

Different surface treatments of carbon fibers and their influence on the interfacial properties of carbon fiber/epoxy composites

Jing Zhang

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> THÈSE présentée par

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Différents traitements de surface des fibres de carbone et leur influence sur les propriétés à l'interface dans les composites fibres de carbone/résine époxyde

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Acronyms and symbols

Acronyms

AFM	atomic force microscopy
APO	atmospheric plasma oxidation
CF	carbon fiber
CNT	carbon nanotube
CVD	chemical vapor deposition
DGEBA	diglycidyl ether of bisphenol A
FTIR/ATR	attenuated total reflectionFourier transform infrared spectroscopy
H/CNT	HTS40 E23 carbon fibers grown with carbon nanotubes
IFSS	interfacial shear strength
IGC	inverse gas chromatography
ILSS	interlaminar shear strength
MWCNTs	multi-walled carbon nanotubes
PAN	polyacrylonitrile
RTM	resin transfer molding
SEM	scanning electron microscope
T/CNT	T700GC carbon fibers grown with carbon nanotubes
TGA	thermogravimetric analysis
VGCNFs	vapor grown carbon nanofibers
XPS	X-ray photoelectron spectroscopy

Symbols

A _{cnt}	specific surface area of CNT-grafted carbon fibers
A_f	specific surface area of desized carbon fibers
at.%	atomic percentage
b	specimen width
d _{cnt}	CNT diameter
d_f	fiber diameter
E_f	fiber module
E_m	matrix module
F	CNT/fiber joint force
F_{max}	maximum applied force
I_D/I_G	Raman spectrum intensity ratio between D and G band
L	distance between electrodes
L _{cnt}	CNT length
ī	average fragment length
l_c	critical fiber length

l_f	fiber length
m _{cnt}	mass of grafted CNTs
m_f	mass of carbon fibers
N _{cnt}	number of CNTs grafted on the fiber surface
N _{fiber}	number of fiber filament in a bundle
R_a	mean surface roughness value
r _{fibe}	fiber radius
S	surface area of desized fiber
Scnt	surface area of CNTs
Sccnt	total cross sectional area of CNTs
S_f	surface area of carbon fibers
t	specimen thickness
W_A	thermodynamic work of adhesion
wt%	weight fraction
α	scale parameters of the Weibull distribution for fiber strength
β	shape parameters of the Weibull distribution for fiber strength
<i>γLV</i> ,	surface free energies of liquid
γsv,	surface free energies of solid
γsl	surface free energies of the solid-liquid interface
σ	electrical conductivity
$\bar{\sigma}$	mean tensile strength
$\sigma_{_{app}}$	stress applied to the composite
σ_{f}	fiber stress
$\sigma_f(\bar{l})$	fiber strength at the average fragment length
$\sigma_f(l_c)$	fiber strength at the critical fiber length
ρ	electrical resistivity
$ ho_{cnt}$	CNT densiy
$ ho_f$	fiber densiy
τ	interfacial shear strength
$ au_{app}$	apparent interfacial shear strength
$ au_{cnt}$	shear strength of CNTs
$ au_{fiber}$	shear strength of CNT/fiber hybrid
$ au_{hybrid}$	shear strength of desized fiber
$ au_{max}$	interlaminar shear strength
Γ	gamma function

General introduction

Carbon fiber (CF)-reinforced polymer composites have many structural applications, including aircraft, sporting equipment, automotive, and civil structures due to their outstanding mechanical properties, light weight and high thermal stabilities. The overall performance of composites significantly depends on the quality of the fiber-matrix interface. Good interfacial adhesion provides composites with structural integrity and efficient load transfer between fiber and matrix. However, untreated carbon fibers are extremely inert and thus have poor adhesion to resin matrices. Meanwhile, the relatively weak transverse and interlaminar properties greatly limit the composite performance and service life. To overcome these barriers, a fiber-based reinforcement which has strong interfacial adhesion to the matrix is highly desired to improve the overall composite properties.

In this thesis, three kinds of surface treatment, including sizing, heat treatment and carbon nanotube (CNT) growth, were applied to CFs.

Firstly, epoxy-based sizing was applied onto the CF surface by the deposition from polymer solutions. Sizing could not only protect the carbon fiber surface from damage during processing but also improve their wettability to polymer matrix. A detailed study was conducted on the influence of the ratio of epoxy and amine curing agent in the sizing formulation. The sizing level on the fiber surface was controlled by varying the concentration of polymer solutions.

Secondly, heat treatment in a gas mixture at 600-750 °C was used to modify the carbon fiber surface. The effect of gas mixture composition, treatment time and temperature on the interface was evaluated systematically.

Thirdly, CNTs were in-situ grafted on the carbon fiber surface by a continuous chemical vapor deposition (CVD) process to obtain hierarchical reinforcement structures. These hybrid structures have the potential to improve the interfacial strength of fiber/epoxy composites due to the increased lateral support of the load-bearing fibers. Meanwhile, the CNT reinforcement could improve the composite delamination resistance, electrical and thermal properties. The CF grown with CNTs

of different morphologies and densities were produced by varying CVD conditions. In particular, CNT-grafted CFs were further treated using the two methods mentioned above. The combining use of the three treatments could improve the CNT-CF hybrid performance and prevent fiber damage during the subsequent handling such as transport and composite preparation.

After the surface treatment, single fiber fragmentation tests were conducted to assess the interfacial shear strength (IFSS) of carbon fiber/epoxy composites. This work could support the development of large-scale approach to CF surface treatment, and throw light on the design of structurally efficient CF/epoxy composites.

Chapter 1 Introduction

1.1 Carbon fibers

Carbon fibers are fiber materials which contain at least 92 wt% of carbon in composition [1]. They are derived from several precursors, such as polyacrylonitrile (PAN), pitch, rayon, polyesters and polyamides. Thousands of carbon fibers with diameters ranging form 4 to15 µm are bundled together to form a tow, which may be used to produce high-performance materials as it is or in other forms (e.g. fabrics). They have been widely used in aerospace, automotive and sport industries due to their excellent properties, such as high tensile strength and stiffness, low densities, high thermal stabilities and favorable electrical conductivity [2].

1.1.1 Manufacture process

Nowadays, PAN and pitch are predominant carbon-fiber precursors. But the conditions to produce carbon fibers from the two precursors are different. Generally, the fabrication of carbon fibers involves pyrolysis of stabilized precursor fibers. Precursor fibers are first stabilized under stress at 200-400 °C in an oxidizing atmosphere. The stabilized fibers are then carbonized at around 1000 °C in an inert atmosphere to remove hydrogen, oxygen, nitrogen, and other non-carbon elements. During the carbonization process, carbon content increases to above 90%. Carbonized fibers can be further graphitized at a higher temperature up to around 3000 °C in an inert environment to achieve higher carbon content and higher Young's modulus in the fiber direction.

Producing carbon fibers from PAN involves polymerization of acrylonitrile, spinning of PAN, oxidation, carbonization, and graphitization (cf. Fig. 1.1). The development of graphite structures during the pyrolysis of thermally stabilised PAN is shown schematically in Fig. 1.2. To circumvent the drawbacks (i.e. the weak adhesion and poor bonding between crude carbon fibers and resin matrix) during the preparation of carbon fiber-reinforced composites, surface treatments and sizing process are usually applied to increase the surface area and surface acidic functional

groups of carbon fibers and hence improve the bonding between the fiber and the matrix [3-5].



Fig. 1.1 PAN-based carbon fiber production process.



Fig. 1.2 Reactions during carbon fiber manufacturing process. (Adapted from [6]) Pitch is produced from destructive distillation of petroleum or coal tar which is

made up of fused aromatic rings. Both isotropic and mesophase pitches are used to produce carbon fibers. Production of pitch-based carbon fibers involves melt spinning of pitch precursor fibers, oxidation, carbonization, and graphitization (cf. Fig. 1.3).



Fig. 1.3 Pitch-based carbon fiber production process.

1.1.2 Structures and properties of carbon fibers

The carbon fiber is made up of basic structural units of turbostratic carbon planes. These layers of hexagonal carbon rings are along the fiber axis with crystallite sizes of several nm [7], as shown in Fig. 1.4.



Fig. 1.4 Unit cell of graphite showing preferred direction of the layer planes with respect to the fibre axis in PAN-based (PAN) and mesophase-pitch-based (MP) carbon fibers [8]. (Reproduced with permission from IOP Publishing Ltd., © 1987)

The crystallite size increases with increasing the heat treatment temperature and they become better aligned with the fiber axis. The schematic of the basic structural units arranged in a carbon fiber is given in Fig. 1.5. On the fiber surface, the carbon layers are highly oriented. But they are less ordered in the core.



Fig. 1.5 Schematic three-dimensional representation of structure in PAN-based carbon fibers [8]. (Reproduced with permission from IOP Publishing Ltd., © 1987)

High-modulus pitch-based carbon fibers exhibit higher orientation than PAN-based carbon fibers. PAN-based carbon fibers have particulate morphology and smaller crystals (cf. Fig. 1.6), whereas pitch-based carbon fibers exhibit graphitic sheet-like morphology and larger crystals (cf. Fig. 1.7). The properties of carbon fibers strongly depend on the fiber microstructures and morphologies. The properties of some commercial carbon fibers are listed in Table 1.1.



Fig. 1.6 Scanning electron micrographs of PAN-based GY-70 carbon fibers at (a) low and (b) high magnification*.



Fig. 1.7 Scanning electron micrographs of pitch-based P-100 carbon fibers at (a) low and (b) high magnification.*

* Springer and Journal of Materials Science, 28, 1993, 423-439, Carbon fibre compressive strength and its dependence on structure and morphology, S. Kumar, D.P. Anderson, A.S. Crasto, Fig. 12, 15, 17, with kind permission from Springer Science and Business Media.

	Fiber	Tensile Strength (GPa)	Tensile Modulus (GPa)	Diameter (µm)	Elongation to Break (%)	Density (g/cm ³)	Thermal Conductivity (W·m ⁻¹ K ⁻¹)	Electrical Resistivity (Ω·cm)
PAN- based	Hextow AS4	4.47	231	7.1	1.8	1.79	6.83	1.7×10 ⁻³
	Hextow IM10	6.96	303	4.4	2.1	1.79	6.14	1.3×10 ⁻³
	Torayca T300	3.53	230	7	1.5	1.76	10.47	1.7×10 ⁻³
	Torayca T700GC	4.9	240	7	1.8	1.8	-	-
	Torayca M35J	4.7	343	5	1.4	1.75	39.06	1.1×10 ⁻³
	Tenax HTS40	4.3	240	7	1.8	1.77	10	1.6×10 ⁻³
Pitch- based	Nippon YSH-50A	3.83	520	7	0.7	2.1	120	7.0×10 ⁻⁴
	Nippon YS-90A	3.53	880	7	0.3	2.18	500	3.0×10 ⁻⁴
	Nippon XN-05	1.1	54	10	2.0	1.65	7.4	2.8×10 ⁻³
	Thornel P-55	1.38	414	10	0.5	2.00	120	8.5×10 ⁻⁴
	Thornel P-30	1.38	207	10	0.8	2.00	62	1.0×10 ⁻³

Table 1.1 Properties of some commercial carbon fibers*

*Source: Reprinted from manufacturer's technical literature.

Carbon fibers exhibit good thermal and electric conductivities along the fiber direction. The electrical and thermal conductivities increase with fiber tensile modulus and carbonization temperature. Pitch-based carbon fibers usually possess higher Young's modulus and better thermal and electrical conductivity in the fiber direction, while PAN-based carbon fibers exhibit a higher tensile strength. Electrical resistivity of high-modulus carbon fibers is about 5-10 $\mu\Omega$ ·m, while that of high-strength carbon fibers is about 15-25 $\mu\Omega$ ·m [7]. For high-modulus pitch-based carbon fibers, the thermal conductivity can be greater than 500 W·m⁻¹K⁻¹ at room temperature. The transverse texture of mesophase carbon fibers is either radial or

flat-layer as shown in Fig. 1.8, which makes the fiber readily develop three-dimensional crystallinity. This structure gives pitch-based fibers superior lattice-dependent properties [9].



Fig. 1.8 Transverse textures of mesophase pitch-based carbon fibers. (Reprinted from Carbon, 36, D.D. Edie, The effect of processing on the structure and properties of carbon fibers, 2373, Copyright (1998), with permission from Elsevier)

1.2 Surface treatment and sizing of carbon fibers

To improve the adhesion between the carbon fibers and the matrix in a composite, different surface treatments and sizing of carbon fibers are often performed after the carbon fibers come out of the carbonization furnace. Generally, surface treatments of carbon fibers can be divided into oxidative and non-oxidative treatments.

1.2.1 Oxidative surface treatments

There are various methods of oxidative treatments, including dry oxidation in the presence of gases, plasma etching and wet oxidation [10].

Dry oxidative treatments are normally performed with air, oxygen and CO₂ at low or elevated temperatures. Herrick et al. [11] treated rayon-based carbon fiber in air at 500 °C for 16 h to slightly improve the interlaminar shear strength (ILSS). ILSS was improved by 45% when the temperature was raised to 600 °C, although a serious weight loss was accompanied. Scola et al. [12] treated the fibers for 60 s in N₂ containing 0.1-1.8% O₂ at 1000-1500 °C to improve their bonding characteristics in a resin. There was no significant degradation of mechanical properties of the fibers. Dai et al. studied the effect of heat treatment on carbon fiber surface properties and fibers/epoxy interfacial adhesion [2]. T300B carbon fibers were heated in a vacuum drying chamber at 150 °C, 180 °C and 200 °C for several hours using controlled processing cycles. It demonstrated that the content of activated carbon atoms (conjunction with oxygen and nitrogen and hydroxyl) on the treated carbon fiber surface and the polar surface energy decreased with increasing the heat treatment temperature. Compared with the untreated fibers, the wettability studied by dynamic contact angle test between carbon fiber and E51 epoxy resin became worse. The results of micro-droplet tests demonstrated that the IFSS of T300B/epoxy reduced after the heat treatment process. This was attributed to the decrement of the amount of reactive functional groups in the interfacial region.

Plasma treatment has become a popular method for improving the fiber-matrix adhesion in recent years [13-23]. Plasma is a partially or fully ionized gas containing electrons, radicals, ions and neutral atoms or molecules. The principle of a plasma treatment is the formation of active species in a gas induced by a suitable energy transfer. Typical gases used to create a plasma include air, oxygen, ammonia, nitrogen and argon. Erden et al. [23] used continuous atmospheric plasma oxidation (APO) to introduce oxygen functionalities on the surface of carbon fibers in order to improve the interfacial adhesion between carbon fibers and polyamide-12 (PA-12). After the APO treatment, carbon fibers became more hydrophilic due to the introduction of polar oxygen-containing groups on the fiber surface, which also resulted in an increase of fiber surface energy. And the fiber tensile strength remained unaffected. The IFSS between carbon fibers and PA-12 increased from 40 to 83 MPa with up to 4 min of APO treatment. This can be attributed to the increase of surface oxygen content from 7 at.% to 16 at.%, which yielded more hydrogen bonds between fibers

and PA-12 matrix.

A number of liquid-phase oxidizing agents (e.g. nitric acid, acidic potassium permanganate, acidic potassium dichromate, hydrogen peroxide and ammonium bicarbonate) have also been used to treat carbon fiber surface. These liquid-phase treatments do not cause excessive pitting and hence degradation of the fiber strength [10].

Anodic oxidation is most widely used for treatment of commercial carbon fibers as it is fast, uniform and suited to mass production [24-27]. Carbon fibers act as an anode in a suitable electrolyte bath. A potential is applied to the fiber to liberate oxygen on the surface. Typical electrolytes include nitric acid, sulfuric acid, sodium chloride, potassium nitrate, sodium hydroxide, ammonium hydroxide and so on.

1.2.2 Non-oxidative surface treatments

Non-oxidative methods, including the deposition of an active form of carbon, plasma polymerization and grafting of polymers onto the fiber surface [28] have been used for the carbon fiber surface treatments.

Whiskerization involves the growth of thin and high strength single crystals, such as silicon carbide (SiC), silicon nitride (Si₃N₄) and titanium dioxide (TiO₂) at right angles to the fiber surface [29].

Many polymerizable organic vapors are used for plasma polymerization process, such as polyamide, polyimide, organosilanes, propylene, and styrene monomers. Plasma polymerization is demonstrated to increase the polar component of surface free energy of carbon fibers [30, 31].

1.2.3 Sizing of carbon fibers

Sizing of carbon fibers refers to the coating of organic materials applied to fiber surface during the manufacture [32-34]. Sizing is reputed to protect the fiber surface

from damage during subsequent textile processing, aid in handling, provide a chemical link between the fiber surface and the matrix and thus to improve the fiber-matrix adhesion [35].

Sizing can be achieved by deposition of polymers from solutions onto the fiber surface. The fibers pass through a sizing bath filled with organic solutions. The choice of sizing materials depends on the fiber type and the matrix resin. They must be compatible with the matrix resin, which allows the resin to penetrate into the fiber bundle and interact with the fiber surface. Typical sizing materials include epoxy, urethane, polyester and others. The sizing amount is 0.5-1.5 wt% of the fiber and the sizing layer is hundreds of nanometers thick [34].

Drzal et al. [36] have studied the effect of sizing on the adhesion of carbon fiber to epoxy matrix. They found that the sizing layer created a brittle interface layer between the fiber and matrix which improved the IFSS.

Dai et al. [37] have investigated the influence of sizing on the carbon fiber/matrix interfacial adhesion by comparing sized and desized T300B and T700SC carbon fibers. They found that the desized carbon fibers presented less concentration of activated carbon atoms (conjunction with oxygen and nitrogen) and lower polar surface energy, but higher dispersive surface energy and IFSS. The sizing agent on T300B and T700SC fiber surface was negative for the interfacial bonding. This is contrary to the general principles. Desizing reduced the acid parameter of carbon fibers surface which promoted bonding strength at the fiber/epoxy interface. The IFSS of T300B/epoxy increased from 63.72 MPa to 87.77 MPa after desizing, with an improvement of 38%. This was attributed to the increment of work of adhesion. The IFSS of desized T700SC/epoxy (89.39 MPa) was 9% greater than that of T700SC/epoxy (81.74 MPa). The thicker sizing might result in weak layer in the interface region. They concluded that IFSS for carbon fiber/epoxy systems depended not only on the chemical bonding but also on the physical and adhesive interactions.

1.3 Carbon fiber-matrix interface

In fiber-reinforced composites, both the fiber and the matrix keep their original physical and chemical properties. Meanwhile, a combination of mechanical properties is produced, which cannot be attained with either of the components acting alone [10]. That is due to the presence of an interface (or more properly named, interphase [38]) between these two constituents [10]. The issue of interface is of great interest in the design and manufacture of composite components.

1.3.1 General introduction to fiber/matrix interface

The interface in fiber-reinforced composites is a surface formed by a common boundary of fiber and matrix for the transfer of loads. The physical and mechanical properties of the interface are different from those of the individual bulk fiber and matrix. Since 1990, the concept of the fiber-matrix interface, which exists as a two-dimensional boundary, has been expanded into that of a fiber-matrix interphase that exists in three dimensions [39]. The interphase is a region different in structure and composition near the fiber-matrix interface. The interphase starts from some point in the fiber through the actual interface into the matrix. Fig. 1.9 schematically illustrates the concept of the three-dimensional interphase between fiber and matrix according to Drzal et al. [40].



Fig. 1.9 Characteristics of the fiber/matrix interphase in a composite material. (Reprinted from Composites, 23, P.J. Herrera-Franco, L.T. Drzal, Comparison of methods for the measurement of fibre/matrix adhesion in composites, 3, Copyright (1992), with permission from Elsevier)

Generally, interfacial adhesion can be attributed to major mechanisms including, adsorption and wetting, electrostatic attraction, chemical bonding, exchange reaction bonding, and mechanical bonding according to Kim [41].

Good wetting of the fiber by the matrix is important for proper consolidation of composites. Bonding due to wetting involves interactions of electrons on an atomic scale. Wetting can be quantitatively expressed in terms of the thermodynamic work of adhesion, W_A , represents the thermodynamic work necessary to create a solid-vapor surface and a liquid-vapor surface by pulling apart the solid-liquid interface.

$$W_A = \gamma_{LV} + \gamma_{SV} - \gamma_{SL} \tag{1-1}$$

where γ_{LV} , γ_{SV} , γ_{SL} are the surface free energies of the liquid, the solid, and the solid-liquid interface, respectively. Good wetting occurs only when the surface energy of the fiber (γ_{SV}) is greater than that of the matrix (γ_{LV}). Contact angle measurements are extremely useful for determining the wettability of the carbon fibers surface by the

resin matrix [42-45].

Chemical reactions occur between constituents at the interface region [46, 47]. A bond is created between the chemical group on the fiber surface and another compatible chemical group in the matrix. The bonds strength is decided by the number and type of bonds. The functional groups existing on the carbon fiber surface include -COOH, C-OH and C=O [48]. Surface oxidative treatments of carbon fibers are widely used to promote chemical bonding with polymer resins [26, 49].

Mechanical bonding is a significant mechanism of bonding in carbon fiber-polymer matrix composites. The interlocking at the fiber surface can be promoted by introducing large number of pits and corrugations to the carbon fiber surface or increasing the carbon surface area. The interfacial shears strength significantly depends on the degree of roughness [50, 51].

