Carbon Fibre Reinforced Poly(vinylidene Fluoride)

Siti Rosminah Shamsuddin

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Department of Chemical Engineering
Imperial College London
South Kensington Campus,
SW7 2AZ London, UK

Declaration

This dissertation is a description of the work carried out by the author in the Department of Chemical Engineering, Imperial College London between July 2008 and February 2012 under the supervision of Prof Alexander Bismarck and Dr Patrick Leevers. Except where acknowledged, the material presented is the original work of the author and no part of it has been submitted for a degree at this or any other university.

Signature

Abstract

The demand for oil in the world is expected to rise by 1.7% in the fourth quarter of 2012 compared to fourth quarter of 2011. In order to cater for this increasing demand, the oil and gas industry continues to explore and develop deep-sea oilfields where oil and gas risers and pipelines encounter extreme conditions. The combination of high pressure and temperature with aggressive media which contains of hydrocarbon, alkanes, acids, sour gas (H_2S), and CO_2, etc., requires superior material performance and durability. Conventional engineering materials, such as steel are heavy and require corrosion protection, which are currently used as risers, flowlines and choke and kill lines have reached their limits. This is because of the poor chemical resistance and damage tolerance and the high costs involved in supporting their own weight. This has motivated the industry to explore non-corroding and lighter alternative materials if deeper sea reservoirs are to be explored. One such material that has the potential to overcome such limitations thus enabling new design strategies for cost effective, weight and energy saving materials is fibre reinforced composites. The remarkable properties and the tailorability of fibre reinforcement along load paths to achieve excellent performance of the composites is an attribute not found in any other material.

The aim of this research was to manufacture novel carbon fibre reinforced polyvinylidene fluoride (PVDF) composites by incorporating atmospheric plasma fluorination of the carbon fibres. Powder impregnation method was adapted for the manufacturing of continuous unidirectional (UD) carbon fibre reinforced PVDF composite prepregs. The resulting composite laminates were characterised through various macro-mechanical tests. The impact of atmospheric plasma fluorination of the carbon fibre on the tensile, flexural, short beam shear and tearing properties of the UD composites were investigated to determine whether the improvements observed in the single fibre model composite can be translated to macro-level composite laminates. Apart from this, the impact of combining both fibre and matrix modifications on the composite were studied and the preliminary results on micro-mechanical scale are presented. Finally, composite pipe structures, made by filament winding technique using unidirectional carbon fibre reinforced PVDF composite prepregs onto a pure PVDF liner were fabricated, and characterised with respect to its mechanical properties.

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My family for their undying love
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List of Publications

Invited book chapters

1. Shamsuddin, S.-R., Ho, K. K. C, Lee, K. –Y., Hodgkinson, J. M. and Bismarck, A., "Carbon Fibres: Properties, Testing and Analysis" in "Wiley Encyclopaedia of Composites". Edited by Nocolais, L., John Wiley & Sons (Germany), 2011.

Invited Refereed Journal Papers

1. Shamsuddin, S.-R., Ho, K. K. C, Lee, K. –Y. and Bismarck, A., "Plasma Treatment of Carbon Fibres: Effect of Fibre Properties, Adhesion and Composite Performance, *Special Issue of the Journal of Adhesion Science and Technology (JAST)*, 2011. *Submitted*.

2. Ho, K. K. C., Shamsuddin, S.-R., Riaz, S., Lamoriniere, S., Tran, M. Q., Javaid, A. and Bismarck, A., "Wet impregnation as route to unidirectional carbon fibre reinforced thermoplastic composites manufacturing", *Plastic, Rubber and Composites*, **40** (2011), 100-107.

3. Shamsuddin, S.-R., Ho, K. K. C, Lamoriniere, S., Lee, A. F. and Bismarck, A., "Impact of In-Line Atmospheric Plasma Fluorination of Carbon Fibres on the Performance of Unidirectional, Carbon Fibre-Reinforced Polyvinylidene Fluoride", *Advances in Polymer Technology-Special Issue*, **29** (2009), 86-97.

Peer-reviewed Journal Papers

1. Shamsuddin, S.-R., Ho, K. K. C., Ng, P., Lee, A. F. and Bismarck, A., "Synergy of matrix and fibre modification on adhesion between carbon fibres and poly(vinylidene fluoride)", *Composites Science and Technology*, **72** (2011), 56-64.

2. Ho, K. K. C., Shamsuddin, S.-R., Laffan, M. and Bismarck, A., “Unidirectional carbon fibre reinforced poly(vinylidene fluoride): Impact of atmospheric plasma on composite performance”, *Composites Part A-Applied Science and Manufacturing*, **42** (2011), 453-461.

Conference Proceedings

1. Shamsuddin, S.-R., Ho, K. K. C., and Bismarck, A., “Carbon fibre reinforced PVDF: Effect of matrix and carbon fibre modification on composite performance”, *Proceedings of the 14th European Conference on Composite Materials,* 7th – 10th June 2010, Budapest, Hungary

2. Shamsuddin, S.-R., Ho, K. K. C., Laffan, M. and Bismarck, A., “Unidirectional Carbon Fibre Reinforced Polyvinylidene Fluoride: Impact of Atmospheric Plasma Fluorination on Composite Performance”, *Proceedings of the 17thInternational Conference on Composite Materials,* 27th – 31st July 2009, Edinburgh, UK.

Oral Presentations at Conferences

1. Shamsuddin, S.-R., Ho, K. K. C., Bismarck, A., “Unidirectional Glass Fibre Reinforced Polyvinylidene Fluoride (PVDF) Composites: Tailoring the Interface the Interface Via Low Pressure Oxygen Plasma”, *ICMAT 2011*, 26th June - 1st July 2011, Singapore.

2. Shamsuddin, S.-R., Bismarck, A., “Unidirectional fibre reinforced polyvinylidene fluoride (PVDF) composites: Impact of constituents’ modifications on the macro-mechanical properties of composite”, *Chemical Engineering PhD Research Symposium*, 29th March 2011, Imperial College, UK.

3. Shamsuddin, S.-R., Ho, K. K. C., Bismarck, A., “Carbon fibre reinforced polyvinylidene fluoride: tailoring adhesion for improving composite performance”, *ICMAC 2011*, 22nd - 24th March 2011, Belfast UK

4. Ho K. K. C., Shamsuddin, S.-R., Bismarck, A., “Short glass fibre reinforced polyvinylidene fluoride: Plasma modification and manufacturing”, *ICMAC 2011*, 22nd - 24th March 2011, Belfast UK.

5. Shamsuddin, S.-R., Ho, K. K. C., Bismarck, A., “Carbon fibre reinforced polyvinylidene fluoride (PVDF): Effect of matrix and carbon fibre modification on composite performance”, *ECCM 14th*, 7th - 10th June 2010, Budapest.

6. Shamsuddin, S.-R., Ho, K. K. C., Bismarck, A., “Carbon fibre reinforced PVDF: Effect of matrix and carbon fibre modification on composite performance”, *SICOMP Conference 201*0, 3rd - 4th June 2010.

7. Ho, K. K. C., Shamsuddin, S.-R., Ng, P., Bismarck, A., “Interface engineering of carbon fibre reinforced poly(vinylidene fluoride)”, *10th European Symposium on Polymer Blends*, 8th - 10th March 2010, Dresden, Germany.

8. Shamsuddin, S.-R., Ho, K.K.C, Laffan, M., Lamoriniere, S., Bismarck, A., “Unidirectional carbon fibre reinforced polyvinylidene fluoride: Impact of atmospheric plasma fluorination on composite performance”, *ICCM 17th*, 27th - 31st July 2009, Edinburgh, Scotland.

Awards

1. 3rd Prize for best oral Presentation in the Chemical Engineering PhD Research Symposium 2011 by Academic and Industrial Panellists and 1st Prize for best oral presentation in the Chemical Engineering PhD Research Symposium 2011 by student votes, Imperial College London, March 2011

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$\hat{\sigma}$, σ^{tu}	Ultimate tensile strength
δ	Load point displacement
γ	Surface free energy
γ^{p}	Dispersive component of surface free energy
γ^{d}	Polar component of surface free energy
θ_r	Receding contact angle
A	Average cross section area
a	Delamination length
a_o	Initial crack length
b, B	Width
C_1 , C_O	Compliances for the critical load and at the elastic portion of the load/displacement curve
D	Central deflection
d, t	Pipe thickness
d_{50}	Average particle size
d_f	Fibre diameter
d_i	Initial inside diameter of the specimen (mm)
E , E^{chord}	Young’s modulus
E_f	Flexural modulus
E_f	Young’s modulus of fibre
E_m	Young’s modulus of matrix
F	Equilibrium force during the steady state tearing process
f	Fibre
F^{d}	Load per unit length at a specific deflection
F^{SBS}	Apparent short beam shear strength
g	Acceleration due to gravity
G_{IC}	The initiation critical energy release rate

h, H, t	Thickness
H_f^0	Heat of Fusion
L	Specimen length
m	Gradient of the initial part of the force-displacement curve
m	Matrix
P	Load, percentage of pipe deflection
P_c	Initiation critical load
P_{Max}	Maximum Load
PS	Pipe stiffness
r	Internal radius of the pipe specimen
S	Span length
S/h	Span to thickness ratio
SF	Stiffness factor
$\mathrm{T_g}$	Glass transition temperature
$\mathrm{T_m}$	Melting temperature
V_f	Fibre volume fraction
W	Weight
W_A	Thermodynamic work of adhesion
W_e	Specific essential work of fracture
W_f	Fibre weight
W_m	Matrix weight
w_p	Non-essential specific plastic work
X_c	Degree of crystallinity
γ_{la}, γ_l	Liquid surface tension
ΔH_m	Heat of melting
Δy	Change in the inside diameter of the specimen in the direction of load
$\Delta\varepsilon$	Difference in tensile strain
$\Delta\theta$	Contact angle hysteresis
$\Delta\sigma$	Difference in tensile stress
θ	Contact angle
θ_a	Advancing contact angle

ρ	Density
ρ_f	Fibre density
ρ_m	Matrix density
σ	Apparent hoop tensile strength
σ_f	Flexural strength
σ_f	Tensile strength of fibre
σ_m	Tensile strength of matrix
τ_{IFSS}	Interfacial shear strength

List of Units

at.-%	atomic percentage
cm	centimetre
°C/min	degree Celsius per minute
°C	degree Celsius
eV	electronvolt
GPa	Giga Pascal
g	gram
g/cm^3	gram per cubic centimetre
h	hour
J/g	Joule per gram
J/m^2	Joule per square metre
kJ/m^2	kilojoule per square metre
kN	kilo Newton
kW/m^2	kilowatt per square metre
L	Litre
L/min	Litre per minute
MJ/m^3	Mega joule per cubic metre
MPa	Mega Pascal
m	metre
m/min	metre per minute
µm	micrometre
µN/m	micro Newton per metre
mN/m	milliNewton per metre
mW	milliWatt
mg	milligram
mL	millilitre
mm/s	millimetre per second
mm	millimetres
min	minute

N	Newton
N/mm	Newton per millimetre
ppm	parts per million
%	percentage
rpm	rotation per minute
t	tonne
W	Watt
wt%	weight per cent

List of Abbreviation

AP	Atmospheric pressure
APC	Aromatic polymer composite
APF	Atmospheric plasma fluorination
APP	Atmospheric pressure plasma
Ar	Argon
ASTM	American Standard of Testing Material
BMI	Bismaleimide
$C_3H_4O_2$	Acrylic acid
$C_3H_5NH_2$	Allylamine
C_3H_8	Propane
$C_4H_2O_3$	Maleic anhydride
$C_4H_8O_2$	Ethyl acetate
$C_6H_{18}OSi_2$	Hexamethyldisiloxane
C_6H_6	Benzene
$C_7H_6O_2$	Benzoic acid
C_8H_{10}	Xylene
CF	Carbon fibre
CF_4	Tetrafluorocarbon
CF4	Tetrafluoromethane
CH_4	Methane
$CHClF_2$	Chlorodifluoromethane
CL	Composite line
ClF_3	Chlorine trifluoride
CO2	Carbon dioxide
CPL	Composite production line
D-band	Disorder finite-sized microcrystalline and/or edge of carbon
DCB	Double cantilever beam
DGEBA	Diglycidyl ether of bisphenol A
DMF	Dimethyl formamide

DSC	Differential scanning calorimetry
ECTFE	Ethylene-chlorotrifluoroethylene
ENF	End-notch flexure
F_2	Fluorine
FEP	Fluorinated ethylene propylene copolymer
G-band	Tangential graphatised carbon
H2S	Hydrogen disulphide
H_2SO_4	Sulphuric acid
He	Helium
HF	Hydrogen fluoride
HNO_3	Nitric acid
IFSS	Interfacial shear strength
ILSS	Interlaminar shear strength
K_2CO_3	Potassium carbonate
$KMnO_4$	Potassium permanganate
KNO_3	Potassium nitrate
KOH	Potassium hydroxide
LP	Low pressure
LPP	Low pressure plasma
MAH	Maleic anhydride
N_2	Nitrogen
NaOH	Sodium hydroxide
NH_4HCO_3	Ammonium Bicarbonate
O_2	Oxygen
O_3	Ozone
PA12	Polyamide
PAN	Polyacrylonitrile
PC	Polycarbonate
PEEK	Polyetheretherketone
PEI	Polyetherimide
PFA	Tetrafluoroethylene-perfluoro alkoxy vinyl ether copolymer

PPS	Polyphenylenesulphide
PTFE	Polytetraflurorethane
PVDF	Polyvinylidene fluoride
RTP	Reinforced thermoplastic pipe
SEM	Scanning electron microscopy
TGDDM	Tetraglicidyl diaminodiphenylmethane
TLP	Tension Leg Platform
UD	Unidirectional
XPS	X-ray photoelectron spectroscopy

1.0 Introduction

Conventional high performance fibre reinforced polymer composites have outstanding mechanical properties, exhibiting high strength and stiffness combined with low weight and susceptibility to fatigue and corrosion. Composites furthermore offer advanced design possibilities, improved safety and extended service life with respect to its resistance to corrosion as well as reduced through life cost [1]. The properties of composites can be tailored to particular applications by incorporation of additional functionality, such as sensors, actuators and self-healing properties [2, 3]. Even switchable stiffness and energy storage can be integrated within composites, making composites truly the materials of the future [4, 5]. The composites use is rising exponentially, not only in the aerospace sector, but also in the oil and gas industry [6]. The application of composites on the sea bed as risers/pipelines for offshore oil and gas is relatively new but very promising. Composites, for pipes, cables, pressure vessels, etc. will be the key technology to exploiting deeper sea, arctic or high temperature reservoirs because of their favourable strength to weight ratio, ability to withstand harsh environments, such as high temperatures, high and fluctuating pressures, sweet and sour well fluids, chemicals and high salinity, and excellent corrosion/wear resistance [7].

Over the past two decades, composite materials have progressed and are now being used in secondary structures on offshore oil platforms such as gratings, staircases, handrails, accommodation modules, high pressure tubing, fire water main and deluge pipes replacing metals [8]. Reduction in weight is directly translated in the savings of structural costs for construction of offshore platforms. It has been reported that weight savings of 50 to 70% are possible when using composites in offshore as compared to conventional steels [9]. In weight sensitive applications, such as Tension Leg Platforms (TLP), a weight reduction of a component by 1 kg translates to 2 kg weight being removed from the rest of the structure [10]. In addition to top-side applications, composite materials have been introduced as an excellent materials choice for column pipes, deep sea umbilical and choke and kill lines over the last 10 years [6] owing to their intrinsic corrosion resistance. Although composite materials have been used in the oil & gas industry, there have been many economical and emotional barriers against increasing use of composite drilling and production risers, stemming from the risks involved in exploration and development, the different failure modes of composites as compared to metals, the need for components to fail safe and the lack of large dedicated composite manufacturing capabilities. However, the successful installation of a composite driller riser joint on the Heidrun Tension Leg Platform in the Norwegian North Sea from 2001 to autumn 2002 has proven that composite materials are a viable alternative to conventional risers creating opportunities for the industry to invest in composite technology [11, 12].

The composite material that was investigated in this research is carbon fibre reinforced polyvinylidene fluoride (PVDF). Of all reinforcing fibres, carbon has been most commonly used as reinforcement in advanced composites to manufacture light, stiff and durable components or structures. Carbon fibre was first introduced by Thomas Edison in the nineteenth century as filaments for light bulbs. However, it was only used in composites in the early 1960s by Shindo in Japan, Watt in England and Bacon and Singer in the United States, focusing mainly on space technology and aeronautics [13]. A market report prepared by a global management consulting and market search firm, Lucintel, shows that the growth rate of the carbon fibre market from 1987 to 2010 was 10% and is now expected to increase 13% per year through to 2015 as new industries are emerging and demanding high performance and lightweight materials [14, 15].

When a composite is in service, it is the matrix that comes into contact with the environment that the material is exposed to. Matrix is the barrier of the composite, determines its inertness and acts as the protection for the reinforcing fibres. Primary characteristics for reinforcing fibres in inert composites are high stiffness and strength, in which carbon fibres outperform other fibres. Furthermore, such properties are unaffected in hostile environments such as elevated temperatures, exposure to common solvents and fluids, and environmental moisture which makes them chemically and mechanically favourable. Therefore, it is important to select the right matrix for the manufacturing and characterising inert composites.

PVDF is an inert thermoplastic fluoropolymer (Fig. 1.1). It was first produced commercially in 1961 by the Pennsalt Chemical Company in the United States. In 1960s, the market for PVDF focused on heat shrinkable tubing for electrical insulation in military applications and heat trace wiring [16]. Today, PVDF continues to be high in demand as material for high purity processing components, such as tank linings, pumps, filtration products, pipes and fittings, flexible tubing, architectural coatings (to provide superior weatherability for buildings), wires and cables as well as a polymer processing aid (added to polymers during extrusion for increased output, lower die pressure, reduced die build-ups, to eliminate melt-fracture and lower processing temperatures, etc.) [16, 17]

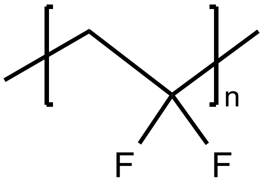

Figure 1.1 Chemical structure of PVDF

Compared to other fluoropolymers, PVDF has the lowest melting point, but has the highest heat deflection temperature under load making it a very suitable for high temperature applications. PVDF can be processed at sufficiently low temperatures using the same equipment and nearly the same conditions as polyethylene and polypropylene. Owing to this and having the wide service temperature window of -20^{o}C to 120^{o}C [16], PVDF has been used as the main sheathing material for flow, choke and kill lines in offshore oil and gas application [18] as well as chemical barriers for offshore flexible risers as it has shown a remarkable characteristic of being able to be in contact with Petroleum for over 20 years [17]. Therefore, the main motivation to study PVDF composites comes from the oil and gas industry. The need to use a material that is not only inert but can provide structural and mechanical performance and is also light-weight especially for deep-sea exploration has turned all attention into investigating composites as an alternative materials for the industry. PVDF has already been used widely within the oil and gas industry due to its intrinsic inertness. Implementing reinforcement into a chemically inert matrix, such as PVDF, will benefit the oil and gas industry with a material that can withstand harsh chemical conditions as well as provide high mechanical strength. Other high performance engineered thermoplastics, such as polyetheretherketone (PEEK) and polyphenylenesulphide (PPS), are very expensive and difficult to process as they require high processing temperatures making PVDF an excellent alternative. However, PVDF has very low inter-molecular interaction. Therefore, adhesion to reinforcements is a major challenge when PVDF is used as a matrix material.

Many studies have been conducted extensively to address the issue of adhesion between PVDF and other materials such as carbon fibres, metals and glass [17-21]. Introducing reactive chemical groups into PVDF has been shown to enhance bonding between PVDF and other surfaces such as glass and metals [17]. It has also been reported that the most promising method to enhance the adhesion between carbon fibres and PVDF is to introduce fluorine functional groups onto the surface of carbon fibres. This can be done by either direct fluorination or by plasma fluorination techniques [20-22]. Direct fluorination is performed in a specially designed reactor by passing through a diluted combination or individual F_2 gases over a batch of carbon fibres for a given period of time. Studies with combinations of F_2, ClF_3 and HF showed that direct fluorination can introduce up to 65% of fluorine groups onto the carbon fibre surface [19, 23]. These studies also show that as the fluorine content on the carbon fibre surface increases, the surface energy of the carbon fibre decreases. This is explained by the presence of covalent $C\text{-}F_x$ bonds on the fibre surface, which increases the surface hydrophobicity [19, 23, 24]. Besides that, a study of adapting the direct fluorination method of carbon fibres and the adhesion between the fluorinated fibres and various fluoropolymers was performed by Ho et al. [21]. The fluoropolymers studied were ethylene-chlorotrifluoroethylene (ECTFE), polyvinylidene fluoride (PVDF), fluorinated ethylene propylene copolymer (FEP) and tetrafluoroethylene-perfluoro alkoxy vinyl ether copolymer (PFA). It was found that the optimum apparent interfacial shear strength between fluorinated fibres and matrices as well as the fluorinated fibre contact angles was observed at F/C ratio of 0.1-0.2. This was true for all the fluoropolymers studied. However, direct fluorination of carbon fibres is not very favourable as it can only be used in a batch system and involves handling F_2 directly.

Apart from direct fluorination, low pressure plasma fluorination is an alternative method for introducing fluorine functional groups onto a substrate. Sahin et al. [25] reported that 30 at.-% of fluorine content was observed on a cellulose surface that was subjected to low pressure plasma fluorination using CF_4 as the feed gas to create super-hydrophobic paper. Similarly, many other studies have been conducted to improve hydrophobicity of carbon nanotubes and polymers such as Polypropylene (PP), Polyester fabrics and Polyethylene terephthalate (PET) [26-28]. However, the low pressure plasma fluorination method requires a complex vacuum system to operate. Therefore, it can also only be applied to batch processes.

Atmospheric plasma fluorination (APF) was developed by Ho et al. [22, 29-31] to introduce small amounts of fluorine into the surface of carbon fibres. This technique is able to treat carbon fibres in a continuous process. The authors studied various plasma feed gases on the surface properties of the fluorinated carbon fibres. It was reported that the water contact angle of the treated carbon fibres was significantly increased when nitrogen (N_2) and chlorodifluoromethane ($CHClF_2$) were used as feed gases in the plasma. The increase in the hydrophobicity of the treated fibres was due to the presence of more fluorine functional groups on the fibre surface. With this feed gas combination, it was also reported that the degree of fluorination depends on the treatment duration. By exposing the carbon fibres to APF for 8 min, as high as 4.9 at.% of fluorine was detected on the carbon fibre surface by X-ray photoelectron spectroscopy [30]. Moreover, X-ray diffraction, Raman spectroscopy and measurements of the tensile strength of APF treated carbon fibres showed that the bulk properties of the fibre were not affected.

Apart from characterising the surface and the bulk properties of APF treated carbon fibres, the apparent interfacial shear strength of the fluorinated carbon fibres and PVDF was studied using single fibre model composites [22]. It was shown that the interfacial shear strength between fluorinated carbon fibres and PVDF reaches the maximum (~16 MPa) after being exposed for 1 min to APF and remains unaffected when exposed for longer time to APF. These studies show that APF only alters the surface properties of the carbon fibres without modifying the bulk properties and is able to overcome the adhesion issues between carbon fibres and PVDF.

The above achievements were demonstrated for single-fibre model composites. Therefore, the main aim of this research was to determine whether these improvements obtained for single-fibre model composites can be translated to a macro-scale composites and ultimately to a composite structure.

1.1 Aims and objectives

The primary aim of this research is to manufacture unidirectional (UD) carbon fibre reinforced polyvinylidene fluoride (PVDF) and characterise the macro-mechanical properties of these composite laminates. The fibre/matrix interface was tailored by APF modification of the fibre surface to enhance the mechanical performance of the composites prepared. The specific objectives include:

a. Continuous manufacturing of UD carbon fibre reinforced PVDF via wet powder impregnation route using our laboratory scale composite production line and incorporating APF in-line;
b. Quantify the degree of improvements on the mechanical properties of UD carbon fibre reinforced PVDF composite laminates by fibre modification through atmospheric pressure plasma fluorination which include axial tensile strength, flexural properties and interlaminar shear properties;
c. Investigate the effect of both fibre and matrix modification on the properties of single-fibre model composites; and
d. Fabricate a reinforced PVDF pipe using filament winding and characterise its mechanical properties.

1.2 Structure of the thesis

The thesis is divided into eight chapters. The first chapter gives the background, previous work and overview of the objectives of the research. This is followed by Chapter 2 which gives an insight into inert composites. The thermal resistance, chemical resistance and interfacial adhesion between inert polymers and carbon fibres are discussed in detail. The challenge with inert polymer composites is mainly compatibilisation with reinforcement, such as carbon fibres. This problem is often addressed by modifications of carbon fibres to exploit the full benefits of inert polymers in the composites. This will be discussed in detail in Chapter 3 which reviews the progress made on the surface modification of carbon fibres using plasma treatments. The effect of plasma treatments on the surface and bulk properties of carbon fibres as well as the interfacial behaviour between the treated fibres and various polymer matrices is presented.

The route chosen to manufacture UD carbon fibre reinforced PVDF was a wet powder impregnation method utilising a laboratory scale composite production line. This technique was chosen because of its simplicity and is an alternative to the melt impregnation method (used in the industry to produce for instance carbon fibre reinforced PEEK (APC2)) where viscous thermoplastics can cause severe damage to the fibres during processing [32, 33]. The key to uniform fibre/matrix content in composites is a homogenous dispersion of polymer powder within the impregnation step of the process. Continuous UD carbon fibre reinforced PVDF composite prepregs with a fibre volume fraction of 60 ± 2% were manufactured and the details are discussed in Chapter 4.

PVDF is inert, hydrophobic and lacks reactive groups. All of these attributes do not favour adhesion to carbon fibres. In order to improve the interaction between carbon fibres and PVDF, atmospheric plasma fluorination (APF) method was incorporated as mentioned previously [22, 29, 30] to modify the surface of carbon fibre by introducing fluorine moieties, decreasing the surface energy and improving the wettability between the treated fibres and PVDF. However, these improvements were demonstrated in detail only at single-fibre model composite level [22]. Therefore, APF treatment was integrated into the continuous manufacturing process of UD composite laminates and the mechanical properties of these composite laminates were studied on the macro scale level. This is described in Chapter 5 where the tensile, flexural, interlaminar shear and tear properties of UD carbon fibre reinforced PVDF laminates are discussed in detailed.

Modifying the fibres alone was shown to have a positive effect on both micro- and macro-mechanical performance of the carbon fibre reinforced PVDF composites. Furthermore, a study made previously by Tran et al. [18] showed that the interfacial shear strength between carbon fibres and PVDF can be improved as much as 184% by modifying the matrix with the addition of maleic anhydride (MAH) grafted PVDF. In Chapter 6, the effect of modifying both constituents is discussed. The results show that a clear synergy exists between APF fibres and matrix modifications on the micro-mechanical properties in single-fibre model composites. A significant improvement was also observed in the interlaminar shear strength of the composite laminates. This study was performed as a proof of concept that tailoring the fibre/matrix interface is possible and this can lead to better mechanical performance of the composite.

Finally, composite pipe structures were fabricated via filament winding. The composite pipe structures were made by winding continuous UD composite prepregs onto the outer surface of a pure PVDF pipe. The details are discussed in Chapter 7. This study was performed to understand the impact of APF treated carbon fibres on the overall mechanical properties of a composite structure fabricated.

The final part of the thesis covers the overall summary and conclusion of the research. This also includes suggestions for future work that could be carried out in order to exploit the full potential these materials can offer. The final goal of this work is to be able to present a composite that is not only inert, but relatively cheap and can provide high mechanical performance for the greater good of the composite community.

2.0 Performance of fibre reinforced inert polymer

Inert composites are defined as composites made with inert matrices where the matrix protects the reinforcing fibres when the composite is exposed to harsh environments such as elevated temperatures, moisture and chemical attack. Thermoplastic polymers, such as PEEK, PPS, PP, various fluoropolymers (PVDF, PTFE, etc.) and other polyolefins are considered as inert polymers because they are chemically inert and possess high mechanical strength at elevated temperatures. However, not all inert polymers are used for the production of composite materials. The main challenge exists in the compatibilisation issues between inert polymers and reinforcing fibres. Many attempts to overcome these issues have been addressed by researchers over the past decades. Surface treatments and polymer sizing of fibre surfaces are some of the approaches which have been shown to improve the interfacial adhesion between reinforcing fibres and inert matrices. In this chapter, the performance of inert composites is presented, which includes the thermal and chemical resistance, as well as the interfacial adhesion between carbon fibres and inert polymers. Furthermore, the effect of crystallinity on the interfacial adhesion is also discussed.

2.1 Introduction

A composite is defined as a combination of two or more chemically distinctive materials, having an engineering performance that exceeds of the individual components, with an explicit interface between the constituents. One of these constituents, the continuous phase, is called the matrix, which can be in the form of polymer, metal, ceramic or cement. Another constituent, the major role in any composite, is termed reinforcement, which can be in the form of fibres or particulates, added to the matrix in order to alter the matrix properties. The reinforcement may also be chemically treated or coated/sized in order to enhance the interfacial bonding between the reinforcement and the matrix and to improve wetting between the two constituents. However, when a composite is in service, it is the matrix that protects the reinforcement surface and has to resist environmental attack such as moisture, chemicals and elevated temperatures [34]. Thermoplastic polymer matrices offer the biggest advantage over other matrices when corrosion resistance is required in the composite [35]. A polymer is said to be inert when it does not react/dissolve/swell, etc. with any substances or when the speed of reaction is extremely slow. Thus when inert polymers are reinforced with fibres, composites which are not only inert, but possess excellent mechanical performance can be created.

Thermosets, such as epoxies cannot be considered inert as they are moisture sensitive [36]. However, not all thermoplastics are inert [37]. High performance thermoplastics, such as polyetheretherketone (PEEK) and polyphenylene sulphide (PPS), exhibit excellent chemical resistance, excellent toughness and have good load bearing properties in harsh environments and at elevated temperatures, making them very attractive to be used as matrices in fibre reinforced polymer composites [38]. Fluoropolymers such as polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE) also exhibit outstanding properties especially in aggressive environments, such as in HF and H_2SO_4 at high temperatures (280 – 450 °C). The excellent chemical and thermal stability of fluoropolymers is due to the strong C – F bonds ($E_B = 481$ kJ/mol) [39] making them attractive for applications where inert properties are required such as in oil fields, chemical processing, corrosion protection, etc.

Carbon fibres have significant advantages as compared to other reinforcing fibres owing to the great flexibility in the properties they can provide. Primary characteristics for reinforcing fibres in inert composites are high stiffness and strength, in which carbon fibres out-perform other reinforcements [40]. Furthermore, these properties should be unaffected in hostile environments such as elevated temperatures, exposure to solvents and fluids, and moisture which makes them chemically and mechanically favourable. Other reinforcing fibres such as boron, aramid and glass are also commonly used as reinforcement in composites with boron and aramid being not so widely used in oil and gas applications because of their high cost (boron) and low compression strength and susceptibility to moisture (aramid) as compared to carbon fibres [35]. Various types and compositions of glass fibres are also available on the market today. Glass fibres remain a strong competitor to carbon fibres for the oil and gas industry. Although the cost per weight or volume of glass fibres is lower than carbon fibres, chemical and galvanic corrosion resistance and electrical properties of carbon fibres are significantly better [41]. The intrinsic disadvantages of glass fibres such as thermal expansion, moisture pick-up and modulus properties will need engineering before it can compete against carbon fibres in composites [42]. This chapter reviews the current and potential usage of carbon fibres reinforced inert polymer composites for application in harsh situations, such as that in chemical processing plants, automotive, aerospace, oil and gas as well as other applications.

2.2 Thermal & chemical resistance of inert composites

Thermoplastics in general are tougher, more ductile and more damage resistant than thermosets. Thermoplastic composites allow for high production rates, because no curing step is involved. However, the thermal history which the polymer experienced during manufacturing can affect the crystallinity and performance of the thermoplastic composite. Furthermore, during service, these materials can be subjected to an array of environmental conditions. Most of which involve a combination of thermal and mechanical loading as well as ageing, degradation and plasticisation of the matrix. The effect and consequences of these environmental exposures are highly material dependent and, therefore, contribute to the overall inertness of the composite.

It has been reported that the fracture behaviour of high performance carbon fibre reinforced thermoplastics such as PEEK and PPS is dominated by the properties of the matrix, which affects both the stability of crack propagation and the magnitude of the measured fracture toughness. When a crack grows parallel to the laminate, the combination of the tough matrix and the strong fibre matrix interface governs the high fracture toughness. Both Gao et al. [43, 44] and Beehag [45] studied the effect of cooling rate and pressure on interlaminar fracture properties of CF/PEEK composites. It was found that there was a positive impact of increased cooling rate (up to 80°C/min) on G_{IC} and G_{IIC} interlaminar fracture toughens. This is attributed to the ductility of the matrix and the good fibre/ matrix interface bond, where both are matrix dependent and affected by matrix crystallinity. Although processing parameters such as temperatures and pressures are crucial, the conditions when the composite is in operation are also important; for example a study by Vieille et al. [46] on PPS laminates revealed the correlation between glass transition temperature (T_g) of PPS (~88-90 °C[*]) and the service temperature of the composite. Quasi-isotropic PPS laminates were mechanically tested at room temperature and at 120°C. A service temperature higher than the T_g seems to have little influence to both the tensile strength and stiffness for notched and un-notched laminates. However, it is detrimental to the compressive, flexural and interlaminar shear properties. Work by Berger et al. [47] suggested that although Mode II interlaminar fracture toughness of CF/PEEK is lowered at elevated temperature, by increasing the loading speed during the test, as much as 25% fracture energy can be recovered.

The effect of hot/ wet conditioning on carbon fibre reinforced thermoplastics has been the focus of many researchers over the years. It was found that CF/PEEK composite absorbs only about 0.21% moisture when exposed to steam for 400 h [48]. Tensile, compression and fatigue properties of CF/PEEK composites conditioned at 23°C, 70°C and 100°C deionised water were tested and it was found that water and temperature had no influence on the mechanical properties [49]. When Zhang et al. [50] did similar studies using CF/PEEK conditioned at 95°C in brine, no statistical differences in compressive properties was reported. However when Hine et al. [51] tested CF/PEEK conditioned at 100°C, they found that this condition in fact led to ~50%

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[*] *Material data. Link in: http://www.matweb.com/search/DataSheet.aspx?MatGUID=f277b224f135406caa973d38d49104ca&ckck=1. Assessed on 13 March 2012*

increase of G_{IC} and G_{IIC} properties, which is due to enhanced resistance to crack growth from large bundles of fibres which became detached from the surface of the crack as well as large amount of fibre breakage observed from SEM analysis of the specimen.

During the service life of the composite material, they are not only restricted to exposure to heat and water. Mahieux et al. [52] investigated the water and oil absorption of CF/PEEK, CF/PPS and CF/PFA composites at various temperatures (25-80 °C). It was observed that CF/PFA composite did not show any water absorption, while CF/PEEK and CF/PPS composites showed moisture uptake of about 0.2% at 80 °C. In addition, when the composites were exposed to industrial oil (VG 46) at 80°C for 2 months, only CF/PEEK resulted in an uptake of about 0.6%. Under the same exposure, the T_g of CF/PFA was reduced by 30 °C from 300 °C, independent of the oil temperature, while the T_g of other composites remained unaffected. The authors commented that this degradation in glass transition of CF/PFA is due to exposure to the industrial oil because there were no decreased in T_g observed when the same test was performed in water. Cogswell [53] in his book discussed the effect of various environments of which CF/PEEK is exposed to on the absorption and mechanical properties of the composite. It was reported that CF/PEEK picks up 4.5% methylene chloride after the composite was exposed to it at 23 °C for 17 months and the transverse tensile strength and modulus of the composite were reduced by 10%. Similarly, CF/PEEK took up 2.4% of paint stripper, which resulted in a reduction of 10% in the open hole tensile and compression properties. When CF/PEEK was exposed to hydraulic fluids for 17 months 0.8% uptake was reported. However, no significant decrease in the open-hole tension and compression properties was observed. Cogswell also reported that the uptake of jet oil by CF/PEEK was 0.85% when the composite was exposed to the chemical at 82 °C for 10 weeks. Although the pick-up was low, the ±45° tensile strength reduced by 10% at 82 °C and 60% at 121 °C. All the studies conducted however did not show any influence on the flexural properties of CF/PEEK. Unfortunately, there is no literature on the thermal and chemical resistance of other carbon fibre reinforced fluoropolymer composites yet. Further reading on the thermal and chemical resistance of pure fluoropolymers can be found in Ref. [39].

2.3 Polymer crystallinity in inert composites

The physical and mechanical properties of semi-crystalline thermoplastic composites depend greatly on the crystal structure of the polymer and its processing history (thermal history of melting and cooling during the manufacturing/fabrication process) [54, 55]. Low crystallinity polymers have high elongation and higher toughness properties but the interfacial bonding to reinforcement is compromised. In contrast, when high crystallinity polymers were used as matrix, the stiffness, chemical resistance and thermal stability of the resulting composite can be enhanced [56]. The degree of crystallinity, X_c in inert polymers is an important area of study as it provides an understanding of the chemical resistance of the polymer. The packing and arrangement of the polymer chains lead to formation of crystals and these results in better chemical resistance. The incorporation of carbon fibres into semi-crystalline polymer matrices promotes nucleation and crystallite growth perpendicular to the fibre axis, which ultimately has an impact in the fibre/matrix adhesion property [57]. The crystal development within semi-crystalline polymer composites is influenced by fibre length, type and content [58].

Sarasua et al. [58] studied the effect of crystallinity on short CF reinforced PEEK produced during cooling in the mould. The crystallinity of both neat PEEK and short CF/PEEK composites was found to be highest (X_c~30%) if the mould temperature was higher than the glass transition temperature (T_g) of PEEK (T_g = 143-148 °C[†]) [58]. This crystallinity was not influenced by annealing the composites at 200 °C and 300 °C nor by the type, length or amount of fibres present in the composite and it is comparable to the crystallinity of AS4/PEEK composites widely known as APC2 (~32%) [59-61]. However, at mould temperatures lower than T_g of PEEK, the crystallinity of the short fibre reinforced PEEK composites containing 10 wt% fibres was found to be (X_c = 18%), which was higher than that of neat PEEK (X_c = 9%). The crystallinity of the short fibre composites also increased with decreasing fibre length. The authors commented that short fibres are able to nucleate crystallization better than longer fibres under certain thermal conditions and therefore increase the crystallinity of the short fibre composites.

[†] *Material data. Link in: http://www.matweb.com/search/DataSheet.aspx?MatGUID=2164cacabcde4391a596640d553b2ebe. Assessed on 13 March 2012.*

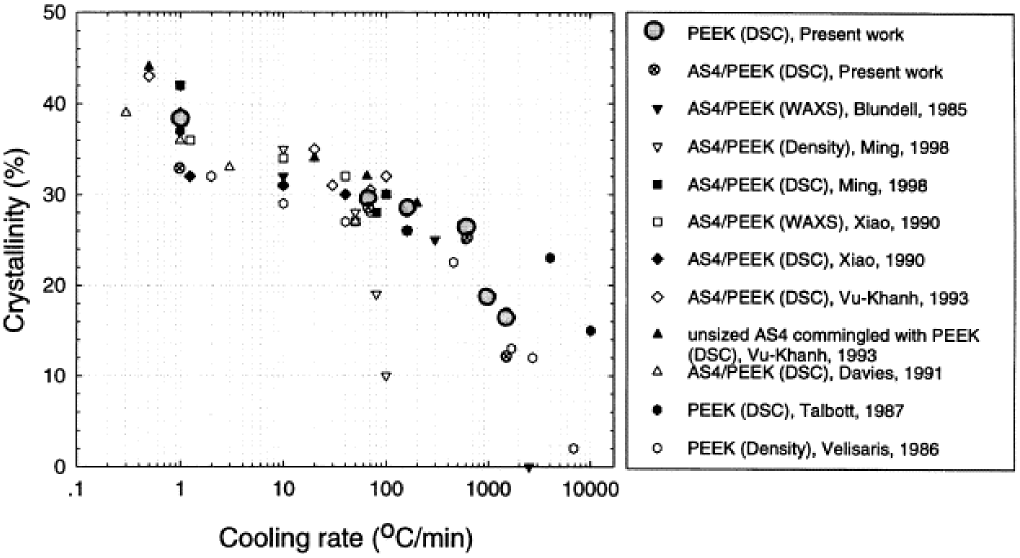


Figure 2.1 Degree of crystallinity as a function of cooling rate for PEEK polymer and CF/PEEK composites [43]

The effect of cooling rate on the crystallinity of CF reinforced PEEK has been studied extensively [43, 55, 62-65]. Figure 2.1 shows clearly a trend of higher degree of crystallinity of both neat PEEK and carbon fibre reinforced PEEK composite if lower cooling rates were used. This phenomenon can be explained by the formation of better defined, denser and larger spherulites (Fig 2.2). However, at higher cooling rates, the ability of crystals forming is limited as the mobility of the polymer chains is reduced by the rapid cooling and, which therefore, results in a lower degree of crystallinity [43, 66].

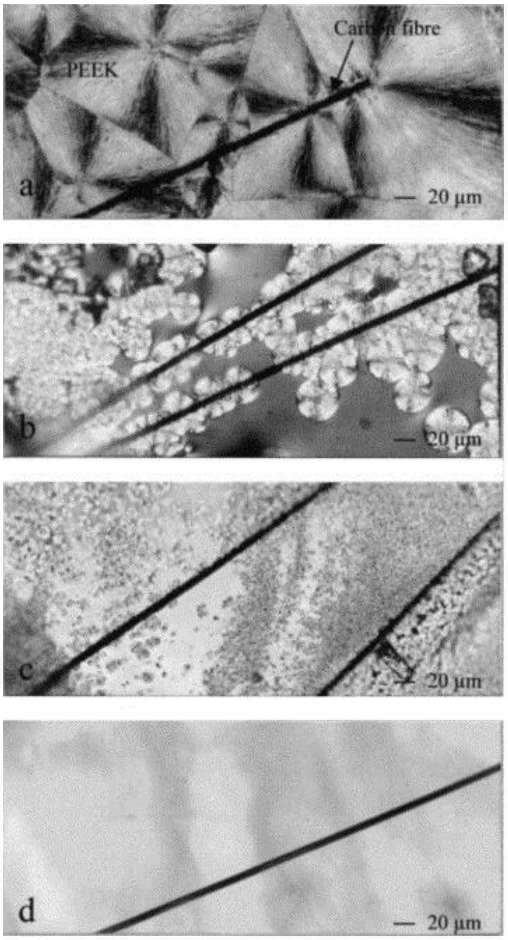


Figure 2.2 PEEK matrix morphologies around a carbon fibre at cooling rates of (a) 1 °/min; (b) 200 °/min; (c) 1000 °/min; and (d) 2000 °/min [43]

Desio et al. [67] studied the crystallization behaviour of unreinforced and various carbon fibre reinforced poly (phenylene sulphide) (PPS) composites. Four different types of carbon fibre reinforced PPS composites were studied which were unsized AS4, sized AS4, graphitized Thornel T300 reinforced PPS composites and a carbon fibre reinforced PPS prepreg from Phillips Petroleum (Fig. 2.3). It was reported that the rate of crystallization of PPS increases for the carbon fibre reinforced PPS composites as compared to unreinforced PPS. This effect is due the presence of carbon fibres which provides heterogeneous nucleating sites (formation of transcrystallites on the fibre surface) thus increasing the crystallization rate [67, 68]. Despite the increase in the rate of crystallisation, the degree of crystalinity of the composites decreased as compared to unreinforced PPS. The authors hypothesised that this is because of trapped impurities (from composite manufacturing) and imperfection produced in the growing crystals during rapid crystallisation. It was found that the crystallization rate of both graphitized Thornel and sized AS4 carbon fibre reinforced PPS composite was independent of the fibre content. The degree of crystallinity however shows that it is constant with fibre loading up to 30-50 wt%, after which the degree of crystallinity decreased with increasing fibre content. The reason for this decline is explained by the small inter-fibre space present which hinders the growth of the crystallites [67].

