important observation is the composition of the complementary fracture surfaces of the

two arms in these samples. The position of black regions in one arm (B) always corresponds to black regions in the other arm (B), and vice versa, while Grey regions (G) are matched by shiny regions (S).

The composition of the different regions could be readily determined from their Raman spectra, taking advantage of the strong Raman intensity and distinctive features of the CNT veils compared with the CF. Considering the low D/G ratio and sharp G band lineshape, grey and dark-black regions can be easily recognized as CNT-rich regions, whereas the shiny areas, with broad D and G bands of similar intensity, correspond to carbon fiber. Thus, the Raman data enable to identify different color tones on the fracture surface to different layers of the composite and ultimately, to different interfaces: S/G represent CF/CNT veil interfaces and B/B represent CNT veil/CNT veil interfaces.

Fig. 4-6 Three different morphologies (marked as S, B and G) identified on the fracture surface of laminates reinforced with as-produced CNT veils and their Raman spectra.

Figure 4-7 shows SEM micrographs of the different region and the crack propagation path derived from the fractography analysis. As shown in the picture, the shiny region (S) consists of pure carbon fibers or fiber bundles. Those fibers debonded from CNT-rich resin areas and left substantial dents on the counterpart (G). Thus, it is of reasonable to conclude that the crack moved forward through the interface of carbon fabric layer and CNT layer, as schematically shown in **Figure 4-7 (II)**. The dark-black (B) region in one arm always correspond to a dark-black region (B) in its counterpart (see **Figure 4-6**), and SEM micrograph (**Figure 4-7 B**) indicates that both regions shared the similar

fracture morphologies with extensive CNTs. The crack, in this case, moves exclusively through the CNT layer, as schematically depicted in **Figure 4-7 (I)**. Following this logic, the propagation route of crack in whole area of interest could be unveiled simply based on the apparent color of fracture surfaces.

Fig. 4-7 Crack propagation path determined from combined fractography by Raman spectroscopy, optical and electron microscopy. Visually dark black areas (BB) correspond to cohesive failure of the interleaf. Matching shiny (S) and grey (G) areas represent adhesive failure at the CNT veil/CF interface. Fracture toughness increases when both modes alternate.

Equipped with this fractography method, the differences in fracture toughness between the two types of CNT-containing samples can be rationalized in terms of their microstructure while tracing back to their fabrication method. **Figure 4-8** presents the fracture surfaces of two different samples and schematics of the different crack propagation paths. In the case of the low toughness samples, the crack progresses almost exclusively along the CNT-rich interlayer, corresponding to a cohesive failure mechanism. A similar behavior is observed in composites produced with CNT veils manufactured semi-industrially, which are supplied as densified free-standing sheets [221]. In contrast, the high toughness CNT interleaf sample showed regular crossings of the interlaminar region through the interlayer. Essentially a combination of adhesive and cohesive failure. These saw-like interlaminar crossings not only increase the total crack propagation length, but also trigger different toughening mechanisms: crack advance through the nanotoughened epoxy, possibly nano-scale bridging, and a good deal of carbon fiber/bundles bridging. Thus, failure in this mode combines pull-out of nano-sized reinforcements, debonding between carbon fiber and resin, as well as carbon fiber pull-out and breakages (see **Figure 4-5b** and **Figure 4-7S/G**). These multiscale mechanisms are usually considered to consume additional energy and hence contribute significantly to the

enhanced interlaminar toughness and thus Mode I fracture behavior.

Fig. 4-8 Fracture surfaces of the two types of composites with CNT veil interleaves. Increases in Mode I fracture toughness correspond to a saw-like crack path alternating between cohesive and adhesive failure in samples with low-density as-produced veils. Pre-densified veils reduced fracture toughness and failed exclusively cohesively.

The envisaged operation of these toughening mechanisms in terms of interlaminar crossing (ligament bridging) is schematically represented in **Figure 4-9a**. The initial crack created by the teflon insert can propagate either through the CNT layer or produce debonding at the carbon fabric/interleave interface. The generation of such type of cracks reduces the stress level in this region allowing the crack to open. The secondary cracks at the carbon fabric/interleave interfaces enlarges and interacts with the crack in the CNT layer producing a ligament spanning both carbon fabric arms. This process repeats continuously to form further ligaments while the crack propagates in the direction of the coupon. Simultaneously, the deformation of the CNT veil ligaments increases due to the crack opening displacement and at the same time veil ligaments tend to align in the through-the-thickness direction enhancing the toughening effect. The energy dissipated by the permanent deformation, rotation and final tearing and rupture of the CNT veil ligaments are the main sources of toughening in these materials. Therefore, there actually exist three level of bridging mechanisms operating at different length scales in CNT/CF/epoxy composite samples, which are involving macro bridging of nanotoughened ligament, micro bridging of carbon fiber and nano bridging of CNT, respectively, as shown in **Figure 4-9b**. Those bridging effects result in an increase of the G_{IC} value of the composite materials which is usually described by the rising R-curve.

Fig. 4-9 (a) The ligament evolution (interlaminar crossing) sequence upon crack growth; (b) Schematic of hierarchical toughening mechanisms involving macro bridging of nanotoughened ligament, micro bridging of carbon fiber and nano bridging of CNT.

The results presented above show evidence of interlaminar reinforcement by adding CNT veils when they are appropriately synthesized and integrated in the laminate. Densification of the CNT veil appears as a critical processing parameter. It is expected that the structure resulting from the compaction of the dry veil has lower density than the veils under capillary-induced solvent densification. Upon resin infiltration the resulting composite interleaf is expected to have different CNT volume fraction and properties such as intrinsic fracture toughness and in general different cohesion in the transverse direction. There is ample work showing the enhancement of CNT fiber properties upon polymer infiltration, with the matrix improving stress transfer between CNT bundles and leading to a complex hierarchical composite structure [222-225]. Further studies on the fracture toughness of CNT fiber interleaves and their composites should shed more light into the relationship between veil properties and interlaminar reinforcement.

4.2 Woven laminates containing industrial-scale CNT interleaves

In this section, a joint work in collaboration with Tortechn Nano-Fibers company is reported. The main difference with previous sections was that the CNT veils used here was provided by the company instead of manufacturing at our lab. In addition, since enough CNT veils were guaranteed, a systematical investigation of interleave thickness effect on the interlaminar properties of woven

CFRP was performed.

4.2.1 Laminate manufacturing and examination

Previous investigations suggested that CNT fiber veils need to be directly (in-situ) deposited onto the surface of fabric (**Section 4.1**), rather than be inserted as a freestanding interleaf material, so as to give full play to its interlaminar toughening. More importantly, if CNT veils are already incorporated onto the carbon fabric or prepreg during the manufacturing process, the extra step of interleaving in composite layup is removed. In other words, carbon fabric/prepreg with CNT veils can be used just as normal fabric/prepreg in the construction of composite structures. Considering that prepreg typically have a limited shelf life under room temperature, we finally chose VARTM method for scale-up trial using the same conditions already described, since dry fabric needs no strict storage requirement and it is earlier to be delivered between our workplace and Tortechnano-Fibers. In order to investigate thickness influence of CNT veil interleaves on the interlaminar properties of woven CFRP composite, three groups of CNT veil produced by Tortechnano were synthesized with a nominal areal density of 0.5, 1.0 and 1.5g/m², respectively. The selection of areal density is based on the fact that previous study has already demonstrated improvements of 60% in Mode-I fracture toughness after integration of CNT veils with an areal density of 0.8/m² [156]. **Figure 4-10** showed a plot of the attenuation signal obtained from the ultrasound inspections, indicating that there exist no obvious defects/voids inside the laminate. The cross-sectional images of the laminates are shown in **Figure 4-11**, which were obtained by means of optical microscope and further confirmed almost void-free laminate production, showing that the CNT veils bridge neighboring two CF plies with a thickness of around 5, 10 and 15 microns, respectively for the nominal areal densities used.

Fig. 4-10 C-scan images of CNT toughened CFRP with a CNT areal density of (a) 0.5, (b) 1.0 and (c) 1.5 g/m^2 , respectively.

Fig. 4-11 Cross-sectional images of CNT toughened CFRP with a CNT areal density of (a) 0.5, (b) 1.0 and (c) 1.5 g/m^2 , respectively.

4.2.2 Mode I interlaminar fracture

Typical load versus displacement curves of DCB tests for the reference laminate and CNT veil reinforced laminates are displayed in **Figure 4-12a**. A brittle fracture at the initial crack occurred for the baseline since the load dropped quickly at this point and the load during the crack propagation also decreased continuously with the increase of the opening displacement. The reinforced laminates with 0.5 g/m^2 and 1.0 g/m^2 CNT veils showed an apparent nonlinear response before crack propagation. The nonlinear response could demonstrate that the integration of the CNT veil increased the toughness of interlaminar resin and a plastic deformation might occur before crack propagation. But, for the sample with 1.5 g/m^2 CNT veil, the fracture behavior was observed to be more brittle, though the load dropped more slowly with the increasing of opening displacement

during the later crack propagation partly due to the low stress level around the crack tip.

The R-curves corresponding to each group of specimens were presented in **Figure 4-12b**. It was found that the baseline (CFRPs without CNT veils) laminate displayed essentially flat R-curves, implying limited micro carbon fiber/bundle bridging within the fracture process zone. In contrast, interleaving thin CNT veils (i.e. 0.5 g/m² and 1.0 g/m²) to the original laminate resulted in significant enhancement of propagation value of mode I fracture toughness. For instance, $G_{IC,prop}$ increased from 263±12 J/m² to 465±53 J/m² after interleaving 0.5 g/m² CNT veils, enhanced by 77%. When using 1.0 g/m² veils, $G_{IC,prop}$ also increased by as much as 76%, from from 263±12 J/m² to 463±52 J/m². This was associated with a significantly ‘rising’ trend of the R-curves (see **Figure 4-12b**), indicating there are extensive carbon fiber bridging within the fracture process zone. However, the mode-I fracture toughness strikingly dropped from 263±12 J/m² to 169±51 J/m² (-36%) as the areal density of the CNT veils reached up to 1.5 g/m². It is also noted that there are large discrepancies of fracture energy among the specimens with 1.5 g/m² CNT veils, possibly due to the lack of impregnation of resin for the thick CNT veil.

Fig. 4-12 Representative Load-extension curves (a) and R-curves (b) of specimens with and without CNT veils; (c) comparison of Mode I interlaminar fracture toughness for CNT-interleaved composites (as-produced and pre-densified CNT veils) and baseline (without CNT veils).

Representative SEM micrographs of the fracture surfaces of the DCB specimens with and without CNT veils are displayed in **Figure 4-13**. Reference specimen (**Figure 4-13a**) showed a typical adhesive failure, in which carbon fibers are mostly debonded from the resin with a smooth fracture surface. In comparison, the fracture surfaces of the thin CNT veil interleaved specimens (**Figure 4-**

13 b and c) were much rougher compared with baseline. A large number of CNTs were observed on the fracture surface with the majority of them being in a long and continuous form, indicating that CNTs are mostly pulled out from the resin. Meanwhile, numerous microcracks can be easily distinguished. These microcracks were generated by the crack deflection mechanism because of the presence of CNTs. In the matrix-rich region, the CNTs resisted matrix cracking by crack bridging, thus increasing the load required for crack initiation and propagation. It should also be noted that carbon fibers on the fractures surfaces are mostly covered by CNTs, suggesting an enhanced interface between CF and resin, and most importantly, these CF are in a “loose” state, indicating they also participated in loading transferring during the cracking, resulting in a micro-fiber bridging mechanism. However, when the areal density of CNT interleaving increased up to 1.5 g/m^2 , no carbon fiber was easily detected at fracture surface (**Figure 4-13c**), which indicates that the thicker CNT layer guided the crack inside and hindered the formation of carbon fiber bridging. This is in agreement with the flat R-curve behaviour obtained for these specimens, and hence, the fracture energy calculated in this case can be endorsed to the intrinsic fracture energy of the CNT layer in the absence of other superior toughening mechanisms.

Fig. 4-13 Representative SEM micrographs of the fracture surfaces under Mode I loading condition: (a) baseline; (b), (c) and (d) are from CNT veils interleaved samples with an areal density of 0.5, 1.0 and 1.5 g/m^2 , respectively

4.2.3 Mode II interlaminar fracture

Figure 4-14 shows load-displacement curves of specimens with and without CNT veils in Mode II tests. Each curve was selected from the set of curves for being the most representative of the average values from the respective sample. The generally observed behaviours show that the maximum load increased with increasing the areal density of CNT veils as shown in **Figure 4-14a**, leading to a rising-trend of Mode II fracture toughness (see **Figure 4-14b**). Specifically, G_{IIC} enhanced from $563 \pm 15 \text{ J/m}^2$ to 699 ± 38 , 712 ± 30 and $756 \pm 14 \text{ J/m}^2$ after interleaving veils with an areal density of 0.5, 1.0 and 1.5 g/m^2 , increased by 24%, 26% and 34%, respectively. Note that the non-interleaved sample shows the lowest loading values with a “flattened” behavior after reaching the elastic limits. In Mode II stress state, the shear induced at the crack tip is very consistent with the layered structure of the CNT veils, so CNTs can effectively transfer load by shear as opposed to the Mode I case, resulting in totally different toughening mechanisms.

Fig. 4-14 Representative Load-displacement curves of specimens with and without CNT veils in Mode II tests; (b) comparison of Mode II ILFT for CNT-interleaved composites and baseline

Representative SEM micrographs of the fracture surfaces of the ENF specimens with and without CNT veils are shown in **Figure 4-15**. The surface of the baseline specimen was clean, as expected, the fracture surfaces of thin CNT veil interleaved laminates (0.5 g/m^2 and 1.0 g/m^2 as shown in **Figure 4-15 b and c**) displayed a rough feature with the fracture path being deflected. This crack

deflection not only increases the total crack propagation length, but also trigger multiscale fiber-bridging mechanisms. Specifically, when the crack advance through the nanotoughened epoxy, numerous CNTs were pulled out from the matrix, triggering CNT bridgings (nano scale); when the crack tries to advance into intralaminar region, a good deal of carbon fiber was stretched and pulled out, resulting in carbon fiber bridgings (micro scale). Thus, failure in this mode combines pull-out of nano-sized reinforcements, debonding between carbon fiber and resin, as well as carbon fiber pull-out and breakages (see **Figure 4-15 b** and **c**). These mechanisms are usually considered to consume additional energy and hence contribute significantly to the enhanced interlaminar toughness and thus Mode II fracture behavior. It is worth noting that the fracture surface of 1.5 g/m² CNT veils interleaved specimen, unlike Mode I case, is still quite rough and multiscale bridging mechanism is also detected there (**Figure 4-15d**), which can well explain the continuous improvement of Mode II ILF as shown in **Figure 4-14b**.

Fig. 4-15 Representative SEM micrographs of the fracture surfaces under Mode II loading condition: (a) baseline; (b), (c) and (d) are from CNT veils interleaved samples with a areal density of 0.5, 1.0 and 1.5 g/m², respectively

4.2.4 Transition from mode I to Mode II

For Mode II ENF specimens, an initial crack was firstly generated by subjecting the specimen first to Mode I crack propagation, thus we have the chance to see the transition region from Mode I to Mode II delamination. As can be seen in **Figure 4-16**, the red dash lines mark the boundaries of mode I and Mode II delaminations in different specimens. There is no much difference of transition region for the baseline sample as well as the specimens interleaved with 0.5 g/m^2 and 1.0 g/m^2 CNT veils. However, for the samples with 1.5 g/m^2 CNT veils, there exists an obvious difference between mode I and mode II delaminations, indicating a change of failure mechanism. Close observation of transition zone (see **Figure 4-17**) confirmed that crack deflection happened when loading condition changing from opening to in-plane shearing, leading to a shift of failure mode from cohesive-dominated to adhesive-dominated. In principle, shearing of the CNT layer becomes more difficult when increasing their areal density so the crack will progress through the weakest path at the CNT/carbon fiber interface.

Fig. 4-16 The fracture surfaces of specimens after suffering both Mode I and II loading condition: (a) baseline; (b), (c) and (d) are from CNT veils interleaved samples with an areal density of 0.5 , 1.0 and 1.5 g/m^2 , respectively. The red dash line mark the boundary of Mode I and Mode II delamination

Fig. 4-17 Representative transition zone from Mode I to Mode II for 1.5 g/m² CNT veil interleaved specimen

4.2.5 Interlaminar shear strength

Figure 4-18a displayed the load-displacement curves of specimens with and without CNT veils. Each kind was at least tested 3 times for obtaining a more reliable statistical value and repetitive behaviors were observed among each group of samples. Statistic results showed that ILSS of woven CFRP laminate samples increase from 32.2 ± 0.7 MPa to 34.6 ± 0.3 MPa when interleaved with 0.5 g/m² CNT veils, enhanced by 7.7% (see **Figure 4-18b**). However, a down trending was observed after areal density is larger than 0.5 g/m². Nevertheless, the ILSS of CNT interleaved specimen is still higher than that of baseline, i.e. 3.6% and 3.2% improvements were also observed when using 1.0 and 1.5 g/m² CNT veil interleaves. The SBS failure of woven CFRP specimen was quite different from that of unidirectional CFRP sample. Many times, failure was not interlaminar shear, instead by indentation and/or flexure. The loading nose caused indentation deformation and concentration of compressive and transverse shear stresses, which either individually or in combination exceed the material strength before the interlaminar failure happened. In addition, the waviness of textile fabric composites further deteriorated the compression strength and caused compression failure on the loading point. In our case, the apparent ILSS depends more on the overall mechanical properties of laminates, rather than the interlaminar properties of middle plane. This is why there is a marginal improvement when introducing a layer of CNT veils in the middle plane of woven CFRP. It can be concluded that ILSS measurement methodology is no longer appropriate for woven laminates.

Fig. 4-18 (a) Representative Load-displacement curves of specimens with and without CNT veils in SBS test and (b) Comparison of interlaminar shear strength (ILSS) for CNT-interleaved composites and baseline (without CNT veils).

4.3 Unidirectional laminates containing lab-scale CNT interleaves

In previous sections, the interlaminar toughening effects of CNT veils in woven fabric architecture has been investigated. The laminates were prepared by optimized VARTM method and CNT veils were mostly well infiltrated taking fully advantages of low viscosity of fresh resin. In industrial application, unidirectional carbon fiber prepreps are also widely used, which is worth to perform a further exploration in terms of interlaminar toughening with CNT veils.

In this section, samples of unidirectional carbon fiber/epoxy matrix composites interleaved with different composition CNT veils were prepared using hot press method and tested for interlaminar fracture toughness (IFT), measured in Mode-I (opening) and Mode-II (in-plane shear), and for interlaminar shear strength (ILSS), evaluated by the short beam shear (SBS) test. The crack propagation mode could be directly determined through fractography analysis by electron microscopy and resin/CNT spatial discrimination by Raman spectroscopy, showing a clear correlation between interlaminar reinforcement and the balance between cohesive/adhesive failure mode at the interlayer region. Composites with full resin infiltration of the CNT veils give a large increase of Mode II IFT (88%) to 1500 J/m^2 and a slight enhancement of apparent interlaminar shear strength (6.5%), but a decrease of Mode I IFT (-21%). The results help establish the role of interlayer infiltration, interlaminar crossings and formation of a carbon fiber bridgings, for interlaminar reinforcement with interleaves.

4.3.1 Laminates preparation and examination

The composite panels were 280×280 mm, and purposely designed to comprise an interleaved area of 140×280 mm and the remaining part free of interleaf. To summarize, baseline panels were manufactured using AS4/8552 prepregs and the results of mechanical tests compared with those laminates interleaved with 8552 epoxy film, as received CNT veils and the combination of both in order to enhance veil impregnation. Reference interleaf-free and CNT-veil specimens were extracted from the same panel to avoid any variations between different batches, although, in general, the fabrication process was optimized to avoid variations between different panels. **Figure 4-19** shows an example of a final CF/CNT veils/epoxy laminate composite produced using the aforementioned hot-press compression molding. A plot of the attenuation signal obtained from the ultrasound inspections (**Figure 4-19a**) showed that there exist no obvious defects/voids inside the laminate, without significant thickness variations proved by a homogeneous attenuation distribution. The cross-sectional of the laminates is shown in (**Figure 4-19b**), which was obtain by means of optical microscope and further confirmed almost void-free laminate production showing that the CNT veil was fully integrated in the composite with a thickness of 10.0 ± 1.0 microns.

Fig. 4-19 (a) Attenuation plot of the laminates containing CNT veils obtained by ultrasound inspection (b) cross-section of the laminate obtained by optical microscopy.

4.3.2 Mode I interlaminar fracture

Two different data-reduction of fracture toughness values can be used to describe the fracture behaviour of the laminates, namely initiation and propagation toughness ($G_{Ic,ini}$ and $G_{Ic,prop}$), respectively. $G_{Ic,ini}$ is determined by the 5%/max point in the force-displacement curve after precracking, while the $G_{Ic,prop}$ is the value where the energy release rate achieves a constant state and

the crack propagates in a self-similar way independent on the crack length [208]. The G value of interest for this experiment was $G_{IC,prop}$, since it is more realistic in practice for determining the likelihood of the crack to continue to propagate.