1.3.2 Effects of interface on composite performance

The final performance of composite materials depends not only on properties of fiber and matrices, but also on the quality of the fiber-matrix interface [52]. Good interfacial adhesion provides composites with structural integrity and efficient load transfer from fiber to matrix [53, 54]. The on-axis properties (such as longitudinal tensile, compressive, and flexural properties) are dominated by fiber properties, whereas the off-axis properties (such as transverse tensile and flexural, in-plane and interlaminar shear) and interlaminar fracture toughness are dominated by matrix and interfacial properties.

Drzal et al. [55] have established the correlation between the interface bond strength and mechanical properties of carbon fiber-epoxy matrix composites. A-4 PAN-based carbon fibers (Hercules, Inc.) with different surface conditions have been used. They have been designated as AU4, AS4 and AS4C which stand for "as received", "surface treated" with an electrochemical oxidation procedure, and "surface treated and coated" with a 100-200 nm thick layer of epoxy. The results obtained from a series of mechanical tests are summarized in Table 1.2 and Table 1.3.

AU4/Epoxy AS4/Epoxy AS4C/Epoxy Properties Interfacial shear 37.2 68.3 81.4 strength (MPa) Longitudinal tensile 130±9 138±5 150 ± 9 modulus (GPa) Longitudinal tensile 1403±107 1890±143 2044±256 strength (MPa) Longitudinal compressive 131 ± 8 126±9 153±8 modulus (GPa) Longitudinal compressive 679 ± 116 911±180 1174±207 strength (MPa) Longitudinal flexural 154 ± 6 136±11 147 ± 5 modulus (GPa) Longitudinal flexural 1662 ± 92 1557 ± 102 1827 ± 52 strength (MPa)

Table 1.2 Summary of on-axis properties of carbon fiber- epoxy matrix composites with different fiber surface treatments [55]

The interfacial shear strengths have been calculated from single fiber fragmentation tests, which also identify failure modes. After the surface treatments, there has been a significant increase in the IFSS. For AU4 fiber, the adhesion level was low, and frictional debonding was detected at failure. Pure interfacial failure occurred after surface treatment in the case of AS4 fiber. AS4C fiber has shown highest adhesion level due to better stress transfer between fiber and matrix and matrix cracking has been observed at fiber breaks. The failure mode has changed from interfacial to matrix.

The longitudinal tensile strength of has been found to increase with interfacial bond shear strength when the failure was interfacial. The compressive strength has been shown to be enhanced as fiber-matrix increase, which was attributed to the increase of the load necessary to cause the interface failure in transverse tension due to the Poisson effect under compression. In contrast, the longitudinal tensile and compressive moduli were insensitive to changes in fiber-matrix adhesion. There has been little change in the flexural strength and moduli with low and intermediate interface. But for AS4C fiber which has shown strongest interface bond strength, there was a significant improvement in the flexural stiffness and strength due to the ability of the high modulus interface to suppress the interlaminar failure.

Table 1.3 Summary of off-axis properties of carbon fiber- epoxy matrix composites with different fiber surface treatments [55]

Properties	AU4/Epoxy	AS4/Epoxy	AS4C/Epoxy
Interfacial shear strength (MPa)	37.2	68.3	81.4
Transverse tensile modulus (GPa)	8.9±0.6	9.8±0.6	10.3±0.6
Transverse tensile strength (MPa)	18.0±3.9	34.2±6.2	41.2±4.7
Transverse flexural modulus (GPa)	10.2±1.5	9.9±0.5	10.7±0.6
Transverse flexural strength (MPa)	21.4±5.8	50.2±3.4	75.6±14.0
[±45] _{3s} in-plane shear modulus (GPa)	9.1±1.5	6.2±0.5	6.0±0.2
$[\pm 45]_{3s}$ in-plane shear strength (MPa)	37.2±1.8	72.2±12.4	97.5±7.4
Iosipescu in-plane shear modulus (GPa)	7.2±0.5	6.4±1.0	7.9±0.4
Iosipescu in-plane shear strength (MPa)	55.0±3.0	95.6±5.1	93.8±3.3
Short beam interlaminar shear strength (MPa)	47.5±5.4	84.0±7.0	93.2±3.8

From the values of the off-axis properties summarized in Table 1.3, it has been shown that all the strength values were sensitive to the interface adhesion, while the modulus values were relatively insensitive to the interface bonding. In particular, the transverse flexural strength can be a good indicator of the interfacial strength. In the case of ILSS, the Iosipescu method showed the least scatter among the three mechanical tests carried out. The failure in Iosipescu and short beam shear test specimens were matrix-dominated, while the $\pm 45^{\circ}$ specimen was relatively insensitive to the change in failure mode.

1.3.3 Characterization of interfacial properties of fiber composites

A large number of experimental techniques have been developed to measure the properties of the interface in fiber composites [56-66]. These methods can broadly be

classified into two groups depending on the nature of specimens employed and the scale of testing: one includes the testing of microcomposites where individual fibers are embedded in matrix, such as the fiber pull-out test [67, 68], the indentation test [69, 70], the single-fiber fragmentation test [71, 72], and the embedded fiber compression test [73], as shown in Fig. 1.10 and Fig. 1.11; and the other uses bulk laminate composites to evaluate the interlaminar/intralaminar properties, some examples are given in Fig. 1.12 [56].



Fig. 1.10 Micromechanical tests in which external load is applied to the matrix: fragmentation test (a) and Broutman test (b)*.



Fig. 1.11 Micromechanical tests in which external load is applied directly to the fiber:

pull-out (a), microbond (b), three-fiber test (c), and push-out (d)*. *Reprinted from Composites Science and Technology, 65, Serge Zhandarov, Edith Mader, Characterization of fiber/matrix interface strength: applicability of different tests, approaches and parameter, 150-151, Copyright (2004), with permission from Elsevier.



Fig. 1.12 Schematic representation of laminate composite shear test. (Reprinted from Composites, 23, P.J. Herrera-Franco, L.T. Drzal, Comparison of methods for the measurement of fibre/matrix adhesion in composites, 22, Copyright (1992), with permission from Elsevier)

The fiber pull-out method has been developed in the early stages of composites research [74]. In this method, a fiber or a fiber bundle is partially embedded in a matrix block, a thin disc, or a droplet firstly. When the fiber is loaded under tension while the matrix block is gripped, the load and displacements are then monitored continuously during the whole debond and pull-out process. Fig. 1.13 shows a typical force-displacement curve. A conventional way to determine the apparent IFSS τ_{app} is
by using the following equation [75]:

$$\tau_{app} = \frac{F_{max}}{\pi d_f l_f} \tag{1-2}$$

where d_f is the fiber diameter and l_f is the embedded length. This technique can be used for almost any fiber-matrix combination. But a relatively large scatter in the test data is obtained, which is attributed mainly to testing parameters such as droplet gripping, faulty measurement of fiber diameters, and so on.



Fig. 1.13. A typical force-displacement curve recorded during a pull-out test. (From the same source as Fig. 1.11 and Fig. 1.12)

Lu et al. [76] have prepared multi-scale CNT-hybridized carbon fibers by a newly developed aerosol-assisted CVD, and the BET surface area of the hybrid fibers was almost three times more than the original carbon fibers. Meanwhile, they have also investigated the interfacial shearing strength of a caron fiber-reinforced polymer composite with the produced CNT-hybridized carbon fiber and an epoxy matrix from the single fiber pull-out tests of micro-droplet composite, as shown in Fig. 1.14. A single fiber was pulled out from the cured epoxy droplet and the force to pull the fiber out of the epoxy was measured and used to calculate the IFSS.



Fig. 1.14 Schematic diagrams of single fiber pull-out test (a) and photograph of sample testing (b) [76].(Reproduced with permission from Elsevier)

The results indicated that the IFSS of the carbon fiber-reinforced polymer composite with the produced CNT-hybridized carbon fiber and an epoxy matrix was about 94% more than the original carbon fibers. The improvement of the IFSS was attributed to the fact that fiber surface area increased with the grafting of CNTs which resulted in the increase of the touching resin matrix region around the carbon fibers and finally provided a stronger interfacial properties.

The fiber fragmentation test is one of the most popular methods to evaluate the interface properties of fiber-matrix composites. It has been developed from the early work of Kelly and Tyson [77]. Here, a single fiber is embedded entirely in the middle of the matrix which is formed into a tensile dog-bone shaped specimen. The failure strain of the matrix material must be at least three times greater than that of the fiber. When the specimen is loaded in tension, the embedded fiber breaks into increasingly smaller fragments at locations where the fiber tensile strength is exceeded. The fragmentation process repeats until all fiber lengths are too short to allow its tensile stress to cause more fiber breakage. The IFSS τ can be estimated from the Kelly-Tyson model [77]:

$$\tau = K \frac{d_f \sigma_f(\bar{l})}{2\bar{l}} \tag{1-3}$$

where K adopts a mean value of 0.75, d_f is the fiber diameter, $\sigma_f(\bar{l})$ is the fiber strength at the sauturation length \bar{l} . This technique yields a large amount of information for statistical sampling and replicates the events in-situ in the composite. But there are also some shortcomings in this method, such as the matrix must have a strain limit and sufficient toughness to avoid fiber fracture induced failure, the fiber strength should be known at the critical length and so on.

The microindentation technique is also popular for measuring the fiber interfacial shear strength [78]. The single fibers perpendicular to a cut and polished surface of an actual composite are compressively loaded using an indenter with various tip shapes and sizes. During the test, the force and indenter tip displacement are continuously monitored until the fiber detaches from the matrix. The IFSS may be obtained from:

$$\tau = \frac{F_{max}}{\pi d_f l_f} \tag{1-4}$$

where F_{max} is the maximum applied force required for debonding and pushing a fiber out of the specimen, d_f is the fiber diameter, l_f is the fiber length (the thickness of the specimen). The microindentation technique is an in-situ interface test for real composites and it reflects actual processing conditions. The drawbacks include crushing and splitting of fibers by the sharp indenter under compression, the inability to observe the failure mode or locus of failure.

Apart from the direct measurements of fiber-matrix interface properties as stated above, a number of methods have been designed to evaluate the fiber-matrix interface bond quality by inference from the gross mechanical properties such as ILSS, transverse tensile strength and translaminar shear strength [10, 40]. These techniques employ laminated composites reinforced with continuous and long fibers, whether unidirectional or cross-plied.

The short beam shear test is one of the most widely used laminate techniques. It is used to measures the ILSS. In this test, a beam fabricated from unidirectional laminate composites is loaded in three-point bending. The specimen has a span-to-width ratio (L/h) chosen to produce interlaminar shear failure. The ILSS is given by:

$$\tau_{max} = \frac{3F_{max}}{4bt} \tag{1-5}$$

where F_{max} is the maximum applied load, *b* is the specimen width and *t* is the specimen thickness. An inherent problem in this technique is that the loading nose of small diameter induces stress concentration and non-linear plastic deformation.

1.3.4 Improvement of the interfacial adhesion between carbon fiber and matrix

The carbon fiber/matrix adhesion is weak due to a chemically stable surface of carbon fiber. A large number of surface treatment techniques for carbon fibers have been developed to improve the carbon fiber-matrix interfacial adhesion through introducing more chemical reactive sites on the surface or increasing the fiber surface area.

Deng et al. [79] have grafted the diblock copolymer hydroxyl-terminated poly (n-butylacrylate)-b-poly (glycidyl methacrylate) (HO-PnBA-b-PGMA) onto the surface of the carbon fibers (cf. Fig. 1.15) and then studied the influence of the grafted polymers on the interfacial properties between carbon fibers and epoxy resin.



Fig. 1.15 Schematic illustration of grafting block copolymer onto carbon fibers [79]. (Reproduced with permission from Elsevier)

The results indicated that the IFSS of the carbon fiber/epoxy resin composites were significantly improved by the introduction of the diblock copolymer. The IFSS value increased with increasing length of the PnBA block in the copolymer when the polymerization degree of PnBA (DPn) was below 180, and then decreased with further increasing of the DPn of PnBA. But the length of PGMS block showed no obvious effect on the IFSS.

The application of a sizing to the carbon fiber surface is an efficient way to increase the fiber/matrix adhesion. Sizing makes the carbon fiber more compatible with the matrix, thus the wetting and impregnation of the fiber tow by the matrix is enhanced.

Marieta et al. [80] have investigated the influence of sizing on a high-strength carbon fiber in respect of interfacial adhesion in composite materials with a cyanate matrix. Fig. 1.16 shows a comparison of the averages of the apparent IFSS values for the analyzed systems. The commercially sized carbon fiber possessed much higher apparent IFSS due to the chemical reactions that took place between the epoxy sizing and the bisphenol-A dicyanate resin during the curing process.



Fig. 1.16 Apparent IFSS data of the microcomposites based on the carbon fibers with different treatments and DCBA matrix by pull out measurements. (Reprinted from Composites Science and Technology, 62, C. Marieta, E. Schulz, I. Mondragon, Characterization of interfacial behaviour in carbon-fibre/cyanate composites, 307, Copyright (2002), with permission from Elsevier)

Zhang et al. [81] have studied the effect of emulsifier content in sizing agent on the carbon fiber surfaces and the interface of carbon fiber/epoxy composites. Carbon fibers were sized with different emulsifier content (10 wt%, 15 wt% and 20 wt%) sizing agent. The result showed that both the surface roughness and surface energy of the sized carbon fibers increased with increasing the emulsifier content in sizing agent. When higher content of emulsifier was used, the carbon fiber tensile strength and the IFSS became greater. They [82] have also studied the effect of emulsifier content of sizing agent on the carbon fiber surface by the atomic force microscopy (AFM) and it indicated that the emulsifier content had the important effect to improving the surface of the fiber. In addition, the surface composition of the fibers has been characterized using X-ray photoelectron spectroscopy (XPS) and it showed that the C-C was the major carbon functional components on the surface of carbon fibers samples and -C-OH, -C-OR and -C=N on the E-3 sized carbon fibers were more than that of other size agent sized carbon fibers. The effects of emulsifier content of sizing agent on the adhesion of surface on the interlaminar shear strength were also examined and it indicated that the 20 wt% of emulsifier content sizing agent (E-3) sized carbon fiber/epoxy resin composite showed better interfacial shear strengths.

Heat treatment is also a kind of surface treatments for carbon fibers to improve fiber/matrix adhesion by changing the fiber surface properties.

Bismarck et al. [83] have produced basic carbon fiber surfaces by heating fibers at 905 °C under nitrogen, cooling to 25 °C and then exposing them to oxygen. They have also produced basic carbon fiber surfaces by heating fibers in air at 385 °C. The contact angle of acidic carbon fibers versus water was lower compared with basic carbon fibers. Since thermoplastic materials contain acidic groups, the adhesion between the thermoplastic matrix and the carbon fiber could be improved due to acid-base interactions by a suitable thermo treatment.

Feih et al. [84] have studied the effect of fire on the tensile properties of carbon fibers and provided new insights into the tensile performance of carbon fiber-polymer composite materials during fire. By determining the reduction to the tensile properties and identifying the softening mechanism of T700 carbon fiber following exposure to simulated fires of different temperatures (up to 700 °C) and atmospheres (air and inert), they concluded that the fiber modulus decreased with increasing temperature (above ~500 °C) in air, which was attributed to oxidation of the higher stiffness layer in the near-surface fiber region. But the fiber modulus was not affected when heated in nitrogen due to the absence of surface oxidation, which indicated that the stiffness loss of carbon fiber composites in fire was sensitive to the oxygen content.

Dai et al. [85] have studied the reaction of the functional groups between the carbon fiber surface and the fiber surface sizing during heat treatment in detailed. The

results indicated that the concentration of epoxy groups in both the fiber surface sizing and the extracted sizing decreased with the increasing heat-treatment temperature, but it was lower in the extracted sizing compared with that of fiber surface sizing after heat treatment under the same conditions. It indicated that the reaction rate between the functional groups of fiber surface was higher than that of sizing system itself. Moreover, the content of C-O bonds and activated carbon atoms on the surface of the desized carbon fibers was highest after the heat treatment at 150 °C, which proved the reaction between the functional groups on the surface of carbon fibers and the sizing materials.

Li et al. [86] have investigated the effect of heat treatments for T700 carbon fiber on properties of nitride matrix composites. T700 carbon fibers were oxidized at 400 °C in air for 1.5 h or heated in an inert atmosphere at 1000 °C for 1 h. After the treatment, the oxidized fibers displayed rough surfaces, whereas the heat treated fibers exhibited relatively smooth surfaces like the as-received fibers. Both flexural strength and elastic modulus of oxidized fiber reinforced composite were visibly improved, and those of heat treated fiber reinforced composite were slightly changed. The interface between fiber and matrix can be effectively improved by the oxidation method.

In addition of the heat treatment, moisture also has effect on the interface between a carbon fiber and an epoxy matrix.

Liu et al. [87] have studied the interfacial toughness after water aging in T300 carbon fiber/5228 epoxy resin composite by the interfacial fracture energy, which was derived from the modified Wagner-Nairn-Detassis model. The results indicated that the interfacial fracture energy decreased obviously after immersion in boiling water and immersion in water at 70 °C and can recovery to the original level after re-drying treatments. The swelling of the resin matrix and interphase resulted in an increase in interphase thickness and a decrease in interphase bonding property, which indicated that the interfacial fracture shad a close relationship with the interfacial fracture energy.

Zafar et al. [88] have prepared single fiber model composites based on an epoxy resin using high modulus carbon fibers and investigated the long term effects of moisture on the interface between a carbon fiber and an epoxy matrix. The results indicated that the glass transition temperature decreased after moisture absorption. The effects of moisture on the axial strain of the carbon fiber within the composite and stress transfer at the interface as a function of exposure time was observed using Raman spectroscopy, and it showed that the decrease in mechanical and interface properties of the model composites under the seawater immersion was more significant than under demineralised water immersion.

Another possible solution developed more recently for increasing IFSS is to graft CNTs directly onto the surface of the fibers via varied techniques [89-92]. As CNTs have a high aspect ratio and desirable thermal, electrical and mechanical properties, it is anticipated to create hybrid fibers with highly tailored surface area and properties.

Agnihotri et al. [93] have grown CNTs on the surface of carbon fiber/fabric using catalytic CVD at 550 °C. Different lengths and quantities of CNTs have been obtained by varying the CVD reaction time from 5 to 25 min. Both the density and length of CNTs on the fiber surface increased as the growth time increased and can attain a length greater than 50µm. After the heat treatment inside the CVD reactor, the elastic modulus and breaking strength of carbon fibers remained unchanged. The Tg of the CNT-coated fiber/polyester composites was same as that of the composite made from as received carbon fibers. The optimum CNT growth time was 15-20 min to improve the storage modulus of the multiscale composite and the pull out strength of single CNT-coated carbon fibers increased by as much as 33% and 88%, respectively. Both of the properties dropped significantly when the growth time was beyond 20 min.

Wang et al. [94] have used electrophoretic deposition method (cf. Fig. 1.17) to deposit vapor grown carbon nanofibers (VGCNFs) on carbon fibers and fabricated composites of the resulting hybrid material (CF-VGCNF) in an epoxy matrix by the vacuum-assisted resin transfer molding process. The results indicated that the electrical conductivities of the composites were significantly improved compared to

those without the VGCNF reinforcement.



Fig.1.17 Principle of electrophoretic deposition process [94]. (Reproduced with permission from Elsevier)

The Taguchi method was used to optimize the electrophoretic deposition process conditions (i.e. deposition time, applied voltage, concentration of VGCNF in a distilled water suspension, and the distance between anode (a carbon fabric) and cathode (a copper plate)) through the analysis of means and the analysis of variance for achieving a highly uniform deposition of carbon nanofibers. The results indicated that electrical conductivity of the CF-VGCNF/epoxy composite had a 51% improvement at the optimum deposition conditions that the deposition time is 5 min, the voltage is 40 V, the concentration of VGCNFs is 0.1 wt%, and the distance between electrodes is 10 mm.

Lv et al. [95] have grafted multi-walled carbon nanotubes (MWCNTs) onto carbon fibers using an injection CVD method to increase the interfacial strength in carbon fiber/epoxy composites. Entangled and highly aligned MWCNTs (cf. Fig. 1.18) with different length were obtained by controlling the surface treatment of the carbon fibers and the growth time. When the carbon fibers were coated by SiO₂ before the nanotube growth, highly aligned MWCNT which were perpendicular to the fibers were gotten. That was because the strong adhesion between the catalyst and SiO₂ coating leads to high density deposition. The length of nanotube array ranged from 16.6 to 108.6µm under the growth time at 30-120 min. The length of the MWCNT alignment increased with the growth time. The carbon fibers strength dropped after the growth of MWCNTs due to the surface damage caused by the catalyst iron etching and the thermal degradation at high temperature (850°C). A steady decrease was observed as the growth time increased. Particularly, for the fibers under 120 min of growth, the tensile strength decreased by around 33.5%. The carbon fibers grown with MWCNTs showed a good wettability according to the contact angle test. Compared to the pristine carbon fibers, there was an improvement of the IFSS between the hybrid fibers and the epoxy resin (Table 1.4). An optimum length (47.2µm) of aligned MWCNTs showed a remarkable improvement of the IFSS of up to 175%.



