

Carbon Fibre Reinforced PVDF and PEEK Nanocomposites

By

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Declaration

This dissertation is a description of the work carried out by the author in the Department of Chemical Engineering and Chemical Technology, Imperial College London between June 2007 and December 2010 under the supervision of Prof Alexander Bismarck, Prof Milo Shaffer and Dr Emile Greenhalgh. 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.

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Abstract

There is currently a well-timed opportunity to create intensely improved structural materials to be used as risers in the offshore oil and gas industry where high mechanical performance along with superior resistance to chemical attack is required. Recent evidence shows that carbon nanotubes (CNTs) are the ideal reinforcement for polymer fine structures and are expected to improve the matrix modulus, which should lead to composites with much improved compression and other matrix dominated properties. By combining conventional reinforcing fibres and CNTs within thermoplastic matrices, a new class of materials with both superior mechanical, environmental, and chemical performance, as well as significantly reduced through-life costs should be possible.

Different formulations of nanocomposites consisting of modified Polyvinylidene difluoride (PVDF) and modified CNTs e.g. Poly methyl methacrylate grafted carbon nanotubes (PMMA-g-CNTs) were fabricated using extrusion and injection moulding up to a maximum CNT content of 10 wt%. CNTs were well distributed within polymers as determined through optical and electron microscopy. Dynamic mechanical analysis was conducted in order to study the effect of CNTs on storage modulus of nanocomposites. The tensile, flexure and compression properties of PVDF nanocomposites were increased with increase in CNT content. Overall, PMMA-g-CNTs based PVDF nanocomposites with a 10 wt% CNT loading showed 20%, 30% and 60% improvement in tensile, compressive and flexural modulus as compared to PVDF nanocomposite containing 10 wt% CNT loading.

The main objective of this research was to optimise processing conditions for fabricating ultra-inert hierarchical fibre reinforced nanocomposites. The CNT modified matrix, prepared by solution precipitation, was reinforced with carbon fibres via continuous composite line setup to manufacture hierarchical reinforced thermoplastic (Polyvinylene difluoride (PVDF) and Poly ether ether ketone (PEEK)) composites. Thermoplastic hierarchical composites containing up to 1.25 wt% CNTs demonstrated improved compression and interlaminar shear

strength whereas a decrease was observed of the same when CNT content was increased up to 5 wt%. A similar trend of decline in mechanical performance at higher loadings of CNTs (>1 wt%) was observed in PEEK based hierarchical composites which indicated that matrix dominated properties were availed without compromising the quality of fibre/matrix interface at an optimum loading of CNTs (1.25 wt%) resulting in enhanced mechanical performance of hierarchical composites. However, further addition of CNTs adversely effected the fibre impregnation by nanocomposite matrix, due to processing issues such as high viscosity of nanocomposites at higher CNT contents, resulting in poor mechanical performance. Moreover, the influence of CNTs on the fracture toughness was also investigated by double cantilever beam testing. Polished cross sections of fracture surfaces of failed composites were analysed to understand how CNTs affected the damage mode. Fractographic analysis of compression and double cantilever beam (DCB) failed PVDF and PEEK hierarchical composites also showed the presence of bare/dry fibres which indicates that nanocomposite's infusion/impregnation in to carbon fibres is being compromised at higher CNT loadings.

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List of Abbreviations and Symbols

ACF	Activated Carbon Fibres
APF	Atmospheric Plasma Fluorination
CC	Compliance Calibration
CFRP(s)	Carbon Fibre Reinforced Polymer Composite(s)
CNT(s)	Carbon Nanotube(s)
CSCNT(s)	Cup Stacked Carbon Nanotube(s)
CTFE	Chloro tri Fluoro Ethylene
DMF	Di Methyl Formamide
DMTA	Dynamic Mechanical Thermal Analysis
DPS	Di Phenyl Sulfone
DSC	Differential Scanning Calorimetry
DWNT	Double Walled Nanotubes
FVC	Fibre Volume Content
GP	General Purpose
GPa	Giga Pascal
HFP	Hexa Fluoro Propylene
HP	High Performance
HRTEM	High Resolution Transmission Electron Microscopy
ICSTM	Imperial College of Science, Technology and Medicine
ILSS	Interlaminar Shear Strength

MAH	Maleic Anhydride
MBT	Modified Beam Theory
MCC	Modified Compliance Calibration
MPVDF	Modified PVDF (containing 25 wt% MAH grafted PVDF)
MPa	Mega Pascal
MWNT	Multi-wall Carbon Nanotubes
NC(s)	Nanocomposite(s)
PaCE	Polymer and Composite Engineering
PAN	Polyacrylonitrile
PECVD	Plasma Enhanced Chemical Vapour Deposition
PEEK	Poly Ether Ether Ketone
PEI	Poly Ether Imide
PES	Poly Ether Sulphone
PI	Poly Imide
PMC	Polymer Matrix Composite
PMMA	Poly Methyl Methacrylate
PmPV	Poly(m-PhenyleneVinylene-co-2,5-dioctyloxy-p- PhenyleneVinylene)
PPS	Poly Phenylene Sulphide
PSD	Particle Size Distribution
PVDF	Poly VinylenediFluoride
RPM	Revolutions per Minute

RPS	Revolutions per Second
SAN	Poly(Styrene-co-Acrylonitrile)
SEM	Scanning Electron Microscope
SBS	Short Beam Shear Strength
SWNT	Single-wall Carbon Nanotubes
TFE	Tetra Fluoro Ethylene
WAXS	Wide Angle X-ray Scattering
XRD	X-Ray Diffraction
m_f	Mass of Fibre
ρ_m	Density of Matrix
ρ_f	Density of Fibre
E^*	Complex Modulus
E'	Storage Modulus
E''	Loss Modulus
λ	Wavelength
F^{tu}	Ultimate tensile strength
σ	Stress
ε	Strain
E_B	Modulus of Elasticity in Bending
P	Load
δ	Crack Length

B	Width of Beam
a	Crack Length
T _g	Glass Transition Temperature
G _{IC,SS}	Steady State Energy Release Rate
μm	Micro-meter
nm	Nano-meter
X _C	Degree of Crystallinity
T _m	Melting Temperature
T _c	Crystallization Temperature
V _f	Fibre Volume Fraction
$\bar{E}$	Normalised Stiffness
μ ϵ	Micro-strain

Chapter 1 – Introduction

1.1 Objective

The objective of this research was to produce ultra-inert high strength hierarchical nanocomposites by combining carbon nanotube (CNT) enhanced thermoplastic matrices with unidirectional carbon fibre reinforcement. The hierarchical composites are expected to exhibit enhanced interlaminar fracture toughness and improved transverse mechanical performance as compared to neat carbon fibre reinforced thermoplastic composites in addition to their inherent outstanding longitudinal properties. Interlaminar fracture toughness of the laminated fibre reinforced composites is of extreme significance due to the presence of high strength fibres in a weak matrix which makes them susceptible to delamination, which in turn is controlled by the interlaminar fracture toughness of the composite material.