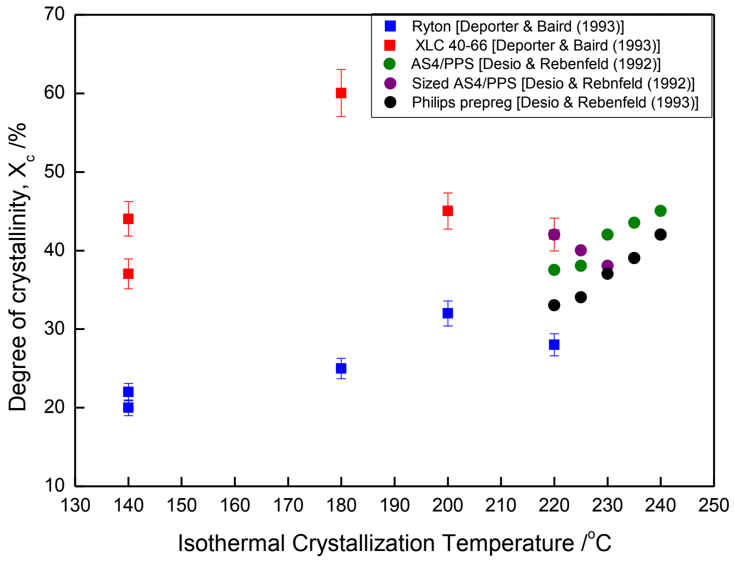


Figure 2.3 Degree of crystallinity, X_c as a function of isothermal crystallization temperature of various CF/PPS composites (Redrawn from Ref. [55, 56])

The effect of isothermal and non-isothermal crystallization on carbon fibre reinforced PPS was studied by Deporter and Baird [66]. The degree of crystallinity reached a maximum of 32% when the crystallisation temperature was increased from 140 °C to 200°C, but at temperatures exceeding 200 °C, the X_c decreased again (Fig. 2.3). The authors explained that this is due to both nucleation-controlled and diffusion-controlled crystallization. At higher crystallisation temperatures, the activation energy in the polymer to form nuclei is low, thus the number of nuclei formed is lower. At lower crystallisation temperatures the mobility of the polymer chain is hindered by the increased viscosity of the polymer melt which results in a decrease of the degree of crystallinity of the matrix. Therefore, for isothermal crystallisation process, the degree of crystallinity of the PPS matrix in composites reaches a maximum at an intermediate temperature (in the case of PPS, it was found to be 180 °C) as a result of balancing the two phenomena mentioned previously.

The effect of carbon fibre loading on crystallinity of short unsized AS4 carbon fibre reinforced polyvinylidene fluoride (PVDF) composites was studied by Ho et al. [69]. It was found that at loading fractions of 5 wt% and 10 wt% of unsized AS4 carbon fibres, the crystallinity of CF/PVDF increased to 45.1% and 47.6%, respectively, as compared to 42.5% of pure PVDF polymer produced using the same processing conditions. However, at carbon fibre loading of 15 wt%, the crystallinity of the composite reduced drastically to 37.4%. The authors commented that the presence of more carbon fibres in PVDF impeded the mobility of the polymer chains and hence reduced the crystallinity. A similar observation was made for short carbon fibre reinforced polypropylene (PP) and PP blended with maleic anhydride grafted PP by Karsli and Aytac [70]; the degree of crystallinity of the PP matrix decreased with increasing carbon fibre content. However, in unidirectional carbon fibre reinforced PVDF, the crystallinity of the PVDF matrix decreased and does not depend on fibre surface treatment [71, 72].

2.4 Interfacial adhesion between carbon fibres and inert polymers

The mechanical performance of composites does not only depend on the intrinsic properties of the constituents but it is determined by the interfacial interaction between fibres and matrix. Adhesion between the fibres and the polymer matrix determines stress transfer and, therefore, enhances the tolerance of a composite to carry external loads. In semi-crystalline thermoplastic composites, the interfacial interactions between carbon fibre and matrix are influenced by various factors, such as, thermal and residual stresses and presence of surface reactive functionalities [43, 73]. The practical adhesion is characterised by the interfacial shear strength (τ_{IFSS}) between the fibres and the matrix. τ_{IFSS} can be determined using various tests, such as single fibre fragmentation [74-76], single fibre pull out [77-79] and single fibre push out [80].

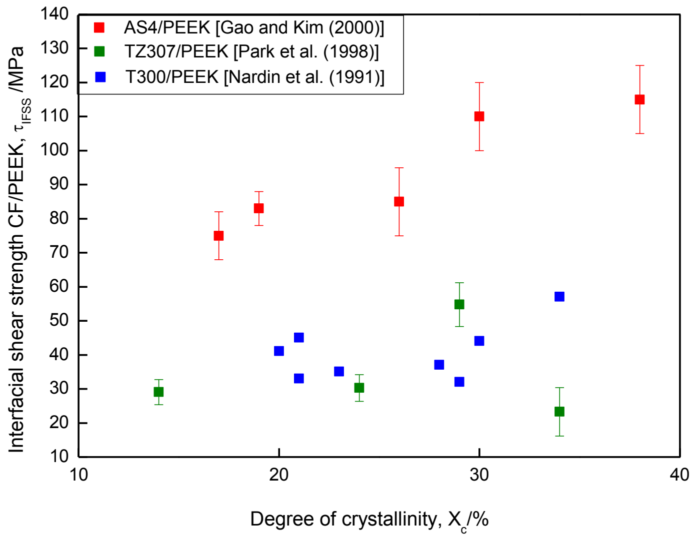


Figure 2.4 Interfacial shear strength as a function of degree of crystallinity of PEEK matrix in CF/PEEK (Redrawn from Ref [43, 63, 81])

It was reported that τ_{IFSS} between CF and PEEK is directly proportional to the degree of crystallinity of PEEK (Fig. 2.4). Gao and Kim [43] reported that τ_{IFSS} between carbon fibres and PEEK is maximal at 38% degree crystallisation of PEEK. Similarly, Park et al. [63] and Nardin et al. [81-83] also reported an improved τ_{IFSS} between carbon fibres and PEEK at higher X_c (Fig. 2.4). These results show that the degree of crystallisation does affect the interfacial adhesion between carbon fibres and PEEK. This is mainly due to the presence of crystals formed within the matrix.

Li [84] studied the influence of ozone and air oxidation of fibres on τ_{IFSS} of carbon fibre/PEEK composites. His study shows that τ_{IFSS} increased with the degree of surface treatment of the fibre surface (Table 2.1). It was found that τ_{IFSS} between high strength carbon fibres and PEEK is enhanced by 60% when the carbon fibres were treated under ozone treatment for 3 min [84]. This improvement is mainly due to the presence of carboxyl functional groups such as C−O and O−C=O on the fibre surface as was evident from X-ray photoelectron spectroscopy (XPS). This strong interfacial adhesion leads to better stress transfer between the matrix and fibre. Similar results were also reported by Nardin et al. [81]. They reported that τ_{IFSS} between oxidised and sized T300 carbon fibres and PEEK was improved by 95% and 68%, respectively, as compared to 37 MPa for as-received T300/PEEK. Zou and Netravali [85] reported that τ_{IFSS} between the AS4 carbon fibres and PEEK was improved by 85% as compared to untreated AS4 and PEEK by treating AS4 fibres in ethylene/ammonia low pressure plasma (mixtures of 1:1 ratio). The enhancement is mainly due to the increased polar nature of the carbon fibres due to the incorporation of amines, carbonyl, ether and hydroxyl while increases the surface energy of the fibre surface. Lamorinière [86] studied the effect of sized T700 and de-sized T700 fibres on the τ_{IFSS} to PEEK. He reported an increase of 100% in τ_{IFSS} between de-sized T700 fibres and PEEK as compared to τ_{IFSS} of sized T700 and PEEK (Table 2.1). This shows that the epoxy sizing on the fibre surface is detrimental to provide a strong fibre/thermoplastic interface.

Table 2.1 Interfacial shear strength (IFSS) of as-received CF and modified CF and PEEK

Composite type	***CF treatment***	***IFSS / MPa***	***Remarks***	***REF***
TZ307/PEEK	As-received	19.6 ± 4.0	Cooling time of 48 min from 250°C	[63]
TZ307/PEEK	As-received	54.7 ± 6.4	Cooling time of 16 min from 260°C	[63]
HS CF/PEEK	As-received	35.0 ± 2.0	-	[84]
HS CF/PEEK	Air oxidised	47.0 ± 2.5	-	[84]
HS CF/PEEK	Ozone treatment	56.0 ± 3.0	-	[84]
T300/PEEK	As-received	37.0	-	[81]
T300/PEEK	Oxidised	72.0	-	[81]
T300/PEEK	Sized	62.0	-	[81]
AS4/PEEK	As-received	45.0		[85]
AS4/PEEK	C_2H_4-NH_3 Plasma	92.2	50% volume fraction of NH_3	[85]
AS4/PEEK	C_2H_4-NH_3 Plasma	90.8	75% volume fraction of NH_3	[85]
AS4/PEEK	As-received	69.0 ± 9.0	-	[86]
T700SC 60E/PEEK	As-received/sized	21.0 ± 1.5	-	[86]
T700/PEEK	De-sized	41.0 ± 10.0	-	[86]

Only one paper was found on the τ_{IFSS} between carbon fibres and PP. Fu et al. [87] reported that the τ_{IFSS} between HTA 5331 (TENAX) and PP was found to be 18 MPa. In addition, a summary of τ_{IFSS} of various carbon fibre reinforced PPS can be found in Table 2.2. Meretz et al. [88] and Ramanathan et al. [89] investigated the effect of crystallinity on the fracture behaviour and the interfacial strength between carbon fibre and PPS. Both high modulus and high strength carbon fibres were used in the study. The results from the two studies were found to be similar. τ_{IFSS} between carbon fibres and PPS were influenced by the morphology or crystallinity of PPS at the interface region [73, 88, 89].

Table 2.2 Interfacial shear strength (IFSS) of as-received and modified CF/PP and CF/PPS

Composite type	***CF treatment***	***IFSS / MPa***	***Remarks***	***REF***
HTA5331/PP	As-received	18.0	-	[87]
HM48.00A/PPS	As-received	31.3 ± 5.2	Quenched in water from T_m of PPS	[89]
HM48.00A/PPS	As-received	16.7 ± 5.0	Slow cooling to RT from T_m of PPS	[89]
HM48.00A/PPS	Industrially modified	55.5 ± 8.4	Quenched in water from T_m of PPS	[89]
HM48.00A/PPS	Industrially modified	48.5 ± 16.3	Slow cooling to RT from T_m of PPS	[89]
C320.00A/PPS	As-received	37.3 ± 5.5	Quenched in water from T_m of PPS	[89]
C320.00A/PPS	As-received	53.1 ± 10.4	Slow cooling to RT from T_m of PPS	[89]
C320.00A/PPS	Industrially modified	46.7 ± 5.7	Quenched in water from T_m of PPS	[89]
C320.00A/PPS	Industrially modified	36.6 ± 2.1	Slow cooling to from T_m of PPS	[89]
M40/PPS	As-received	18.3 ± 4.2	-	[90]
M40/PPS	O_2 Plasma	18.3 ± 4.2	Plasma conditions: 50 W for 30 min	[90]
M40/PPS	Ar Plasma	18.3 ± 4.2	Plasma conditions: 50 W for 30 min	[90]
T300/PPS	As-received	33.1 ± 7.7	-	[91]
T300/PPS	Styrene Plasma	43.5 ± 6.5	Plasma conditions: 5 W for 10 min	[91]
T700/PPS	As-received	35.0 ± 13.0	Cooling from 320°C at 20°C/min	[88]
T700/PPS	As-received	36.0 ± 6.0	Cooling from 320°C at 1°C/min	[88]
T700/PPS	As-received	39.0 ± 14.0	At transcrystallinity	[88]

When single fibre model composites were subjected to isothermal crystallisation process, τ_{IFSS} between the fibre and PPS matrix increased. The results show that τ_{IFSS} values obtained were dependent on the embedded length which indicates brittle failure. Ramanathan et al. [89] hypothesised that the brittle failure was due to the increased degree of crystallinity at the fibre/matrix interface [43, 89]. Ductile failure behaviour was found when the specimens were prepared by quenching in water or slow cooling, which shows that ductile interface was observed at lower degree of crystallinity of the polymer. τ_{IFSS} of high modulus HM48.000A carbon fibre/PPS model composite was found to increase with fibre surface modification by thermal oxidation [89]. The result is in agreement to the study performed by Yuan et al. [90] who measured τ_{IFSS} between high modulus M40 (Toray) carbon fibre/PPS which was increased by 33.6% and 67.5% when the fibre was subjected to oxygen and argon plasma treatment, respectively (Table 2.2). The effect of various annealing procedures on the τ_{IFSS} of high modulus and high strength carbon fibre/PPS model composites were studied by Meretz et al. [88]. It was reported that the high modulus carbon fibres act as nucleating agent. Therefore, the crystallinity of the bulk matrix increased which resulted in brittle failure behaviour at the interface as reported by Gao and Kim [43] and Ramanathan et al. [89]. High strength carbon fibres had very high τ_{IFSS} of up to 80 MPa [88] while exhibiting ductile fracture behaviour during the single fibre pull out test. The authors hypothesised that this is due to the nature of the high strength fibre not having a high density of nucleation sites hence could not form a crystalline later at the interphase.

Compared to other inert thermoplastics, the adhesion between carbon fibres and fluoropolymers is generally poor due to the inert nature and lack of reactive groups in the matrix. For example, τ_{IFSS} between carbon fibres and PVDF was found to be only about 10 MPa [71, 92]. Similarly, τ_{IFSS} between carbon fibre and PTFE was found to be about 10.7 MPa [93]. Therefore, in order to improve the interfacial adhesion between the constituents, different surface treatments of carbon fibres and blending maleic anhydride grafted PVDF (MAH-g-PVDF) to neat PVDF have been studied. Bismarck and Schulz [20] and Ho et al. [94] studied the effect of direct fluorination of carbon fibres on the interfacial adhesion to various fluoropolymer matrices. It was reported that τ_{IFSS} between fluorinated C320.00A carbon fibres and PVDF reaches a maximum of 35 MPa at carbon fibre surface F/C content of 0.8 [20]. No further improvement was found beyond this F/C content. The authors hypothesised that the reason for the improved interfacial adhesion of fluorinated fibres at F/C content of 0.8 could be due to the physical compatibilisation between the fluorinated fibres and PVDF as the F/C content of PVDF was found to also be ~0.85. Ho et al. [94] studied the effect of fluorination of T300 carbon fibres on the τ_{IFSS} to polyvinylidene fluoride (PVDF), ethylene-chlorotrifluoroethylene (ECTFE), fluorinated ethylene propylene copolymer (FEP) and tetrafluoroethylene-perfluoro alkoxy vinyl ether copolymer (PFA) was reported (Table 2.3). τ_{IFSS} between fluorinated T300 fibres and all the fluoropolymers studied also reaches an optimum value 24-27 MPa at intermediate degrees of fibre surface fluorination (F/C content of ~ 0.1-0.2) except for T300/PFA which improved up to 128% to 18.7 MPa at F/C content of 0.2. This shows that interfacial adhesion between fluorinated fibres and fluropolymers depends on the degree of fluorination of both fibres as well as the matrix used for optimum compatibility.

Table 2.3 Interfacial shear strength (IFSS) of as-received and modified CF/Fluoropolymer composites

Composite type	***CF treatment***	***IFSS / MPa***	***Remarks***	***REF***
T300/PVDF	As-received	10.2	-	[21]
T300/PVDF	Direct fluorination	27.7	With F/C ratio of 0.1	[21]
T300/ETCFE	As-received	18.4	-	[21]
T300/ETCFE	Direct fluorination	27.74	With F/C ratio of 0.2	[21]
T300/PFA	As-received	8.2	-	[21]
T300/PFA	Direct fluorination	18.7	With F/C ratio of 0.2	[21]
T300/FEP	As-received	14.9	-	[21]
T300/FEP	Direct fluorination	23.5	With F/C ratio of 0.2	[21]
C320.00A/PVDF	As-received	27.7 ± 1.7	-	[20]
C320.00A/PVDF	Direct fluorination	34.9 ± 2.9	With F/C ratio of 0.8	[20]
AS4GP/PVDF	As-received	17.5 ± 2.0	-	[18]
T700/PVDF	As-received	10.2	-	[22]
T700/PVDF	Plasma fluorination	16.0	With 1.1 at.-% of F on CF surface	[22]
AS4/PVDF	As-received	10.8 ± 0.4	-	[92]
AS4/PVDF	Plasma fluorination	14.5 ± 1.2	With 2.8 at.-% of F on CF surface	[92]
CF/PTFE	As-received	10.7	-	[93]
CF/PTFE	PTFE coated	29.7	PFTE coated through plasma chemical deposition	[93]

Apart from direct fluorination, atmospheric plasma fluorination (APF) was developed by Ho et al. [95]. This was found to be an effective method of introducing a small concentration of fluorine moieties onto carbon fibre surface to improve compatibility to PVDF matrix in a continuous process. It was reported that τ_{IFSS} between APF treated T700 carbon fibres and PVDF increased by 56% from 10.2 MPa to 16.0 MPa after exposing the fibres to APF for 1 min only [71]. The fluorine content on the fibre was found to be only 1.1 at.-% by XPS analysis. Shelestova et al. [93] studied the effect of plasma chemical deposition of a PTFE-like polymer onto carbon fibres and the adhesion behaviour towards PTFE matrix. The authors reported that the τ_{IFSS} improved 178% from 10.7 MPa for untreated carbon fibre reinforced PTFE composite to 29.7 MPa for the PTFE coated carbon fibre reinforced PTFE composite. This improvement was due to the compatibilisation of the fibre surface to the surrounding matrix.

The interfacial interaction between carbon fibres and PVDF was also studied by using various blends of maleic anhydride grafted PVDF (MAH-g-PVDF) [18, 92]. It was found that AS4 GP carbon fibre exhibited the highest τ_{IFSS} with MAH-g-PVDF as the interfacial adhesion between the fibre and this matrix was reported to increase 155% as compared to AS4-GP in unmodified PVDF [18]. However AS4-GP is a sized carbon fibre, which is compatibilised to commercially available epoxy based thermosets.

2.5 Summary

The demand for composite materials to be used in high-end applications has been increasing over many years due to its remarkable intrinsic properties such as light weight, high strength and stiffness to weight ratio, and the tailorability of fibre reinforcement along load paths to achieve excellent performance of the composites. However, not all composites perform well in harsh environments, such as high temperature or to chemicals and moisture. Inertness of composites is an attribute governed by the matrix material. Hence, polymer and ceramic matrices are considered more inert compared to metal matrix composites. But when high performance composites are considered, all the attention is turned to carbon fibre reinforced polymers. This review focused on carbon fibre reinforced high performance semi-crystalline thermoplastic polymers, such as PEEK, PPS, PVDF, PTFE, FEP, ECTFE, FEP and PP. The mechanical properties of fibre reinforced polymers can be influenced by the degree of crystallinity, size of spherullites and the crystallinity around fibres. The intimate contact between fibres and the surrounding polymer matrix is also vital to boost the mechanical performance of composites. This is mainly because when load is applied to composite, it is transferred from fibres to matrix through the interface. The interfacial adhesion at the fibre/matrix interface can be enhanced through various means such as surface modifications and heat treatment. The improvement made at micro-scale of the composite can be translated to macro-mechanical properties. This has been shown by the improvement on the interface dominated mechanical properties such as transverse tensile and flexural properties of the composite as a direct result of improvement in the interfacial shear strength.

3.0 Plasma Treatment of Carbon Fibres: Effect on Fibre Properties, Adhesion and Composite Performance

Surface modification of carbon fibres is necessary to improve interfacial adhesion between carbon fibre and matrix. Plasma treatment of carbon fibres has attracted much interest as a means to tailor the adhesion of the constituents in high performance composites. Through plasma treatment, the surface energy of carbon fibres can be altered, which determines the wettability between the plasma treated fibres and polymer matrices. This chapter reviews current progress on the surface treatment of carbon fibres in low pressure and atmospheric pressure plasmas. In this chapter the effect of both plasma treatments on the surface and bulk properties of the fibres; namely surface morphology, surface composition, fibre wettability and surface free energies, carbon graphitic order and the fibre tensile properties are discussed. The micro- and macro-mechanical performance of composites containing plasma treated carbon fibres is also presented. Comparisons of both surface and bulk characterisations of the fibres are drawn between low and atmospheric pressure plasma treatments. This chapter also highlights the suitability of continuous atmospheric plasma treatment of carbon fibres to tailor the fibre-matrix interface during composite manufacturing.

3.1 Introduction

Advanced fibre reinforced polymer composite materials are often used in load-bearing and structural applications nowadays due to their high strength, high modulus and low density (1.55 g cm^{-3}). These composites consist of a continuous matrix phase, a reinforcing phase and an interface/interphase between the two constituents. The matrix protects the fibres, holds them in place (in the desired alignment) and determines the chemical and thermal resistance of the composite while the reinforcing phase, i.e. the fibres, carries the majority of load acting in the fibre direction [13, 96]. The overall performance of composite materials does not only depend intrinsically on the properties, alignment and orientation of the fibres and properties of the matrix but also on the adhesion at the fibre/matrix interface. Adequate adhesion allows for sufficient stress to be transferred from the matrix through the interface to the reinforcing fibres when load is applied. The easiest way to quantify adhesion is to determine the thermodynamic work of adhesion W_A (Eq. 2.1) by measuring the contact angle θ of a (pre-) polymer wetting the fibres and knowing (or measuring) the liquid surface tension γ_{la} [96].

$$W_A = \gamma_{la}(1 + cos\theta) \tag{3.1}$$

Sufficient adhesion between fibres and matrix can be achieved when hydrogen and covalent bonds form between the fibre surface functionalities and the matrix and/or through mechanical interlocking [97-99]. Untreated carbon fibres are known to be microporous and generally have imperfect graphite crystalline structure along the fibre axis [100, 101]. Untreated carbon fibres also are chemically inert, therefore, difficult to bond to the matrix [98, 101, 102]. In order to enhance the fibre-matrix interfacial bonding, carbon fibres that are available on the market are always surface treated and often also sized. To guarantee an optimum adhesion between carbon fibres and thermosets, commercially available carbon fibres are modified by electrochemical surface oxidation (using NH_4HCO_3 or K_2CO_3/KOH or KNO_3 as electrolytes) [103-106] and sized [101, 107-111].

The majority of the market is dominated by thermosetting matrices because of the low viscosity of thermoset systems, making them easy to process and form into any shape. The processing advantages as well as the market's demand require commercially available carbon fibres generally engineered to be compatible with thermosetting resins. Nevertheless, the application of thermoplastic as matrix should not be ignored in order to exploit the full advantages that these matrices can offer for the composite industry. Thermoplastic materials are tough and offer enhanced impact and abrasion properties, enhanced moisture and corrosion resistance, unlimited shelf life, clean processing with no exothermic reactions, they do not emit volatile organic vapours, are recyclable and can be processed using one-step moulding as compared to thermosetting composites. However, the problem associated with thermoplastic matrix systems is often the poor adhesion between carbon fibres and thermoplastics. Therefore, various surface treatments of carbon fibres are employed to improve the interfacial adhesion between fibres and matrix. Further oxidation of carbon fibres in dry environment (using O_2 or O_3) [100, 112], wet (HNO_3) [100] or electrochemical (using HNO_3, $KMnO_4$, H_2SO_4, NaOH) oxidation [100] and other post-surface treatments such as electrocoating (PMMA, MPD) [113, 114], plasma (air, O_2, N_2, He, Ar, CF_4, $CHClF_2$) [22, 29, 30, 40, 115-118], plasma polymerization ($C_3H_5NH_2$, $C_4H_8O_2$, C_8H_{10}, $C_3H_4O_2$, $C_6H_{18}OSi_2$, $C_4H_2O_3$, $C_7H_6O_2$) [100, 119-123] and plasma enhanced chemical vapour deposition (CH_4, C_3H_8, C_6H_6) [100, 124], deposition of active form of pyrolytic carbon or carbon nanotubes [125, 126] and polymer grafting on the fibre surface [127], have been explored to improve the interaction between thermoplastic matrices and the reinforcing fibres. However, compared to most carbon fibre surface modifications, plasma treatments of carbon fibres offer many advantages [97-99]; they are:

- dry, clean and environmental friendly compared to wet oxidation process.
- efficient in altering the chemistry of materials without affecting the bulk properties of the material and, therefore, allow tailoring of the surface properties of materials.
- versatile because many feed gases can be used to introduce various active functional groups or plasma polymer layers that are chemically bonded onto the fibre surface.

Although low pressure plasma (LPP) treatments are the more established route for surface modification of carbon fibres, they have a low-productivity due to the use of sealed vacuum chambers allowing often only for batch treatments [29, 128]. Atmospheric pressure plasma (APP) treatment, however, is more adaptable for continuous in-line modification because it can be operated without the need for complex vacuum systems [29, 128]. In addition to the ability for continuous processing, APP also allows sustainable plasma glow discharge using various feed gases which is important for any continuous treatment [29, 129]. Bismarck et al. [130], Park et al. [131], Erden et al. [132] and Ho et al. [29] have demonstrated that the surface free energy of carbon fibres can be increased using both LPP and APP treatments. Such increased in fibre surface energy led to enhanced interface between the plasma treated fibres and polymer matrices, which results in better composites performance [40, 97, 131]. In this chapter, the focus is on surface treatment of carbon fibres using plasma treatment to enhance the compatibility between the fibres and polymer matrices. The impact of both APP and LPP on surface and bulk fibre properties is discussed.

3.2 Plasma surface treatments of carbon fibres

Plasma, also known as the fourth state of matter, is a partially or fully ionised gas medium consisting of positively charged ions and electrons [99, 133]. The accelerated atoms in the plasma stream cause the valence electrons to be freed as a result of atomic collision and generate free radicals [40, 99]. Although scientists have utilised plasma technology in materials science since the 1960s, it was not applied to carbon fibres until the mid-80s [134, 135]. The main aim of plasma treatments of carbon fibres is to modify the surface chemistry and morphology without affecting the bulk properties of the fibres. Plasma treatments remove amorphous carboneous materials from the surface of carbon fibres via sputtering and etching [97]. This roughens the surface of the fibre, allowing for better mechanical interlocking between the fibres and the matrix, as well as increasing the fibre surface area [97].

Carbon fibre surfaces have also been modified using plasma polymerisation, which is a technique popular among researchers for tailoring the surface functionalities of carbon fibres by grafting polymers onto the fibre surface [99]. The advantages associated with plasma polymerisation include low operating temperature, it is solvent-free and, therefore, less expensive to operate. In addition to this, plasma polymerisation has the ability to deposit ultra-thin films of controlled composition on fibre surfaces [120, 121, 136]. This method has been extensively studied to improve the interfacial adhesion between carbon fibres and thermosetting matrices [119-122, 136]. However, this chapter reviews current progress in plasma oxidation, fluorination and etching of carbon fibres. For plasma polymerisation of carbon fibres, the readers can refer to reviews by Jones [111] and Liston et al. [99].

Both LPP and APP treatments of carbon fibres are used to modify the surface chemistry of the fibres via the implantation of covalent C-F_x functional groups or active polar functional groups such as hydroxyl, carboxyl, carbonyl etc. This creates new surface functional groups and alters the surface energy of the treated fibres, which then allows for better chemical interaction between the plasma treated carbon fibres and polymer matrices [40, 97, 131]. The most notable flexibility of plasma treatments of carbon fibres is the ability to use a diverse range of feed gases to produce the desired surface properties. The type of feed gas used determines the final characteristics of the treated fibre surface. LPP and APP oxidation have been used for surface treatment of carbon fibres due to its simplicity and effectiveness of introducing oxygen-based functional groups on carbon fibre surfaces. Both oxygen and air plasmas are capable of incorporating various reactive and non-reactive surface oxides onto the surface of carbon fibres [40, 97, 132, 137-139]. Kusano et al. [140] reported that plasma treatment of PAN-based HTA5001 (Tenax) carbon fibres using helium as feed gas showed significant increase in the oxygen functional groups of carbon fibres after a treatment time of just one second. It was reported that using inert gases such as Ar or He as plasma gases generates radicals on the fibre surface which are very reactive and when exposed to air, surface oxygen functional groups were formed on the treated carbon fibre [100]. As a result of this treatment, the hydrophilicity of the carbon fibres increased, which led to improved adhesion between the treated carbon fibres and an epoxy matrix. Double cantilever beam (DCB) tests showed that the fracture energy of the plasma treated carbon fibre reinforced composites increased by 18% when compared to as-received carbon fibre reinforced composites [140]. Jang [117] observed surface etching of PAN-based AU4 (Hercules) carbon fibres after exposure to argon plasma. The degree of surface etching by argon was found to be similar to that of carbon fibres after oxygen plasma treatment as observed under SEM. After 20 min of argon LPP treatment of AU4 carbon fibres, the atomic concentration of oxygen on the surface of the fibre increased from 10.5% for as-received fibres to only 17.9% as compared to 27.5% when treated in LP oxygen plasma. However, the author showed that the transverse tensile strength of both argon and oxygen plasma treated carbon fibre reinforced bismaleimide (BMI) composites almost doubled.

Using different plasma feed gases allows the surface properties of plasma treated carbon fibres to be tailored [131]. Park et al. [131] reported that the hydrophilicity as measured by a significant drop in the water contact angle of PAN-based TZ-307 (Taekwang) carbon was significantly enhanced when treated in AP helium/oxygen plasma. The surface free energy of plasma treated carbon fibres improved tremendously (by up to 50%). The increase in the surface free energy of the treated fibres can be explained by the incorporation of oxygen functional groups into the carbon fibre surfaces. Nitrogen plasma treatment of PAN-based T700 (Toray) and TSX-111 (Jilin Carbon) carbon fibres led to the formation of various amines, namely $-CNH_2$, $R_2C{=}NR$ and $-C{=}NH$, on the fibre surfaces which results in a less acidic surface character [29, 141]. Streaming ζ-potential measurements of the nitrogen plasma treated PAN-based T700 (Toray) carbon fibres showed a shift of the isoelectric point towards higher pH from pH 3.7 to pH 4.1 as compared to as-received T700 [29]. Furthermore, the $\zeta_{plateau}$ of the plasma treated fibres increased compared to untreated fibres. The authors hypothesised that the number of surface oxides on the fibres decreased upon nitrogen plasma treatment. A similar trend was reported by Huang et al. [141] who performed X-ray photoelectron spectroscopy (XPS) measurements of nitrogen APP-treated vapour grown carbon fibres. A decrease in the oxygen content from 8.32 at.-% for the as-received PAN-based TSX-111 carbon fibres to 6.6 at.-% for the 10 min AP nitrogen plasma treated fibres was observed. Nitrogen-based functional groups ($C{=}NH$, $-NH_2$ and $C{=}N$) on the other hand increased from 1.85 at.-% for as-received fibres to 2.13 at.-% for 10 min nitrogen APP treated fibres.

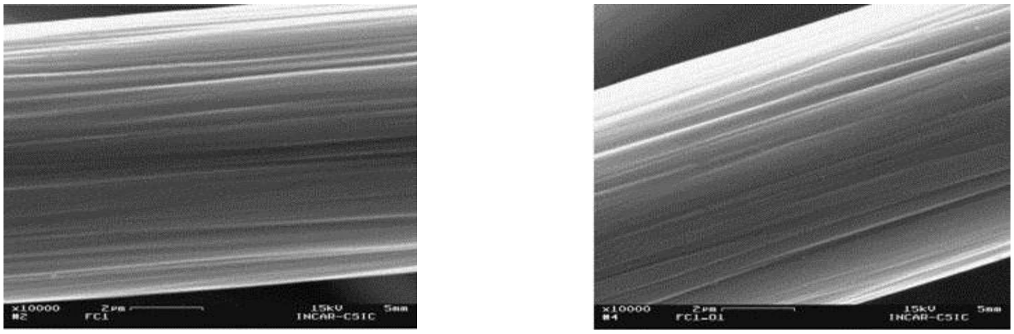
Plasma treatments on carbon fibres can also increase the hydrophobicity of the treated fibres. This could be achieved by using a mixture of nitrogen (N_2) and chlorodifluoromethane (CFC Freon 22) [22, 29, 30], a mixture of helium and tetrafluoromethane (CF_4) or helium and fluorine (F_2) [118, 142] as the feed gas for APP and LPP treatment of carbon fibres. It has been shown that the degree of surface chemistry alteration from plasma treatments depends on the type of carbon fibres used as well as the variables used during the treatment process. These include high strength or high modulus fibres, treatment time, plasma power and plasma gases used.

Fluorinated carbon fibres allow for a better bonding to fluoropolymer matrices [20, 21, 143, 144]. The mentioned advantages make plasma treatments of carbon fibres attractive as a mean to modify the surface of carbon fibres in order to enhance interactions between the fibres and different matrices. The following sections will discuss the implications of LPP and APP on the surface and bulk properties of treated carbon fibres.

3.3 Surface properties of plasma treated carbon fibres

3.3.1 Fibre surface morphology

The surface morphology of carbon fibres is commonly studied using scanning electron microscopy (SEM). Some commercially available standard strength carbon fibres exhibit a circular cross-section with shallow crenulations parallel to the fibre axis [113, 145]. These crenulations are attributed to the differential contraction of carbon fibres during the cooling step in the manufacturing process, which led to the buckling of the surface skin because of the high thermal expansion coefficient of the graphitic planes in the interior of the fibres [115, 146, 147] (Fig. 3.1). The surface morphology of PAN-based carbon fibres after AP oxygen plasma treatment showed no apparent surface damage, as reported by Erden et al. [132] and Park et al. [131] while the surface area of the treated carbon fibres increased threefold compared to neat fibres but remains well below 1 $m^2 g^{-1}$.



(a) (b)

Figure 3.1 Surface morphology of untreated (a) and oxygen LPP treated (b) high strength (HT) PAN-based carbon fibres [116]

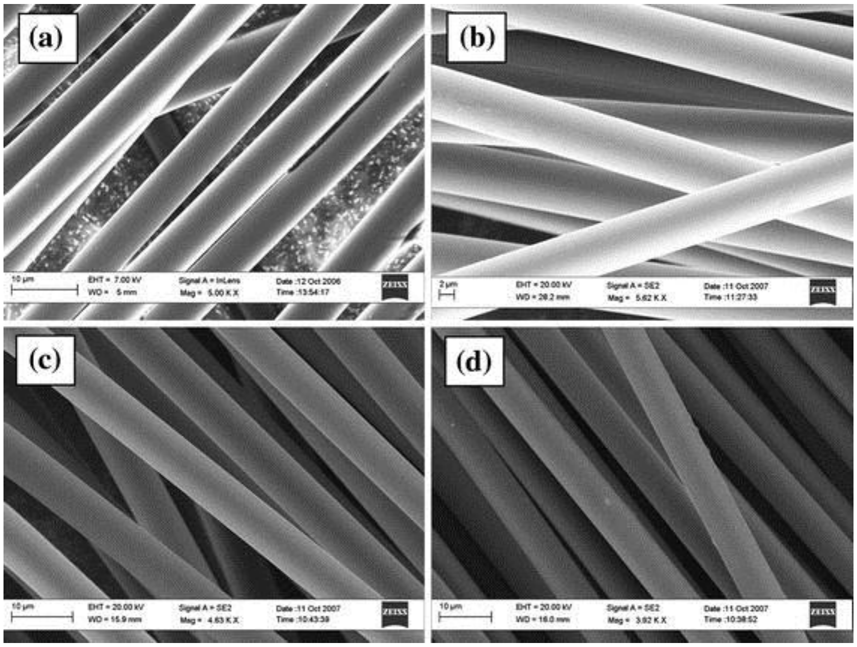
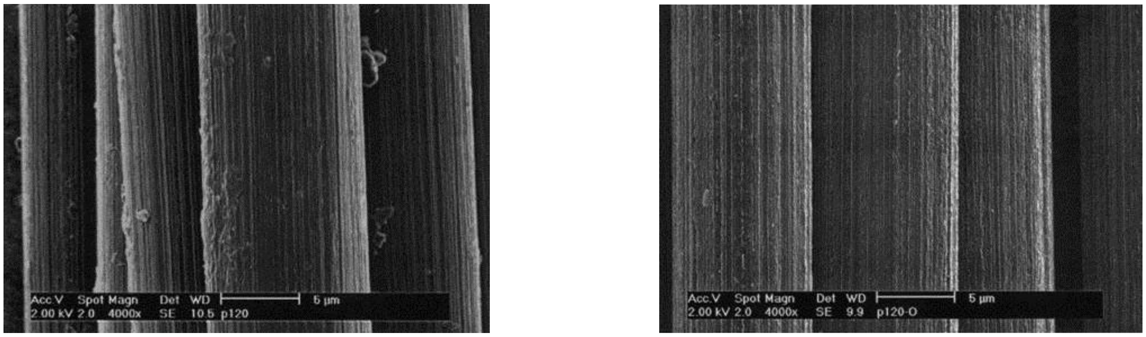


Figure 3.2 Surface morphology of untreated and oxygen APP treated PAN-based AS4 carbon fibres [132]

Bismarck et al. [106] and Bogoeva-Gaceva et al. [148] reported that LP oxygen plasma treatment resulted in slight deepening of the crenulations on high modulus PAN-based HM48.00A (Sigri) and HM-S/6K (Grafil) carbon fibre surfaces. This however did not influence the overall fibre diameter or the surface area of the treated fibres, which is also observed after oxygen APP treatment of carbon fibres (Fig. 3.2). However, the surface morphology of pitch-based P120 (Amoco) carbon fibres treated with LP oxygen plasma showed no etching and pitting effects, no increment in surface area nor deepening of crenulations on the fibre surface were observed by SEM (Fig. 3.3). Such an observation might possibly be due to the more graphitic nature of pitch-based carbon fibres [137, 149].



(a) (b)

Figure 3.3 Surface morphology of untreated (a) and oxygen LPP treated (b) pitch-based P120 carbon fibres [150]

Plasma fluorination of carbon fibres also affects the surface morphology of PAN-based AS4 (Hexcel) and T700 (Toray) carbon fibres, as shown in Figures 3.4 and 3.5. It can be seen that atmospheric plasma fluorination resulted in pitting of the surface of carbon fibres due to carbon sputtering effect in plasma environment. However, extending the treatment time resulted in a more smooth fibre surface due to the removal of amorphous carbon from the fibre surface [29, 30, 151].

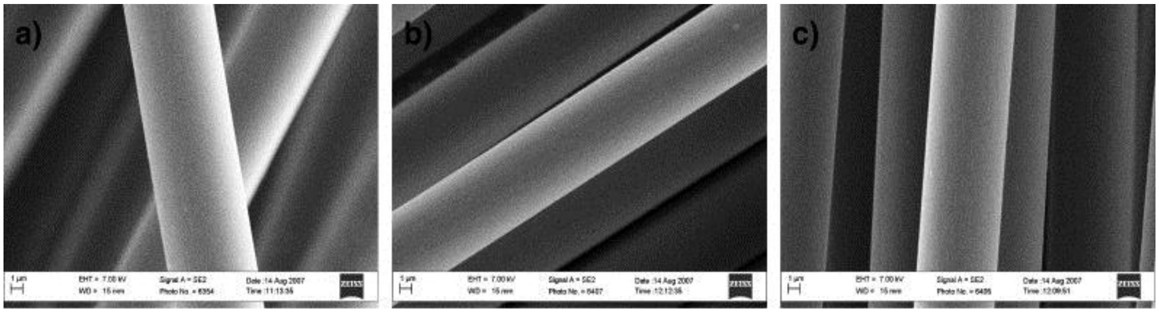


Figure 3.4 Surface morphology of untreated (a) and atmospheric pressure plasma fluorinated batch (b) and continuous (c) treated PAN-based AS4 carbon fibres [30]

To-date, there are no morphological studies conducted in low pressure plasma fluorinated carbon fibres [152]. A few studies showed that the carbon fibre surface was significantly damaged by direct fluorination using a mixture of HF-F_2 or N_2-F_2 for an extended period of time of up to 60 min [23, 151]. Ho et al. [23] observed a 33% decrease in the tensile strength of T300 (Toray) carbon fibre treated with N_2-F_2 as compared to as-received T300 fibres. In this context and the fact that direct fluorination is only a batch process, atmospheric plasma fluorination of carbon fibres is a better suited method [30].