Fig. 1.18 SEM images of unsized carbon fibers (a) before and (b) after the surface treatment, and carbon fibers grafted by (c) entangled MWCNTs (sample 1) and (d–h) aligned MWCNTs (samples 2–6) with different length controlled by the growth time. (Reprinted from Carbon, 49,

P. Lv, Y. Feng, P. Zhang, H. Chen, N. Zhao, W. Feng, Increasing the interfacial strength in carbon fiber/epoxy composites by controlling the orientation and length of carbon nanotubes grown on the fibers, 4668, Copyright (2011), with permission from Elsevier)

Sample	CNTs Orientation	CNTs Length (µm)	$\tau_{\rm IFSS}(MPa)$
а	-	-	17.4
c	Entangled	N/A	22.3
d	Aligned	16.6	25.2
e	Aligned	23.1	32.3
f	Aligned	47.2	47.8
g	Aligned	63.5	46.1
h	Aligned	108.6	42.9

Table 1.4. Single fiber fragmentation test results

A study of wetting and fiber fragmentation of CNT grafted carbon fibers was conducted by Qian et al. [42]. CNTs were grown on IM7 carbon fibers using a chemical vapor deposition method at 750°C for 1h. After the grafting process, the BET surface area increased by three times compared to the pristine carbon fibers. At the same time, the fiber tensile strength decreased by around 15% (depending on gauge length) which was resulted from the dissolution of iron particles into the carbon fiber surface during the high temperature growth reaction. The modulus was almost unchanged. Contact angles between carbon fibers and poly (methylmethacrylate) were directly measured using a drop-on-fiber systems and indicated that the CNT grafted carbon fibers possessed good wettability by the polymer. The results of single fiber fragmentation tests demonstrated a significant improvement (26%) of the apparent interfacial shear strength after CNT grafting, which correlated directly with a reduced contact angle between fiber and matrix. This was attributed to a more efficient stress transfer between the carbon fibers and surrounding matrix, through the grafted CNT layer.

Storck et al [96] reported that shorter, higher density nanotube forests on the fiber surface yielded increases in interlaminar strength of the composite. Gains of up 36.2% in IM7 carbon fiber were seen. Conversely, nanotubes longer than two times the fiber diameter reduced interlaminar strength.

1.4 Carbon fiber-reinforced composites

In a carbon fiber-reinforced composite, at least one of the reinforcements is carbon fiber, short or continuous, unidirectional or multidirectional, woven or nonwoven and the matrix is usually a polymer, a metal, a carbon, a ceramic, or a combination of different materials [97-104]. Polymer-matrix composites are much easier to fabricate than composites made up with other matrix. Epoxy resins are the most common polymer matrix used with carbon fibers and currently constitute over 90% of the matrix resin material used in advanced composites [7, 105].

1.4.1 Manufacture process

There are numerous methods for fabricating fiber composites. The selection of a method will depend on the materials, the part design and the end-use.



Fig 1.19 Diagram of a typical vacuum bag lay-up [28].

Continuous fiber composites are commonly fabricated by hand lay-up of fibers and impregnation with a resin. The fiber tapes or woven fabrics are placed in a die and high-pressure gases or a vacuum is introduced via a bag to force the plies together as shown in Fig. 1.19. The vacuum bagging process consolidates the plies and significantly reduces voids due to the off-gassing that occurs during the matrix curing stages.

Resin transfer molding (RTM) involves transferring the resin through injection ports, under moderate pressure (0.35-0.70 MPa) into a closed and clamped mold in which the reinforcement has already been placed (cf. Fig 1.20). This method can be used to produce continuous carbon fiber composites of intricate shapes. But it is limited to low-viscosity resins, such as epoxy. The dry reinforcements and resins used in RTM are less expensive than prepreg materials and they can be stored at room temperature.



Fig. 1.20 Resin transfer molding [106].

Pultrusion is a relatively simple, low-cost, continuous process, producing a profile of constant cross-section. The fibers is typically pulled through a heated resin bath for impregnation, and gathered together to produce a particular shape before entering a heated die.

Filament winding is primarily used for hollow, generally circular or oval sectioned components. Fiber tows are wound continuous from a spool onto a mandrel in a variety of orientations. The fibers can be impregnated with a resin before or after winding. Three basic types of filament winding are hoop, helical and multi-directional winding.

1.4.2 Applications

Carbon fiber-reinforced composites have a wide range of applications because of their high performance and their ability to tailor fiber architecture to meet final performance requirements [107-111]. Nowadays, carbon fiber is indispensable in the aircraft/aerospace, sports, and recreation industries [112-116]. The main applications are shown in Fig. 1.21.



Fig. 1.21 Applications of carbon fiber-reinforced composites

Aircraft remains the dominant market for carbon fibers, where high specific properties have always been at a premium. Light weight, thermal stability and high

rigidity make carbon fiber a critical part in the modern aircraft/aerospace applications including primary and secondary structure for Boeing and Airbus civil aircraft, the International Space Station, satellites etc [117]. For the latest Boeing 777, carbon-fiber composites made up 7% of the total materials.

In the automotive industry, carbon fiber polymer-matrix composites are mainly used for saving weigh. Carbon fibers have been used in leaf springs and in transmission shafts on light trucks [7].

Another most significant application for carbon fiber composites is in sporting goods. These applications started early, and they were the largest market before significant aerospace applications existed. Typical products include golf club shafts, tennis racquets, fishing rods, bicycle components and skiing equipment.

The electrically conductive characteristic of carbon fiber polymer-matrix composites makes them suitable for elimination of static, electrodes, batteries and fuel cells [118-122]. In addition, carbon fiber polymer-matrix composites are used for the protection of aircraft from lightning strike [121]. The high thermal conductivity and low thermal expansion of carbon fiber composites make them attractive for heat dissipation components [123-127]. New applications of carbon fibers are developing at a rapid pace and the potential uses for carbon fiber are virtually limitless.

1.5 References

[1] Huang X. Fabrication and Properties of Carbon Fibers. Materials. 2009;2:2369-2403.

[2] Dai Z, Zhang B, Shi F, Li M, Zhang Z, Gu Y. Effect of heat treatment on carbon fiber surface properties and fibers/epoxy interfacial adhesion. Applied Surface Science. 2011;257:8457-8461.

[3] Jacobasch H-J, Grundke K, Uhlmann P, Simon F, MÄDER E. Comparison of surface-chemical methods for characterizing carbon fiber-epoxy resin composites. Composite Interfaces. 1995;3:293-320.

[4] Sherwood PMA. Surface analysis of carbon and carbon fibers for composites. Journal of Electron Spectroscopy and Related Phenomena. 1996;81:319-342.

[5] Weitzsacker CL, Xie M, Drzal LT. Using XPS to Investigate Fiber/Matrix Chemical Interactions in Carbon-fiber-reinforced Composites. Surface and Interface Analysis. 1997;25:53-63.

[6] Goodhew PJ, Clarke AJ, Bailey JE. A review of the fabrication and properties of carbon fibres. Materials Science and Engineering. 1975;17:3-30.

[7] Dorey G. Carbon fibres and their applications. Journal of Physics D: Applied Physics. 1987;20:245-256.

[8] Johnson DJ. Structure-property relationships in carbon fibres. Journal of Physics D: Applied Physics. 1987;20:286-291.

[9] Edie DD. The effect of processing on the structure and properties of carbon fibers. Carbon. 1998;36:345-362.

[10] Kim JK, Mai YW. Engineered Interfaces in Fiber Reinforced Composites. Oxford: Elsevier Science Ltd; 1998.

[11] Herrick JW, Gruber PE, Mansur FT. Surface treatments for fibrous carbon reinforcements. 1966. p. AFML-TR-66-178, Part I.

[12] Scola DA, Basche M. Treatment of carbon fibers. United States Patent 3720536; 1970.

[13] Morra M, Occhiello E, Garbassi F, Nicolais L. Surface studies on untreated and plasma-treated carbon fibers. Composites Science and Technology. 1991;42:361-372.

[14] Commerçon P, Wightman JP. Surface characterization of plasma treated carbon fibers and adhesion to a thermoplastic polymer. The Journal of Adhesion. 1992;38:55-78.

[15] Yuan LY, Chen CS, Shyu SS, Lai JY. Plasma surface treatment on carbon fibers. Part 1: Morphology and surface analysis of plasma etched fibers. Composites Science and Technology. 1992;45:1-7.

[16] Yuan LY, Shyu SS, Lai JY. Plasma surface treatments of carbon fibers. Part 2: Interfacial adhesion with poly(phenylene sulfide). Composites Science and Technology. 1992;45:9-16.

[17] Allred RE, Schimpf WC. CO2 plasma modification of high-modulus carbon fibers and their adhesion to epoxy resins. Journal of Adhesion Science and Technology. 1994;8:383-394.

[18] Dilsiz N, Ebert E, Weisweiler W, Akovali G. Effect of Plasma Polymerization on

Carbon Fibers Used for Fiber/Epoxy Composites. Journal of Colloid and Interface Science. 1995;170:241-248.

[19] Vaidyanathan NP, Kabadi VN, Vaidyanathan R, Sadler RL. Surface Treatment of Carbon Fibers Using Low Temperature Plasma. The Journal of Adhesion. 1995;48:1-24.

[20] Chand N, Schulz E, Hinrichsen G. Adhesion improvement of carbon fibres by plasma treatment and evaluation by pull-out. Journal of Materials Science Letters. 1996;15:1374-1375.

[21] Bogoeva-Gaceva G, Mäder E, Haüssler L, Dekanski A. Characterization of the surface and interphase of plasma-treated HM carbon fibres. Composites Part A: Applied Science and Manufacturing. 1997;28:445-452.

[22] Pittman Jr CU, Jiang W, He G-R, Gardner SD. Oxygen plasma and isobutylene plasma treatments of carbon fibers: Determination of surface functionality and effects on composite properties. Carbon. 1998;36:25-37.

[23] Erden S, Kingsley KCH, Lamoriniere S, Lee AF, Yildiz H, Bismarck A. Continuous atmospheric plasma oxidation of carbon fibres: influence on the fibre surface and bulk properties and adhesion to polyamide 12. Plasma Chemistry and Plasma Processing. 2010;30:471-487.

[24] Yumitori S, Nakanishi Y. Effect of anodic oxidation of coal tar pitch-based carbon fibre on adhesion in epoxy matrix: Part 2. Comparative study of three alkaline solutions. Composites Part A: Applied Science and Manufacturing. 1996;27(11):1059-1066.

[25] Yumitori S, Nakanishi Y. Effect of anodic oxidation of coal tar pitch-based carbon fibre on adhesion in epoxy matrix: Part 1. Comparison between H2SO4 and NaOH solutions. Composites Part A: Applied Science and Manufacturing. 1996;27(11):1051-1058.

[26] Fukunaga A, Ueda S. Anodic surface oxidation for pitch-based carbon fibers and the interfacial bond strengths in epoxy matrices. Composites Science and Technology. 2000;60(2):249-254.

[27] Liu X, Yang C, Lu Y. Contrastive study of anodic oxidation on carbon fibers and graphite fibers. Applied Surface Science. 2012;258(10):4268-4275.

[28] Morgan P. Carbon Fibers and Their Composites: CRC Press; 2005.

[29] Goan JC, Prosen SP. Interfacial bonding in graphite fiber-resin composites. Interfaces in Composites, Philadelphia: ASTM; 1969. p. 3-26.

[30] Donnet JB, Guilpain G. Surface characterization of carbon fibres. Composites. 1991;22(1):59-62.

[31] Dagli G, Sung N-H. Properties of carbon/graphite fibers modified by plasma polymerization. Polymer Composites. 1989;10:109-116.

[32] Fitzer E, Weiss R. Effect of surface treatment and sizing of c-fibres on the mechanical properties of cfr thermosetting and thermoplastic polymers. Carbon. 1987;25(4):455-467.

[33] Yumitori S, Wang D, Jones FR. The role of sizing resins in carbon fibre-reinforced polyethersulfone (PES). Composites. 1994;25(7):698-705.

[34] Broyles NS, Chan R, Davis RM, Lesko JJ, Riffle JS. Sizing of carbon fibres with

aqueous solutions of poly(vinyl pyrollidone). Polymer. 1998;39(12):2607-2613.

[35] Sugiura N, Maki N. Sizing agent for carbon fiber, method for sizing carbon fiber by said sizing agent, sized carbon fiber and knitted or woven fabric using said carbon fiber. United States Patent 7135516: Mitsubishi Rayon Co., Ltd. (Tokyo, JP); 2006.

[36] Drzal LT, Rich MJ, Koenig MF, Lloyd PF. Adhesion of Graphite Fibers to Epoxy Matrices: II. The Effect of Fiber Finish. The Journal of Adhesion. 1983;16:133-152.

[37] Dai Z, Shi F, Zhang B, Li M, Zhang Z. Effect of sizing on carbon fiber surface properties and fibers/epoxy interfacial adhesion. Applied Surface Science. 2011;257:6980-6985.

[38] Drzal LT, Rich MJ, Lloyd PF. Adhesion of Graphite Fibers to Epoxy Matrices: I. The Role of Fiber Surface Treatment. The Journal of Adhesion. 1983;16:1-30.

[39] Drzal LT. Interfaces and Interphases In: Daniel B. Miracle SLD, editor. ASM Handbook, Volume 21-Composites: ASM International; 2001

[40] Herrera-Franco PJ, Drzal LT. Comparison of methods for the measurement of fibre/matrix adhesion in composites. Composites. 1992;23(1):2-27.

[41] Kim J-K, Mai Y-W. Interfaces in Composites. In: Chou TW, editor. Structure and Properties of Fiber Composites, Materials Science and Technology, Weinheim, Germany: VCH Publication; 1993. p. 239-289.

[42] Qian H, Bismarck A, Greenhalgh ES, Shaffer MSP. Carbon nanotube grafted carbon fibres: A study of wetting and fibre fragmentation. Composites Part A: Applied Science and Manufacturing. 2010;41:1107-1114.

[43] Dilsiz N, Erinç NK, Bayramli E, akovali G. Surface energy and mechanical properties of plasma-modified carbon fibers. Carbon. 1995;33(6):853-858.

[44] Bismarck A, Kumru ME, Springer J, Simitzis J. Surface properties of PAN-based carbon fibers tuned by anodic oxidation in different alkaline electrolyte systems. Applied Surface Science. 1999;143(1–4):45-55.

[45] Ho KKC, Lamoriniere S, Kalinka G, Schulz E, Bismarck A. Interfacial behavior between atmospheric-plasma-fluorinated carbon fibers and poly(vinylidene fluoride). Journal of Colloid and Interface Science. 2007;313(2):476-484.

[46] Nakayama Y, Soeda F, Ishitani A. XPS study of the carbon fiber matrix interface. Carbon. 1990;28(1):21-26.

[47] Atkinson KE, Farrow GJ, Jones C. Study of the interaction of carbon fibre surfaces with a monofunctional epoxy resin. Composites Part A: Applied Science and Manufacturing. 1996;27(9):799-804.

[48] Dilsiz N, Wightman JP. Surface analysis of unsized and sized carbon fibers. Carbon. 1999;37:1105-1114.

[49] Guo H, Huang YD, Meng LH, Liu L, Fan DP, Liu DX. Interface property of carbon fibers/epoxy resin composite improved by hydrogen peroxide in supercritical water. Materials Letters. 2009;63(17):1531-1534.

[50] Bénard Q, Fois M, Grisel M. Roughness and fibre reinforcement effect onto wettability of composite surfaces. Applied Surface Science. 2007;253(10):4753-4758.

[51] Song W, Gu A, Liang G, Yuan L. Effect of the surface roughness on interfacial properties of carbon fibers reinforced epoxy resin composites. Applied Surface Science. 2011;257(9):4069-4074.

[52] Schultz J, Lavielle L, Martin C. The Role of the Interface in Carbon Fibre-Epoxy Composites. The Journal of Adhesion. 1987;23(1):45-60.

[53] Piggott MR. The effect of the interface/interphase on fiber composite properties. Polymer Composites. 1987;8:291-297.

[54] Piggott MR. The interface in carbon fibre composites. Carbon. 1989;27(5):657-662.

[55] Drzal LT, Madhukar M. Fibre-matrix adhesion and its relationship to composite mechanical properties. Journal of Materials Science. 1993;28:569-610.

[56] Herrera-Franco PJ, Drzal LT. Comparison of methods for the measurement of fibre/matrix adhesion in composites. Composites. 1992;23:2-27.

[57] Kim JK, Zhou, L.M. ,Mai, Y.W. Techniques for Studying Composite Interfaces. In: Cheremisinoff NP, editor. Handbook of Advanced Materials Testing New York: Marcel Dekker; 1994. p. 327-366.

[58] Domnanovich A, Peterlik H, Kromp K. Determination of interface parameters for carbon/carbon composites by the fibre-bundle pull-out test. Composites Science and Technology. 1996;56(9):1017-1029.

[59] Yu A, Gupta V. Measurement of in situ fiber/matrix interface strength in graphite/epoxy composites. Composites Science and Technology. 1998;58(11):1827-1837.

[60] Montes-Morán MA, Young RJ. Raman spectroscopy study of high-modulus carbon fibres: effect of plasma-treatment on the interfacial properties of single-fibre–epoxy composites: Part II: Characterisation of the fibre–matrix interface. Carbon. 2002;40(6):857-875.

[61] Zafeiropoulos NE, Baillie CA, Hodgkinson JM. Engineering and characterisation of the interface in flax fibre/polypropylene composite materials. Part II. The effect of surface treatments on the interface. Composites Part A: Applied Science and Manufacturing. 2002;33(9):1185-1190.

[62] Brandstetter J, Peterlik H, Kromp K, Weiss R. A new fibre-bundle pull-out test to determine interface properties of a 2D-woven carbon/carbon composite. Composites Science and Technology. 2003;63(5):653-660.

[63] Zhandarov S. Characterization of fiber/matrix interface strength: applicability of different tests, approaches and parameters. Composites Science and Technology. 2005;65:149-160.

[64] Nishikawa M, Okabe T, Hemmi K, Takeda N. Micromechanical modeling of the microbond test to quantify the interfacial properties of fiber-reinforced composites. International Journal of Solids and Structures. 2008;45:4098-4113.

[65] You JH, Lutz W, Gerger H, Siddiq A, Brendel A, Höschen C, et al. Fiber push-out study of a copper matrix composite with an engineered interface: Experiments and cohesive element simulation. International Journal of Solids and Structures. 2009;46(25–26):4277-4286.

[66] Godara A, Gorbatikh L, Kalinka G, Warrier A, Rochez O, Mezzo L, et al. Interfacial shear strength of a glass fiber/epoxy bonding in composites modified with carbon nanotubes. Composites Science and Technology. 2010;70(9):1346-1352.

[67] Pitkethly MJ, Doble JB. Characterizing the fibre/matrix interface of carbon

fibre-reinforced composites using a single fibre pull-out test. Composites. 1990;21(5):389-395.

[68] DiFrancia C, Ward TC, Claus RO. The single-fibre pull-out test. 1: Review and interpretation. Composites Part A: Applied Science and Manufacturing. 1996;27(8):597-612.

[69] Ramanathan T, Bismarck A, Schulz E, Subramanian K. Investigation of the influence of surface-activated carbon fibres on debonding energy and frictional stress in polymer-matrix composites by the micro-indentation technique. Composites Science and Technology. 2001;61(16):2511-2518.

[70] Desaeger M, Verpoest I. On the use of the micro-indentation test technique to measure the interfacial shear strength of fibre-reinforced polymer composites. Composites Science and Technology. 1993;48(1–4):215-226.

[71] Huang Y, Young RJ. Analysis of the fragmentation test for carbon-fibre/epoxy model composites by means of Raman spectroscopy. Composites Science and Technology. 1994;52(4):505-517.

[72] Baillie CA, Bader MG. Strength studies of single carbon fibres in model composite fragmentation tests. Composites. 1994;25(6):401-406.

[73] Park J-M, Kim J-W, Yoon D-J. Interfacial evaluation and microfailure mechanisms of single carbon fiber/bismaleimide (BMI) composites by tensile and compressive fragmentation tests and acoustic emission. Composites Science and Technology. 2002;62(6):743-756.

[74] Broutman LJ. Measurement of the Fiber-Polymer Matrix Interfacial Strength.
Interfaces in Composites: American Society for Testing and Materials; 1969. p. 27-41.
[75] Miller B, Muri P, Rebenfeld L. A microbond method for determination of the shear strength of a fiber/resin interface. Composites Science and Technology. 1987;28(1):17-32.

[76] An F, Lu CX, Li YH, Guo JH, Lu XX, Lu HB, et al. Preparation and characterization of carbon nanotube-hybridized carbon fiber to reinforce epoxy composite. Materials & Design. 2012;33:197-202.

[77] Kelly A, Tyson WR. Tensile properties of fibre-reinforced metals: Copper/tungsten and copper/molybdenum. Journal of the Mechanics and Physics of Solids. 1965;13(6):329-350.

[78] Mandell JF, Chen J-H, McGarry FJ. A Microdebonding Test for In-situ Fiber Matrix Bond Strength and Moisture Effects. Research report: Department of Materials Science and Engineering, Massachusetts Institute of Technology; 1980.

[79] Deng SH, Zhou XD, Fan CJ, Lin QF, Zhou XG. Release of interfacial thermal stress and accompanying improvement of interfacial adhesion in carbon fiber reinforced epoxy resin composites: Induced by diblock copolymers. Composites Part a-Applied Science and Manufacturing. 2012;43(6):990-996.

[80] Marieta C, Schulz E, Mondragon I. Characterization of interfacial behaviour in carbon-fibre/cyanate composites. Composites Science and Technology. 2002;62(2):299-309.

[81] Zhang RL, Huang YD, Liu L, Tang YR, Su D, Xu LW. Effect of emulsifier content of sizing agent on the surface of carbon fibres and interface of its composites.

Applied Surface Science. 2011;257:3519-3523.

[82] Zhang RL, Huang YD, Liu L, Tang YR, Su D, Xu LW. Influence of sizing emulsifier content on the properties of carbon fibers and its composites. Materials & Design. 2012;33:367-371.

[83] Bismarck A, Wuertz C, Springer J. Basic surface oxides on carbon fibers. Carbon. 1999;37(7):1019-1027.