1.2 Introduction

Oil has become a diminishing resource and focus is on uncovering reserves in increasingly inhospitable regions everywhere around the world. The offshore oil industry involves massive resources and installations and has amassed considerable experience in drilling in deep water using steel piping and casings. As water depths increase, however, the weight of the steel structures used to bring the oil to the surface becomes a serious limitation to what is feasible. At depths greater than 1500 m the weight becomes a major problem, both for transporting the parts to the offshore site but also because the structure has to be supported by the floating

platform. The equipment to be used in an oilfield must maintain its structural integrity in high pressure, high temperature and ultra-deep well environments as well [1]. Composite materials have been used in oilfield applications since 1960s owing to their unique advantages such as light weight, high strength to weight ratio, excellent corrosion resistance, long fatigue life and design flexibility [1]. For composites to be used in the oil and gas industry it is not only important to meet the required mechanical performance but they should also be highly resistant to chemical attack [2, 3]. The low density of carbon fibre composites as compared to steel makes the buoyancy due to Archimedes effect considerable. Moreover they can match the strength and rigidity of steel and provide greater resistance to corrosion. Furthermore, their better thermal insulation help them in preventing the blocking of the riser (pipe which brings the oil to the surface) due to high viscosity of oil at lower temperatures as the oil leaves the seabed at 100°C but surrounding sea water is at 4°C. Advanced carbon fibre reinforced polymer composites (CFRPs) are set to make a big impact in this area as there is really no alternative for extracting oil in depths of water down to 3000m [4]. When employed in the off-shore oil and gas industry, as reinforcement for risers, tubing, tanks, choke and kill lines, CFRPs were declared to be the only possible choice for exploitation of deposits at depths greater than 1500 m [4]. Recently, demand and applications of these composites have grown extensively in the oil and gas industry ranging from grids and gratings, composite piping, pressure vessels, risers and flexible tubing to even high-pressure down hole applications. A typical offshore oil platform design is shown in Figure 1-1.

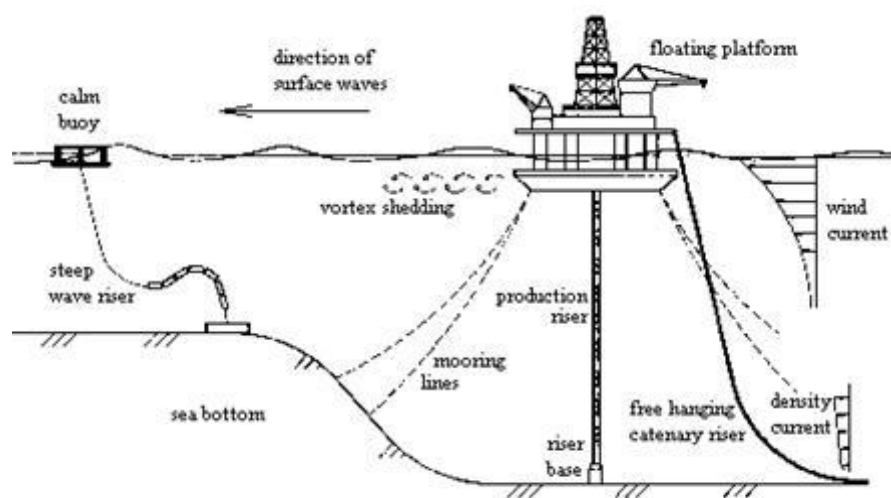


Figure 1-1: Offshore oil platform design [5]

Thermosets, like polyesters and epoxy resins have been used as polymer matrices in CFRPs for a long time, but their rigid brittle properties and poor chemical resistance, make them less suitable for applications in the offshore oil and gas industry [6, 7]. However, high performance fibre reinforced thermoplastic composites, such as poly ether ether ketone (PEEK) and polyphenylene sulphide (PPS) display excellent mechanical properties in addition to their light weight with superb resistance when exposed to extreme chemical and mechanical conditions [8, 9]. Principally because of these factors, thermoplastics have become the matrix of choice for many composite applications, including offshore oil and gas industries, where high performance under extreme temperature and pressure conditions is required.

Polyvinylene difluoride (PVDF), a fluoropolymer, is one of the most extensively used thermoplastics in industry. Its high service temperature, high resistance to abrasion, UV and chemical attack in addition to its thermal stability makes it suitable for oil field applications at higher temperatures. Due to the presence of C-F bonds, which are significantly stronger than conventional C-H bonds, it is extremely inert. PPS and PEEK also display the desired properties but are expensive and are difficult to process because of their higher service temperatures. The lower cost and superior mechanical properties of PVDF give it an advantage over both PPS and PEEK when used subsea. In this research, out of these high performance thermoplastics, PVDF and PEEK are chosen as matrices for fabrication of nanocomposites in the first place and then hierarchical nanocomposites.

On the other hand, polymers are becoming extensively reinforced with carbon nanotubes (CNTs) to enhance their mechanical properties. The outstanding features of the CNTs like high aspect ratio, high purity, extraordinary resilience, thermal stability and high electrical conductivity make them really a significant reinforcement for nanocomposites.

Most research focuses on the use of CNT solely as the reinforcement of polymer matrices to produce nanocomposites. Individual CNTs have been predicted and observed to have remarkable properties [10-12]. PVDF matrices have been primarily investigated as a means to enhance piezoelectric response [13] but recently its exceptional mechanical performance has become the most attracting subject for researchers. Conventional monolithic materials which are being used in deep sea applications currently will reach their limit if deeper reservoirs are to be exploited [4]. The primary emphasis of this project was to enhance the properties of thermoplastic matrix of PVDF and PEEK by incorporating CNTs into the resin and

reinforcing the resulting nanomatrix (PVDF/CNT) with carbon fibres. It is anticipated that the multiscale carbon fibre reinforced thermoplastic nanocomposite will provide good chemical and thermal stability along with outstanding toughness which are ideal for oil field applications. These are termed as hierarchical composites due to the formation of multiscale hierarchy in carbon fibre reinforced thermoplastic nanomatrix and can be used in applications where chemical resistance and toughness are both required, such as in oil and gas industry.

PVDF nanomatrix was prepared in the laboratory by incorporating CNTs in PVDF which is itself quite challenging, as there were some difficulties in the production processes. However, prepregs of PEEK nanomatrix (already fabricated by a senior PhD student, Steven Lamoriniere [14], in polymer and composite engineering group (PaCE)) were consolidated during this research to characterise their mechanical performance. The problem with the nanocomposites is that when high aspect ratio CNTs are incorporated in to a polymer melt or solution, high viscosity results, which cannot be processed by the normal techniques of polymer melt processing such as slurry processing or injection moulding used for conventional polymers. In order to process this high viscosity suspension, a solution precipitation method was adopted which is believed to possess good dispersion of CNTs needed for mechanical reinforcement [15].