Figure 20a and **b** displayed the representative load-displacement curves for mode I interlaminar fracture tests. All the test exhibited a stable and smooth crack propagation. The corresponding R-curves of the different samples, respectively were obtained following the data-reduction methods aforementioned. For the control baseline samples (AS4/8552 prepregs without interleaf), a relatively large increase in G_I with the increasing crack length is observed which is predominately attributed to carbon fiber bridging. Conversely, the samples interleaved with CNT veils showed a relatively flat R-curve behaviour which was an indicative of fiber bridging suppression. More specifically, the $G_{IC,prop}$ values decreased as much as 71% (compared with control samples) when directly interleaving CNT veils. Such significant knock-down in Mode I fracture toughness can be ascribed to the poor resin infiltration of the prepreg resin bleeding into the CNT veils. This fact was confirmed by the SEM picture of the corresponding fracture surface as shown in **Figure 20e** and by the Raman analysis (see **Section 3.3.5**). It seems that resin bleeding from the AS4/8552 prepreg was not enough to produce good infiltration into the CNT veil. To alleviate such effect, 8552 resin films were intercalated together with the as-produced CNT veil in the middle layer of the manufactured panels. Interestingly, it was found the intercalation of such resin film improved significantly the resin infiltration of the CNT veils (see **Section 3.3.5**), thus enhancing the Mode I mechanical performance. Compared with samples only interleaved with CNT veils, $G_{IC,prop}$ values were improved as much as 170%. It is worth noting that the $G_{IC,ini}$ value of CNT veil/resin film laminates maintained at the same level as the control sample without interlaminar reinforcement while the $G_{IC,prop}$ value was 21% smaller. In addition, 8552 epoxy films were also intercalated in the baseline AS4/8552 laminates to isolate its influence on the fracture behavior. In this case, the Mode I fracture toughness of the only resin-interleaved specimen showed no significant statistic changes compared with that of control samples (see **Figure 20c**). Therefore, the results suggest that CNT veils require a minimum of resin impregnation to transfer some load between crack wakes.

Fig. 4-20 Representative load-displacement curves (a) and the corresponding R-curves (b) of specimens with and without CNT veils in Mode I loading case; (c) comparison of Mode I ILFT for CNT-interleaved composites and baseline; (d) (e) and (f) are the corresponding SEM micrographs of the fracture surfaces.

To summarize, the inclusion of CNT veils seems to provide a preferential path for crack propagation hampering carbon fiber bridging, which is known to be one of the major contributions to mode I interlaminar fracture toughness. The carbon fiber bridging observed in CNT interleaved samples was negligible, thus any contribution to the fracture toughness from this source is likely to be minimal. Although both CNT interleaved laminates exhibited a significant decrease of the fracture toughness, and this fact was attributed to the absence of fiber bridging, the reduction obtained in the case of the CNT film interleaved laminates with the supplementary 8552 resin film was less pronounced indicating some rudimentarily CNT stress transfer.

Moreover, it should be emphasized that toughening of resins with dispersed CNT is often perceived to be the result of CNTs being oriented orthogonal to the fracture plane acting as a kind of ‘nano-stitches’[15]. However, the CNTs used in this work are predominantly oriented parallel to the plane of the veil, therefore, the loading of the CNTs during mode I crack propagation was not optimal. As the crack is initiated in the CNT modified interlayer growing in mode I, the CNT veils are loaded transversally and subjected to out-of-plane peeling forces. The CNTs in the fracture surface did not exhibit neither stretching nor loading alignment (see **Figure 20e and f**), suggesting that most of the

CNTs seem to have been peeled off from the matrix resin without significant deformation. The introduction of the CNT veil interleaf gave rise to coupled detrimental effects: a low energy-dissipation path tracking the crack propagation and at the same time limiting the extension of carbon fiber bridging as the main contributor to the interlaminar material toughness. Those mechanisms produced the substantial reduction of the carbon fiber bridging as compared with the baseline laminates.

4.3.3 Mode II interlaminar fracture

For the Mode II ENF tests, specimens were extracted from the previously tested Mode I coupons according to the standard requirements. Representative load-displacement curves and the corresponding Mode II IFT (G_{IIC}) for each laminate configuration (baseline, resin interleaf-AS4/8552, CNT interleaf-AS4/8552 and CNT/resin interleaf-AS4/8552) are given in **Figure 4-21**. It was found that resin interleaved samples also showed the similar mechanical responses with control specimens under mode II loading condition as it was observed in mode I tests. However, only the introduction of both CNT veil and resin film resulted in a higher maximum load at the onset of fracture and thus in a higher G_{IIC} value. In this case, an 88% enhancement was obtained as compared with baseline samples without interleaves. It should be pointed out that when using the as-produced CNT veils alone without 8552 epoxy resin film (CNT interleaf-AS4/8552), only a slightly improvement of G_{IIC} of 12% is measured. Again, the AS4/8552 epoxy prepreg resin bleeding was not enough to fully impregnate the CNT interleaf, resulting in a minor improvement. By scrutinizing the fracture surfaces, three different failure mechanisms can be distinguished which are schematically shown in **Figure 4-21 (f, g and h)**. The failure mechanism for the baseline is shear dominated interfacial failure at the fiber/matrix interface, which was confirmed by SEM image (**Figure 4-21c**). The G_{IIC} in this case strongly depends on the bond strength between carbon fiber and resin. The introduction of a CNT veil in the mid-plane of the laminates resulted in the formation of an interlaminar region with a thickness of around 10 μm . When CNT veil is poorly infiltrated by the resin, a preferential crack path is created in this layer, resulting in a cohesive dominated failure (**Figure 4-21g**). The high-resolution micrograph of the fracture surface presented in **Figure 4-21d** showed that the crack exclusively propagates through the CNT veil interlayer. This phenomenon was also observed in our previous work [221], in which commercial CNT film was used. It should

be noted, in this case, that the CNTs were highly aligned with the mode II shear loads at the crack tip so some effective bridging could occur resulting in a 12% improvement of G_{IIC} as previously mentioned. When CNT veil is well infiltrated, crack tip is deflected away from the CNT toughened interlayer into the interface of CF ply and toughened interlayer (adhesive failure), resulting in interlaminar crossing and effective CNT crack bridging (**Figure 4-21e and h**). In this scenario, the failure mechanism not only includes the debonding of carbon fiber from CNT modified matrix, but also interlaminar crossing and bridging at points where the crack passes from one side of the interlayer to the other, significantly enhancing the Mode II IFT.

Fig. 4-21 Representative Load-displacement curves of specimens with and without CNT veils in Mode II tests; (b) comparison of Mode II ILFT for CNT-interleaved composites and baseline; (c), (d) and (e) are the corresponding fracture surfaces under SEM; (f), (g) and (h) sketches of possible fracture mechanisms of the three specimens analyzed.

4.3.4 Interlaminar shear strength

The small size of the ILSS test specimen combined with the ease of testing make the test method

more attractive than other shear tests [226]. The short span of the beam reduces the bending effects loading the mid-plane under shear dominated forces. **Figure 4-22a** displays the representative load-displacement curves of each composite configuration. They are almost linear and elastic, except at the peak load. The maximum force attained during the tests was used to determine the interlaminar shear strength of the laminate according to the standard assuming the maximum shear stress produces cracking at the mid-plane position of the laminate. The ILSS statistical results shown in **Figure 4-22b** are average values of at least 3 individually tested specimens for each laminate configuration. In all the cases, single/multiple cracks propagating parallel to the span direction were observed emanating from one of the supports of the beam and not necessarily located in the mid-plane of the laminate. Thus, the ILSS strength obtained via **Formula (4-1)** based on ASTM standard D2344 [154] should be treated as an apparent value of the shear strength. Not surprisingly, the statistic results showed that interleaving thin resin film exerts negligible influence on the interlaminar shear properties of control laminate.

$$ILSS = \frac{3}{4} \frac{F_{max}}{wt} \quad (4-1)$$

The apparent ILSS of unidirectional laminate samples decreased from 101.1±2.1 MPa to 93.1±3.7 MPa when interleaved with only CNT veils. Such relative decrease was around -7.9% (see **Figure 4-22b**). When looking into their specific failure modes as shown in **Figure 4-22c** and **d**, multiple shear cracks were found running along the fiber direction of the control sample included the mid-plane one (**Figure 4-22c**). As a contrast with baseline samples, only one crack was observed just in the middle plane of the CNT veils interleaved sample (**Figure 4-22d**). When interleaving with resin films and as-produced CNT veils in the mid-plane of the specimen, the apparent ILSS increased from 101.1±2.1 MPa to 107.1±2.4 MPa, enhanced then by 6.5%. Cross-sectional micrograph in **Figure 4-22e** showed that the multiple cracks were developed near the mid-plane, meanwhile this interface itself still kept intact, indicating that CNT toughened region bears higher ILSS than the control interlayer.

Fig. 4-22 Representative Load-extension curves of specimens with and without CNT veils in short beam shear test; (b) comparison of apparent ILSS for CNT-interleaved composites and baseline; (c) (d) and (e) are the corresponding cross-sectional images under optical microscope.

It should be emphasized that the ILSS determination using Formula (1) is on the condition that crack was initiated in the middle plane. For samples interleaved with both CNT veil and resin film, cracks were initiated and propagated near the middle layer, while the middle layer itself still kept intact. In

this case, Formula (1) is not applicable. Based on linear and elastic calculations and some basic assumptions as shown in **Figure 4-23a**, following inequality was finally obtained:

$$\tau_{max}^{CNTR} \geq \frac{\tau_{max}^{BL}}{1-\alpha^2} \quad (4-2)$$

Where, α is the ratio of the distance between the crack initiation plane and the middle plane to the half thickness of the laminate, τ_{max}^{CNTR} and τ_{max}^{BL} are ILSS of CNT veil/resin film interleaved specimen and baseline, respectively.

Formula (4-2) provides the lower limit of ILSS for CNT veil/resin film interleaved specimens. In this section, τ_{max}^{BL} is determined as 101.1MPa (**Figure 4-22b**). The distance between the crack initiation plane and the middle plane is around 300 μm as shown in **Figure 4-23b**, and the thickness of laminate (t) is around 3.65 mm, so α is calculated as 0.16. Thus, $\tau_{max}^{CNTR} \geq 103.8 \text{ MPa}$.

Fig. 4-23 (a) ILSS distribution of SBS specimen along the through-the-thickness direction, in which red and blue lines stand for crack plane and middle CNT layer, respectively; (b) cross-sectional images of tested SBS specimen interleaved with both CNT veils and resin film.

4.3.5 Discussion

Resin film and veil impregnation

It was found that interleaving thin 8552 resin film exerted negligible influence on the interlaminar properties of 8552/AS4 composite laminate. G_{IC} , G_{IIC} and ILSS were nearly unchanged after film integration. **Figure 4-24** showed the cross-sectional image of resin-interleaved laminate, in which no significant difference was found between the mid-plane region (interleaved with resin film) and other interlaminar regions. The film in this case is very thin (~ 25 microns) so resin can be easily distributed during the cure cycle.

Fig. 4-24 AS4/8552 laminate interleaved with thin 8552 resin film showing no apparent increase of interlaminar thickness or resin rich regions in the middle ply compared with other interlaminar regions

Interestingly, locally interleaving with thin resin films together with the CNT veils can significantly improve its resin infiltration. This fact was confirmed subsequently by the SEM high resolution images of the corresponding fracture surfaces as shown in **Figure 4-20 (e) and (f)**. The composition of the different regions could be readily determined from their Raman spectra taking advantage of the strong Raman intensity and distinctive features of the CNT veils compared with the carbon fiber and the polymer resin. Considering together the low D/G band ratio and the sharp G band line-shape as displayed in **Figure 4-25a**, the fracture surface of only CNT veil interleaved sample can be easily recognized as dry CNT-dominated regions in the fracture surface. In comparison, a prominent fluorescence effect was recorded during the Raman analysis on the fracture surfaces of CNT veil/resin film interleaved specimens which confirmed the adequate infiltration of resin into the CNT veils.

These findings also provide us a clue of prepreg selection for specific application in the future. Maybe, the prepreg will be designed with an excess of resin bleeding to account for the resin that will be incorporated into the dry CNT veil interleaves.

Fig. 4-25 Raman spectra of fracture surfaces in different specimens

Toughening mechanisms

It is common that laminate composites incorporated with same interleaf materials perform quite differently in Mode I and Mode II loading conditions [86, 89]. Some material properties may exert a positive or a negative influence on each mode of interlaminar failure. Both kinds of failures are complicated, with Mode I case being prevailed by peel stress and Mode II being dominated by shear stress, and it is really a challenge to figure out which material properties or their combinations are most likely to affect crack initiation and propagation behaviors, thus changing the final fracture toughness.

The remarkable enhancement of Mode II IFT of CNT veil interleaved laminates (well-infiltrated) can be attributed to the ideal loading case for the CNT veils. The CNT veils used in this section are primarily oriented parallel to the fracture plane, which is designed to carry load in the plane, rather than out of plane. Under Mode II loading condition, stresses are effectively transferred to the veil by membrane mechanisms which enhance the interlaminar toughness G_{IIC} values as it was demonstrated in the previous paragraphs. On contrast, under Mode I loading condition CNTs are mostly peeled out from the assembly, which cannot take full advantage of their real strength. Our previous work [156] demonstrated improvements of 60% in Mode I fracture toughness after interleaving similar

CNT veils into woven carbon fabrics. It was this woven structure that reshaped the CNT veil configuration after compression, which was prove to be favor of stress transferring under Mode I loading state.

Toughening effect, to a considerable degree, depends on crack behavior [156] and the ability of the material for crack bridging. As shown in **Figure 4-26**, the Mode I fracture surface of CNT veil toughened samples was quite smooth (**Figure 4-26a, up**) and CNTs were universally found in both arms of fracture samples (**Figure 4-26b, right**). Thus, it can be concluded that the crack progresses almost exclusively along the CNT-rich interlayer, corresponding to a cohesive failure (**Figure 4-26c, up**). Under the Mode II load condition, a “banded” structure in the specimen loading direction on the fracture surface was found (**Figure 4-26a, bottom**). Closed examination under SEM showed that adhesive failure was dominated in this case (**Figure 4-26b, left**). It should be noted that those adhesive failure regions were not uniformly distributed along one side of CNT veils, but alternately distributed in the both sides, which leads to a lot of interlaminar crossings (**Figure 4-26c, bottom**). In fact, the black bands in bottom picture of **Figure 4-26a** are originated from those interlaminar crossings. Moreover, the interfaces between CF and resin are modified by the CNTs (**Figure 4-26b, left**), which could have a huge contribution to the Mode II IFT.

Fig. 4-26 (a) Mode I and Mode II fracture surfaces of CNT veil interleaved specimen (well-infiltrated); (b) Some details of transition zone from Mode I to Mode II and (c) different cracking behaviors under Mode I and Mode II loading condition.

The toughening effect of CNT veils also depends on the architectures of the host fabrics. In unidirectional laminate, the fabric ply is quite flat and smooth, hence the majority of CNTs are parallel with the delamination plane of the DCB specimen. As the crack is driven by Mode I (opening) loading condition, the CNTs are loaded transversally and subjected to peeling forces. It is worth noting that similar phenomena were also observed when using electrospun nanofiber veils in UD composites[89, 227]. Daelemans et al. [89], for example, reported that the presence of the electrospun nanofibrous veils between UD plies blocked the formation of a carbon fiber bridging zone and most of the nanofibers seem to have been peeled off from the matrix resin without much deformation during the crack propagation under Mode I loading condition. Interestingly, they also found if a zone of carbon fiber bridging was able to develop before the delamination encountered

the nanofiber modified region, the Mode I fracture toughness increased notably in this nanofiber modified region.

In our previous work [156], when 5H satin woven fabric was utilized, Mode I interlaminar fracture toughness was enhanced as much as 60%. In this scenario, the woven architecture of the fabrics probably resulted in tiny regions where the local crack growth was not purely Mode I or where the crack growth direction was not perfectly parallel with the plane of the interlayer, triggering a better load transfer to the CNTs and more fiber-bridgings, resulting in a significant enhancement of fracture energy consumption.

Originality and innovative aspects

The novelty of this section can be rooted in three sides. One is Mode II toughening factor (η_{II}), which can be defined as the improvement of Mode II interlaminar fracture toughness ($\Delta G_{IIC}/G_{IIC}$) divided by relative-to-ply interleaf thickness. In this work, an 88% improvement of G_{IIC} was achieved by interleaving a layer of 10um thick CNT veils (veil/ply ratio $\sim 5.5\%$). The calculated η_{II} value ($88/5.5 \approx 15.8$) ranked top among other interleaf materials listed in the **Table 3-2**. It should also highlight that weight/thickness penalty can also be minimized when thinner interleaved are used, as well as the possible influence of other mechanical performance (i.e bending, in-plane shear, etc.)

Tab. 4-2 Comparison of Mode II toughening factor (η_{II}) by using different interleaf materials

<i>Interleaf material</i>	<i>Interleaf thickness/ ply thickness ($\mu\text{m}/\mu\text{m}$)</i>	<i>Mode II improvement (%)</i>	<i>η_{II}</i>	<i>REF.</i>
<i>Nylon 6,6 nanofibrous mat</i>	<i>40/210</i>	<i>61</i>	<i>3.2</i>	<i>[228]</i>
<i>Nanotubes/epoxy film</i>	<i>150/200</i>	<i>126.7</i>	<i>1.7</i>	<i>[229]</i>
<i>As-prepared CNT BP/laminate</i>	<i>20/200</i>	<i>34</i>	<i>3.4</i>	<i>[230]</i>
<i>Cross-linked CNT BP/laminate</i>	<i>20/200</i>	<i>74</i>	<i>7.4</i>	<i>[230]</i>
<i>Nylon veils surface-loaded with silver nanowires</i>	<i>53/125</i>	<i>227</i>	<i>5.4</i>	<i>[231]</i>
<i>CNT veils</i>	<i>10/180</i>	<i>88</i>	<i>15.8</i>	<i>This work</i>

Note: only research works using unidirectional CFRP composites were compared here to avoid other possible influences.

Another merit of this section is that a facile and scalable manufacturing method was demonstrated, in which CNT veil is directly wound onto the prepreg surface. Most of reported interleaving materials/methods are either complicated to make/execute, or difficult to be realized in large scale. In this work, I try to avoid any post-processing to the materials and scale-limited steps, even though I know some of them (i.e. functionalization [148]) would exert a positive influence on the fracture behaviors. In addition, the integration of pre-assembled CNT veils without recourse to solvents is also potentially compatible with standard composite manufacturing methods and essentially analogous to the introduction of electrospun thermoplastic veils already utilized industrially [92]. Recently, this method has been successful applied in a joint research work with a company. We not only demonstrated a significant improvement of interlaminar fracture toughness, but also proved the scalability of this technique. Related results will be published soon.

Last but not least, we emphasize that our aim is not only to demonstrate an increase in toughness, but also to provide a rationale for the observed results. The new Raman fractography method and systemic test campaigns of interlaminar properties, are examples of developments that improve general understanding of interlaminar reinforcement with CNT veils.

4.4 Summary

In this chapter, the possible effects of CNT veil interleaves on interlaminar properties of woven and unidirectional CFRP laminate composites were systematically investigated. A facile and scalable VARTM as well as a hot press protocol was successfully built to make CNT/CF/epoxy composites, by which void-free laminates can be manufactured. The IFT under Mode I and Mode II loading cases and ILSS are investigated and discussed comparatively, followed by a systematic analysis of failure and toughening mechanisms.

In VARTM system (**Section 4.1 and 4.2**), the CNT veils interleaved into woven laminates can be generally divided into three different categories: as produced (lab-scale), densified via solvent exposure (lab-scale) and mechanically densified (industrial-scale). The following conclusions can be reached:

- The degree of densification of the CNT veil exerts a profound influence on resin infiltration process, and consequently the interlaminar properties of resultant laminates. As-produced

low-density “fluffy” CNT veils (0.8 gsm) consistently led to woven CFRP laminates with as much as 60% enhancement of $G_{IC,prop}$. In contrast, integrating liquid densified CNT veils deteriorated their interlaminar mechanical performances. It should be pointed out that mechanical densification exerts much less impact on the porosity/microstructure of CNT veils compared with liquid exposure methods, and resultant CNT interleaves are still suitable for VARTM application.

- The thickness of CNT veils exerts a clear influence on the interlaminar properties of woven CFRP composites. $G_{IC,prop}$ increased as much as 77% and 76% after interleaving CNT veils with a thickness of 5μm and 10μm, respectively. These were associated with a significantly ‘rising’ trend of the R-curves, indicating there are extensive carbon fiber bridging within the fracture process zone. However, $G_{IC,prop}$ strikingly dropped by 36% as the thickness of the CNT veils reached up to 15 μm, which might be ascribed to the uncompleted resin infiltration of CNT veils. In comparison, the mode-II fracture toughness (G_{IIC}) improved continuously with increasing the thickness of CNT veils. Specifically, G_{IIC} enhanced by 24%, 26% and 34%, after interleaving veils with a thickness of 5, 10 and 15μm, respectively.
- A new methodology combining Raman analysis and surface observation was proposed to study the crack propagation behavior, which was proven to be feasible and can determine the failure position, precisely and readily. The analysis results showed that interlaminar crossing play a paramount role in toughening mechanism. The crack front alternately propagates above and below the CNT-toughened interlayer, significantly improving the fracture toughness of resultant laminate.