[84] Feih S, Mouritz AP. Tensile properties of carbon fibres and carbon fibre-polymer composites in fire. Composites Part a-Applied Science and Manufacturing. 2012;43(5):765-772.

[85] Dai ZS, Zhang BY, Shi FH, Li M, Zhang ZG, Gu YZ. Chemical interaction between carbon fibers and surface sizing. Journal of Applied Polymer Science. 2012;124(3):2127-2132.

[86] Li B, Zhang C-R, Cao F, Wang S-Q, Chen B, Li J-S. Effects of fiber surface treatments on mechanical properties of T700 carbon fiber reinforced BN–Si3N4 composites. Materials Science and Engineering: A. 2007;471(1–2):169-173.

[87] Liu HX, Gu YZ, Li M, Zhang ZG. Characterization of interfacial toughness in carbon fiber/epoxy resin composite subjected to water aging using single-fiber fragmentation method in an energy-based model. Polymer Composites. 2012;33(5):716-722.

[88] Zafar A, Bertocco F, Schjodt-Thomsen J, Rauhe JC. Investigation of the long term effects of moisture on carbon fibre and epoxy matrix composites. Composites Science and Technology. 2012;72(6):656-666.

[89] Qian H, Bismarck A, Greenhalgh ES, Shaffer MSP. Carbon nanotube grafted silica fibres: Characterising the interface at the single fibre level. Composites Science and Technology. 2010;70(2):393-399.

[90] Wicks SS, de Villoria RG, Wardle BL. Interlaminar and intralaminar reinforcement of composite laminates with aligned carbon nanotubes. Composites Science and Technology. 2010;70(1):20-28.

[91] An F, Lu C, Li Y, Guo J, Lu X, Lu H, et al. Preparation and characterization of carbon nanotube-hybridized carbon fiber to reinforce epoxy composite. Materials & amp; Design. 2012;33(0):197-202.

[92] Coleman JN, Khan U, Blau WJ, Gun'ko YK. Small but strong: A review of the mechanical properties of carbon nanotube–polymer composites. Carbon. 2006;44(9):1624-1652.

[93] Agnihotri P, Basu S, Kar KK. Effect of carbon nanotube length and density on the properties of carbon nanotube-coated carbon fiber/polyester composites. Carbon. 2011;49:3098-3106.

[94] Wang YQ, Byun JH, Kim BS, Song JI, Chou TW. The use of Taguchi optimization in determining optimum electrophoretic conditions for the deposition of carbon nanofiber on carbon fibers for use in carbon/epoxy composites. Carbon. 2012;50(8):2853-2859.

[95] Lv P, Feng Y, Zhang P, Chen H, Zhao N, Feng W. Increasing the interfacial strength in carbon fiber/epoxy composites by controlling the orientation and length of carbon nanotubes grown on the fibers. Carbon. 2011;49:4665-4673.

[96] Storck S, Malecki H, Shah T, Zupan M. Improvements in interlaminar strength: A carbon nanotube approach. Composites Part B: Engineering. 2011;42:1508-1516.

[97] Chung DDL. Carbon Fiber Composites. Newton: Butterworth-Heinemann; 1994.

[98] Akihama S, Suenaga T, Banno T. The behaviour of carbon fibre reinforced cement composites in direct tension. International Journal of Cement Composites and Lightweight Concrete. 1984;6(3):159-168.

[99] Christ K, Hüttinger KJ. Carbon-fiber-reinforced carbon composites fabricated with mesophase pitch. Carbon. 1993;31(5):731-750.

[100] Dhami TL, Bahl OP, Jain PK. Carbon-carbon composites made with oxidised PAN (Panex) fibers. Carbon. 1995;33(11):1517-1524.

[101] Bianchi V, Goursat P, Ménessier E. Carbon-fiber-reinforced YMAS glass-ceramic-matrix composites—IV. Thermal residual stresses and fiber/matrix interfaces. Composites Science and Technology. 1998;58(3–4):409-418.

[102] Tsotra P, Friedrich K. Electrical and mechanical properties of functionally graded epoxy-resin/carbon fibre composites. Composites Part A: Applied Science and Manufacturing. 2003;34(1):75-82.

[103] Rams J, Ureña A, Escalera MD, Sánchez M. Electroless nickel coated short carbon fibres in aluminium matrix composites. Composites Part A: Applied Science and Manufacturing. 2007;38(2):566-575.

[104] Yang WS, Biamino S, Padovano E, Fuso L, Pavese M, Marchisio S, et al. Microstructure and mechanical properties of short carbon fibre/SiC multilayer composites prepared by tape casting. Composites Science and Technology. 2012;72(6):675-680.

[105] Stenzenberger HD. Recent developments of thermosetting polymers for advanced composites. Composite Structures. 1993;24(3):219-231.

[106] Gruit Guide to Composites. http://www.gurit.com/composite-materials-and-technology.aspx.

[107] Zhang Q, Liu J, Sager R, Dai L, Baur J. Hierarchical composites of carbon nanotubes on carbon fiber: Influence of growth condition on fiber tensile properties. Composites Science and Technology. 2009;69:594-601.

[108] Larson BK, Drzal LT, Sorousian P. Carbon fibre-cement adhesion in carbon fibre reinforced cement composites. Composites. 1990;21(3):205-215.

[109] Selzer R, Friedrich K. Mechanical properties and failure behaviour of carbon fibre-reinforced polymer composites under the influence of moisture. Composites Part A: Applied Science and Manufacturing. 1997;28(6):595-604.

[110] Davis DC, Wilkerson JW, Zhu J, Hadjiev VG. A strategy for improving mechanical properties of a fiber reinforced epoxy composite using functionalized carbon nanotubes. Composites Science and Technology. 2011;71(8):1089-1097.

[111] Ho KKC, Shamsuddin S-R, Laffan M, Bismarck A. Unidirectional carbon fibre reinforced poly (vinylidene fluoride): Impact of atmospheric plasma on composite performance. Composites Part A: Applied Science and Manufacturing. 2011;42(5):453-461.

[112] Wan YZ, Wang YL, Zhou FG, Cheng GX, Han KY. Three-dimensionally

braided carbon fiber-epoxy composites, a new type of materials for osteosynthesis devices. II. Influence of fiber surface treatment. Journal of Applied Polymer Science. 2002;85(5):1040-1046.

[113] Dhakate SR, Bahl OP. Effect of carbon fiber surface functional groups on the mechanical properties of carbon-carbon composites with HTT. Carbon. 2003;41(6):1193-1203.

[114] Sharma SP, Lakkad SC. Effect of CNTs growth on carbon fibers on the tensile strength of CNTs grown carbon fiber-reinforced polymer matrix composites. Composites Part a-Applied Science and Manufacturing. 2011;42(1):8-15.

[115] Manocha LM, Bhatt H, Manocha SM. Development of carbon/carbon composites by co-carbonization of phenolic resin and oxidised pan fibers. Carbon. 1996;34(7):841-849.

[116] He H, Wang J, Li K, Wang J, Gu J. Mixed resin and carbon fibres surface treatment for preparation of carbon fibres composites with good interfacial bonding strength. Materials & Design. 2010;31(10):4631-4637.

[117] Lee SM. Handbook of Composite Reinforcements. John Wiley & Sons; 1993. p. 76-78.

[118] Lodge KJ. The electrical properties of joints in carbon fibre composites. Composites. 1982;13(3):305-310.

[119] Baker AA, Jones R, Callinan RJ. Damage tolerance of graphite/epoxy composites. Composite Structures. 1985;4(1):15-44.

[120] Meier U. Strengthening of structures using carbon fibre/epoxy composites. Construction and Building Materials. 1995;9(6):341-351.

[121] Hirano Y, Katsumata S, Iwahori Y, Todoroki A. Artificial lightning testing on graphite/epoxy composite laminate. Composites Part A: Applied Science and Manufacturing. 2010;41(10):1461-1470.

[122] Deierling PE, Zhupanska OI. Experimental study of high electric current effects in carbon/epoxy composites. Composites Science and Technology. 2011;71(14):1659-1664.

[123] Korb G, Koráb J, Groboth G. Thermal expansion behaviour of unidirectional carbon-fibre-reinforced copper-matrix composites. Composites Part A: Applied Science and Manufacturing. 1998;29(12):1563-1567.

[124] Fukai J, Kanou M, Kodama Y, Miyatake O. Thermal conductivity enhancement of energy storage media using carbon fibers. Energy Conversion and Management. 2000;41(14):1543-1556.

[125] Gallego NC, Edie DD, Nysten B, Issi JP, Treleaven JW, Deshpande GV. The thermal conductivity of ribbon-shaped carbon fibers. Carbon. 2000;38(7):1003-1010.

[126] Gandikota V, Jones GF, Fleischer AS. Thermal performance of a carbon fiber composite material heat sink in an FC-72 thermosyphon. Experimental Thermal and Fluid Science. 2010;34(5):554-561.

[127] Wang Q, Han XH, Sommers A, Park Y, T' Joen C, Jacobi A. A review on application of carbonaceous materials and carbon matrix composites for heat exchangers and heat sinks. International Journal of Refrigeration. 2012;35(1):7-26.

Chapter 2 Sizing of carbon fibers and the influence on the carbon fiber/epoxy matrix interface

2.1 Introduction

It is well known that mechanical properties of carbon fiber reinforced polymer composites significantly depend on interfacial properties of fibers and resin matrices. Untreated carbon fibers which are extremely inert normally have poor adhesion to resin matrices [1], resulting in composites with relatively low mechanical properties. The sizing technique which provides an interface between fibers and matrices has been developed to optimize the properties of composites [2-4]. The advantage for the carbon fiber sizing treatments is that they could not only protect the carbon fiber surface from damage but also improve the wetting of the carbon fiber by the matrix [5].

When the carbon fibers treated with sizing technique are subsequently used for composites, the carbon fiber surface participates in forming the interface/interphase region between the matrix and the fiber [1]. It has been recognized that the composition of sizing formulation play an important role in the final performance of the composites.

Drzal et.al. [5] demonstrated that the sizing formulation which contained a less than stoichiometric amount of curing agent created a layer of higher modulus and lower fracture toughness than the bulk resin and promoted better stress transfer and hence higher interfacial shear strength. The results were different from our present study which indicated that the optimal amount of curing agent in the sizing formulation is a little more than the stoichiometric amount.

In the present study, we report on the effect of sizing formulation on interfacial properties between carbon fibers and matrices, and the IFSS of carbon fiber/epoxy composites was evaluated by single fiber fragmentation test. Surfaces morphologies and chemistry of desized and sized carbon fibers were studied by scanning electron microscope (SEM), atomic force microscopy (AFM), attenuated total reflection-fourier transform infrared spectroscopy (FTIR/ATR) and thermo gravimetric analysis (TGA).

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2.2 Experimental

2.2.1 Materials

T700GC provided by Toray Carbon Fibers America, Inc. and HTS40 E23 (HTS for short) provided by Toho Tenax America, Inc. were used in this study. Both of them are PAN-based carbon fibers and commercially available as "sized". Some typical properties of the carbon fibers are listed in Table 2.1.

Table 2.1 Properties of T700GC and HTS40 E23 carbon fibers. (Reprinted from manufacturer's technical literature)

Fiber type	T700GC	HTS40 E23
Brand name	Torayca®	Tenax®
Number of filaments	12K	12K
Tensile Strength (MPa)	4900	4300
Tensile Modulus (GPa)	240	240
Elongation at break (%)	1.8	1.8
Filament diameter (µm)	7	7
Density (g/cm3)	1.80	1.77
Sizing Type & Amount	epoxy-based sizing, 0.3-0.9 %	epoxy-based sizing, 1.3 %

The as-received fibers were heat treated at 700 °C under inert atmospheres for around 10 minutes to remove the commercial sizing and they were defined as desized carbon fibers. The desized fibers would be resized with epoxy resin later.

Diglycidyl ether of bisphenol A (DGEBA) L14817 (Alfa Aesar) epoxide monomer was used as sizing material in this study and polyetheramine EC310 (Baxxodur) was used as curing agent. The chemical structures of the epoxide monomer and the amine are shown in Fig. 2.1.



Polyetheramine

Fig. 2.1 Chemical structure of DGEBA epoxide and EC310 polyethertriamine curing agent.

In single fiber fragmentation test, WWA/WWB4 epoxy system (Resoltech) was used as the matrix resin. In single fiber tensile test, diglycil ether bisphenol A based, EP-502 (Polymer Gvulot) and diethylene tetramine based, EPC-9 curing agent (Polymer Gvulot) were used for sample preparation.

2.2.2 Sizing process

Different proportions of epoxy DGEBA and hardener EC310 were mixed and dissolved in acetone to prepare the sizing material. Subsequently, desized fibers were soaked in the solution for several minutes. Finally, the fibers were dried at room temperature for 24 h.

To investigate the effects of different proportions of epoxy and hardener on the interfacial properties, 2 wt% acetone solutions with epoxy-amine composition of 0, 23.7, 47.3, 94.7 and 110 parts EC310 per 100 parts DGEBA were prepared.

Sizing thickness was controlled by changing the concentration of sizing solution with the epoxy-amine ratio of 100 : 94.7. Four concentrations were investigated: 0.5 wt%, 1 wt%, 2 wt%, and 4 wt%.

2.2.3 Characterization methods

The surface morphologies of carbon fibers were examined by SEM (LEO Gemini 1530).

AFM (Digital Instruments Nanoscope IIIa) was used to obtain topographic imaging of the carbon surface and estimate the surface roughness.

The sizing amount was investigated by TGA using a thermal gravity analyzer/differential scanning calorimeter (NETZSCH STA449 F3). Fiber samples were degraded in nitrogen and oxygen at a constant heating rate of 20 °C/min.

FTIR/ATR (Nexus, Thermo Electron) was used to characterize the chemical structure of sizing materials and the carbon fiber surface.

2.2.4 Evaluation of the interfacial shear strength of carbon fiber/epoxy composites

Single fiber fragmentation test was used to determine IFSS of carbon fiber/epoxy composites. The fragmentation test is widely used for measuring the effect of different surface treatments on the interfacial shear strength of carbon fibers because the specimen preparation and testing procedures are relatively simple and wealth of information can be obtained in terms of damage processes [5-7].

When an external stress is applied to a matrix where a single fiber is embedded, the tensile stress is transferred into the fiber through an interfacial shear stress. The tensile strain in the fiber increases with the increase of tensile load. Once the tensile strain exceeds the failure strain of the fiber, the fiber will fracture. As the load increases, the fiber continues to fracture into shorter lengths until the fragments becomes too short to break, as illustrated in Fig. 2.2 [8]. This situation is defined as the saturation state in the fiber fragmentation process. This shortest fragment length that breaks due to a stress application is defined as the critical length fiber fragment. The interfacial shear strength τ can be estimated from the Kelly-Tyson model [9]:

$$\tau = \frac{d_f \sigma_f(l_c)}{2l_c} \tag{2-1}$$

where d_f is the fiber diameter, $\sigma_f(l_c)$ is the fiber strength at the critical fiber length l_c .

The critical fiber length is determined by:

$$l_c = \frac{4}{3}\overline{l} \tag{2-2}$$

where \bar{l} is the average fragment length.



Fig. 2.2 Schematic representation of the single fiber fragmentation process. (Reprinted from Composites, 23, P.J. Herrera-Franco, L.T. Drzal, Comparison of methods for the measurement of fibre/matrix adhesion in composites, 3, Copyright (1992), with permission from Elsevier)

A group of mould was designed for the single-fiber composite fabrication as shown in Fig. 2.3. Stoichiometric proportions of epoxy WWA and hardener WWB4 were mixed (WWA : WWB4 = 100 : 40 by weight) and degassed in a vacuum cell at room temperature in order to allow the trapped air bubbles to escape from the system. A single fiber was carefully separated from a yarn and both ends of the fiber were fastened to a 0.1 mm thick steel shim with double sided adhesive tape in order to keep the fiber straight. Six such fibers could be aligned on the shim. Another 0.1 mm thick shim was placed on the first shim. The shims were then covered by two plates. The epoxy was injected into the mould through the inlets in the top plate (cf. Fig. 2.4).



Fig. 2.3 Mould used to prepare single-fiber composite.



Fig. 2.4 Single-fiber composite fabrication.

After curing for 15 h at 60 °C and then cooling slowly to room temperature, a 0.2mm thick single composite sheet was prepared. Finally the individual specimens were cut from this sheet into dog-bone shape using a specially designed cutter, as shown in Fig. 2.5. The gauge length of all samples was about 10 mm. The fragmentation tests were performed by using INSTRON 5544 tensile testing apparatus equipped with a load cell of 2000 N under an optical microscope fitted with a video

camera. The samples were tested at a rate of 0.1 mm/min until saturation (no more breaks occur when applying further strain to the specimen) was reached. The number of fiber breaks within the gauge length was counted for calculating the average fragment lengths using an optical microscope (Leica Aristomet DC300). Meanwhile, an image of the fractured sample was taken with a camera while mounting on the microscope.



Fig. 2.5 Specimen of dog-bone shape for fragmentation test.

To calculate IFSS, the fiber strength at the critical length should be known. In the original model of Kelly and Tyson, the fiber strength was assumed to be deterministic and constant, which is experimentally incorrect. The fiber strength is a statistical parameter which cannot be fully described by a single value and it is length-dependent. There are two ways to measure the size effect in single fibers. The conventional way is to perform extensive tensile tests with single fiber at different gauge length, followed by extrapolation to the critical length, which is usually inaccessible in a tensile test [10-12]. The other way is to perform a real-time fragmentation test, which is proposed by Wagner and coworkers [13, 14]. The latter method was adopted in this study as it is much simpler and has similar accuracy as the former. In the real-time fragmentation test, the number and length of fragments was recorded at any desired level of stress. We were able to assess how the average fragment length varies with the applied stress. As the test can be viewed as a multiple

"in-series" tensile test of single fibers of varying lengths, it is named as single fiber tensile test here. Assuming that the strength of a fiber obeys the Weibull/weakest link model, the mean tensile strength $\overline{\sigma}$ of fibers having an average length *L* is given by:

$$\overline{\sigma} = \alpha L^{-1/\beta} \Gamma \left(1 + \frac{1}{\beta} \right)$$
(2-3)

where α and β are the scale and shape parameters of the Weibull distribution for strength, respectively, and Γ is the gamma function. The relationship between the average fragment length \bar{l} and the fiber stress σ_f is given by inverting Equation (2-3):

$$\bar{l} = \alpha^{\beta} \sigma_{f}^{-\beta} \left\{ \Gamma \left(1 + \frac{1}{\beta} \right) \right\}^{\beta}$$
(2-4)

or,
$$\ln \bar{l} = -\beta \ln \sigma_f + \beta \ln \left\{ \alpha \Gamma \left(1 + \frac{1}{\beta} \right) \right\}$$
(2-5)

 σ_{f} , may be obtained from the stress applied to the composite σ_{app} :

$$\sigma_f = \sigma_{app} \left(\frac{E_f}{E_m} \right) \tag{2-6}$$

where E_f and E_m are the fiber and matrix module, respectively.

The values of α and β can easily be obtained from a plot of ln (\bar{l}) against ln (σ_f) , which allows to calculate the fiber strength at the critical length.

The specimen manufacture for single fiber tensile test is quite like that of fragmentation test as mentioned before. Stoichiometric proportions of epoxy EP-50 and hardener EPC-9 were mixed and degassed in a vacuum cell at room temperature. A single fiber was aligned on a polycarbonate plate $(35 \times 70 \times 2 \text{ mm}^3)$. Fiber straightening was achieved by gluing one end of the fiber, fastening with light weight at the other end and then gluing. A spacer was aligned in the middle of the plate.
Fibers were aligned on both sides. Liquid epoxy resin was spread on the plate, covered and a load of about 1 kg was applied carefully on the top of the plate. The sample was cured for 5 h at 80 °C and then allowed to cool slowly to room temperature to avoid the formation of internal stresses. After curing, the epoxy film was cut to size using a specially designed cutter. The gauge length of all samples was about 15 mm. The single fiber tensile tests were performed by using a minimat 2000 (Rheometric Scientific) tensile testing apparatus equipped with a load cell of 200 N under a microscope with crossed polarized light, fitted with a video camera. The samples were tested at a rate of 0.05 mm/min, the fracture events were recorded as a function of applied load. When a break occurred, the corresponding stress was recorded and the mean length of the fragments present was calculated by dividing the initial gauge length of the specimen by the number of breaks (plus one) present at that stress.

2.3 Results and discussion

2.3.1 Surface characterization

The morphologies of carbon fibers were studied using SEM and some of the characteristic micrographs are given in Fig. 2.6-Fig. 2.8.

For T700GC fibers (cf. Fig. 2.6), it could be clearly seen that desized fibers had no more polymer patches adhered to surface compared with as-received fibers. There were longitudinal, discontinuous ridges extending parallel to the fiber axis on the surface. For the resized fibers, the longitudinal streaks on the surface became less clear. Polymer grains were found on the surface of resized fibers when a mixture of epoxy and hardener was used as sizing material (cf. Fig. 2.7). When the concentration of sizing solution was below 4%, all fibers were uniformly coated with a thin layer of epoxy resin. As the concentration increased to 4%, the coating became nonuniform and many sizing bridges were created between fibers. The resulting filament clumping or filament/filament cohesion must be kept to a minimum as it is unfavorable for composite processing.



Fig. 2.6 SEM pictures of T700GC fibers: (a) as-received; (b) desized; (c) resized with pure epoxy.



Fig. 2.7 SEM pictures of T700GC fibers resized using different sizing concentrations (a) 0.5%;
(b) 1%; (c) 2%; (d) 4%.