Although much progress has been made in addressing the processing issues involved in producing nanocomposites, the preparation of satisfactory high strength thermoplastic hierarchical composites is still a great challenge. The high strength and ultra-inertness of thermoplastic hierarchical composites is expected to be achieved by overcoming the main challenges involved in processing such homogeneous dispersion of CNTs in a matrix. CNTs tend to aggregate into bundles by van der Waals forces, and hence they are difficult to disperse in polymer matrices. The weak interfacial adhesion between CNTs and the polymer leads to inefficient load transfer to the CNTs. As a result, the mechanical performance of the nanocomposites is not as good as envisaged. Moreover, when a load is applied to a fibre reinforced nanocomposite (hierarchical composites), it is transferred from the nanocomposite matrix to the carbon fibre. If the fibre to matrix interaction is weak, it will result in poor mechanical performance, such as low interlaminar shear strength [16]. A procedure is investigated to improve overall mechanical performance of fibre reinforced nanocomposites by ensuring a uniform distribution of CNTs in the matrix, which is achieved by a solution precipitation method. Laminates of carbon fibre reinforced thermoplastic nanomatrices were

prepared through the continuous composite line designed by Tran et al. [14, 17]. The good impregnation of nanomatrix on to the carbon fibre ensures adhesion/compatibility at the fibre and thermoplastic nanomatrix interface which guarantees effective load transfer from the matrix to fibres [18] and improves the mechanical performance of the thermoplastic hierarchical composites.

1.3 Aim of Project

This project attempts to design and fabricate a new class of high strength composite materials that should both be extremely resistant to chemicals and capable of withstanding intense situations with extreme fluctuation in temperatures and pressures, when subjected to oil field applications, for instance in risers for exploitation of oil deposits. The primary aim of this project is to develop a new high performance thermoplastic composite material in which the matrix is additionally reinforced with CNTs and to study their interactions with a high performance thermoplastic polymer (PVDF and PEEK) to gain a better understanding of their behaviour. Moreover, high strength to weight ratio of the pipes/risers of such polymer based composites could provide easy control while mining down in oil deposits or deep sea reservoirs as compared to steel risers in addition to lowering the cost for adjusting this entire setup. The outstanding properties of CNTs such as low-weight, very high aspect ratio, high electrical conductivity, elastic moduli in the TPa range, tensile strength in GPa range [19] and much higher fracture strain make them an attractive candidate for advanced composite materials. Firstly, the interaction and effect of various CNT loadings on the mechanical properties of fabricated nanocomposites were investigated. Secondly, the nanocomposite matrix (NC) were produced and impregnated with carbon fibres to produce hierarchical nanocomposites. It was anticipated that conventional fibres and CNTs within thermoplastic polymers could be combined to develop a structural material with superior mechanical, environmental and chemical performance, in addition to significantly reduced service life costs. However, the preparation of hierarchical composites based on CNT reinforced matrix (prepared through solution precipitation method), with envisaged exceptional mechanical performance, is still a great challenge as only unsatisfactory results have been obtained so far [14, 17]. There is still need to resolve some important processing issues in order to develop hierarchical composites with outstanding mechanical performance.

The specific objectives of this research are:

- To develop PVDF nanocomposites with up to 10 wt% CNT loading using extrusion and injection moulding, and to characterise their mechanical performance.
- To synthesize PVDF nanocomposite powder with up to 5 wt% CNT loading suitable to be used on the powder impregnation line.
- To develop ways to optimise composite tape (prepreg) fabrication with homogeneous impregnation of the carbon fibre with nanocomposite powder by running the powder impregnation line provided. The prepreg should have a matrix rich surface layer to ensure proper consolidation.
- To optimise the processing conditions (temperature and pressure) of composites when being formed into laminates during consolidation. It is important to obtain good resin impregnation on carbon fibres during consolidation in order to obtain laminates with improved stiffness and strength.
- To develop hierarchical nanocomposite laminates based on PVDF and PEEK with up to 5 wt% CNTs by compression moulding.
- To examine the mechanical properties especially the delamination resistance and compression strength of the hierarchical composite laminates produced. Other mechanical properties for the fibre reinforced nanocomposites such as short beam shear strength (SBS) and flexural strength were also determined.

1.4 Structure of the Thesis

The thesis is divided into eight chapters. This Chapter describes the motivation, brief background, aim and objectives of the thesis. Chapter 2 reviews the relevant background literature. It starts with the background of composite materials (specifically carbon fibre reinforced polymer composites), their applications, earlier efforts and possible materials for composite structures. Then, the significance of the basic raw materials involved in this project such as carbon fibres, thermoplastic polymers and carbon nanotubes will be discussed. Experimental materials and methods are explained in Chapter 3. It begins with raw materials, followed by fabrication procedures of PVDF nanocomposites via extrusion and injection moulding. Then the PVDF nanocomposite powder preparation as a route to fabricate hierarchical nanocomposite through a powder impregnation line is explained. Next, processing details of PEEK hierarchical nanocomposites along with the characterisation techniques such as fractography of composites studied by scanning electron microscope

(SEM), thermal behaviour of nanocomposites studies by dynamic mechanical thermal analysis (DMTA) etc. will be explained. Finally, the test methods used to determine the mechanical performance of PVDF and PEEK nanocomposites and hierarchical composites will be described. The three following chapters are results and discussion. Chapter 4 focuses on the mechanical performance of PVDF nanocomposites with CNT loadings of up to 10 wt%. Chapter 5 discusses the suitability of particle size of PVDF nanocomposite powder produced via solution precipitation for fabrication of hierarchical composites. Next, optimisation issues of processing for PVDF hierarchical nanocomposites fabricated through powder impregnation line is addressed followed by a detailed explanation of mechanical performance of PVDF hierarchical composites. Chapter 6 details the mechanical performance of hierarchical composites based on modified PVDF (MPVDF) containing 25 wt% maleic anhydride grafted PVDF. The hierarchical nanocomposites of MPVDF were tested for compression, flexure and short beam shear strength in addition to fracture toughness, which will be discussed in detail in Chapter 6. Chapter 7 discusses the mechanical characterisation of PEEK hierarchical nanocomposites in detail. Fractography of the respective composites is explained in each of the Chapter 4 to 7. Finally, Chapter 8 presents conclusions and future work.

Chapter 2 - Background and Literature Review

The basic theories, background knowledge, and previous research which are related to this project are explained in this chapter. To begin with an explanation of composite materials followed by detailed descriptions of carbon fibres, PVDF/PEEK (thermoplastics) and CNTs, which are used for fabricating hierarchical nanocomposites, is presented. Furthermore, the role of fibre/matrix adhesion and the challenges involved in fabrication of thermoplastic hierarchical nanocomposites are discussed in this chapter.