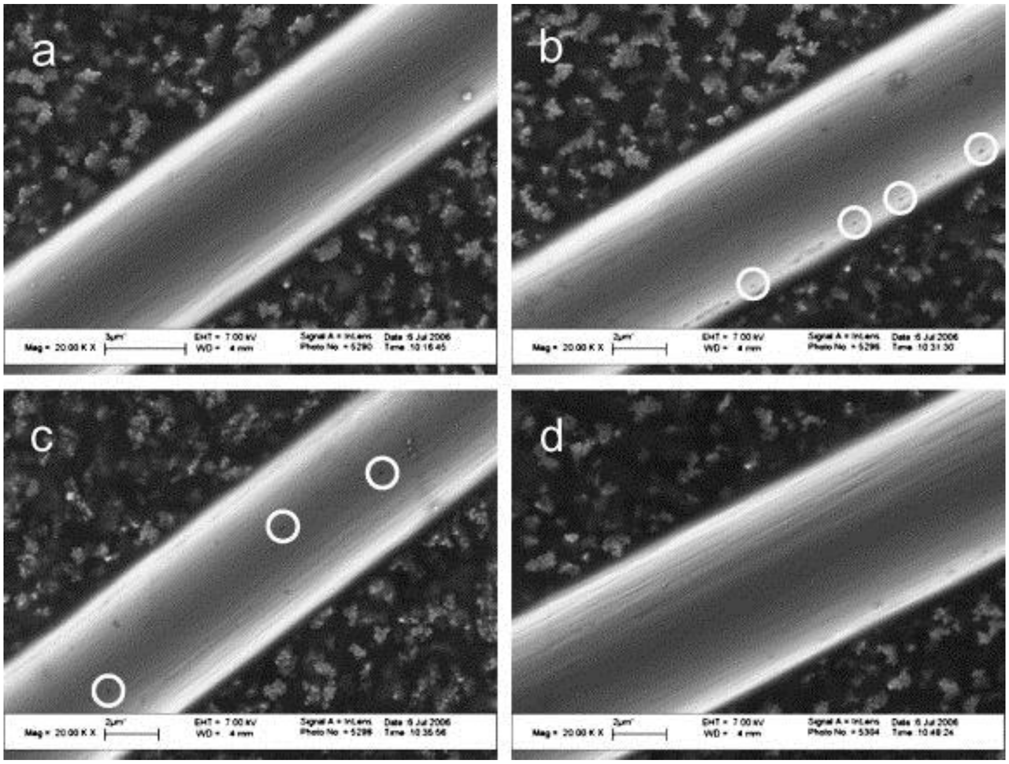


Figure 3.5 Surface morphology of untreated (a) and atmospheric pressure plasma fluorinated 2 min (b) 4 min (c) and 8 min (d) of PAN-based T700 carbon fibres [29]

3.3.2 Surface composition of LP and AP plasma treated carbon fibres

X-ray photoelectron spectroscopy (XPS) is a technique that allows the composition of the outermost few atomic layers of solid surfaces to be analysed. Generally, carboxyl (–COOH), phenolic, quinine, hydroquinone, aldehyde, fluorescene- and normal-type lactones, ethers, peroxides and ester groups are present on as-received carbon fibre surface [153]. Although electrochemical oxidation is commonly applied to most (if not all) commercially available carbon fibres by the manufacturers to introduce oxygen functional groups onto carbon fibre surfaces to improve fibre-matrix adhesion, researchers often prefer to use of plasma treatments as a post manufacturing process to further increase the surface oxygen content of carbon fibres. This is because plasma treatments of carbon fibres are an effective method to clean the fibre surface from organic contamination, increase fibre surface area by micro-etching, cross-linking to strengthen carbon fibre surface cohesively and modify the surface chemistry of the treated fibres [99]. This is to improve the interfacial adhesion of carbon fibre to thermosetting and thermoplastic polymer matrices including unconventional matrices such as fluoropolymers [116].

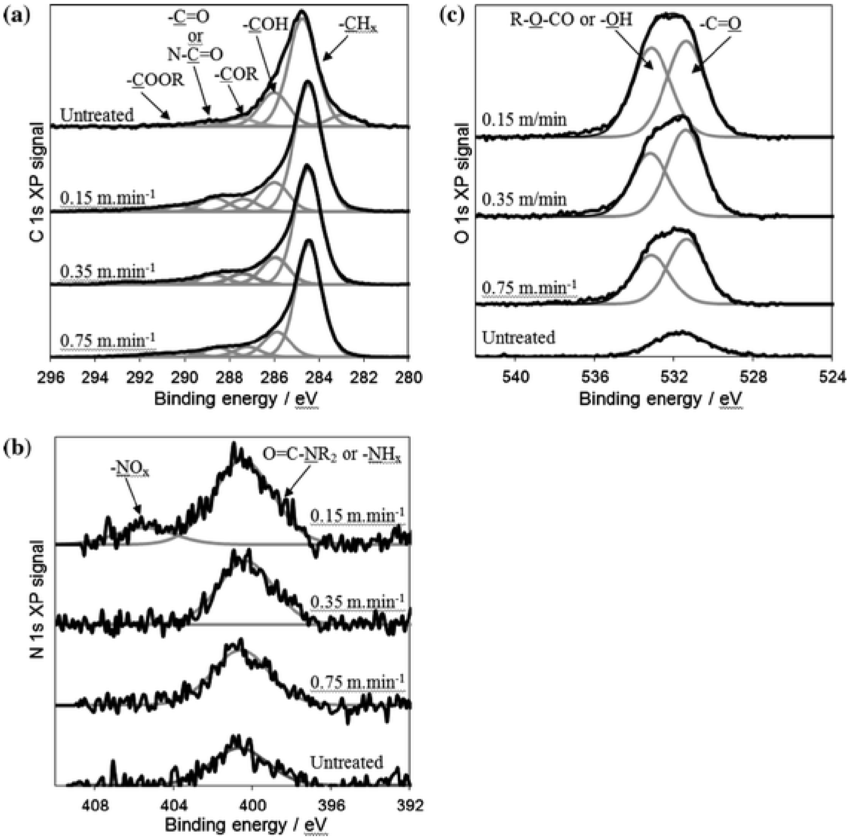


Figure 3.6 High resolution (a) C1s, (b) O1s and (c) N1s spectra of atmospheric pressure oxygen plasma treated PAN-based AS4 carbon fibres [132]

An example of high-resolution C1s spectra (Fig. 3.6) shows various oxygenated species present in AP oxygen plasma treated PAN-based AS4 (Hexcel) carbon fibres; alcohols/ethers (−COH or −COR or C−O) at binding energies of 286-287 eV, carboxylic acids (−COR), esters and ketones (−C=O) at binding energies 288-290 eV and $–CO_2R$ at binding energies of 290-292 eV [132].

The elemental composition of carbon fibres after atmospheric plasma oxidation showed an increase in the oxygen concentration, expressed as the O/C ratio as a function of plasma exposure time (Table 3.1). Erden et al. [132] reported that the O/C ratio of continuous AP oxygen plasma treatment of unsized AS4 (Hexcel) carbon fibres increased from 0.08 to 0.20 after the fibres were exposed to 4 min plasma treatment compared to as-received fibres. It should be noted that the amount of oxygen functionalities that can be introduced is very dependent on the type of fibres used as well as the exposure time, plasma power and the feed gas. Park et al. [131] showed that when PAN-based TZ-307 (Taekwang) carbon fibres were treated in He/O_2 (1:1) atmospheric plasma for 30 min, an increase in the O/C content from 0.15 up to 0.30 could be achieved.

Table 3.1 Surface composition of as-received and APP air treated carbon fibres

Carbon fibres	***Plasma treatment***	***Treatment time/s***	***Surface composition/ at.-%***			***O/C ratio/ %***	**REF**
			C 1s	***O 1s***	***N 1s***		
Standard	As-received	0	90.87	9.12	0.01	0.10	[154]
Standard	APP air	30	73.63	24.02	2.35	0.33	[154]
Standard	APP air	60	72.40	25.13	2.47	0.35	[154]
Standard	APP air	90	72.26	25.19	2.55	0.35	[154]
Grafil HM-S	As-received	0	85.00	15.00	0	0.18	[148]
Grafil HM-S	APP air	300	89.00	15.00	0	0.12	[148]
Grafil HM-S	APP air	600	86.40	13.60	0	0.16	[148]
Grafil HM-S	LPP N_2	60	75.70	14.70	9.50	0.19	[148]
Grafil HM-S	LPP N_2	600	75.30	14.80	9.60	0.20	[148]

Another study by Kusano et al. [140] using the same feed gas for the plasma treatment of PAN-based HTA5001 (TENAX) carbon fibres, resulted in an increase of O/C ratio from 0.04 for as-received fibres to only 0.11 after 3 min of treatment time. These results are comparable to the surface oxygen content of other industrially oxidised PAN-based carbon fibres (such as Grafil HM-S, IM7, HTA, UHMS, C320, M40 and T300) treated in oxygen LPP treatment [91, 116, 148, 155-157]. When pitch-based S-233 (Donacarbo) and P120 (Amoco) carbon fibres and were treated in oxygen LPP, similar findings were made [137, 150]. However, with increasing exposure to low pressure oxygen plasma and higher plasma power, the surface oxygen content of

S-233 carbon fibres reaches saturation point and decreases slightly by 10%. The authors hypothesised that the reason behind the decline of the O/C ratio of the fibre surface at higher plasma power and longer treatment time is due to the reduction of micro-pore volume, at which oxygen functionalities can no longer be chemisorbed [137].

In addition to AP oxygen plasma, air was also used as the plasma feed gas to modify the fibre surface. AP air plasma treatment creates essentially the same surface functionalities on the surface of carbon fibres as AP oxygen plasma, with the exception that nitrogen functional groups were also introduced onto the fibre surfaces. Li et al. [154] reported that air APP treatment of carbon fibres showed an increase in the oxygen and nitrogen content after only 30 s of plasma treatment. The surface composition reaches its saturation limit and no further increase in oxygen content was observed after 60 s treatment time (Table 3.1). The O/C ratio increased from 0.1 for untreated carbon fibres to 0.33 for 30 s, 0.35 for 60 s and 0.35 for 90 s of treatment time in air plasma. This resulted in increased hydrophilicity of the fibres as more solid carbon oxides were formed [148, 154]. Kusano et al. [140] showed that air APP treatments increased the surface N/C content of HTA5001 (Toho Tenax) carbon fibres without affecting the O/C content as compared to as-received fibres. Comparing atmospheric pressure to low pressure air plasma, Bogoeva-Gaceva et al. [148] reported that by treating PAN-based Grafil HM-S (Courtaulds) carbon fibres in low pressure air plasma for 5 and 10 min, the O/C ratio decreased from 0.18 to 0.12 and 0.16, respectively. More importantly, no traces of nitrogen were found on the fibre surface by XPS. This shows that the low power output of LPP did not result in the functionalisation of carbon fibre surfaces with either oxygen- or nitrogen-based functional groups instead it is more likely that the carbon fibres were simply etched during the plasma treatment. This is supported by the decrease in the ratio of oxidised carbon to graphitic carbon from 0.54 for as-received Grafil HM-S to 0.47 and 0.45 for 5 and 10 min treatment time, respectively. On the other hand, air APP runs at much higher power output and this resulted in the generation of both oxygen and nitrogen radicals, which eventually functionalise the surface of carbon fibres, as observed by Li et al. [154] and Kusano et al. [140].

By using fluoride-containing gases, fluorine moieties can be introduced onto the carbon fibre surface [29, 30, 144]. It can be seen that up to 1.1 at.-% of fluorine can be introduced into the surface of as-received AS4 (Hexcel) carbon fibres when subjected to 1 min of APF and an increase of up to 4.7 at.-% when the exposure time to APF was increased to 4 min (Table 3.2) [158]. High resolution C1s XP spectra showed 3 different C-F species after fluorination of carbon fibres, namely C-F at 290 eV, $C-F_2$ at 292 eV and $C-F_3$ at 294 eV. The F1s high resolution spectra showed a single peak at a binding energy of 689 eV indicating that the fluorine is covalently bonded to the carbon surface [29]. This is in contrast to direct fluorination treatments which commonly result in the formation of C–F bonds with ionic, semi-ionic and covalent character [24, 159]. As a result of fluorination in APP, the surface oxygen content of the industrially oxidised carbon fibres was reduced. This can be seen from the reduction in the amount of $R-O_x$ groups while $C-F_x$ functional groups are introduced onto the fibre surface [29].

Table 3.2 Surface compositions of carbon fibres from fluorine APP treatment

Carbon fibre	***Plasma treatment***	***Plasma gas***	***Treatment time/min***	***C 1s***	***N 1s***	***O 1s***	***F 1s***	***Si 1s***	***Cl 1s***	***C/F ratio***	***REF***
T700 GC-91	As-received	-	0	74.9	6.7	18.4	0	0	0	0	[144]
T700 GC-91	APP	N_2:$CHCl_2F$	0.6	74.5	4.97	18.8	1.71	0	0	0.44	[144]
T700 GC-91	APP	N_2:$CHCl_2F$	0.8	76.1	5.67	16.5	1.76	0	0	0.43	[144]
T700 GC-91	APP	N_2:$CHCl_2F$	1.8	75.9	5.2	15.2	3.74	0	0	0.20	[144]
T700SC	As-received	-	0	75.4	1.2	18.0	0	5.4	0	0	[29]
T700SC	APP	N_2:$CHCl_2F$	1	82.4	1.6	12.5	1.1	0.6	0	0.75	[29]
T700SC	APP	N_2:$CHCl_2F$	4	80.8	2.0	13.6	1.6	1.3	0	0.51	[29]
T700SC	APP	N_2:$CHCl_2F$	8	84.5	1.8	9.5	1.5	0.8	0	0.56	[29]
AS4	APP	N_2:$CHCl_2F$	0	90.6	2.4	7.0	0	0	0	0	[30]
AS4	APP	N_2:$CHCl_2F$	4	77.4	1.8	12.9	4.7	0	3.2	0.17	[30]
P120	LPP	CF_4	-	76.0	0	1.8	19.0	0	0	0.04	[118]
IPCL	LPP	CF_4	-	60.0	0	2.5	35.0	0	0	0.02	[118]
Thornel 300	LPP	He:CF_4	60	-	-	-	-	-	-	0.91	[142]
Thornel 300	LPP	He:F_2	60	-	-	-	-	-	-	0.77	[142]

Table 3.2 shows the chemical composition of carbon fibres after being subjected to fluorination in LPP and APP treatment. Tressaud et al. [118] reported the low pressure plasma fluorination of carbon fibres with CF_4. This resulted in a very thin fluorinated layer on the outmost surface of the carbon fibre. This plasma fluorination did not affect the bulk fluorination of the fibres when compared to direct fluorination, where significant bulk penetration occurs and in some cases

fluorine was intercalated into the bulk of the fibres [159]. This can be explained by the observation of a drastic change in the relative intensities from the C 1s and F 1s XPS spectra as well as decreased electrical conductivity [21, 23, 118, 151]. Loh et al. [142] carried out LPP fluorination on Thornel 300 (Union Carbide Co.) carbon fibres in both mixtures of CF_4-He and F_2-He. The authors showed that with the same gas flow rate of 30 sccm and treatment time of 60 min, the F/C ratio on the carbon fibre surface was 0.91 for CF_4-He plasma and 0.77 for F_2-He plasma. CF_4-He plasma was more efficient in removing surface oxides and introduces more fluorine onto the carbon fibre surface compared to F_2-He because the oxygen atoms in CF_4 gas plasma, react with the carbon-containing species in the plasma. This results in the formation of stable volatile components before the oxygen could react with the carbon fibres. The increase in F/C ratio of CF_4-He plasma treated carbon fibres also lead to the reduction of O/C ratio from 0.13 for as-received fibres to 0.06 for CF_4-He treated fibres.

3.3.3 Wettability of plasma treated carbon fibres

Wetting is defined as the extent to which a liquid spreads over a solid surface thereby displacing another fluid, in most cases, air [160]. By using water as the test liquid, it is possible to determine whether a solid surface is either hydrophilic or hydrophobic. Characterisation of carbon fibres by contact angle measurements has been one of the most popular methods adopted by many researchers, as the information derived from these measurements is only determined by the outermost surface layer [161].

Erden et al. [132] showed that 4 min AP oxygen plasma treatment of unsized carbon fibre (AS4, Hexcel) resulted in a reduction of advancing water contact angles (θ_a) from 77° to 58°. θ_a is characteristic for the wetting of dry surfaces and represents the low energy fraction of the surface, while the receding contact angle θ_r is the characteristic for the de-wetting of a wet surface and reflects the properties of the high energy fraction of the same surface. A similar trend was also reported when PAN-based carbon fibres were treated using low pressure oxygen plasma, where a drastic drop of θ_a was also observed (see Table 3.3) [146, 156, 162]. The same behaviour was also seen for θ_r, though the magnitude of the contact angle was lower (Table 3.3).

The authors suggested that the reduction of the contact angle values is related to the increase in the carboxylic (–COOH) and hydroxyl (–OH) functional groups as observed by XPS.

Table 3.3 Advancing θ_a and receding θ_r contact angles of untreated and oxygen plasma treated carbon fibres against water

Carbon fibre	***Plasma treatment***	***Treatment time/sec***	θ_a ***, W/ °***	θ_r***, W/ °***	***REF***
C320.00A	As-received	0	82.5 ± 2.9	56.3 ± 3.1	[162]
C320.00A	LPP, 16.5 W	60	56.2 ± 4.3	38.6 ± 5.9	[162]
C320.00A	LPP, 16.5 W	300	52.7 ± 1.4	34.9 ± 5.0	[162]
C320.00A	LPP, 16.5 W	600	46.7 ± 3.5	30.7 ± 8.2	[162]
C320.00A	LPP, 16.5 W	1200	39.5 ± 3.5	32.2 ± 3.8	[162]
UHMS	As-received	0	78.0 ± 5.0	49.0 ± 5.0	[156]
UHMS	LPP, 100W	20	36.0 ± 5.0	14.0 ± 5.0	[156]
IM7S	As-received	0	44.0 ± 5.0	32.0 ± 5.0	[156]
IM7S	LPP, 100W	20	29.0 ± 5.0	10.0 ± 5.0	[156]
IM7U	As-received	0	80.0 ± 5.0	59.0 ± 5.0	[156]
IM7U	LPP, 100W	20	32.0 ± 5.0	12.0 ± 5.0	[156]
HTA	As-received	0	34.0 ± 5.0	20.0 ± 5.0	[156]
HTA	LPP, 100W	20	28.0 ± 5.0	10.0 ± 5.0	[156]
HM-35	As-received	0	60.0 ± 5.0	41.0 ± 5.0	[156]
HM-35	LPP, 100W	20	33.0 ± 5.0	15.0 ± 5.0	[156]
IM-500	As-received	0	66.0 ± 5.0	60.0 ± 5.0	[156]
IM-500	LPP, 100W	20	37.0 ± 5.0	26.0 ± 5.0	[156]
HTA-7	As-received	0	62.0 ± 5.0	52.0 ± 5.0	[156]
HTA-7	LPP, 100W	20	35.0 ± 5.0	19.0 ± 5.0	[156]
AS4	As-received	0	77.2 ± 4.4	58.3 ± 3.5	[132]
AS4	APP, 2.1 kW	240	58.5	49.0	[132]

The contact angle hysteresis ($\Delta\theta$), which is the difference between θ_a and θ_r, also reduced after oxygen plasma treatment. Contact angle hysteresis is mainly due to chemical surface inhomogeneity. Although micro-roughness can also contribute to $\Delta\theta$, the effect is minor except for extremely low or high contact angles [105]. Oxygen plasma treatment using LPP and APP resulted in a decrease of the water contact angle hysteresis as the oxygen content on treated fibre surfaces increased, with oxygen APP resulting in a more significant decrease compared to oxygen LPP (Fig. 3.7). It was proposed by Erden et al. [132] that the decrease in $\Delta\theta$ was attributed to the more uniform distribution of surface oxides onto the surface of carbon fibres with APP treatment thus leading to greater surface homogeneity.

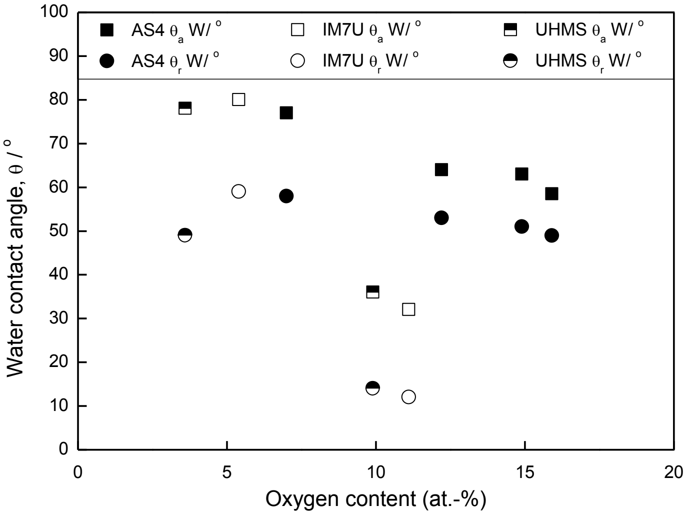


Figure 3.7 Advancing θ_a and receding θ_r water contact angles of AS4, IM7U and UHMS carbon fibres with the corresponding oxygen content after oxygen plasma treatment on the carbon fibre surface (Redrawn from Ref. [132, 156])

By measuring the contact angle of various test liquids against carbon fibres, the surface free energy, γ of the plasma treated carbon fibres can be calculated. γ is the sum of the dispersive component γ^d and polar component γ^p of surface energy [163]. Both oxygen APP as well as LPP resulted in a decrease of γ^d and increased γ^p significantly [131, 132, 155, 162]. γ^d indicates the essential surface characteristics of the graphitic framework of carbon fibres [132]. The decrease in γ^d is due to the disruption of the carbon fibre surface by bombarding the fibre surface with plasma species. The polar component of the surface free energy on the other hand increases with oxygen plasma treatment due to the introduction of polar oxygen functional groups on the carbon fibre surface (Table 3.4), which agrees with the measured ζ-potential; the $\zeta_{plateau}$-values, which increased from -14.9 mV for as-received AS4 (Hexcel) carbon fibres to -8.9 mV for 4 min oxygen APP treated AS4 fibres as reported by Erden et al. [132]. The decrease in $\zeta_{plateau}$-values is due to the fact that the treated fibres are more hydrophilic and adsorb more water which results in a loss of adsorption sites for ions. [145].

Table 3.4 Surface energy γ, dispersive γ^d and polar γ^p components of untreated and oxygen plasma treated carbon fibres

Carbon fibre	***PAN/ Pitch***	***Plasma treatment***	***Treatment time/min***	***γ /mN/m***	***γ^p /mN/m***	***γ^d /mN/m***	***REF***
C320.00A	PAN	As-received	0	37.5 ± 2.3	10.0 ± 1.6	27.5 ± 1.7	[162]
C320.00A	PAN	LPP, 16.5 W	1	47.4 ± 2.9	27.7 ± 2.9	19.7 ± 0.2	[162]
C320.00A	PAN	LPP, 16.5 W	5	49.4 ± 1.2	30.8 ± 1.1	18.6 ± 0/6	[162]
C320.00A	PAN	LPP, 16.5 W	10	53.4 ± 2.6	34.2 ± 2.4	19.2 ± 0.8	[162]
C320.00A	PAN	LPP, 16.5 W	20	57.9 ± 3.3	39.4 ± 3.2	18.5 ± 0.5	[162]
P120J	Pitch	As-received	0	-	1.0 ± 0.2	28.0 ± 3.0	[155]
P120J	Pitch	LPP, 75 W	3	-	2.4 ± 0.5	31.2 ± 2.0	[155]
P120J	Pitch	LPP, 75 W	10	-	5.4 ± 0.3	32.0 ± 2.0	[155]
P120J	Pitch	LPP, 75 W	3	-	3.6 ± 0.4	34.0 ± 2.0	[155]
P120J	Pitch	LPP, 75 W	3	-	2.8 ± 0.5	33.0 ± 1.0	[155]
P120J	Pitch	LPP, 75 W	10	-	2.7 ± 0.3	33.0 ± 4.0	[155]
TZ-307	PAN	As-received	0	47.0	-	-	[131]
TZ-307	PAN	APP, 100 W	0.5	49.0	-	-	[131]
TZ-307	PAN	APP, 200 W	0.5	56.0	-	-	[131]
TZ-307	PAN	APP, 250 W	0.5	67.5	-	-	[131]
AS4	PAN	As-received		34.0 ± 0.9	9.8 ± 0.4	24.3 ± 0.6	[132]
AS4	PAN	APP, 2.1 kW	0.8	43.3 ± 0.6	16.0 ± 0/4	27.4 ± 0.2	[132]
AS4	PAN	APP, 2.1 kW	1.8	44.0 ± 0.7	16.3 ± 0.4	27.7 ± 0.3	[132]
AS4	PAN	APP, 2.1 kW	4	47.3 ± 0.5	19.6 ± 0.4	27.7 ± 0.1	[132]

In contrast to oxygen APP, the wettability of carbon fibres decreased as a result of atmospheric plasma fluorination due to the introduction of covalent C-F_x moieties and the reduction of hydrophilic C-O_x groups. This was seen in the de-convolution of the high resolution XPS of C 1s of fluorine APP treated T700SC (Toray) carbon fibres. The two peaks of C-O_x functional groups at 286.7 eV and C-F_x functional groups at 288.9 eV were clearly visible (Fig. 3.8) where the XPS intensity of the former reduced with increasing treatment time. As a result, the surface of the fibre becomes more hydrophobic. Ho et al. [29] reported that θ_a of industrially oxidised, but desized T700 (Toray) carbon fibres in water was 73°. The contact angle increased to 104° after exposure to $CHClF_2$:N_2 in APP for 4 min (Table 3.5). The surface free energy of APF treated carbon fibres decreased from 50 to 35 mN/m due to the incorporation of fluorine moieties into and the reduction of the C-O_x on the fibre surface, which is expected to result in a reduction of the polar component γ^p of the surface energy (Table 3.6).

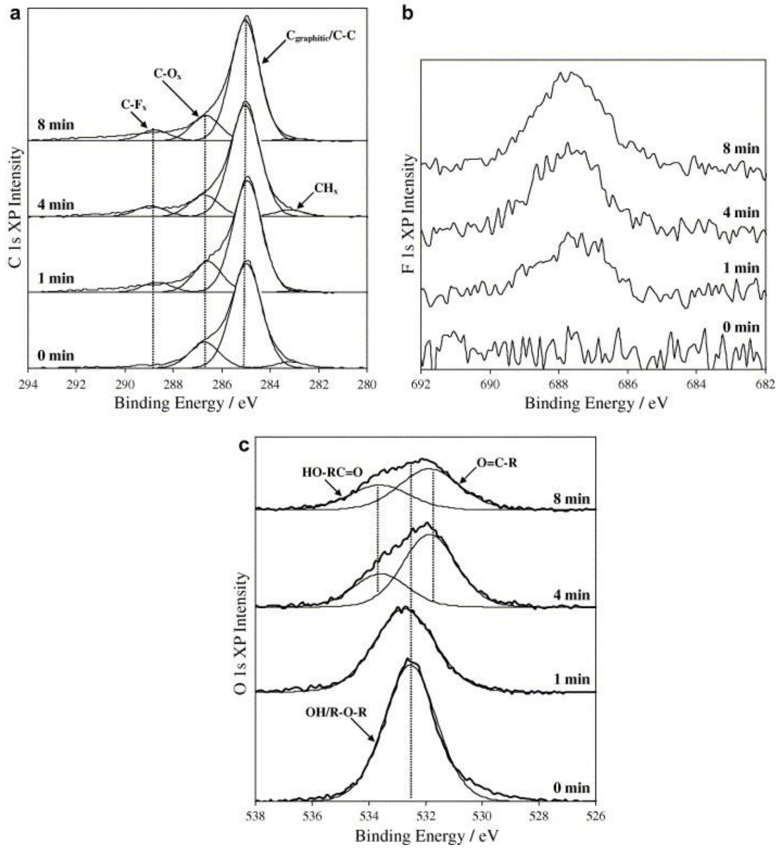


Figure 3.8 C 1s, F 1s and O1s XP spectra of fluorine APP treated carbon fibres [29]

Table 3.5 Advancing θ_a and receding θ_r contact angles of fluorine APP treated carbon fibre against water

Carbon fibre	***Fluorination method***	***Fluorination gas***	***Treatment time/min***	***$\theta_{a,}$ W/°C***	***$\theta_{r,}$ W/°C***	***REF***
T700SC	As-received	-	0	72.9 ± 2.7	43.6 ± 4.8	[29]
T700SC	APP	N_2:SF_6	4	61.2 ± 3.2	47.6 ± 3.3	[29]
T700SC	APP	N_2:$CHCl_2F$	2	94.3 ± 0.5		[29]
T700SC	APP	N_2:$CHCl_2F$	4	102.7 ± 2.1	36.8 ± 6.2	[29]
T700SC	APP	N_2:$CHCl_2F$	8	86.4 ± 3.2		[29]
AS4	As-received	-	0	77.2 ± 4.4	56.8 ± 5.7	[30]
AS4	APP	N_2:$CHCl_2F$	4	90.9 ± 8.3	45.9 ± 4.5	[30]

This decrease is caused by both the reduction of the number of high energy surface oxides and the disruption of the graphitic character of the carbon fibre surfaces after APF [22, 151]. Similar results were also obtained when AS4 carbon fibres were treated in $CHClF_2$:N_2 APP [30]. An increase in the θ_a from 77° to 91° was found when the fibres were plasma treated for 4 min. $\Delta\theta$ increased from 20° for the untreated fibres to 45° for the fluorinated fibres, which indicates a significant increase in the surface inhomogeneity after exposure to APF.

Table 3.6 Surface energy γ, dispersive γ^d and polar γ^p components of untreated and fluorine APP treated carbon fibres

Carbon fibre	***Fluorination method***	***Fluorination gas***	***Treatment time/min***	***γ /mN/m***	***γ^p /mN/m***	***γ^d /mN/m***	***REF***
T700SC	As-received	-	0	49.8 ± 2.8	38.6 ± 1.7	11.2 ± 1.1	[29]
T700SC	APP	N_2:SF_6	4	47.9 ± 6.0	-	-	[29]
T700SC	APP	N_2:$CHCl_2F$	2	48.7 ± 1.2	43.2 ± 0.9	5.5 ± 0.2	[29]
T700SC	APP	N_2:$CHCl_2F$	4	35.3 ± 2.6	31.7 ± 1.7	3.6 ± 0.8	[29]
T700SC	APP	N_2:$CHCl_2F$	8	46.8 ± 2.2	440.9 ± 0.9	5.8 ± 1.2	[29]
AS4	As-received	-	0	37.5 ± 6.1	-	-	[30]
AS4	APP	N_2:$CHCl_2F$	4	36.6 ± 7.7	-	-	[30]

3.4 Bulk properties of atmospheric plasma treated carbon fibres

3.4.1 Graphitic order of plasma treated carbon fibres

Raman spectroscopy is a useful tool for the characterisation of structural disorder of the carbon fibres with an estimated analysis depth of 100 nm [137, 164]. The most common well-resolved bands observed by Raman spectroscopy of carbon are at wavenumbers of around 1350 cm^{-1} and 1580 cm^{-1}, which are associated with the disorder finite-sized microcrystalline and/or edge of carbon (D-band) and tangential graphatised carbon (G-band), respectively [165, 166]. Table 3.7 summarises the D- to G-band (D/G) ratio of different carbon fibres after being exposed to different types of plasma treatments.

Table 3.7 D- to G-band (D/G) ratio of untreated and oxygen plasma treated carbon fibres. Δ D/G indicates the percentage of increase in the D- to G-band ratio of treated fibres relative to the as-received fibres

Carbon fibre	*Plasma condition*	*Treatment time/min*	*Raman laser power/mW*	*D/G ratio*	*Δ D/G (%)*	*REF*
AS4 – PAN based	As-received	0	-	4.61 ± 0.33	-	[132]
AS4 – PAN based	APP, 2.1 kW	0.8	-	4.73 ± 0.20	2.60	[132]
AS4 – PAN based	APP, 2.1 kW	1.8	-	4.82 ± 0.16	4.56	[132]
AS4 – PAN based	APP, 2.1 kW	4.0	-	4.87 ± 0.04	5.64	[132]
S-233 – Pitch based	As-received	0	20	3.80	-	[137]
S-233 – Pitch based	As-received	0	100	4.19	-	[137]
S-233 – Pitch based	LPP, 50 W	1.0	20	4.19	10.26	[137]
S-233 – Pitch based	LPP, 50 W	1.0	100	4.39	4.77	[137]
S-233 – Pitch based	LPP, 150 W	5.0	20	4.29	12.89	[137]
S-233 – Pitch based	LPP, 150 W	5.0	100	4.06	-3.10	[137]
T50 – PAN based	As-received	0	-	0.88	-	
T50 – PAN based	LPP, 75 W	3.0	-	1.66	88.63	
P100 – Pitch based	As-received	0	-	0.64		[150]
P100 – Pitch based	LPP, 75 W	3.0	-	1.16	81.25	[150]
P120 – Pitch based	As-received	0	-	0.34	-	[150]
P120 – Pitch based	LPP, 75 W	3.0	-	1.39	308.82	[150]

It can be seen from Table 3.7 that the D/G ratio increased after plasma oxidation for all carbon fibres. This increase in D/G ratio can be attributed to the breaking of graphitic bonds, resulting in the formation of more edge carbon atoms [164] and reduction of the surface crystallinity [137]. The percentage increase in the D/G ratio of AP oxygen plasma treated fibres is lower than that of LP oxygen plasma treated fibres when compared to the as received fibres. This implies that APP treatment does not as severely disrupt the graphitic carbon planes of the fibres. In this context, AP oxygen plasma treatment of carbon fibres is a preferable route to modify carbon fibre surfaces without damaging the bulk properties of the fibres.

Table 3.8 D- to G-band (D/G) ratio of fluorine APP treated carbon fibres

Carbon fibre	*Plasma condition*	*Treatment time/min*	*D/G ratio*	*REF*
T700 – PAN based	As-received	0	1.06	[29]
T700 – PAN based	APP	1.0	1.30	[29]
T700 – PAN based	APP	2.0	1.10	[29]
T700 – PAN based	APP	4.0	0.94	[29]
T700 – PAN based	APP	8.0	0.80	[29]
AS4 – PAN based	As-received	0	5.10	[30]
AS4 – PAN based	APP-batch	4.0	3.60	[30]
AS4 – PAN based	APP-continuous	1.3	5.00	[30]
AS4 – PAN based	APP-continuous	0.8	4.50	[30]
AS4 – PAN based	APP-continuous	4.0	4.80	[30]

Atmospheric plasma fluorination of T700 fibres also resulted in an increase of the D/G ratio with short treatment time but it decreased after increasing the exposure to APF (Table 3.8). The authors suggested that this is due to the significant damage of the carbon fibre surface caused by the sputtering action of highly energised and ionised plasma gas during the first minute of treatment time. However, with increasing plasma exposure time, more ordered graphitic structures were exposed and, therefore, the D/G ratio decreases [29]. AS4 fibres, on the other hand, showed no difference in the D/G ratio with increasing APF treatment time in continuous treatment process (see Fig. 3.9). A decrease of D/G ratio was observed for APF of the fibres using a batch process. This was due to the removal of amorphous carbon by the sputtering effect of the plasma jet [30].

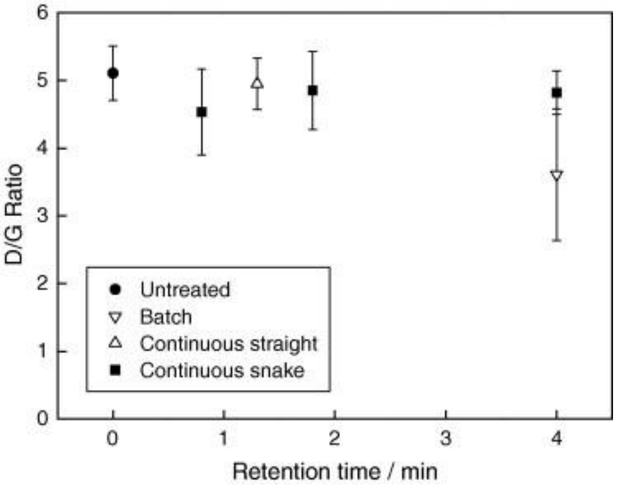


Figure 3.9 D- to G-band (D/G) ratio of atmospheric pressure plasma fluorinated PAN-based AS4 carbon fibres as a function of plasma treatment time [30]

3.4.2 Single fibre tensile properties of plasma treated carbon fibres

Many researchers showed that plasma oxidation of PAN-based carbon fibres does not significantly affect the tensile strength of the fibres even after 20 min of treatment time [148, 149, 155, 162]. However, Jang et al. [117] showed that when AU4 (Hercules) carbon fibres were treated for 20 min in low pressure oxygen plasma, the tensile strength of the fibres reduced from 3,800 MPa to 3,010 MPa [117]. Similarly, Erden et al. [132] reported a decrease of the tensile strength of AS4 (Hexcel) carbon fibres from 4,370 MPa to 3,660 MPa after AP oxygen plasma treatment for 4 min (Table 3.9). The decline in the fibre tensile strength can be explained by the fact that the fibres were exposed to various highly energetic species in the plasma jet for a longer period of time, which leads to the creation of surface defects that ultimately reduce the strength of the carbon fibres.

Table 3.9 Fibre diameter d_f, gauge length, tensile strength, Weibull single filament tensile strength for untreated and oxygen plasma treated carbon fibres

Carbon fibre	***Plasma condition***	***Treatment time/min***	***Fibre diameter, d_f (μm)***	***Gauge length (mm)***	***Tensile strength (MPa)***	***REF***
AS4 – PAN based	As-received	0	7.1 ± 0.1	20.0	3,810 ± 200	[132]
AS4 – PAN based	APP, 2.1 kW	0.8	7.1 ± 0.1	20.0	3,653 ± 550	[132]
AS4 – PAN based	APP, 2.1 kW	1.8	7.1 ± 0.1	20.0	3,582 ± 361	[132]
AS4 – PAN based	APP, 2.1 kW	4.0	7.1 ± 0.1	20.0	3,136 ± 667	[132]
P120J – Pitch based	As-received	0	9.6 ± 1.3	21.0	1,960 ± 200	[155]
P120J – Pitch based	LPP, 75 W	3.0	9.2 ± 1.2	20.0	1,620 ± 200	[155]
P120J – Pitch based	LPP, 75 W	10.0	8.9 ± 1.1	20.0	1,870 ± 200	[155]
P120J – Pitch based	LPP, 150 W	3.0	8.8 ± 1.4	21.0	1,660 ± 200	[155]

Table 3.10 Tensile strength and Young’s modulus for atmospheric pressure plasma fluorinated carbon fibres under various treatment time

Carbon fibre	***Treatment time/ min***	***Gauge length/ mm***	***Tensile strength/ MPa***	***Young’s modulus/ GPa***	***REF***
T700SC*	0	20	4900 ± 500	230 ± 5	[29]
T700SC	8.0	20	4500 ± 500	225 ± 5	[29]
AS4	As-received	20	3810 ± 200	215 ± 7	[30]
AS4-batch	4	20	3930 ± 100	187 ± 5	[30]
AS4-continuous	1.3	20	3939 ± 190	221 ± 7	[30]

*Data from manufacturer

Table 3.10 shows the tensile strength and modulus of atmospheric plasma fluorinated carbon fibres. It can be seen that that the tensile strengths and Young’s moduli of both T700 and AS4 fibres were not significantly affected by plasma fluorination up to 8 min of treatment time [22, 30]. Therefore, fluorinating the carbon fibres with APP treatment introduces fluorine functional groups onto the fibre surface without damaging the bulk properties of the fibres [23].

3.5 Effect of plasma modification of carbon fibres on adhesion between fibres and polymer matrices and composite performance

The fibre matrix adhesion determines the overall performance of composites [162]. When a composite is subjected to load, the load is transferred to the fibre through the matrix via the interface. A good interface will ensure good load transfer and this can be determined by quantifying the interfacial shear strength between fibre and the matrix. The effect of plasma treatments on the interfacial shear strength, as a measure of practical adhesion between the fibres and the matrix, as well as interface dominated properties of the composite manufactured will be discussed.

3.5.1 Interfacial shear strength between plasma treated carbon fibres and polymer matrices

The interfacial shear strength (IFSS) can be determined using for example, single fibre-pull out and single fibre fragmentation tests [97]. Table 3.11 summarises the results of various studies on the effect of low pressure and atmospheric pressure plasma oxidations of carbon fibres on the adhesion between the plasma treated fibres and different matrix systems studied using the single fibre fragmentation test. Bismarck et al. [162] observed a 39% decrease in the IFSS between 1 min oxygen LPP treated C320.00A (Sigri SCL) carbon fibres and as-received C320.00A (Sigri SCL) carbon fibres and polycarbonate (PC) matrix. This decrease was in good agreement with the decrease in the work of adhesion W_a calculated from the surface tension, γ_{la} between untreated and 1 min oxygen LPP treated C320.00A fibres. The result of single fibre fragmentation test include adhesive interactions and also plastic yielding from the matrix thus the IFSS values obtained from such tests should be considered as a ranking tool for this particular system [162]. Paiva et al. [155] reported that the IFSS between oxygen LPP treated pitch-based P120J (Amoco) carbon fibres and PC increases with the treatment time, but at longer plasma exposure time, the IFSS between treated fibres and PC reduced slightly (Table 2.11). This is due to the physical and chemical changes through the incorporation of oxygen functionalities (−OH, R−O−R, R−COOH, C=O) into the fibre surface.

Table 3.11 Fibre diameter d_f, critical fibre length l_c, Weibull strength at critical length σ (l_c) and corresponding interfacial shear strength (IFSS), $\tau_{Weibull}$ of various as-received and oxygen plasma treated carbon fibres

Carbon fibre	***Matrix***	***Surface condition***	***Treatment time/min***	***Fibre diameter, d_f/µm***	***Critical fibre length, l_c/µm***	***Weibul strength, $\sigma(l_c)$/GPa***	***IFSS, $\tau_{Weibull}$/ MPa***	***REF***
C320.00A	PC	As-received	0	8.0	1110 ± 50	3.06 ± 0.48	11.1 ± 1.2	[162]
C320.00A	PC	LOP 16.5W	1	7.0	1560 ± 90	3.04 ± 0.39	6.8 ± 0.5	[162]
C320.00A	PC	LOP 16.5W	5	7.5	1180 ± 50	3.19 ± 0.57	10.1 ± 1.4	[162]
C320.00A	PC	LOP 16.5W	10	7.5	1000 ± 50	3.01 ± 0.48	11.3 ± 1.2	[162]
C320.00A	PC	LOP 16.5W	20	7.5	1170 ± 30	3.06 ± 0.53	9.8 ± 1.4	[162]
C320.00A	PC	LOP 75 W	3	7.8 ± 0.5	639 ± 26	4.54 ± 0.16	28.0 ± 2.0	[162]
P120J	PC	As-received	0	9.6 ± 1.3	1361 ± 78	3.47 ± 0.16	12.0 ± 1.0	[155]
P120J	PC	LOP 75 W	3	9.2 ± 1.2	487 ± 17	4.94 ± 0.26	47.0 ± 3.0	[155]
P120J	PC	LOP 75 W	10	8.9 ± 1.1	652 ± 44	4.59 ± 0.31	31.0 ± 3.0	[155]

Plasma oxidation of carbon fibres in most cases increases the interfacial shear strength in model composites due to the incorporation of oxygen surface functionalities on the carbon fibre surface and thus providing more sites for hydrogen bonding to epoxy and polar thermoplastics such as polyamide (PA12) matrices [116, 132, 150, 155, 167]. A significant increase of IFSS from 6 MPa for untreated to 38 MPa for 3 min low pressure oxygen plasma treated pitch-based P120 carbon fibres (Amoco) and epoxy matrix (1,4-butadienol diglycidyl ether resin) was reported by Montes-Moran et al. [150]. They concluded that the increase of the IFSS was due to the incorporation of surface functional groups (such as C−OR, C=O and O=C−OR) that led to acid-base interactions between the treated fibres and epoxy resin. Furthermore, LPP treatment of pitch based P120 fibres increases their surface roughness, improving the mechanical interlocking between the two constituents. Erden et al. [132] reported that the IFSS between 4 min AP oxygen plasma treated AS4 carbon fibres to PA12 matrix as compared to as-received AS4 carbon fibres to PA12 doubled from 40 MPa to 83 MPa. This corresponds to the increase in the oxygen content of the fibre surface from 7 at.-% to 16 at-% after AP oxygen plasma, which promotes hydrogen bonding between the treated fibres and the PA12 matrix [132]. Yuan et al. [91] studied the interface between oxygen LPP treated T300 carbon fibres (Toray) and polyphenylene sulphide (PPS). After 10 min of LP oxygen plasma treatment of T300 carbon fibres, the IFSS between the treated fibres and PPS increased by 20%. The authors hypothesised that this effect is due to the attraction of hydroxyl groups on the treated fibre surface to the sulphide links in PPS through hydrogen bonding thus increasing the IFSS between the treated fibres and PPS.