HTS fibers had more clear ridges and striations on the surface along the main fiber direction compared with T700GC fibers. Polymer particles were observed on the

surface of as-received fibers (cf. Fig. 2.8). After desizing, there were no more sizing materials on the fiber surface in the form of polymer particles. For resized fibers, the surface had thicker and less frequent up-and-downs.



Fig. 2.8 SEM pictures of HTS fibers: (a) as-received; (b) desized; (c) resized with epoxy.

The topographies of the desized and epoxy-sized carbon fibers were further examined by AFM. AFM can characterize non-conductive materials as well as conductive materials, which is ideal to study polymeric coatings on carbon fibers. Fig. 2.9 shows that when the carbon fiber was resized by epoxy, the original features of the surface topography changed. The resulting structure became rougher and the longitudinal streaks on the desized fibers become less clear on the resized fibers. This change in surface topography is probably due to the variations in the thickness of the polymer coating.



Fig. 2.9 AFM images of a T700GC carbon fiber surface: (a) desized; (b) resized.

Table 2.2 summarizes the results of a roughness analysis of desized and epoxy-sized carbon fibers, which were obtained from the images of a 1 μ m \times 1 μ m area. The results indicate that the mean surface roughness value (R_a) is 9.5 nm for the desized carbon fiber. The resized surface became rougher with R_a higher than that of the desized carbon fiber.

	Desized carbon fiber	Resized carbon fiber
RMS	11.2 nm	31.3 nm
R _a	9.5 nm	24.9 nm
R _{max}	43.0 nm	217.1 nm
Dimensions	$1 \ \mu m \ \times \ 1 \ \mu m$	1 μm × 1 μm

Table 2.2 Surface roughnessof desized and epoxy-sized carbon fibers

(RMS is the root mean square deviation of the roughness curve profile; R_a is the mean value of the roughness curve relative to the center line; and R_{max} is the difference in height between the highest and lowest points on the cross-sectional profile relative to the center line over the length of the profile.)

The mass loss of T700GC carbon fiber was determined using TGA during heated in the mixture of oxygen and nitrogen, and the results are presented in Fig. 2.10 and Fig. 2.11. For as-received fibers, a small weight loss over the temperature range of 200-500 °C was found. It was resulted from the decomposition of the commercial sizing on the carbon fiber surface. The carbon fiber experienced a large mass loss when heated between about 600-900 °C due to oxidation [15]. There was no evident weight loss for desized fibers before 600 °C, which means the sizing was completely removed after the heat treatment. The fibers which were resized using different sizing bath concentration were also investigated. There was also a small loss in mass over the temperature range of 200-500 °C due to decomposition of the epoxy-based sizing compounds on the carbon fiber surface. The amounts of mass loss between 200 °C and 500 °C are listed in Table 2.3. It is shown that the weight loss increased as the concentration of sizing solution increased, which means the sizing level could be controlled by changing the sizing bath concentration [3]. When a sizing concentration of 2% was used, the sizing level was close to that of as-received fibers.



Figure 2.10 Mass loss-temperature curves for T700GC as-received fibers and desized fibers.



Figure 2.11 Mass loss-temperature curves for T700GC fibers resized using different sizing solution concentration.

T700GC Fiber	Sizing concentration	Weight loss (%)
As-received	Commercial sizing	0.57
Epoxy-resized No.1	0.5%	0.39
Epoxy-resized No.2	1%	0.51
Epoxy-resized No.3	2%	0.61
Epoxy-resized No.4	4%	1.31

Table 2.3 The values of weight loss between 200°C and 500 °C

The components of sizing formulation (i.e. epoxide resin (DGEBA) and amine curing agent (EC310)), desized and resized carbon fibers have been studied by attenuated total reflection-Fourier transform infrared spectroscopy (FTIR/ATR), cf. Fig. 2.12. And the assignments of characteristic bands are listed in Table 2.4.



Fig. 2.12 FTIR/ATR spectra of DGEBA, EC310, desized and resized carbon fibers.

	Band (cm ⁻¹)	Assignment	
	2970-2870	C-H stretching	
	1610	C=C stretching of aromatic rings	
DGEBA	1510	C-C stretching of aromatic rings	
	1240, 1035	Ar-O-C stretching of ethers	
	915, 831	epoxide ring vibration	
	3330	NH ₂ stretching	
	2970, 2870	C-H stretching	
EC210	1590	N-H deformation vibrations	
EC310	1450	CH ₂ deformation vibration of -OCH ₂ -	
	1370	C-H deformation vibration of R-CH ₃	
	1110	C-N stretching	
	3660	O-H stretching	
	2990, 2900	C-H stretching	
Resized carbon fiber	1390	C-H deformation vibration of R-CH ₃	
	1240	Ar-O-C stretching of ethers	
	1070	C-N stretching	

Table 2.4 Characteristic bands of DGEBA, EC310 and resized carbon fiber

It can be seen that DGEBA has the epoxide ring vibration absorbance peaks at 915 cm⁻¹ and 831 cm⁻¹; the C-H stretch at 2970 cm⁻¹-2870 cm⁻¹; the C=C stretch and C-C stretch of aromatic ring at 1610 cm⁻¹ and 1510 cm⁻¹, respectively; and the Ar-O-C stretch at 1035 cm⁻¹. For EC310, NH₂ stretch, N-H deformation vibrations and C-N stretch are observed at 3330 cm⁻¹, 1590 cm⁻¹ and 1110 cm⁻¹, respectively.

As to the desized carbon fibers, the absorbance increases with decreasing the wavenumbers. It could be attributed to the fact that the penetration depth of the electric field into a conducting solid is inversely proportional to the wavenumber [16], which makes the absorbance higher at lower wavenumbers than at higher wavenumbers.

The resized carbon fibers were prepared by the sizing of the desized carbon

fibers with DGEBA and EC310 (with the ratio 100 : 94.7 by weight), and networks with ring and branched structures [17] formed on the surface of carbon fibers. It can be confirmed by the FTIR/ATR spectra of the resized carbon fibers. It has been observed that O-H group with absorbance peak at 3660 cm⁻¹ was formed from epoxide-amine addition reactions. And Ar-O-C and C-N bonds have also been observed at 1240 cm⁻¹ and 1070 cm⁻¹, which originated from the bonds of DGEBA and EC310, respectively.

2.3.2 Influence of sizing on the carbon fiber/epoxy matrix interface

2.3.2.1 Determination of carbon fiber tensile strength

In the single fiber tensile tests, the number and length of fragments can be obtained at any level of stress. The relation between the average fragment length and the fiber stress can be created, as shown in Fig. 2.13. The continuously monitored fragmentation procedure provides a simple way to measure the shape parameter for strength rather than extensive measurements of single fibers at different gauge length.



Fig. 2.13 Typical ln-ln plot of the mean fragment length against fiber stress. The shape parameter for strength is the opposite of the slope.

The tensile strength of T700GC carbon fibers with different surface conditions are listed in Table 2.5. As-received fibers with commercially sizing, desized fibers without any sizing and resized fibers with epoxy sizing were tested. For all these three kinds of fibers, the tensile strength at critical length was around 10 GPa, regardless of the fiber surface condition. MARSTON et al. [18] also reported that the tensile strength of the single carbon filaments was relatively insensitive to the epoxy sizing.

T700GC carbon fiber	As-received	Desized	Resized
Fiber diameter (μm)	7.2	7.1	6.9
Rang of fiber stress (GPa)	6.5-11.5	6.0-10.0	6.0-12.0
Average fiber fragment length at sauturation (mm)	0.71	0.95	0.71
Fiber strength at average saturation length (GPa)	11.0	10.3	10.1

Table 2.5 Tensile strengths obtained from real-time single fiber fragmentation tests

According to Tagawa and co-workers [19], tensile strength of carbon fibers exhibits statistical Weibull type distribution and the size effect in axial direction was almost similar for all carbon fibers. Weibull shape parameters in axial direction are almost constant, irrespective of the carbon precursor and the strength level. The tensile strength obtained for a certain gauge length can be generalized as a representative strength of the fiber strength. In this study, a constant value (4.7) of the Weibull shape parameter β will be used to calculate the value of the fiber fragment strength at the critical length according to the following equation [20].

$$\sigma_f(l_c) = \sigma_f(l_f) \left(\frac{l_f}{l_c}\right)^{-\frac{1}{\beta}}$$
(2-7)

where $\sigma_f(l_c)$ is the fiber strength at the critical fiber length l_c , $\sigma_f(l_f)$ is the average strength of a fiber fragment of length l_f .

2.3.2.2 Effect of stoichiometry

The interface is an essential aspect in governing the overall performance of a fiber matrix composite. It arises through the interaction of the fiber and the resin and controls the micromechanics of failure. It is important to design the interface to give a desired composite property [21]. It is well known that there are different activities between matrix resins and fiber surfaces, and the presence of a sizing coating on the fiber surface is the most important aspect of the formation of interface. The sizing can be composed of a pure resin without a curing agent or being a mixture consisting of resin and curing agent. Changing the ratio of curing agent component in the mixture can vary the interfacial properties of composites. Effect of stoichiometry on the adhesion of carbon fibers to resin was studied by using the fragmentation method which simulates the failure of a unidirectional composite.

The results of single fiber fragmentation test for the T700GC carbon fibers are listed in Table 2.6. It is demonstrated that after desizing, the IFSS decreased from 57.8 MPa to 34.1 MPa. The epoxy resizing of carbon fibers gave rise to varied extents of increase in the IFSS, which can be attributed to the increased surface roughness and the better chemical compatibility with the matrix. An increasing roughness may provide more points of contact between the fiber and the matrix. The matrix compatible sizing might enhance wetting of the fibers by the matrix.

T700GC carbon fibers	Hardener content (phr)	Mean fragment length (µm)	IFSS (MPa)
As-received	-	456	65.4
Desized	-	778	34.2
Epoxy-resized Formula 1	0	492	59.7
Epoxy-resized Formula 2	23.7	512	56.9
Epoxy-resized Formula 3	47.3	536	53.8
Epoxy-resized Formula 4	94.7	357	87.9
Epoxy-resized Formula 5	110	441	68.1

Table 2.6 Single fiber fragmentation test results for T700GC carbon fibers

The amount of curing agent in the sizing formulation can influence the IFSS of composites, which was shown in Fig. 2.14.



Fig. 2.14 IFSS of T700GC carbon fiber composites using different sizing formulations: epoxy/hardener ratio varying from 100:0 to 100:110.

When an epoxy/hardener ratio of 100 : 94.7 was used for sizing, there was a largest improvement of 115 % in the IFSS. A lower or a higher ratio only gave an increment of 44 %-74 %. It might be attributed not only to the network structures [17] but also to compositions of the sizing coatings on the fiber surface. When the epoxy/hardener ratio is 100 : 0 or 100 : 23.7 in the sizing formulations, the sizing coatings are composed mainly of linear structures or branched structures which do not so tightly adhere to the fiber surface but have faire effect to improve IFSS by 56 % or 51 %. For the sizing coatings with the epoxy/hardener ratio of 100 : 47.3, it is mainly composed of networks of interconnected rings on the fiber surface as almost all the amine groups and epoxy groups reacted completely. In this case there are seldom chemical interaction between the sizing coatings and matrix resins. When the epoxy/hardener ratio increases to 100 : 94.7, the interconnected ring structures of sizing coatings could tightly adhere to the fiber surface and the excess of amine groups could react with the epoxy groups in the matrix resins, which result in the strongest interfacial properties and largest enhancement of IFSS. But the IFSS decreased when the epoxy/hardener ratio increased to 100 : 110, this is because more branched and linear structures existed in the sizing coatings and they would reduce the adhesion of sizing coatings on the fiber surface.

It is important to note that the change in the level of fiber/matrix adhesion induced an accompanying change in the interfacial failure mode. The morphology associated with the fiber breaks can provide valuable information regarding the interface strength. According to Mullin et al. [22], three modes of fracture may arise in a single-fiber composite during a fragmentation test, depending on the strength of interfacial adhesion, as shown in Fig. 2.15. Two failure modes have been observed in our studies: (i) In the case of high levels of adhesion, the initial fiber break is followed by a double cone matrix crack perpendicular to the fiber axis. (Fig. 2.15(b)); (ii) In the case of a relatively weaker interface, the initial fiber break is followed by an interfacial debonding (Fig. 2.15 (c)).

The optical micrographs of T700GC carbon fiber breaks after the fragmentation

test were shown in Fig. 2.16. The composite specimens with desized carbon fibers exhibited significant interfacial debonding and no matrix damage around the fiber breaks, implying a relatively weak interface. Apparent interfacial debonding was also observed for the composites containing resized carbon fibers using a sizing formulation of 100 : 47.3. But the final fragment length was much smaller than that of desized fibers. In the case of as-received fibers and resized fibers using a sizing formulation of 100 : 94.7 and 100 : 110, the failure mode was altered from interfacial debonding to local matrix crack, which indicated a strong interface bond.



Fig. 2.15 The three failure modes in a single-fiber composite during a fragmentation experiment, according to Mullin et al. [22, 23]: (a) and (b) strong interface-the initial fiber break is followed by a matrix crack; (c) weak interface-the initial fiber break is accompanied by interfacial debonding.



Fig. 2.16 Typical optical micrographs of T700GC carbon fiber breaks in epoxy matrix after the fragmentation test. The arrows indicate the fragment length.

The optimum sizing formulation was then adopted to resize HTS carbon fibers. The results of single fiber fragmentation test are listed in Table 2.7. It is interesting to note that, not like in the case of T700GC carbon fibers, the resizing did not improve the interface between HTS carbon fibers and epoxy matrix. The possible reason is that the surface chemical composition of these two kinds of fibers is different from each other.

HTS carbon fibers	Hardener content (phr)	Mean fragment length (µm)	IFSS (MPa)
As-received	-	322	99.6
Desized	-	463	64.5
Epoxy-resized Formula 1	0	539	53.9
Epoxy-resized Formula 2	23.7	519	56.2
Epoxy-resized Formula 4	94.7	478	62.1

Table 2.7 Single fiber fragmentation test results for HTS carbon fibers

2.3.2.3 Effect of sizing level

The TGA analysis of resized T700GC carbon fibers demonstrated that the sizing level on the fiber surface could be well controlled by changing the sizing concentration. The results of fragmentation tests for resized T700 carbon fibers are given in Table 2.8. The IFSS increased after resizing, no matter which sizing concentration was used. When the sizing solution concentration of 2% was used, the single-fiber composite attained the maximum value of IFSS (cf. Fig. 2.17). This is because the 2% sizing solution sized fiber gave the most uniform polymer coating. For the 0.5% and 1% sizing solution sized fibers, the fiber surface was not totally covered by the sizing material. When the concentration was up to 4%, the IFSS had little increase. From the SEM pictures we can see that too much sizing made the fiber surface become less uniform and the sizing was peeled off in some place on the fiber surface. This could influence the penetration of the matrix resin into the epoxy sizing and the formation of interface between the fiber and the matrix.

T700GC carbon fiber	Sizing concentration (%)	Mean fragment length (µm)	IFSS (MPa)
As-received	-	456	65.4
Desized	-	778	34.2
Epoxy-resized No.1	0.5	450	66.4
Epoxy-resized No.2	1	390	79.1
Epoxy-resized No.3	2	357	87.9
Epoxy-resized No.4	4	507	57.4

Table 2.8 Single fiber fragmentation test results for T700GC carbon fibers



Fig. 2.17 IFSS of T700GC carbon fiber composites using different sizing concentration.

2.4 Conclusions

Different sizing formulations composed of varied proportions of epoxy and amine curing agent were used for the sizing of desized T700GC and HTS carbon fibers and the interfacial shear strength of carbon fiber/epoxy composites was evaluated by single fiber fragmentation test. The results indicated that the sizing formulations with the concentration of 2 wt% in acetone and epoxy/amine ratio of 100 : 94.7 endowed the resized T700GC fibers with the optimal interfacial properties. The IFSS was increased by 35% compared with as-received fibers. It could be attributed to the fact that the interconnected ring structures of sizing coatings could tightly adhere to the fiber surface and the excess of amine groups could react with the epoxy groups in the matrix resins when the optimal sizing formulation was used, which result in the strongest interfacial properties and largest enhancement of IFSS. However, in the case of HTS fibers, no improvement in the interfacial strength was found after the sizing process. From the SEM pictures and TGA results, it could be seen that the sizing level on the fiber surface could be well

controlled by changing the sizing concentration. But too much sizing made the fiber surface become less uniform and the sizing was peeled off in some place on the fiber surface, which would decrease the interfacial properties between the carbon fibers and matrix.

2.5 References

[1] Oyama HT, Wightman JP. Surface characterization of PVP-sized and oxygen plasma-treated carbon fibers. Surface and Interface Analysis. 1998;26(1):39-55.

[2] Marieta C, Schulz E, Mondragon I. Characterization of interfacial behaviour in carbon-fibre/cyanate composites. Composites Science and Technology. 2002;62(2):299-309.

[3] Broyles NS, Chan R, Davis RM, Lesko JJ, Riffle JS. Sizing of carbon fibres with aqueous solutions of poly(vinyl pyrollidone). Polymer. 1998;39(12):2607-2613.

[4] T.H. CHENG JZ, S. YUMITORI, F.R. JONES, C.W. ANDERSON. Sizing resin structure and interphase formation in carbon fibre composites Composite. 1994;7:661-670.

[5] Drzal LT, Rich MJ, Koenig MF, Lloyd PF. Adhesion of Graphite Fibers to Epoxy Matrices: II. The Effect of Fiber Finish. The Journal of Adhesion. 1983;16:133-152.

[6] Drzal LT, Rich MJ, Lloyd PF. Adhesion of Graphite Fibers to Epoxy Matrices: I. The Role of Fiber Surface Treatment. The Journal of Adhesion. 1983;16:1-30.

[7] Tripathi D, Chen FP, Jones FR. A comprehensive model to predict the stress fields in a single fibre composite. J Compos Mater. 1996;30(14):1514-1538.

[8] Kim BW, Nairn JA. Observations of fiber fracture and interfacial debonding phenomena using the fragmentation test in single fiber composites. J Compos Mater. 2002;36(15):1825-1858.

[9] Kelly A, Tyson WR. Tensile properties of fibre-reinforced metals: Copper/tungsten and copper/molybdenum. Journal of the Mechanics and Physics of Solids. 1965;13(6):329-350.

[10] Hitchon JW, Phillips DC. The dependence of the strength of carbon fibres on length. Fibre Science and Technology. 1979;12(3):217-233.

[11] Phani KK. The strength-length relationship for carbon fibres. Composites Science and Technology. 1987;30(1):59-71.

[12] El Asloun M, Donnet J, Guilpain G, Nardin M, Schultz J. On the estimation of the tensile strength of carbon fibres at short lengths. Journal of Materials Science. 1989;24(10):3504-3510.

[13] Wagner HD, Eitan A. Interpretation of the fragmentation phenomenon in single-filament composite experiments. Applied Physics Letters. 1990;56(20):1965-1967.

[14] Yavin B, Gallis HE, Scherf J, Eitan A, Wagner HD. Continuous monitoring of the fragmentation phenomenon in single fiber composite materials. vol. 12: Polymer Composites; 1991. p. 436-446.

[15] Feih S, Mouritz aP. Tensile properties of carbon fibres and carbon fibre–polymer composites in fire. Composites Part A: Applied Science and Manufacturing. 2011.

[16] Sellitti C, Koenig JL, Ishida H. Surface characterization of graphitized carbon fibers by attenuated total reflection fourier transform infrared spectroscopy. Carbon. 1990;28(1):221-228.

[17] Morgan RJ, Kong F-M, Walkup CM. Structure-property relations of polyethertriamine-cured bisphenol-A-diglycidyl ether epoxies. Polymer.

1984;25:375-386.

[18] Marston C, Gabbitas B, Adams J. The effect of fibre sizing on fibres and bundle strength in hybrid glass carbon fibre composites. Journal of Materials Science. 1997;32(6):1415-1423.

[19] Tagawa T, Miyata T. Size effect on tensile strength of carbon fibers. Materials Science and Engineering: A. 1997;238(2):336-342.

[20] Zhou XF, Wagner HD, Nutt SR. Interfacial properties of polymer composites measured by push-out and fragmentation tests. Composites Part a-Applied Science and Manufacturing. 2001;32(11):1543-1551.

[21] Jones C. The chemistry of carbon fibre surfaces and its effect on interfacial phenomena in fibre/epoxy composites. Composites Science and Technology. 1991;42:275-298.

[22] Mullin J, Berry JM, Gatti A. Some Fundamental Fracture Mechanisms Applicable to Advanced Filament Reinforced Composites. J Compos Mater. 1968 (2):82-103

[23] Zhou XF, Nairn JA, Wagner HD. Fiber-matrix adhesion from the single-fiber composite test: nucleation of interfacial debonding. Composites Part a-Applied Science and Manufacturing. 1999;30(12):1387-1400.

Chapter 3 Heat treatment of carbon fibers and the effect on the interfacial properties of composites

3.1 Introduction

A desirable fiber/matrix interface is important for the mechanical properties of carbon fibers reinforced composites. As the interfacial properties strongly depend on the carbon fiber surface, many researches have focused on the surface treatment of carbon fibers to enhance the bonding between fibers and the matrix in a composite [1]. Heat treatment of carbon fibers is a popular surface treatment technique. It could affect the physico-chemical properties and the morphology of carbon fibers [1-3]. W.H. Lee et al [4] studied the role of heat treatment in improving the properties of a carbon fiber composite. The as-received carbon fibers were treated in a gas mixture of $O_2/(O_2+N_2)$ at 550 °C for 15 min. The interlaminar shear strength (ILSS) of the composite which employs surface treated carbon fiber.