2.1 Composite Materials

A composite is a mixture of two or more physically distinct and mechanically separable phases on a microscopic scale, separated by a distinct interface. The overall properties are superior to those of the individual components. The constituents of a composite are generally divided into two categories, matrix and reinforcements, separated by a distinct interface. The first constituent which is normally continuous throughout the composite (with sandwich structure as an exception) is the matrix, which can be ceramic, metallic or polymeric. The matrix transfers stress between the fibres, provides a barrier against an adverse environment and protects the fibres from wear and abrasive damage. The second phase is termed reinforcement as it generally is the load bearing constituent for the composite [20] and enhances one or more of the material characteristics of the matrix. The form of reinforcement can be fibrous (discontinuous or continuous fibre) or particulate (particles which have similar dimensions in all directions), as shown in Figure 2-1.

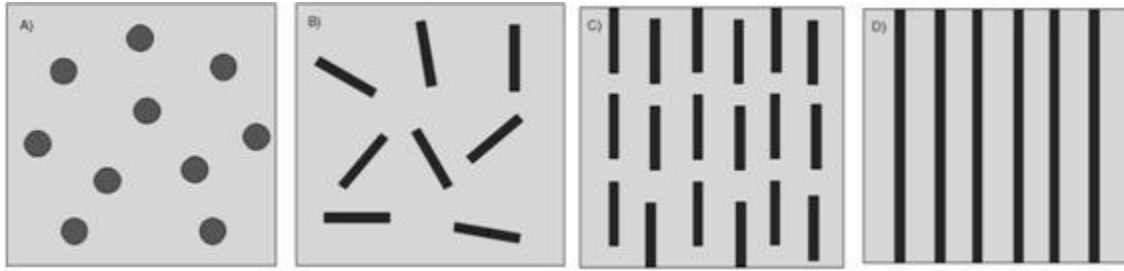


Figure 2-1: Example of composites: (A) particulate, random; (B) discontinuous fibres, random; (C) discontinuous fibres, unidirectional; (D) continuous fibres, unidirectional

Composite performance is determined by several factors, such as the interaction between the reinforcement and matrix, fibre volume fraction, fibre aspect ratio, the orientation of the reinforcement. The interface which transfers load from the matrix to the fibre can directly affect the mechanical performance of composites, especially shear and delamination resistance [21], and it can be maximized once effective load transfer from the matrix to the fibre is guaranteed. The high aspect ratio of fibres allows for an increase in the surface area at the interface between the reinforcement and the matrix, which can improve the mechanical performance of composites. The single direction of reinforcement with a high aspect ratio can increase the efficiency of load transfer by increasing interfacial contact area in the relevant direction. Thus, continuous unidirectional carbon fibres are usually used as reinforcement in the majority of high performance fibre reinforced composite applications.

Composites materials are now relatively common place around the world, particularly for structural applications in the aircraft, automobile and medical industries. Furthermore, fibre reinforced polymer largely replace conventional materials, such as metal, because of their much improved mechanical properties, such as high specific modulus and specific strength. Moreover, composites materials have other potential advantages for common application areas, such as fatigue resistance, corrosion resistance, and low expansion coefficient.

2.2 Carbon Fibre Reinforced Polymer Composites-CFRPs

2.2.1 Introduction

Polymers are of great interest due to their low density, good processability and reasonable cost. They are extensively used in many important applications such as packaging materials, coatings, transparent, optical, biological and medical materials except for structural use where high strength is the major requirement. However, this limitation can be overcome by the

incorporation of some kind of reinforcement in to the polymers to make composites. Broad areas of application of reinforced polymers include the electronic, automobile, aeronautic and astronautic industries. Polymer matrix composites, (PMCs) whether the polymer is a thermoset or a thermoplastic, have received particular attention over the years and make the biggest proportion of composite materials [22]. One of the major reasons is their easier processing as compared to carbon-matrix, ceramic-matrix, and metal-matrix composites [22]. There is also less degradation of the reinforcement during manufacturing of polymer matrix composites. Although the mechanical properties of polymers are inadequate for many structural purposes, the benefit polymer matrices gain from reinforcement are more significant compared to any other type of matrix [22]. In this instance, a polymer is typically combined with a high aspect ratio material with superior strength and stiffness, such as glass, carbon and aramid fibres, which has the largest volume fraction and take the main load acting on a composite structure. Carbon fibres when used in polymer-matrix composites as reinforcement, the resulting aircraft saves fuel because of its light weight. So, it can be concluded that carbon fibre composites, particularly those with polymeric matrices, have become the dominant advanced materials for aerospace, automobile, sporting goods and other applications due to their high strength, high modulus, low density, rational cost and ease of fabrication.

Polymer matrices can be classified into three classes; thermoset, thermoplastic and elastomer [20]. Thermosets (especially epoxy resins) have long been used as polymer matrices for carbon fibre composites making the largest portion of PMCs. During curing, usually performed in the presence of heat and pressure, a thermoset resin hardens gradually due to the completion of polymerisation and the crosslinking of polymer molecules. These generic characteristics of thermosets create a strong bond resulting in a brittle polymer composite and cannot be reshaped after curing has finished. For thermosets, such as epoxy, polyester, and phenolic resin, the processing temperature typically ranges from room temperature to about 200°C [22].

Thermoplastics on the other hand are not cross linked which makes them flow under high temperature and solidify when cooled to room temperature [20]. This makes thermoplastic quite interesting as the material can be heated and remoulded repeatedly with little loss of material properties. Recycling of thermoplastics is also possible unlike thermosetting polymers. Thermoplastic can furthermore be classified as crystalline thermoplastic, semi

crystalline thermoplastic and amorphous thermoplastic. Thermoplastics need time to cool down after melting as the cooling rate will have a huge impact on the crystallinity of the thermoplastics [23]. Unlike thermosets where the strength of the polymer is from chemical links, thermoplastics need time to arrange and organize to increase the crystallinity which determines their mechanical properties. Reinforced thermoplastics, as a consequence of the trend towards environmental protection and material recycling, have attracted progressively more attention from scientists and engineers of composite materials as compared to reinforced thermosets [22].

Thermoplastics have recently become important as matrices for carbon fibre composites because of their greater ductility and processing speed compared to thermosets, and the recent availability of thermoplastics that can withstand high temperatures. The processing temperature for thermoplastics, such as polyimide (PI), Polyethersulphone (PES), Poly ether ether ketone (PEEK), polyether imide (PEI), and polyphenylene sulphide (PPS), typically ranges from 300°C to 400°C. The higher processing speed of these thermoplastics is due to that fact that thermoplastics soften immediately upon heating above the glass transition temperature (T_g) and the softened material can be shaped easily. Subsequent cooling completes the processing. However, the curing reaction for a thermoset resin occurs gradually as compared to the thermoplastics.