In AS4/8552 prepreg system, integration of thin 8552 resin film exerted negligible influence on the interlaminar properties of AS4/8552 composite laminate. G_{IC} , G_{IIC} and ILSS were proved to be unchanged after film interleaving. Only interleaving as-produced fluffy CNT veils into unidirectional CFRP system led to an increase of Mode II IFT (12%) but a significant decrease of Mode I IFT (71%), as well as a slight degradation of ILSS (-7.9%). It is common for a same interleaving system varies dramatically in Mode I and Mode II toughening effects because of totally different stress state under respective mode, with Mode I being dominated by peel forces and Mode II being dominated by shear forces. Locally adding resin film near CNT veils can substantially

improve the infiltration condition and thus interlaminar properties. Compared with samples only interleaved CNT veil, $G_{IC,prop}$ was improved as much as 170% after supplementing a thin resin film. Compared with control samples, the Mode II IFT and apparent ILSS were increased by 88% and 6.5%, respectively. The depreciation of $G_{IC,prop}$ value probably was due to the in-plane orientation of the CNT veil within the ply that caused the low peeling resistance.

CHAPTER 5

Integrated energy storage in laminated composites by CNT networks

“What makes life dreary is the want of motive”

- George Eliot

In this chapter, CNT veils as essential part of supercapacitor were integrated into FRP composites to achieve simultaneously both load-carrying and electrochemical energy storage capabilities. Section 5.1 introduces the first generation of Structural SC in our lab, in which aluminum foils were utilized as current collectors and carbon fabrics were employed as structural reinforcement. Section 5.2 presented the second generation of Structural SC, in which CNT veils functioned as both electrodes and current collectors. The avoidance of metallic current collectors results in an ultrathin SC interleaf with a thickness of around 100 μm . In Section 5.3, a demonstrator of Structural SC was successful built, in which 15 EDLC devices (24.5 cm^2) were interleaved inside a $\sim 1000 \text{ cm}^2$ laminated composite, confirming the scalability of the proposed manufacturing method. Finally, the section 5.4 reports on the optimization of interlaminar epoxy rivets in structural power composites through FEM simulation and experimental validation.

It should be mentioned that the electrochemical characterization was performed by Dr. Evgeny Senokos and Dr. Moumita Rana.

5.1 The first generation of structural SC

5.1.1 Fabrication of self-standing all-solid EDLC devices

The fabrication of EDLC interleaves was carried out using the method recently reported by our research group [213], as schematically shown in **Figure 5-1**. After deposition of CNT fibers on aluminum current collector, the polymer electrolyte membrane is consolidated between the two electrodes by simply applying desired pressure of 2.5 MPa during 15 minutes. The next step consists in sandwiching a pre-formed PE membrane between two CNT fiber electrodes of similar weight and applying a small pressure during 10 minutes with a uniaxial press. The membranes have a composition of 70% of $\text{PYR}_{14}\text{TFSI}$ and 30% of PVDF-co-HFP and are fabricated by doctor blading.

Fig. 5-1 Scheme of the fabrication of devices by pressing a polymer electrolyte membrane between two CNT fiber sheet electrodes and two Al current collectors [213]

5.1.2 Energy storing composite fabrication and in situ electrochemical characterization.

The structural SC devices were fabricated by VARTM methods with lay-up of preform shown in **Figure 5-2a**. The laminates consisted of 8 layers of 5H satin carbon fabrics with 3 EDLC interleaves laid down between CF fabric layers, using insulating plastic tape to avoid the CF short circuiting the device (**Figure 5-2b**). The EDLC interleaves were manually introduced in the lay-up, with aluminium current collector extending out for electrical connection. **Figure 5-2c** shows a photograph of the composite during fabrication, with the cables attached to the devices. The procedure of structural SC fabrication achieves good integration of the components in the CF/EDLC/ epoxy laminate. **Figure 5-2d** shows optical and electron micrographs of the laminate cross-section showing the EDLC interleaf inbuilt between CF layers in the cured sample. The resin was able to fill the carbon fabric with the EDLC device, allowing formation of a continuous ply structure without large voids and defects.

In situ galvanostatic charge-discharge tests were performed during infusion, gelation and further curing of epoxy resin in order to evaluate the impact of these processes on electrochemical performance of the supercapacitor. CD profiles in **Figure 5-3a** shows negligible changes in electrochemical behavior of EDLC after infusion. Coulombic efficiency remains high, at 99%, and

equivalent series resistance (ESR) low, at 24 Ohm cm^2 . After curing of epoxy, which takes 48 hours at room temperature, there is a small ESR increase to 35 Ohm cm^2 , which we attribute to local damage to the sample after removal the peel-ply and distribution media layers used for fabrication of the composites. Nevertheless, as **Figure 5-3b** shows, energy density remains fairly constant at 6.40 Wh/kg (normalized by mass of active material) during epoxy infusion and after curing.

Fig. 5-2 (a) Infusion of epoxy into CF/EDLC/CF lay-up. (a) the lay-up of preform; (b) Details of highlighted region in (a) showing the embedding locations of SCs (c) Photographs of a CF/EDLC/CF lay-up during epoxy infusion and of the 4 cm^2 EDLC interleaf embedded in it (inset). (d) Optical micrograph of composite cross-section (top) showing successful integration of EDLC/CF/epoxy in the laminate and scanning electron micrograph (bottom) of integrated EDLC interleaf.

Fig. 5-3 Electrochemical properties of structural EDLC composite during fabrication by vacuum bag resin infusion. (a) Charge-discharge profiles at 5 mA cm^{-2} of EDLC before infusion, after infusion and after curing of epoxy resin. (b) Energy density obtained for different stages of infusion and curing.

5.1.3 In situ electrochemical characterization of structural EDLC during mechanical tests

The high efficiency of the structural EDLC composite shown above enables the simultaneous study of electrochemical and mechanical properties. For this work, we have chosen to carry out in situ charge-discharge and impedance spectroscopy measurements during 4-point bending on rectangular cross-section beams according to ASTM D7262 standard [214]. Maximum flexural stress σ and strain ϵ in the beams were calculated from the total force recorded with the load cell and the displacement of the actuator of the testing frame. In order to study different ply level stress states, we produced a composite with 8 CF layers $[0]_8$ and three 4 cm^2 EDLC interleaves. The EDLC interleaves were placed between the first and second layer, (SC_1T), in the neutral plane (SC_2M) and between seventh and eighth layers (SC_3B), respectively (see **Figure 5-2b**). They were tested individually after composite fabrication and showed nearly identical electrochemical performance (see **Figure 5-4**) and could, for example, power three red LEDs (see **Figure 5-5**). Their position in the laminate enables studying their properties under compression (SC_1T), neutral (SC_2M) and tension (SC_3B) stress states.

Fig. 5-4 Electrochemical performance of the embedded EDLC interleaves. (a) CD profiles measured at 5 mAcm^{-2} , (b) specific capacitance and (c) Ragone plot obtained for SC_1T, SC_2M and SC_3B integrated into the structural composite.

Fig. 5-5 Photograph of three EDLC device embedded into structural composite independently powering red LEDs.

Figure 5-6a shows photographs of the sample in the unstrained state and under a large deflection (~ 30 mm). In the elastic regime we observed no indication of mechanical reduction of bending modulus. The chord modulus obtained from the σ - ϵ curve (**Figure 5-6b**) was about 52 GPa, which was within the range of the control sample without interleaf. This fact indicates a good stress transmission between the plies of the CF and the EDLC interleaves during bending.

Overall, the observed change in the electrochemical properties of the interleaves is relatively small after loading cycles considering the large deformation of the composite structure. **Figure 5-6c** showed that the energy density and capacitance of the EDLC interleaf under tension (SC_3B) increase by around 30% and 12%, respectively and then remains constant throughout the test. The transverse compaction during 4-point bending test results in enhanced capacitance probably due to improved infiltration of the polymer electrolyte into the porous CNT fiber electrode, as previously observed in CNT fiber-based flexible thin EDLCs under severe bending [213]. Smaller increment in energy density is also observed in the interleaves in the neutral plane and the compressive region, and thus, it is attributed to a better electrical contact in the EDLC layers, probably caused by the pressure applied during 4-point bending.

The only pronounced change of electrochemical properties is observed at high bending stresses for the interleaf under compression (SC_1T), which shows a drop in energy density of 22%. This is again due to a change in ESR, which increases by about 60% relative to the unstrained state (**Figure 5-6d**). This increase is due to local losses of electrical contact, attributed to transverse opening deformation of the device caused by the in-plane compressive stresses at this ply. The fact that the

final value of ESR is lower than in the strained states suggests that most of the contact losses are reversible. **Figures 5-6e** and **f** show SEM micrographs of cross sections of interleaves in the compressive ply (buckled device) and tensile ply, respectively. They show significant deformation of the interleaf under compression, in agreement with the observed changes in electrical resistance.

Fig. 5-6 In situ electrochemical characterization during four point bending flexural test of the structural supercapacitor composite. (a) Photographs of the flexural test setup at the initial and bent states. (b) Comparison of stress-strain curves obtained for the structural composite containing three embedded EDLC interleaves and a reference composite produced without interleaves. (c) Relative energy and (d) ESR obtained from CD at 5 mA cm^{-2} measured during bending, for the interleaves under compression (SC_1T), neutral (SC_2M) and tensile (SC_3B) stress states. (e) and (f) SEM images of the composite cross-section after the bending test. The micrographs correspond to areas near the interleaf edge, for the samples subjected to compression (SC_T) (e) and tension (SC_B) (f) stresses.

5.1.4 Mechanical interconnection using perforated interleaves

While having very high power and energy densities, the EDLC interleaf layer in the composite can act as an internal defect. The polymer electrolyte in the EDLC layer is very soft, with a tensile modulus of 14 MPa. Its correspondingly low shear modulus implies that the EDLC essentially acts as a delamination, as the resistance to the opening/sliding between adjacent layers is very small. Yet, the simple structure and fabrication method used here open the possibility to produce engineered structures that mitigate the reduction in interlaminar properties. As an example, we produced an EDLC interleaf with a grid structure, that upon fabrication lead to a composite structure with adjacent lamina mechanically joined by stiff epoxy connectors (**Figure 5-7a and b**). This joining method ensures a more efficient transmission of shear stresses through the interfaces of the beam. The sample consisted of a 32 cm² EDLC with 18 holes of 1 cm diameter (18 cm² of effective electrode area), interleaved in a composite as described above.

Fig. 5-7 Structural supercapacitor composite with mechanically interconnected plies via the use of grid EDLC interleaves. (a) Photograph of a 32 cm² grid EDLC interleaf. (b) Schematic of the envisaged structure. (c) Bending stress-strain curves obtained for reference composite and structural supercapacitor containing a grid EDLC interleaf. (d) 3D tomography image confirming penetration of epoxy resin through channels in the interleaf.

Synchrotron X-ray tomography was used to confirm that epoxy resin successfully flowed in the through-the-thickness direction between the adjacent plies via the machined interleaf holes. **Figure**

5-7d presents a 3D image of a section of the sample after the bending test. The brighter section corresponds to the EDLC interleaf, which has higher X-ray absorbance. It is clearly delimited by a region where epoxy interconnected two adjacent plies, thus demonstrating successful production of the envisaged structure. Further characterization of this complex structure is included in **Figure 5-8**, as color-coded 2D images extracted from different parts of the volume and as a video of the volume inspected under rotation. Inspection of the EDLC edge shows the presence of voids, which according to X-ray tomography analysis account for 1% of the volume in the full composite. These voids are undesired defects, mainly caused by the presence of dielectric tapes used to insulate the electrodes electrically from the CF layer.

Fig. 5-8 High-resolution a) 2D and b) 3D tomography image of CFs/epoxy composite, confirming penetration of epoxy resin through channels in the interleaf and showing the volume fraction of voids appearing at the edge of the EDLC.

The composite with the grid EDLC interleaf was subjected to 4-point bending tests and compared

against a control sample without EDLC interleaves. Bending stress-strain curves (**Figure 5-7c**) show that both samples had a similar elastic response and bending modulus, indicating effective shear stress transmission through the CF plies. The supercapacitor composite showed evidence of non-linear deformation at around 60 MPa and failure by localized buckling at 153 MPa, whereas the control sample presented linear-elastic behavior up to fracture at 215 MPa. In the multifunctional composite failure was triggered at the interleave edges (see **Figure 5-9a**). With the Al support and tape layers, the interleaf thickness is comparable (0.56 mm) to that of a CF lamina (0.4 mm), thus, plies are distorted in this region in order to accommodate the thickness variation imposed by the EDLC interleaf, producing stress concentrations that generate damage and local ply buckling upon loading.

Fig. 5-9 Electrochemical performance of structural SC before bending test and after buckling. (a) Photos of 4-point bending test setup and (b) Charge-discharge curves obtained before and after buckling of the structural SC.

Charge-discharge profiles demonstrate nearly identical electrochemical properties for whole and perforated EDLC interleaves, proportional to the effective electrode area (see **Figure 5-10a**). Differences observed in the Ragone plot for the two samples (**Figure 5-10b**) are mostly attributed to the difference in effective electrode area (32 cm² and 18 cm² for entire and perforated EDLC, respectively). Interestingly, the supercapacitor could still be charged and discharged after composite fracture, retaining its efficiency of 99%, 93% of power density and 69% of energy density as shown in **Figure 5-9b**.

Fig. 5-10 Comparison of electrochemical performance of regular 32 cm^2 EDLC interleaf and a modified samples with grid structure containing 18 holes. (a) Charge-discharge profiles and (b) Ragone plots (energy and power are normalized by the total mass of composite) obtained for structural SCs containing entire and modified EDLC devices. The energy and power densities of the grid electrode are pro rata with effective area.

5.2 The Second generation of structural SC

In previous section we presented a route for manufacturing structural supercapacitors through interleaving a self-standing all-solid EDLC device into a FRP laminate. However, further studies on coupled mechanical and electrochemical studies were hampered by the large presence of defects in the structure, most notably those arising from the presence of metallic current collectors, which essentially act as severe delaminations.

In this section, we present results on the fabrication of structural supercapacitor composites by resin infusion of glass fiber (GF) fabrics after integration of thin layers of CNTF fabric and polymer electrolyte without metallic current collectors. Coupled mechanical and electrochemical measurements are conducted under various loading conditions to assess the robustness of the multifunctional composite, showing resilience to fatigue in bending and no degradation of electrochemical properties. The multifunctional composite outperforms control samples with metallic current collectors with respect to both energy/power density and durability, highlighting the differences between multifunctional materials and multifunctional systems.

5.2.1 EDLC layer assembly and structural SC fabrication

The structural supercapacitors produced in this section consist of laminates of woven glass fiber fabric containing an integrated layer that can store energy by acting as an EDLC. The first step is

producing the EDLC by simply pressing two CNT fiber fabrics separated by a polymer electrolyte membrane comprised of ionic liquid and polymer electrolyte (PVDF-co-HFP).

After its assembly, the EDLC layer was laid up between GF plies and the whole lay-up vacuum infused with the Derakane thermosetting polymer. In addition to its impact on mechanical and electrochemical properties, the choice of matrix and polymer must be taken into account to ensure adequate compatibility between the components. CD and EIS measurements can be conveniently performed in situ during resin infusion to assess compatibility and other possible effects during fabrication. Indeed, when using a free-standing EDLC without any external current collector or insulation, the resin dissolved IL from the electrolyte membrane and caused electrochemical failure after composite fabrication, as proved in **Figure 5-11**. Replacing the IL-based electrolyte with an aqueous one is a possible simple solution. However, the higher operating voltage of IL and the corresponding higher power density of the devices, makes it is of interest to develop a general method for integration of IL-based ELDC layers in structural supercapacitor composites.

Fig. 5-11 (a) Digital image of the experimental set up used during in situ electrochemical test during resin infusion process. (b) Plot of Energy and coulombic efficiency over CD cycles during the in-situ infusion experiment, where a free-standing device without encapsulation was embedded in glass fibers. (c) Charge-discharge profiles of the device at different time after the infusion. (d) Schematic representation of the device failure mechanism showing percolation of liquid resin through the polymer electrolyte membrane during the infusion process, which leads to dilution of the electrolyte, followed by solidification of the membrane.

Our strategy is to encapsulate EDLC via two thin PVA film, as shown in **Figure 5-12a**. The resulting EDLC is extremely flexible (see **Figure 5-12b**) and has a thickness of $\sim 100 \mu\text{m}$ (see **Figure 5-12c**). Such current collector-free, flexible configuration leads to EDLC with $\sim 624 \text{ mF/g}$ capacitance, 656 W/kg power density, 1.12 Wh/kg energy density, as well as 98.6 % retention of capacitance after 10000 charge-discharge cycles at high current density of 5 mA/cm^2 (see **Figure 5-12d**).

Fig. 5-12 EDLC layer for integration in structural supercapacitor composite (a) Schematic of the EDLC composition; (b) Digital image of a thin, flexible EDLC, lighting a red LED; (c) Digital image of a free-standing EDLC during thickness measurement using a screw gage and (d) Relative energy density of the EDLC upon galvanostatic cycling at current densities of 5 mA/cm^2 for 10,000 galvanostatic cycles. Inset shows ragone plot.

The new EDLC with PVA encapsulation was then interleaved inside laminate through VARTM method (similar with **Figure 5-11a**). In situ electrochemical test during resin infusion process was conducted again. **Figure 5-13** shows the energy density and coulombic efficiency of an EDLC measured in situ during the infusion process. As can be seen in highlighted area, no change in energy density or columombic efficiency was observed when resin front flow through the EDLC region, which indicates a successful infusion process without influence on the electrochemical performance of the composite. Coupons were extracted from the panel using an electric saw and edges were polished by manual grinding with sand paper, as shown in **Figure 5-14c**. The fabrication method and laminate lay-up were purposely designed to produce samples for in-situ electrochemical studies

under mechanical loading, the main objective of this section.

Fig. 5-13 Plot of Energy and columbic efficiency over CD cycles during the in-situ infusion experiment

From a mechanical perspective, the introduction of a flexible and deformable film inside the composite laminate can induce strong displacement distortions because of the presence of non-connected plies. Shear connectors can alleviate such distortions caused by the presence of the supercapacitors. The strategy consists in using EDLC layers with a pattern of holes as supercapacitor interleaves. Upon infiltration, resin fill the empty spaces created by the holes interconnecting the adjacent laminate layers with resin structural rivets enabling an effective shear transmission between the plies [232].

There are almost endless combinations of different size, shape and number of holes. As a rational strategy to select a relevant combination of parameters close to an optimum, FEA (finite element analysis) simulation was performed on double slotted single-lap shear specimens (see **Section 5.4**). Based on simulation results, equally spaced, circular rivets of 0.8cm in diameter were chosen, producing an array with ~83% areal fraction of SC material (containing ~17% of rivets for shear transmission). This architecture provides relatively large power/energy density while retaining around 20% the shear strength relative to the fully connected laminate strength. Laminates containing supercapacitors without rivets were also produced for comparison. To understand the role of current collector and the riveting area of the EDLC on the electrochemical performance under the action of mechanical load, four types of samples were produced, as summarised in **Table 5-1**. The laminates consist of composite samples with the different combinations of supercapacitors: with and without rivets, and with either aluminium foil as current collector or with the CNT fiber material itself as current collector (see **Figure 5-14**).

Tab. 5-1 List of samples subjected to mechanical three point bending tests and electrochemical measurements.

Samples	A_{EDLC}	Current collector
CNTCC-100	100%	no
CNTCC-83	83%	no
AlCC-100	100%	Al
AlCC-83	83%	Al

Note: Al and CC are the abbreviations of Aluminium and Current collector, respectively

Fig. 5-14 (a) Schematics of Structural SC with and without Aluminium current collector; (b) Digital image of the EDLC after curing of resin. The four laminated samples named as device Al CC-100, Al CC-83, CNT CC-100 and CNT CC-83 as tabulated in Table 5-1.

5.2.2 In situ electrochemical characterization of structural EDLC during mechanical tests

The prepared four devices were then subjected to electrochemical measurements during quasi-static three-point bending tests (Figure 5-15a). The sequential testing protocol consisted in: i) in-situ CD and EIS during progressive 1mm deflection up to 8 mm deflection ii) 50 load/unload cycles to 5 mm deflection and CD and EIS every 10 cycles, iii) loading to sufficiently large deflection (12 mm deflection) until hearing acoustic emissions indicating a possible onset of fiber fracture. This latter step was followed by CD and EIS in the unloaded state.