In the present work, PAN-based T700GC and HTS40 E23 carbon fibers were heat treated under controlled atmosphere. The effect of different treatment parameters (i.e. gas mixture ratio of H₂/Ar, treatment time and temperature) on the interfacial properties of carbon fiber/epoxy composites were studied systematically. The changes of fiber surface morphology after treatments were examined using SEM and the surface chemistry was studied by X-ray photoelectron spectroscopy (XPS). The IFSS of carbon fibers/epoxy composites was investigated by single-fiber fragmentation test. Furthermore, the results of micro-scale interfacial studies were compared with the macro ILSS of the corresponding bulk composites.

3.2 Experimental

3.2.1 Materials

T700GC and HTS40 E23 (HTS for short) carbon fibers were used in the present study.

M21 epoxy prepreg (Hexply) was used as matrix to prepare unidirectional carbon fiber-reinforced composites. It is a high performance, very tough epoxy matrix for use in primary aerospace structures.

3.2.2 Heat treatment of carbon fibers under controlled atmosphere

The heat treatment of the as-received carbon fibers was carried out at 600-750 °C for 4-32 min in a gas mixture of H_2/Ar . The total gas flow rate was 1.8 L/min.

3.2.3 Fabrication of unidirectional carbon-fiber reinforced composites

Vacuum bagging method used for the composite fabrication and the sample preparation process is shown in Fig. 3.1. A rotating assembly was used to form the M21/carbon fiber prepreg in a filament winding process. Then the prepreg was placed in a mold with a dimension of 40×40 cm and cured under pressure at 180 °C for 2 hours. The pressure was maintained until the sample cooled down to the room temperature.



Fig. 3.1 Flow chart of composite sample preparation.

3.2.4 Characterization methods

Possible changes in the fiber surface morphology after treatments were examined on SEM (LEO Gemini 1530).

The surface composition of the carbon fibers was determined by XPS. The spectra were measured using a Thermo VG Scientific ESCALAB 250 system equipped with a micro-focused, monochromatic Al K α X-ray source (1486.6 eV). The samples were stuck on sample holders using conductive double-sided adhesive tapes. The spectra were calibrated by setting the main C1s component at 285 eV.

In order to evaluate the changes in the interfacial properties of the fiber/epoxy composites after the heat treatment, single fiber fragmentation test was carried out. The principle and the testing procedure have been introduced detailedly in Chapter 2.

The ILSS of bulk composites was measured using EN ISO standard 14130 with span to depth ratio of 5. The specimens were cut from the fiber composite plate using a cutting machine. Crosshead speed was constant at 2 mm/min. At least five

specimens were tested for each kind of fiber. The ILSS was calculated using the following equation:

$$\tau = \frac{3}{4} \times \frac{F_{max}}{bt} \tag{3-1}$$

where F_{max} is the maximum load, b is specimen width, t is specimen thickness.

3.3 Results and discussion

3.3.1 Surface properties of heat treated carbon fibers

The carbon fiber surfaces were examined by SEM and the pictures are shown in Fig. 3.2 and Fig. 3.3.



Fig. 3.2 SEM pictures of T700GC after heat treatment: (a) without H_2 ; (b) with H_2 .



Fig. 3.3 SEM pictures of HTS after heat treatment: (a) without H_2 ; (b) with H_2 .

Even at the magnification of 10000 (Fig. 3.2 a-2, b-2), the surface morphological changes can hardly be seen from the micrographs. After the treatment, T700GC fibers showed smooth and clean surface, regardless of the use of H₂ during the treatment. The commercial sizing was eliminated by means of combustion. Some shallow striations in the fiber direction can be found on the surfaces, due to the manufacturing process based on PAN-precursors [5].

For HTS fibers, the striation pattern along the fiber axis appeared more clearly and the depth was observed to be lager than that of T700GC fibers. The morphological changes caused by the introduction of H_2 in the treatment gas were not observed.

XPS is an effective and powerful technique for the investigation of the surface functionalities of carbon fibers as illustrated by a number of studies [6-8]. Sherwood [9] has investigated the effects of carbon fiber surface modification by electrochemical and plasma oxidation on composite properties using XPS. The sampling depth for a XPS measurement on carbon fibers was reported to be about 10-15 nm. The combination of XPS data from different regions indicated differences in chemical composition with depth into the surface. REIS et al. [10] have used XPS to study the mechanism of adhesion between the surface of carbon fibers and resins in composites. They found that the oxidative surface treatment increased the oxidized functions at the fiber surface. The commercial sizing did not entirely cover the fiber surface and only a part of it is covalent. The chemical reaction between the epoxidic group of the resin and the fiber surface may occur mainly through the alcoholic group at the surface.

In this study, the change of surface functionalities due to different heat treatment conditions was investigated. XPS full range scan spectra of T700GC and HTS are shown in Fig. 3.4 and Fig. 3.5, respectively. Wide scan spectra in the binding energy range of 0-1100 eV were obtained to identify the surface elements and carry out a quantitative analysis. The XPS spectra indicate that the major peaks were due to the C1s and O1s photoelectrons. Relatively weak peaks of N1s were also observed, which arises from the residual nitrogen present in the fibers. No other major elements were detected from wide scan spectra on the surface of all samples.



Fig. 3.4 A full range XPS spectra of heat treated T700GC carbon fibers



Fig. 3.5 A full range XPS spectra of surface treated HTS carbon fibers

Fig 3.6 and 3.7 show XPS narrow scan spectra of T700GC and HTS, respectively. Carbon atoms differ in their binding energies depending on their conjunction with oxygen atom (by a single bond or a double bond). The C1s signals exhibited an asymmetric tailing toward high binding energy, which was partially attributed to the intrinsic asymmetry of the graphite peak and also to the chemical shift of photoelectron peaks associated with functionalized carbons [11, 12]. The spectra shape of fibers treated in H₂/Ar have little difference with that of fibers treated in Ar.





Fig. 3.6 High-resolution C1s, N1s and O1s XPS spectra of T700GC carbon fibers.



Fig. 3.7 High-resolution C1s, N1s and O1s XPS spectra of HTS carbon fibers.

Table 3.1 summaries the elemental compositions (at.%) on the surface of heat

treated carbon fibers or over the sampling depth of several atomic layers from the surface. Carbon and oxygen were the most abundant elements at the PAN-based carbon fiber surface and there is a considerable amount of nitrogen [11]. Carbon was the primary element in both T700GC and HTS fibers. There were more N present on T700GC than on HTS. The surface activity of carbon fiber is determined by many factors such as the O/C atomic ratio, the concentration of oxygen atom, C1s binding state and O1s binding state [1]. For both T700GC and HTS, the carbon-oxygen composition on the fiber surface was almost consistent regardless the use H₂ during the treatment.

Samples	C1s (at. %)	O1s (at. %)	N1s (at. %)	O/C (%)
T700GC (with H ₂)	91.94	5.61	2.45	0.061
T700GC (without H ₂)	91.97	5.50	2.52	0.059
HTS (with H ₂)	93.97	4.49	1.54	0.048
HTS (without H ₂)	93.68	5.06	1.26	0.054

Table 3.1 XPS element analysis data of heat treated carbon fibers

3.3.2 Effect of H_2/Ar ratio, treatment temperature and time on the interfacial properties

Single fiber fragmentation test was conducted to assess the effect of heat treatment parameters (H_2 /Ar ratio, treatment temperature and time) on the carbon fiber/matrix interface. H_2 /Ar ratio was controlled by the H_2 flow rate and total H_2 /Ar flow rate was 1.8 L/min. The results are listed in Table 3.2.

Fiber		IFSS (MPa)		
	H ₂ (L/min)	Temperature (°C)	Time (min)	-
	0	600	8	50.2
	0.1	600	8	61.9
	0.3	600	8	71.7
	0.5	600	8	96.5
	0.3	600	8	71.7
T700CC	0.3	650	8	58.1
170060	0.3	700	8	50.1
	0.3	750	8	56.6
	0.3	600	4	81.5
	0.3	600	8	71.7
	0.3	600	16	114.3
	0.3	600	32	77.7
		As-received		
HTS	H ₂ (L/min)	Temperature (°C)	Time (min)	-
	0	600	8	60.6
	0.3	600	8	58.4
	0.5	600	8	54.5
	As-received			99.5

Table 3.2 Fragmentation test results of heat treated fiber/epoxy composites

Firstly, the influence of the H_2/Ar ratio in the mixture gas (or the H_2 flow rate) was studied in the case of T700GC fibers (cf. Fig. 3.8). The treatments were conducted at 600°C for 8min using a H_2 flow rate varying from 0 L/min to 0.5 L/min.



Fig 3.8 Effect of H_2 flow rate on the IFSS of treated T700GC carbon fiber/epoxy composites.

The results shown in Fig 3.8 indicated that the value of IFSS increased with increasing the H_2 flow rate. When the H_2 flow rate was less than 0.3 L/min, the value of IFSS was lower than that of as-received fibers. A H₂ flow rate ≥ 0.3 L/min resulted in a larger value of IFSS, compared with as-received fibers. Higher H₂ flow rate during the heat treatment was helpful to the improvement of IFSS. There was an improvement of 43% when the H_2 flow rate increased from 0 L/min to 0.3 L/min. It is well known that carbon fiber/epoxy adhesion results from not only chemical but also physical interactions with the matrix. Adhesion is the force of attraction between a solid surface and a second phase which leads to adsorption on a surface or adsorption into a surface layer. Surface chemical functionality may lead to a chemical reaction with the matrix in appropriate cases. Topographical changes resulted from surface treatments could make matrix material be able to penetrate into any pits and slits in the fiber, giving better physical adhesion. According to the results of quantitative surface element analysis, the concentration of oxygen atom and the O/C atomic ratio were almost the same for the fibers treated with a H₂ flow rate of 0 L/min and 0.3 L/min. The improvement in IFSS caused by the increase of H₂ flow rate could be attributed to the change in the physical interactions between fiber and matrix. Generally, the prepolymers used in the fabrication of the carbon fiber-reinforced composites have relatively high molecular weight and a large molecular size to maintain a proper viscosity [2]. As a result, the resins molecules may hardly access the micropores on the carbon fiber surfaces due to the steric hindrance effect. The higher H₂ flow rate may provide more effective adhesion area at the fiber/matrix interface through creating relative larger pore of resin accessible size on the fiber surface. Although the surface morphology of the treated fiber seems to remain unchanged through the SEM characterization, the change of micropore size on the fiber surface could be observed by other characterization techniques such as AFM and TEM. Further studies will be conducted to prove the hypothesis. Another important way to investigate and model interactions at the interface is to determine dispersive and polar contributions to the surface free energies of the fibers [13]. Inverse gas chromatography (IGC) is a promising approach and allows us to calculate the free energy of adsorption leading to the dispersive contribution of the surface free energy, as well as acid-base properties of the studied material. Dai et al. [14] have investigated carbon fiber changes during the manufacture of carbon fiber/resin matrix composite by means of IGC, XPS and dynamic contact angle test. It was concluded that the wettability of resin on carbon fiber depended not only on the surface energy values of carbon fiber and resin, but also on the polarity match of surface energy.

Secondly, the influence of the heat treatment temperature on the interface was studied (cf. Fig. 3.9). The H₂ flow rate and treatment time were kept at a constant value (0.3 L/min and 8 min, respectively). It is shown that a temperature higher than 600 °C is unfavorable for improving the IFSS. Moreover, for the fibers treated at 600 °C, the IFSS results show much smaller error bar, which means the treatment effect was uniform on the fibers.


Fig 3.9 Effect of heat treatment temperature on the IFSS of treated T700GC carbon fiber/epoxy composites by fragmentation tests.

Thirdly, the effect of treatment time was also investigated (cf. Fig. 3.10). The H_2 flow rate and temperature were 0.3 L/min and 600 °C, respectively. The results indicated that IFSS increased compared with as-received fibers, no matter how long was the treatment (in the range of 4 to 32 min). When the fibers were treated for 16 min, a highest value of IFSS was obtained (75 % higher than that of as-received fibers).



Fig 3.10 Effect of heat treatment time on the IFSS of treated T700GC carbon fiber/epoxy composites by fragmentation tests.

The heat treatment in mixture gas of H₂/Ar was also applied to HTS fibers.

Contrary to T700GC, no improvement in IFSS was observed even when a high H_2 flow rate of 0.5 L/min was used (cf. Fig. 3.11), with which a highest value of IFSS was obtained in the case of T700GC fibers. This may be explained by their difference in surface morphologies and reactivity. There are more striations along the fibers axis on the HTS and the striations are much deeper. When the striated fiber surface was wetted by the resin, small amounts of residual air could have been sealed in the bottom of the valleys and was not eliminated during the curing process [12]. The incomplete filling of valleys of the fiber surface striations by the matrix resin could lead to a reduction of interfacial area.



Fig 3.11 Effect of H_2 flow rate on the IFSS of treated HTS carbon fiber/epoxy composites by fragmentation tests.

3.3.3 Comparison of the interfacial properties between single-fiber composites and bulk composites

A comparison of the interfacial properties between single-fiber composites and the corresponding bulk composites was made by using as-received and two kinds of heat treated T700GC fibers (cf. Fig. 3.12). Overall, the values of ILSS are higher than that of IFSS. The effect of heat treatment on the interfacial properties was not

significant for bulk composites. A 1 : 1 correlation between the single fiber adhesion strength and the composite shear strength was not demonstrated. One possible reason could be that the bulk composite performance is dependent not only on the constituent properties, but also on the processing parameters such as temperature, pressure, heat-up rate and so on. Another possible reason is that the matrix resins used for the single fiber composites and the bulk composites were different. Both of them were epoxy-based resins, but the chemical composition is different from each other. However, the single fiber test is still very useful as it provides valuable insight into adhesion fundamentals, and the failure mechanisms involved in corresponding composites.



Fig. 3.12 Comparison of ILSS (bulk composites) and IFSS (single fiber composites) of T700GC fibers reinforced composites.

3.4 Conclusions

Heat treatments of carbon fiber in the gas mixture of H_2/Ar have been carried out. The morphology and surface chemistry of treated fibers have been investigated using SEM and XPS. T700GC fiber showed smooth and clean surface, while the surface of HTS was rougher due to the deeper striations along the fiber axis. Carbon fiber surface XPS results revealed that carbon, oxygen and nitrogen were the three major elements detected at the fiber surface. The oxygen content was around 5% for both T700GC and HTS fibers. The nitrogen concentration was higher on T700GC (around 2.5%) than on HTS (around 1.4%). The surface morphology and composition was not influenced by the change of H_2/Ar ratio in the gas mixture. The effects of the H_2/Ar ratio in the gas mixture, treatment temperature and time on the interfacial properties of composites have been investigated. The IFSS of treated carbon fiber/epoxy composites has been evaluated by single fiber fragmentation test. The results indicated that after the treatment at 600 °C for 16min using a H₂ flow rate of 0.3 L/min, the optimal interfacial properties were obtained for T700GC fibers. Heat treatments alter the inert nature of carbon fiber surfaces. The IFSS was increased by 75% compared with as-received fibers. In the case of HTS fibers, the heat treatment has not been found to lead to any improvement in composite interfacial properties. The relationship between the IFSS of single fiber composites and the ILSS of the corresponding bulk composites was also studied. It was found that there was little correlation between the single fiber adhesion strength and the composite shear strength, probably because the matrix resins used are very different.

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3.6 References

[1] Wang S, Chen Z-H, Ma W-J, Ma Q-S. Influence of heat treatment on physical-chemical properties of PAN-based carbon fiber. Ceramics International. 2006;32(3):291-295.

[2] Lee JS, Kang TJ. Changes in physico-chemical and morphological properties of carbon fiber by surface treatment. Carbon. 1997;35(2):209-216.

[3] Donnet JB, Wang TK, Shen ZM. Atomic scale STM study of pitch-based carbon fibers: Influence of mesophase content and heat treatment temperature. Carbon. 1996;34(11):1413-1418.

[4] Lee WH, Lee JG, Reucroft PJ. XPS study of carbon fiber surfaces treated by thermal oxidation in a gas mixture of O2/(O2+N2). Applied Surface Science. 2001;171(1–2):136-142.

[5] Bismarck A, Wuertz C, Springer J. Basic surface oxides on carbon fibers. Carbon. 1999;37(7):1019-1027.

[6] Weitzsacker CL, Xie M, Drzal LT. Using XPS to Investigate Fiber/Matrix Chemical Interactions in Carbon-fiber-reinforced Composites. Surface and Interface Analysis. 1997;25:53-63.

[7] Nakayama Y, Soeda F, Ishitani A. XPS study of the carbon fiber matrix interface. Carbon. 1990;28(1):21-26.

[8] Dilsiz N, Wightman JP. Surface analysis of unsized and sized carbon fibers. Carbon. 1999;37:1105-1114.

[9] Sherwood PMA. Surface analysis of carbon and carbon fibers for composites. Journal of Electron Spectroscopy and Related Phenomena. 1996;81:319-342.

[10] Reis MJ, Botelho Do Rego AM, Lopes Da Silva JD, Soares MN. An XPS study of the fibre-matrix interface using sized carbon fibres as a model. Journal of Materials Science. 1995;30(1):118-126.

[11] Chiang Y-C, Lee C-Y, Lee H-C. Surface chemistry of polyacrylonitrile- and rayon-based activated carbon fibers after post-heat treatment. Materials Chemistry and Physics. 2007;101(1):199-210.

[12] Zhuang H, Wightman JP. The Influence of Surface Properties on Carbon Fiber/Epoxy Matrix Interfacial Adhesion. The Journal of Adhesion. 1997;62(1-4):213-245.

[13] Lindsay B, Abel M-L, Watts JF. A study of electrochemically treated PAN based carbon fibres by IGC and XPS. Carbon. 2007;45(12):2433-2444.

[14] Dai Z, Zhang B, Shi F, Li M, Zhang Z, Gu Y. Effect of heat treatment on carbon fiber surface properties and fibers/epoxy interfacial adhesion. Applied Surface Science. 2011;257:8457-8461.

Chapter 4 Effect of CNTs on the interfacial properties of CNT-grafted carbon fiber/epoxy composites

4.1 Introduction

Carbon nanotubes (CNTs) are ideal candidates for developing novel high performance composites due to their unique mechanical, thermal and electrical properties [1, 2]. The introduction of CNTs into fiber-reinforced composites results in multiscale hybrid composites which consist of reinforcements having diameter of micro-scale (fibers) and nano-scale (CNTs). The combination of a micro-scale with a nano-scale reinforcement is expected to enhance the mechanical performance of composites.

Recently, there has been a growing interest in developing hierarchical structures by grafting CNTs directly onto the surface of long carbon fibers. The hierarchical structures have the potential to improve the interfacial strength of conventional fiber/polymer composites due to the increased lateral support of the load-bearing fibers [3]. Thostenson et al.[4] reported an improvement in the interfacial load transfer for the epoxy composites containing CNTs grafted carbon fibers. In the other hand, this grafting method alleviates the problem of agglomeration and allows the dispersion of a high volume fraction of carbon nanotube (CNT) through out the composite [5].

A number of methods have been used to fabricate CNT-grafted fibers, such as direct growth of CNTs onto fibers [4, 6-9] and chemical reactions between modified fibers and CNTs [10]. Among those methods, chemical vapor deposition (CVD) provides an efficient way to graft CNTs directly onto carbon fibers, which can be then used in traditional fiber-reinforced polymer composites [11, 12].

So far, most researchers have grafted CNTs on small-scale fiber tows or woven in a static way. In the present study, the continuous grafting of CNTs onto the surface of carbon fiber tows was achieved by the CVD process and the CNT morphologies can be varied widely depending on the growth conditions. The morphology of CNTs grown on carbon fibers was examined by scanning electron microscope (SEM). The CNTs content in the hybrid carbon fibers were determined by thermogravimetric analysis (TGA). The interfacial shear strength (IFSS) of single hybrid carbon fiber/epoxy composites was studied by the single fiber fragmentation tests. The effect of the CNT morphology on the interfacial properties of composites was evaluated. The carbon fibers grafted with CNTs were further heat treated and resized. The combining use of the three treatments endowed carbon fibers with superior interfacial adhesion to the tested epoxy matrix.

4.2 Experimental

4.2.1 Materials

The carbon fibers used in this study were PAN-based T700GC (Toray) and HTS40 E23 (HTS for short, Tenax).

WWA/WWB4 epoxy system (Resoltech) was selected as the matrix resin in single fiber fragmentation tests, which requires a relatively high strain at break.

4.2.2 Growth of CNTs on carbon fibers using a continuous CVD method

The graft of CNTs onto carbon fibers has been conducted using a CVD method [9, 13, 14]. The reactions were performed in a horizontal quartz tube (around 10 cm in diameter) equipped with an electrical furnace, as shown in Fig 4.1.



Fig. 4.1 Schematic diagram of the CVD reactor for the growth of CNTs on the carbon fibers.

Nitrogen, hydrogen and acetylene were used as precursor gases. The ferrocene catalyst dissolved in xylene was fed by a syringe system and carried into the reaction tube by the carrier gases in the form of spray. The reactions were performed at 600-650 °C in dynamic mode. By varying the growth condition (e.g. reaction time, reaction temperature and catalyst formulation), CNTs of different morphologies were grafted onto T700GC fibers to get 6 kinds of hybrid fibers named T/CNT-a, T/CNT-b, T/CNT-c, T/CNT-d, T/CNT-e, T/CNT-f, or onto HTS fibers to get 5 kinds of hybrid fibers named H/CNT-a, H/CNT-b, H/CNT-c, H/CNT-e. The furnace was then cooled down to room temperature under the protection of argon gas.