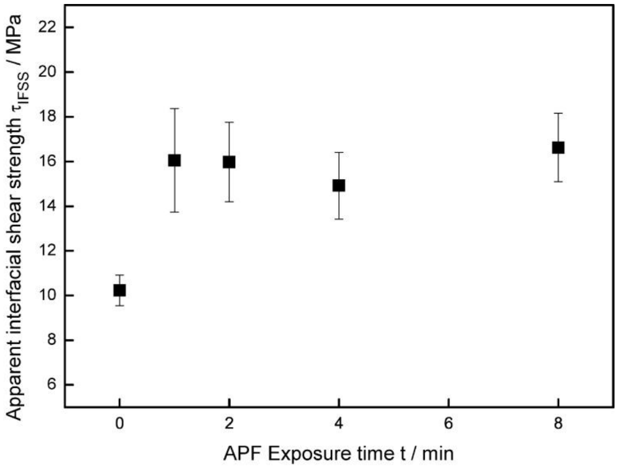


Figure 3.10 Interfacial shear strength as a function of fluorine APP treatment time for T700 fibres[71]

Fluorinating the surface of carbon fibres can improve physical compatibilisation between fluorinated fibres and fluoro-polymers [20]. APF treatment of carbon fibres resulted in a significant increase of the IFSS between fibres and polyvinylidene fluoride (PVDF) matrix [22]. Exposing T700 (Toray) carbon fibres for 1 min to fluorine APP resulted in an increase of the IFSS between carbon fibres and PVDF from 10 MPa to 16 MPa (Fig. 3.10). Further increase in the fluorine APP treatment time however had no effect on the IFSS. The authors also observed an increase in the fibre surface area from 0.22 $m^2 g^{-1}$ for untreated fibres to 0.44 $m^2 g^{-1}$ for 8 min fluorine APP treated fibres, caused by the sputtering effect of plasma jet. However, this increased surface area did not affect the IFSS. Instead, the pitting on the fibre surface could result in the formation of voids at the fibre/matrix interface if not fully wetted by PVDF.

The observed improvement in IFSS between APF treated carbon fibres and PVDF is in agreement with the IFSS of direct fluorinated C320.00A (Sigri SGL) fibres and PVDF, where the

IFSS increases 30% with F/C content of 0.8 (Fig. 3.11), which indicates the improved physical compatibilisation between the fibres and PVDF [20]. However, for the case of direct fluorination of C320.00A fibres, the IFSS between carbon fibres and PVDF shows a drop at higher F/C ratio (>1.5).

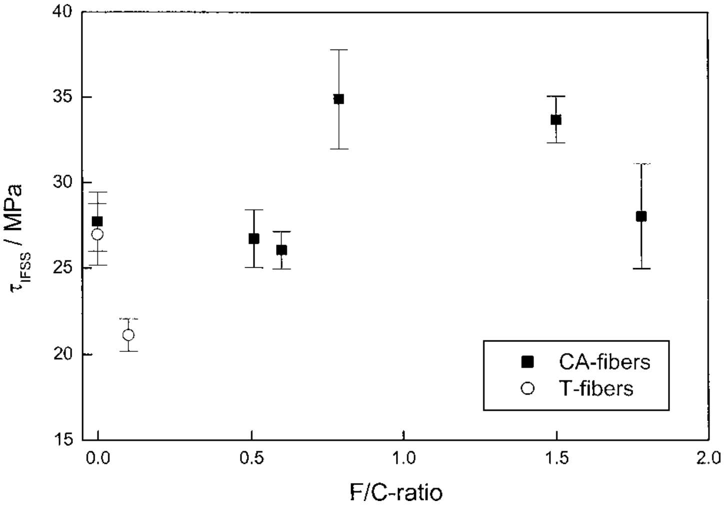


Figure 3.11 Interfacial shear strength as a function of F/C ratio of direct fluorinated CA320 and T300 fibres [20]

3.5.2 Interface dominated properties of plasma treated carbon fibre reinforced polymer composites

The most widely used mechanical test to study the adhesion properties in real composites is the short beam shear test to determine the interlaminar shear strength (ILSS) of a composite. Pittman et al. [167] measured a 6.6% increase of the ILSS between LP oxygen plasma treated T300 carbon fibres and an epoxy system. A more significant increase in short beam shear strength was reported by Fukunaga et al. [149]; the ILSS of LP oxygen plasma treated ultra-high modulus pitch carbon fibres and epoxy increased drastically from about 30 MPa to almost 80 MPa. This increase shows that oxygen plasma treated carbon fibres have much better adhesion as compared to electrochemically oxidised carbon fibres if incorporated into an epoxy [168]. A similar trend was also observed by Jang et al. [169], who used LP oxygen plasma treated hybrid fibres (co-woven with T300 carbon fibres (Toray) and PEEK fibres (Nittobo)) reinforced PEEK composite.

The ILSS increases significantly for fibres treated up to 3 min in LP oxygen plasma (Fig. 3.12) [169]. This increase is attributed to the polar functional groups on the carbon fibre surfaces as a result of oxygen plasma treatment [169].

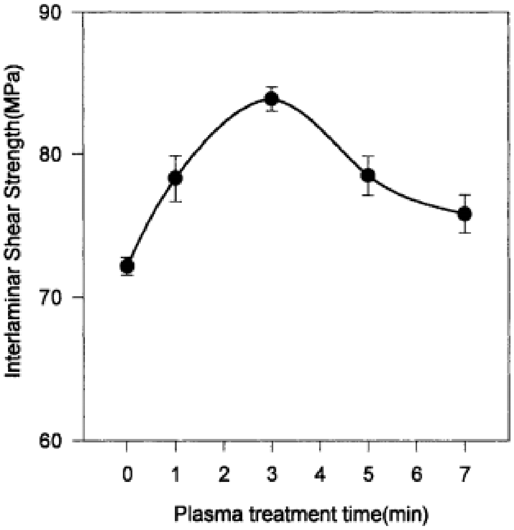


Figure 3.12 Interlaminar shear strength between atmospheric oxygen plasma treated T300/PEEK hybrid fibre reinforced PEEK composite as a function of plasma treatment time [169]

Apart from short beam shear, there are many other tests that were carried out to study the composite performance containing plasma treated carbon fibre. Li [170] reported enhanced flexural strength of AP oxygen plasma treated carbon fibre/polypropylene composites by 53% due to effective load transfer between fibre and matrix through a good interface. Jang [117] studied the interface between LP oxygen plasma treated carbon fibre/bismaleimide (BMI) composites using transverse tensile tests. The study showed a significant increase of the transverse tensile strength from 2.20 MPa for untreated carbon fibre/BMT composite to 4.71 MPa for composites containing fibres treated for 20 min in LP oxygen plasma [117]. This improvement in transverse strength implies an improvement in the interfacial adhesion between the plasma treated fibres and the matrix.

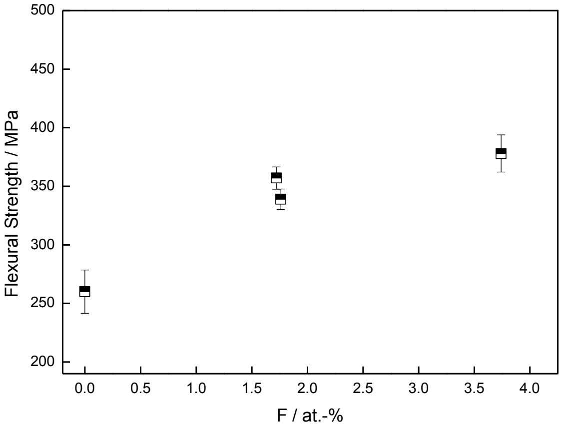


Figure 3.13 Flexural strength of laminated T700 carbon fibre reinforced PVDF composites as function of fibre surface fluorine content [144]

Atmospheric treated T700 carbon fibre reinforced PVDF composites led to an increase of up to 45% in the composite flexural strength (Fig. 3.13) [144]. This improvement was correlated to the improved fibre/matrix interface as a result of the introduction of fluorine functionalities into the treated fibres.

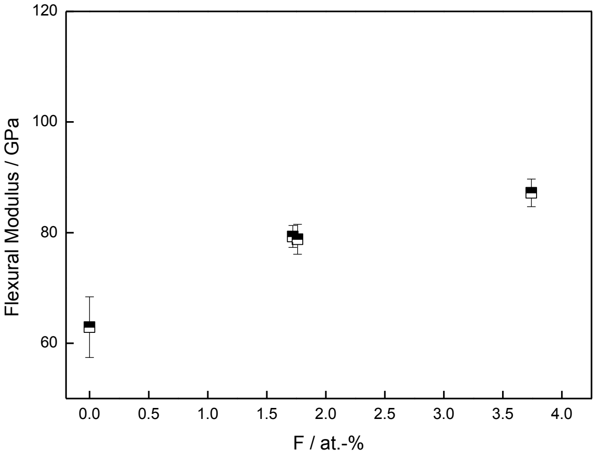


Figure 3.14 Flexural modulus of laminated T700 carbon fibre reinforced PVDF composites as function of fibre surface fluorine content [144]

The same improvement was seen for the flexural modulus where the moduli increased from 63 GPa for as-received T700 reinforced PVDF composites to 87 GPa for 1.8 min of APF treated T700 carbon fibre reinforced PVDF composites (Fig. 3.14). The authors also analysed the effect of ILSS of the APF treated carbon fibre reinforced PVDF composites using the short beam shear test (Fig. 3.15). The results showed an increase of 72% from 7.8 MPa for as-received T700 fibre reinforced PVDF to 13.4 MPa for 1.8 min of APF treated T700 fibre reinforced PVDF. These improvements indicate that good fibre/matrix adhesion properties can be achieved through APF.

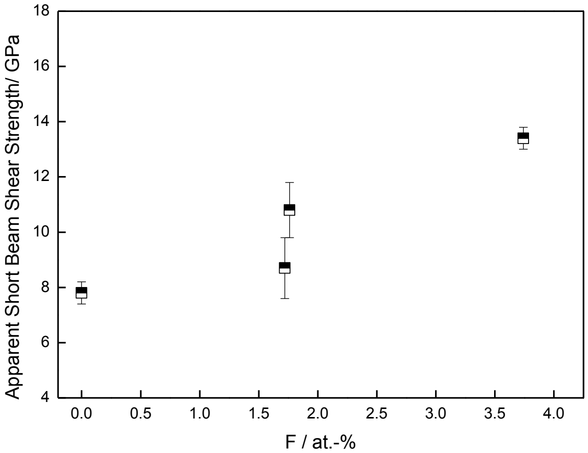


Figure 3.15 Apparent short beam shear strength of laminated T700 carbon fibre reinforced PVDF composites as function of fibre surface fluorine content [144]

3.6 Summary

The need for high performance lightweight materials has sparked the use of carbon fibre reinforced composites to replace conventional materials for structural applications. Plasma treatment of carbon fibres is a promising route to utilise the full potential of fibres in composite applications through enhancing the fibre-matrix interface. This review compares low pressure plasma (LPP) and atmospheric pressure plasma (APP) treatments of carbon fibres to improve the fibre-matrix interface in composites. However, there are pros and cons associated with each method; Low pressure plasma is the more established plasma treatment route because the treatment can be performed at low (or ambient) temperature and the flexibility of controlling each process variable in order to attach selective functional groups onto the treated surface. However, pressure vessels, seals and vacuum pumps required for the LPP system make the process more complicated and increases the cost significantly compared to APP. LPP treatment is mainly a batch process (although could also be adapted to a continuous treatment using integrated vacuum logs or transfer systems) and will also suffer from the problem of batch-to-batch variability whereas fibres treated in an APP system can be processed in a continuous manner, ensuring consistency of the final product. LPP systems, on the other hand, require a significant amount of preparation time to achieve the desired pressure before the plasma treatment can begin. In addition to this, LPP systems are limited by the size of the plasma reactor/vacuum chamber.

Even though there are significant differences in terms of the plasma systems used and operation for LPP and APP treatments, the characteristics (surface and bulk properties) of the plasma treated fibres are similar for both. The wettability, surface free energy, surface morphology of the plasma treated fibres showed similar trends regardless whether APP or LPP treatments were applied. XPS has also verified that similar functional groups can be introduced into the surface of carbon fibres independent of the types of plasma treatment when using the same feed gas. Although the above is true for the same carbon fibres used, the success of the treatments depends massively on the type of the carbon fibre used, e.g. PAN- or pitch-based. The single fibre tensile properties of APP and LPP treated fibres showed insignificant changes compared to the neat carbon fibres. However, differences between oxygen APP and LPP can be seen in the D/G ratio (the graphitic nature of carbon fibres) of plasma treated fibres. With APP treatment, the D/G ratio increased (which signifies more defective carbon formed) but this increase is lower than that of LPP treated carbon fibres. This implies that APP treatment of carbon fibres does not as severely disrupt the graphitic carbon planes in the fibre surfaces. In this context, oxygen APP treatment is preferable to modify carbon fibre surfaces without damaging the bulk properties of the fibres.

It has also been shown that through plasma treatments (both APP and LPP) of carbon fibres, the IFSS, as a measure of practical adhesion between treated fibres and the matrix improved significantly. The reason for this improvement is the incorporation of different functional groups onto the surface of the plasma treated fibres, which has led to the formation of chemical interactions, such as hydrogen bonding and van der Waals interactions between the treated fibres and polymer matrices. The types of functional groups introduced into the fibres depend on the feed gas used; for oxygen and air, the most widely used feed gases, –COOH, -OH and C=O have been incorporated. Dichlorofluoromethane and nitrogen have also been studied intensively. These gases result in the introduction of fluorine (such as $C\text{-}F_x$) and nitrogen (such as $-CNH_2$ and -C=NH) moieties onto the fibre surface. These modifications have a positive impact on the final composite performance as indicated by interlaminar shear and flexural properties of plasma treated carbon fibre reinforced composites. Inert gases such as argon were used to etch the surface of carbon fibres and introduce similar functional groups as oxygen plasmas from oxidation with air and therefore improved the interfacial bonding between treated fibres and epoxy matrices.

APP treatment of carbon fibres, meets the industrial demand to produce high performance composite materials, because of its intrinsic scalability, high production throughput, versatility and low operating costs compared to LPP systems. Structural multifunctional composites are the next step forward in the high performance composites field. The most important advantage of APP treatments of carbon fibres is the possibility to tailor the composite interfaces during production and, therefore, keeping the know-how in-house and gain competitive advantages over competitors.

4.0 Wet Impregnation as route to unidirectional carbon fibre reinforced thermoplastic composites[‡]

This chapter discusses the processing of unidirectional (UD) carbon fibre reinforced thermoplastic composites using a laboratory scale modular composite line (CL). Thin continuous prepregs were manufactured from a 12k carbon fibre tow via wet impregnation of carbon fibres by a polymer suspension. Hardware design, processing parameters influencing the prepreg quality and the fibre volume content of the resulting prepregs are discussed. UD carbon fibre reinforced Polyvinylidene fluoride (PVDF) composite prepregs and laminates were prepared via compression moulding and tested. Results from short beam strength and flexural tests are presented. The flexibility of the process is demonstrated showing the simplicity of the manufacturing route to achieve UD carbon fibre reinforced PVDF composite prepregs with qualities comparable to commercially available APC2.

[‡] *Based on a paper: Ho, K. K. C., Shamsuddin, S.-R., Riaz, S., Lamoriniere, S., Tran, M. Q., Javaid, A. and Bismarck, A., "Wet impregnation as route to unidirectional carbon fibre reinforced thermoplastic composites manufacturing", Plastic, Rubber and Composites,* ***40*** *(2011), 100-107.*

4.1 Introduction

Thermoset resins account for over 90% of the polymeric composite market share whereas thermoplastic matrices occupy only 10% of matrices used in advanced composites [40]. This is primarily because thermoset systems, epoxy in particular, have relatively low viscosities and can be processed easily. However, epoxy systems suffer from their intrinsic properties, such as brittleness, chemical instability, short pot (or shelf) life and they are difficult to recycle [171]. Thermoplastic matrices are a good alternative for advanced structural composite systems because of their intrinsic characteristics such as improved toughness, low moisture absorption, rapid production, unrestricted shelf life and moreover thermoplastic composites can be reprocessed, thermoformed and welded [40].

Uniform impregnation of reinforcing fibres with the matrix during processing is critical as it ensures that all fibres are wetted out and homogeneously distributed. This can avoid defect sites within the composite, such as fibres in contact, fibre misalignment, fibre waviness and voids etc. [172]. Manufacturing of fibre reinforced thermoplastic composites began in the mid-1970s using processes such as film stacking/ hot compaction, melt pultrusion, wet and dry powder impregnation etc. [173]. Film stacking has been a standard process for making fibre reinforced thermoplastic composites for several decades. The process requires the reinforcing fibres being laminated between layers of thermoplastic films, this stack is then fused together under heat and pressure (in excess of 10 bar) over a period of time (typically 1h) [171] to form a prepreg. Issues often encountered with film stacking include incomplete wet-out (impregnation) of the fibres by the matrix, which is correlated with the viscosity of the resin. Furthermore, damage to the reinforcing fibres is also known to occur [33]. Nevertheless, film stacking has remained the most widely used technology for manufacturing small quantities of fibre reinforced thermoplastic composites.

Fabrication of unidirectional (UD) fibre reinforced prepregs via pultrusion [33, 174], dry [175] and wet [172] powder impregnation routes are fairly similar; all three processes involve a continuous fibre tow being pulled through a medium (a thermoplastic melt in pultrusion, a dry powder bed in dry impregnation or a polymer powder suspension in wet powder impregnation) to impregnate the fibre with the thermoplastic matrix. Dry and wet processing require in-line post heat treatment to melt the polymer and consolidate the prepregs but the wet powder impregnation process requires an extra heating step to remove the liquid in which the polymer powder was suspended. The melt pultrusion process faces similar problems as film stacking, i.e. impregnation of fibres is dependent on the viscosity of the thermoplastic melt. It follows that dry powder impregnation technique should be a better route to manufacture thermoplastic prepregs. However, impregnating a dry fibre tow with a dry polymer powder has its disadvantages. Friction between fibres and die is high and causes fibre and prepregs to fracture. Furthermore impregnation relies on electrostatic forces, which do not allow good process control due to the fact that polymer powder may be lost after impregnation and prior to polymer melting and, therefore, it is difficult to make prepregs with consistent fibre volume fraction. On the contrary, the wet impregnation process relies mainly on surface tension, capillary forces, powder size and its size distribution and is easy to operate providing that a suitable liquid medium is available [176]. The liquid phase present in this process not only reduces the frictional force between the fibre tow and the impregnation pins, minimising fibre damage, but also helps in interlocking the polymer powder within the fibre tow when exiting the impregnation bath due to capillary action.

Advanced composite materials such as carbon fibre reinforced polyetheretherketone (PEEK) and polyphenylene sulphide (PPS) manufactured via melt pultrusion are used in load-bearing and structural applications because of their high strength, high modulus, and low density. Hence the interest in developing a modular flexible and compact system to investigate the potential to manufacture unique fibre reinforced thermoplastic (and other matrix) composites as well as the impact of in-line modification of reinforcing fibres on composite performance were initiated. In this chapter, a processing route to manufacture UD carbon fibre reinforced thermoplastic composites using a wet powder/ slurry route is presented. Processing parameters, including polymer powder bath concentration, speed, tension and temperature are discussed. The flexibility of the module to manufacture carbon fibre/PVDF prepregs is demonstrated and the quality of fabricated composites was assessed by measuring the macromechanical properties.

4.2 Materials and Methods

4.2.1 Materials

The carbon fibres used in this study were high strength and strain, unsized but industrially carbonised and oxidised continuous PAN-based carbon fibres kindly supplied by Hexcel Corporation (Hextow^{TM} AS4 12k, Cambridge, UK). In addition, PVDF Kynar® 711 ($T_m \approx$ 165-170 °C) powder from Arkema (Serquigny, France) was used. Cremophor® A 25 (BASF Ludwigshafen, Germany) was used as surfactant to disperse PVDF Kynar® 711 polymer powder in water.

4.2.2 Preparation of slurry based polymer suspension for wet impregnation

An aqueous PVDF slurry was prepared by dissolving 3.6 g of Cremophor® A 25 (2 wt% with respect to the polymer) in 2 L of deionised water before 180 g of Kynar® 711 PVDF powder (approximately d_{50} = 5µm [177]) was added (9 wt% with respect to the mass of water). The suspension was then left to be stirred at room temperature using a magnetic stirrer overnight to ensure that a homogenous PVDF slurry was obtained.

Similarly, concentrated PVDF slurry was prepared by dissolving 4.0 g of Cremophor® A 25 surfactant (2 wt% with respect to the polymer) in 1 L of deionised water. After which, 200 g of Kynar® 711 PVDF powder was added (20 wt% with respect to the mass of water). The suspension was then left to be stirred at room temperature using a magnetic stirrer overnight to ensure homogenous PVDF slurry was obtained.

4.2.3 Particle size analysis

The particle size of polymer slurry suspension used for wet impregnation was measured using a Mastersizer 2000 particle size analyser (Malvern, Worcestershire, UK). The measurements were performed on a 2 wt% of PVDF slurry made by diluting the 9 wt% aqueous PVDF powder suspension with deionised water. All measurements were repeated 3 times per condition. The mean diameter of the maximum volume of the particles in the suspension is represented as d_{50}.

4.2.4 The modular laboratory scale composite production line

A modular laboratory scale composite line (CL) incorporating the wet powder impregnation technique was built enabling the production of continuous UD carbon fibre reinforced thin thermoplastic composite prepregs.

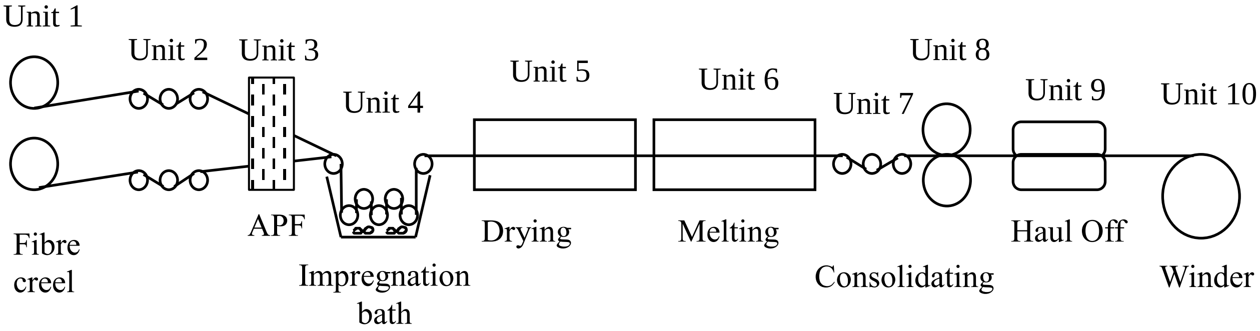


Figure 4.1 Schematic of modular laboratory scale composite production line (CPL) based on wet powder impregnation

The CL consists of ten units (Fig. 4.1), which can be arranged to form a continuous composite manufacturing line. Units 1 and 2 together form a creel with close loop tension control (Izumi International, USA), which can hold four spools of carbon fibres in an isometric frame. Up to 10 N of tension on individual fibre tows can be generated and controlled. Unit 3 is the atmospheric plasma fluorination jet where fibre modifications were performed (Details of the APF process can be found in the subsequent chapters).

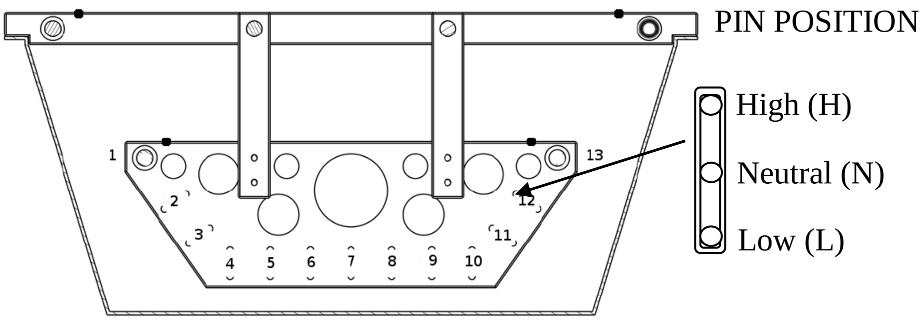


Figure 4.2 Schematic of the impregnation pins used to spread the fibre tows inside the

impregnation bath (side view)

The wet slurry impregnation bath (Unit 4) can hold up to 3 L of the impregnation medium in which up to 13 removable pins are fitted (Figure 4.2). The position of individual pins can be adjusted by up to 10 mm from the neutral position, which allows for different wrap angles to influence fibre spreading. This provides greater flexibility to control the impregnation process, which is governed by the number of filaments in the fibre tow, the particle size of polymer powder as well as the powder concentration in the bath. The polymer slurry was continuously stirred to ensure homogenous dispersion of polymer particles within the bath. Given that a water based slurry impregnation route is used, the water must be removed. Unit 5 is a 1 m long drying oven, which houses two infrared heaters. These medium wave infrared heaters (Model B, fast response medium wave emitters, Heraeus, Kleinostheim, Germany) emit up to 150 kW/m^2 of power and are extremely efficient for drying water in a very short period of time. The melting oven (Unit 6) is identical to Unit 5 only the temperature setting is higher in order to melt the polymer. The power output for both Unit 5 and 6 are controlled independently using programmable logic controllers (3508 Eurotherm PID temperature controllers, UK). Unit 7 consists of three heated pins, which are arranged 30 mm apart and can be adjusted up to 25 mm horizontally (Figure 4.3).

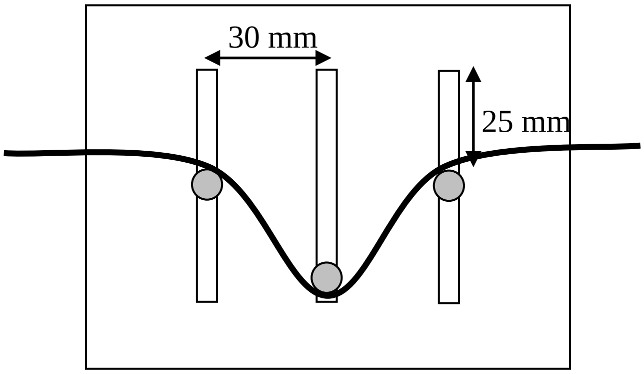


Figure 4.3 Schematic diagram of the heated shear pins used to spread the molten polymer on the carbon fibre tow (side view)

The main purpose of the heated shear pins is to further spread the polymer giving a smooth finish to the composite prepregs. The tension generated from the wrap angle of the heated pins also spreads the fibres further, driving the polymer into the tow and eliminating voids. Any fibre "fuzzes" that are produced during manufacturing can also be collected here. Unit 8 is a water-cooled rolling die (15 mm width) which is used to consolidate the hot, smooth carbon fibre polymer melt tow into a thin prepregs. The pressure exerted onto the prepregs while passing through Unit 8 can be adjusted by adding additional weights onto the upper roller to maximise the effect. The haul off device (Unit 9) is a belt-drive pulling unit (Model 110-3; RDN Manufacturing Co., Bloomingdale, USA), which controls the whole processing speed. Finally the as-produced continuous UD carbon fibre reinforced thermoplastic composite prepregs is wound up onto a spool using a VEXTA Gear Head Drive (GFB5G2000, Oriental Motor Co, Ltd. Japan) (Unit 10).

4.2.5 Manufacturing of UD carbon fibre reinforced PVDF composite prepregs

Continuous UD carbon fibre reinforced thermoplastic composite prepregs (10.5 mm wide and 0.1 mm thick) were manufactured using our CL described above. A 12k carbon fibre roving was fixed into the creel and a pre-tension of 1.5 N was applied. The fibre tows were then passed through the impregnation bath containing the powder slurry, which was agitated using two 60 mm magnetic stirring bars. The wet polymer impregnated fibre tow was then passed into the drying oven set to 130°C. The fibres were dried completely before melting to ensure no water is entrapped within the composite. Once the water was removed, the tow then entered the second (melting) oven. This oven was set to operate at 220°C for fibre reinforced PVDF composites (CF/PVDF) in order to melt the polymer. The prepreg coming out from the melting oven was passed over the shear impregnation pins operated at 220°C for the CF/PVDF. The melt impregnated prepreg was passed through the water-cooled consolidation unit to consolidate the prepregs. The prepreg was pulled through the line by the haul-off at 1 m/min and wound up onto a spool. During manufacturing, the width and the thickness, as determined by the spreading of the fibres, of the composite prepregs, produced was monitored using a calliper (Series 500, Mitutoyo, Hampshire, UK; accuracy = 0.02 mm). The fibre volume content (V_f) of the as-produced composite prepregs was measured using the methods explained in section 4.2.6.1.

4.2.6 Effects of processing conditions

4.2.6.1 Determination of optimum bath concentration for consistent resin content of carbon fibre/ PVDF composite prepregs

Initial bath concentrations of 9 wt% and 10 wt% were used to identify the optimum concentration for consistent carbon fibre/PVDF composite prepregs with V_f of 60 % to be produced. The time required to reach steady state; a continuous composite prepregs of at least 15 m having a uniform V_f, for each experimental run using different bath concentrations was recorded. The V_f was determined by cutting 1 m long samples of UD carbon fibre reinforced thermoplastic composite prepregs and weighing them using an analytical balance (HR-120-EC, A&D Instruments, Oxford, UK). V_f was calculated using the following equation:

$$V_f = \frac{\rho_m W_f}{\rho_f W_m + \rho_m W_f} \bullet 100\% \tag{4.1}$$

where ρ and W are the density and the weight and f and m correspond to the fibre and the matrix, respectively. W_f of 1 m 12k AS4 carbon fibre tow[§] = 0.858 g, ρ_f = 1.79 gcm^{-3}, $\rho_{m(PVDF,\ Kynar®\ 711)}$[**] = 1.80 gcm^{-3}.

During manufacturing, the V_f of the manufactured composite prepregs changes as a function of processing time because the PVDF powder from the impregnation bath is consumed. This causes the V_f of the produced composite prepregs to increase. Therefore, for a consistent carbon fibre/ PVDF composite with V_f of 60 % to be produced, the concentration of PVDF powder in the impregnation bath must be maintained as constant as possible. Different bath concentrations throughout the manufacturing process were confirmed by extracting 5 ml of the polymer slurry from the bath during steady state and evaporating off the water using a hot plate.

[§] *HexTow AS4 carbon fibres product data sheet. Link in: http://www.hexcel.com/NR/rdonlyres/5659C134-6C31-463F-B86B-4B62DA0930EB/0/HexTow_AS4.pdf accessed on 28.07.10*

[**] *Kynar® & Kynar Flex® PVDF performance characteristics & Data. Link in: http://www.arkema-inc.com/kynar/literature/pdf/743.pdf accessed 28.07.10*

4.2.6.2 Pin configurations within the impregnation bath

The tension applied on the fibre tow directly influences the spreading of the fibre tow and, therefore, the polymer powder pick up rate. Tensions of 3 N, 6 N and 9 N were induced by adjusting the pins located inside the impregnation bath (Figure 3.2), details of individual configurations can be found in Table 4.1. The tow tension was logged in the Izumi tension control system throughout individual experimental runs while the as-produced prepregs were visually monitored and the width, thickness and V_f were measured.

Table 4.1 Details of pin locations and their corresponding positions for induced tension

Tension/ N	***Position***	***Pin locations***
0.3	H/H/H	1,7,13
0.6	H/H/H/H/H	1,4,7,10,13
0.9	H/H/H/H/H/H/H	1,3,5,7,9,11,13

4.2.7 Preparation of composite test specimen

UD carbon fibre reinforced PVDF composite laminates were prepared by cutting the as-produced composite prepreg into 20 cm long sections. For flexural and short beam shear specimens, 34 layers of the cut composite prepregs were stacked and tightly wrapped using a release film (Upilex 25S, UBE Industries Ltd., Tokyo, Japan) before placing them into a stainless steel mould (200 mm × 12 mm). The mould containing the stacked composite prepregs was then heated for 10 min in a hot press (Model# 4126, Carver Inc., Indiana, USA) at 190°C followed by a slow increase in pressure to 1 t, which was held for 2 min before transferring the mould to hot press (Model# 4126, Carver Inc., Indiana, USA) operated at 80°C and held for 10 min at 0.5 t. The specimen was then removed from the mould after it was cooled to ambient temperature. A diamond blade cutter (Diadisc 4200, Mutronic GmbH & Co, Rieden am Forggensee, Germany) was used to cut test specimens to the required dimensions (please see section 4.2.10 and 4.2.11) for mechanical testing. The edges of the test specimens were smoothed by grinding using P60 grit sandpaper.

4.2.8 Microscopic analysis of composite test specimens

Transverse sections of compression moulded specimens were embedded into a polyester resin (Kleer Set, MetPrep, Coventry, UK). The resin was cured at room temperature for 24 h before being polished using resin bonded diamond grinding discs (ApexDGD 60µm Buehler Ltd, Illinois, USA). Specimens were ground first using a water medium for 2.5 min at a pressure of 0.2 MPa and a speed of 220 rpm. This was followed by a diamond suspension (MetaDi 6 µm, Buehler) for 2 min. In order to obtain a scratch and void free surface finish of the cross section of composites for optical analysis, specimens were further polished using a 3 µm and 1 µm diamond suspension, respectively, for 5 min at a pressure of 0.27 MPa and a speed of 150 rpm. Processed specimens were then examined under an optical microscope (BH2, Olympus, Tokyo, Japan).

4.2.9 Crystallinity of composite specimens

The melting and crystallisation profiles of the manufactured specimens were determined using dynamic differential scanning calorimetry (DSC) in a nitrogen atmosphere at a heating rate of 10 °C/min over the range from -100 to 220 °C for carbon fibre/PVDF. Samples (typically 10 mg) were sealed in a Tezro-aluminium pan. An empty sealed pan was used as reference. The melting temperature (T_m) and heat of melting (ΔH_m) were determined from the heat flow curves. The degree of crystallinity (X_c) was calculated as follows:

$$X_c = \frac{\Delta H_m}{H_f^0} 100\% \tag{4.2}$$

where H_f^0 is the heat of fusion of 100 % crystalline PVDF (104.5 J/g)[178].

4.2.10 Flexural testing

Flexural moduli and flexural strengths are of importance in engineering practice because composites are often subjected to bending load. Individual test specimens with dimensions of 95 mm × 10 mm × 2 mm were prepared. The specimens were loaded into a three-point bending rig (span-to-thickness ratio of 32:1) equipped with a 5 kN load cell (model 4466, Instron, Buckinghamshire, UK). The test was carried out according to the ASTM D790-03 standard [179] with a crosshead speed of 1 mm/min until failure. The flexural strength σ_f and flexural modulus E_f were calculated using the following equations:

$$\sigma_f = \frac{3P_{MAX}S}{2bh^2}\left[1+6\left(\frac{D}{S}\right)^2 - 4\left(\frac{h}{S}\right)\left(\frac{D}{S}\right)\right] \tag{4.3}$$

and

$$E_f = \frac{S^3 m}{4bh^3} \tag{4.4}$$

where D is the central deflection of the specimen at failure load P_{MAX}, S the span length, m the gradient of the initial part of the force-displacement curve, b the specimen width and h the specimen thickness. The flexural strength and modulus of composite laminates were calculated from eight measurements in order to obtain statistically relevant values.

4.2.11 Short beam strength testing

The short beam strength test was chosen as a screening/ ranking test to characterise the interlaminar shear characteristics of the manufactured composites because it is one of the simplest and most commonly used test methods [180]. It should be noted that the ASTM 2344 [181] states that although the dominant failure during the test is purely shear, the internal stresses are complex and various failure modes can occur. Thus the results of this test are termed "apparent" short beam strength or "apparent" interlaminar shear strength. Test specimens of carbon fibre/PVDF laminates with dimensions of 20 mm × 10 mm × 2 mm were loaded under three-point bending using a jig with a 10 mm span (i.e. span-to-thickness ratio S/h of 5:1). Such recommended S/h allows for interlaminar shear failure to be induced. The test was carried out with an Instron equipped with 1 kN load cell (model 4466, Instron, Buckinghamshire, UK). The loading rate was set to 1 mm/min and the test was carried out following ASTM D2344 [181]. The apparent interlaminar shear strength (ILSS) was calculated using the following equation:

$$F^{SBS} = ILSS = 0.75\frac{P_{MAX}}{bh} \tag{4.5}$$

where P_{MAX} is the maximum load observed during the test, b is the specimen width and h is the specimen thickness. The test was repeated eight times to obtain a statistical average and the error reported are standard deviations.

4.3 Results and Discussion

4.3.1 Particle size distribution of slurry polymer for wet impregnation

The particle size of a PVDF powder slurry during wet impregnation process in the production of unidirectional carbon fibre reinforced thermoplastic composite laminates is crucial for an optimum polymer pickup by the fibre tow [182]. Different particle sizes behave differently during wet impregnation of the carbon fibre tow. Polymer powders with small particle size may be filtered through the spread carbon fibre tow inside the impregnation bath and polymer powder with larger particle size may rest on the surface of the tow which leads to an uneven resin rich layer of the produced prepreg. Such partial or imperfect, i.e. impregnation due to resin rich regions or fibre contacts will result in mechanical weak points in the fabricated composites [172].

The average particle size d_{50} of PVDF (Kynar® 711) was measured to be 5 µm (Figure 4.4) which is similar to that quoted by Arkema [177]. In order to obtain the desired prepregs with V_f of 60%, 9 wt% polymer powder concentration was utilised for manufacturing of continuous CF/PVDF prepregs.

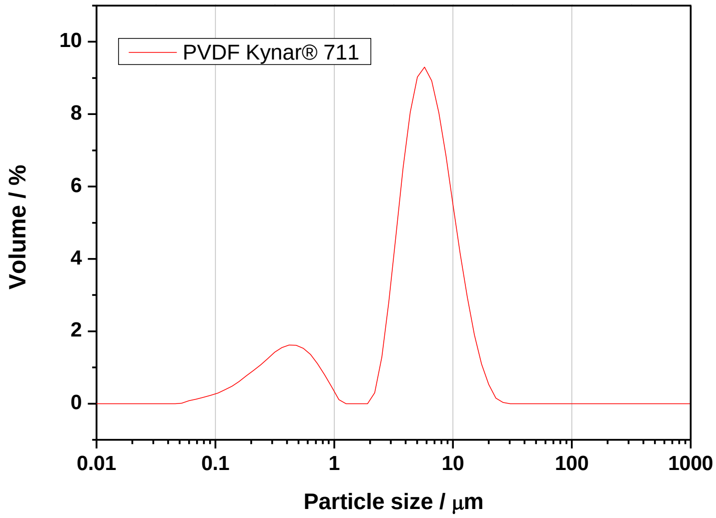


Figure 4.4 Particle size distribution of PVDF Kynar® 711 powder suspended in water

4.3.2 Influence of processing parameters

The effect of the initial polymer bath concentrations (9 wt% and 10 wt%) on polymer pick up (impregnation) during manufacturing was studied. A preliminary run with 10 wt% of PVDF bath concentration was carried out. However, it was realised that 10 wt% is not the desired bath concentration to manufacturing carbon fibre reinforced PVDF with V_f of 60%. 10 wt% of bath concentration gave significantly lower V_f (in the range of 50-55%). Therefore, a lower bath concentration of 9 wt% was selected which resulted in consistent V_f of 60% with minimal top up frequency. It was established that a top up of 50 ml of concentrated polymer suspension containing 20 wt% of polymer suspension had to be added periodically to the impregnation bath. This bath concentration enabled steady state to be maintained after 10 min of stabilisation time. Composite prepregs manufactured with 0.3 N tension caused only by the friction between the tow and impregnation pins located inside the powder impregnation bath had a poor quality of impregnation. This is assessed by observing the composite manufactured. With low tension in the impregnation bath, there were patches of dry fibres along the length of the prepreg manufactured. The width of the produced composite prepregs also fluctuated. Furthermore, when such composite prepregs were flexed by hand, it could be observed that the inner part of the fibre tow consisted of dry fibres. The quality of composite prepregs manufactured with 0.6 N tension induced by the tow/ impregnation pin friction was found to vary as a function of time. Steady state was not achievable even after 60 min of manufacturing time. The V_f of the composite prepregs manufactured fluctuated from 55-68% throughout the duration of the experiment, which made it difficult to identify the corresponding bath concentration required to give a consistent V_f of 60%. Carbon fibre reinforced PVDF prepregs manufactured with higher induced tension of 0.9 N resulted in much better composite prepregs as compared to those manufactured with 0.3 N and 0.6 N induced tensions. The V_f as well as the width of fabricated composite prepregs was consistent throughout and could easily be controlled. This pin configuration allows for increased fibre residence time in the polymer suspension and promoted good fibre spreading for efficient polymer pick-up by the fibre tow.

The manufacturing speed was varied from 1 m/min, 2 m/min to 3 m/min. It was observed that at a processing speed of 3 m/min, the PVDF powder could not be sufficiently melted, as could be seen by the white powder situated within the fibre tow exiting the melting oven. This is governed by the residence time of the impregnated tow inside the oven, which was too short. At 2 m/min manufacturing speed, patches of dry polymer powder and melted polymer were observed on the impregnated prepreg at random intervals. This indicated that a lower processing speed was required and at 1 m/min, good quality composite prepregs with consistent V_f over time were produced.

4.3.3 Quality of UD carbon fibre reinforced PVDF composites

UD carbon fibre reinforced PVDF composites possessed a uniform fibre volume fraction of 58-62% (Table 4.2) confirming that carbon fibre/PVDF manufactured using the CL was of consistent quality. It can be seen from Table 4.2 that the crystallinity X_c of the carbon fibre/PVDF composites laminates manufactured in-house was 18%. However, it is worth mentioning that X_c is highly relevant in this study because PVDF is a semi-crystalline thermoplastic and was used as the matrix. X_c of the polymer matrix can influence mechanical (higher X_c means stiffer matrix) as well as thermal properties since re-processing the composite prepreg into laminates requires melting and consolidation.

Table 4.2 Properties of investigated unidirectional carbon fibre reinforced thermoplastic composites

Specimens	***FVC/ %***	***Xc/ %***	***T_{m1}/ °C***	***ΔH/ $Jmol^{-1}$***
In-house manufact. CF/PVDF Kynar® 711	58-62	18.7	166	1.5

The cross-sectional view of the composite laminates (Fig. 4.5) gives an insight into the quality of the produced composite prepregs. This cross-sectional image of the in-house manufactured carbon fibre/PVDF reveals that the reinforcing fibres were evenly distributed within the matrix with minimal voids.