The changes in mechanical and electrochemical properties throughout progressive deflection of patterned samples with and without aluminium current collector (Al-CC) are summarised in Figure 5-15(b-d). Their mechanical behaviour was almost identical, with a nearly linear and elastic behaviour and minor evidences of plastic deformation or damage. Possible differences in bending

stiffness can be attributed to sample preparation although they have no significant effect on the interpretation of electrochemical data recorded. Throughout the load and unload process the EDLCs without Al-CC show a negligible change ($<1.8\%$) in energy density; in contrast, the EDLCs with Al-CC undergo significant loss ($>30\%$) in energy density (**Figure 5-15c**). The main cause of this degradation is a continuous increase in electrical resistance, which in terms of ESR determined from EIS (**Figure 5-15d**) can increase by as much as 180%. For reference, the change in ESR of EDLCs without Al-CC is a drop of 9%.

Fig. 5-15 Electrochemical measurements during three-point bending (a) Digital image of the setup used for in situ measurements, with the sample under a deflection of 12 mm. (b) Load-displacement curves of the three-point bending specimens. CD and EIS measurements are performed during progressive deflection. (c) Plot of energy density against deflection for the different types of samples (d) Plot of energy density against deflection. Both (c) and (d) show no major changes for the CNTF samples, and rapid degradation for those with Al current collector.

The data in **Figure 5-15d** also indicate that the deterioration of the Al-CC sample continues during unloading. This mechanism was further studied by performing a “fatigue” test consisting of 50 bending cycles with 5 mm mid-span deflection, with CD and EIS collected every 10 bending cycles. Again, a nearly constant bending stiffness (**Figure 5-16a**) suggests no major change in mechanical properties of the overall composite that could propagate to the EDLC layer. A comparison of CD

cycles before and after the test shows that the CNT-CC sample remains unaltered, whereas the Al-CC specimen degrades from an already poorer performance (**Figure 5-16b, c**). As suspected, the latter undergoes continuous loss of energy density due to constant increase in ESR during repeated load/unload cycles (**Figure 5-16d**).

Fig. 5-16 Load/unload bending cycles to 5 mid-span deflection, and in-situ electrochemical measurements. (a) No major changes in bending stiffness are observed, indicating no degradation of mechanical properties. (b) CD profiles show no degradation of samples with CNTF current collector, but poor performance for Al-CC control samples. (c) Plot of energy density against bending cycle showing progressive damage during cycling when using Al-CC. (d) ESR determined from EIS is constant for CNTF devices but increases continuously during fatigue cycling and is the main cause for electrochemical deterioration of Al-CC comparator.

Finally, a more extreme bending test was performed by bending each laminate up to a large deflection distance of 12 mm, at a force of ~450 N (**Figure 5-17a**). Under this large deflection, fracture of glass fibers could be heard and white crack marks in the laminate could be observed. In spite of producing a large deflection reaching the onset of GF fracture, CD profiles (see **Figure 5-17b, c, d and e**) of the EDLCs before and after the test show that the composite can store energy and the sample with CNT-CC shows no electrochemical degradation. In contrast, the EDLCs with aluminium CC experienced a significant drop in the discharge time.

Fig. 5-17 (a) Plot of force over deflection distance for the extreme bending test. (Comparison of charge discharge profiles of the EDLCs before and after extreme bending experiments (deflection length 12 mm).

Figure 5-18 shows the relative change in energy density and in ESR throughout the complete testing procedure. As noted before, the samples with CNT-CC show no degradation of electrochemical properties, neither in continuous planar ELDC layer configuration nor with hole patterns for interply. In contrast, the samples with Al-CC, analogous to embedded devices, show a loss of energy density, mainly through an increase in ESR, causing an overall 80% decrease in energy density. Since this degradation occurs continuously during both loading and unloading cycles, it is related to failure of interfaces.

Fig. 5-18 Variation of (a) deflection length, (b) relative energy density and (c) relative resistance during in-situ electrochemical load/unload bending cycles.

To further investigate the origin of the electrical/electrochemical degradation mechanism, 3D X-ray tomography was performed to inspect the central part of supercapacitor composites with and without current collector. **Figure 5-19** shows the reconstructed image of a composite from 3D X-ray tomography experiments. The EDLC with Al-CC shows prominent areas of voids between the GF layer and the EDLC (**Figure 5-19d**, red arrow), but very importantly, there is extensive internal delamination of the ELDC. Electron micrographs confirm that there is detachment of the CNTF

layer from the Al CC (**Figure 5-20**), which we identify as the origin of the increase in electrical resistance and progressive degradation of electrochemical performance in the composite through successive loading. In contrast, the devices without metallic CC adapt to the wavy shape of the GF plies (**Figure 19 f and h**).

Fig. 5-19 Results of 3D X-ray tomography experiments. Reconstructed image of a composite containing EDLC (a) with Al CC and (e) without CC from 3D X-ray tomography experiments. (b-d, f-g) Representative cross sectional images of the area around EDLC. The red arrow in (d) shows buckling of CC due to bending.

Fig. 5-20 FESEM image of the EDLC with Al CC showing its detachment from the CNT-electrolyte membrane layer

5.3 Demonstrator of structural SC

In previous chapter, the possibility of removing metallic current collector has been successfully demonstrated, thus enabling to make ultrathin SC interleaves for structural power application. Considering the requirements of high voltage and high current for its practical application, it is important to scale up the fabrication process and design suitable connection among the supercapacitor components by series/parallel. However, unlike making test specimens, manufacturing a demonstrator with more embedded SCs will be more complicated and difficult since people need considering how to lay out and connect them.

Traditionally, copper wire is used to connect the component devices because of its high electrical conductivity. However, it may not be an ideal candidate in structural power system for the following reasons: First, the embedded wires inside laminates may function as delamination sources, which are harmful to the mechanical properties of structural power composites. Second, the use of a copper wire doesn't serve the purpose of weight-saving and will result in a compromise on the energy/power density of the laminate. Replacing copper wire with CNT strips can be a sound option because of their network structure of high aspect ratio building blocks, which endows them with a combination of electrical conductivity in the range of metals, with density similar to that of polymer and toughness above that of carbon fiber [197]. More importantly, interleaving thin CNT sheet will not increase the thickness of laminate and even enhance the interlaminar properties if a good infiltration

of resin is guaranteed, as discussed in **Chapter 4**.

To use CNT strips as connectors, it is important to establish a method for secured electric connection. Since CNT strips can be simply connected by solvent evaporation among overlapping area, first, the resistance before and after overlapping need to be checked. Secondly, resin will infiltrate through the CNT sheet during the vacuum bag infusion process because of its high porosity. This infiltration of resin might also alter the electrical resistance of CNT sheet.

In order to investigate the influence of both CNT overlapping and resin infiltration on its electrical resistance, a delicate experiment was performed as shown in **Figure 5-21a**, in which two CNT strips were simply connected by solvent evaporation and the overlapping region was then embedded inside a GFRP laminate via a mini bag infusion method. Several wires were soldered on the two sides of CNT strip for the convenience of resistance measurement though 4-probe method. As shown in **Figure 5-21b**, the electrical resistance increases linearly with increasing the measure length, indicating overlapping CNT strips produce functional electrical connection.

Fig. 5-21 (a) measurement of electrical resistance of CNT strip with 4-probe method and (b) the variation of electrical resistance of CNT strip with respect to length

After solving the connection issue, we can start to make preparation for the demonstrator manufacturing. **Figure 5-22** shows an example of multiple patterned EDLC layers tested in series before integration as a structural laminate supercapacitor. A significant benefit of the nanofabric route for multicell assembly is the possibility to assemble and test laminated EDLC layers as a

separate stage, before full integration as a structural device, which enables optimization of each process separately.

Figure 5-22 Patterned nanofabric EDLC layers assembled and tested in series before fabrication of structural laminate supercapacitor

A VARTM method was employed to fabricate the final demonstrator as shown in **Figure 5-23a**. Specifically, 16 layers of plain-woven glass fabrics with an approximate area of 1000 cm² was used as structural reinforcement. The choice of glass rather than carbon fabric was due to its transparency. Five EDLC devices were integrated in the top (between 1st and 2nd layers), mid-plane (between 8th and 9th layers) and bottom (between 15th and 16th layers) of laminate. The connectors (“tabs”) of each EDLC electrodes were CNT strips extended outside of the laminate to enable connections in series and/or parallel. These integrated conductors of CNT nanofabric provided more robust electrical connections and less disruption than metallic materials. No change was observed in the electrochemical performance of the EDLCs before and after the resin infusion process, which confirmed effective protection of the polymer electrolyte from the structural epoxy vinyl ester resin through the use of a thin PVA encapsulation, even though the thermoplastic was patterned to enable through-the-thickness resin flow. Finally, the structural supercapacitor laminate was subjected to several tests for emergency power cut systems. These included charging at different voltages, up to 30 V. Discharge profiles were measured at different charging voltages (**Figure 5-23 b and c**), including tests with different series/parallel connections to demonstrated successful operation and flexibility for electrical reconfiguration.

Fig. 5-23 Structural supercapacitor demonstrator: electronics box for aerospace power network. A) Fabrication of the structural device based on nanofabric EDLC layers and a $[0^\circ]_{16}$ plain-woven glass fabric laminate. B) Photograph of test set-up during operation and C) Discharge profiles of the structural supercapacitor charged at different voltages

5.4 Laminated structural power composites (SPCs) with interconnecting rivets: interlaminar properties and multifunctional design

The rivet interlocking route (**Figure 5-24**) has proved to be very effective in enhancing the shear properties of structural power composites [232, 233]. It also enables rapid progress on SPC development by circumventing the intrinsic challenges in making a structural polymer electrolyte [9]. However, there are multiple questions about the relationship between interlaminar properties and the unusual composite structure in SPCs, that remain open. These include aspects such as the effect of the rivet shape, the number/area of rivets required to meet design specification of strength and stiffness, the importance of location and shape within the composite structure to maximize the reinforcement effects, etc.

Fig. 5-24 3D schematic illustration of (a) Structural Supercapacitor and (b) Structural lithium-ion battery. An array of through-thickness rivets is used to interlock a stack of typical Li-ion battery electrodes three-dimensionally. These rivets are securely anchored on the encapsulating CFRP facesheets, allowing the entire unit to act as a mechanically-efficient sandwich structure.

The objective of this section is to answer the aforementioned questions, thus providing a guidance for rivet structure design when similar reinforcing strategies were used. In this work, double-notch shear simulations were employed to evaluate the shear properties of structural power composites with different rivet structures. In parallel, experimental tests were performed to valid the proposed simulation model. The resulting model is particularly useful to design SPCs with tailored balance between the energy/power densities and structural properties, thus opening the multifunctional spectrum.

5.4.1 A numerical framework for rivet design

Model description

A finite element analysis (FEA) was carried out to address the effect of the rivet structure on the mechanical performance of laminated materials containing EDLC devices using Abaqus (2016). The geometry corresponded to the dimensions of the double slotted single lap shear specimens was presented in **Figure 5-25a** with length, width and thickness of 200 mm, 48 and 3.1mm, respectively. Two CFRP symmetric adherents with a total thickness of 1.5 mm were modelled as linear elastic with 8-node linear brick elements with reduced integration (C3D8R) through the thickness. The material of the adherents corresponded to a linear and elastic orthotropic solid with the representative properties $E_1 = E_2 = 70GPa$; $E_3 = 7GPa$; $\nu_{12} = \nu_{13} = \nu_{23} = 0.3$; $G_{12} = G_{13} = G_{23} = 5.5GPa$.

A 100 μm adhesive layer was inserted between two adherends and modelled with 8-node three-dimensional cohesive elements (COH3D8). Both adherent and cohesive meshes were conformal sharing common node positions at the interface between them. The cohesive layer geometry was partitioned in three regions: connecting epoxy rivets, EDLC material and perfect interface between the CFRP adherends as appears in **Figure 5-25b**. A traction-separation constitutive response was adopted for the complete cohesive layer with different mechanical properties corresponding to the three aforementioned regions.

Figure 5-25c shows a typical bi-linear traction-separation law of cohesive elements. The n-subscript refers to the normal direction of the cohesive element; s and t subscripts are the first and second in-plane shear directions, respectively. The cohesive element constitutive law relates the traction components transmitted by the cohesive elements, namely t_n , t_s and t_t with the corresponding components of the relative displacement δ_n , δ_s , and δ_t . An initial response of the cohesive elements is assumed to be linear and elastic following the stiffness matrix:

$$\begin{bmatrix} t_n \\ t_s \\ t_t \end{bmatrix} = \begin{bmatrix} K_n & 0 & 0 \\ 0 & K_s & 0 \\ 0 & 0 & K_t \end{bmatrix} \begin{bmatrix} \delta_n \\ \delta_s \\ \delta_t \end{bmatrix} \quad (5-1)$$

where K_n , K_s and K_t stand for the stiffness components in normal and shear opening,

Fig. 5-25 (a) Schematic of double-notch shear test specimen; (b) Material assignment; (c) Typical bilinear traction-separation law and (d) Schematic of the mixed-mode cohesive zone model, in which stress interaction law maps the damage initiation and BK fracture criterion maps the delamination growth.

respectively. It is assumed that the cohesive response in the plane s-t will be isotropic, thus $K_s = K_t$. In addition, normal n and shear s-t opening modes will be fully decoupled. The onset of the elastic behavior is attained when the tractions transmitted by the cohesive elements achieve a damage initiation criterion. In this work, the quadratic interaction criterion (QUADS) was selected to this end.

$$\left(\frac{\langle t_n \rangle}{N}\right)^2 + \left(\frac{t_s}{S}\right)^2 + \left(\frac{t_t}{S}\right)^2 = 1 \quad (5-2)$$

where N and S are the normal and shear strength of the cohesive elements under pure normal and shear opening. In the latter expression, $\langle \quad \rangle$ stands for the McCauly bracket defined as $\langle x \rangle = (x + |x|)/2$ which is introduced to avoid damage of the cohesive element under normal compressive forces. After fulfilling the damage initiation criterion, the interface degrades depending on the traction-displacement history. A damage variable d is introduced in the elastic constitutive law:

$$\begin{bmatrix} t_n \\ t_s \\ t_t \end{bmatrix} = (1 - d) \begin{bmatrix} K_n & 0 & 0 \\ 0 & K_s & 0 \\ 0 & 0 & K_t \end{bmatrix} \begin{bmatrix} \delta_n \\ \delta_s \\ \delta_t \end{bmatrix} \quad (5-3)$$

with extreme damage variable ranging between $d = 0$ (perfect behavior) and $d = 1$ (fully damaged cohesive elements). Such damage d variable evolves under a mixed-mode loading history according to the Benzeggagh-Kenane fracture criterion [234], where the critical fracture energy under mixed-mode G_c depends on the mixed-mode ratio according to

$$G_c = G_{Ic} + (G_{IIc} - G_{Ic}) \left(\frac{G_s + G_t}{G_n + G_s + G_t} \right)^\eta \quad (5-4)$$

where η is the BK power exponent and G_n , G_s and G_t the reciprocal work released during the loading history.

The properties assigned to each of the material partitions created in the cohesive layer stated as following: first, for the perfect interface, the strength of the material was assumed to be high enough to suppress any possibility of damage as it occurs during testing; second, the EDLC interface was assumed to be extremely weak so the stress between the adherents is transferred entirely by the epoxy rivets; third, the epoxy rivets will behave following the cohesive crack model. **Table 5-2** gives the normal cohesive properties, corresponding to epoxy rivets. Then the normal and shear stiffness of the cohesive elements will be computed as $K_n = E_{Adh}/t_{Adh}$ and $K_s = K_t = G_{Adh}/t_{Adh}$, where $G_{Adh} = E_{Adh}/(2(1 + \nu_{Adh}))$ stands for the shear moduli and $t_{Adh} = 100\mu m$ is the adhesive layer

thickness.

Table 5-2 Material properties of epoxy film adhesive (Hysol® EA 9695™) [235]

Tensile strength	T_{Adh}	48 MPa
Maximum elongation at break	ϵ_{tmax}	11.5 %
Tensile modulus	E_{Adh}	2019 MPa
Poisson ratio	ν_{adh}	0.34
Critical strain energy release rate (Mode I)	G_{IC}	1.019 kJ/m ²
Critical strain energy release rate (Mode II)	G_{IIC}	0.783 kJ/m ²

The two notches were introduced in the specimen at opposite surface of the specimens via the assign-seam method in Abaqus. The seam method automatically duplicates mesh nodes in the notch area allowing for the displacement discontinuity between two opposite free surfaces. At the left side all six degrees of freedom (DoF) are fixed, while on the right side, solely longitudinal displacement is allowed (x-direction).

5.4.2 Preliminary verification of FEA model

Sample preparation and testing

The CFRP adherends with stepped shape come from previous lap shear test of slotted samples, as shown in **Figure 5-26**. Before preparation, the surfaces were carefully cleaned by polishing machine. Then two adherends were glued together by epoxy film adhesive (Hysol® EA 9695™). A thin Teflon film was inserted to serve as EDLC embedment. In this work, 4 different Teflon inserts were prepared, on which 2 holes were generated by laser cutting machine. These holes allow the epoxy penetrate through the Teflon film during the curing process and create a rivets to join the adherends together. After laser cutting, Teflon inserts were covered with release oil to avoid possible adhesive force with resin. Finally, all the samples were cured in oven (120 °C) for 2 hours under vacuum condition. A lapshear shear test was carried out in a universal electromechanical testing machine (INSTRON 3384), using a loading rate of 0.1mm/min.

Figure 5-26 Details for preparing single lap shear specimen

Comparison of simulation and experimental results

The effective area ratio (η) was defined as energy storing area (real area of supercapacitor) divided by the total shear area (see **Figure 5-27**). During the experimental lap-shear test, 5 groups of samples were prepared, namely $D = 3, 6, 8$ and 16 mm and baseline (fully banded), corresponding to an effective area ratio of 99%, 95%, 91%, 65% and 0%, respectively. In comparison, 7 different cases were simulated with rivet sizes of $D = 3, 6, 8, 12, 16$ and 22 mm, as well as a fully banded case. The comparison analysis showed that the simulation model gave good predictions of shear force with a variation less than 5% when effective area ratio $\eta > 30\%$.

Fig. 5-27 Comparison of simulation and experimental results, in which different rivet sizes were tested and simulated.

However, there was considerable discrepancy between simulation and experimental values of fully banded specimens. This prominent variation can be ascribed to the complicated failure mechanisms of fully banded specimens, which are difficult to capture during the simulation. **Figure 5-28** detailed the fracture surfaces of single lap shear samples with different rivet structure. When the diameter of the pin is less than 16 mm, the cohesive failure is dominated. While when using bigger pins (i.e. D=16mm or full banded), both cohesive and adhesive can be observed on the fracture surfaces. Sometimes, the crack even propagates inside the CFRP adherend and triggers carbon fiber bridgings (**Figure 5-28e**), leading to a more complicated failure mechanism.

Fig. 5-28 Failure surfaces of single lap shear specimens showing that different failure mechanisms

5.4.3 Parameter analysis

Effects of rivet shape

Three different shapes of rivet geometries were considered in this section as listed in **Figure 5-29a**, including circular, ellipse and square with different alignments. Their areas were kept constant and equal to the area of 2 circular rivets with a diameter of 8 mm. Ellipse (0°) means that the angle between the major axis of ellipse and the force direction is zero, while Square (0°) stands for that the angle between the bottom edge of square and the force direction is zero, as illustrated in **Figure 5-29a** (alignment).

Figure 5-29 b and **c** displayed the simulated results of single lap shear tests with different rivet shapes and alignments. Specifically, Square (0°) and Circle shared the very similar shear behaviors with two force-displacement curves near coincided with each other. Ellipse (90°) showed the highest relative shear strength, followed by Square (0°)/Circle, Square (45°) and Ellipse (0°), respectively. In terms of relative shear energy (the area under the relative force-displacement curve), Square (0°) and Circle were top-ranked, followed by Square (45°), Ellipse (90°) and Ellipse (0°), respectively. It should be emphasized that the shear performance of ellipse rivets with a large eccentricity (i.e. $e=0.968$) displayed a prominent directional sensitivity. Specifically, Ellipse (90°) far outweighed Ellipse (0°) in terms of relative shear strength and shear energy. Although square shaped rivets

showed different shear behavior along different directions, this directional sensitivity is marginal. In general, circle rivet presented the best shear performance, which can be attributed to its least significant stress concentration effect.

Fig. 5-29 The definition of rivet shape and alignment; (b) Relative shear force vs. displacement curves of single lap-shear simulation with different rivet shapes and alignments and (c) Comparison of relative shear properties.

Note: all values were normalized by corresponding maximum value

Effect of rivet distribution

In this section, the total area of circle rivets was kept as constant. The diameter of rivets varied from 1.5 mm to 12 mm, with numbers of rivets correspondingly changing from 36×18 to 2×1 , as shown in **Figure 5-30**. It is interesting to note that, with increasing the degree of homogenization, the relative shear rigidity (the slope of relative shear force vs. displacement curve) increases significantly at initial stage, and then gradually converge toward a constant. In comparison, the relative shear strength decreases considerably at first, and then levels off too. It seems with homogenizing the distribution of rivet structure (increasing the number density of rivet), the shear performance will finally converge to a single state, relating to the inherent properties of materials.