4.2.3 Characterization methods

The morphological features of the hybrid fibers were characterized by SEM (LEO Gemini 1530).

The thermal stability of carbon fibers and the content of CNTs in the hybrid fibers were investigated by thermogravimetric analysis (TGA) using a thermal gravity analyzer/differential scanning calorimeter (NETZSCH STA449 F3). The TGA measurements were conducted from 30 to 900 °C using a heating rate of 20 °C/min in the mixture of nitrogen and oxygen (volume ratio: 1 : 1).

Raman spectrometer (Labram, Horiba) with He-Ne laser source with a

wavelength of 632.8 nm was used to determine the quality of CNTs synthesized.

The anchorage between CNTs and carbon fibers was tested after the growth process. The hybrid fibers were immersed into acetone and processed with ultrasonic bath (VWR, USC500D, 45 kHz). All the treatments lasted for 20 min.

The single fiber fragmentation test was used to assess the properties of the fiber/matrix interface.

High temperature conditions involved with the CVD could induce the degradation of the fiber and result in shorter fragment lengths. It was found that degradation can be significant for low-modulus fibers at temperatures between 800 °C and 900 °C, but high modulus fibers were stable at much higher temperatures [4]. The carbon fibers used in this study are standard modulus PAN-based fibers (E = 240 GPa). Degradation in fiber strength as a result of CNT growth should be minimal, given the relative low reaction temperature (maximum: 650 °C).

DC voltage-current measurement was carried out by using Keithley Multimeter equipped with two copper electrodes. The distance between the two electrodes was kept at 20 cm. The oxidation effect of the copper electrodes was minimized by polishing the surface before each measurement. The electrical conductivity of carbon fiber σ is calculated by using the following equation:

$$\sigma = \frac{1}{\rho} = \frac{L}{R \times \pi \times r_{fiber}^2 \times N_{fiber}}$$
(4-1)

where ρ is electrical resistivity, R is electrical resistance, L is distance between electrodes, r_{fiber} is radius of carbon fiber filament, N_{fiber} is number of fiber filament in a bundle.

The measurement was also performed by applying silver paste on the fibers where they come into contact with copper electrodes. It is compared with the previous method for purpose of evaluating the influence of the contact mode on the electrical conductivity.

4.3 Results and discussion

4.3.1 CNT morphologies

The fibers were examined with SEM to verify the CNT grafting. The images shown in Fig 4.2 revealed that both T700GC and HTS carbon fibers were uniformly coated with CNTs after the continuous CVD process. Randomly-oriented, curly CNTs were successfully grafted onto the carbon fiber surface, which could be attributed to the homogeneous coverage of catalyst particles. The CNT diameters were between 10nm and 20 nm.

Most of the current research on CNT-grafted fibers is based on small-scale fiber materials and the grafting process is static. In our studies, CNT-grafted fibers were successfully produced in a continuous way. This will allow the preparation of hierarchical composites for macro-scale mechanical testing, including shear, compression, and delamination test.



Fig. 4.2 SEM images of CNT-grafted carbon fibers: (a) T700GC; (b) HTS.

Surface morphologies of CNT-grafted T700GC carbon fibers, using different growth conditions are shown in Fig. 4.3. The thickness of the nanotube region surrounding the fiber is in the range of 230-700 nm. The results of SEM indicated that

CVD can be successfully used to grow CNTs on carbon fibers with selectable CNT morphology by controlling growth conditions such as temperature, reaction time and source flow rate. For T/CNT-a (Fig. 4.3 (a)), the CNTs were relative long, but the density was low, as the fiber surface was not completely covered by CNTs. There were more CNTs on the T/CNT-b surface as shown in Fig. 4.3 (b), but CNTs were shorter as compared to T/CNT-a. From T/CNT-c to T/CNT-f, the CNT density increased gradually, and the fiber surface is difficult to be observed. But CNTs length was almost the same. In the case of T/CNT-d and T/CNT-e, clumpy microstructures presented at the CNT ends, which were believed to be carbonaceous impurities.





Fig. 4.3 SEM images of CNT-grafted T700GC carbon fibers with varied CNT morphologies: (a) *T/CNT-a;* (b) *T/CNT-b;* (c) *T/CNT-c;* (d) *T/CNT-d;* (e) *T/CNT-e;* (f) *T/CNT-f;* (g)T/CNT-g.

SEM images of HTS carbon fibers grafted with CNTs of different morphologies are shown in Fig. 4.4. In (a) and (b), entangled CNTs are sparsely distributed on the fiber surface and the density is relatively low. CNTs shown in (c) were shorter but denser. Carbon fibers were entirely covered with long, thick CNTs for H/CNT-d and H/CNT-e.



Fig. 4.4 SEM images of CNT-grafted HTS carbon fibers with different CNT morphologies: (a) H/CNT-a; (b) H/CNT-b; (c) H/CNT-c; (d) H/CNT-d; (e) H/CNT-e.

4.3.2 CNT content on the carbon fiber surface

TGA was applied to assess the oxidation temperature and weight fraction of the CNTs grafted onto the carbon fibers. Fig. 4.5 displays the weight loss results for carbon fibers grown with CNT of different morphologies upon the surface. The onset oxidation temperatures for weight loss, corresponding to the combustion of the CNTs were around 500 $^{\circ}$ C.



Fig 4.5 TGA curves of carbon fibers grafted with CNTs: (a) T700GC; (b) HTS.

Table 4.1 and 4.2 listed the CNTs mass fraction in different hybrid carbon fibers. The results demonstrated that CVD can be successfully used to synthesize CNTs on carbon fibers with different densities, and selectable CNT morphology by controlling growth conditions.

T700GC carbon fibers	CNT morphology	Weight loss (%)	
T/CNT-a	Long, sparse	1.75	
Т/СМТ-b	Short, dense	1.9	
T/CNT-c	Relatively long, dense	2.13	
T/CNT-d	Long, dense, some impurities	2.64	
T/CNT-e	Long, dense, more impurities	2.84	
T/CNT-f	Long, dense, pure	3.12	

Table 4.2 The values of weight loss caused by the combustion of CNTs on HTS.

HTS carbon fibers	CNT morphology	Weight loss (%)	
H/CNT-a	Long, spare	1.03	
H /CNT-b	Long, relatively dense	1.83	
H /CNT-c	Short, dense	1.92	
H /CNT-d	Long, dense	2.02	
H /CNT-e	Very long, dense	6.74	

Assuming a regular array of CNTs possessing the measured average diameter and length, the change of specific surface area of the carbon fiber after CNT grafting could be calculated through the CNTs mass fraction. CNTs occupied some fiber areas after CNT growth (cf. Fig 4.6), assuming that both the fiber and the CNTs are cylindrical. The relative values for the calculation of T/CNT-c are listed in Table 4.3.



Fig. 4.6 Schematic representation of CNT-grafted fiber. The small circles on fiber surface represent the areas of CNT growth.

d _f (Fiber diameter)	7 μm
d _{cnt} (CNT diameter)	10 nm
ρ _f (Fiber densiy)	1.8 g/cm^3
ρ _{ent} (CNT densiy)	1.4 g/cm^3
L _{cnt} (CNT length)	595 nm
CNT content in the hybrid fiber	2.13 wt%

Table 4.3 Values used for calculation of the specific surface area.

The specific surface area of desized fiber without CNTs, A_f , can be evaluated from the following equations:

$$A_f = \frac{S_f}{m_f} = \frac{\pi \times d_f \times L_f}{\pi \times \left(\frac{d_f}{2}\right)^2 \times L_f \times \rho_f}$$
(4-2)

And the specific surface area of CNT-grafted carbon fibers, A_{cnt} , is calculated from:

$$A_{cnt} = \frac{S_{cnt} + S_f}{m_{cnt} + m_f} = \frac{\pi \times d_{cnt} \times L_{cnt} \times N_{cnt} + \pi \times d_f \times L_f - \pi \times \left(\frac{d_{cnt}}{2}\right)^2 \times N_{cnt}}{\pi \times \left(\frac{d_{cnt}}{2}\right)^2 \times L_{cnt} \times N_{cnt} \times \rho_{cnt}/0.0213}$$
(4-3)

where m_{cnt} and m_f are the masses of the grafted CNTs and carbon fibers, respectively. S_{cnt} and S_f are the surface area of CNTs and carbon fibers, respectively. N_{cnt} is the number of CNTs grafted on the fiber surface.

By the calculation, the specific surface areas of desiziedT700GC and T/CNT-c are $0.32 \text{ m}^2/\text{g}$ and $6.37 \text{ m}^2/\text{g}$, respectively. And the surface area of T/CNT-c is around 20 times more than that of desized fiber. The large increase in surface area is resulted from the high aspect ratio of CNT which endows it opportunities to increase the interfacial area if the CNTs are welled fixed on the fiber surface.

4.3.3 Raman characterization

Raman spectra of T700GC carbon fibers before and after CNT grafting in different conditions are shown in Fig. 4.7. The spectra showed two main bands, which are assigned to the disorder D mode (~1320 cm⁻¹) induced by sp^3 carbon atoms hybridization and the tangential G mode (~1599 cm⁻¹) for the stretching vibrations of sp^2 carbon atoms [15, 16].



Fig. 4.7 Raman spectra of T700GC carbon fibers before and after carbon nanotube grafting in different conditions.

The D : G intensity ratio, I_D/I_G , can be used to evaluate the degree of order of carbon material. And the I_D/I_G ratio for T700GC carbon fibers before and after CNT grafting is shown in Fig. 4.8. Higher I_D/I_G ratio corresponds to less ordered structure and more structure defects while lower I_D/I_G ration corresponds to more ordered structure and less structure defects [15, 17]. For T700GC carbon fibers before CNT, the I_D/I_G ration value is 1.12, while the values decrease to 1.03 and 0.96 for T/CNT-a and T/CNT-b, respectively. It is demonstrated that the grafting of CNTs on the surface of carbon fibers in the certain conditions (T/CNT-a and T/CNT-b) could remedy the existing defects of the unmodified carbon fibers from T/CNT-c to T/CNT-f, I_D/I_G ration values become higher than that of T/CNT-b. It may be attributed to the fact that the denser CNTs cover the surface of carbon fibers and form a new carbon surface, which bring new disordered structures and defects. The evolution, however, is quite small for all situations.



Fig. 4.8 Relative Raman intensity ratios (I_D/I_G) of T700GC carbon fibers before and after CNT grafting in different conditions.

4.3.4 Adhesion of CNT on carbon fiber

To use the CNT/carbon fiber hybrid reinforcement in matrix, a strong anchorage between CNTs and carbon fibers is mandatory. It has been reported that CNTs, which were grown on thin (15 nm) Ni films deposited by plasma vapor deposition technique, were entirely removed by the ultrasonic treatment in acetone due to the weak attachment strength [11, 18]. In our studies, for assessing the relative attachment strength of the CNT to the carbon fiber surface, the hybrid fibers were exposed to an ultrasonic bath in acetone for 20 min. The SEM images (cf. Fig. 4.9) after the tests demonstrated a good adhesion between the two components. The CNTs still anchored to the carbon fiber surface and the network of CNTs surrounding the carbon fiber was unchanged. It could be attributed to the fact that the catalyst particles have the potential to react with and/or diffuse into fiber substrates during the growth reaction [5]. The good bonding between the CNT and the carbon fiber surface is quite beneficial to the dipping process of the hybrid fibers into a polymeric matrix.



Fig 4.9 SEM images of CNT/carbon fiber after the ultrasonic bath in acetone for 20 min: (a) CNT/T700GC; (b) CNT/HTS.

4.3.5 Effect of CNT morphology on the interfacial properties

The growth of CNTs changes not only the characteristics of fiber surface but also the fiber/matrix interface. Single fiber fragmentation tests were conducted to evaluate the interface strength of the CNT coated carbon fiber/epoxy resin matrix. In the case of T700GC, as shown in Table 4.4 and Fig 4.10, carbon fibers without CNTs presented the lowest IFSS. In contrast, CNT grafted hybrid fibers, regardless of the morphology of CNTs, exhibited improved IFSS.

T700GC	CNT content (%)	Mean fragment length (µm)	IFSS (MPa)
As-received	-	456	65.4
Without CNTs	-	778	34.2
T/CNT-a	1.75	402	76.3
T/CNT-b	1.9	530	54.5
T/CNT-c	2.13	315	102.5
T/CNT-d	2.64	672	40.8
T/CNT-e	2.84	594	47.5
T/CNT-f	3.12	385	80.4

Table 4.4 Single fiber fragmentation test results for T700GC carbon fibers.



Fig. 4.10 IFSS of single fiber composites containing T700GC carbon fibers grown with CNTs of different morphologies.

The introduction of CNTs at the fiber-matrix interface could enhance the fiber-matrix bonding by providing mechanical interlocking between the fibers and the

matrix, resulting in an efficient transfer of tensile load to the fibers in the epoxy composites. Moreover, the presence of CNTs at the fiber surface also increased the overall interfacial area. Therefore, the interface was strengthened due to the presence of CNTs at the fiber/matrix interface.

Fig 4.11 demonstrates that the CNT morphology plays an important role in the interfacial properties of the hybrid composites. T/CNT-c possesses optimal nanotube geometry which results in the highest IFSS value.



Fig. 4.11 IFSS plotted as a function of CNT content in hybrid T700GC carbon fibers.

Low density CNTs (T/CNT-a) and short CNTs (T/CNT-b) have quite limited effect on the improvement of interfacial strength. As the CNT density and length increased, the IFSS of T/CNT-c increased significantly, which could be attributed to the high specific surface area (20 times larger than that of desized fibers) of the hybrid fibers. The increasing contact area could result in the improvement of Van der Waals interaction at the composite interface [19]. Meanwhile, more anchoring sites were created due to the large presence of CNTs and led to micromechanical interlocking effect at the interface regions. As the CNTs were randomly oriented on the carbon fiber surface, some of the CNTs were aligned with the principal tensile stress direction, resulting in greater load transfer and higher yield strength [20].

During the continuous CVD process, the catalyst may not be always deposited uniformly on the surface of the individual fiber. As a consequence, there may be amorphous carbon instead of nanotubes deposited on some areas on the fiber surface as shown in the case of T/CNT-d and T/CNT-e. These impurities of amorphous carbon are unfavorable to the interface. In addition, the fracture mode turned from type a to type b (cf. Fig. 4.12) in this case, where the interfacial debonding occurred. For T/CNT-f, there were more CNTs on the surface as compared with T/CNT-c, but the IFSS was smaller. It may be attributed to the fact that the high-density of CNTs made the wetting of resin on the CNTs more difficult. As CNTs are hundreds of times thinner than the carbon fiber, the resulting gap between CNTs is approximately hundreds of smaller than the gap between fibers [21]. This will make the resin more difficult to flow between CNTs.



Fig. 4.12 Typical optical micrographs of hybrid T700GC carbon fiber breaks in epoxy matrix after the fragmentation test: (a) matrix crack; (b) interfacial debonding; (c) higher magnification of (a); (d) higher magnification of (b).

In the case of HTS, the IFSS values were also influenced by the CNT

morphologies. From the results of fragmentation tests (Table 4.5 and Fig 4.13), the IFSS values of H/CNT-c and H/CNT-d increased as compared with that of desized fibers.

HTS	CNT content (%)	Mean fragment length (µm)	IFSS (MPa)	
As-received	-	322	99.6	
Without CNTs	-	463	64.5	
H/CNT-a	1.03	600	46.9	
H /CNT-b	1.83	538	53.9	
H /CNT-c	1.92	301	110.3	
H /CNT-d	2.02	323	99.6	
H /CNT-e	6.74	844	37.9	

Table 4.5 Single fiber fragmentation test results for HTS carbon fibers.



Fig. 4.13 IFSS of single fiber composites containing HTS carbon fibers grown with CNTs of different morphologies.

The decrease in the interfacial properties (H/CNT-a and H/CNT-b) can be attributed to the fact that these low-density CNTs simply acts as defects rather than the true reinforcement (cf. Fig. 4.14). The catalyst particles deposited on the carbon fiber surface could create defects, which are unfavorable to the fiber/matrix interface [9]. As the CNT content increased, the effect was negligible. When high-density, long CNTs were grafted on H/CNT-c and H/CNT-d, the IFSS increased by 71% and 54%, respectively. As the CNT content increased to 6.74% (H/CNT-e), the lowest IFSS was obtained. It may be because the CNTs were too dense on the carbon fiber surface and the matrix resin could not sufficiently penetrate into the CNT array, resulting in a poor interface between the matrix and the fiber.



Fig. 4.14 IFSS plotted as a function of CNT content in hybrid HTS carbon fibers.

According to the observations of the fiber breaks of CNT coated HTS fibers, as shown in Fig. 4.15, there was no interfacial failure and therefore good adhesion for H/CNT-c and H/CNT-d.



Fig. 4.15 Typical optical micrographs of hybrid HTS carbon fiber breaks in epoxy matrix after the fragmentation test: (a) matrix crack; (b) interfacial debonding.

Possible failure mechanisms are given in Fig. 4.16. In the present composites, there are two types of interfaces: the fiber/matrix and the CNT/matrix. As strong interfacial adhesion between CNT and the polymer have been reported by other researchers [22-26], the strength of fiber/matrix interface becomes critical. For a medium CNT density, the CNTs are not too long, which allows the polymer molecules to percolate into the spaces between the CNTs and thereby lead to a stronger interface [27]. As shown in Fig. 4.16 (a), in these cases, failure in fragmentation tests occurred by fracture in the matrix. On the other hand, when the CNTs were longer and denser (Fig. 4.16 (b)), poor percolation by polymer molecules reduced the fiber/matrix interfacial area dramatically and failure occurred at the interface. This is further evidenced by the fiber pullout when the fragmentation test was continued until the sample fracture, as shown in Fig. 4.17. To allow fiber pullout, the fiber must be broken and the fiber/matrix interface must be debonded. If the CNT/fiber joint is relatively weak, CNTs will be detached from the fiber surface and the fractured CNT remains buried inside the matrix. If the fiber/CNT joint is strong and the CNT bonding with the matrix is relatively weak, CNT pullout could occur.



Fig. 4.16 Possible failure mechanisms in fragmentation tests of CNT-coated HTS carbon fibers in an epoxy matrix.



Fig. 4.17 Fiber pulledout after the sample failure.

4.3.6 Influence of CNT on the electrical conductivity

Two methods were used to evaluate the influence of CNT on the electrical conductivity of carbon fibers. In one method, electrodes were in contact with fibers directly, while in the other, silver paste was applied on the fibers where they come into contact with copper electrodes. Fig 4.18 shows the electrical conductivity of T700GC fibers with different surface conditions.



Fig. 4.18 Comparison of electrical conductivity of T700GC carbon fibers.

It is indicated that when silver paste was used, the electrical conductivity increased for all kinds of fibers. This may be because the silver paste made better contact between fiber filaments. In particular, the value of electrical conductivity of as-received fibers increased by about 5 times. The possible reason is that the commercial sizing on the fiber surface has poor conductivity, which resulted in relatively high resistance between filaments. When the silver paste was applied on the fiber, the electric conduction between filaments became stronger.

Regardless of the use of silver paste, the conductivity of CNT grafted fibers was higher than that of as-received fibers. Whereas compared with desized fibers, the introduction of CNT on the fiber surface changed the conductivity slightly. This is because carbon fibers themselves have high conductivity. The effect of CNT on conductivity could be limited. When no silver paste was used, the conductivity of desized fibers and all CNT grafted fibers was around 5×10^4 S/m and it increased

to 6×10^4 S/m once silver paste was applied. Although no significant improvement in the conductivity of carbon fibers was observed after the CNT growth, it is expected that the hybrid fibers will lead to a substantial enhancement of the electrical conductivity of the composites. Bekyarova et al. [28] reported that there was a 2-fold improvement in the out-of plane electrical conductivity for CNT/carbon fiber/epoxy composites when compared to the carbon fiber/epoxy composites as a result of the reinforcement of the electron transport channels.

4.3.7 Combining use of CNT grafting, heat treatment and sizing

CNT grafting has been proved to be an effective method to improve the interfacial properties of carbon fiber/epoxy composites by increasing the fiber surface area, creating mechanical interlocking, and/or local stiffening at the fiber/matrix interface. At the same time, the excellent electrical and thermal conductivities of CNTs enable the hierarchical composites to be developed into and new generation of multifunctional structural composite materials. Nevertheless, the potential and questionable risks of the CNT composites for workers and consumers are great barriers to the application. Coating the CNT grafted carbon fibers with a thin polymer layer (sizing) could be an ideal way to better fix the CNTs on the fiber surface and improve the CNT performance. Moreover, sizing maintains tow integrity and makes the filament handling easier. Therefore, a combining use of CNT grafting, heat treatment and sizing was carried out for the purpose of improving the CNT safety and tailoring the interface.

T700GC fibers were selected for the combining treatment study because the individual treatment was more effective for T700GC fibers than for HTS fibers in improving the interfacial strength. The fragmentation test results and micrographs of the treated fibers were shown in Table 4.6 and Fig. 4.19.

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T700GC	Mean fragment length (µm)	IFSS (MPa)
As-received	456	65.4
Without CNTs (desized)	778	34.2
CNT grafting	619	45.2
CNT grafting + heat treatment	502	58.2
CNT grafting + heat treatment + sizing	338	94.1

Table 4.6 Fragmentation test results of multi-treated T700GC fibers/epoxy composites.



Fig 4.19 Effect of combining treatments on the interfacial properties.