A large increase in the strength and modulus of the composite results, when thermoplastics are reinforced macroscopically by carbon fibres. Thus, in order to obtain a high-strength, high-modulus and heat-resistant polymer composite, a high fibre content (up to 60% by volume) is required. Unlike fibre-reinforced thermosets such as reinforced epoxies and polyimides, reinforced thermoplastics are usually fabricated by means of extrusion and injection-moulding, whereby polymer melts are blended with reinforcing fibres and are processed at elevated temperatures. The high fibre content is expected to worsen the inherently poor melt processability of matrix resins, increasing wear on processing machines and using more energy. These drawbacks occur particularly for the case of advanced engineering polymers requiring high processing temperatures. In practice, the processability of advanced engineering polymers affects their theoretically estimated exceptional performance.

Semicrystalline thermoplastic composites have been comprehensively evaluated because of their high toughness and exceptional solvent resistance. They are comparatively more

efficiently reinforced than amorphous thermoplastics (e.g. poly ether sulfone (PES)). This is because the fibres act as nucleation sites for crystallisation; the fibre becomes surrounded by a microcrystalline structure, which binds the fibre more firmly to the polymer and improves the modulus. A few drawbacks exist, however, with respect to processing, in particular for those potential semicrystalline thermoplastics, e.g. PEEK, used for high-performance composites. Thermoplastic polymers usually possess a very high melting point (which can be close to their decomposition temperature), so that an adequate drop in viscosity by raising the processing temperature is often not achievable. In addition, the viscosity of thermoplastics in the molten state is usually much higher than that of thermosets during processing [24]. These characteristics are considered to be responsible for limiting the use of high-temperature, semicrystalline, thermoplastic matrices for making flexible pre impregnated tapes due to lack of good processing techniques. However, during the last decade, great efforts have been made to overcome the difficulties of impregnation with thermoplastic resins for manufacturing fibre-reinforced thermoplastic composites [25].

2.2.2 PVDF & PEEK: Applications and use as Matrix for CFRPs

Polyvinylene difluoride (PVDF) and poly ether ether ketone (PEEK) are considered among those semicrystalline thermoplastics, which are capable of withstanding intense situations and thus are best suitable options for high performance composites. PVDF is the homopolymer of 1, 1-difluoroethylene, and is available in molecular weights between 60,000 and 534,000. This structure, which contains alternating $--CH_2--$ and $--CF_2--$ groups along the polymer backbone, gives the PVDF material polarity that contributes to its unusual chemical and insulation properties in addition to its high resistance (solvent resistance, weather resistance, corrosion resistance, creep and fatigue resistance) and low coefficient of friction [26]. It is one of the fluoropolymers that have received much attention in academic research and industrial application (e.g., cable jacketing, insulation for wires and in chemical tanks and other equipment). Its benefits include chemical and thermal stability along with melt processability and selective solubility. PVDF offers low permeability to gases and liquids, low flame and smoke characteristics and other beneficial characteristics. In addition to forming a homopolymer, the monomers of PVDF can also form co-polymers with other monomer families, most commonly with the co-monomers hexafluoropropylene (HFP), chlorotrifluoroethylene (CTFE), and tetrafluoroethylene (TFE). The properties of the copolymers are strongly dependent on the type and fraction of the co-monomers as well as the

method of polymerization. For example, HFP makes a homogenous copolymer with PVDF. On the other hand, the PVDF copolymer phase segregates if the other monomer is not fluorinated [27]. It exhibits at least four crystalline phases (α , β , γ and δ) [27]. The α phase is most common for PVDF crystallized from the melt, whereas the β phase is technologically most important because of its better pyroelectric and piezoelectric properties [26]. However the mechanical properties in term of modulus and strength are quite low as compared to PEEK (see Table 2-1). In order to be reinforced, several issues including interfacial adhesion need to be addressed to achieve a composite with the desired mechanical performance [28].

Polymer	Tensile Strength [MPa]	Flexural Strength [MPa]	Compressive Strength [MPa]	Tensile Elastic Modulus (Young's Modulus) [GPa]	Flexural Modulus [GPa]	Reference
PVDF	31-49	59-65	80	1.10	0.62-1.158	[29, 30]
PEEK	100	170	118	3.6	4.06~4.09	[31, 32]

Table 2-1: Mechanical properties of PVDF and PEEK

On the other hand, significant interest in the mechanical properties of poly ether ether ketone (PEEK) based CFRPs has compelled researchers to make innovations in this field as PEEK is also a high performance, semicrystalline thermoplastic. It is slowly replacing metals and other materials in high performance application such as in the aerospace industry (particularly leading edges of A350 Airbus wings) because of its high strength, high thermal properties and excellent chemical resistance [33, 34]. This polymer is ideal for highly aggressive environments. It can withstand a continuous temperature of 260°C and even higher temperatures for short duration. It also has outstanding wear resistance over wide ranges of pressure, velocity and temperature [35].

More importantly, it has excellent chemical resistance to jet fuels, salt spray and chemical/biological agents at elevated temperatures along with its attractive mechanical properties [36]. One of the major applications of PEEK based CFRPs include bearing and slider materials. Moreover, its relatively stiff backbone gives exceptional high-temperature stability. Its high glass transition temperature and high melting point in addition to a high continuous service temperature offers the advantages of easy processability by injection moulding and other techniques common to thermoplastic polymers [35]. Despite the

advantages offered by PEEK based CFRPs, they are rather expensive and difficult to process, when considered for oil field applications, as compared to PVDF when reinforced with carbon fibres to make high performance composites.

2.2.2.1 Carbon Fibres: Responsible for Strength and Stiffness of CFRPs

In any composite, fibres carry the load and their type, amount, orientation and alignment determine their effectiveness. Carbon fibres refer to fibres which are at least 92 wt% carbon in composition [37]. They can be used for applications where high strength and stiffness is required [1]. The atomic structure of a carbon fibre is similar to that of graphite, consisting of sheets of carbon atoms (graphene sheets) arranged in a regular hexagonal pattern. Graphite is a crystalline material in which the sheets are stacked parallel to one another in regular fashion. The chemical bonds between the sheets are relatively weak van der Waals forces, so the carbon layers can easily slide with respect to one another. The high modulus of carbon fibres stems from the fact that the carbon layers, though not necessarily flat, tend to be parallel to the fibre axis. This crystallographic orientation, aligned parallel to fibre axis, provides carbon fibres higher modulus and strength.