Fig. 5-30 the evolution of shear performance with changing the degree of homogenization (η remains constant)

Effect of effective area ratio

2x1 configuration

The simulation campaign started with the simplest case, 2x1 configuration, as shown in **Figure 5-31**. With increasing the diameter of round rivet from 3 to 22 mm, the effective area ratio varies from 98.8% to 34.0%. Full bonded sample (without SC) was set as baseline. When no epoxy rivet was used, the shear strength was proved to be negligible. A prominent non-linear relationship between relative shear strength and effective area ratio was obtained, which can be ascribed to the localization of rivet distribution. Noting that relative shear stiffness dropped nearly 50% when effective area ratio reaches up to 97.8%, which is detrimental to the structural rigidity when suffered shear loads. It should also be emphasized that shear stiffness is extremely important in structural power design with embedded technology. Since energy storage devices are essentially interleaved in the interlayers. Lower shear stiffness means larger shear deformation under constant shear loads, and larger shear deformation very likely would fail the energy storage devices.

Fig. 5-31 the evolution of shear performance with changing the effective area ratio (2x1 configuration)

16x8 configuration

Previously, we found that when the number density of rivet is bigger than $(16 \times 8)/(48 \times 24) = 1/9 \text{ mm}^{-2} \approx 1.1 \times 10^5 \text{ m}^{-2}$, shear properties (i.e. shear strength and stiffness) of resultant sample will convergent to constant values, which can be treated as its inherent material properties. In this section, 16x8 is selected as basic distribution of circle rivet within a $48 \times 24 \text{ mm}^2$ region. A systematic simulation campaign was performed with effective area ratio varying from 0 to 1, as schematically exemplified in **Figure 5-32**. It was worth noting that the relative shear stress of 16x8 configuration, in sharp contrast to that of 2x1 configuration, decreased quasi-linearly with increasing the effective area ratio. More interestingly, relative shear stiffness only showed a marginal drop when η changing from 0 to 80%, which far outperforms that of 2x1 configuration.

Fig. 5-32 the evolution of shear performance with changing the effective area ratio (16x8 configuration)

Discussion

It is obvious that number density of rivet exerts huge influence on the evolution of shear behavior. When this value is small, i.e. $(2 \times 1) / (48 \times 24) \times 10^6 \approx 1.7 \times 10^3 \text{ m}^{-2}$, there is a clear non-linear relationship between relative shear stress and effective area ratio. While a large number density was selected, for instance, $(16 \times 8) / (48 \times 24) \times 10^6 \approx 1.1 \times 10^5 \text{ m}^{-2}$, a quasi-linear relationship was distinguished. Thus it can be inferred that a linear relationship will be infinitely approached with increasing the number density of rivet as shown in **Figure 5-33**. When the rivet has a relatively large size and its number density is small (the degree of homogenization is low), there exist two types of nonlinearity: 1. Nonlinear Geometry: the changing shape of a model when large deformations exists provides nonlinear changes in the components stiffness; 2. Nonlinear Boundary Condition: boundary conditions that involve components in contact with one another often produce disproportionate changes in deformation. Thus the geometric shape and spatial distribution of rivets will exert a significant influence on the damage evolution of rivets (see **Figure 5-34a**). The obtained relative shear stress vs. effective area ratio curve thus depends not only the inherent material properties, but also the structure properties. With increasing the degree of homogenization (decreasing the diameter of the rivet), the structural influence of rivet is gradually weakened and the damage evolution of

rivets are more inclined to behave in a linear way (see **Figure 5-34b**). The homogenized rivet-reinforced laminate will finally can be treated as a regular laminate, which has constant material parameters and can be characterized by standard testing protocol.

Fig. 5-33 the evolution of relative shear stress vs. effective area ratio curve with increasing the degree of homogenization

Fig. 5-34 damage evolution during lap shear simulation: (a) 2x1 configuration and (b) 16x8 configuration

5.4.4 Shear properties of perforated Structural supercapacitor: experimental investigation and modeling prediction

In **Section 5.4.2**, we conduct a preliminary verification of FEA model through experimental investigation. The single lap shear specimens were manufactured by simply bonding two CFRP adherends with epoxy film adhesive. A Teflon film was used to simulate the SC configuration. However, in real structural power application (i.e. the demonstrator shown in **Section 5.3**), the configuration and mechanical environment of SCs are much more complicated, which are hardly replicated by the test campaign described in **Section 5.4.2**. In this section, the lap shear specimens were directly derived from the structural SC. The real lap shear strengths (LSS) of specimens with different effective area ratios were obtained, which were then utilized for generating the real envelope of LSS for perforated Structural SC.

Sample preparation

Hole pattern design

In **Section 5.4.3**, we found that when the number density of rivet is bigger than $1.1 \times 10^5 \text{ m}^{-2}$, the shear property of resultant laminate will be independent with rivet distribution, which can be served as its inherent material properties. So 16x8 is selected as basic distribution of circle rivet within a 48 x 24 mm² region, similar with simulation campaign detailed in **Section 5.4.3 (Effect of effective area ratio/16x8 configuration)**. Considering the technical difficulties with the laser cutting resolution and the process of resin infusion, small holes were avoided. The diameters of the holes were selected to be 1.5, 2.0 and 2.5 mm, corresponding an effective area ratio of 80.4%, 65.1% and 45.5%, respectively. Hole patterns were produced by cutting EDLC layers with a ZING 16/24 laser cutting machine (Epilog Laser) as shown in **Figure 5-35c**.

The preparation of Double-Notch Shear test specimen for perforated Structural SC

The choice of glass fabric rather than carbon fabric is because of its transparency (see **Figure 5-35f**), which makes it relative easy to locate the middle plane of structural supercapacitor. The notches were cut utilizing a water-refrigerated milling machine as displayed in **Figure 5-35g**. **Figure 5-35h** demonstrated a representative slotted single lap-shear specimen embedded with a perforated EDLC. The notches were carefully milled up to the surface of EDLC layer. A cross-sectional image collected under optical microscope (**Figure 5-35i**) showed an interleaf thickness of 200 μm , corresponding the shear thickness.

Fig. 5-35 The preparation of slotted single lap-shear specimen from perforated Structural supercapacitors: (a) EDLC layer assembly; (b) hole pattern design via Inkscape software; (c) laser cutting execution; (d) preform lay-ups with a perforated EDLC interleaf; (e) epoxy infusion; (f) demolding of laminates after curing at room temperature for 72 hours; (g) notch generation; (h) well-prepared slotted single lap-shear specimen and (i) cross-sectional images of structural SC.

Single lap-shear test

As shown in **Figure 5-36a**, the single lap-shear test was carried out in a universal electromechanical testing machine (INSTRON 3384), using a loading rate of 0.1mm/min. An extensometer with a 12.5mm gauge length was used to measure the notch opening of the specimens. An infrared level meter was employed to vertically align the specimens during the installation. Digital Image Correlation (DIC) was also adopted to investigate the possible influence of rivet structure on the strain distribution of the specimen surface. To this end, a white paint was first sprayed followed by the dispersion of black dots to create the speckle pattern necessary for the measurements. **Figure 5-36c** presented the representative shear force-displacement curves of double-notch shear test specimens with 16x8 rivet pattern. Noting that the shear rigidity changes marginally with increase the diameter of rivets, in line with the simulation results of **Section 5.4.3 (Effect of effective area ratio/16x8 configuration)**. The vertical displacement obtained through DIC analysis was presented

in **Figure 5-36b**. The color distribution indicates that the rivet structure exerts negligible influence on the strain distribution and the point shear force transmitted by the rivet is homogeneously transferred to both specimen halves.

Fig. 5-36 (a) Testing setup; (b) DIC analysis and (c) Representative force-displacement curves of double-notch shear test

Figure 5-37 displayed the fracture surfaces of lap shear test specimens. In the three cases analyzed, the fracture surfaces are very similar indicating an effective connection of the tested specimens by the epoxy resin rivet structure. A closer observation of the epoxy rivet area suggested two different fracture mechanisms: firstly, some of the rivets showed fiber imprints, indicating that fiber/matrix debonding was the dominant damage mechanism; secondly, numerous hackles in epoxy rivets (or ‘cusps’ as they are alternatively known) can also be distinguished, suggesting a shear stress state transmitted through them. “Hackle markings” are one of the most important fractographic features observed in polymer composites, frequently found in mode-II and mixed-mode(I/II) delamination growth because of the shear stress [236, 237].

Results and Discussions

Figure 5-38a displayed the comparison of experimental results and model prediction of single lap shear test. It should be pointed out that the input data of new simulation campaign were tuned based on the experimental results of D=1.5 mm (16x8) and other two cases (D=2.0 mm and D=2.5 mm) are simulation predictions using tuned input data. The predicted shear properties are in good agreement with the experimental results in terms of shear rigidity (the slope of shear force vs. displacement curve) and lap shear strength (LSS). Specifically, the shear rigidity nearly maintains

the same with increasing the diameter of rivets from 1.5mm to 2.5mm, in line with the experimental findings. The predicted LSS values are within 6% margin of Error (see **Figure 5-38b**), which is precise enough for most of the engineer applications.

Fig. 5-37 (a-c) The fracture surface of the lap shear specimens; (d) the woven fabric imprint in the epoxy rivets can be easily observed; (e-g) SEM images with details of the fracture surfaces at the rivet connection.

Previous study, **Section 5.4.3 (Effect of effective area ratio/16x8 configuration)**, has already predicted a quasi-linearly relationship between LSS and effective area ratio (η) when 16x8 rivet configuration was adopted, especially when η is within a range of 0-0.8. In order to obtain the real envelop of LSS for perforated structural supercapacitor, a linear fitting was firstly used for 3 simulated points. The intersection with y axis in the left could be the Lap shear strength of non-interleaved laminate. The change of energies with respect to the effective area ratio can be found in our previous research [238]. Thus the envelope of multifunctional properties of the grid-shaped EDLC interleaf architectures was created as shown in **Figure 5-38b**, which can be served as a guidance for Structural SC design.

Fig. 5-38 (a) Comparison of experimental investigation and model prediction of shear test and (b) Envelope of multifunctional properties for Structural SC design

5.5 Summary

In this chapter we present the fabrication of a novel structural composite supercapacitor based on CNT fibers/polymer electrolyte interleaves embedded between fabrics and infused by epoxy. The method is simple and compatible with industrial composite fabrication techniques.

In section 5.1, we reported the first generation of structural SC in our lab, in which aluminum foil was used as current collector. Once embedded in the composite structure, the EDLC interleaves had identical electrochemical properties as before, with Coulombic efficiency of 98% and low ESR of 35 Ohm cm² even when charged at 3.5V. In situ electrochemical measurements during 4-point bending were performed on composites with EDLC interleaves at different ply positions in order to study the tensile, neutral and compressive scenarios. The results show that electrochemical properties were essentially retained under high flexural deformations and stresses (70 MPa). Changes in ESR produce 10-37% increases in energy density upon initial loading, and a drop of 22% at large strains. Even after sample failure by buckling the devices could still be charged and discharged, with 69% and 93% of the initial energy and power densities, respectively.

In section 5.2, the second generation of structural SCs were fabricated by vacuum bag resin infusion of a lay-up containing glass fiber, CNT fiber fabrics and an IL-based polymer electrolyte, without metallic current collectors. Mechanical interconnection of GF plies through the EDLC can be achieved by patterning holes in the EDLC layers, which are subsequently filled with resin during infusion and form resin plugs, or rivets. With a pattern of circular holes of 8 mm diameter and a fraction of 17% holes relative to EDLC, projected power and energy densities of 172 W/kg and 0.3 Wh/kg, respectively, could be reached, combined with an estimated 20% of interlaminar shear strength relative to the fully connected composite layers. The robustness of the structural supercapacitor composites was evaluated by a three-point bending protocol including progressive deflection, repeated load/unload cycles and deflection up to GF fracture, combined with in/ex situ electrochemical measurements. The multifunctional material developed in this work shows no appreciable degradation of its electrochemical properties, a consequence of the use of the CNT fiber fabric electrode as current collector. In contrast, control samples with Al current collectors,

analogous to embedded devices, show rapid and progressive degradation of their properties, mainly caused by an increase in electrical resistance through internal delamination of the ELDC components.

In section 5.3, a demonstrator of structural SC was successfully manufactured, confirming the scalability of our proposed method for structural SC fabrication. The demonstrator was then subjected to several tests according to specifications by Airbus and showed a good performance.

Finally, section 5.4 reports on the use of FEM simulation and experimental tests to study the micromechanics of interlaminar epoxy rivets in SPCs. It explores the effect of multiple rivet parameters (size, area, shape) on single-lap shear strength/energy, and the transition from materials to shape-dominated interleaf properties. The results provide a validated methodology to design laminated structural composites with tailored balance of multifunctional properties of wide application to structural power composites of different constituents, with storage either as capacitors or batteries.

CHAPTER 6

Conclusions and future works

“There is no such thing as a great talent without great will-power”

- Balzac

6.1 General conclusions

In this thesis, CNT veils were integrated inside FRP composites for both interlaminar toughening and energy storage purposes. For the sake of a better understanding, the main conclusions that can be drawn from this thesis have been associated to the specific aspects and are listed as follows:

CNT veils for interlaminar toughening

Assembling micro CNTs to macro fiber veils is a promising way to fully explore the excellent properties of these nanomaterials on a macroscopic scale. Furthermore, since there is no need to disperse them into the matrix, there exists no disadvantages such as an increased viscosity or inhomogeneous dispersion which makes them suited candidates for most laminate manufacturing routes. In general, CNT veil based approaches provide completely new fields for the application of CNT with advantages not only simplifying the integration process but also significant mechanical enhancement. Next to the highly effective use of nanofiller reinforcement materials, it bears the feasibility of scale-up for real industrial manufacturing.

A simple new methodology combining Raman analysis and direct optical observation was used to study crack propagation in different samples. Effectively, Raman spectroscopy can be used as a convenient and powerful tool for fractography analysis by unambiguously providing compositional information over large areas of the fracture surface and relating it directly to the color of the distinctive regions. The analysis results showed that interlaminar crossing plays a dominant role amongst toughening mechanisms. The crack front propagates alternately between interfaces of the laminate, triggering multi-level fiber bridging and significantly improving the fracture toughness of the laminate.

The toughening effects of CNT veils depend highly on their degree of compaction and thickness. The densification of CNT veil via solvent exposure will lower its permeability and thus inhibit the through-thickness percolation of the resin in infusion methods. While mechanical densification exerts much less impact on the porosity/microstructure of CNT veils compared with liquid exposure methods, and resultant CNT interleaves were proved to be suitable for VARTM application. $G_{IC,prop}$ increased as much as 77% and 76% after interleaving mechanically-densified CNT veils with a thickness of 5 and 10 μm , respectively. These were associated with a significantly ‘rising’ trend of the R-curves, indicating there are extensive carbon fiber bridging within the fracture process zone. However, $G_{IC,prop}$ strikingly dropped by 36% as the thickness of the CNT veils reached up to 15 μm , which might be ascribed to the uncompleted resin infiltration of CNT veils.

The host fabric architectures and loading conditions also exert a clear influence on the toughening effects of CNT veils. In unidirectional laminate, the fabric ply is quite flat and smooth, hence the majority of CNTs are parallel with the delamination plane of the DCB specimen. As the crack is driven by Mode I (opening) loading condition, the CNTs are loaded transversally and peeled off from the matrix resin without much deformation. In woven laminate, the woven architecture of the fabrics probably resulted in tiny regions where the local crack growth was not purely Mode I or where the crack growth direction was not perfectly parallel with the plane of the interlayer, triggering a better load transfer to the CNTs and more fiber-bridgings, resulting in a significant enhancement of fracture energy consumption. It was also found that laminate composites incorporated with same interleaf materials perform quite differently in Mode I and Mode II loading conditions. Some material properties may exert a positive or a negative influence on each mode of interlaminar failure. Both kinds of failures are complicated, with Mode I case being proved by peel stress and Mode II being dominated by shear stress, and it is really a challenge to figure out which material properties or their combinations are most likely to affect crack initiation and propagation behaviors, thus changing the final fracture toughness.

CNT veils for structural power application

CNT fiber veils, with their high specific surface area, excellent mechanical properties as well as the remarkable electrical conductivity, could be ideal candidates of electrodes and current collectors for

structural power application. This thesis has successfully demonstrated CNT veils as essential part of supercapacitor were integrated into FRP laminates, achieving simultaneously and synergistically both load-carrying and energy storage capabilities. A simple and scalable fabrication method was developed, in which CNT veils-based EDLC interleaves were imbedded between carbon/glass fabrics, followed by resin infusion and curing of a thermosetting polymer. Electrochemical behaviour of the device was evaluated during epoxy infusion, after resin curing and during flexural deformation. It was found that a high coulombic efficiency and stability of EDLCs can be maintained during resin infusion. However, further studies on coupled mechanical and electrochemical properties were hampered by defects arising from the presence of thick metallic current collectors. By using CNT veils not only as active material but also as current collectors, the total thickness can be saved and a true multifunctional composite material was produced, which can sustain mechanical deformations without degradation of electrochemical properties even under high-deflection bending and repeated load/unload cycles.

Structural power composites (SPC) can be made by introducing energy-storing layers in composite laminates, either as embedded devices or as thin integrated interleaves simultaneously performing load-bearing and electrochemical energy storage functions. However, the solid electrolyte in these layered architectures is typically a soft polymer, thus making the SPC prone to delamination, especially under unfavorable loading conditions like out-of-plane tension and in-plane compression. Mechanical interconnection using structural matrix bridges between lamina, analogous to epoxy rivets, provides a solution for alleviating the delamination risks and maintaining the structural integrity of SPC even under most unfavorable combinations of loads.

A finite element model approach was employed to explore the effect of rivet structures on the lap shear behaviour of laminated materials containing EDLC devices. In parallel, experimental tests were performed to valid the proposed simulation model. It was revealed that interconnecting rivets in circle shape outperformed in other shapes in terms of comprehensive shear performance under double-notch shear test. The average lap shear strength of rivet reinforced structural power composites depends on not only the rivets area (or effective area ratio) but also the distribution of the rivet structure. With homogenizing the distribution of rivet, the shear performance will shift from

non-linear to quasi-linear, and finally converge to a single state, more related to the inherent properties of materials, rather than structural properties.

6.2 Future works

Crack-bridging and CNT pull-out play an essential role in toughening of CNT based composites and their dominance is generally dictated by the adhesion between the reinforcing CNT and surrounding polymer and the intrinsic strength of the CNT. Crack-bridging is favored when the adhesive strength exceeds the strength of the CNT whereas the pull-out toughening mechanisms favors a weak interface. Both mechanisms present great potential to improve the fracture toughness of the CNT-toughened composite. Therefore, it becomes desirable to investigate the properties of the interface between CNT and matrix in order to provide greater insight into these key toughening mechanisms. The pull-out test [239] or microdroplet test [240] may be employed.

Conducting in-situ Mode I (opening) test under optical microscope or SEM can not only enable us observe the crack propagation behavior of hierarchical CF/CNT veils/epoxy laminate at micro scale so as to get a deep insight into the toughness mechanisms of nanocomposites, but also provide with a direct way to measure the critical length of process-zone [241], which plays an important role in modeling verification. However, carrying out DCB test under optical microscope or SEM is impossible due to the space and loading issues. Wedge-insert fracture (WIF) test, which transfer the opening behavior into compression one, offers a solution. This method was first proposed with the aim of applying to dynamic fracture test [242], and recent trials involving specimen preparation and pre-testing under optical microscope as shown in **Figure 6-1** and **6-2**, have confirmed the feasibility.

Fig. 6-1 Theory, specimen preparation method and grips design of the mini WIF test

Figure 6-2 Set-up of the mini WIF test

The development of multiscale modeling strategies enables us deal with the inherent complexity of hierarchical materials, in which the structure and properties at small length scales determine the macroscopic behaviour. CF/CNT veils/epoxy composite bears hierarchical structure as schematically shown in **Figure 6-3**, which leads to three different length scales: (i) nanotoughened epoxy (nm), (ii) nanotoughened interlaminar region (μm), and (iii) nanotoughened laminate (mm).

This clear separation of length scales is very useful to carry out multiscale modelling by computing the properties of one entity (e.g., nano-toughened epoxy) at the relevant length scale, homogenizing the results into a constitutive model, and passing this information to the simulations at the next length scale to determine the mechanical behaviour of the larger entity. (e.g. nano-toughened interlaminar region).

Fig. 6-3 Multiscale approach for analyzing the toughening mechanisms in composites interleaved with carbon nanotube veils.

Since CNTs possess exceptional mechanical properties as well as excellent electrical conductivity and piezoresistivity, they can be utilized not only to toughen the weak interlaminar layer, but also to enable FRP structures with damage sensing capability. Though abundant works have been performed in damage sensing field with CNTs, a comprehensive understanding of utilizing CNT veils/mats in FRP for both interlaminar toughening and structural health monitoring purposes remains lacking. Not to mention the gap between lab-scale findings and real engineering applications, and how to interpreting existed knowledge to real industrial practice in structural components.