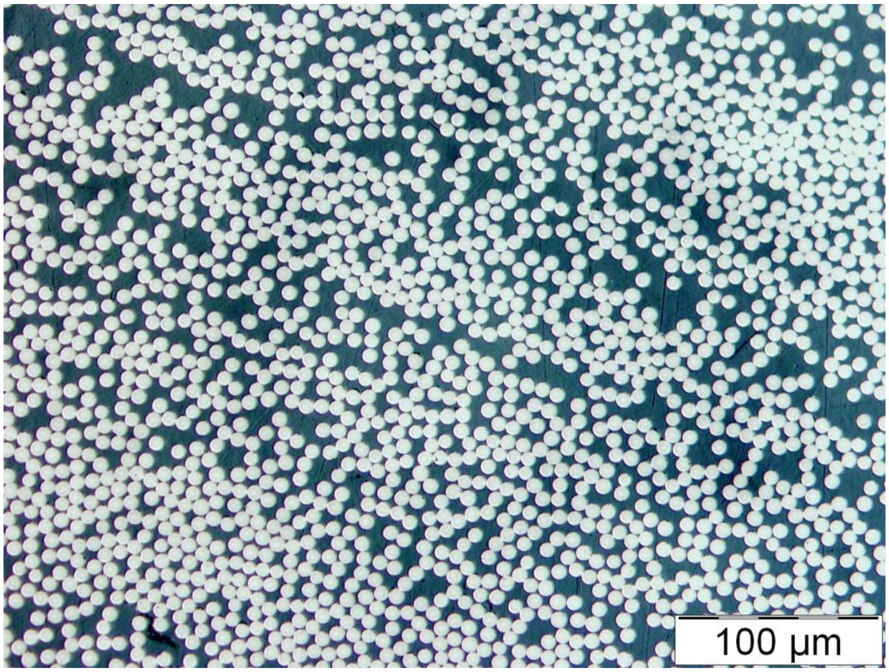


Figure 4.5 Polished cross section (×50) of manufactured CF/PVDF laminate

4.3.4 Mechanical properties of carbon fibre reinforced PVDF composites

Industrial scale manufacturing of APC2 involves tens of tows of carbon fibres to produce 15 cm wide prepregs, therefore, the presence of twists within the carbon fibre tow can be compensated for when multi-tows are used and overlap among each other. However, only one carbon fibre tow was used to manufacture composites using the CL and hence, the effect of twists present within the fibre tow is more likely to magnify the influence on the alignment of the fibres compromising the strength. Having said this, UD carbon fibre reinforced PVDF composites, with reasonable prepreg quality were successfully manufactured and the mechanical performance data are presented in Table 3, however, no baseline data exist for comparison purposes.

Table 4.3 Mechanical properties of investigated unidirectional carbon fibre reinforced PVDF composites

Specimens	***ILSS/ MPa***	***Flex Strength/ MPa***	***Flex. Modulus/ GPa***
In-house manufact. CF/PVDF Kynar® 711	7 ± 0.2	225 ± 7	80 ± 2

The values obtained from short beam shear and flexural tests showed that the values obtained for the strength of the carbon fibre reinforced PVDF are low compared to conventionally available carbon fibre reinforced epoxy composites. This may be attributed from the low adhesion between the constituents leading to a poor interface and ultimately low mechanical performance. However, carbon fibre/PVDF is of interest for use in oil and gas applications because of its chemical inertness [183]. Due to this intrinsic property of PVDF together with its superior melt processing characteristics compared to other inert fluoropolymers such as polytetraflurorethane, (PTFE), it was demonstrated that it is viable to manufacture continuous UD carbon fibre reinforced PVDF prepregs within reasonable quality in both microscopic level as well as its macro-mechanical properties.

4.4 Summary

A laboratory scale modular composite line for manufacturing continuous UD carbon fibre reinforced PVDF composite prepregs was developed. The process uses a wet impregnation route for polymer impregnation to produce prepregs (10.5 mm wide and 0.2 mm thick) with consistent fibre volume content between 58 to 62%. However, this can be tailored by controlling the polymer powder concentration in the impregnation bath and manufacturing speed. Manufacturing other thermoplastic composites is also possible provided that polymer powder is available or can be produced by cryogenic grinding of polymer pellets. For example, in this chapter, carbon fibre reinforced PVDF prepregs were produced using this laboratory scale modular composite line. The same setup can be adopted for any other thermoplastic composites by adjusting processing parameters such as slurry based polymer powder suspension and temperature. However, more research is required to fully optimise the mechanical properties of CF/PVDF composites in order to utilise the advantages this composite has to offer.

5.0 Unidirectional carbon fibre reinforced poly(vinylidene fluoride): Impact of atmospheric plasma fluorination on composite performance[††]

A powder impregnation process with integrated inline continuous atmospheric plasma fluorination (APF) of carbon fibres (CF) to produce unidirectional carbon fibre/polyvinylidenefluoride (PVDF) prepregs with a fibre volume fraction of 60 % was developed. The prepregs were processed into test laminates by compression moulding. The short-beam strength improved by up to 200 % for the specimens containing atmospheric plasma fluorinated carbon fibres with a fluorine content of 3.7 at.-%, as determined by XPS. The flexural strength and modulus of the laminated CF/PVDF composites containing APF treated carbon fibres also increased by 110 % and 37.5 %, respectively. The composite laminates were also subjected to tension loads and 10% improvement of the tensile strength was observed for composites containing APF treated fibres as compared to those containing as-received CF. The essential and non-essential work of fracture of the composites containing fluorinated CF/PVDF determined using the trousers test increased by 140% and 104%, respectively. An attempt was made to measure the interlaminar fracture toughness of the composite. However, due to complications of the nature of PVDF material being tough, the results obtained correlates the flexural strength of the composite. The details will be discussed in the chapter.

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

5.1 Introduction

Exploring deep-sea oilfields remains challenging, which is partially due to the harsh environments encountered requiring superior materials performance and durability. Scientists and engineers are aiming to design and fabricate materials that can deliver exceptional mechanical and chemical performance in the most severe environments that are at the same time cost effective and provide weight and energy savings [12, 184-187]. Carbon fibres have become very important as reinforcement for composites over the last 40 years because of their high strength, high modulus and low density [188]. Fibre reinforced composites can be found in load-bearing and structural applications such as coiled tubing, drill rods, field flow lines for deep sea oil and gas explorations [188, 189]. Epoxy matrices are commonly used in high volume industrial applications such as pipes, tanks, boats etc., because of their relatively good mechanical properties and ease of manufacturing [190]. However, the common drawbacks are that fibre reinforced epoxies are very brittle, cannot withstand high temperatures, are non-recyclable and have a limited chemical stability [191, 192]. Alternatively, high temperature resistant thermoplastics have been developed to enhance both heat resistance and overcome problems related to brittleness [193, 194].

High performance thermoplastic matrices such as polyphenylenesulphide (PPS), polyetheretherketone (PEEK) and polyetherimide (PEI) have high maximum service temperature of 220°C, 250°C, 171°C, respectively, compared to typical standard epoxy resin system, such as diglycidyl ether of bisphenol A (DGEBA) and tetraglicidyl diaminodiphenylmethane (TGDDM), which have the maximum service temperatures of 123°C and 190°C [195]. Although PEEK is very tough and has a service temperature of up to 250°C, it is rather expensive and also difficult to process as it requires a processing temperature of around 400°C [196, 197]. On the other hand, polyvinylidene fluoride (PVDF) like many other fluoropolymers not only exhibits excellent toughness but also has the same heat deflection temperature of 140°C at 0.46 MPa as polyamide 12 (PA12). In addition, PVDF has a much lower water absorption (0.03 %) compared to PA 12 (1.5 %)[‡‡], which is the key parameter for deep-sea oil and gas pipelines. PVDF is resistant to

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[‡‡] *MatWeb Material Property data: Arkema Group Kynar® 710 PVDF; EMS-Grivory Grilamid® L20W20 Nylon 12, As Conditioned. Link in:* http://www.matweb.com/search/DataSheet.aspx?MatGUID=7378d6bf9bf84f2b8dcc1f49d40eeb44*;* http://www.matweb.com/search/DataSheet.aspx?MatGUID=5bdf8fa7f0b64e08bc0f3adad214a35a *Accessed on 28.07.2010.*

corrosion under severe environmental stresses and it costs much less compared to PEEK and yet it is still fairly easy to process [198-201]. However, PVDF exhibits the same problems as other fluoropolymers; namely low adhesion which causes incompatibility at the fibre-matrix interface [19, 202], which is critical for efficient load transfer from the matrix to the fibres via the interface. The performance of a composite is governed by the fibre-matrix adhesion which directly affects the shear and delamination resistance [203]. Nevertheless, PVDF has the potential to be an alternative matrix used in composite materials [204, 205] because the surface chemistry of carbon fibres can be tailored to suit the matrix to be reinforced [206]. There is increasing evidence that fluorination of carbon fibres leads to a much improved interface due to increased Van der Waals interaction between the fluorinated carbon fibre and the PVDF matrix [18, 20, 207]. A method has recently been reported allowing for the continuous fluorination of carbon fibres using an atmospheric pressure plasma system [21] and has shown that atmospheric plasma fluorination of carbon fibres indeed enhances the adhesion to PVDF [71].

This chapter describes how carbon fibres are continuously atmospheric plasma fluorinated (APF) during composite production using a powder-impregnation method [176, 182, 208-211]. Thin (0.2 mm) unidirectional (fluorinated) carbon fibre reinforced PVDF prepregs were produced. Conventional interface dominated mechanical tests were performed to study the adhesion between the reinforcing fibres and matrix.

5.2 Experimental

5.2.1 Materials

From the patent literature [212], it has been reported that high temperature thermoplastic polymers exhibit a better adhesion to unsized carbon fibres. Therefore, commercially available high tensile strength, unsized but otherwise standard industrially carbonised and oxidised polyacrylonitrile (PAN) based carbon fibres (HexTow™ AS4 12K and Torayca T700GC-91), supplied by Hexcel Corporation (Duxford, Cambridge, UK) and Toray Industries (Tokyo, Japan) were used for this study. The polyvinylidenefluoride (PVDF) used was Kynar® 711, supplied by Arkema (Arkema Inc., Philadelphia, US). Average particle size $d_{50} = 5.5$ μm). The surfactant used to stabilise the suspension of PVDF powder in water was Cremophor® A25 (BASF GmbH, Ludwigshafen, Germany). Gases used as feed gas during the plasma modification were chlorodifluoromethane (Freon 22) and nitrogen (N_2) (BOC Ltd Co., Surrey, UK).

5.2.2 Inline carbon fibre modification while manufacturing unidirectional carbon fibre/PVDF prepregs

Unidirectional carbon fibre reinforced PVDF prepreg with a fibre volume fraction of 60% was manufactured using a laboratory scale composite line (CPL) based on the powder impregnation technique used for thermoplastic composites manufacturing. A tension controlled 12K carbon fibre roving was looped three times inside a borosilicate glass tee piece over phenolic polymer roller pins while exposed to the atmospheric plasma jet (Openair-Plasma-Technology system, single rotating FLUME Jet RD1004, Plasmatreat, Steinhagen, Germany). The plasma jet was generated by ionising a feed gas mixture of chlorodifluoromethane and N_2 in a 1:70 ratio with a flow rate of 35 L / min creating a pressure drop of 2.3 bar at the jet nozzle. A detailed description of the setup and operational parameters can be found in Ref. [158, 213].

The fibres were spread using a series of set pins located in the powder impregnation bath, which contained 9 wt% PVDF and 2 wt% of surfactant with respect to the polymer in 2.5 L of deionised water. The polymer impregnated carbon fibre tow was first passed through a drying oven to evaporate the water followed by a second oven to melt the polymer. The polymer melt impregnated fibre tow was then passed over a set of three heated pins to spread the molten polymer along the fibre tow before being consolidated by water cooled rollers and into a continuous unidirectional carbon fibre reinforced composite prepreg with dimensions of 10 ± 2 mm width and 0.2 ± 0.05 mm thickness. Finally the prepreg was wound up. Three different manufacturing speeds (0.33 m/min, 0.75 m/min and 1.0 m/min) were chosen. The processing speed was controlled using a belt-drive pulling unit (Model 110-3, RDN manufacturing Co. lllonis, USA), which also determined the residence time (1.8 min, 0.8 min and 0.6 min) of the carbon fibres within the glass chamber for APF.

5.2.3 Ensuring consistent fibre volume content of as produced prepregs

Various methods were used to ensure the quality of the manufactured composite prepreg. Samples of the polymer impregnated fibre tow were taken at different stages during the drying and melting stages on the CPL and were observed using an optical microscope (BH2, Olympus, Tokyo, Japan). This allowed optical inspection of the polymer-impregnated fibre tow to ensure the temperature in the drying and the melting ovens were adequate with respect to the processing speed. In the meantime, the width and the thickness, as determined by the spreading of the fibres, of the composite prepreg, produced was closely monitored using a calliper (Series 500, Mitutoyo, Hampshire, UK; accuracy= 0.02 mm). The fibre in matrix distribution in the composite laminates was also studied.

Preliminary experiments were performed to determine the PVDF powder concentration required in the impregnation bath to produce composite prepregs with a volume fraction of 60%. Different PVDF powder concentrations (9 wt% and 10 wt%) were chosen and prepregs manufactured. The CPL was operated at a speed of 1 m/min while the atmospheric plasma system was off during this exercise. Unidirectional carbon fibre reinforced PVDF prepregs produced were collected, cut into 1 m long samples and weighed using an analytical balance (HR-120-EC, A&D Instruments, Oxford, UK). To calculate the fibre volume content V_f, the following equation was used:

$$V_f = \frac{\rho_m W_f}{\rho_f W_m + \rho_m W_f} \bullet 100\% \tag{5.1}$$

where ρ and W are the density and the weight and f and m correspond to the fibre and the matrix, respectively. W_f of 1 m AS4 carbon fibre[§§] = 0.858 g, ρ_f = 1.79 gcm^{-3}, ρ_m[***] = 1.80 gcm^{-3}.

PVDF powder from the impregnation bath is consumed during the manufacturing process causing V_f of the produced composite prepreg to increase. For a consistent composite with a V_f of 60% to be produced, the PVDF powder in the impregnation bath must be maintained as constant

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[§§] *HexTow AS4 carbon fibres product data sheet. Link in: http://www.hexcel.com/NR/rdonlyres/5659C134-6C31-463F-B86B-4B62DA0930EB/0/HexTow_AS4.pdf Accessed on 28 July 2010*

[***] *Kynar ® & Kynar Flex ® PVDF performance characteristics & Data Link in: http://www.arkema-inc.com/kynar/literature/pdf/743.pdf Accessed 28 July 2010*

as possible. The polymer concentration in the impregnation bath was maintained by adding 50 ml of concentrated polymer suspension containing 20 wt% of PVDF to the impregnation bath every 10, 15 and 20 min when the manufacturing speed was set at 1 m/min, 0.75 m/min and 0.33 m/min respectively. These time intervals were established by monitoring the V_f of the composite produced.

5.2.4 Preparation of composite test specimen

Test specimens of unidirectional carbon fibre reinforced PVDF composite laminates were prepared by cutting the as-produced composite prepreg into 15 and 20 cm long strands. For flexural and short beam shear specimens, a total 34 layers of the cut composite prepregs were stacked and tightly wrapped using a release polyimide film (Upilex 25S, UBE Industries Ltd., Japan) before placing them into a stainless steel mould (200 mm × 12 mm). For Mode I specimens, 5 pieces of as produced plies were overlapped and welded together using a soldering iron (WECP-20 Weller, Cooper Group, Germany) to create a combined ply width of 25 mm. Forty of such unidirectional carbon fibre reinforced PVDF plies with a width of 25 mm were layed up and at the opening end, a release film separator (60 mm x 25 mm x 0.13 mm, Upilex 12.5 SN, UBE Industries Ltd., Japan) was inserted at mid plane. The layup was then placed into a stainless steel mould (150 mm × 25 mm). For Mode II specimens, a stainless steel mould (150 mm x 12 mm) was used to prepare individual test specimens and this was done by laying 40 plies of unidirectional carbon fibre reinforced PVDF composite which were separated in the mid plane by a 60 mm x 10 mm release film (Upilex 12.5 SN, UBE Industries Ltd., Japan) at the opening end. For tensile test specimens, a total of 11 layers of composite prepregs were stacked into a steel mould (200 mm x 12 mm x 10 mm).

The mould containing the stacked composite prepregs was then placed in to a hot press (Model# 4126, Carver Inc., Indiana, USA) at 190°C and pre-heated for 10 min. After which the pressure was increased slowly and held for 2 min before transferring the mould to a hot press (Model# 4126, Carver Inc., Indiana, USA) operated at 80°C and held for 10 min. The mould was then allowed to cool for 15 min to ambient temperature before the specimen was removed from the mould. Test specimens were cut to the required dimensions for mechanical testing using a diamond blade cutter (Diadisc 4200, Mutronic GmbH, Rieden am Forggensee, Germany). The quality of the edges was improved by grinding using P60 grid sandpaper. All specimens were annealed in a vacuum oven (8465F, Weiss Gallenkamp, Loughborough, UK) overnight at 80°C.

5.2.5 Flexural testing

For details on the flexural tests, please refer to section 4.2.10 in Chapter 4.

5.2.6 Short beam strength testing

The short beam strength method is the simplest and, therefore, the most commonly used test to characterise interlaminar shear behaviour. During the short beam strength test, interlaminar shear is generated through a three-point bending mode in order to characterise the apparent interlaminar shear properties of unidirectional fibre reinforced composites. Short beam strength testing is very similar to flexural testing only that the span-to-thickness ratio is much smaller. This test allows large shear stresses to be introduced through the thickness of the test specimen while reducing the tensile and compressive flexural stresses. For details on the short beam shear tests, please refer to section 4.2.11 in Chapter 4

5.2.7 Mode I double cantilever beam interlaminar fracture toughness

The effect of APF on composites resistance to delamination was studied using the Mode I non-modified double cantilever beam theory (DCB) test according to ASTM 5528 [214]. Individual test specimens were fractured using an Instron 4466 (Buckinghamshire, UK) equipped with a 10 kN load cell at a constant rate of 1.0 mm/min until failure [214]. The initiation critical energy release rate, G_{IC} was calculated from the modified beam theory (MBT):

$$G_{IC} = \frac{3P\delta}{2ba} \tag{5.2}$$

where P is the load at which the crack growth initiated as observed through the travelling microscope, δ is the load point displacement, b and a are the specimen width and delamination length, respectively. The initiation critical energy release rate was determined from at least 8 measurements per condition in order to obtain a statistically significant average values and the error bars show the standard deviations.

5.2.8 Mode II end notched flexure interlaminar fracture toughness

The Mode II interlaminar fracture toughness was determined by means of a 3-point bend or also known as end notched flexure (ENF) test on the unidirectional carbon fibre reinforced PVDF laminates. Unidirectional carbon fibre reinforced PVDF laminates of 150 mm x 10 mm x 3.0 mm were used as test specimens which were mounted onto a 3-point bend test rig. The span length was set to 100 mm. The test was carried out in an Instron 4466 (Buckinghamshire, UK) equipped with a 5 kN load cell at a constant rate of 0.5 mm/min until failure according to JIS Standard K 7086 [215]. The calculated crack length for the critical load to fail the composite in shear is given by the equation:

$$a_1 = [\frac{C_1}{C_0} a_0{}^3 + \frac{2}{3}(\frac{C_1}{C_0} - 1)L^3]^{1/3} \tag{5.3}$$

where C_1 and C_O are the compliances for the critical load and at the elastic portion of the load/displacement curve respectively, a_o is the initial crack length and L is the specimen length. The initiation stage interlaminar fracture toughness of Mode II, G_{IIC} was calculated using the equation:

$$G_{IIC} = \frac{9a_1{}^2 P_c{}^2 C_1}{2B(2L^3 + 3a_1{}^2)} \tag{5.4}$$

where P_c is the initiation critical load and B is the specimen width. The Mode II interlaminar fracture toughness was determined from at least 8 measurements per condition to obtain a statistically meaningful average value and the error bars indicate standard deviations.

5.2.9 Axial tensile properties of unidirectional carbon fibre reinforced PVDF

The tensile specimens were prepared according to ASTM D3039 [216] with a laminate dimension of 200 mm x 12 mm x 0.7 mm. Four strips of 50 mm long ±45° glass fibre reinforced epoxy composite tabs were used as end tabs leaving 100 mm gauge length on the test specimen. The surface of the end tabs and specimen to which the end tabs were glued were sand blasted to ensure a good adhesion between the two surfaces. The end tabs were then glued onto the test specimen by using CN Adhesive (General purpose, Tokyo Sokki Kenkyujo Co. Ltd., Japan). A strain gauge, FLA 2-11 (Tokyo Sokki Kenkyujo Co. Ltd., Japan) was placed in the centre of the gauge length of the specimen and glued using CN adhesive. Tensile tests were carried out at a crosshead speed of 2 mm/min in an Instron 4505 (Instron, High Wycombe, Buckinghamshire, UK), equipped with 100 kN load cell. Every effort was made to correctly align the specimens in the jaws of the machine, thus ensuring a width-wise uniform stress field. The test was carried out until failure and the ultimate tensile strength σ^{tu} and tensile chord modulus of elasticity (Young's modulus E^{chord}) were calculated based on the following equations;

$$\sigma^{tu} = \frac{P_{MAX}}{A} \tag{5.5}$$

and

$$E^{chord} = \frac{\Delta\sigma}{\Delta\varepsilon} \tag{5.6}$$

where P_{MAX} is the maximum load at failure (N), A is the average cross section area (mm^2), $\Delta\sigma$ and $\Delta\varepsilon$ are the difference in tensile stress and strain between strain points of 0.001 and 0.003, respectively. The test was carried out on 8 specimens to obtain statistical average values and the errors presented are standard deviations.

5.2.10 Tearing properties of unidirectional carbon fibre reinforced PVDF composite prepregs

The tearing properties of the unidirectional carbon fibre reinforced PVDF prepregs were assessed using a trouser leg tearing test, a method originally developed for rubber material [217, 218] to study the essential work of fracture [219-221]. A crack length of 50 mm was cut along the axial direction of a 100 mm x 10 mm x 0.2 mm ply using a sharp pen knife. The ends of the 2 legs were fixed onto a tensile jig mounted onto an Instron (model 4466, Instron, Buckinghamshire, UK) using a 1 kN load cell and were displaced in opposite directions at a constant rate of 20 mm/min until failure. The corresponding force required to fail individual specimens were logged using a computer and the specific essential work of fracture, W_e as well as non-essential specific plastic work, w_p were determined using the following equation:

$$W_e = \frac{F}{t^2} = 2w_p t \tag{5.7}$$

where F is the equilibrium force during the steady state tearing process and t is the specimen thickness. The test was repeated 8 times per condition to obtain a statistically significant average.

5.3 Results and Discussion

Previously conducted single fibre pull-out tests have shown that batch APF of carbon fibres leads to an improved apparent interfacial shear strength between the fluorinated carbon fibres and PVDF [71]. In this chapter, the continuous APF was incorporated into the manufacturing process to produce unidirectional carbon fibre (AS4) reinforced PVDF composites and this allowed an examination of whether the increased interfacial shear strength translates into improved mechanical properties. X-ray photoelectron spectroscopy (XPS) was used to determine the surface fluorine content of APF treated carbon fibres. Fluorine contents of 3.7 at.-%, 2.8 at.-% and 1.7 at.-% were recorded for AS4 carbon fibres fluorinated at processing speeds of 0.33 m/min, 0.75 m/mm and 1 m/mm [158]. A detailed discussion of the surface composition and corresponding XP spectra as well as the surface and bulk properties of the fibres continuously fluorinated in atmospheric plasma can be found in Ref [158]. Similarly, fluorine content of 3.7 at.-%, 1.8 at.-% and 1.7 at.-% was determined for T700 carbon fibres [144] when fluorinated at the same processing speeds at stated above, respectively (Table 5.1).

Table 5.1 Surface composition (in at.%) of APF AS4 and T700 carbon fibres determined by XPS

Processing speed/mmin^{-1}	***AS4 F/at.-%***	***T700 F/at.-%***
0.33	3.7	3.7
0.75	2.8	1.8
1.00	1.7	1.7

Initially the optimum PVDF powder concentration in the impregnation bath was determined to be 9 wt% so that unidirectional carbon fibre reinforced PVDF composite prepregs with fibre volume fraction of 60 % could be manufactured consistently. The microscope images of the powder impregnated carbon fibres taken from the drying stage show that the fibres in the tow are well impregnated by PVDF powder and that all water is removed in the drying section (Fig. 5.1a). The microscope image of the polymer melt impregnated fibre tow also suggests that the temperature control in the heating oven is sufficient to melt the polymer (Fig. 5.1b). The composite laminates produced from the prepregs by compression moulding show that fibre-in-matrix distribution was generally uniform (Fig. 5.1c). The shape of the original individual composite prepregs moulded to form the laminates remains clearly evident, as shown by the presence of resin-rich layers between the layers of composite prepregs. Nevertheless, no significant voids can be observed within the composite samples. The crystallinity X_c of the PVDF matrix was determined using DSC measurements (for experimental details see [71]). The degree of crystallinity X_c of the matrix in the composites manufactured was constant at 19 ± 2 %. The fibre volume fraction of as-produced carbon fibre reinforced PVDF prepregs was found to vary slightly during the process duration (2 h) for each manufacturing speed and the produced composite had $V_f = 60 \pm 2$ %.

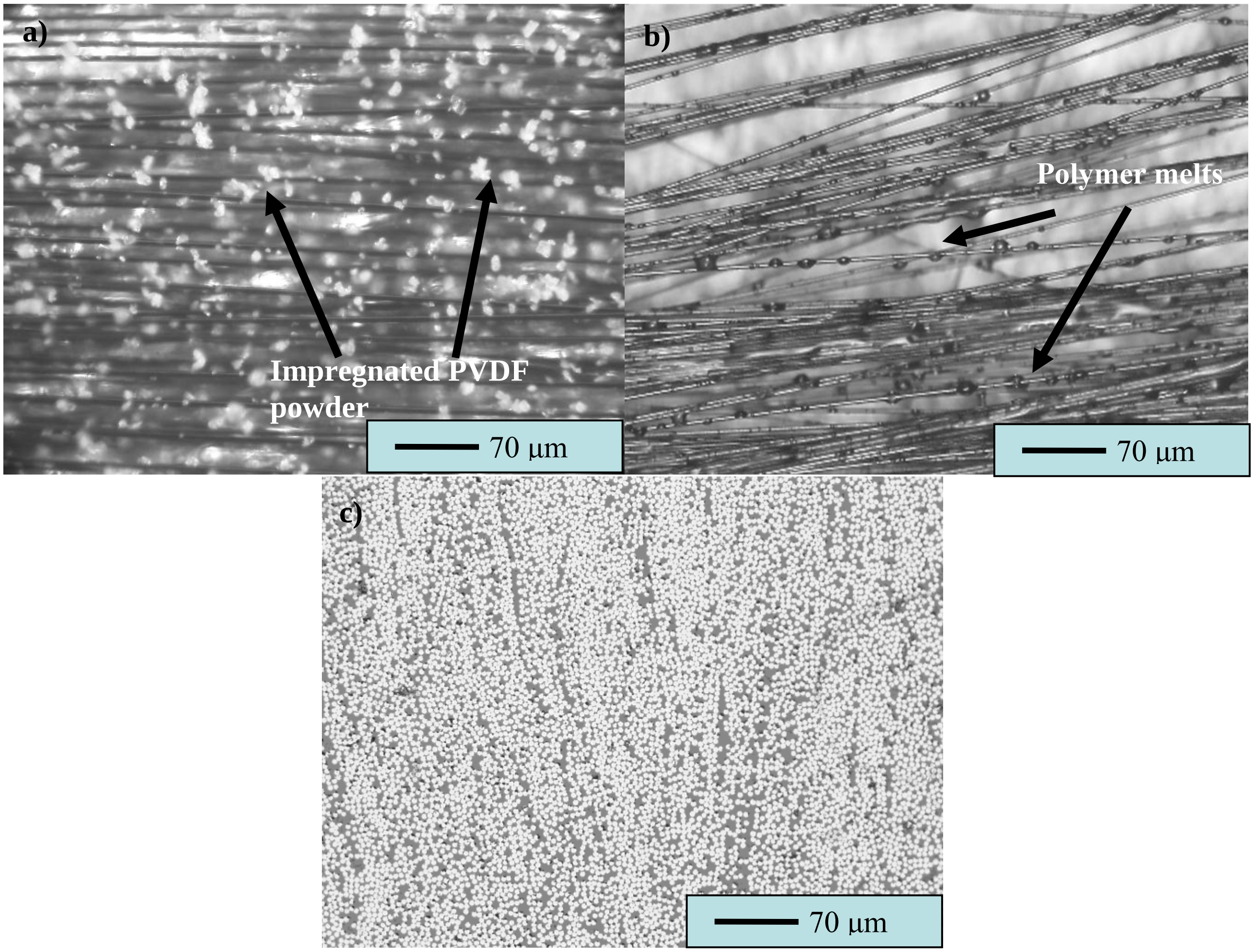
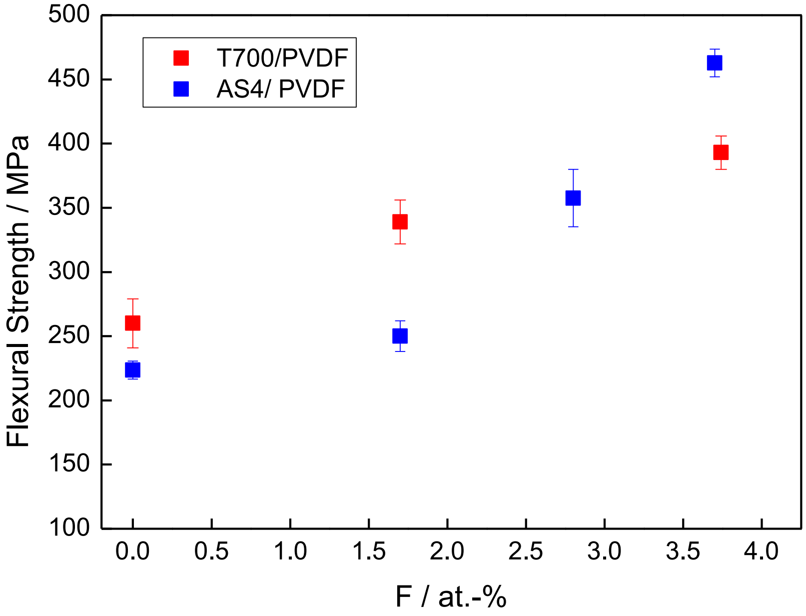


Figure 5.1 Microscope images of powder impregnated carbon fibre tow before a) during drying, b) during melting and c) after consolidation and compression moulding into a laminate

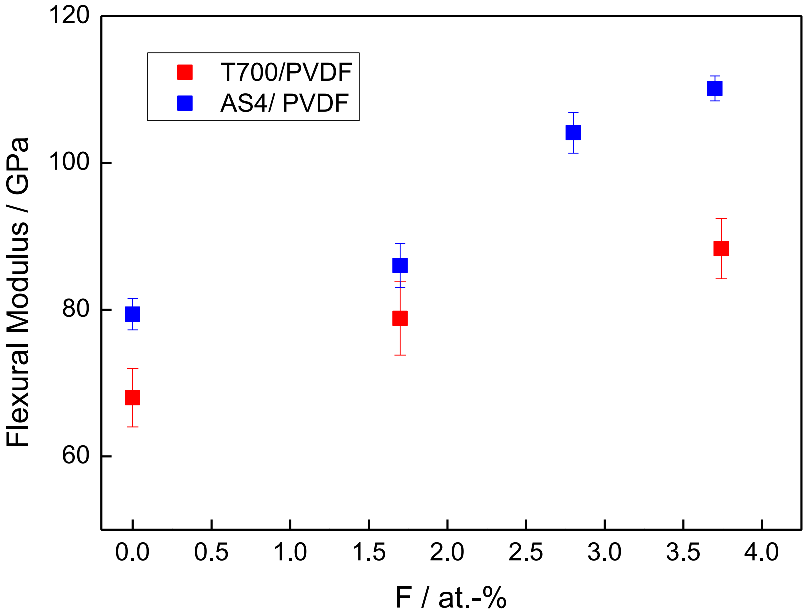
The effect of APF on the interface dominated properties of the laminated composites was examined. The effect of increasing degree of fibre fluorination, which was adjusted by varying the processing speed, on the mechanical performance of unidirectional carbon fibre reinforced PVDF is discussed below.

5.3.1 Effect of APF on flexural properties of carbon fibre reinforced PVDF

Flexural properties are important in engineering practice and are used a lot a) to obtain design data, b) for quality control and c) for specification purposes. If the bonding between the fibre and the matrix is weak, which is the case for carbon fibres and fluoropolymers, composites will not support load in shear or compression. The flexural properties of carbon fibre reinforced PVDF composites increased with content of fluorine functionalities on the fibre surface (Fig. 5.2). All tested specimens underwent compressive buckling failure on the top surface of the tested laminates. A typical load – displacement curve can be found in Appendix A. A flexural strength and modulus of 260 ± 18 MPa and 68 ± 4.0 GPa were obtained for standard industrially oxidised but unsized T700/ PVDF composites produced at a line speed of 1 m/min (Fig. 5.2a). For the composites containing T700 carbon fibres that were continuously APF treated with a degree of fluorination of 1.8 at.-% (produced at 0.75 m/min), the flexural strength and modulus increased to 339 ± 9 MPa and 79 ± 5.0 GPa respectively, which corresponded to 30% and 16% improvement. As the fluorine content of the carbon fibres increased to 3.7 at.-% (produced at 0.33 m/min), the flexural strength and modulus of the composites were found to increase further by 45% and 29% to 378 ± 16 MPa and 88 ± 4.1 GPa.



(a)



(b)

Figure 5.2 Flexural strength (a) and modulus (b) of laminated AS4/T700 carbon fibre reinforced PVDF composites as function of fibre surface fluorine content

A similar trend was also observed for the flexural strength of AS4/ PVDF composites. For specimens processed at 1 m/min, containing standard industrially oxidised but unsized AS4 fibres, the measured flexural strength and modulus were 225 ± 7 MPa and 80 ± 2 GPa, respectively. When APF was incorporated into the manufacturing process at 1 m/min, corresponding to carbon fibre fluorine content of 1.7 at.-%, the flexural strength and modulus increased by 10% and 7.5% (to 250 ± 12 MPa and 86 ± 3 GPa). As the manufacturing speed was decreased (0.75 m/min and 0.33 m/min), the fluorine content of the carbon fibres increased to 2.8 at.-% and 3.7 at.-%. This led to further increase in the flexural strength of the composites to 357 ± 22 and 462 ± 10 MPa which indicate an improvement by 60 % and 110 %, respectively. A similar trend was also observed as the measured flexural modulus increased to 105 ± 3 GPa and even further to 110 ± 2 GPa for composites containing carbon fibres with 3.7 at.-% fluorine content.

From the flexural results obtained, we can see that by increasing the fluorine content of both AS4 and T700 fibres, there is a positive impact on the flexural properties of the reinforced PVDF composite laminates. Since the flexural test is an interface dominated property test, by examining the stress acted upon the surface of the specimen at failure, which is accompanied by the breaking of fibres, the results suggest enhancement in interfacial strength between carbon fibres and PVDF.

5.3.2 Effect of APF on short beam strength of carbon fibre reinforced PVDF

The ASTM Standard [39] states that during conventional short beam strength testing of unidirectional fibre reinforced thermoplastics, the stress that is induced in the specimen is neither a pure shear stress nor a pure flexural type stress but a mixture of both stresses. Nevertheless, the failure mode observed during the test represents shear failure, and should be known as apparent short beam shear failure, rather than flexural when the standard is followed strictly [222]. Figure 5.3 clearly indicates that APF of carbon fibres improves the resistance of unidirectional carbon fibre reinforced PVDF to deformation between two outer rollers when specimens were loaded in a three point configuration. The apparent short beam shear strength (SBS) increases from 7.8 MPa for the standard oxidized but unsized T700/PVDF composites to 10.8 MPa for composites containing carbon fibres with a degree of fluorination of 1.7 at.-% (Fig. 5.3). As the surface fluorine content of the reinforcing carbon fibre continues to increase to 3.7 at.-%, the apparent SBS was found to increase further to 13.4 ± 0.4 MPa. The results obtained indicate that appropriate degree of inline carbon fibre modification improves the interface dominated mechanical properties of unidirectional T700 carbon fibre reinforced PVDF. The short beam strength increases from 7 ± 0.2 MPa for the standard oxidized but unsized AS4/PVDF composites to 9.5 ± 0.5 MPa and to 11 MPa for composites containing carbon fibres with a degree of fluorination of 1.7 at.-% and 2.8 at.-%, respectively. As the surface fluorine content of the reinforcing carbon fibre continues to increase to 3.7 at.-%, the short beam strength was found to increase further to 20.6 ± 0.2 MPa.

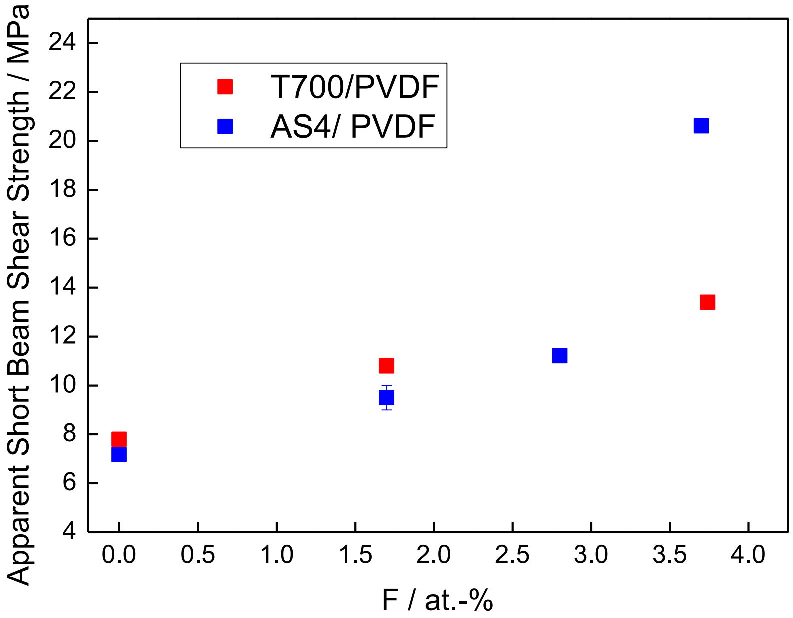


Figure 5.3 Apparent short beam shear strength of laminated AS4/ T700 carbon fibre reinforced PVDF composite as function of fibre surface fluorine content

The improvement may be attributed to the interface compatibility which is a clear effect as the surface fluorine content of the reinforcing fibre increases. By applying the SBS test to examine the interlaminar shear strength of carbon fibre reinforced PVDF composites, the fibre matrix adhesion can be investigated. Once again the apparent SBS results obtained showed that by increasing the fluorine content of both AS4 and T700 fibres, there is a positive impact on the interlaminar shear strength of the reinforced PVDF composite laminates, i.e. improvement in interfacial adhesion. However, from the flexural and SBS results obtained above, it was observed that AS4/PVDF composites exhibit higher mechanical performance than T700/PVDF composites, and therefore only AS4/PVDF laminates will be analysed further in the subsequent sections.

5.3.3 Impact of APF on Mode I and Mode II interlaminar fracture toughness of carbon fibre reinforced PVDF

Carbon fibre reinforced PVDF coupons were fabricated and loaded under both Mode I DCB and Mode II ENF tests to measure the fracture toughness of the specimen. However no crack growth was observed during the test. The main reason for this observation can be hypothesised due to the toughness of PVDF matrix. PVDF is a tough semi-crystalline polymer with a glass transition temperature (T_g) of -40 °C. Therefore, PVDF behaves ‘rubbery’ at room temperature. This attribute of the polymer resulted in a tough composite material. When a crack is introduced in such composite, it is difficult or almost impossible to obtain a stable crack growth. Therefore, the material will fail in the weakest point of the composite. During the DCB test, the arms of the DCB coupon underwent flexural failure ahead of the crack tip shortly after crack initiation for all the specimens (Fig. 5.5). Therefore what was measured was only the flexural strength of the arm. There is also a possibility that a resin fillet ahead of the crack tip was present, which hindered the specimen to crack under load. Similarly in Mode II test, there was no crack observed during the three-point bend test which again indicates the toughness of the matrix material. Hence, instead of interlaminar fracture toughness measurement, all that was measured was actually merely flexural strength of the composite. When the results from the tests were analysed, it fits perfectly to the flexural strength of the composite as reported in section 5.3.1.

(A)

(B)

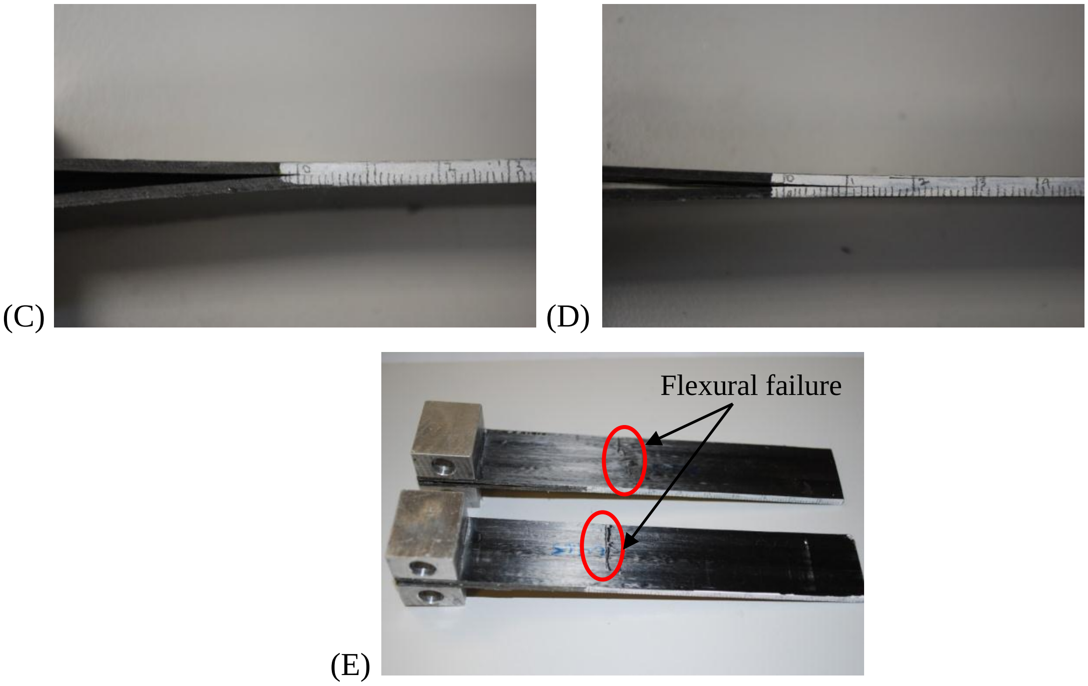


Figure 5.4 Photographic images of failed specimen indicating the crack initiation process (A-D) and flexural failure feature on the surface of the specimens after testing (E)

5.3.4 Impact of APF on tensile properties of carbon fibre reinforced PVDF

The tensile properties of UD carbon fibre composites are mainly a fibre dominated property. The tensile strength of as-received AS4 UD carbon fibre reinforced PVDF was found to be 1130 ± 53 MPa. By subjecting the carbon fibre to APF modification, the tensile strength of the UD composite increased slightly by 10% to 1261 ± 70 MPa for carbon fibre with fluorine content of 1.7 at.-%. However, when the fibres were further exposed to APF modification, the tensile strength did not increase further (Fig. 5.5). All the unmodified and APF treated carbon fibre reinforced PVDF laminates tested in this study resulted in similar values of Young’s modulus. The Young’s modulus of unmodified UD carbon fibre reinforced PVDF was found to be 133 ± 4.5 GPa (Fig. 5.5). An observation during the test that is worth mentioning is the specimens failed catastrophically, almost explosive while releasing large amount of elastic energy stored.