Carbon fibres that are commercially available are divided into three categories (based on their structure), namely general-purpose (GP), high performance (HP), and activated carbon fibres (ACF). The general-purpose type is characterised by an amorphous and isotropic structure, low tensile strength, low tensile modulus, and low cost. Their applications include sealing materials, electrically conducting materials, heating elements, electrodes, filters and as reinforcement of concrete in short fibre form. The high performance type can be used in various applications such as effective reinforcements in different types of matrix materials such as polymers, metals and ceramics because of their relatively high strength and modulus. Their higher modulus is associated with a higher proportion of graphite and more anisotropy. However, activated carbon fibres have poor strength and modulus and are characterised by the presence of a large number of open micro pores, which act as adsorption sites. The adsorption capacity of activated carbon fibres is comparable to that of activated carbons which allows the adsorbate to get to the adsorption site faster, thus accelerating the adsorption and desorption processes [22].

Carbon fibres can alternatively be classified on the basis of their tensile strength and modulus. The following nomenclature is formulated by IUPAC

- UHM (ultra high modulus type): carbon fibres with modulus greater than 500 GPa
- HM (high elastic modulus type): carbon fibres with modulus greater than 300 GPa and strength to modulus ratio less than 1%
- IM (intermediate elastic modulus type): carbon fibres with modulus up to 300 GPa and strength to modulus ratio above 1×10^{-2}
- Low modulus type: carbon fibres with modulus as low as 100 GPa and low strength. They have an isotropic structure.
- HT (high strength type): carbon fibres with strength greater than 3 GPa and strength-to-modulus ratio between 1.5 and 2×10^{-2}

The on-going development of the PAN carbon fibre market since 1950s has led to the foundation of carbon fibres global expansion. The main suppliers of carbon fibres are setting up new factories and selling their products all around the world. The major companies which are manufacturing carbon fibres are Toray, Toho Tenax, Mitsubishi, Hexcel and Cytec industries [38].

2.2.3 Carbon Nanotubes: Significance, Classification and Role in Fabricating Nanocomposites

Although Iijima [39] is often credited as the discoverer of CNTs, carbon nanofibres and nanotubes have been reported to be synthesised in as early as 1960 by Roger Bacon [40, 41]. There are even reports in the catalysis literature of the 1950's of attempts to remove troublesome fibrous carbon deposits [10]. One can hypothesis that nanotubes were likely present in his experiments as a by-product, when he used the electric arc method to produce graphite whiskers, although unobserved. A few earlier reports in literature also showed the emergence of tubular carbon structures while hydrocarbon decomposition was being carried out by Endo, in 1976. However, in 1991, Iijima observed the graphitic tubular structure of CNTs in the arc discharge apparatus that was used to produce C_{60} and other fullerenes. This structural richness of the CNTs i.e. coaxial tubes with a hollow core were realised for the first time when observed under high resolution transmission electron microscopy (HRTEM), while

examining the carbon produced by the arc evaporation of graphite in an atmosphere of helium [39]. To date, almost more than 50,000 papers have been written with CNTs as the major issue, including a large fraction on polymer composites. This important discovery led to the realization that with graphene tubes parallel to the filament axis, these highly crystallized tubular carbon structures would inherit several important properties of “intraplane” graphite [42].

Carbon nanotubes and nanofibres are graphitic filaments/whiskers (large molecules of pure carbon that are long and thin), with diameters ranging from 0.4 - 500 nm [43], and lengths in the range of several micrometres to millimetres. They are usually grown by diffusion of carbon through a metal catalyst and its subsequent precipitation as graphitic filaments. The diffusion of carbon occurs via catalytic decomposition of carbon containing gases or vaporized carbon from arc discharge or laser ablation. There are three distinct structural types of filaments which have been identified based on the angle of graphene layers with respect to the filament axis, namely herringbone (or cup-stacked), stacked and nanotubular [43].

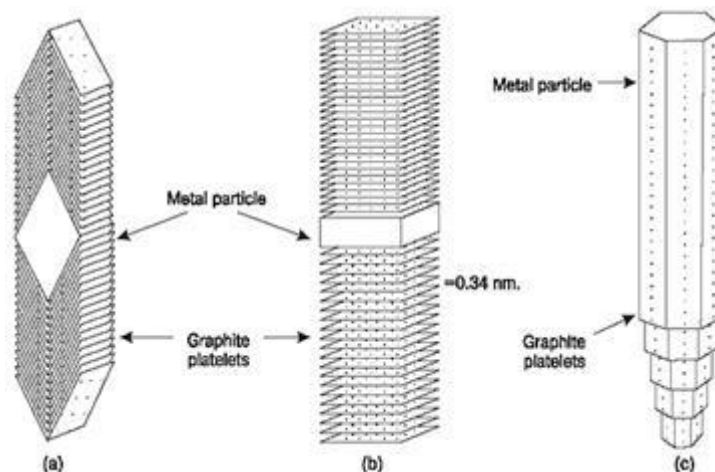


Figure 2-2: Schematic diagram of A) herring-bone, B) stacked or platelet, C) tubular structures produced by the thermal decomposition of carbon containing gases over selected metal catalyst particles classified on the basis of angle of graphene layers with respect to the filament axis [43]

In particular, nanotubes exhibit high electrical conductivity, thermal conductivity and mechanical strength along filament axis [44]. More specifically some of them can be extremely efficient conductors of electricity depending on their configuration, whereas some act as semiconductors. As there are very few open edges and dangling bonds in the structure nanotubes are also very inert. They can have a length-to-diameter ratio greater than 1,000,000 [43]. They are considered to be one of the stiffest and strongest nanoreinforcements known,

with Young's moduli as high as 1 TPa for SWCNT and 200 GPa for MWCNTs and tensile strengths of up to 11 GPa for SWCNT and 270 GPa for MWCNTs [17, 45]. As individual molecules, nanotubes are 100 times stronger-than-steel and one-sixth of its weight. These properties make carbon nanotubes a technologically important material for various mechanical applications. Their characteristic of having low density in addition to these features, suggests that CNTs are ideal candidates for high performance polymer composites.

As shown in Figure 2-2, graphite platelets are at an angle to the filament axis in herringbone structure, whereas perpendicular to the filament axis in the stacked form and they are parallel to the filament axis in the nanotube. In literature today, herring-bone and stacked structure of the graphene whiskers are classified under the name of carbon nanofibres, whereas nanotubes is used to describe the case where tubular graphene walls are parallel to the filament axis.

CNTs have structures closely related to those of fullerenes. The terms 'zigzag' and 'armchair' refer to the arrangement of hexagons around the circumference (as shown in Figure 2-3). There is a third class of structure, 'chiral', in which the hexagons are arranged helically around the tube axis, as shown in Figure 2-3C. Experimentally, the CNTs are generally less perfect than the idealised versions shown in Figure 2-3 and may be either multi-walled or single-walled i.e. the various configurations of graphene cylinders (CNTs) obtained, when graphitic filaments or whiskers are grown by diffusion of carbon through a metal catalyst with subsequent precipitation afterwards [43, 46].