Nowadays electromagnetic interference (EMI) shielding and lightning strike protection (LSP) are pressing issues in aerospace industry. Currently aerospace parts employ a layer of a metallic mesh for such function without any structural contribution. However, metal meshes with high mass density and roughness will unavoidably increase total weight and airflow resistance during the flight, leading to increase of fuel consumption. Furthermore, metallic materials may introduce breakage or exfoliation in the long-term application, because of their easy corrosion and inferior resin compatibility. CNT veils, in comparison, are flexible and extremely light, which can be interleaved in any composite structure to simultaneously provide LSP and EMI shielding functions with minimal weight penalty. Most importantly, the integration of CNT veils into FRP composites does not require any special techniques and can be easily realized by employing standard fabrication methods. In addition, CNT veils with micron pores and large surface area has better resin compatibility than metal materials in the model process of CFRP composites, which can also contribute to structural function.

CHAPTER 7

List of publications and conferences

“Our destiny offers not the cup of despair, but the chalice of opportunity”

- Richard Nixon

1) International Peer-reviewed Journal Papers:

1. **Yunfu Ou**, Carlos González*, and Juan José Vilatela*. Understanding interlaminar toughening of unidirectional CFRP laminates with carbon nanotube veils. *Composites Part B: Engineering*, 2020, <https://doi.org/10.1016/j.compositesb.2020.108372>.
2. **Yunfu Ou**, Carlos González* and Juan José Vilatela*. Interlaminar toughening in structural carbon fiber/epoxy composites interleaved with carbon nanotube veils. *Composites Part A: Applied Science and Manufacturing*, 2019, 124: 105477.
3. Moumita Rana†, **Yunfu Ou**†(co-first authors), Federico Sket, Carlos González, Juan J. Vilatela*. Damage-tolerant, laminated structural supercapacitor composites enabled by integration of carbon nanotube fibers. *Multifunctional Materials*, 2020, 3(1): 015001.
4. Evgeny Senokos, **Yunfu Ou**, Juan J. Vilatela* et al. Energy storage in structural composites by introducing CNT fiber/polymer electrolyte interleaves. *Scientific Reports*, 2018, 8(1): 1-10.
5. **Yunfu Ou**, Moumita Rana, Carlos González*, and Juan José Vilatela*. Laminated structural power composites with interconnecting rivets: interlaminar properties and multifunctional design (to be submitted).
6. **Yunfu Ou**, Carlos González*, and Juan José Vilatela*. Thickness effect of carbon nanotube interleaves on interlaminar properties of woven CFRP composite laminate (under preparation).

2) International Conference Proceedings

1. **Yunfu Ou**, Carlos González* and Juan José Vilatela*, CNT FIBER VEIL INTERLEAVED CARBON FIBER/EPOXY LAMINATE COMPOSITE, *22nd International Conference on Composite Materials (ICCM22)*, Melbourne, Australia, August 11-16, 2019. (Oral presentation)
2. **Yunfu Ou**, Carlos González* and Juan José Vilatela*, Enhanced interlaminar fracture toughness

of woven carbon fabric/epoxy composites by interleaving home-made CNT veils, *MATCOMP19*, Vigo, Spain, July 3-5, 2019. (Oral presentation)

3. **Yunfu Ou**, Carlos González* and Juan José Vilatela*, Understanding interlaminar toughening mechanisms in structural carbon fiber/epoxy composites interleaved with CNT veils. *18th European conference on composite materials (ECCM18)*, Athens, Greece, June 24-28, 2018 (Oral presentation)

4. **Yunfu Ou**, Carlos González* and Juan José Vilatela*, CNT fiber veils for CFRP-hybrids with enhanced interlaminar fracture toughness and integrated multifunctionalities, *8th International Conference on Carbon NanoParticle based Composites(CNPCOMP2019)*, London, UK, July 17-19, 2019. (Poster)

5. **Yunfu Ou**, Carlos González* and Juan José Vilatela*, Hierarchical Carbon fiber/epoxy structural composites interleaved with CNT fiber veils. *Airbus PhD day*, Hamburg, Germany, September 11, 2018 (Poster)

6. Moumita Rana, **Yunfu Ou** and Juan José Vilatela*, Structural power composite based on nanostructured fabrics of CNTs: enhanced charge storage capability and design optimization. *55th Society of Engineering Science (SES) Technical Meeting*, Madrid, Spain, October 10-12, 2018

References

- [1] J. Holbery and D. Houston, "Natural-fiber-reinforced polymer composites in automotive applications," *JOM Journal of the Minerals, Metals and Materials Society*, vol. 58, pp. 80-86, 2006.
- [2] C. E. Bakis, L. C. Bank, V. Brown, E. Cosenza, J. Davalos, J. Lesko, *et al.*, "Fiber-reinforced polymer composites for construction—State-of-the-art review," *Journal of composites for construction*, vol. 6, pp. 73-87, 2002.
- [3] G. Williams, R. Trask, and I. Bond, "A self-healing carbon fibre reinforced polymer for aerospace applications," *Composites Part A: Applied Science and Manufacturing*, vol. 38, pp. 1525-1532, 2007.
- [4] Z. Huang, Y. Zhang, M. Kotaki, and S. Ramakrishna, "A review on polymer nanofibers by electrospinning and their applications in nanocomposites," *Composites science and technology*, vol. 63, pp. 2223-2253, 2003.
- [5] M. Richardson and M. Wisheart, "Review of low-velocity impact properties of composite materials," *Composites Part A: Applied Science and Manufacturing*, vol. 27, pp. 1123-1131, 1996.
- [6] J. Rogelj, C. Chen, J. Nabel, K. Macey, W. Hare, M. Schaeffer, *et al.*, "Analysis of the Copenhagen Accord pledges and its global climatic impacts—a snapshot of dissonant ambitions," *Environmental research letters*, vol. 5, p. 034013, 2010.
- [7] L. E. Asp, M. Johansson, G. Lindbergh, J. Xu, and D. Zenkert, "Structural battery composites: a review," *Functional Composites and Structures*, vol. 1, p. 042001, 2019.
- [8] J. Snyder, D. O'Brien, and E. Wetzel, "Structural Batteries, Capacitors and Supercapacitors," in *Handbook of Solid State Batteries*, ed: World Scientific, 2016, pp. 657-699.
- [9] N. Shirshova, H. Qian, M. S. Shaffer, J. H. Steinke, E. S. Greenhalgh, P. T. Curtis, *et al.*, "Structural composite supercapacitors," *Composites Part A: Applied Science and Manufacturing*, vol. 46, pp. 96-107, 2013.
- [10] S. Ekstedt, M. Wysocki, and L. Asp, "Structural batteries made from fibre reinforced composites," *Plastics, rubber and composites*, vol. 39, pp. 148-150, 2010.
- [11] L. E. Asp and E. S. Greenhalgh, "Structural power composites," *Composites science and*

- technology*, vol. 101, pp. 41-61, 2014.
- [12] A. Leif, A. Bismarck, G. Lindberg, S. Leijonmarck, T. Carlson, and M. Kjell, "Battery half cell, a battery and their manufacture," ed: Google Patents, 2015.
- [13] R. Guzman de Villoria, P. Hallander, L. Ydrefors, P. Nordin, and B. Wardle, "In-plane strength enhancement of laminated composites via aligned carbon nanotube interlaminar reinforcement," *Composites Science and Technology*, vol. 133, pp. 33-39, 2016.
- [14] A. Mikhalech, T. Gspann, and A. Windle, "Aligned carbon nanotube–epoxy composites: the effect of nanotube organization on strength, stiffness, and toughness," *Journal of Materials Science*, vol. 51, pp. 10005-10025, 2016.
- [15] S. S. Wicks, R. G. de Villoria, and B. L. Wardle, "Interlaminar and intralaminar reinforcement of composite laminates with aligned carbon nanotubes," *Composites Science and Technology*, vol. 70, pp. 20-28, 2010.
- [16] S. C. Joshi and V. Dikshit, "Enhancing interlaminar fracture characteristics of woven CFRP prepreg composites through CNT dispersion," *Journal of Composite Materials*, vol. 46, pp. 665-675, 2012.
- [17] Q. An, A. N. Rider, and E. T. Thostenson, "Electrophoretic deposition of carbon nanotubes onto carbon-fiber fabric for production of carbon/epoxy composites with improved mechanical properties," *Carbon*, vol. 50, pp. 4130-4143, 2012.
- [18] A. Warrier, A. Godara, O. Rochez, L. Mezzo, F. Luizi, L. Gorbatikh, *et al.*, "The effect of adding carbon nanotubes to glass/epoxy composites in the fibre sizing and/or the matrix," *Composites Part A: Applied Science and Manufacturing*, vol. 41, pp. 532-538, 2010.
- [19] M. Tehrani, A. Boroujeni, T. Hartman, T. Haugh, S. Case, and M. Al-Haik, "Mechanical characterization and impact damage assessment of a woven carbon fiber reinforced carbon nanotube–epoxy composite," *Composites Science and Technology*, vol. 75, pp. 42-48, 2013.
- [20] F. H. Gojny, M. H. Wichmann, B. Fiedler, W. Bauhofer, and K. Schulte, "Influence of nano-modification on the mechanical and electrical properties of conventional fibre-reinforced composites," *Composites Part A: Applied Science and Manufacturing*, vol. 36, pp. 1525-1535, 2005.
- [21] S. van der Heijden, L. Daelemans, B. De Schoenmaker, I. De Baere, H. Rahier, W. Van Paepegem, *et al.*, "Interlaminar toughening of resin transfer moulded glass fibre epoxy laminates by

- polycaprolactone electrospun nanofibres," *Composites Science and Technology*, vol. 104, pp. 66-73, 2014.
- [22] Y. Li, I. A. Kinloch, and A. H. Windle, "Direct spinning of carbon nanotube fibers from chemical vapor deposition synthesis," *Science*, vol. 304, pp. 276-278, 2004.
- [23] X. H. Zhong, Y. L. Li, Y. K. Liu, X. H. Qiao, Y. Feng, J. Liang, *et al.*, "Continuous multilayered carbon nanotube yarns," *Advanced materials*, vol. 22, pp. 692-696, 2010.
- [24] J. J. Vilatela, R. Khare, and A. H. Windle, "The hierarchical structure and properties of multifunctional carbon nanotube fibre composites," *Carbon*, vol. 50, pp. 1227-1234, 2012.
- [25] N. Sela and O. Ishai, "Interlaminar fracture toughness and toughening of laminated composite materials: a review," *Composites*, vol. 20, pp. 423-435, 1989.
- [26] R. O. Ritchie, "The conflicts between strength and toughness," *Nature materials*, vol. 10, pp. 817-822, 2011.
- [27] R. Sills and M. Thouless, "Cohesive-length scales for damage and toughening mechanisms," *International Journal of Solids and Structures*, vol. 55, pp. 32-43, 2015.
- [28] D. Vashishth, J. Behiri, and W. Bonfield, "Crack growth resistance in cortical bone: concept of microcrack toughening," *Journal of biomechanics*, vol. 30, pp. 763-769, 1997.
- [29] L. Chan, J. Gillham, A. Kinloch, and S. Shaw, "Rubber-Modified Epoxies. I. Cure, Transitions, and Morphology," PRINCETON UNIV NJ DEPT OF CHEMICAL ENGINEERING 1984.
- [30] K. T. Tan, N. Watanabe, and Y. Iwahori, "X-ray radiography and micro-computed tomography examination of damage characteristics in stitched composites subjected to impact loading," *Composites Part B: Engineering*, vol. 42, pp. 874-884, 2011.
- [31] A. P. Mouritz, M. K. Bannister, P. J. Falzon, and K. H. Leong, "Review of applications for advanced three-dimensional fibre textile composites," *Composites Part A: Applied Science and Manufacturing*, vol. 30, pp. 1445-1461, 1999.
- [32] W. HOWARD, J. GOSSARD, T. and R. JONES, "Reinforcement of composite laminate free edges with U-shaped caps," in *27th Structures, Structural Dynamics and Materials Conference*, 1986, p. 972.
- [33] A. Mouritz, M. Bannister, P. Falzon, and K. Leong, "Review of applications for advanced three-dimensional fibre textile composites," *Composites Part A: applied science and manufacturing*, vol. 30, pp. 1445-1461, 1999.

REFERENCES

- [34] F. Pegorin, K. Pingkarawat, and A. Mouritz, "Comparative study of the mode I and mode II delamination fatigue properties of z-pinned aircraft composites," *Materials & Design*, vol. 65, pp. 139-146, 2015.
- [35] C. A. Steeves and N. A. Fleck, "In-plane properties of composite laminates with through-thickness pin reinforcement," *International Journal of Solids and Structures*, vol. 43, pp. 3197-3212, 2006.
- [36] A. Mouritz, "Review of z-pinned composite laminates," *Composites Part A: applied science and manufacturing*, vol. 38, pp. 2383-2397, 2007.
- [37] R. Bagheri, B. Marouf, and R. Pearson, "Rubber-toughened epoxies: a critical review," *Journal of Macromolecular Science®, Part C: Polymer Reviews*, vol. 49, pp. 201-225, 2009.
- [38] W. G. Perkins, "Polymer toughness and impact resistance," *Polymer Engineering & Science*, vol. 39, pp. 2445-2460, 1999.
- [39] J. Wang, X. Zhang, L. Jiang, and J. Qiao, "Advances in toughened polymer materials by structured rubber particles," *Progress in Polymer Science*, vol. 98, p. 101160, 2019.
- [40] R. A. Pearson and A. F. Yee, "Toughening mechanisms in thermoplastic-modified epoxies: 1. Modification using poly (phenylene oxide)," 1993.
- [41] J. L. Hedrick, I. Yilgör, G. L. Wilkes, and J. E. McGrath, "Chemical modification of matrix Resin networks with engineering thermoplastics," *Polymer Bulletin*, vol. 13, pp. 201-208, 1985.
- [42] A. J. Kinloch, M. L. Yuen, and S. Jenkins, "Thermoplastic-toughened epoxy polymers," *Journal of Materials Science*, vol. 29, pp. 3781-3790, 1994.
- [43] R. A. Pearson, "Toughening Epoxies Using Rigid Thermoplastic Particles: A Review," ed: ACS Publications, 1993.
- [44] G. Di Pasquale, O. Motto, A. Rocca, J. Carter, P. McGrail, and D. Acierno, "New high-performance thermoplastic toughened epoxy thermosets," *Polymer*, vol. 38, pp. 4345-4348, 1997.
- [45] D. Hourston, J. Lane, and H. Zhang, "Toughening of epoxy resins with thermoplastics: 3. An investigation into the effects of composition on the properties of epoxy resin blends," *Polymer international*, vol. 42, pp. 349-355, 1997.
- [46] R. Venderbosch, T. Peijs, H. Meijer, and P. Lemstra, "Fibre-reinforced composites with tailored interphases using PPE/epoxy blends as a matrix system," *Composites Part A: Applied Science and Manufacturing*, vol. 27, pp. 895-905, 1996.

REFERENCES

- [47] P. Huang, S. Zheng, J. Huang, Q. Guo, and W. Zhu, "Miscibility and mechanical properties of epoxy resin/polysulfone blends," *Polymer*, vol. 38, pp. 5565-5571, 1997.
- [48] A. Saalbrink, A. Lorteije, and T. Peijs, "The influence of processing parameters on interphase morphology in polymer composites based on phase-separating thermoplast/epoxy blends," *Composites Part A: Applied Science and Manufacturing*, vol. 29, pp. 1243-1250, 1998.
- [49] J. Spanoudakis and R. Young, "Crack propagation in a glass particle-filled epoxy resin," *Journal of Materials Science*, vol. 19, pp. 473-486, 1984.
- [50] H. Azimi, R. Pearson, and R. Hertzberg, "Role of crack tip shielding mechanisms in fatigue of hybrid epoxy composites containing rubber and solid glass spheres," *Journal of applied polymer science*, vol. 58, pp. 449-463, 1995.
- [51] P. Rosso, L. Ye, K. Friedrich, and S. Sprenger, "A toughened epoxy resin by silica nanoparticle reinforcement," *Journal of Applied Polymer Science*, vol. 100, pp. 1849-1855, 2006.
- [52] H. Zhang, Z. Zhang, K. Friedrich, and C. Eger, "Property improvements of in situ epoxy nanocomposites with reduced interparticle distance at high nanosilica content," *Acta Materialia*, vol. 54, pp. 1833-1842, 2006.
- [53] Y. T. Park, Y. Qian, C. Chan, T. Suh, M. G. Nejhad, C. W. Macosko, *et al.*, "Epoxy toughening with low graphene loading," *Advanced Functional Materials*, vol. 25, pp. 575-585, 2015.
- [54] B. Geisler and F. Kelley, "Rubbery and rigid particle toughening of epoxy resins," *Journal of Applied Polymer Science*, vol. 54, pp. 177-189, 1994.
- [55] B. Wetzell, P. Rosso, F. Hauptert, and K. Friedrich, "Epoxy nanocomposites—fracture and toughening mechanisms," *Engineering fracture mechanics*, vol. 73, pp. 2375-2398, 2006.
- [56] F. Campbell, "Chapter 2-Fibers and Reinforcements: The String that Provides the Strength," *Manufacturing Processes for Advanced Composites*, Elsevier Science, Amsterdam, 2003.
- [57] W. Bascom, m. J. Bitner, R. Moulton, and A. Siebert, "The interlaminar fracture of organic-matrix, woven reinforcement composites," *Composites*, vol. 11, pp. 9-18, 1980.
- [58] B. Schrauwen and T. Peijs, "Influence of matrix ductility and fibre architecture on the repeated impact response of glass-fibre-reinforced laminated composites," *Applied Composite Materials*, vol. 9, pp. 331-352, 2002.
- [59] B. Briscoe, R. Court, and D. Williams, "The effects of fabric weave and surface texture on the interlaminar fracture toughness of aramid/epoxy laminates," *Composites science and technology*,

- vol. 47, pp. 261-270, 1993.
- [60] T. Ebeling, A. Hiltner, E. Baer, I. Fraser, and M. Orton, "Delamination failure of a woven glass fiber composite," *Journal of composite materials*, vol. 31, pp. 1318-1333, 1997.
- [61] S. Bazhenov, "Strong bending in the DCB interlaminar test of thin, E-glass woven-fabric-reinforced laminates," *Composites*, vol. 22, pp. 275-280, 1991.
- [62] J.-K. Kim and M.-L. Sham, "Impact and delamination failure of woven-fabric composites," *Composites Science and Technology*, vol. 60, pp. 745-761, 2000.
- [63] F. Stig and S. Hallström, "Spatial modelling of 3D-woven textiles," *Composite Structures*, vol. 94, pp. 1495-1502, 2012.
- [64] S. Drapier and M. R. Wisnom, "Finite-element investigation of the compressive strength of non-crimp-fabric-based composites," *Composites Science and Technology*, vol. 59, pp. 1287-1297, 1999.
- [65] D. Falconnet, P.-E. Bourban, S. Pandita, J.-A. Manson, and I. Verpoest, "Fracture toughness of weft-knitted fabric composites," *Composites Part B: Engineering*, vol. 33, pp. 579-588, 2002.
- [66] K.-Y. Kim, J. I. Curiskis, L. Ye, and S.-Y. Fu, "Mode-I interlaminar fracture behaviour of weft-knitted fabric reinforced composites," *Composites Part A: Applied Science and Manufacturing*, vol. 36, pp. 954-964, 2005.
- [67] K. Dransfield, C. Baillie, and Y.-W. Mai, "Improving the delamination resistance of CFRP by stitching—a review," *Composites Science and Technology*, vol. 50, pp. 305-317, 1994.
- [68] L. Lee, S. Rudov-Clark, A. Mouritz, M. Bannister, and I. Herszberg, "Effect of weaving damage on the tensile properties of three-dimensional woven composites," *Composite Structures*, vol. 57, pp. 405-413, 2002.
- [69] J. Brandt, K. Drechsler, and F.-J. Arendts, "Mechanical performance of composites based on various three-dimensional woven-fibre preforms," *Composites science and technology*, vol. 56, pp. 381-386, 1996.
- [70] R. E. Evans and K. R. Hirschbuehler, "Thermoplastic interleaved resin matrix composites with improved impact strength and toughness," ed: Google Patents, 1986.
- [71] K. N. Shivakumar, R. Panduranga, and M. Sharpe, "Interleaved polymer matrix composites-A review," in *54th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference*, 2013, p. 1903.