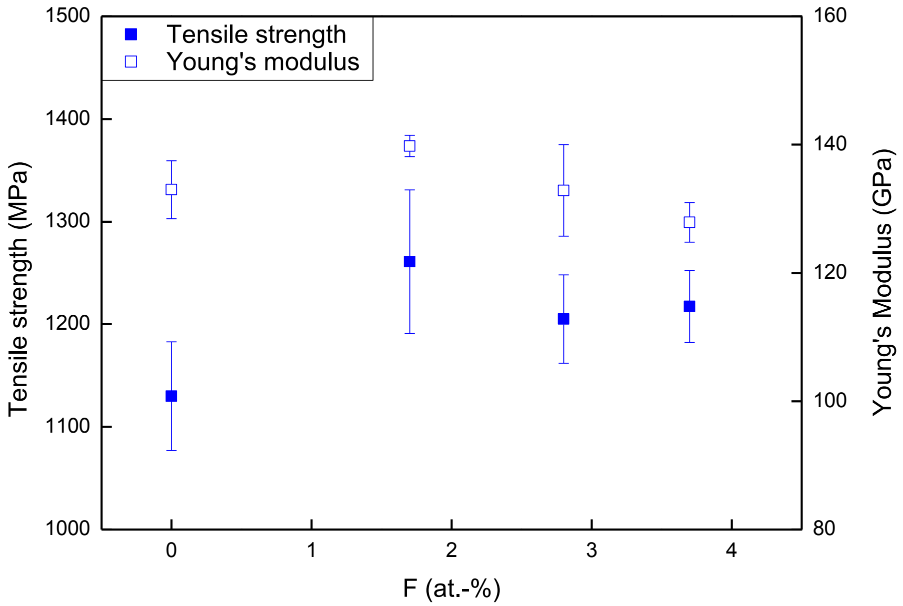


Figure 5.5 Tensile strength and Young's Modulus of UD carbon fibre reinforced PVDF as a function of fluorine content on the fibre surface

By using the simple rule of mixture, and by taking the fibre volume fraction to be 60%, the Young's modulus and tensile strength of a UD carbon fibre reinforced polymer can be predicted using the equation:

$$E_{comp} = V_f E_f + (1 - V_f) E_m \tag{5.8}$$

Similarly, the tensile strength of the UD composite can also be predicted using the equation:

$$\sigma_{comp} = V_f \sigma_f + (1 - V_f) \sigma_m \tag{5.9}$$

where V_f is the fibre volume fraction, E_f and σ_f the Young's modulus (231 GPa[†††]) and tensile strength (4,433 MPa[†††]) of the fibre and E_m and σ_m is the Young's modulus (2.31 GPa[‡‡‡]) and

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[†††] *Hexcel HexTow® AS4 Product data. Link in: http://www.hexcel.com/resources/datasheets/carbon-fiber-data-sheets/as4.pdf. Accessed on 1 March 2012*

tensile strength (48.3 MPa[‡‡‡]) of the matrix. The predicted Young's Modulus of carbon fibre reinforced PVDF should be 139.5 GPa, which is similar to the experimental values. The predicted tensile strength should be 2679 MPa. This predicted composite strength is 100% higher than that obtained experimentally. This is mainly because the rule of mixture is an estimate taking into account the maximum tensile properties of each constituent while assuming perfect bonding between the fibres and the matrix. Besides that, the rule of mixture neglects any flaws in fibre misalignments, void content and imperfect distribution of fibres within the matrix such as fibre-rich or resin-rich areas within the composites [226, 227]. However, the compression moulding technique which was employed during the specimen preparation stage will induce inhomogeneous distribution of the fibres within the matrix (see Fig. 5.6).

Nevertheless, when the tensile strength obtained in the carbon fibre reinforced PVDF laminate was compared to the tensile strength of a single carbon fibre reinforced PVDF prepreg, the results are similar. It was reported previously that the tensile strength of a single carbon fibre reinforced PVDF prepreg was 1,050 MPa [228]. Therefore, the tensile strength measured is considered valid. The stress-strain curves can be found in Appendix B. The strain to failure obtained during the experiments for as-received AS4 and different degrees of fluorine content on APF treated carbon fibre reinforced PVDF laminates was found to be between 0.84 - 0.94%. This result is quite low considering the strain to failure of AS4 carbon fibres which is quoted to be 1.8%[†††]. However, a lower failure strain is expected since the overall failure stress of the composite laminate is also relatively low.

[‡‡‡] *Arkema Kynar® 710 PVDF Homopolymer Product data. Link in: http://www.matweb.com/search/DataSheet.aspx?MatGUID=7378d6bf9bf84f2b8dcc1f49d40eeb44&ckck=1. Accessed on 1 March 2012*

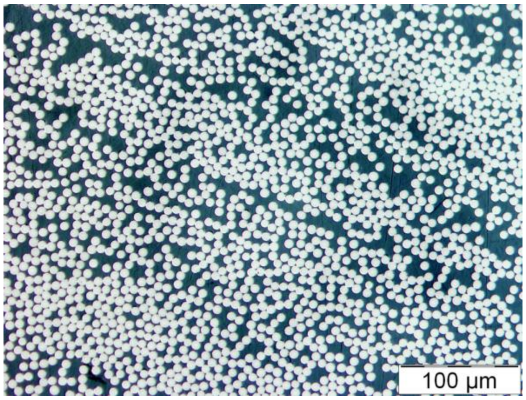

Figure 5.6 Optical microscope image of a cross-sectional section of the UD composite laminate after compression moulding

5.3.5 Effect of APF on tearing of carbon fibre reinforced PVDF

The essential work of fracture via tearing W_e and non-essential work (plastic deformation) W_p [229], which are also known as out-of plane or Mode III deformation of a trouser leg test are shown in Figure 5.7 and 5.8. Such a method is very useful in the characterisation of the plane stress toughness of ductile polymers and related systems [230], i.e. PVDF composites. The W_e of AS4/PVDF composite prepregs containing as-received fibres were found to be independent of manufacturing speed (0.77 ± 0.06 kJ/m^2). However, when carbon fibres were treated with APF, the resulting prepregs showed a significant improvement in the W_e from 0.79 ± 0.05 to 1.56 ± 0.01 kJ/m^2 when the manufacturing speed was reduced from 1 m/min to 0.33 m/min, which corresponds to 1.7 at.-% and 3.7 at.% of fluorine content on the carbon fibre surface. According to the literature [231], the W_e of a 50 µm thick PVDF film was 43.6 kJ/m^2 as compared to 65 kJ/m^2 (300 µm) when measured in-house.

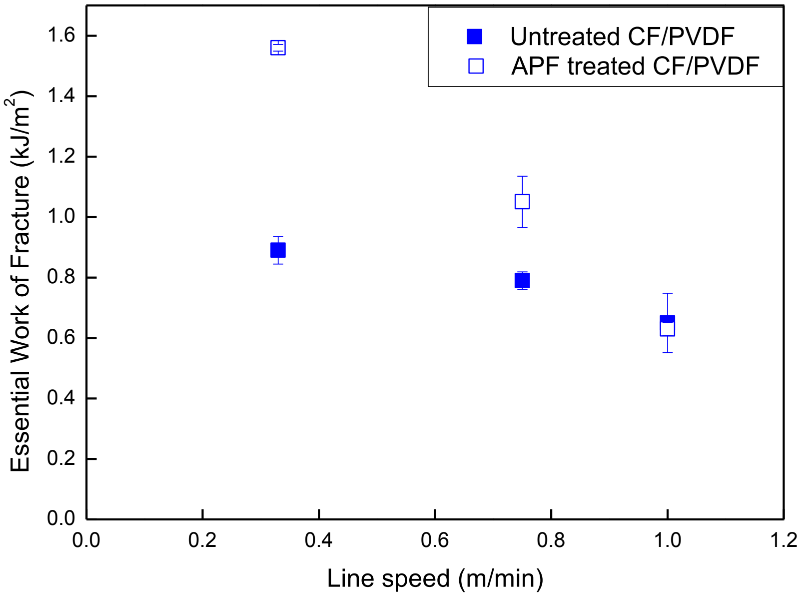

Figure 5.7 Essential work of fracture of as-received and APF treated AS4 CF/PVDF composite prepregs as a function of manufacturing speed

It can be seen that the W_e values obtained for AS4/PVDF composite prepregs were relatively low when compared to the W_e of pure PVDF polymer. This may be due to the fact that when carbon fibre was introduced unidirectionally into the matrix, the presence of fibres aids the tearing by occupying 60% of the volume and thus provide a crack path parallel to the fibres orientation because it is more energy favourable. Nevertheless, upon APF of the carbon fibre surface, it is noteworthy that the composite resistance to fracture was indeed improved because of the stronger adhesion between fibre and matrix. Figure 5.8 shows the W_p for unmodified and APF treated AS4/PVDF composite prepregs as a function of manufacturing speed. The W_p of composite prepregs containing as-received carbon fibres are largely unaffected by the different manufacturing speeds, between 2.26 MJ/m^3 and 2.92 MJ/m^3. By introducing 1.7 at.-% of fluorine functionalities on the carbon fibre surface (manufactured at 1m/min), the W_p was found to be 2.95 ± 0.4 MJ/^{3}. By reducing the manufacturing speed, i.e. allowing carbon fibre to be exposed longer to APF, the W_p increased by 28.6% and 56.6% to 3.79 ± 0.5 and 4.62 ± 0.3 MJ/m^3, respectively. These results show that composite prepregs containing fluorinated carbon fibre have a higher tear resistance as indicated by both the essential/ non-essential work of fracture criteria.

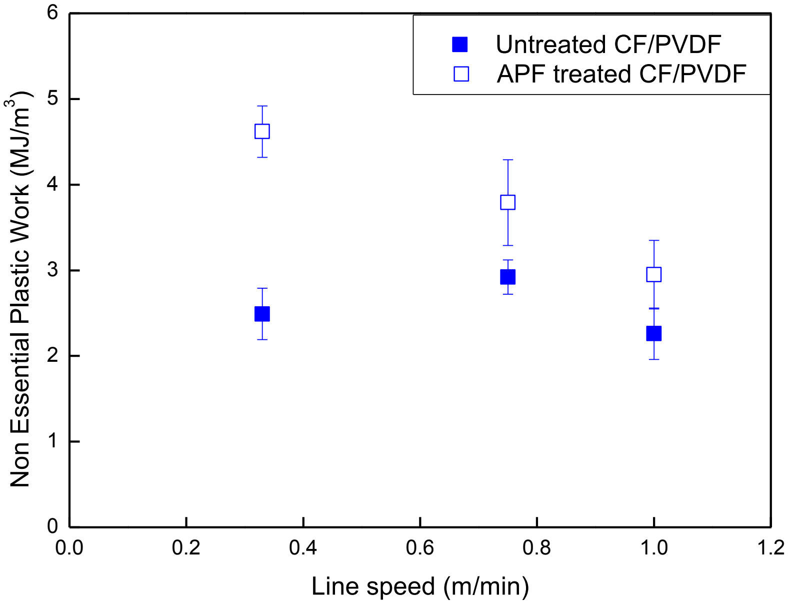

Figure 5.8 Non-essential plastic work of as-received and APF treated AS4 CF/PVDF composite prepregs as a function of manufacturing speed

5.4 Summary

The macro-mechanical properties of unidirectional (fluorinated) carbon fibre reinforced PVDF composites were investigated. Thin composite prepregs with a fibre volume fraction of 60 ± 2 % were manufactured using the powder-impregnation route. In order to modify the carbon fibres while manufacturing composites, continuous inline atmospheric plasma fluorination was integrated into the process. The level of fluorination of the fibres (up to 3.7 at-%) was controlled by the manufacturing speed. Interface dominated composite properties were characterised using flexural, short beam strength, Mode I/ II interlaminar fracture toughness and trousers tests. It was found that increasing the fluorine content of the fibres resulted in significant improvement of the mechanical properties of unidirectional carbon fibres reinforced PVDF composite laminates. The flexural strength increased from 225 MPa for the standard oxidised but unsized AS4/PVDF composites to 465 MPa for the composites containing APF carbon fibres with a degree of fluorination of 3.7 at-%. The flexural modulus was also found to increase from 80 GPa to 110 GPa with increasing degree of fluorination. When compared to T700 carbon fibre reinforced PVDF composite, an improvement of 45% and 38% were obtained in the flexural strength and modulus respectively. The short-beam shear test showed improvements of up to 72 and 200 % in apparent short beam shear strength for the composite laminates containing APF T700 and AS4 carbon fibres, respectively. Both of these carbon fibres have a fluorine content of up to 3.7 at.-%, as determined by XPS. However, as AS4 carbon fibre performed better than T700 fibres, only AS4 carbon fibre reinforced PVDF composites were subjected to tensile, Mode I and Mode II interlaminar fracture toughness and tearing test. There was no crack propagation observed during when the composite laminate was subjected to both Mode I DCB and Mode II ENF tests. It could be concluded that this is mainly due to the toughness of the matrix (being rubbery-like at room temperature) when the tests were performed.

AS4 reinforced PVDF laminates were also loaded under tension along the fibre direction. The tensile strength and Young’s modulus of the UD carbon fibre reinforced PVDF composites was found to be 1130 MPa and 133 GPa, respectively. The incorporation of APF treated carbon fibre into PVDF surface did not significantly improve the tensile strength of the composites as axial tensile is a fibre dominated property. The essential work of fracture increased from 0.79 kJ/m^2 to 1.56 kJ/m^2 for composites containing AS4 carbon fibres with a degree of fluorination of 3.7 at.-% as compared to composites with surface degree of 1.7 at.-%. The non-essential work of fracture or the plastic work of fracture increased with increasing fluorine content of the AS4 carbon fibres from 2.95 MJ/m^3 to 4.62 MJ/m^3. Both the essential and non-essential work of fracture for unmodified AS4 carbon fibre reinforced PVDF prepregs were independent of the manufacturing speed which suggests that fluorination on the carbon fibre surface enhances the composites resistance to fracture. It can be concluded that interface dominated mechanical properties of unidirectional fibre reinforced PVDF composites can be significantly improved by fluorinating the carbon fibres mildly, which is mainly due to increased Van der Waals interaction between the fibre and the matrix.

6.0 Synergy of matrix and fibre modification on adhesion between carbon fibres and poly(vinylidene fluoride)[§§§]

Interfacial properties between carbon fibres and poly(vinylidene fluoride) (PVDF) were tuned by modifying both constituents. Atmospheric plasma fluorination (APF) was utilised to tailor the surface composition of carbon fibres, which resulted in an incorporation of up to 3.7 at-% of fluorine functionalities in to the fibre surfaces. The PVDF matrix was modified by blending pure PVDF with maleic anhydride (MAH) grafted PVDF. Both fibre and matrix modifications act in synergy with improvements of up to 50 % in the apparent interfacial shear strength (IFSS) above the level of pure fibre or matrix modification. Modification of both constituents led to the formation of various interactions at the fibre/matrix interface namely dispersive and polar (H-bonds) between (modified) PVDF and the fluorine as well as oxygen functionalities on the fibre surfaces. The apparent IFSS between the modified fibres and matrix reaches a maximum of 42 MPa, which is almost the tensile strength of the pure PVDF. The improvements in apparent IFSS in single fibre model composites for both fibre and matrix modifications translated to a seven times improvement in the interlaminar shear strength of unidirectional composites.

[§§§] *Based on: Shamsuddin, S.-R., Ho, K. K. C., Ng, P., Lee, A. F. and Bismarck, A., "Synergy of matrix and fibre modification on adhesion between carbon fibres and poly (vinylidene fluoride)", Composites Science and Technology,* ***72*** *(2011), 56-64.*

6.1 Introduction

Advanced composite materials are becoming more and more accepted in load-bearing and structural applications, due to their high strength, high modulus and low density [35]. For composites to be used in deep sea oil and gas applications such as risers, coiled tubing, drilling systems and flow lines, they should be (ultra)-inert, moisture tolerant and able to withstand high and fluctuating pressures and temperatures while remaining durable [187]. In composites, it is usually the matrix which determines the temperature and chemical resistance. Polyvinylidene fluoride (PVDF), a semi-crystalline thermoplastic [187, 232], has a high maximum service temperature (T_S=129°C)[****] and might be the matrix of choice to produce very inert composites for load bearing structural applications in challenging environments. Composites, like all materials, fail when the load exceeds the limit to which it can be subjected. Catastrophic failure in composites occurs when the fibres, being the load bearing component in a composite, fail [233-236]. Moreover, the mechanical properties of a composite depend intrinsically on the quality and performance of the fibre/matrix interface [237].

Although PVDF appears a prime candidate for use as a matrix, the adhesion between PVDF and untreated carbon fibres is poor [20]. It has been shown previously that fluorination of carbon fibres improves fibre/fluoropolymer adhesion [20, 71, 207]. Direct [19, 202, 238-242] or plasma fluorination [142, 243, 244] are the most common methods used to introduce up to 80 at.% fluorine moieties onto carbon fibres. However, both direct and low-pressure plasma fluorination [142, 239] of carbon fibres are batch processes, as they require special reaction vessels or vacuum chambers and can therefore not easily be integrated into existing continuous manufacturing processes [30, 71]. In order to address these manufacturing issues, a continuous atmospheric plasma fluorination (APF) procedure was developed [21], which allows for the introduction of a small amount of fluorine functionalities (up to 5 at.%) in to the surface of carbon fibres. An alternative route to tailor the adhesion between carbon fibres and fluoropolymers is by matrix modification. For example, it has been reported that maleic anhydride (MAH) grafted PVDF can result in up to 155% improvement of the adhesion to

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[****] *The Texloc Library PVDF Detailed Properties; Link in: http://www.texloc.com/closet/cl_pvdf_properties.htm Accessed on 03.06.2011.*

carbon fibres [18]. Here we investigate the influence of both a matrix modification by using a blend of MAH-grafted PVDF with PVDF and an APF carbon fibre modification on the resulting adhesion properties in a single fibre model composite and unidirectional carbon fibre/PVDF composites.

6.2 Experimental

6.2.1 Materials

HexTow™ AS4 12k continuous, high strength and strain, unsized, industrially oxidised PAN-based carbon fibre (F_0) were used in this study. The carbon fibres were kindly supplied by Hexcel Corporation (Cambridge, UK). Poly(vinylidene) fluoride (PVDF) Kynar® 711 powder and maleic anhydride MAH-grafted PVDF ADX® 121 pellets were kindly supplied by Arkema (Serquigny, France). Nitrogen (N_2) and chlorodifluoromethane (Freon 22), used as the plasma feed gas for carbon fibre fluorination, were supplied by BOC (UK). General purpose grade dimethyl formamide (DMF) and ethanol (purity > 99%) used to dissolve MAH-grafted PVDF and flushing the solvent were purchased from VWR (UK).

6.2.2 Modification of the composite constituents

6.2.2.1 Atmospheric plasma fluorination of carbon fibres

Atmospheric plasma fluorination (APF) of carbon fibres was performed using an Openair-Plasma-Technology system (single rotating FLUME Jet RD1004, Plasmatreat, Steinhagen, Germany). The plasma jet was generated by ionising a feed gas mixture of Freon 22 and N_2 (1:70 ratio). The gas mixture was ionised at 2.5 bar with a flow rate of 35 l/min and a power of 2.1 kW (296 ± 3 V, 7 ± 0.2 A). The continuous carbon fibre roving was passed through the plasma jet 3 times, using phenolic resin roller pins to maximise the fibres' exposure to APF. The top fibre tow was 15 mm away from the tip of the plasma nozzle, inside a 20 cm long borosilicate glass 3.3 unequal tee piece. A schematic of the continuous plasma fluorination setup can be found in reference [30]. APF of carbon fibres was conducted at speeds of 0.33 m/min (F_3), 0.75 m/min (F_2) and 1 m/min (F_1), which corresponded to a residence time in the active zone of the plasma jet of 1.8 min, 0.8 min and 0.6 min, respectively.

6.2.2.2 Preparation of MAH-g-PVDF/PVDF blends

Three different blends of PVDF were investigated: as received Kynar®711 PVDF (P_0), a blend of Kynar® 711 and Kynar®ADX 121 PVDF ($P_{2.5}$) and as received Kynar®ADX 121 (P_5). The pure PVDF (Kynar® 711) contains no MAH-grafted moieties and the commercially available MAH-g-PVDF (Kynar®ADX 121) contains about 5 ppm of MAH-grafted [245]. Master batches of PVDF Kynar® 711 and Kynar® ADX 121 blend (containing 2.5 ppm of MAH-grafting on PVDF – as a result of blending 50% pure PVDF with 50 % MAH-grafted-PVDF) were prepared by dissolving the polymers in DMF to make a 10 wt.% solution. The mixture was homogenised (L4R Silverson, Chesham, UK) throughout and cooled using liquid nitrogen while a non-solvent, a ratio of 80:20 wt% of DMF to deionised water was added drop-wise via a separation funnel to induce polymer precipitation. The precipitate was filtered under vacuum and washed with ethanol before being dried in a vacuum oven at 50°C for 12 h and then 120°C for 12 h. The PVDF/MAH-grafted-PVDF blend formed from this solvent precipitation process was a fine powder. The same procedure was adapted to the as-received MAH-grafted-PVDF (P_5) to obtain fine powder which will be used throughout the experiments. More information can be found in Ref. [245].

6.2.3 Characterisation of constituents

6.2.3.1 Determination of fibre diameters

The modified Wilhelmy-technique [246-248] was used to determine the diameters of (APF) carbon fibres. This gravimetric approach measures the wetting force exerted on the fibre as the fibre is immersed in or withdrawn from n-dodecane (γ_l = 25.4 mN/m, 99 % purity, Fisher Scientific), which wets the fibres completely and, therefore, allows the fibres' diameter d_f to be determined according to the following equation:

$$d_f = \frac{mg}{\pi \gamma_l} \tag{6.1}$$

where g is the acceleration due to gravity and γ_l is the surface tension of the test liquid. Measurements were conducted on at least 25 individual fibres to obtain a significant statistical average and standard deviation. Details of the experimental procedure have been reported previously and can be found in references [21, 249].

6.2.3.2 Surface Composition of fluorinated carbon fibres and different blends of PVDF

XPS of the modified carbon fibres and blends of PVDF matrices were performed using a Kratos AXIS HSi spectrometer equipped with magnetic focussing at normal emission using a Mg K_{α} (1253.6 eV) source operated at 160 W. Survey and high resolution spectra were recorded with analyser pass energies of 160 and 20 eV, respectively. Elemental compositions of carbon fibres and matrices were determined using appropriate instrumental response factors (C 1s = 0.278, F 1s = 1.000, N 1s = 0.477 and O 1s = 0.780). Spectra were Shirley background-subtracted and fitted using CasaXPS version 2.3.15. The minimum number of components to achieve a good fit was used, with a common Gaussian-Lorentzian (70:30 mix) line shape adopted for all elements and a common FHWM for each component (C 1s = 1.15 eV, F 1s = 1.67 eV, N 1s = 2.8 eV and O 1s = 1.83 eV, respectively). Reference values for functional groups were taken from the NIST Standard Reference Database [250].

6.2.3.3 Effect of matrix modification on matrix crystallinity

Differential scanning calorimetry (DSC) (TA Instruments Q2000 DSC, Manchester, UK) was used to determine the melting/recrystallisation behaviour of single carbon fibre/PVDF model composites. The DSC scans were performed in N_2 atmosphere at a heating rate of 10°C/min between -100 to 220°C. An appropriate amount of sample (typically ~5 mg) was sealed in a Tzero-aluminium pan and placed in the heating chamber together with an empty reference pan. The melting temperature (T_m) and heat of melting (ΔH_m) were determined from the heat flow curves. The degree of crystallinity (X_c) was calculated as follows:

$$X_c = \frac{\Delta H_m}{H_f^0} 100\% \tag{6.2}$$

where H^0_f is the heat of fusion of 100 % crystalline PVDF (104.5 J/g) [251].

6.2.4 Wettability of carbon fibres by PVDF melt

Understanding the wetting behaviour of polymer melts on carbon fibres enables prediction of the fibre/matrix adhesion [252, 253]. Three single carbon fibres were attached to a stainless steel frame by an epoxy adhesive (Adhesive weld, J-B Weld, Slough, UK) and cured at room temperature for 24 h. PVDF powder was sprinkled over the fibres before the frame was carefully loaded into a hot stage (THM600, Linkam Scientific Instruments, Surrey, UK) and heated to 205°C. PVDF melt droplets on carbon fibres were examined using an optical microscope (BH2, Olympus, Tokyo, Japan). Digital images of these droplets were captured. Contact angles were determined from at least 60 captured images. Detailed procedures on contact angle determination for drop on fibre systems can be found in reference [254].

6.2.5 Microscopic analysis of composite test specimens

Failed sections of short beam shear tested specimens were embedded into a polyester resin (EpoxyCure, Buehler Ltd, Illinois USA). The resin was cured for 24 h at room temperature before being polished using resin bonded diamond grinding discs (ApexDGD 60 μm Buehler Ltd, Illinois, USA). Specimens were ground first using a water medium for 20 min at a pressure of 0.2 MPa and a speed of 150 rpm. Then the specimen was ground using a diamond suspension (MetaDi 6 μm, Buehler) for 2 min. To obtain a scratch and void-free surface finish of the polished specimens, the entire process was repeated using 3 μm and 1 μm diamond suspensions, respectively at the same polishing parameters. Polished specimens were then examined under an optical microscope (BH2, Olympus, Tokyo, Japan).

6.2.6 Mechanical testing of matrix and model composites

6.2.6.1 Processing and tensile testing of PVDF polymer blends

The PVDF powder, P_0 and P_5 prepared using solvent precipitation (section 6.2.2) were dried in a vacuum oven for 24 h at 60°C prior to injection moulding into dog-bone shaped tensile specimens (with dimensions in accordance to ASTM standard D638 type V [255]) using a laboratory injection moulding machine (Haake Minijet, Thermo Scientific, UK) equipped with a single gated injection mould at a melting temperature of 205°C, pressure of 300 bar and a mould temperature of 105°C. The tensile properties of injection moulded PVDF blends were determined using a tensile screw-driven test frame equipped with a 50 kN load cell (model 3369, Instron, UK) following ASTM D638-3 [255]. Tensile specimens were loaded at a stroke of 1 mm/min until failure, while the loading force versus deformation was recorded. Ultimate tensile strength $\hat{\sigma}$ and Young's modulus E of each specimen was calculated following the standard [255]; the tensile moduli were determined between applied strains of 0.05 to 0.25%. Measurements were repeated on eight nominally identical samples to obtain a statistical average. The values presented represent these averages, with their errors are associated with standard deviations.

6.2.6.2 Single fibre pull-out tests

Single fibre pull-out was used to determine the apparent interfacial shear strength (τ_{IFSS}) as a measure of 'practical' adhesion at the fibre/matrix interface [256]. A single fibre was partially embedded to a pre-determined length between 50-150 μm into a PVDF melt droplet using a home-made embedding apparatus. Solid PVDF was placed on an aluminium sample carrier, heated to and held at 205°C while a fibre was pushed into the melt. The sample was subsequently cooled to room temperature using an air jet. The fibre pull-out test was performed using a piezo-motor fixed on a very stiff frame to avoid energy storage in the free fibre length between the matrix surface and clamping device. The fibre was loaded at a speed of 0.2 μm/s and pulled out of the matrix while the force was recorded throughout the experiment by a load cell. The schematic of the test and a typical load-displacement curve for the single fibre pull out test can be found in Appendix C. τ_{IFSS} was be calculated from F_{MAX} required to trigger de-bonding of the embedded carbon fibre from the matrix using the following equation:

$$\tau_{IFSS} = \frac{F_{MAX}}{\pi d_f L} \tag{6.3}$$

where d_f is the fibre diameter (determined using the modified Wilhelmy method, section 5.3.1) and L the embedded fibre length (determined from the load vs. displacement curve). The apparent shear strength between fluorinated carbon fibres and PVDF was determined from at least 10 pull-out measurements in order to obtain a statistically significant average. Average values are presented with errors presented as standard errors.

6.2.6.3 Short Beam Shear Test

The simplest and most common test method used to rank the effect of constituent modifications on the interlaminar strength of a composite is short beam shear test. The short beam shear test was conducted according to ASTM D2344 standard [257]. The details of the test method and the specimen dimensions can be found in section 4.2.11 of Chapter 4.

6.3 Results and discussion

6.3.1 X-ray photoelectron spectroscopy

6.3.1.1 Surface composition of atmospheric plasma fluorination (APF) carbon fibres

The impact of APF on the carbon fibre surface composition was determined by XPS. The surface compositions of APF treated carbon fibres are summarised in Table 6.1. The as-received, unsized but industrially oxidised AS4 fibre contained nitrogen and oxygen, but no traces of fluorine on its surface. Fluorinating the carbon fibres in atmospheric pressure plasma results in the removal of some surface material by sputtering of high energy species generated in plasma and chemical incorporation of fluorine, oxygen and nitrogen moieties. This is apparent from the reduction in surface carbon content with increasing fluorine surface concentration. The surface fluorine content reaches a maximum of 3.7 at.-% when exposed to 1.8 min continuous APF. The degree of fluorine surface functionalisation of carbon fibres can be simply controlled by increasing APF exposure time, as previously reported [21, 30], which is inversely proportional to the processing speed as anticipated (longer plasma exposure times permitting greater surface bombardment by the ionised plasma feed gas).

Table 6.1 Surface composition of atmospheric plasma fluorinated carbon fibres in at.-% from XPS

Fibres	***C (at.-%)***	***N (at.-%)***	***O (at.-%)***	***F (at.-%)***	***Cl (at.-%)***	***S (at.-%)***
F0	88.5	2.4	10.6	0.0	0.0	0.0
F1	87.5	2.2	7.9	1.7	0.6	0.1
F2	79.3	2.7	12.1	2.8	0.0	0.0
F3	76.4	1.8	12.7	3.7	0.0	0.0

6.3.1.2 Surface composition of maleic anhydride (MAH)-grafted PVDF

Maleic anhydride (oxygen) content in PVDF was also assessed by XPS. Table 6.2 presents the surface compositions of PVDF, MAH-grafted PVDF and PVDF/MAH-grafted PVDF blend. The as-received PVDF (P_0) is indeed indicative of a pure fluorohydrocarbon polymer, with a C:F atomic ratio of 1.3, close to the theoretical value of unity expected for a polymer backbone comprising only repeating $–CF_2–$ and $–CH_2–$ units [258].

Table 6.2 Surface composition of different matrices in at.-% from XPS

Matrix	***C (at.-%)***	***N (at.-%)***	***O (at.-%)***	***F (at.-%)***
P_0	56.52	0	0.21	43.27
$P_{2.5}$	58.81	0	1.99	39.20
P_5	57.15	0.15	8.19	34.50

The high-resolution C1s XP spectrum in Fig. 6.1a is also fully consistent with the parent polymer structure, exhibiting two components at 286.0 eV and 290.4 eV in excellent agreement with the literature [259]. The C:F atomic ratio increased upon MAH addition from 1.3 (P_0) to 1.7 ($P_{2.5}$) as expected from dilution of the PVDF matrix. This change coincided with the emergence of a new, weak carbon state at 288.6 eV, consistent with the -O-C(CH)=O ester function in MAH and incorporation of significant surface oxygen giving rise to two O1s states at 532.1 eV and 533.4 eV associated with the carbonyl and ether moieties of the anhydride (Fig. 1b). The latter O1s states were present in a 1.33:1 (-C=O):(-C-O-C-) ratio in sample P_5, lower than the anticipated value of 2 based upon the molecular formula of maleic anhydride which is indicative of significant reactively-formed -OH during the sample preparation and processing.

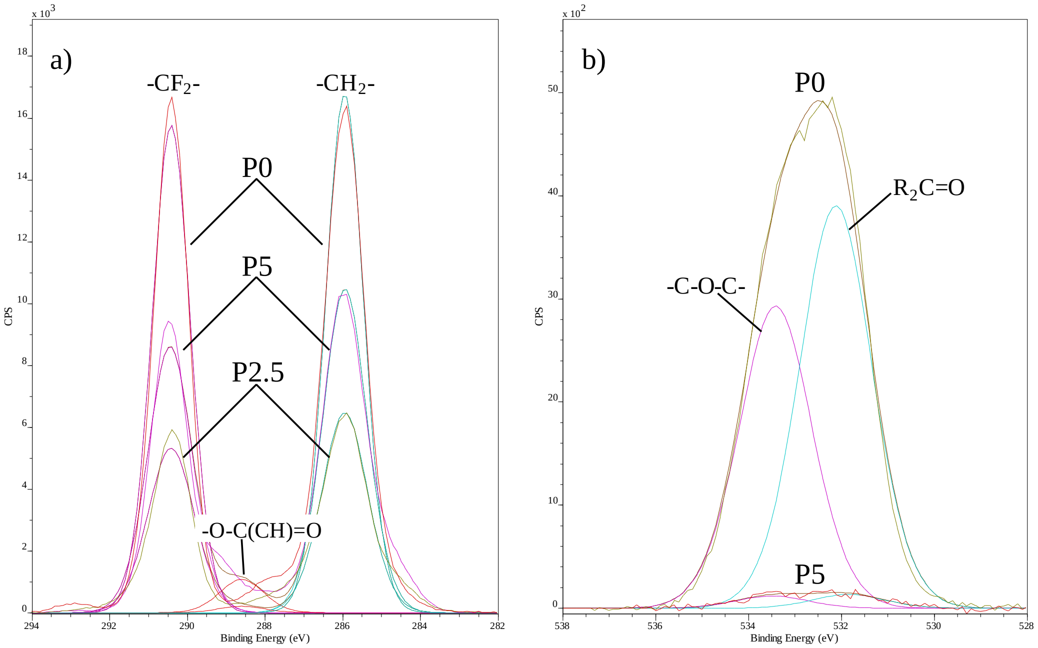


Figure 6.1 High-resolution a) C1s and b) O1s XP spectra of P0, P2.5 and P5 PVDF matrices containing with fitted components

In terms of the absolute anhydride content, XPS reveals the surface of P_5 contains ~14 % (14,000 ppm) MAH, much greater than the notional bulk value of 5 ppm. This dramatic surface enrichment reflecting the grafting methodology used to incorporate MAH functionality. In contrast, the surface of $P_{2.5}$ contains only ~2.5% MAH, less than the 7 % expected based upon a simple two-fold dilution of sample P_5, suggesting that the PVDF/Kynar® ADX 121 blend is rather inhomogeneous with preferential surface segregation of PVDF. A single fluorine chemical environment was present in samples P_0, $P_{2.5}$ and P_5 in line with expectations for PVDF [260], with a binding energy of 687.5 eV. Trace nitrogen (0.15 at.%) was only observed in sample P_5, demonstrating that neither MAH-grafting nor co-polymer blending protocols introduced significant surface contaminants.

6.3.2 Thermal and mechanical properties of maleic anhydride (MAH)-grafted PVDF

The influence of MAH-grafted-PVDF on crystallite formation was studied using DSC. Results show that grafting MAH onto PVDF led to a marginal drop in overall crystallinity X_c (Table 6.3), when compared to pure PVDF. The crystallinity decreased by 2.7% from 47.8% for P_0 to 45.1% for P_5. Although the morphology of the matrix that surrounds the reinforcing fibres can have a strong impact on the interfacial behaviour of the model composite, such small variation (< 3%) is not expected to influence interfacial shear properties [261].

Table 6.3 Melting point (T_m), Heat of Melting (H_m) and degree of crystallinity (X_c) of pure PVDF (P0), blend of 50: 50 PVDF and MAH-grafted PVDF (P2.5) and 100% MAH- grafted PVDF (P5)

Samples	***T_m (°C)***	***H_m (J/g)***	***X_c (%)***
P_0	170	49.85	47.8
$P_{2.5}$	172	48.02	45.9
P_5	169	47.09	45.1

The tensile strength and modulus of the polymer matrices PVDF Kynar® 711 (P_0) and MAH-grafted-PVDF (P_5) were measured to study the influence of grafting MAH to PVDF on the mechanical properties of the matrix. The tensile strength of both pure and MAH-grafted-PVDF was found to be 50 ± 0.7 MPa, which shows that grafting MAH to PVDF does not affect the tensile properties of the polymer. The tensile strength of $P_{2.5}$ was not measured as no significant change was found from the extremes, pure PVDF (P_0) and 5 ppm MAH grafted PVDF (P_5). The stiffness of the P_5 is however slightly compromised; the tensile modulus dropped by 10% from 1.9 GPa for P_0 to 1.7 GPa.

6.3.3 Wetting of carbon fibre by PVDF melts

The receding wetting behaviour between carbon fibres and modified PVDF melt droplets was characterised from drop-on-fibre systems (Fig. 6.2). The receding contact angle (θ_r) is characteristic for the high energy part of a surface as all attractive interactions will have to be overcome during de-wetting. A smaller contact angle indicates better wettability of the fibres by the matrix and better fibre/matrix contact, which should translate to better adhesion between fibre and matrix [3].

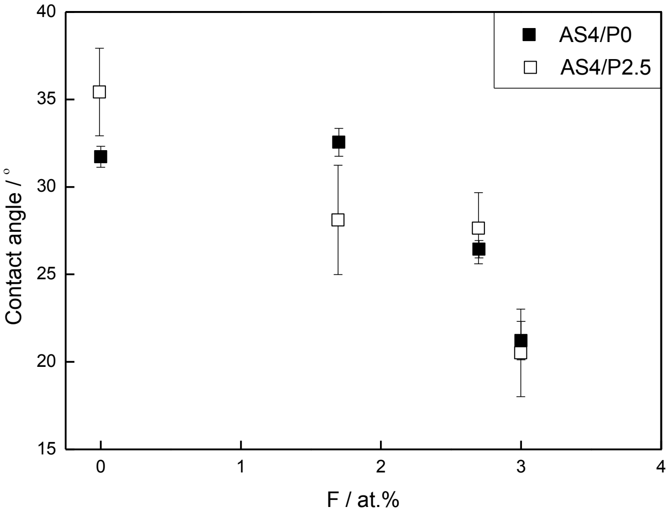
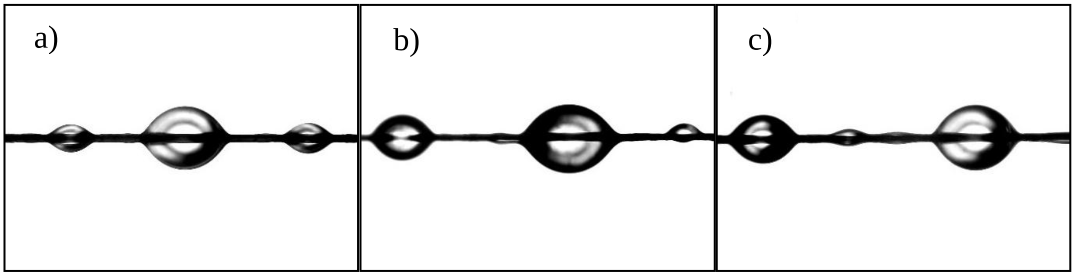


Figure 6.6.2 Contact angle of PVDF melt droplets on APF AS4 carbon fibres, P0 and P2.5 as a function of fluorine content on the carbon fibre surface

The PVDF/carbon fibre contact angle decreased with increasing fluorine content on the carbon fibre for both pure PVDF (P_0) and MAH-grafted-PVDF ($P_{2.5}$). A noteworthy decrease of 9º of the contact angle was observed from 32º for as-received AS4 (F_0)/P_0 to 23º for AS4 (F_0)/$P_{2.5}$. When MAH-grafted-PVDF (P_5) was used, all the carbon fibres were completely wetted by the matrix; i.e. no individual droplets formed, which indicated that the compatibility between the two constituents is very good indeed (Fig. 6.3i-j).



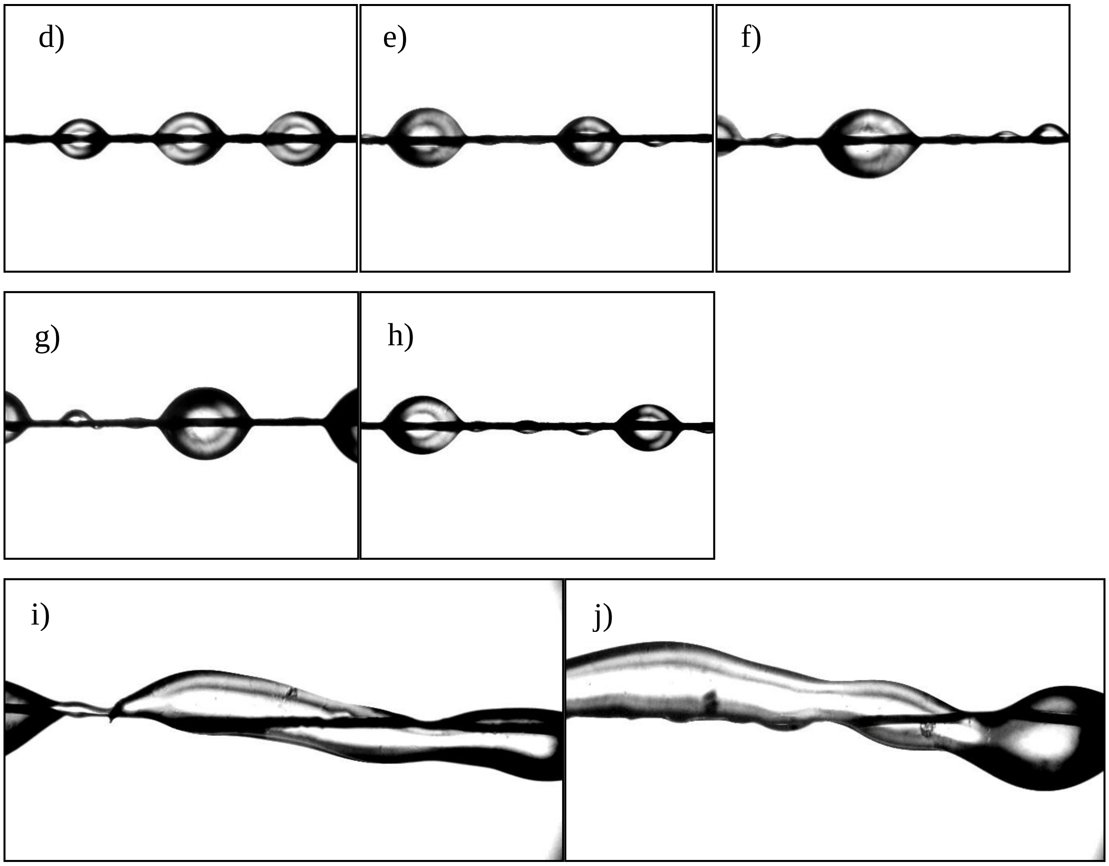


Figure 6.3 PVDF melt droplet on APF AS4: (a) F0/P0, (b) F1/P0, (c) F2/P0, (d) F3/P0, (e) F0/P2.5, (f) F1/P2.5, (g) F2/P2.5, (h) F3/P2.5, (i-j) complete wetting of P5 on AS4 (F0) fibres

6.3.4 Adhesion between (APF-treated) carbon fibres and (modified) PVDF

By fluorinating the carbon fibres, τ_{IFSS} between the fibres and PVDF increased by 34% from 10.8 ± 0.4 MPa to 14.5 ± 1.2 MPa for AS4 containing 2.8 at.% fluorine (Fig. 6.4). This result confirms previous findings of APF-treated T700 carbon fibres/PVDF model composites for which we found an improvement of 57% in τ_{IFSS} [71]. The increased interaction between the carbon fibres and PVDF is due to the enhanced dispersive interactions between the fluorine groups on the fibre and those of the matrix [31].