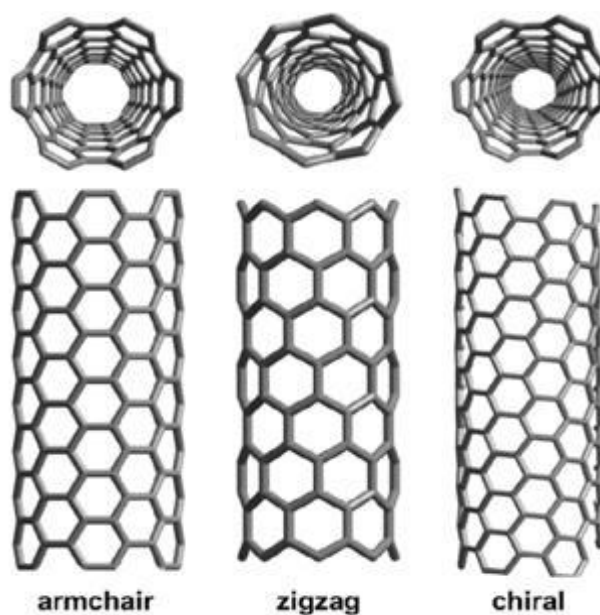


Figure 2-3: Three classes of CNTs on the basis of structure: A) armchair, B) zigzag, C) chiral [46]

CNTs can be further classified as single or multi-walled carbon nanotubes. Single-wall carbon nanotubes (SWCNT) is formed by rolling-up of rectangular strips of hexagonal graphite monolayers and their special properties emerge from the strong one-dimensionality and crystalline perfection of the structure and multi-wall carbon nanotubes (MWCNT) consisting of concentric, coaxial graphene cylinders. The ends of the tubes are usually closed off by a carbon end-cap (Figure 2-4)

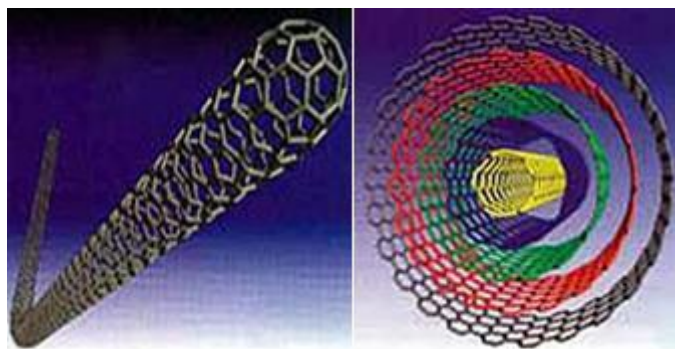


Figure 2-4: a) single-wall nanotube b) multi-wall nanotube [47]

SWNTs agglomerate more easily than MWNTs due to their smaller diameter and greater surface area and can form ropes or aligned bundles of SWNTs. SWNTs often require more specialization to produce than MWNTs. Therefore, the cost of purified SWNTs tends to be greater than that of MWNTs. The MWNTs, on the other hand, have been found to demonstrate lower mechanical, electrical, and thermal properties due to the ability of the concentric nanotubes to slide past each other. Due to the inherent tube within a tube structure, MWNTs tend to have a larger diameter (10 nm) as compared with SWNTs (1 nm). However, advancements in nanotube fabrication have led to MWNTs with more precise, smaller diameters. This may lead to nanotubes with improved properties over larger diameter MWNTs with less agglomeration than SWNTs [48].

The nanomaterials drastically add to the electrical conductivity as well as to the mechanical strength of the original material. Nanocomposites are a class of composites that are part of the growing field of nanotechnology and are created by introducing nanoreinforcements into a macroscopic matrix material [49]. The small size of the nanofillers ensures an excellent surface finish and can enable reinforcement of fine structures such as fibres, films and even the matrices of conventional composites. However, nanoreinforcements induce difficulty in processing because of the resulting high viscosity suspension which is a major drawback. The percentage by weight of the nanomaterials (carbon nanotubes and carbon nanofibres)

introduced often remains very low (on the order of 0.5% - 5%) due to the incredibly high surface area to volume ratio of the particles.

2.3 Fibre/matrix Adhesion in CFRPs

2.3.1 Fibre/Matrix Adhesion

One of the fundamental parameters for fibre reinforced composites is to ensure sufficient adhesion between the matrix and the fibre, in order to obtain good mechanical performance. The mechanical properties of the fibre reinforced composites depend not only on the properties of the fibre and the matrix itself but also on the nature of the interfacial region between them. If the interface is strong enough the load applied will be transferred from matrix to the reinforcing fibres via the interface. Otherwise this load will just separate the matrix from the reinforcing fibre resulting in poor mechanical performance. For example, in the case of thermosets such as epoxies (a brittle matrix) the interfacial strength between the matrix and the reinforcing fibre is compromised while designing composites, to optimize toughness. Whereas, on the other hand, thermoplastics which shrink tightly on to the fibre, a weak interface will attempt to disintegrate the matrix from the fibres due to transverse flexure or delamination, on the application of load. Quality of interfacial interaction can be considered as a measure of mechanical performance of a composite. So a strong interface is important to guarantee good load transfer from the matrix to the fibres. In an attempt to fabricate fibre reinforced composites with a strong interface, either the fibres or the matrix can be modified. Although polymer modification by surface treatments is a well-established area, but due to hydrophobic recovery [50], they get dispossessed of their hydrophilic character after a certain time. Many researchers are focussing on either modifying the matrix or the fibre to obtain an improved quality fibre/matrix interface.

Due to the lower surface energy of the thermoplastic fluoropolymers, it is difficult to bond to, and to have good adhesion with reinforcing carbon fibres. PVDF, which belongs to the fluoropolymers, is a relatively inert matrix, as compared to other thermoplastic polymers, due to the lack of reactive groups, which limits the level of interaction between the fibre and the matrix. Thus, when the fabrication of carbon fibre reinforced PVDF composites is taken in to account, the question of difficulty in compatibility between matrix and the fibre arises. There have only been a few studies so far, that have investigated routes to improve the interaction between fluoropolymers and carbon fibres. But recently, some progress has been made in

modifying the PVDF matrix and the carbon fibres for enhancing the interfacial interaction between the carbon fibre and the PVDF matrix.

2.3.2 Carbon Fibre Modification

Various surface treatments can be applied to carbon fibres for improving CF/polymer interfacial adhesion and hence the mechanical properties of the carbon fibre reinforced composites. The preferred type of treatment depends on the matrix material, which can be a polymer (thermoset or thermoplastic), a metal, a carbon or a ceramic. Oxidative surface treatments typically add functional groups; texture the fibre surface by removing the weak outer layers of fibre, thus increasing the interfacial area. In general, there are three main methods of surface treatment, namely wet oxidation (e.g., HNO_3 , 110°C , 10 min to 150 h.), dry oxidation (e.g., air, O_2 , $500\text{--}800^\circ\text{C}$, 30 sec to 2 h.) and anodic oxidation (e.g., air, H_2SO_4 , K_2SO_4 , NaOH , 1-10 min.) [51]. Whereas coupling agents, wetting agents, and/or sizings (coatings/finishes) are other sources utilized for surface treatment of carbon fibres. Carbon fibres need treatment both for thermosets and thermoplastics. However, non-oxidative treatments involve a deposition of materials on the fibre surface such as whiskers, pyrolytic carbon, or grafting of polymer chains for example “whiskerization”, involves growth of single crystals of silicon carbide, silicon nitride or CNTs on the surface of carbon fibre [52].