REFERENCES

- [72] N. Odagiri, "T800H/3900-2 toughened epoxy prepreg system: Toughening concept and mechanism," in *Pros. Amer. Soc. Composites 6th Technical Conf.*, 1991, pp. 43-52.
- [73] N. Odagiri, H. Kishi, and M. Yamashita, "Development of TORAYCA prepreg P2302 carbon fiber reinforced plastic for aircraft primary structural materials," *Advanced Composite Materials*, vol. 5, pp. 249-254, 1996.
- [74] E. Woo and K. Mao, "Evaluation of interlaminar-toughened poly (etherlmiide)-modified epoxy/carbon fiber composites," *Polymer composites*, vol. 17, pp. 799-805, 1996.
- [75] S.-Y. Fu, X.-Q. Feng, B. Lauke, and Y.-W. Mai, "Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate-polymer composites," *Composites Part B: Engineering*, vol. 39, pp. 933-961, 2008.
- [76] M. Hojo, T. Ando, M. Tanaka, T. Adachi, S. Ochiai, and Y. Endo, "Modes I and II interlaminar fracture toughness and fatigue delamination of CF/epoxy laminates with self-same epoxy interleaf," *International journal of fatigue*, vol. 28, pp. 1154-1165, 2006.
- [77] S. Singh and I. Partridge, "Mixed-mode fracture in an interleaved carbon-fibre/epoxy composite," *Composites Science and Technology*, vol. 55, pp. 319-327, 1995.
- [78] S. Matsuda, M. Hojo, S. Ochiai, A. Murakami, H. Akimoto, and M. Ando, "Effect of ionomer thickness on mode I interlaminar fracture toughness for ionomer toughened CFRP," *Composites Part A: Applied Science and Manufacturing*, vol. 30, pp. 1311-1319, 1999.
- [79] O. Ishai, H. Rosenthal, N. Sela, and E. Drukker, "Effect of selective adhesive interleaving on interlaminar fracture toughness of graphite/epoxy composite laminates," *Composites*, vol. 19, pp. 49-54, 1988.
- [80] J. W. Gillespie, L. A. Carlsson, and A. J. Smiley, "Rate-dependent mode I interlaminar crack growth mechanisms in graphite/epoxy and graphite/PEEK," *Composites Science and Technology*, vol. 28, pp. 1-15, 1987.
- [81] A. Smiley and R. Pipes, "Rate effects on mode I interlaminar fracture toughness in composite materials," *Journal of composite materials*, vol. 21, pp. 670-687, 1987.
- [82] K. Shivakumar, S. Lingaiah, H. Chen, P. Akangah, G. Swaminathan, and L. Russell, "Polymer nanofabric interleaved composite laminates," *AIAA journal*, vol. 47, pp. 1723-1729, 2009.
- [83] A. Greiner and J. H. Wendorff, "Electrospinning: a fascinating method for the preparation of ultrathin fibers," *Angewandte Chemie International Edition*, vol. 46, pp. 5670-5703, 2007.

REFERENCES

- [84] J. s. Kim and D. H. Reneker, "Mechanical properties of composites using ultrafine electrospun fibers," *Polymer composites*, vol. 20, pp. 124-131, 1999.
- [85] L. Daelemans, S. van der Heijden, I. De Baere, H. Rahier, W. Van Paepegem, and K. De Clerck, "Using aligned nanofibres for identifying the toughening micromechanisms in nanofibre interleaved laminates," *Composites Science and Technology*, vol. 124, pp. 17-26, 2016.
- [86] L. Daelemans, S. van der Heijden, I. De Baere, H. Rahier, W. Van Paepegem, and K. De Clerck, "Damage-resistant composites using electrospun nanofibers: a multiscale analysis of the toughening mechanisms," *ACS applied materials & interfaces*, vol. 8, pp. 11806-11818, 2016.
- [87] J. Zhang, T. Lin, and X. Wang, "Electrospun nanofibre toughened carbon/epoxy composites: Effects of polyetherketone cardo (PEK-C) nanofibre diameter and interlayer thickness," *Composites Science and Technology*, vol. 70, pp. 1660-1666, 2010.
- [88] S. van der Heijden, L. Daelemans, K. De Bruycker, R. Simal, I. De Baere, W. Van Paepegem, *et al.*, "Novel composite materials with tunable delamination resistance using functionalizable electrospun SBS fibers," *Composite Structures*, vol. 159, pp. 12-20, 2017.
- [89] L. Daelemans, S. van der Heijden, I. De Baere, H. Rahier, W. Van Paepegem, and K. De Clerck, "Nanofibre bridging as a toughening mechanism in carbon/epoxy composite laminates interleaved with electrospun polyamide nanofibrous veils," *Composites Science and Technology*, vol. 117, pp. 244-256, 2015.
- [90] Y. A. Dzenis, "Structural nanocomposites," *Faculty Publications from Nebraska Center for Materials and Nanoscience*, p. 83, 2008.
- [91] A. Zucchelli, M. L. Focarete, C. Gualandi, and S. Ramakrishna, "Electrospun nanofibers for enhancing structural performance of composite materials," *Polymers for Advanced Technologies*, vol. 22, pp. 339-349, 2011.
- [92] R. Palazzetti and A. Zucchelli, "Electrospun nanofibers as reinforcement for composite laminates materials—a review," *Composite Structures*, vol. 182, pp. 711-727, 2017.
- [93] S. Sihn, R. Y. Kim, W. Huh, K.-H. Lee, and A. K. Roy, "Improvement of damage resistance in laminated composites with electrospun nano-interlayers," *Composites Science and Technology*, vol. 68, pp. 673-683, 2008.
- [94] E. Ozden, Y. Z. Menciloglu, and M. Papila, "Engineering chemistry of electrospun nanofibers and interfaces in nanocomposites for superior mechanical properties," *ACS applied materials &*

- interfaces*, vol. 2, pp. 1788-1793, 2010.
- [95] K. Bilge, E. Ozden-Yenigun, E. Simsek, Y. Menceloglu, and M. Papila, "Structural composites hybridized with epoxy compatible polymer/MWCNT nanofibrous interlayers," *Composites Science and Technology*, vol. 72, pp. 1639-1645, 2012.
- [96] G. Li, P. Li, C. Zhang, Y. Yu, H. Liu, S. Zhang, *et al.*, "Inhomogeneous toughening of carbon fiber/epoxy composite using electrospun polysulfone nanofibrous membranes by in situ phase separation," *Composites Science and Technology*, vol. 68, pp. 987-994, 2008.
- [97] K. Magniez, T. Chaffraix, and B. Fox, "Toughening of a carbon-fibre composite using electrospun poly (hydroxyether of bisphenol A) nanofibrous membranes through inverse phase separation and inter-domain etherification," *Materials*, vol. 4, pp. 1967-1984, 2011.
- [98] J. Zhang, T. Yang, T. Lin, and C. H. Wang, "Phase morphology of nanofibre interlayers: Critical factor for toughening carbon/epoxy composites," *Composites Science and Technology*, vol. 72, pp. 256-262, 2012.
- [99] S. Jiang, G. Duan, J. Schöbel, S. Agarwal, and A. Greiner, "Short electrospun polymeric nanofibers reinforced polyimide nanocomposites," *Composites Science and Technology*, vol. 88, pp. 57-61, 2013.
- [100] R. Palazzetti, X. Yan, and A. Zucchelli, "Influence of geometrical features of electrospun nylon 6,6 interleave on the CFRP laminates mechanical properties," *Polymer Composites*, vol. 35, pp. 137-150, 2014.
- [101] R. Palazzetti, A. Zucchelli, C. Gualandi, M. L. Focarete, L. Donati, G. Minak, *et al.*, "Influence of electrospun Nylon 6,6 nanofibrous mats on the interlaminar properties of Gr-epoxy composite laminates," *Composite Structures*, vol. 94, pp. 571-579, 2012.
- [102] I. Rafique, A. Kausar, Z. Anwar, and B. Muhammad, "Exploration of epoxy resins, hardening systems, and epoxy/carbon nanotube composite designed for high performance materials: a review," *Polymer-Plastics Technology and Engineering*, vol. 55, pp. 312-333, 2016.
- [103] D. Bethune, C. H. Kiang, M. De Vries, G. Gorman, R. Savoy, J. Vazquez, *et al.*, "Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls," *Nature*, vol. 363, pp. 605-607, 1993.
- [104] S. Iijima, "Helical microtubules of graphitic carbon," *nature*, vol. 354, p. 56, 1991.
- [105] Z. Zhu, N. Wei, W. Cheng, B. Shen, S. Sun, J. Gao, *et al.*, "Rate-selected growth of ultrapure

- semiconducting carbon nanotube arrays," *Nature communications*, vol. 10, pp. 1-8, 2019.
- [106] J. J. Vilatela García, "Structure, Properties and Treatments of Carbon Nanotube Fibres," University of Cambridge, 2009.
- [107] B. I. Yakobson, C. Brabec, and J. Bernholc, "Nanomechanics of carbon tubes: instabilities beyond linear response," *Physical review letters*, vol. 76, p. 2511, 1996.
- [108] L. Venema, J. Wildöer, C. Dekker, G. Rinzler, and R. Smalley, "STM atomic resolution images of single-wall carbon nanotubes," *Applied Physics A*, vol. 66, pp. S153-S155, 1998.
- [109] J.-C. Charlier, X. Blase, and S. Roche, "Electronic and transport properties of nanotubes," *Reviews of modern physics*, vol. 79, p. 677, 2007.
- [110] P. Lambin, L. Philippe, J.-C. Charlier, and J.-P. Michenaud, "Electronic band structure of multilayered carbon tubules," *Computational Materials Science*, vol. 2, pp. 350-356, 1994.
- [111] L. X. Benedict, V. H. Crespi, S. G. Louie, and M. L. Cohen, "Static conductivity and superconductivity of carbon nanotubes: Relations between tubes and sheets," *Physical Review B*, vol. 52, p. 14935, 1995.
- [112] A. Bachtold, M. Fuhrer, S. Plyasunov, M. Forero, E. H. Anderson, A. Zettl, *et al.*, "Scanned probe microscopy of electronic transport in carbon nanotubes," *Physical review letters*, vol. 84, p. 6082, 2000.
- [113] E. Pop, D. Mann, Q. Wang, K. Goodson, and H. Dai, "Thermal conductance of an individual single-wall carbon nanotube above room temperature," *Nano letters*, vol. 6, pp. 96-100, 2006.
- [114] P. Kim, L. Shi, A. Majumdar, and P. L. McEuen, "Thermal transport measurements of individual multiwalled nanotubes," *Physical review letters*, vol. 87, p. 215502, 2001.
- [115] W. Lu, M. Zu, J. H. Byun, B. S. Kim, and T. W. Chou, "State of the art of carbon nanotube fibers: opportunities and challenges," *Advanced materials*, vol. 24, pp. 1805-1833, 2012.
- [116] M. Endo, H. Muramatsu, T. Hayashi, Y. Kim, M. Terrones, and M. Dresselhaus, "'Buckypaper' from coaxial nanotubes," *Nature*, vol. 433, pp. 476-476, 2005.
- [117] B. Vigolo, A. Penicaud, C. Coulon, C. Sauder, R. Pailler, C. Journet, *et al.*, "Macroscopic fibers and ribbons of oriented carbon nanotubes," *Science*, vol. 290, pp. 1331-1334, 2000.
- [118] M. Zhang, K. R. Atkinson, and R. H. Baughman, "Multifunctional carbon nanotube yarns by downsizing an ancient technology," *Science*, vol. 306, pp. 1358-1361, 2004.
- [119] D. Wang, P. Song, C. Liu, W. Wu, and S. Fan, "Highly oriented carbon nanotube papers made of

- aligned carbon nanotubes," *Nanotechnology*, vol. 19, p. 075609, 2008.
- [120] Y.-L. Li, I. A. Kinloch, and A. H. Windle, "Direct spinning of carbon nanotube fibers from chemical vapor deposition synthesis," *Science*, vol. 304, pp. 276-278, 2004.
- [121] B. Alemán, V. Reguero, B. Mas, and J. J. Vilatela, "Strong carbon nanotube fibers by drawing inspiration from polymer fiber spinning," *ACS nano*, vol. 9, pp. 7392-7398, 2015.
- [122] B. Alemán and J. J. Vilatela, "Multiscale Engineering of Carbon Nanotube Fibers," in *Nanotube Superfiber Materials*, ed: Elsevier, 2019, pp. 113-147.
- [123] J. Stallard, W. Tan, F. Smail, T. Gspann, A. Boies, and N. Fleck, "The mechanical and electrical properties of direct-spun carbon nanotube mats," *Extreme Mechanics Letters*, vol. 21, pp. 65-75, 2018.
- [124] D. Janas and K. K. Koziol, "Carbon nanotube fibers and films: synthesis, applications and perspectives of the direct-spinning method," *Nanoscale*, vol. 8, pp. 19475-19490, 2016.
- [125] A. Mikhalech and J. J. Vilatela, "A Perspective on High-performance CNT fibres for Structural Composites," *Carbon*, 2019.
- [126] T. Gspann, F. Smail, and A. Windle, "Spinning of carbon nanotube fibres using the floating catalyst high temperature route: purity issues and the critical role of sulphur," *Faraday discussions*, vol. 173, pp. 47-65, 2014.
- [127] M. Motta, A. Moisala, I. A. Kinloch, and A. H. Windle, "High performance fibres from 'dog bone' carbon nanotubes," *Advanced Materials*, vol. 19, pp. 3721-3726, 2007.
- [128] A. Lekawa-Raus, J. Patmore, L. Kurzepa, J. Bulmer, and K. Koziol, "Electrical properties of carbon nanotube based fibers and their future use in electrical wiring," *Advanced Functional Materials*, vol. 24, pp. 3661-3682, 2014.
- [129] K. Y. Khromov, A. Knizhnik, B. Potapkin, and J. Kenny, "Multiscale modeling of electrical conductivity of carbon nanotubes based polymer nanocomposites," *Journal of Applied Physics*, vol. 121, p. 225102, 2017.
- [130] K. Krukiewicz, J. S. Bulmer, K. K. Koziol, and J. K. Zak, "Charging and discharging of the electrochemically swelled, aligned carbon nanotube fibers," *Electrochemistry Communications*, vol. 64, pp. 30-34, 2016.
- [131] A. Lekawa-Raus, K. Walczak, G. Kozłowski, M. Wozniak, S. C. Hopkins, and K. K. Koziol, "Resistance-temperature dependence in carbon nanotube fibres," *Carbon*, vol. 84, pp. 118-123,

- 2015.
- [132] A. Lekawa-Raus, K. Walczak, G. Kozłowski, S. C. Hopkins, M. Wozniak, B. A. Glowacki, *et al.*, "Low temperature electrical transport in modified carbon nanotube fibres," *Scripta Materialia*, vol. 106, pp. 34-37, 2015.
- [133] J. Wang, X. Luo, T. Wu, and Y. Chen, "High-strength carbon nanotube fibre-like ribbon with high ductility and high electrical conductivity," *Nature communications*, vol. 5, pp. 1-8, 2014.
- [134] E. Borowski, E. Soliman, U. F. Kandil, and M. R. Taha, "Interlaminar fracture toughness of CFRP laminates incorporating multi-walled carbon nanotubes," *Polymers*, vol. 7, pp. 1020-1045, 2015.
- [135] F. Inam, D. W. Wong, M. Kuwata, and T. Peijs, "Multiscale hybrid micro-nanocomposites based on carbon nanotubes and carbon fibers," *Journal of Nanomaterials*, vol. 2010, p. 9, 2010.
- [136] M. H. Wichmann, J. Sumfleth, F. H. Gojny, M. Quaresimin, B. Fiedler, and K. Schulte, "Glass-fibre-reinforced composites with enhanced mechanical and electrical properties—benefits and limitations of a nanoparticle modified matrix," *Engineering Fracture Mechanics*, vol. 73, pp. 2346-2359, 2006.
- [137] P. Karapappas, A. Vavouliotis, P. Tsotra, V. Kostopoulos, and A. Paipetis, "Enhanced fracture properties of carbon reinforced composites by the addition of multi-wall carbon nanotubes," *Journal of Composite Materials*, vol. 43, pp. 977-985, 2009.
- [138] A. Godara, L. Mezzo, F. Luizi, A. Warrier, S. V. Lomov, A. Van Vuure, *et al.*, "Influence of carbon nanotube reinforcement on the processing and the mechanical behaviour of carbon fiber/epoxy composites," *Carbon*, vol. 47, pp. 2914-2923, 2009.
- [139] K. Kepple, G. Sanborn, P. Lacasse, K. Gruenberg, and W. Ready, "Improved fracture toughness of carbon fiber composite functionalized with multi walled carbon nanotubes," *Carbon*, vol. 46, pp. 2026-2033, 2008.
- [140] T. R. Pozegic, K. D. G. I. Jayawardena, J. S. Chen, J. V. Anguita, P. Balocchi, V. Stolojan, *et al.*, "Development of sizing-free multi-functional carbon fibre nanocomposites," *Composites Part A: Applied Science and Manufacturing*, vol. 90, pp. 306-319, 2016.
- [141] E. J. Garcia, B. L. Wardle, and A. J. Hart, "Joining prepreg composite interfaces with aligned carbon nanotubes," *Composites Part A: Applied Science and Manufacturing*, vol. 39, pp. 1065-1070, 2008.

-
- [142] H. Zhang, Y. Liu, M. Kuwata, E. Bilotti, and T. Peijs, "Improved fracture toughness and integrated damage sensing capability by spray coated CNTs on carbon fibre prepreg," *Composites Part A: Applied Science and Manufacturing*, vol. 70, pp. 102-110, 2015.
- [143] J. Williams, N. Graddage, and S. Rahatekar, "Effects of plasma modified carbon nanotube interlaminar coating on crack propagation in glass epoxy composites," *Composites Part A: Applied Science and Manufacturing*, vol. 54, pp. 173-181, 2013.
- [144] F. Shan, Y. Gu, M. Li, Y. Liu, and Z. Zhang, "Effect of deposited carbon nanotubes on interlaminar properties of carbon fiber-reinforced epoxy composites using a developed spraying processing," *Polymer Composites*, vol. 34, pp. 41-50, 2013.
- [145] K. Almuhammadi, M. Alfano, Y. Yang, and G. Lubineau, "Analysis of interlaminar fracture toughness and damage mechanisms in composite laminates reinforced with sprayed multi-walled carbon nanotubes," *Materials & Design*, vol. 53, pp. 921-927, 2014.
- [146] P. R. Thakre, D. C. Lagoudas, J. C. Riddick, T. S. Gates, S.-J. V. Frankland, J. G. Ratcliffe, *et al.*, "Investigation of the effect of single wall carbon nanotubes on interlaminar fracture toughness of woven carbon fiber—epoxy composites," *Journal of Composite Materials*, vol. 45, pp. 1091-1107, 2011.
- [147] F. Nguyen, S. Tun, A. Haro, N. Hirano, K. Yoshioka, and R. Ovalle-Robles, "Interlaminar Reinforcement by Aligned Carbon Nanotubes in Carbon Fiber Reinforced Polymer Composites," in *19th International Conference on Composite Materials (ICCM)*.
- [148] A. Nistal, B. G. Falzon, S. C. Hawkins, R. Chitwan, C. García-Diego, and F. Rubio, "Enhancing the fracture toughness of hierarchical composites through amino-functionalised carbon nanotube webs," *Composites Part B: Engineering*, vol. 165, pp. 537-544, 2019.
- [149] M. Shaffer and I. A. Kinloch, "Prospects for nanotube and nanofibre composites," *Composites Science and Technology*, vol. 64, pp. 2281-2282, 2004.
- [150] H. Qian, A. Bismarck, E. S. Greenhalgh, G. Kalinka, and M. S. Shaffer, "Hierarchical composites reinforced with carbon nanotube grafted fibers: the potential assessed at the single fiber level," *Chem. Mater*, vol. 20, pp. 1862-1869, 2008.
- [151] W. Down and R. Baker, "Modification of the surface properties of carbon fibers via the catalytic growth of carbon nanofibers," *Journal of materials research*, vol. 10, pp. 625-633, 1995.
- [152] R. Sager, P. Klein, D. Lagoudas, Q. Zhang, J. Liu, L. Dai, *et al.*, "Effect of carbon nanotubes on

- the interfacial shear strength of T650 carbon fiber in an epoxy matrix," *Composites Science and Technology*, vol. 69, pp. 898-904, 2009.
- [153] S. A. Steiner III, R. Li, and B. L. Wardle, "Circumventing the mechanochemical origins of strength loss in the synthesis of hierarchical carbon fibers," *ACS applied materials & interfaces*, vol. 5, pp. 4892-4903, 2013.
- [154] S. Wang, R. Downes, C. Young, D. Haldane, A. Hao, R. Liang, *et al.*, "Carbon fiber/carbon nanotube buckypaper interply hybrid composites: manufacturing process and tensile properties," *Advanced Engineering Materials*, vol. 17, pp. 1442-1453, 2015.
- [155] P. Latko, W. Rumiński, and A. Boczkowska, "Carbon nanotubes-doped veils," *Composite Structures*, vol. 134, pp. 52-59, 2015.
- [156] Y. Ou, C. González, and J. J. Vilatela, "Interlaminar toughening in structural carbon fiber/epoxy composites interleaved with carbon nanotube veils," *Composites Part A: Applied Science and Manufacturing*, p. 105477, 2019.
- [157] S. Di Leonardo, A. Nistal, G. Catalanotti, S. C. Hawkins, and B. G. Falzon, "Mode I interlaminar fracture toughness of thin-ply laminates with CNT webs at the crack interface," *Composite Structures*, p. 111178, 2019.
- [158] W. Xin, F. Sarasini, J. Tirillò, I. Bavasso, F. Sbardella, L. Lampani, *et al.*, "Impact and post-impact properties of multiscale carbon fiber composites interleaved with carbon nanotube sheets," *Composites Part B: Engineering*, vol. 183, p. 107711, 2020.
- [159] E. F. R. da Costa, A. A. Skordos, I. K. Partridge, and A. Rezai, "RTM processing and electrical performance of carbon nanotube modified epoxy/fibre composites," *Composites Part A: Applied Science and Manufacturing*, vol. 43, pp. 593-602, 2012.
- [160] H. Zhang, Y. Liu, S. Huo, J. Briscoe, W. Tu, O. T. Picot, *et al.*, "Filtration effects of graphene nanoplatelets in resin infusion processes: Problems and possible solutions," *Composites Science and Technology*, vol. 139, pp. 138-145, 2017.
- [161] M. D. Yadav, K. Dasgupta, A. W. Patwardhan, and J. B. Joshi, "High Performance Fibers from Carbon Nanotubes: Synthesis, Characterization, and Applications in Composites □ A Review," *Industrial & engineering chemistry research*, vol. 56, pp. 12407-12437, 2017.
- [162] H. Xu, X. Tong, Y. Zhang, Q. Li, and W. Lu, "Mechanical and electrical properties of laminated composites containing continuous carbon nanotube film interleaves," *Composites Science and*