Firstly, relatively short and dense CNTs were grown onto fiber surfaces. The IFSS was increased by 32% compared with desized fibers. It is contributed to the increasing surface area and mechanical interlocking created by CNTs. And then, heat treatment was applied to the CNT grafted fibers. The SEM pictures demonstrated no change in fiber surface morphologies. A further improvement in IFSS of 29% was obtained compared with the hybrid fibers. The impurity introduced by the CVD

process could be burned out during the heat treatment, which made the fiber/matrix interface more efficient. Finally, sizing was deposited on the hybrid fibers after the heat treatment. The polymer layer was observed on the CNT and fiber surfaces and the CNT morphology became less distinct. As to the IFSS, a highest value (94.1 MPa) was obtained, which is even 44% larger than that of as-received fibers. This may be attributed to the fact that the sizing improved the fiber/matrix and CNT/matrix interface at the same time.

4.4 Estimate of CNT/carbon fiber joint force

For the hierarchical composites consisting of CNTs grafted carbon fiber, the adhesion between the CNT and the carbon fiber is a key factor which will influence the load-transfer behavior and interlaminar properties [21]. To fully explore the potential of CNT in improving the interfacial properties of composites, it is important to estimate the CNT/carbon fiber joint force.

Assume that both the fibers and the CNTs are cylindrical and CNTs are vertically adhered on the fiber surface. Other CNT grafting morphologies also exist, for example, the CNT is entirely laid down on the fiber (0.35 wt% of CNT of 10nm in diameter will be needed to cover the whole fiber surface), which is not considered in this study. During the fragmentation test, while a CNT grafted fiber is pulled, the CNT/fiber joints are subjected to shear forces. The increase of IFSS compared with desized fibers (without CNTs) is supposed to be contributed by the shear stress of the CNTs, the force to detach a CNT from the fiber F can be calculated using the following equation:

$$F = \tau_{cnt} \times S_{ccnt} / N_{cnt} \tag{4-4}$$

where τ_{cnt} is the shear strength of CNTs, S_{ccnt} is the total cross sectional area of CNTs, or the fiber surface area occupied by CNTs, N_{cnt} is the number of CNT grown on the fiber with a length of 10 mm, which is the gauge length of the specimen for fragmentation tests.

 τ_{ent} may be obtained from:

$$\tau_{cnt} = [(\tau_{hybrid} \times S - \tau_{fiber} \times (S - S_{ccnt})]/S_{ccnt}$$
(4-5)

where τ_{hybrid} and τ_{fiber} are the shear strength of CNT/fiber hybrid and desized fiber respectively, S is the surface area of desized fiber.

 τ_{hybrid} and τ_{fiber} were measured through fragmentation tests, S_{cent} can be calculated by using the method introduced in the section 4.3.2. The results of T700GC hybrid fibers are listed in Table 4.7 and the IFSS of hybrid fibers are plotted as a function of CNT/fiber joint force (cf. Fig. 4.20).

	CNT radius (nm)	CNT length (nm)	CNT Number density (/μm²)	CNT coverage fraction	τ _{cnt} (MPa)	F (nN)	IFSS (MPa)
T/CNT-a	5	270	1926	15%	313	25	76.3
T/CNT-b	5	125	4439	35%	92	7	54.5
T/CNT-c	5	595	1048	8%	865	68	102.5
T/CNT-d	5	550	1412	11%	94	7	40.8
T/CNT-e	5	705	1188	9%	177	14	47.5
T/CNT-f	5	680	1357	11%	468	37	80.4

Table 4.7 Parameters for the modeling of the CNT/fiber adhesion



Fig 4.20 IFSS plotted as a function of CNT/fiber joint force in T700GC fibers.

It was found that the IFSS increased with increasing CNT/fiber joint force. The

joint strength is critical for the interfacial properties of composites and the highest value of IFSS (102.5 MPa) was obtained when the estimated joint strength was 68 nN. As the CNT/fiber joint strength are determined by the CVD process, there is a great potential to further enhance the interfacial strength of the hierarchical composites by optimizing the CVD parameters. The relationship between the CNT number density and the IFSS was also studied (cf. Fig. 4.21). The results indicated that the optimal density was around $1000/\mu m^2$. When the density was too high, the improvement in the IFSS became quite limited. To improve the interfacial properties of hierarchical composites, a strong CNT/fiber joint force and a suitable CNT number density are desirable.



Fig 4.21 IFSS plotted as a function of CNT number density in T700GC fibers.

4.5 Conclusions

CNTs were grown successfully on the surface of carbon fibers by a continuous CVD process and the resulting materials showed a uniform deposition of CNTs. The CNT densities and morphologies were varied with grafting parameters, such as temperature, growth time and precursor gas flow rate etc. The interfacial properties of hybrid carbon fiber/epoxy composites were assessed using the single fiber fragmentation test. It was found that the presence of CNTs at the fiber/matrix interface have profound effect in the IFSS of the composites. CNTs provided larger contact area and mechanical interlocking between the fibers and the matrix. An optimal CNT content in the hybrid fibers of 2% leads to significant improvement in the IFSS of the resulting hybrid composites (increased by around 200% for T700GC and 71% for HTS, comparing with desized carbon fibers). The CNT-grafted carbon fibers combine the advantage of nano-scale reinforcement with that of micro-scale fibrous reinforcements. Furthermore, it solves the problem of CNT agglomeration, which could create stress concentration sites which initiate failure and reduce the load carrying capacity of the composite. It was also found that a combing surface treatment (CNT grafting followed by heat treatment and sizing) endowed fibers with superior interfacial adhesion to the tested epoxy matrix. The combination can improve the CNT-carbon fiber hybrid performance and prevent fiber damage during the subsequent handling. The continuous CVD process provides industrial potential for the preparation of hierarchical composites. There is a great potential to further enhance the interfacial properties of the multi-scale reinforced composites by strengthening the fiber/CNT joint through the CVD process.

4.6 Acknowledgements

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4.7 References

[1] Lau AK-T, Hui D. The revolutionary creation of new advanced materials—carbon nanotube composites. Composites Part B: Engineering. 2002;33(4):263-277.

[2] Thostenson ET, Ren Z, Chou T-W. Advances in the science and technology of carbon nanotubes and their composites: a review. Composites Science and Technology. 2001;61(13):1899-1912.

[3] Lv P, Feng Y, Zhang P, Chen H, Zhao N, Feng W. Increasing the interfacial strength in carbon fiber/epoxy composites by controlling the orientation and length of carbon nanotubes grown on the fibers. Carbon. 2011;49:4665-4673.

[4] Thostenson ET, Li WZ, Wang DZ, Ren ZF, Chou TW. Carbon nanotube/carbon fiber hybrid multiscale composites. J Appl Phys. 2002;91(9):6034-6037.

[5] Qian H, Greenhalgh ES, Shaffer MSP, Bismarck A. Carbon nanotube-based hierarchical composites: a review. Journal of Materials Chemistry. 2010;20:4751.

[6] Qian H, Bismarck A, Greenhalgh ES, Shaffer MSP. Carbon nanotube grafted carbon fibres: A study of wetting and fibre fragmentation. Composites Part A: Applied Science and Manufacturing. 2010;41:1107-1114.

[7] Zhao J, Liu L, Guo Q, Shi J, Zhai G, Song J, et al. Growth of carbon nanotubes on the surface of carbon fibers. Carbon. 2008;46(2):380-383.

[8] Zhu S, Su C-H, Lehoczky SL, Muntele I, Ila D. Carbon nanotube growth on carbon fibers. Diamond and Related Materials. 2003;12(10–11):1825-1828.

[9] Zhao Z-G, Ci L-J, Cheng H-M, Bai J-B. The growth of multi-walled carbon nanotubes with different morphologies on carbon fibers. Carbon. 2005;43(3):663-665.

[10] He X, Zhang F, Wang R, Liu W. Preparation of a carbon nanotube/carbon fiber multi-scale reinforcement by grafting multi-walled carbon nanotubes onto the fibers. Carbon. 2007;45(13):2559-2563.

[11] Zhang Q, Liu J, Sager R, Dai L, Baur J. Hierarchical composites of carbon nanotubes on carbon fiber: Influence of growth condition on fiber tensile properties. Composites Science and Technology. 2009;69(5):594-601.

[12] Ci LJ, Zhao ZG, Bai JB. Direct growth of carbon nanotubes on the surface of ceramic fibers. Carbon. 2005;43(4):883-886.

[13] Bai JB. PROCEDE DE SYNTHESE DE NANOTUBES DE CARBONE SUR MATERIAUX MICROMETRIQUES LONGS ET PARTICULAIRES. FR 2939422, France2008.

[14] Bai JB, Ci LJ, Zhao ZG. PROCEDE D'OBTENTION DE NANOTUBES DE CARBONE SUR DES SUPPORTS ET COMPOSITES LES RENFERMANT FR 2865739 France2004.

[15] Rong H, Han K, Li S, Tian Y, Muhuoyu. A novel method to graft carbon nanotube onto carbon fiber by the use of a binder. Journal of Applied Polymer Science. 2012:1-5.

[16] Qian H, Bismarck A, Greenhalgh ES, Shaffer MSP. Synthesis and characterisation of carbon nanotubes grown on silica fibres by injection CVD. Carbon.48(1):277-286.
[17] Sharma SP, Lakkad SC. Effect of CNTs growth on carbon fibers on the tensile strength of CNTs grown carbon fiber-reinforced polymer matrix composites. Composites Part a-Applied Science and Manufacturing. 2011;42(1):8-15.

[18] Riccardis MFD, Carbone D, Makris TD, Giorgi R, Lisi N, Salernitano E. Anchorage of carbon nanotubes grown on carbon fibres. Carbon. 2006;44(4):671-674. [19] Zhang F-H, Wang R-G, He X-D, Wang C, Ren L-N. Interfacial shearing strength and reinforcing mechanisms of an epoxy composite reinforced using a carbon nanotube/carbon fiber hybrid. Journal of Materials Science. 2009;44(13):3574-3577.

[20] Sager RJ, Klein PJ, Lagoudas DC, Zhang Q, Liu J, Dai L, et al. Effect of carbon nanotubes on the interfacial shear strength of T650 carbon fiber in an epoxy matrix. Composites Science and Technology. 2009;69(7-8):898-904.

[21] Hung KH, Kuo WS, Ko TH, Tzeng SS, Yan CF. Processing and tensile characterization of composites composed of carbon nanotube-grown carbon fibers. Composites Part A: Applied Science and Manufacturing. 2009;40:1299-1304.

[22] Barber AH, Cohen SR, Eitan A, Schadler LS, Wagner HD. Fracture Transitions at a Carbon-Nanotube/Polymer Interface. Advanced Materials. 2006;18(1):83-87.

[23] Wong M, Paramsothy M, Xu XJ, Ren Y, Li S, Liao K. Physical interactions at carbon nanotube-polymer interface. Polymer. 2003;44(25):7757-7764.

[24] Lau K-t. Interfacial bonding characteristics of nanotube/polymer composites. Chemical Physics Letters. 2003;370(3–4):399-405.

[25] Barber AH, Cohen SR, Wagner HD. Measurement of carbon nanotube--polymer interfacial strength. Applied Physics Letters. 2003;82(23):4140-4142.

[26] Cooper CA, Cohen SR, Barber AH, Wagner HD. Detachment of nanotubes from a polymer matrix. Applied Physics Letters. 2002;81(20):3873-3875.

[27] Agnihotri P, Basu S, Kar KK. Effect of carbon nanotube length and density on the properties of carbon nanotube-coated carbon fiber/polyester composites. Carbon. 2011;49:3098-3106.

[28] Bekyarova E, Thostenson ET, Yu A, Kim H, Gao J, Tang J, et al. Multiscale Carbon Nanotube–Carbon Fiber Reinforcement for Advanced Epoxy Composites. Langmuir. 2007;23(7):3970-3974.

General conclusions and perspectives

General conclusions

This thesis aimed at developing different methods (i.e. sizing, heat treatment, and CNT grafting) for the surface treatments of carbon fibers to improve the interfacial properties of carbon fiber/epoxy composites. Various conditions for the surface treatments have been investigated and the optimal conditions to improve the interfacial properties have been obtained. In more details, the main results obtained during this research are summarized as following:

Sizing of carbon fibers:

Different sizing formulations composed of varied proportions of epoxy and amine curing agent were used for the sizing of desized T700GC and HTS carbon fibers, and their effects on the IFSS of carbon fiber/epoxy composites were investigated by single fiber fragmentation tests. The results indicated that the sizing formulations with the concentration of 2 wt% in acetone and epoxy/amine ratio of 100 : 94.7 endowed the resized T700GC fibers with the optimal interfacial properties. The IFSS was increased by 35% compared with as-received fibers. It could be attributed to the fact that the interconnected ring structures of sizing coatings could tightly adhere to the fiber surface and the excess of amine groups could react with the epoxy groups in the matrix resins when the optimal sizing formulation was used. However, in the case of HTS fibers, no improvement in the interfacial strength was found after the sizing process. The SEM pictures and TGA results indicated that the sizing level on the fiber surface could be well controlled by changing the sizing concentration. But too much sizing made the fiber surface become less uniform and the sizing was peeled off in some place on the fiber surface, which would decrease the interfacial adhesion between the carbon fibers and the matrix.

Heat treatment of carbon fibers:

The effects of the H₂/Ar ratio in the gas mixture, treatment temperature and

time during the heat treatment on the interfacial properties of carbon fiber/epoxy composite were investigated. The results indicated that after the treatment at 600 °C for 16 min using a H₂ flow rate of 0.3 L/min, the optimal interfacial properties were obtained for T700GC fibers. Heat treatments alter the inert nature of carbon fiber surfaces. The IFSS was increased by 75% compared with as-received fibers. In the case of HTS fibers, the heat treatment has not been found to lead to any improvement in the interfacial properties of composites. The relationship between the IFSS of single fiber composites and the ILSS of the corresponding bulk composites was also studied. It was found that there was little correlation between the single fiber adhesion strength and the shear strength of composite, probably because the matrix resins used are very different. The SEM and XPS studies of carbon fiber surface revealed that the surface morphology and composition was not influenced by the change of H₂/Ar ratio in the gas mixture.

Growth of CNTs on carbon fibers:

CNTs of different morphologies were grown on the surface of carbon fibers by a continuous CVD process and the resulting materials showed a uniform deposition of CNTs. An optimal CNT content in the hybrid fibers of 2% led to significant improvement in the interfacial properties of the resulting hybrid composites (IFSS increased by around 200% for T700GC and 71% for HTS, comparing with desized carbon fibers). The CNT-grafted carbon fibers combine the advantage of nano-scale reinforcement with that of micro-scale fibrous reinforcements. Furthermore, it solves the problem of CNT agglomeration, which could create stress concentration sites which initiate failure and reduce the load carrying capacity of the composite.

Additionally, a combining use of CNT grafting, heat treatment and sizing endowed fibers with superior interfacial adhesion to the tested epoxy matrix. Meanwhile, the combination can improve the CNT-carbon fiber hybrid performance and prevent fiber damage during the subsequent handling.

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Perspectives

The surface treatments of carbon fibers to improve the interfacial properties of carbon fiber/epoxy composites developed in this thesis have promising applications in the field of composite materials. The following aspects would be interesting for the future research:

- More investigations are proposed to study the mechanism of heat treatment of carbon fibers to improve the interfacial properties of composites.
- More efforts are encouraged to develop and characterize the CNT-grafted carbon fiber-based bulk compositions.
- It is promising to establish more accurate model to envisage the relationship between the surface treatments and the interfacial properties.

Résumé

Les matériaux composites à base de fibres de carbone (CF) sont actuellement très utilisés dans le domaine de l'aérospatiale, de la construction et du sport grâce à leurs excellentes propriétés mécaniques, une faible densité et une haute stabilité thermique. Les propriétés des composites dépendent fortement de la nature et de la qualité de l'interface fibre/matrice. Une bonne adhérence interfaciale permet un meilleur transfert de charge entre la matrice et les fibres. Les CFs sans traitement sont chimiquement inertes et présentent donc une faible adhérence vis-à-vis de la résine époxyde. Par ailleurs, les faibles propriétés transversales et interlaminaires limitent sensiblement la performance et la durée de vie des composites. Par conséquent, un type de renfort à base de fibres traitées est fortement souhaité pour améliorer les propriétés globales des composites, en particulier l'adhésion interfaciale entre les fibres et la matrice. Dans cette thèse, trois types de traitement de surface, l'ensimage, le traitement thermique et la croissance de nanotubes (CNTs), ont été appliqués aux CFs. En particulier, les CFs greffées de CNTs, se combinant avec les deux autres traitements, montrent la meilleure adhérence interfaciale avec la matrice époxyde. L'ensimage proposé peut améliorer la performance du CNT-CF hybride et minimiser les dommages aux fibres lors de la manipulation ultérieure tels que le transport et la préparation de composites.

Tout d'abord, l'ensimage a été réalisé sur la surface des fibres par dépôt de résine époxyde en solution. L'ensimage permet de protéger les filaments au cours de la mise en œuvre et favorise également la liaison fibre/matrice. Différentes formulations d'ensimage selon les proportions époxy/durcisseur ont été utilisées. La quantité d'ensimage déposée sur les fibres de carbone a été contrôlée en faisant varier la concentration de la solution d'ensimage.

Ensuite, un traitement thermique, effectué sous un mélange de gaz à 600-750 °C, a permis de modifier la surface des CFs. L'influence de la composition du gaz, du temps de traitement et de la température sur les propriétés interfaciales des composites CFs/époxy a été systématiquement quantifiée.

Enfin, des CNTs ont été greffés sur les CFs par une méthode de dépôt chimique en phase vapeur en continu afin d'obtenir un nouveau type de renfort hybride multi-échelle. Les CNTs greffés permettent d'augmenter la surface de contact et d'améliorer l'accrochage mécanique de la fibre avec la résine. De plus, ils pourraient améliorer la résistance au délaminage, les propriétés électriques et thermiques des composites. Les CFs greffées de CNTs de différentes morphologies et densités ont été produites en faisant varier les conditions de croissance.

Après le traitement de surface, les essais de fragmentation ont été menés afin d'évaluer la résistance au cisaillement interfacial (IFSS) des composites CFs/époxy. Par rapport aux fibres vierges, l'ensimage et le traitement thermique ont contribué à une augmentation de l'IFSS de 35% et de 75%, respectivement. L'adhésion interfaciale entre la matrice époxyde et les fibres greffées avec CNTs pourrait être adaptée en faisant varier la morphologie, la densité de nombre et la longueur de CNT. Les CFs greffées avec 2% en masse de CNTs (10nm de diamètre) ont entraîné une amélioration de l'IFSS de 60%. Un traitement thermique et un ensimage pourraient contribuer à une augmentation supplémentaire de 108%. Il convient de mentionner que la dégradation des fibres n'a pas été observée après les divers traitements précédemment évoqués. Les résultats de ces travaux pourraient mener au développement de ces techniques à plus grande échelle pour la conception de structures à base de composites CFs/époxy.

Abstract

Carbon fiber (CF)-reinforced polymer composites are widely used in aerospace, construction and sporting goods due to their outstanding mechanical properties, light weight and high thermal stabilities. Their overall performance significantly depends on the quality of the fiber-matrix interface. A good interfacial adhesion provides efficient load transfer between matrix and fiber. Unfortunately, untreated CFs normally are extremely inert and have poor adhesion to resin matrices. Meanwhile, poor transverse and interlaminar properties greatly limit the composite performance and service life. Therefore, a new kind of fiber-based reinforcement is highly desired to improve the overall composite properties, especially the interfacial adhesion between fiber and matrix. In this thesis, three kinds of surface treatment, including sizing, heat treatment and carbon nanotube (CNT) growth, were applied to CFs. In particular, CFs grafted with CNTs, combining with the other two treatments demonstrate superior interfacial adhesion to the tested epoxy matrix. The proposed epoxy sizing can improve the CNT-CF hybrid performance and prevent fiber damage during the subsequent handling such as transport and composite preparation.

Firstly, epoxy-based sizing was applied onto the CF surface by the deposition from polymer solutions. Sizing could not only protect the carbon fiber surface from damage during processing but also improve their wettability to polymer matrix. A detailed study was conducted on the influence of the ratio of epoxy and amine curing agent in the sizing formulation. The sizing level on the fiber surface was controlled by varying the concentration of polymer solutions.

Secondly, heat treatment in a gas mixture at 600-750 °C was used to modify the carbon fiber surface. The effect of gas mixture composition, treatment time and temperature on the interface was evaluated systematically.

Thirdly, CNTs were in-situ grafted on the carbon fiber surface by a continuous chemical vapor deposition (CVD) process to obtain hierarchical reinforcement structures. These hybrid structures have the potential to improve the interfacial strength of fiber/epoxy composites due to the increased lateral support of the load-bearing fibers. Meanwhile, the CNT reinforcement could improve the composite delamination resistance, electrical and thermal properties. The CF grown with CNTs of different morphologies and densities were produced by varying CVD conditions.

After the surface treatment, single fiber fragmentation test was used to assess the interfacial shear strength (IFSS) of carbon fiber/epoxy composites. Compared with the as-received CFs, the epoxy sizing and the heat treatment contributed to an improvement in IFSS of up to 35% and 75%, respectively. The interfacial adhesion between epoxy matrix and CNT-grafted fibers could be tailored by varying the CNT morphology, number density and length. The CFs grafted with 2 wt% CNTs of 10 nm in diameter resulted in an improvement in IFSS of around 60%. A further heat treatment and epoxy sizing could contribute to an additional increase of 108%. It's worth to mention that no significant strength degradation of the fibers was observed after the surface treatments. This work could support the development of large-scale approach to CF surface treatment, and throw light on the design of structurally efficient CF/epoxy composites.