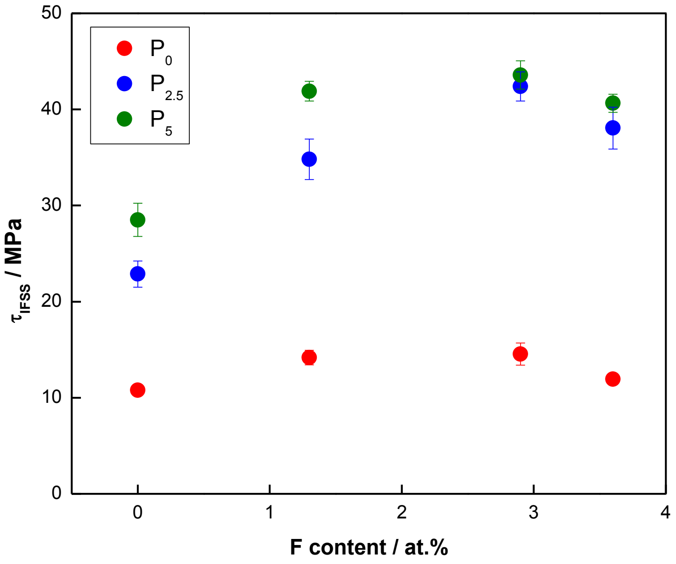


Figure 6.4 Apparent interfacial shear strength between APF AS4 carbon fibres and PVDF as a function of fluorine content for PVDF containing different amounts of MAH-grafted PVDF

By grafting 5 ppm of MAH to the PVDF matrix, the τ_{IFSS} between the original carbon fibres increased by 130% as compared to the single fibre model composite with pure PVDF. It was reported by the manufacturer that grafting of MAH on to PVDF enhances the adhesion of PVDF to metal surfaces[††††]. Our previous findings suggested that the PVDF modification by incorporating MAH-grafted-PVDF also leads to better adhesion between PVDF and carbon fibres [18]. In addition, by using fluorinated carbon fibres containing 2.8 at.% fluorine (F_2) in a modified PVDF matrix (P_5), the τ_{IFSS} increased further to 43.6 MPa. This suggested that the τ_{IFSS} is approaching its maximum, i.e. the tensile strength of the pure matrix. Therefore, by tailoring the interface in composites by controlling the fibre surface and matrix composition, at least the model composite performance can be optimised.

To understand the possible influence of fibre and matrix modification on the failure mode of single fibre model composite during pull out test, τ_{IFSS} was plotted against the embedded fibre length (Fig. 6.5). When using pure PVDF as matrix (P_0), the τ_{IFSS} is independent of the embedded fibre length indicating a ductile failure behaviour of the interface, which suggests that

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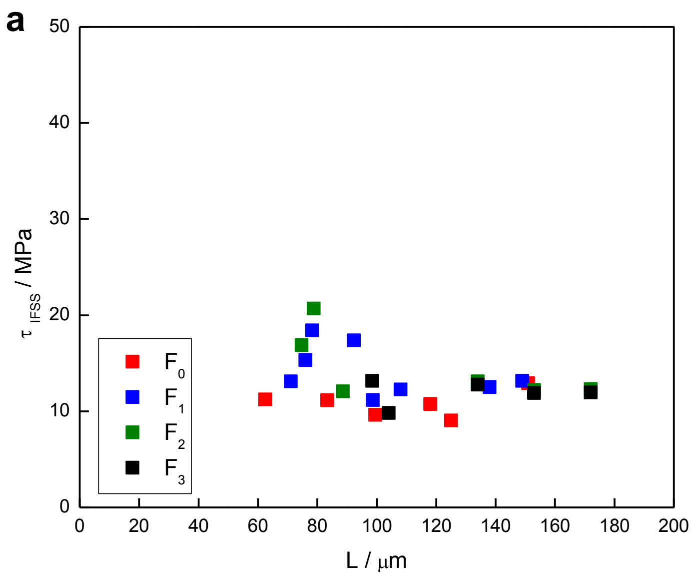
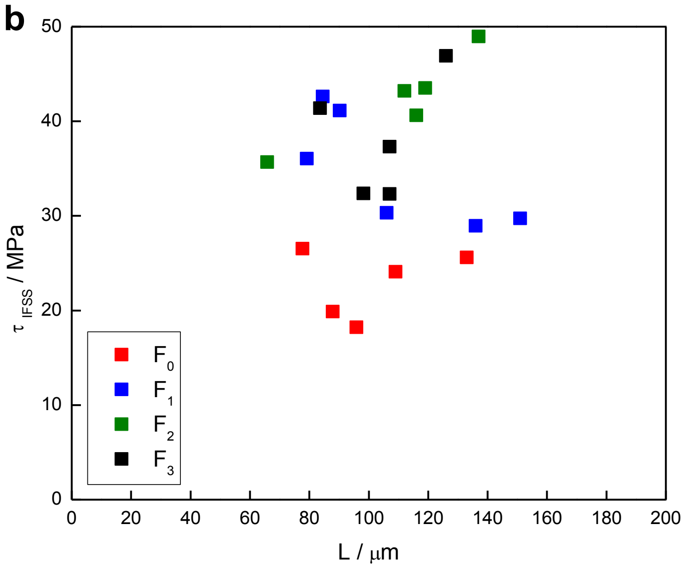
[††††] *Source: http://www.arkema-inc.com/kynar/literature/pdf/761.pdf Accessed on 28 May 2011*

the interface was mostly amorphous [262]. This finding is expected since the elongation at break for pure PVDF was found to be 70% from the tensile test, which is within the range of 20-100% as suggested by the PVDF supplier[‡‡‡‡]. However, incorporating MAH moieties into PVDF affected the failure mode; a mixed-mode of brittle and ductile interface failure was observed. The as-received AS4 $(F_0)/P_5$ composite shows a clear brittle fracture, as τ_{IFSS} increases with decreasing embedded length (Fig. 6.5c). The model composite containing carbon fibres with 3.7 at.% fluorine content on their surface and 5 ppm MAH grafting on PVDF showed however again a more ductile fracture behaviour as τ_{IFSS} was independent of the embedded length.



[‡‡‡‡] *Kynar® and Kynar® Flex PVDF performance characteristic and data. Link in: http://www.arkema-inc.com/kynar/literature/pdf/743.pdf Accessed on 13 June 2011*



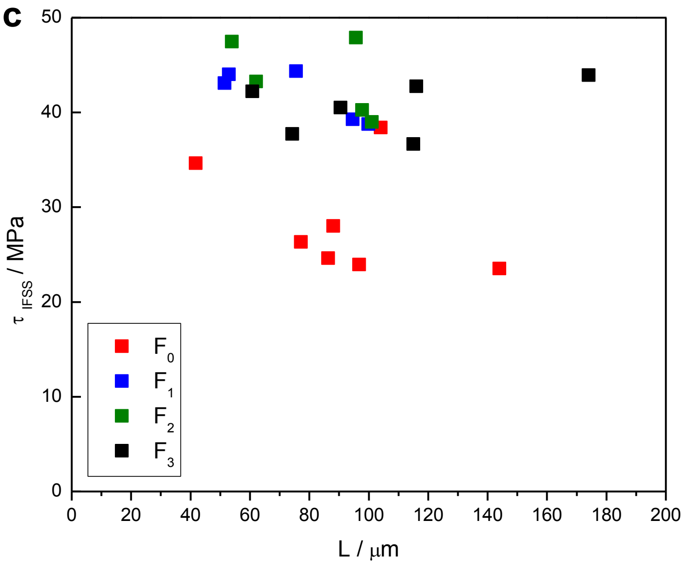


Figure 6.5 Apparent interfacial shear strength as a function of fibre embedded length for single fibre model composites consisting of unmodified (F_0) and APF treated carbon fibres (F_1, F_2 and F_4) and (modified) PVDF: (a) P0, (b) P2.5 and (c) P5

A similar trend was also found for the model composites containing carbon fibres with 2.8 at.% fluorine content on their surface (F_2) and 2.5 ppm MAH grafting on PVDF. The different fracture behaviour of such semi-crystalline systems could be explained by the dominating type of interactions, such as dispersive or polar, at the fibre/matrix interface. Furthermore, τ_{IFSS} between the fibre and matrix increases as contact angle decreases for both P_0 and $P_{2.5}$ (Fig. 6.6). This shows that modifying either or both constituents in the composite leads to better wettability (lower contact angle) which then resulted in better adhesion.

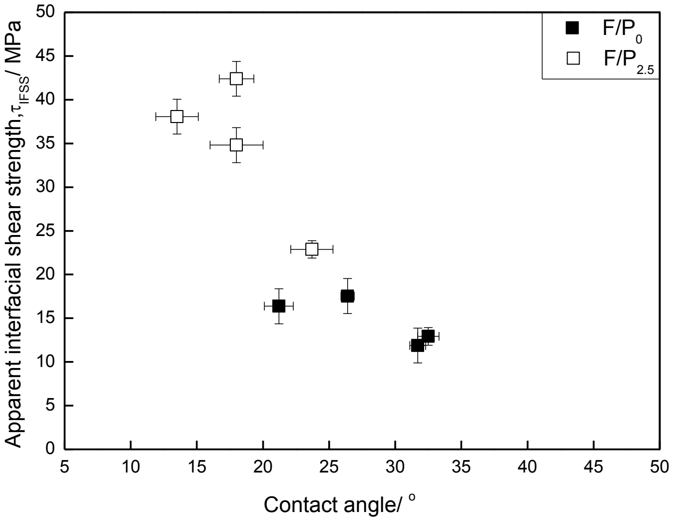


Figure 6.6 Apparent interfacial strength as a function of contact angle for different degrees of carbon fibre fluorination and various matrix blends

6.3.5 Interlaminar strength of unidirectional carbon fibre reinforced PVDF composites

The effect of both matrix and fibre modifications on the interlaminar shear strength of unidirectional carbon fibre reinforced PVDF composites with a fibre volume fraction of 60 ± 2% was studied using short beam shear test. The interlaminar shear strength (ILSS) of AS4 (F_0)/PVDF (P_0) composites was only 7.2 ± 0.2 MPa (Fig. 6.7). By using MAH-grafted-PVDF as matrix, the ILSS of AS4 (F_0)/P_5 composites increased significantly to 53.8 ±1.3 MPa, a 7 times improvement as compared to ILSS of F_0/P_0 composites. Improvements of the ILSS over that of F_0/P_0 can also be seen by introducing fluorine onto the surface of carbon fibres for every degree of matrix modification; $P_{2.5}$ and P_5. The ILSS of composites made with carbon fibres (F_1) containing 1.7 at.-% of fluorine on their surface with pure PVDF (P_0) improved by 32% as compared to F_0/P_0 composite. An improvement of 5.4% and 3.7% of the ILSS was obtained for composites manufactured using carbon fibres (F_1) with 1.7 at.-% of fluorine content with 2.5ppm

MAH grafted PVDF ($P_{2.5}$) and 5 ppm MAH grafted PVDF (P_5), respectively. Only carbon fibres with 1.7 at.-% of fluorine content (F_1) was chosen for this study to ease the manufacturing process (faster speed for better productivity).

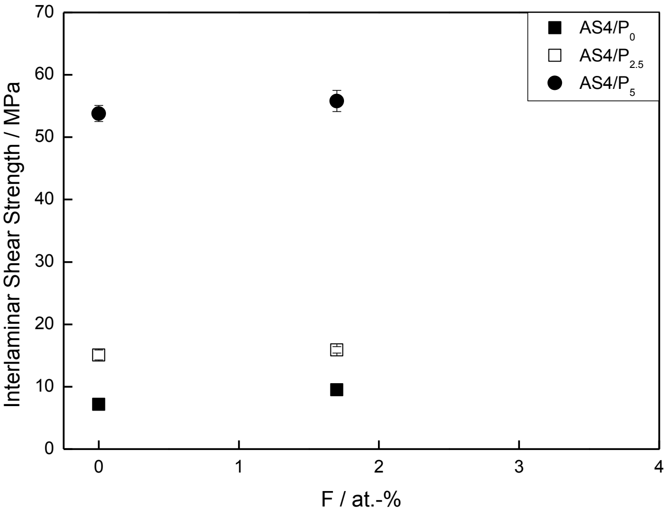


Figure 6.7 Interlaminar shear strength of unidirectional carbon fibre reinforced PVDF composites as a function of fluorine content on carbon fibre surface

The improvements in ILSS of the composites manufactured by modifying either the fibres, or the matrix or both indicates that the stresses induced in these composites can be transferred more efficiently and this can only be achieved by an sufficient interfacial interaction at fibre/matrix interface. Fracture surfaces from short beam shear test specimens can be found in Fig. 6.8. The specimens were prone to delamination and splitting as they were subjected to high shear forces [225]. This is clearly shown in the fracture morphology as each tested specimen showed clear delamination between the laminates within the composite.

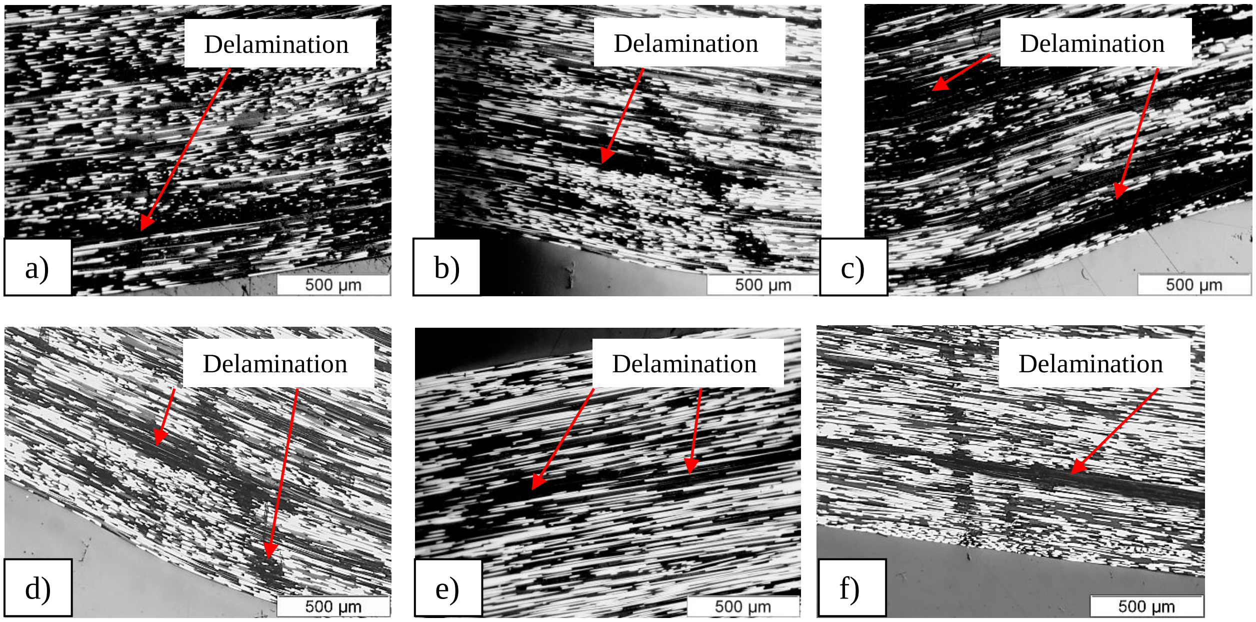


Figure 6.8 Microscopic images of fracture surfaces of UD carbon fibre reinforced PVDF composites during interlaminar shear test: (a) F0/P0, (b) F1/P0, (c) F0/P2.5 (d) F1/P2.5, (e) F0/P5 and (f) F1/P5

A plot of ILSS as a function of apparent IFSS is shown in Fig. 6.9. Both fibre and matrix modifications resulted in significant improvements of the fibre/matrix interface in both unidirectional as well as single fibre model composites. The synergy of both modifications on the ILSS UD composites still exists, although small. The apparent IFSS of single fibre composites increased by fluorinating the fibres alone and this increase is also indicated in the resistance to delamination in the UD composite material. When using a modified matrix, i.e. a blend of MAH-grafted-PVDF with PVDF ($P_{2.5}$), fluorinating the carbon fibres does not influence the ILSS values but significantly increase the apparent IFSS. However, when P_5 was used as the matrix, the composites resistance to delamination increases significantly but again fluorinating the fibres did not affect the ILSS. Nevertheless, the ILSS is property of a real composite and the improvement in the composite's resistance to delamination is noteworthy.

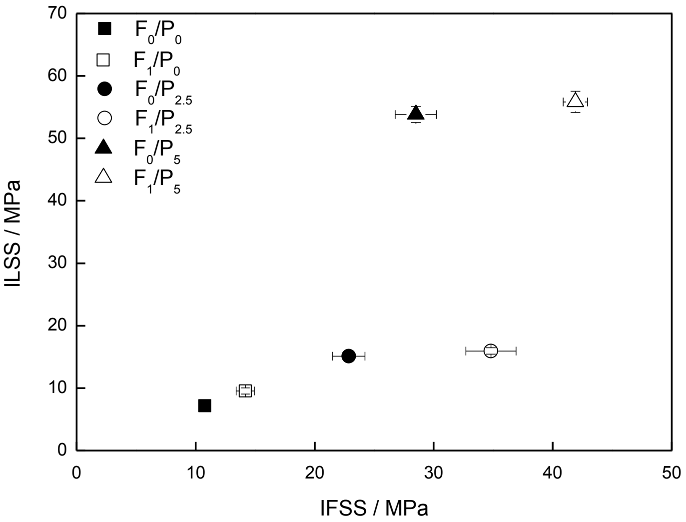


Figure 6.9 Interlaminar shear strength of unidirectional carbon fibre reinforced PVDF composite laminates as a function of apparent interfacial shear strength of single fibre model composite

6.4 Summary

The effect of fibre and matrix modification on the interfacial properties of single carbon fibre/ PVDF model composites and ILSS of unidirectional carbon fibre/PVDF composites was characterised. Carbon fibres with surface fluorine and oxygen contents of up to 3.7 at.% and 12.7 at.%, determined using XPS, were obtained using continuous atmospheric plasma fluorination. The matrix was modified by blending PVDF with/ or using MAH-grafted-PVDF. A significant amount of oxygen (up to 8.19 at.%) was present in MAH-g-PVDF corresponding to 5 ppm MAH grafting. Contact angles as well as the apparent interfacial shear strength measured between single APF carbon fibres and PVDF showed better interfacial adhesion between fluorinated carbon fibres and modified PVDF due to the improved dispersive and H-bonding interactions between the fluorine and oxygen groups on the carbon fibres and matrix. A clear synergy between carbon fibres and matrix modifications was observed resulting in improvements beyond the additive effect caused by either matrix or fibre modification. τ_{IFSS} improved significantly from 10.6 MPa for PVDF model composite containing as-received AS4 to 42 MPa for model composites consisting of carbon fibres containing 2.8 at.% fluorine and 5 ppm MAH-grafting on PVDF. ILSS of UD composites improved significantly from 7.2 MPa for as-received

AS4/PVDF composites to 55.8 MPa for composites containing carbon fibres with 1.7 at.% fluorine on their surface and 5 ppm MAH grafting on PVDF. Such optimised interface matches the tensile strength of the pure matrix, as determined by tensile tests and has resulted in carbon fibre reinforced PVDF composites with much improved interlaminar properties.

7.0 Mechanical performance of carbon fibre reinforced poly(vinylidene fluoride) pipes

Unidirectional (UD) carbon fibre reinforced polyvinylidene fluoride (PVDF) was manufactured using a laboratory scale composite line with in-line carbon fibre surface treatment. The carbon fibres were fluorinated using an atmospheric plasma fluorination (APF) method. The resulting continuous UD carbon fibre reinforced PVDF prepregs were used to fabricate reinforced thermoplastic pipes (RTPs) via filament winding method. Winding angle of ±55° was employed as a preliminary study. The impact of APF treatment of carbon fibres on the hoop tensile strength as well as stiffness of the RTP is presented. The results showed that the hoop tensile strength of the reinforced thermoplastic pipe can be enhanced by 18% by tuning the fibre/matrix interface through incorporation of fluorine functional groups on the fibre surface. An improvement of 15% in the pipe stiffness factor with RTPs made with APF treated carbon fibres was also observed. This indicates the ability of stress transfer between the fibres and the matrix through the interface is enhanced and this is due to the improved adhesion between the fibres and the matrix by incorporating APF on the fibre surface.

7.1 Introduction

The global demand for crude oil and natural gas showed a very stable yearly growth rate averaging 1% in the 20th century. However, the demand of oil and gas has now increased to an average of 1.7% per annum from 2009 due to the increased energy demand especially in developing countries such as China and India. The most critical area that requires special attention directly relating to the final price of consumed oil or gas is transportation [263, 264]. Pipelines are generally the most economical way to transport large quantities of oil or natural gas over land. Compared to shipping by railroad, they have lower cost per unit length and higher capacity. However, to build transportation pipelines on the sea-bed is more complicated due to the harsh environment especially in deep sea. High and fluctuating pressures, exposure to sweet and sour crude oil and other corrosive chemicals are a few of the main challenges to be taken into consideration when designing pipelines for deep-sea offshore oil and gas facilities. The key task for scientists and engineers is to design and fabricate materials which can offer excellent mechanical and chemical properties and at the same time are cost effective. This does not only include the material cost, but the overall manufacturing and delivery of the product must also be considered [265-268]. Oil and gas transportation pipelines are conventionally made from steel or polymers. However, composites can offer a better balance between service weight and mechanical and chemical performance than steel and polymers. This has motivated the oil and gas industry to explore possibilities of using composites on offshore oil and gas platforms.

Carbon fibres have been one of the most commonly used reinforcement in engineered composites over the past 40 years [269-271]. Exceptional mechanical properties as well as outstanding chemical stability make them an ideal material for use as reinforcement for polymers and, therefore, are widely used in structures and in load bearing applications including the flow lines for deep sea oil and gas exploration [268, 272, 273]. High modulus and excellent fatigue and chemical resistance are also some of the advantages of carbon fibres as compared to other reinforcements such as glass and aramid fibres. Though aramid fibres have the highest strength to weight ratio, they are not suitable for deep sea applications because they are very susceptible to water absorption and have poor compression properties when compared to carbon fibres [274-277].

The most widely used matrices for composites are polymers. This is because polymer materials are easy to process and do not require high pressure and temperature during composite manufacturing. Furthermore, polymers are known for their low density, and can be used either as solution or in molten state to impregnate the reinforcement, thus easing the manufacturing process [278]. This makes a low density composite with low manufacturing cost and diversity of material to choose from for different applications. For offshore application, the selection of the polymer matrix is based on the sustainability of the material to perform under environmental and mechanical loads, resistance to moisture and having a reasonable glass transition temperature (T_g) to make sure the polymer can withstand a reasonably wide temperature range during its service [279]. Polyvinylidene fluoride (PVDF), which is a fluorinated thermoplastic is widely used in the high purity semiconductor market as well as for the manufacturing of pipes, valves and ultrafiltration membranes [16]. As a fluoropolymer, PVDF exhibits not only great toughness but also a reasonable thermal performance. Besides that, PVDF has excellent chemical resistance, low permeability to gases and liquids and low water absorption (0.03%) which are the key parameters for deep sea oil and gas applications. Furthermore, in the oil and gas industry, PVDF has already been recognised and used as pipe liner especially where the material has to withstand highly corrosive fluids [280]. To exploit the full benefits such as inertness and other outstanding characteristics of PVDF, it has been reported previously that PVDF can be used as matrix in carbon fibre reinforced polymer composites [18, 20]. The mechanical performance of carbon fibre reinforced PVDF is relatively low as compared to aromatic polymer composites (APC2), however, studies conducted previously have shown that it is possible to improve performance of the composite by adopting atmospheric plasma fluorination (APF) of carbon fibres or by modifying the surrounding matrix by incorporating maleic anhydride grafted PVDF [18, 92, 281]. In this chapter, a preliminary study on the mechanical performance of reinforced thermoplastic pipes (RTPs) fabricated by filament winding of carbon fibre reinforced PVDF composite prepregs at ±55° angle onto a PVDF liner is presented and discussed.

7.2 Materials and method

7.2.1 Materials

Commercially available high strength, unsized, but industrially oxidized polyacrylonitrile (PAN) based carbon fibres (Hexcel, AS4 12K) supplied by Hexcel Corporation (Duxford, Cambridge, UK) were used in this study. Kynar® 711 Polyvinylidene fluoride (PVDF) was used as the matrix material and was kindly supplied by Arkema (King of Prussia, USA). Due to the hydrophobic nature of PVDF, a surfactant was used to stabilise the suspension of PVDF powder in water. The surfactant used was Cremophor® A25 (BASF, Ludwigshafen, Germany). Gases used as feed gas for the atmospheric plasma fluorination were chlorodifluoromethane (Freon 22) and nitrogen (N_2) (BOC, London, UK). An unreinforced PVDF pipe (2” Schedule 80 x 6 m pipe) was purchased from Professional Plastics, Fullerton, California, USA and was used as internal liner for the composite pipe fabrication.

7.2.2 Manufacturing of unidirectional (UD) carbon fibre reinforced PVDF composite prepregs with inline atmospheric plasma fluorination (APF) modification of carbon fibres

The method used for the manufacturing of UD carbon fibre reinforced PVDF composite prepregs was a wet powder/slurry impregnation route. This method was chosen from previous study [282] and it has demonstrated to produce composites comparable to commercially available carbon fibre reinforced PEEK composite such as APC2. A spool of 12K AS4 carbon fibres was set under a tension of 100 g from a tension let-off unit (Izumi International, Greenville, SC) and was passed through a continuous atmospheric plasma treatment jet (FLUME Jet RD1004; Plasmatreat, Steinhagen, Germany) for the inline APF modification of the carbon fibres. A detailed description of APF treatment on carbon fibres can be found in [95]. The treated fibres were then passed through an impregnation bath filled with 9 wt% of PVDF powder (with respect to water) and 2 wt% of surfactant (with respect to PVDF powder) in 2.5 L of deionised water. The polymer suspension in the bath was continuously stirred to ensure homogenous distribution of the polymer throughout the impregnation process. The impregnated fibres were then passed through a series of infrared-heated ovens. The fibres were subjected to a drying oven operating at

125 °C to remove all the water from the fibres before entering a second oven operating at 205 °C to melt the PVDF powder on the fibres. The polymer-impregnated fibres were then passed through a series of heated pins operating at 220 °C to spread the molten polymer homogenously within the fibre tow. The resulting continuous UD composite prepregs (10 mm wide, 0.2 mm thick) was then allowed to consolidate at room temperature while being pulled using a belt haul-off unit (Model 110-3, RDN Manufacturing Co., Bloomingdale, IL, USA). The UD composite prepregs were manufactured using three different manufacturing speeds; 1 m/min, 0.75 m/min and 0.33 m/min to study the effect of different fluorine contents on the fibre surface when subjected to APF on the mechanical properties of the composites produced. During the manufacturing process, the polymer powder in the impregnation bath is consumed by the continuous fibre tow, which leads to a potential variation in the composite's fibre volume fraction, V_f, which is determined by the formula;

$$V_f = \frac{\rho_m W_f}{\rho_f W_m + \rho_m W_f} \tag{7.1}$$

where ρ and W corresponds to the density and weight and f and m are the fibre and matrix properties respectively (ρ_m = 1.78 g/cm^3, ρ_f = 1.80 g/cm^3 and W of 1 m fibre = 0.858 g). Therefore, to ensure a consistent fibre volume fraction of the unidirectional composite prepregs, the concentration of the impregnation bath has to be kept constant throughout the manufacturing process. This was achieved by addition of 50 ml of concentrated polymer suspension (20 wt%) at regular intervals. Only carbon fibre reinforced PVDF composite prepregs with V_f of 60 ± 2% were chosen for further characterisation.

7.2.3 Production of reinforced thermoplastic pipes

(This work was carried out in Swerea SICOMP AB, Piteå, Sweden)

Reinforced thermoplastic pipes (RTP) were fabricated using a continuous filament winding technique. Pure (unreinforced) PVDF pipe (2" Schedule 80 PVDF) having an outside diameter of 60.4 ± 0.1 mm and average thickness of 5.75 mm was mounted and secured onto a steel mandrel using a heat resistant flash tape. This pipe served as the internal liner for the composite pipe. The

UD carbon fibre reinforced PVDF prepregs where then mounted onto a purpose-built pneumatic tension let-off unit, which was regulated to 2 bar pressure. The UD composite prepregs were then passed through a series of horizontal pins and onto a PTFE roller exiting into an angle control unit before it was secured onto the pure PVDF liner by direct heating of the prepregs on the PVDF liner. The winding process was controlled using a filament winding machine (Type: LW11-50/200 Retrofit, Waltritsch & Wachter GmbH, Bodnegg-Rotheidlen, Germany). The winding angle and speed were set to ±55° and 25 mm/s, respectively. During the winding process, two heater units were used; one set at 100 °C and placed underneath the PVDF liner and one that is set to 200 °C travelling with the prepreg as it was wound onto the PVDF liner. The filament winding process was continued until the desired composite wall thickness (~3.5 mm) was obtained.

Figure 7.1 Photographic image of filament winding unit used to fabricate reinforced thermoplastic pipe

7.2.4 Preparation of RTP sections for mechanical testing

The filament wound composite pipes were then cut into sections of 25 mm width using a diamond blade cutter (Diadisc 4200; Mutronic GmbH &Co., Rieden, Germany). To ensure a good and parallel surface of the composite sections, the cut sections were further polished (ApexDGD 60 μm Buehler Ltd, IL, USA) using a P1200 sandpaper and diamond suspension

(MetaDi 6 µm, Buehler Ltd., IL, USA). The pipe sections were then trimmed and cleaned using ethanol to remove any burrs and contamination. The polished RTP sections were left to dry in a vacuum oven (operating at 0.1 bar pressure) overnight at temperature 40 °C to remove any water or solvent from the composite prior to characterisation.

7.2.5 Mechanical characterisation of RTP

7.2.5.1 Hoop tensile tests of RTP sections

Hoop tensile tests were conducted on pipe sections by using the split disk method according to ASTM D2290 [283]. A pipe section having an outside diameter of 65.0 mm, a thickness of 8.5 mm and a width of 25 mm was mounted into a self-aligning split disk test fixture (Fig. 7.1). The composite ring was loaded into the jig without drilling a reduced section according to the standard [283]. Hoop tensile tests were carried out in an Instron 5581 (Instron, High Wycombe, Buckinghamshire, UK) equipped with 50 kN load cell. The cross head speed was set to 12.5 mm/min and the specimen was loaded until failure. The apparent hoop tensile strength σ of the RTP section was calculated based on the equation below:

$$\sigma = \frac{P_{\max}}{(b_1 d_1 + b_2 d_2)} \tag{7.2}$$

where P_{max} is the maximum load at failure, b_1 and b_2 are the width of the specimen at the midpoint of disks which are located 180° apart, d_1 and d_2 are the thickness of the specimen at the midpoint of disks which are located 180° apart. The test was conducted on at least five specimens to obtain a statistically significant average and the errors presented are standard deviations.

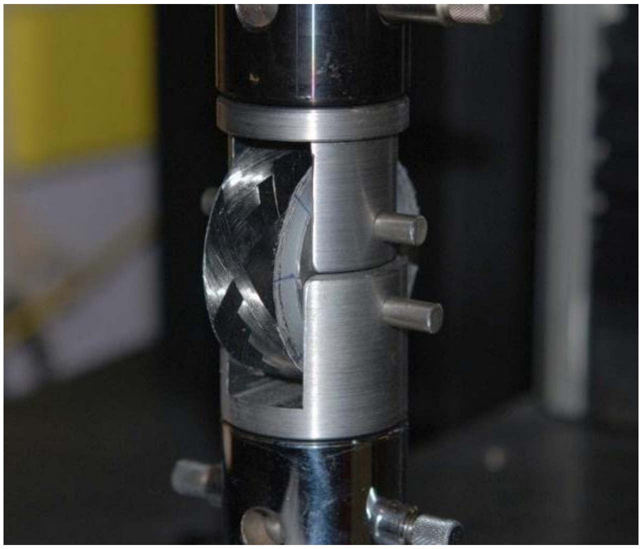


Figure 7.2 Fixture configuration of apparent tensile test using split disk method according to ASTM D2290

7.2.5.2 Compression tests of RTP sections

The compressive properties of RTP sections were determined from external load-deflection characteristics of the composite pipe under parallel plate loading according to ASTM D2412 [284]. This test method was used to determine the pipe stiffness and stiffness factor which can be used for engineering design. A RTP section of the same dimensions as stated in section 7.2.5.1 was placed between two parallel plates. The compression test was carried out at a crosshead speed of 12.5 mm/min in an Instron 5581 (Instron, High Wycombe, Buckinghamshire, UK) equipped with a 50 kN load cell, until the specimen deflection reached 30% of the average inside diameter of the composite pipe. The pipe stiffness *PS* and stiffness factor *SF* were calculated as follows:

$$PS = \frac{F^d}{\Delta y} \tag{7.3}$$

$$SF = 0.149 r^3 \cdot PS \tag{7.4}$$

where F^d is the load per unit length at a specific deflection (N/mm) (in this case, at 30% deflection), Δy is the change in the inside diameter of the specimen in the direction of load (mm) and r is the internal radius of the pipe specimen (mm). The percentage of pipe deflection, P can be calculated as follows:

$$P = \frac{\Delta y}{d_i} \times 100 \tag{7.5}$$

where d_i is the initial inside diameter of the specimen (mm). The stiffness factor can also be written as a function of the materials flexural modulus E (GPa) and overall wall thickness of the pipe t (mm);

$$SF = EI = E \cdot \frac{t^3}{12} \tag{7.6}$$

At least 5 specimens were tested to obtain a statistical average pipe stiffness and stiffness factor. The errors presented are standard deviations.

7.2.8 Microscopic analysis of composite test specimens

RTP sections which were subjected to compression loading were cut into 2 cm long sections using a diamond blade cutter (Diadisc 4200; Mutronic GmbH & Co., Rieden, Germany). The cut sections were embedded into a polyester resin (EpoxyCure, Buehler Ltd, IL, USA). The resin was cured for 24 h at room temperature before being polished using resin bonded diamond grinding discs (ApexDGD 60 μm Buehler Ltd, IL, USA). Specimens were ground first using a water medium for 20 min at a pressure of 0.2 MPa and a speed of 150 rpm. After that the specimens were polished using a diamond suspension (MetaDi 6 μm, Buehler) for 2 min, afterwards using 3 μm and 1 μm diamond suspensions, respectively, using the same polishing parameters. Polished specimens were then examined under an optical microscope (BH2, Olympus, Tokyo, Japan).

7.3 Results and discussion

It has been shown previously that the manufacturing speed of 1 m/min, 0.75 m/min and 0.33 m/min corresponds to retention times of 0.6, 0.8 and 1.8 min, respectively, in the active zone of APF jet [72, 92]. It has also been shown that the amount of fluorine functional groups present on the fibre surface increased with the retention time. Table 7.1 summarises these findings.

Table 7.1 Line speed, retention time and fluorine content of fibre exposed to inline APF modification

Line speed (m/min)	*Retention time (min)*	*F (at.-%)*
1.00 (unmodified)	0.6	-
1.00	0.6	1.7
0.75	0.8	2.8
0.33	1.8	3.7

7.3.1 Mechanical properties of ±55° filament wound carbon fibre reinforced PVDF composite pipe sections

The winding angle is the major dominating factor influencing the mechanical performance of RTPs [285]. Higher winding angle contributes to higher hoop modulus and, therefore, can resist higher buckling load when the RTP is subjected to external pressure. Lower winding angle on the other hand contributes to higher axial strength and modulus [286]. A winding angle of ±55° was chosen for this preliminary study, as it is widely used and has been established as the optimum winding angle for a tubular section where the hoop-to-axial stress ratio can be as high as 2:1 [286, 287]. The methods chosen for characterising the RTPs fabricated were hoop tensile strength determined using a split disk test and compression determined using parallel plate loading tests. According to the ASTM D2290 standard, the split disk test fixture may impose a bending moment at the split during the test and, therefore, the results do represent the apparent tensile strength rather than the true tensile strength of the material. When applied to a composite structure such as used in this study, it is more complex because the composite pipe was made using a ductile PVDF liner and an outer layer consisting of a UD carbon fibre reinforced PVDF that is wound around the liner at an angle of ±55°. The apparent tensile strength of the neat PVDF pipe and RTPs fabricated using UD composite prepregs manufactured at different processing speeds which correspond to various degrees of fluorination on the carbon fibre surface are presented in Table 7.2. The apparent tensile strength of the pure PVDF pipe was determined to be 52.9 ± 0.3 MPa, which is similar to the tensile strength of Kynar® 711 PVDF as quoted by the manufacturer[§§§§] as well as previously reported results [92]. By adding a 3 mm thick layer of ±55° carbon fibre reinforced PVDF around the pure PVDF pipe, the apparent hoop tensile strength increased by 8% to 57 ± 1.2 MPa.

Table 7.2 Apparent tensile strength of pure PVDF pipe and RTPs fabricated using UD composite prepregs manufactured at different degrees of fluorine content on fibre surface

Specimen	***Apparent tensile strength (MPa)***
Pure PVDF	52.9 ± 0.3
Unmodified CF/PVDF	57.2 ± 1.2
APF treated CF/PVDF (1.7 at.-% fluorine content on CF surface)	58.7 ± 2.0
APF treated CF/PVDF (2.8 at.-% fluorine content on CF surface)	59.7 ± 1.0
APF treated CF/PVDF (3.7 at.-% fluorine content on CF surface)	63.0 ± 2.0

The effect of APF treatment of the carbon fibre on the apparent tensile strength of the composite structure was also quantified. As expected from previous results, the improvement in the apparent hoop tensile strength is not significant if the PVDF composite contained carbon fibres with a low degree of fluorination, i.e. carbon fibre with surface fluorine content of 1.7 at.-%, the apparent hoop tensile strength of the RTP was 58.7 ± 2.0 MPa. However, it is notable that the apparent hoop tensile strength improved up to 19% to 63.0 ± 2.0 MPa when carbon fibre reinforced PVDF containing carbon fibres with surface fluorine content of 3.7 at.-% was used. The reason for this improvement of the tensile strength is the enhanced interfacial adhesion between fluorinated fibres and PVDF matrix [20, 71, 92, 281] resulting in an enhanced load transfer between the fibre and the matrix. Some observations were noted when performing the split disk tensile test. Firstly, due to the fact that a relatively thick internal PVDF liner (~5.5 mm

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[§§§§] *Kynar® 710 Homopolymer, Matweb. Link in: http://www.matweb.com/search/DataSheet.aspx?MatGUID=7378d6bf9bf84f2b8dcc1f49d40eeb44. Last accessed on 03.03.2012* thick) was used, the plastic yielding of the polymer pipe occurred before the ultimate failure of the RTP. Secondly, the tensile strength of pure PVDF is said to be about 50-55 MPa and because of this reason, the internal liner was subject to fail first before the composite layer fails.

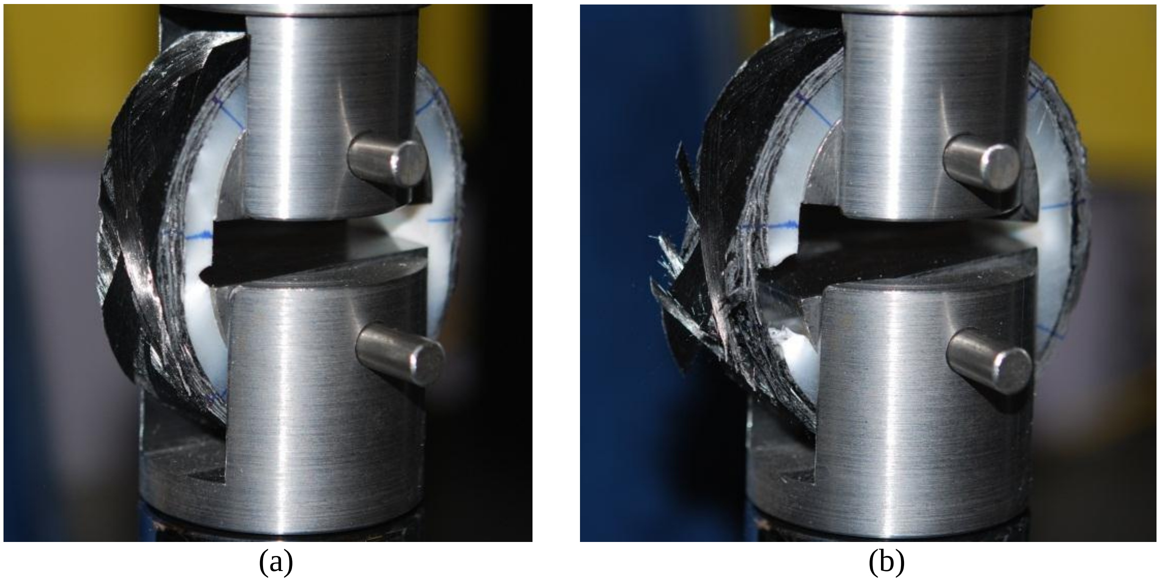
(a) (b)

Figure 7.3 RTP during the split disk tensile test (a) the internal liner which consisted of pure PVDF pipe underwent plastic yielding and started to crack (b) the entire composite failed catastrophically when the internal liner failed as it can no longer withstand the stress

Therefore, when the pure PVDF liner elongated and failed at its maximum stress, it causes a catastrophic failure of the entire structure (See Fig. 7.2). Hence, the composite layer failed with the PVDF liner when in principle, it should withstand more stress than the pure PVDF pipe (Fig. 7.3). Furthermore, it is worth mentioning that the apparent tensile strength obtained from this test is somewhat low for a composite structure with ±55° layup when compared to literature [288, 289]. Kaynak et al. [288] studied various winding angle on two different carbon fibre reinforced epoxy composite pipes. The authors reported that the apparent hoop tensile strength of the composite pipe made from carbon fibre reinforced epoxy with ±45° winding angle was about 180 MPa. Separate work by Sobrinho et al. [289] on ±55° winding angle of glass fibre reinforced epoxy composite pipe resulted in apparent hoop tensile strength of 731 MPa. Both studies utilised composite pipes made without a polymer liner to understand the stress of the composite. Therefore, further study on composite laminate with ±55° layup and RTP sections without a

PVDF liner should be conducted to understand the failure behaviour of only the composite when subjected to tensile load. The load vs. displacement curves can be found in Appendix D.