- Technology*, vol. 127, pp. 113-118, 2016.
- [163] C. Tseng, C. Wang, and C. Chen, "Functionalizing carbon nanotubes by plasma modification for the preparation of covalent-integrated epoxy composites," *Chemistry of Materials*, vol. 19, pp. 308-315, 2007.
- [164] A. T. Seyhan, M. Tanoglu, and K. Schulte, "Mode I and mode II fracture toughness of E-glass non-crimp fabric/carbon nanotube (CNT) modified polymer based composites," *Engineering Fracture Mechanics*, vol. 75, pp. 5151-5162, 2008.
- [165] F. H. Gojny, M. H. Wichmann, B. Fiedler, and K. Schulte, "Influence of different carbon nanotubes on the mechanical properties of epoxy matrix composites—a comparative study," *Composites Science and Technology*, vol. 65, pp. 2300-2313, 2005.
- [166] Y. Zhou, F. Pervin, L. Lewis, and S. Jeelani, "Fabrication and characterization of carbon/epoxy composites mixed with multi-walled carbon nanotubes," *Materials Science and Engineering: A*, vol. 475, pp. 157-165, 2008.
- [167] E. T. Thostenson and T.-W. Chou, "Processing-structure-multi-functional property relationship in carbon nanotube/epoxy composites," *Carbon*, vol. 44, pp. 3022-3029, 2006.
- [168] N. Yu, Z. H. Zhang, and S. Y. He, "Fracture toughness and fatigue life of MWCNT/epoxy composites," *Materials Science and Engineering: A*, vol. 494, pp. 380-384, 2008.
- [169] R. Andrews and M. C. Weisenberger, "Carbon nanotube polymer composites," *Current Opinion in Solid State and Materials Science*, vol. 8, pp. 31-37, 2004.
- [170] J. Blanco, E. J. García, R. Guzmán de Villoria, and B. L. Wardle, "Limiting mechanisms of mode I interlaminar toughening of composites reinforced with aligned carbon nanotubes," *Journal of Composite Materials*, vol. 43, pp. 825-841, 2009.
- [171] T. Hsieh, A. Kinloch, A. Taylor, and I. Kinloch, "The effect of carbon nanotubes on the fracture toughness and fatigue performance of a thermosetting epoxy polymer," *Journal of Materials Science*, vol. 46, p. 7525, 2011.
- [172] S. Hashemi, A. Kinloch, and J. Williams, "The analysis of interlaminar fracture in uniaxial fibre-polymer composites," in *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, 1990, pp. 173-199.
- [173] W. S. Johnson and P. Mangalgiri, "Investigation of fiber bridging in double cantilever beam specimens," *Journal of Composites, Technology and Research*, vol. 9, pp. 10-13, 1987.

REFERENCES

- [174] G. Bao, B. Fan, and A. Evans, "Mixed mode delamination cracking in brittle matrix composites," *Mechanics of materials*, vol. 13, pp. 59-66, 1992.
- [175] Z. Suo, G. Bao, and B. Fan, "Delamination R-curve phenomena due to damage," *Journal of the Mechanics and Physics of Solids*, vol. 40, pp. 1-16, 1992.
- [176] S. Spearing and A. G. Evans, "The role of fiber bridging in the delamination resistance of fiber-reinforced composites," *Acta metallurgica et materialia*, vol. 40, pp. 2191-2199, 1992.
- [177] R. F. Gibson, "A review of recent research on mechanics of multifunctional composite materials and structures," *Composite structures*, vol. 92, pp. 2793-2810, 2010.
- [178] B. K. Kim, S. Sy, A. Yu, and J. Zhang, "Electrochemical supercapacitors for energy storage and conversion," *Handbook of Clean Energy Systems*, pp. 1-25, 2015.
- [179] J. Zhang, L. Zhang, H. Liu, A. Sun, and R.-S. Liu, *Electrochemical Technologies for Energy Storage and Conversion, 2 Volume Set* vol. 1: John Wiley & Sons, 2011.
- [180] H. Du, X. Lin, Z. Xu, and D. Chu, "Electric double-layer transistors: a review of recent progress," *Journal of Materials Science*, vol. 50, pp. 5641-5673, 2015.
- [181] S. Shiraishi, "Electric double layer capacitors," in *Carbon Alloys*, ed: Elsevier, 2003, pp. 447-457.
- [182] T. Morimoto, K. Hiratsuka, Y. Sanada, and K. Kurihara, "Electric double-layer capacitor using organic electrolyte," *Journal of Power Sources*, vol. 60, pp. 239-247, 1996.
- [183] H. Ji, X. Zhao, Z. Qiao, J. Jung, Y. Zhu, Y. Lu, *et al.*, "Capacitance of carbon-based electrical double-layer capacitors," *Nature communications*, vol. 5, pp. 1-7, 2014.
- [184] T. Pereira, Z. Guo, S. Nieh, J. Arias, and H. T. Hahn, "Embedding thin-film lithium energy cells in structural composites," *Composites Science and Technology*, vol. 68, pp. 1935-1941, 2008.
- [185] H. Qian, A. R. Kucernak, E. S. Greenhalgh, A. Bismarck, and M. S. Shaffer, "Multifunctional structural supercapacitor composites based on carbon aerogel modified high performance carbon fiber fabric," *ACS applied materials & interfaces*, vol. 5, pp. 6113-6122, 2013.
- [186] C. González, J. Vilatela, J. Molina-Aldareguía, C. Lopes, and J. LLorca, "Structural composites for multifunctional applications: Current challenges and future trends," *Progress in Materials Science*, vol. 89, pp. 194-251, 2017.
- [187] Q. Li, Y. Q. Zhu, and S. J. Eichhorn, "Structural supercapacitors using a solid resin electrolyte with carbonized electrospun cellulose/carbon nanotube electrodes," *Journal of Materials*

- Science*, vol. 53, pp. 14598-14607, 2018.
- [188] H. Qian, H. Diao, M. Houllé, J. Amadou, N. Shirshova, E. Greenhalgh, *et al.*, "Carbon fibre modifications for composite structural power devices," in *ECCM 15–15th European conference on composite materials*, 2012.
- [189] B. K. Deka, A. Hazarika, J. Kim, Y.-B. Park, and H. W. Park, "Multifunctional CuO nanowire embodied structural supercapacitor based on woven carbon fiber/ionic liquid–polyester resin," *Composites Part A: Applied Science and Manufacturing*, vol. 87, pp. 256-262, 2016.
- [190] B. K. Deka, A. Hazarika, O. Kwon, D. Kim, Y.-B. Park, and H. W. Park, "Multifunctional enhancement of woven carbon fiber/ZnO nanotube-based structural supercapacitor and polyester resin-domain solid-polymer electrolytes," *Chemical Engineering Journal*, vol. 325, pp. 672-680, 2017.
- [191] N. Shirshova, A. Bismarck, S. Carreyette, Q. P. Fontana, E. S. Greenhalgh, P. Jacobsson, *et al.*, "Structural supercapacitor electrolytes based on bicontinuous ionic liquid–epoxy resin systems," *Journal of Materials Chemistry A*, vol. 1, pp. 15300-15309, 2013.
- [192] J.-H. Shin, W. A. Henderson, and S. Passerini, "PEO-based polymer electrolytes with ionic liquids and their use in lithium metal-polymer electrolyte batteries," *Journal of the Electrochemical Society*, vol. 152, p. A978, 2005.
- [193] K.-S. Liao, T. E. Sutto, E. Andreoli, P. Ajayan, K. A. McGrady, and S. A. Curran, "Nano-sponge ionic liquid–polymer composite electrolytes for solid-state lithium power sources," *Journal of Power Sources*, vol. 195, pp. 867-871, 2010.
- [194] H. S. Kim, J. S. Kang, J. S. Park, H. T. Hahn, H. C. Jung, and J. W. Joung, "Inkjet printed electronics for multifunctional composite structure," *Composites Science and Technology*, vol. 69, pp. 1256-1264, 2009.
- [195] J. Sun, V. Gargitter, S. Pei, T. Wang, Y. Yan, S. G. Advani, *et al.*, "Mechanical and electrochemical performance of hybrid laminated structural composites with carbon fiber/solid electrolyte supercapacitor interleaves," *Composites Science and Technology*, p. 108234, 2020.
- [196] J. Thomas, S. Qidwai, W. Pogue III, and G. Pham, "Multifunctional structure-battery composites for marine systems," *Journal of Composite Materials*, vol. 47, pp. 5-26, 2013.
- [197] J. J. Vilatela and R. Marcilla, "Tough electrodes: carbon nanotube fibers as the ultimate current collectors/active material for energy management devices," *Chemistry of Materials*, vol. 27, pp.

- 6901-6917, 2015.
- [198] Z. Yang, J. Ren, Z. Zhang, X. Chen, G. Guan, L. Qiu, *et al.*, "Recent advancement of nanostructured carbon for energy applications," *Chemical reviews*, vol. 115, pp. 5159-5223, 2015.
- [199] M. Yang, B. Cheng, H. Song, and X. Chen, "Preparation and electrochemical performance of polyaniline-based carbon nanotubes as electrode material for supercapacitor," *Electrochimica Acta*, vol. 55, pp. 7021-7027, 2010.
- [200] G. Wang, R. Liang, L. Liu, and B. Zhong, "Improving the specific capacitance of carbon nanotubes-based supercapacitors by combining introducing functional groups on carbon nanotubes with using redox-active electrolyte," *Electrochimica Acta*, vol. 115, pp. 183-188, 2014.
- [201] M. Hahn, M. Baertschi, O. Barbieri, J.-C. Sauter, R. Kötz, and R. Gallay, "Interfacial capacitance and electronic conductance of activated carbon double-layer electrodes," *Electrochemical and Solid State Letters*, vol. 7, p. A33, 2003.
- [202] K. h. An, K. K. Jeon, W. S. Kim, Y. S. Park, S. C. Lim, D. J. Bae, *et al.*, "Characterization of supercapacitors using singlewalled carbon nanotube electrodes," *JOURNAL-KOREAN PHYSICAL SOCIETY*, vol. 39, pp. S511-S517, 2001.
- [203] X. Chen, R. Paul, and L. Dai, "Carbon-based supercapacitors for efficient energy storage," *National Science Review*, vol. 4, pp. 453-489, 2017.
- [204] M. Antonietti, T. Bandoz, G. Centi, R. Costa, R. Cruz-Silva, J. Di, *et al.*, *Nanocarbon-inorganic hybrids: next generation composites for sustainable energy applications*: Walter de Gruyter GmbH & Co KG, 2014.
- [205] A. S. Wu and T.-W. Chou, "Carbon nanotube fibers for advanced composites," *Materials Today*, vol. 15, pp. 302-310, 2012.
- [206] E. Senokos, R. Marcilla, and J. J. Vilatela, "Materials science of multifunctional supercapacitors based on nanocarbon networks," in *Carbon Based Nanomaterials for Advanced Thermal and Electrochemical Energy Storage and Conversion*, ed: Elsevier, 2019, pp. 249-278.
- [207] V. Reguero, B. n. Alemán, B. Mas, and J. J. Vilatela, "Controlling carbon nanotube type in macroscopic fibers synthesized by the direct spinning process," *Chemistry of Materials*, vol. 26, pp. 3550-3557, 2014.
- [208] J. Hodgkin, G. P. Simon, and R. J. Varley, "Thermoplastic toughening of epoxy resins: a critical

- review," *Polymers for advanced technologies*, vol. 9, pp. 3-10, 1998.
- [209] P. J. Minguet, M. J. Fedro, and C. K. Gunther, "Test methods for textile composites," *National Aeronautics and Space Administration, Langley Research Center*, 1994.
- [210] P. Davies, "Fracture of marine composites," in *Key Engineering Materials*, 1996, p. 583.
- [211] R. H. Martin, "Delamination characterization of woven glass/polyester composites," *Journal of Composites, Technology and Research*, vol. 19, pp. 20-28, 1997.
- [212] W. Liu, X. Zhang, G. Xu, P. D. Bradford, X. Wang, H. Zhao, *et al.*, "Producing superior composites by winding carbon nanotubes onto a mandrel under a poly (vinyl alcohol) spray," *Carbon*, vol. 49, pp. 4786-4791, 2011.
- [213] E. Senokos, V. Reguero, L. Cabana, J. Palma, R. Marcilla, and J. J. Vilatela, "Large-Area, All-Solid, and Flexible Electric Double Layer Capacitors Based on CNT Fiber Electrodes and Polymer Electrolytes," *Advanced Materials Technologies*, vol. 2, p. 1600290, 2017.
- [214] I. ASTM, "Standard test methods for flexural properties of unreinforced and reinforced plastics and electrical insulating materials," *ASTM D790-07*, 2007.
- [215] A. Standard, "D6272–10: Standard Test Method for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials by Four Point Bending," *ASTM International*, 2010.
- [216] M. Kersemans, E. Verboven, J. Segers, S. Hedayatrasa, and W. V. Paepegem, "Non-destructive testing of composites by ultrasound, local defect resonance and thermography," in *Multidisciplinary Digital Publishing Institute Proceedings*, 2018, p. 554.
- [217] Y.-N. Liu, M. Li, Y. Gu, K. Wang, D. Hu, Q. Li, *et al.*, "A modified spray-winding approach to enhance the tensile performance of array-based carbon nanotube composite films," *Carbon*, vol. 65, pp. 187-195, 2013.
- [218] S. Li, X. Zhang, J. Zhao, F. Meng, G. Xu, Z. Yong, *et al.*, "Enhancement of carbon nanotube fibres using different solvents and polymers," *Composites Science and Technology*, vol. 72, pp. 1402-1407, 2012.
- [219] A. F. Gill, P. Robinson, and S. Pinho, "Effect of variation in fibre volume fraction on modes I and II delamination behaviour of 5HS woven composites manufactured by RTM," *Composites Science and Technology*, vol. 69, pp. 2368-2375, 2009.
- [220] F. Narducci, K.-Y. Lee, and S. Pinho, "Interface micro-texturing for interlaminar toughness

- tailoring: a film-casting technique," *Composites Science and Technology*, vol. 156, pp. 203-214, 2018.
- [221] Y. Ou, C. González, and J. J. Vilatela, "Understanding interlaminar toughening mechanisms in structural carbon fiber/epoxy composites interleaved with CNT veils," in *Proceeding of ECCM18 Conference.*, Athens, July, 2018.
- [222] R. J. Mora, J. J. Vilatela, and A. H. Windle, "Properties of composites of carbon nanotube fibres," *Composites Science and Technology*, vol. 69, pp. 1558-1563, 2009.
- [223] J. J. Vilatela, L. Deng, I. A. Kinloch, R. J. Young, and A. H. Windle, "Structure of and stress transfer in fibres spun from carbon nanotubes produced by chemical vapour deposition," *Carbon*, vol. 49, pp. 4149-4158, 2011.
- [224] B. Mas, A. Monreal-Bernal, and J. J. Vilatela, "Understanding the Enhancement of Young's modulus of Macroscopic Carbon Nanotube Fibers After Polymer Infiltration," in *AIP Proceedings CNT-NET*, Dresden, 2017.
- [225] A. Mikhalech, T. Gspann, J. Terrones, and A. Banas, "From single CNT fibre to high volume fraction reinforced composites: insights into epoxy infiltration and curing via direct chemical imaging," in *1st International Conference on Multifunctional Nanocarbon Fibres (MNF2018)*, Madrid, Spain, 2018.
- [226] P. Dadras and J. McDowell, "Analytical and experimental evaluation of double-notch shear specimens of orthotropic materials," *Experimental mechanics*, vol. 30, pp. 184-189, 1990.
- [227] G. W. Beckermann and K. L. Pickering, "Mode I and Mode II interlaminar fracture toughness of composite laminates interleaved with electrospun nanofibre veils," *Composites Part A: Applied Science and Manufacturing*, vol. 72, pp. 11-21, 2015.
- [228] T. Brugo and R. Palazzetti, "The effect of thickness of Nylon 6, 6 nanofibrous mat on Modes I–II fracture mechanics of UD and woven composite laminates," *Composite Structures*, vol. 154, pp. 172-178, 2016.
- [229] Y. C. Shin, W. I. Lee, and H. S. Kim, "Mode II interlaminar fracture toughness of carbon nanotubes/epoxy film-interleaved carbon fiber composites," *Composite Structures*, vol. 236, p. 111808, 2020.
- [230] L. Liu, L. Shen, and Y. Zhou, "Improving the interlaminar fracture toughness of carbon/epoxy laminates by directly incorporating with porous carbon nanotube buckypaper," *Journal of*

- Reinforced Plastics and Composites*, vol. 35, pp. 165-176, 2016.
- [231] M. Guo, X. Yi, G. Liu, and L. Liu, "Simultaneously increasing the electrical conductivity and fracture toughness of carbon–fiber composites by using silver nanowires-loaded interleaves," *Composites Science and Technology*, vol. 97, pp. 27-33, 2014.
- [232] E. Senokos, Y. Ou, J. J. Torres, F. Sket, C. González, R. Marcilla, *et al.*, "Energy storage in structural composites by introducing CNT fiber/polymer electrolyte interleaves," *Scientific reports*, vol. 8, pp. 1-10, 2018.
- [233] P. Ladpli, R. Nardari, F. Kopsaftopoulos, and F.-K. Chang, "Multifunctional energy storage composite structures with embedded lithium-ion batteries," *Journal of Power Sources*, vol. 414, pp. 517-529, 2019.
- [234] M. L. Benzeggagh and M. Kenane, "Measurement of mixed-mode delamination fracture toughness of unidirectional glass/epoxy composites with mixed-mode bending apparatus," *Composites science and technology*, vol. 56, pp. 439-449, 1996.
- [235] J. Kupski, S. T. de Freitas, D. Zarouchas, P. Camanho, and R. Benedictus, "Composite layup effect on the failure mechanism of single lap bonded joints," *Composite Structures*, vol. 217, pp. 14-26, 2019.
- [236] J. Bonhomme, A. Argüelles, J. Viña, and I. Viña, "Fractography and failure mechanisms in static mode I and mode II delamination testing of unidirectional carbon reinforced composites," *Polymer Testing*, vol. 28, pp. 612-617, 2009.
- [237] R. Mohammadi, M. A. Najafabadi, H. Saghafi, and D. Zarouchas, "Mode-II fatigue response of AS4/8552 carbon/epoxy composite laminates interleaved by electrospun nanofibers," *Thin-Walled Structures*, vol. 154, p. 106811, 2020.
- [238] M. Rana, Y. Ou, C. Meng, F. Sket, C. González, and J. J. Vilatela, "Damage-tolerant, laminated structural supercapacitor composites enabled by integration of carbon nanotube fibres," *Multifunctional Materials*, vol. 3, p. 015001, 2020.
- [239] C. DiFrancia, T. C. Ward, and R. O. Claus, "The single-fibre pull-out test. 1: Review and interpretation," *Composites Part A: Applied Science and Manufacturing*, vol. 27, pp. 597-612, 1996.
- [240] M. Zu, Q. Li, Y. Zhu, M. Dey, G. Wang, W. Lu, *et al.*, "The effective interfacial shear strength of carbon nanotube fibers in an epoxy matrix characterized by a microdroplet test," *Carbon*, vol.

REFERENCES

- 50, pp. 1271-1279, 2012.
- [241] A. Hillerborg, M. Moder, and P.-E. Petersson, "Analysis of crack formation and crack growth in concrete by means of fracture mechanics and finite elements," *Cement and concrete research*, vol. 6, pp. 773-781, 1976.
- [242] T. Kusaka and T. Kurokawa, "Estimation of mode I interlaminar fracture toughness of CFRP laminates by using wedge insert fracture test," *Journal of the Society of Materials Science, Japan*, vol. 45, pp. 484-489, 1996.