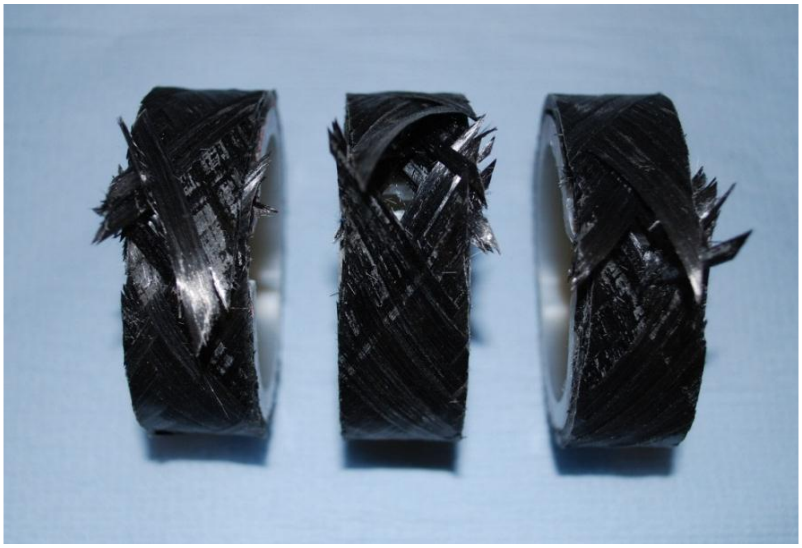

Figure 7.4 RTP consisting of a PVDF liner reinforced with layers of ±55° carbon fibre reinforced PVDF after subjected to split disk tensile test

The stiffness factor, $E \cdot I$ at 10% deflection of the pure PVDF pipe and PVDF pipes reinforced with carbon fibres with varying degree of fluorination is presented in Table 7.2. The stiffness factor of the pure PVDF pipe was 39 ± 2.0 μN/m. Based on this result, the PVDF flexural modulus can be calculated using equation 12, and was found to be 2.3 GPa. This value is comparable to the Young's modulus of Kynar® 711 PVDF material[****]. The stiffness factor of the RTP made with as-received AS4 fibres was found to be similar to that of the pure PVDF pipe. It was reported that the flexural stiffness of RTPs are usually comparable with unreinforced systems [290] and, therefore, the reinforcement does not have any effect on the stiffness factor of the overall structure. Furthermore, it is difficult to calculate the flexural modulus of the structure as it is made of two different materials (pure PVDF liner and carbon fibre reinforced PVDF). However, by introducing fluorine onto the carbon fibre surface, the pipe stiffness factor increased up to 15% to 43 ± 0.6 μN/m when carbon fibres with surface fluorine content of 1.7 at.-% was used to reinforce the PVDF pipe. Further increase in the degree of fluorination does not have any influence on the composite pipe stiffness factor as the values observed were within the error (Table 7.3). However, it can be seen that APF does have a positive impact on the stiffness factor of the RTP, hence making the RTP stiffer. This observation indicates that the composites made with fluorinated fibres allow for better utilization of fibres by enhancing the stress transfer and, therefore, able to withstand higher stresses when subjected to external load. On the contrary, the RTP made from unmodified CF/PVDF prepreg is less stiff and has less effective fibre/matrix interface, allowing for certain amount of fibre/matrix slippage when load is applied. The load vs. displacement curves can be found in Appendix E.

Table 7.3 Stiffness factor, *E·I* of pure PVDF pipe and RTPs fabricated using UD composite prepregs manufactured at different degrees of fluorine content on fibre surface

Specimen	***Stiffness factor, E·I (μN.m)***
Pure PVDF	38.8 ± 0.5
Unmodified CF/PVDF	38.7 ± 0.3
APF treated CF/PVDF (1.7 at.-% fluorine content on CF surface)	43.2 ± 0.7
APF treated CF/PVDF (2.8 at.-% fluorine content on CF surface)	45.2 ± 0.3
APF treated CF/PVDF (3.7 at.-% fluorine content on CF surface)	43.6 ± 1.0

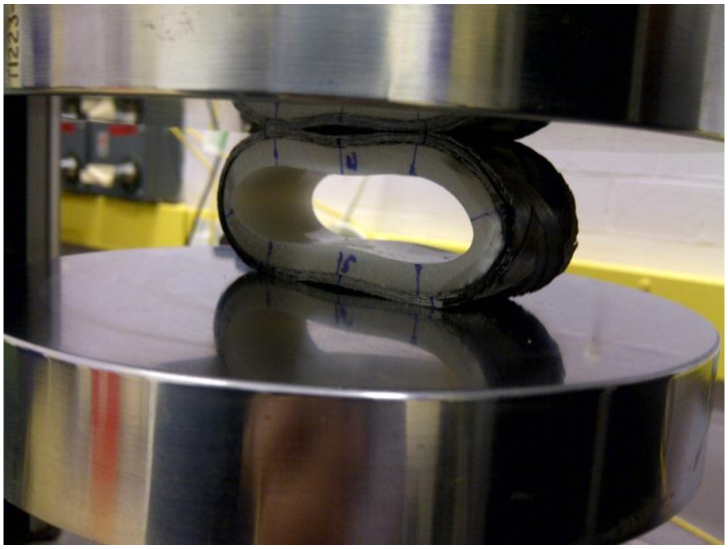

Figure 7.5 RTP specimen loaded under parallel plate according to ASTM D2412. No rupture was observed even at 50% of pipe deflection

During the test, no rupture, cracking, or crazing was observed on all the specimens even after being compressed of up to 50% of the internal diameter of the pipe (Figure 7.4). In order to understand if there any delamination or cracks formed within the tested specimens, the specimens subjected to loading between parallel plates were analysed using optical microscopy (Figure 7.5). The micrographs show that there were a number of voids present in all the specimens after testing. However, no visual delamination or apparent failures in the composite structure were observed after testing.

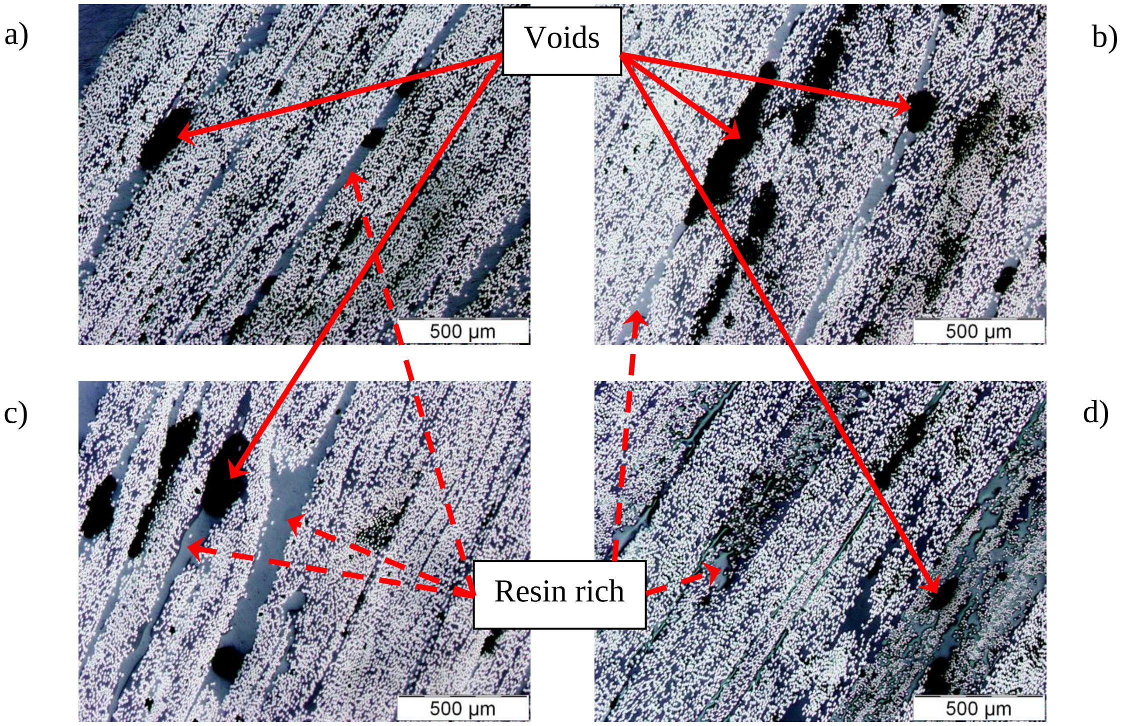

Figure 7.6 Optical microscope images of the composite layer of (A) as-received carbon fibre reinforced PVDF manufactured at 1 m/min, (B) APF treated carbon fibre reinforced PVDF with 1.7 at.-% fluorine content on fibre surface, (C) APF treated carbon fibre reinforced PVDF with 2.8 at.-% fluorine content on fibre surface and (D) APF treated carbon fibre reinforced PVDF with 3.7 at.-% fluorine content on fibre surface

7.4 Summary

The search for a strong, lightweight material to replace heavy and corrodible alloy pipes used for the exploration of deep-water offshore oil fields has motivated the oil and gas industry over the past few decades. PVDF, a polymer approved by the oil and gas industry to be used as internal liner in offshore pipelines and risers, has yet to be utilised completely. However, due to the inertness of PVDF, adhesion to carbon fibre has always been a challenge. This is tackled by fluorinating the carbon fibre surfaces in APF which was proven to improve the interfacial adhesion between the fluorinated fibres and PVDF. To study if the improvements observed in single fibre model composites and composite laminates reported previously are translated into a composite structure, RTPs were fabricated by filament winding UD carbon fibre reinforced PVDF prepregs with a winding angle of ±55° onto a pure PVDF liner. Unreinforced PVDF pipe and the fabricated RTPs were subjected to hoop tensile and compression tests. The apparent hoop tensile strength improved up to 18% for RTP made with carbon fibre reinforced PVDF containing APF treated fibres with surface fluorine content of 3.7 at.-% as compared to as-received fibres. Similar improvement was observed in the stiffness factor of RTP when the composite pipe structure was loaded under compression. These enhanced mechanical properties show that APF treatment of carbon fibres can tailor the fibre-matrix interface leading to better stress transfer between the fibres and matrix leading to improvement in the overall composite performance.

8.0 Conclusion and Suggestions for Future Work

The primary aim of this research was to develop and manufacture continuous unidirectional carbon fibre reinforced polyvinylidene fluoride (PVDF) by incorporating atmospheric plasma fluorination (APF) of carbon fibres to confirm that the improvements achieved previously on the single fibre model composite level can be translated to improvements on the composite laminate level. The findings obtained here will hopefully provide novel composites that could be used in applications which require excellent chemical inertness as well as high strength and toughness. The study of composites can be divided into micro-scale where the characteristics of the composite are studied at single-fibre level, macro-scale which covers the properties obtained on composite laminates and finally the application-scale, where the composites are made into a structure and its performance is demonstrated. Within the scope of this research, the macro-mechanical properties of carbon fibre reinforced PVDF laminates manufactured in-house were characterised to understand the effect of APF treatment on the performance of the composites.

Continuous unidirectional carbon fibre reinforced PVDF with a fibre volume fraction of 60 ± 2% were manufactured using a laboratory-scale composite production line via a wet impregnation method. APF treatment of carbon fibres was performed in-line during the manufacturing process prior to the fibres entering the impregnation bath. The manufacturing speed was altered to study the effect of various degrees of fluorination of the carbon fibre surfaces on the composite mechanical properties. It was found that both the flexural and interlaminar shear strength of the composite can be enhanced by as much as 110% and 200%, respectively, for composites made with fluorinated carbon fibres with surface fluorine content of 3.7 at.-% as compared to unmodified carbon fibre reinforced PVDF. Although an attempt was made to measure the critical energy release rate from Mode I, G_{IC} and Mode II, G_{IIC} interlaminar fracture toughness of the composites manufactured, both tests only indicate a flexural strength of the composite. This is mainly due to the nature of PVDF matrix as being tough at room temperature. Further work has to be done in order to measure the true interlaminar fracture properties of the composite. By carefully design the test specimen (having a thicker arm or using a stiff arm material such as aluminium plate), the problem with tough matrices could be tackled. However, it is worth to note that the improvements from the test results indicates the improvements in the flexural strength of the composite and these improvements can be directly related to the enhancement of the fibre/matrix interface by APF treatment on the fibre surface. In order to understand the axial tension behaviour of this novel composite, UD carbon fibre reinforced PVDF was subjected to tensile tests along the fibre axis. It was observed that the axial tensile strength and Young's modulus of the composite, being a fibre dominated property was 1,130 ± 53 MPa and 133 ± 6 GPa for the unmodified carbon fibre reinforced PVDF composite. By incorporating fluorine into the carbon fibre surface, the axial tensile strength and modulus improved by 8% and 5% to 1,260 ± 70 MPa and 140 ± 2 GPa, respectively, for composites made with carbon fibres containing fluorine content of 1.7 at.-% on the fibre surface. The results observed at the macro-scale demonstrated that APF treated carbon fibres has a positive impact on the overall mechanical performance of the composites manufactured over those made with as-received fibres. Therefore, the next step was taken to test whether these properties also translate into a composite structure, in this case, a reinforced thermoplastic pipes (RTP) with improved properties. RTPs were made by filament winding of continuous unidirectional carbon fibre reinforced PVDF prepregs onto pure PVDF liners. The winding pattern chosen was helical with a winding angle of ±55°. The composite pipe was cut into 25 mm wide ring sections and subjected to hoop tension and compression tests. The hoop tensile strength of the unmodified carbon fibre reinforced PVDF RTP increased by 8% to 57.2 ± 1.1 MPa from 52.9 ± 0.3 MPa for the PVDF pipe. The hoop tensile strength of reinforced PVDF pipes made with fluorinated carbon fibres containing 3.7 at.-% fluorine content on the fibre surface was improved by 10% to 63 ± 2 MPa. Similarly, the RTP stiffness factor was also enhanced by 11% when APF surface treated carbon fibre containing PVDF was used as compared to the PVDF pipe. All of these improvements show that by tailoring the fibre/matrix interface through APF surface treatment, the mechanical performance of the composite can be improved. This improvement indicates the ability of load to be transferred from matrix to fibre through the improved adhesion at the fibre/matrix interface. This was proven to be true from the micro-scale, macro-scale as well as at the application level.

A separate study was conducted to evaluate the effect of both fibre and matrix modification on the interfacial adhesion between fibre and matrix. The fibre was modified by atmospheric plasma fluorination (APF) while the matrix was modified by addition of maleic anhydride (MAH) grafted PVDF. A synergy between fibres and matrix modifications was observed on the interfacial shear strength (τ_{IFSS}). τ_{IFSS} was found to improve up to 300% for fibres with 2.8 at.-% fluorine content on its surface and matrix 5 ppm of MAH grafted PVDF. The improvement in τ_{IFSS} was found to match the ultimate tensile strength of PVDF. An enhancement was also observed in the interlaminar shear strength of UD carbon fibre reinforced PVDF laminates. These improvements show that the fibre matrix interface can be tailored further to optimise the interfacial adhesion which leads to overall improvement in the composite's performance. Although the improvements obtained were overwhelming, it was not possible to further characterise the mechanical properties of the laminates. This is mainly due to lack of resources especially of the MAH grafted PVDF. The MAH grafted PVDF that was used in this study was a research grade material that was kindly supplied by Arkema (Serquigny, France) and is not available on the market yet. However, this study showed synergy of both modifications as proof of concept. Further work should be carried out in the future if sufficient material can be obtained from Arkema.

8.1 Suggestions for future work

The results obtained from this research are very encouraging and open up the possibilities for further work which would help to further improve and understand carbon fibre reinforced PVDF better. We embarked on this research with a mind-set of developing an alternative material for the oil & gas and chemical industry, which requires inert composites that are relatively cheap and able to meet the industry's requirements. The future work laid out in this section can be divided into three areas, namely the optimisation of the manufacturing process, the tailoring of the interface by incorporating both fibre and matrix modifications as well as an outlook towards the composite pipe characterisation.

8.1.1 Optimisation of the composite production line to increase overall productivity as well as improving the APF treatment and wet powder impregnation process

There is room for improvement within the scope of the composite production line (CPL) that was used throughout this research. The first that should be improved is the overall productivity of composite prepregs. The entire length of the CPL at present is about 5 m while utilising two-units of infrared (IR) heaters. The maximum manufacturing speed that can be achieved without compromising the quality of the prepregs produced is 3 m/min. However, it is important to note here that the speed quoted can only be achieved when continuous composite prepregs were manufactured without APF treatment of carbon fibres. To further improve the productivity of the composite prepregs, the CPL should be expanded in length. In order to maintain an acceptable composite prepreg quality at high manufacturing speed, an extra IR heater is also required to ensure excess water can be removed completely from the polymer impregnated fibre tows during the manufacturing process.

As far as increasing the productivity is concerned, the possibility to improve the APF also has to be taken into consideration. At present, a plasma nozzle of 4.0 mm diameter is used and is located vertically on top of the carbon fibre tow. By modifying the plasma nozzle to have a horizontal opening (instead of a round one) of 25.0 mm long x 2.0 mm wide would increase the exposure of the fibres to the plasma jet hence the fluorination process can be improved. Increasing the exposed fibre area during the APF treatment is favourable to ensure efficient and homogenous modification of the fibre surface. This can be achieved by spreading the fibre tows better.

A fibre spreading machine has been purchased from Izumi (Japan) utilizing air flow to gently and evenly spread the fibres and is expected to arrive in April 2012. This equipment is said to have the capability of expanding the width of the original carbon fibre tow by as much as 4-5 times. By incorporating this equipment prior to the APF treatment, it is anticipated that the carbon fibre surface will be more evenly treated during APF. This unit is also expected to improve the ability of the fibres to pick-up polymer particles within the wet impregnation bath during the manufacturing process as the surface area of the fibres is enhanced.

8.1.2 Improvement at fibre/matrix interface adhesion and demonstrate its impact on the composite performance at a macro-scale level.

MAH is a reactive molecule; hence grafting this reactive substance onto an inert material such as PVDF is expected to improve the chemical interaction between a substrate (such as carbon fibres) and PVDF at the interface. The concept of enhancing the interfacial adhesion by using MAH grafted PVDF with fluorinated carbon fibres was proven to be successful, at least at micro-scale; i.e. model composite level. However, the question still remains if this improvement translates into the laminate or macro-scale composite level. The preliminary results obtained from the short beam shear test showed tremendous improvement in the interlaminar shear strength of the composites made with carbon fibres containing 3.7 at.-% fluorine and MAH grafted PVDF. However, more extensive characterisation is needed to understand effect of fibre and matrix modifications on the composite properties. The results obtained from these studies will then be a means of comparing the improvements achieved by solely modifying the fibres.

One aspect that could be further improved is to obtain a MAH grafted PVDF in powder form (with particle size of 5-40 μm) instead of pellets. This is to facilitate the powder impregnation process and to have homogenously distributed PVDF particles throughout the impregnated fibres. By using the polymer in powder form, one can omit the powder precipitation process and all the uncertainties and experimental errors involved therein.

8.1.3 In-depth study on different winding angles and various mechanical and chemical characterization of the composite pipe

The ±55° winding angle was chosen based on internal pressure criterion of a tubular structure, where the hoop stress is doubled than the axial stress [291]. However, due to the absence of high pressure testing rigs within the College, the internal pressure test on the composite pipes fabricated could not be conducted. There are a few technical issues that have to be addressed if such facility is to be built. Despite having to build a pressure test rig, one important issue that has to be looked into is the end fittings or joints which are required to seal and connect the RTPs. This has to be carefully designed especially for inert RTP, with an irregular outer surface to omit any leakage during the pressure test. Having made suitable jigs and fixtures, the composite pipe can be subjected to various tests to determine the burst pressure, time-to-failure at constant internal pressure as well as its ability to withstand cyclic pressures. The characterisation methods will then determine the design criteria of the fabricated composite pipe to demonstrate the feasibility of using composites as an alternative material for applications in harsh environments.

Besides pressure tests on the RTP, various other mechanical properties should also be studied. These could include bending under external pressure, impact, torsion, axial compression and tension. Although winding angle of ±55° was chosen as a preliminary study, different winding angles should also be employed. By varying the winding angle, the composite’s behaviour towards different loadings can be assessed. For example, axial modulus is highest at 0° fibre angle, hoop modulus is greatest in 90° fibre angle whereas shear modulus is enhanced using a ±45° fibre angle. However, since most previous studies in the RTP were conducted on glass fibre/epoxy or carbon fibre epoxy system, the study of these properties on novel carbon fibre reinforced PVDF pipe will be new and exciting as PVDF has already been accepted as an approved polymer for pipe liners and barriers in the oil and gas industry.

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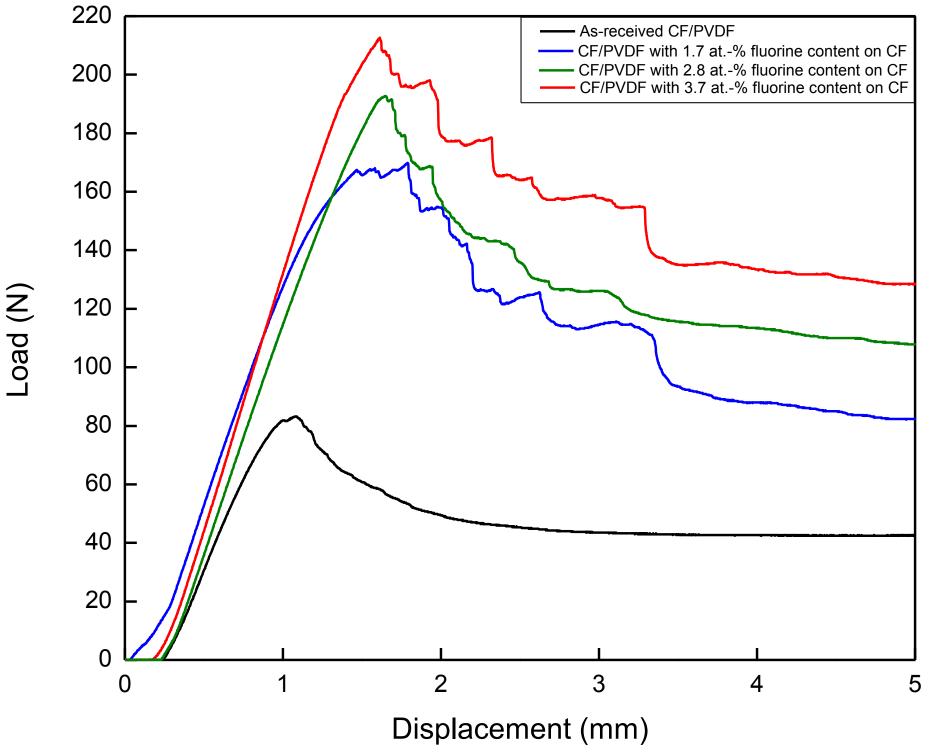
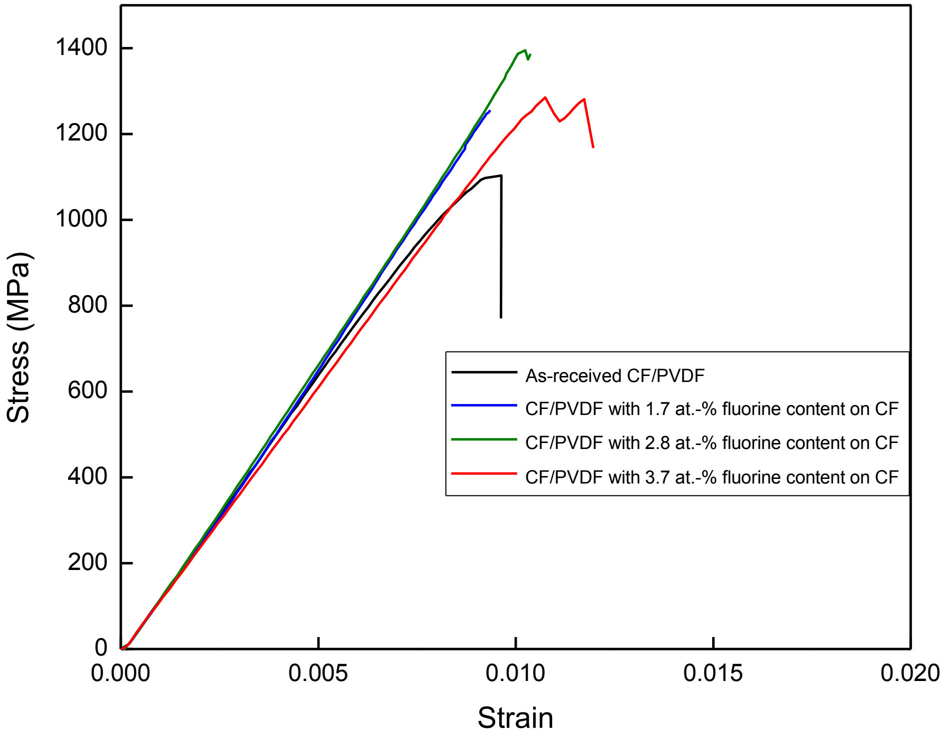
APPENDIX A

Typical load vs. displacement curves for each flexural test specimens



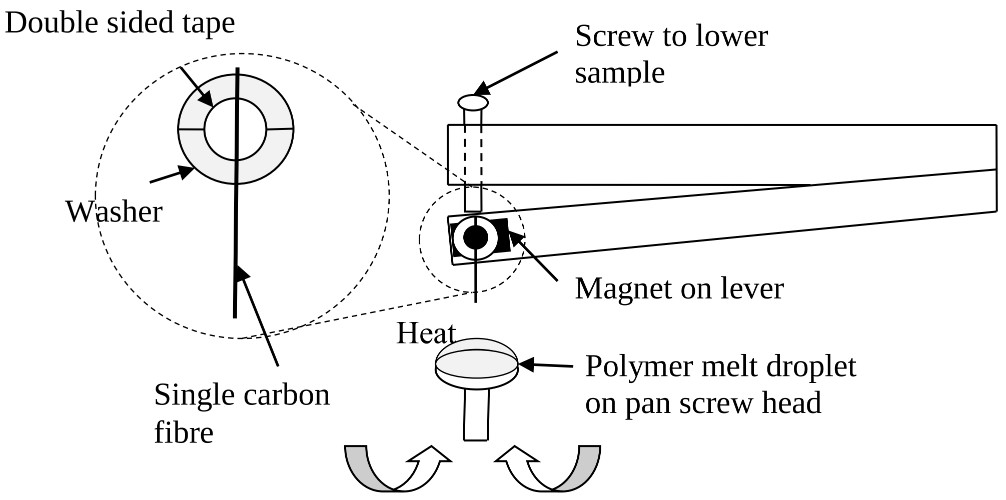
APPENDIX B

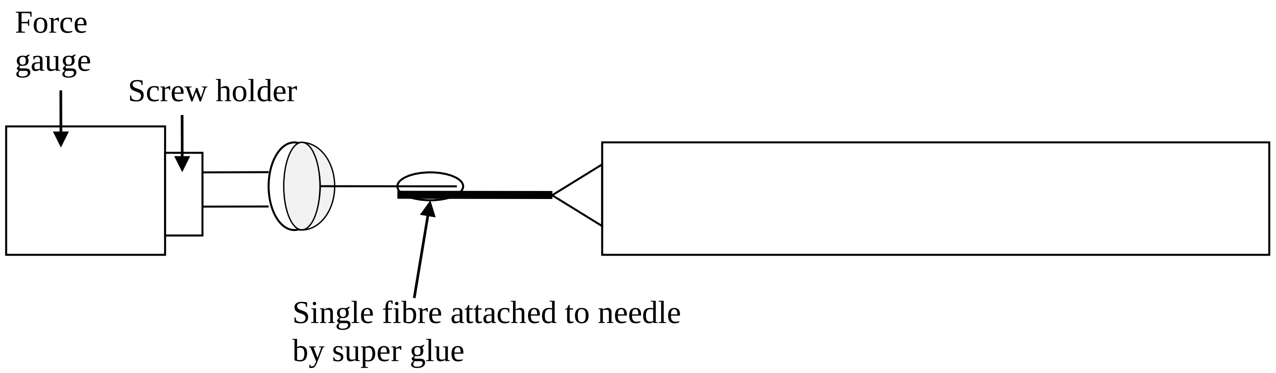
Typical stress vs. strain curves for each UD tensile test specimens



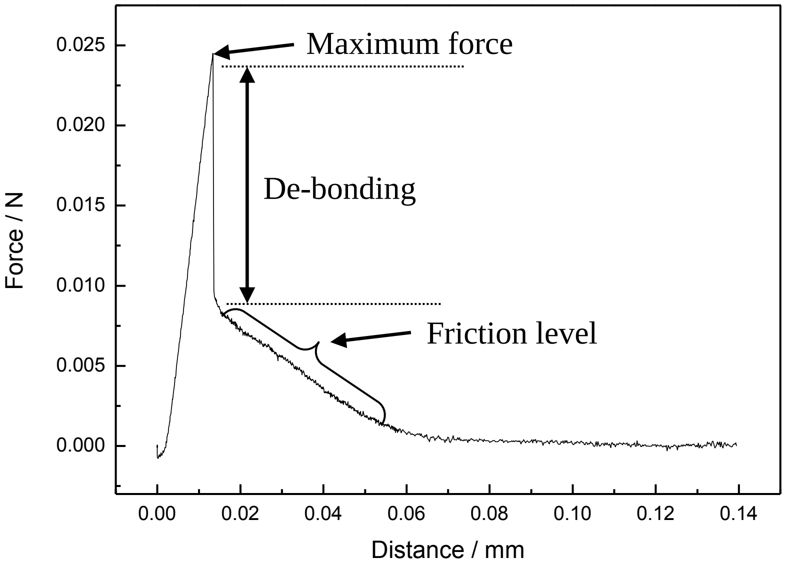
APPENDIX C

Schematic of Single Fibre Pull Out tests



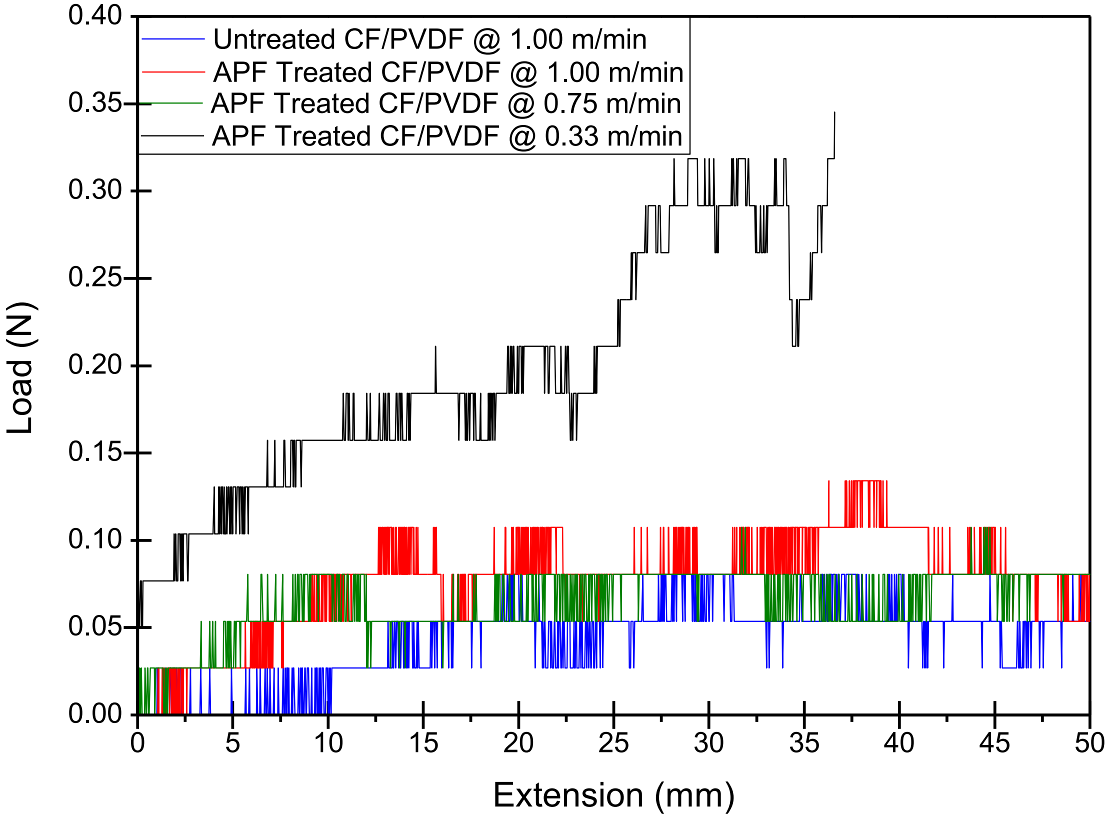


Typical force changes as a function of distance (displacement) during single fibre pull out test



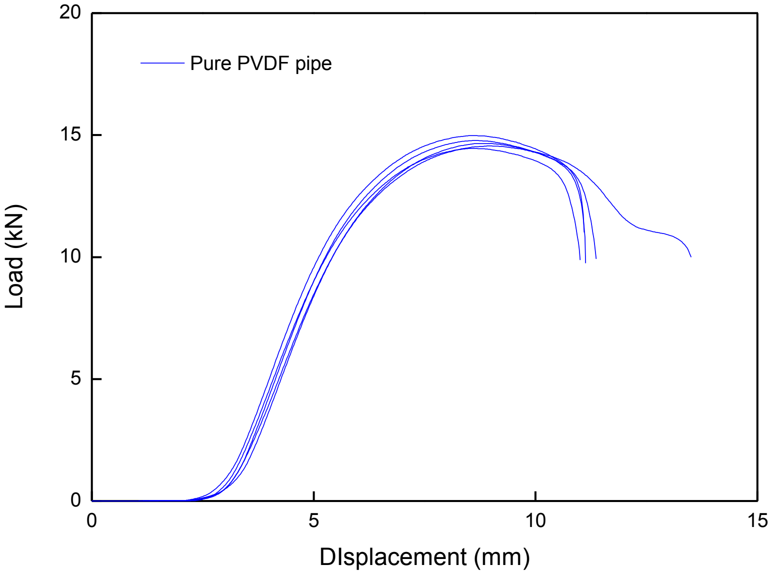
APPENDIX D

Typical load vs displacement for the trousers test.

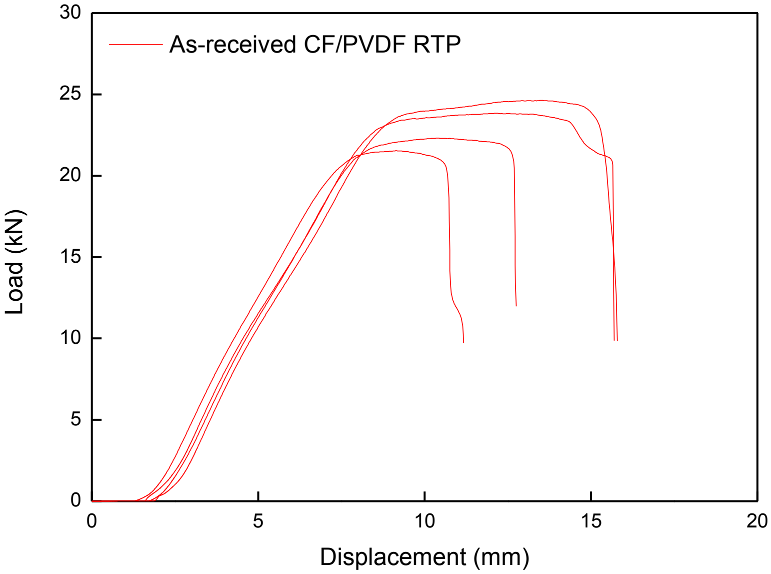


APPENDIX E

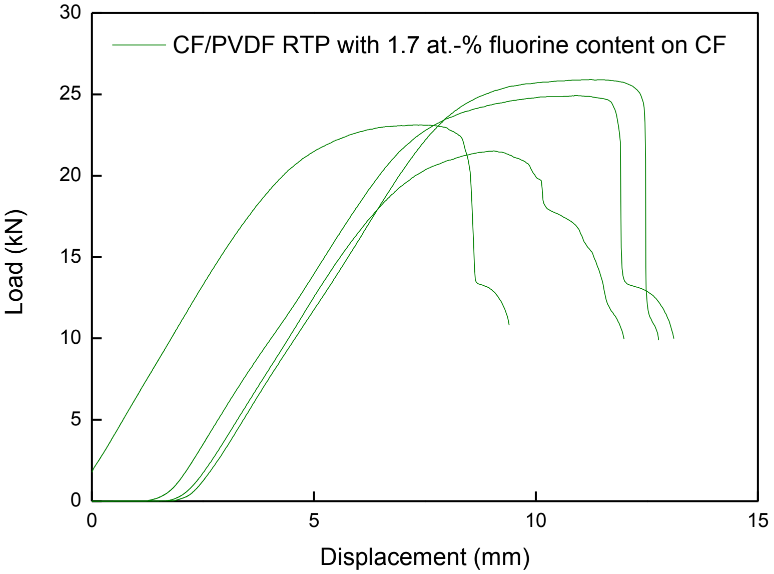
Load vs. displacement curves for (a) pure PVDF pipe, (b) Unmodified RTP and (c) RTP made with 1.7 at.-% fluorine content on carbon fibre surface from the split disk tensile test.



(a)



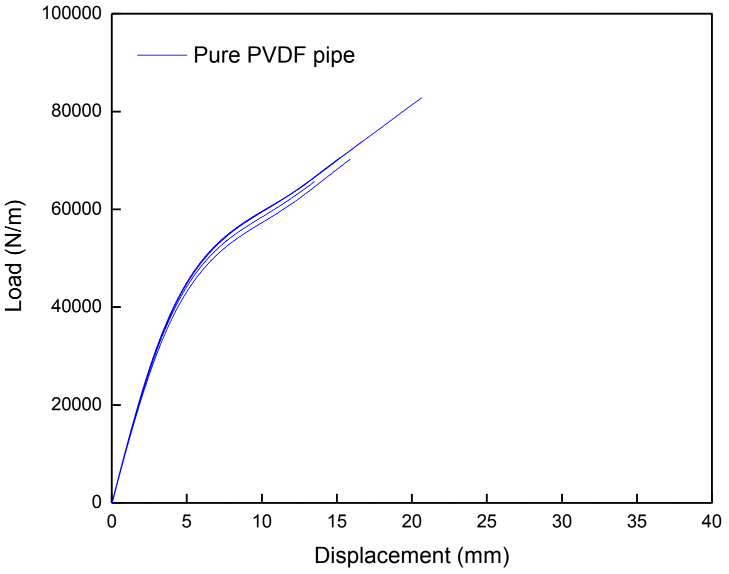
(b)


CF/PVDF RTP with 1.7 at.-% fluorine content on CF
Load (kN)
Displacement (mm)
0
5
10
15
20
25
30
0
5
10
15

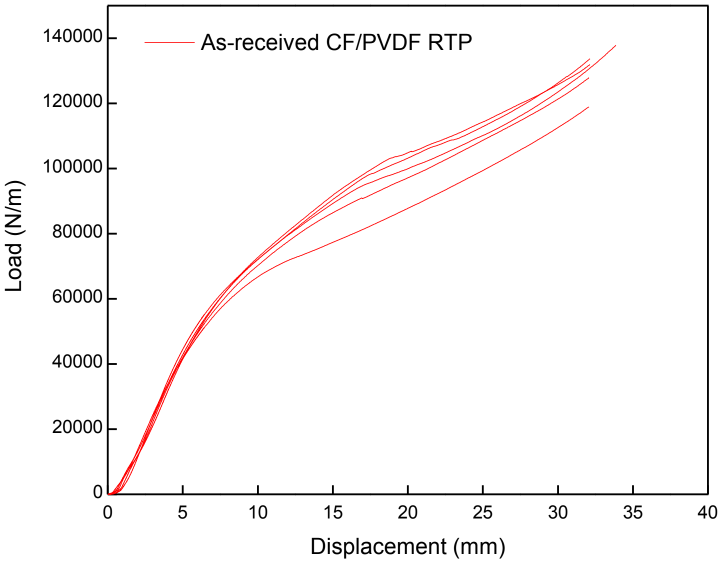
(c)

APPENDIX F

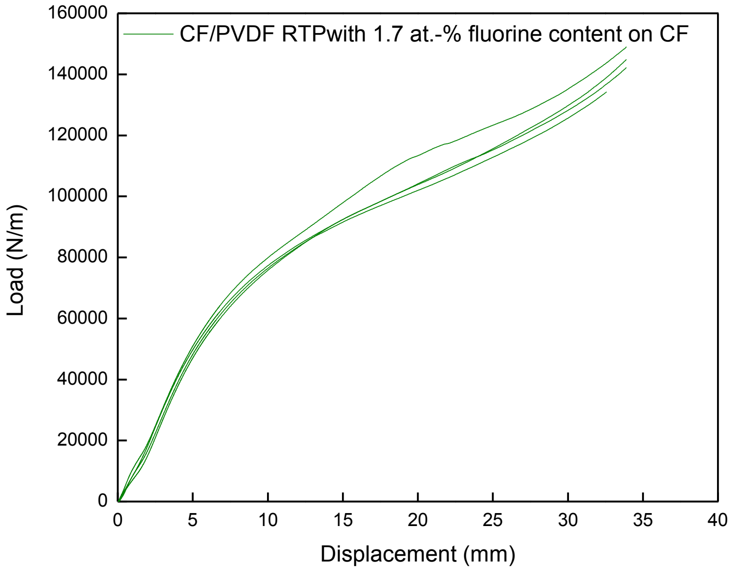
Load vs. displacement curves for (a) pure PVDF pipe, (b) Unmodified RTP and (c) RTP made with 1.7 at.-% fluorine content on carbon fibre surface from the compression test under parallel loading.



(a)



(b)


CF/PVDF RTPwith 1.7 at.-% fluorine content on CF
Load (N/m)
0
20000
40000
60000
80000
100000
120000
140000
160000
Displacement (mm)
0
5
10
15
20
25
30
35
40

(c)