Oxidation treatments can be applied by gaseous, solution, electrochemical, and plasma methods. They serve mainly to remove a weak surface layer from the fibres resulting in a rough surface, thereby enhancing the mechanical interlocking between the fibres and the matrix. Chemical modification (producing carbonyl, carboxyl and hydroxyl groups etc. on fibre surface) contributes little to the fibre/matrix adhesion. However, in the case of fluoropolymers, studies revealed that functionalisation of carbon fibres improved wettability between the fibres and fluoropolymer melts, which is an indicator for an improved thermodynamic adhesion [53]. Thus fluorinated carbon fibres, when used as reinforcement in the composites based on fluoropolymers as their matrix material, are expected to show superior mechanical properties due to superior interfacial adhesion achieved via enhanced mechanical interlocking at the interface.

When considering a PVDF matrix, poor interfacial bonding/interaction will, undoubtedly, hinder mechanical performance and is the main obstacle to be faced in developing high performance PVDF composites. Ho, K.C. et al, [54] recently studied the fluorination of

carbon fibres to enhance the interfacial attraction between the fibres and fluoropolymer matrix. Atmospheric plasma fluorination (APF) was used because it was capable of generating and sustaining stable plasma at atmospheric pressure and thus can control the surface chemistry of carbon fibres more efficiently than direct fluorination and low plasma treatments. It turned out that fluorination of carbon fibres compatibilised the fibre/matrix interface by introducing fluorine functionalities on to the surface of CFs. The study revealed the wettability and interfacial shear strength values of the final composites. It was found that wettability of fluorinated carbon fibres with PVDF melts increased when carbon fibres were exposed to APF for a short time period as determined from contact angle measurements. Moreover, an increase of 65% was observed in interfacial shear strength, as a measure of practical adhesion, under optimal conditions. There was neither formation of any transcrystalline regions around the fibres nor a change of bulk matrix crystallinity [28]. Moreover, there was no increase in surface roughness. It turned out that APF caused compatibilization of the interface between fluorinated carbon fibre and the fluoropolymer.

Coupling agents are mostly short chain hydrocarbon molecules, one end of which is compatible or interacts with the polymer while the other end interacts with the carbon fibre. A coupling agent molecule has the form X-R, where X interacts with the fibre and R interacts with the polymer. A few examples include organosilanes $R-Si(OX)_3$, organotitanates, and organozirconates. An application of a coating is normally termed a size and can be accomplished by; deposition from polymer solution, deposition of a polymer onto the carbon fibres surface by electro deposition (electro polymerisation) and plasma polymerisation [55]. Sizings usually serve to improve fibre-polymer adhesion and fibre handle ability. The choice of sizing material depends on the polymer matrix. Sizing materials include prepolymers/polymers, carbon, SiC, and metals. Due to the relative ease of application, polymers are the most common sizing materials. Sizing thicknesses typically range from 0.1 to 1 μ m.

2.3.3 Matrix Modification

In order to enhance the interfacial interaction between the fibre and matrix, the matrix can be modified either by introducing miscible secondary polymer into the primary matrix or by introducing moieties to the homopolymer that enhance the adhesion. For example, PMMA is miscible in PVDF in the molten state but does not enhance the adhesion [17] of the modified matrix with carbon fibres. However, in a recent study, PVDF was blended with various

amounts of reactive compatibilising agents such as MAH-g-PVDF, to investigate its influence on the interfacial interaction between the fibre and the matrix. Contact angle measurement of polymer melt droplets and single fibre pull out tests are considered as tools to quantify the practical adhesion. The best wetting and adhesion behaviour was achieved between PVDF containing 5 ppm grafted maleic anhydride (MAH) and epoxy sized carbon fibre (modified fibre). Fibre/matrix interaction of continuous unidirectional fibre composites has been shown to correlate with interlaminar performance of the composite laminates.

2.4 Fabrication of CNT Polymer Nanocomposites

Polymer matrices have been reinforced with carbon fibres in the past, to meet the requirements of superior mechanical properties for high strength applications [56]. However, recently, carbon nanotubes are being employed as reinforcement in polymers at a very fast pace. Their nano scale dimensions, high aspect ratio [57], and particularly their high modulus [57-59] and strength [57] (owing to the perfectly orientated defect-free graphene layers along their filament axis) makes them excellent reinforcement for nanocomposites. Even the presence of very small number of CNTs has reported to induce significant changes in the mechanical performance of nanocomposites. Researchers have been employing a large number of methods for the production of CNT polymer nanocomposites such as melt mixing of the CNTs with polymers via extrusion, injection moulding, electrospinning, in situ polymerisation in the presence of CNTs, surfactant-assisted processing of CNT polymer nanocomposites, coagulation spinning, and solid-state shear pulverisation after the discovery of very first polymer nanocomposite (using CNTs as a reinforcement) which was reported in 1994 by Ajayan [60]. Some other commonly used methods for fabricating polymer nanocomposites include solution evaporation and emulsion polymerisation. Solution evaporation method is based on mixing both the polymer solution and CNTs suspension prepared in the same solvent, for fabricating both MWCNT and SWCNT based polymer-matrix nanocomposites. In order to make the outstanding properties of CNTs really available in the nanocomposites, they must be dispersed well in the solvent to let them thoroughly reinforce the matrix (polymer solution). This is what makes difficulty in fabricating polymer nanocomposites out of a few thermoplastic polymers because of the technical difficulties associated with their limited solubility. CNT polymer nanocomposites can also be prepared by merely mixing CNTs with the melt polymer. Sometimes an appropriate chemical treatment

e.g. attaching functional groups to the nanotube surfaces helps improving the bonding or mechanical interlocking between the polymer and CNTs [61].

2.4.1 Challenges involved in Fabrication of CNT Polymer Nanocomposites

The fabrication of a uniform carbon nanotube reinforced polymer nanocomposite is quite challenging due to the small size and flocculating nature of carbon nanotubes. The following key issues need to be resolved:

- a. Processing issues related to the increased melt (or solution) viscosity due to incorporation of CNTs
- b. Homogeneous dispersion of CNTs in polymer matrices
- c. Efficient load transfer from the polymer matrices to CNTs
- d. Alignment of carbon nanotubes when fabricating nanocomposites

2.4.1.1 Processing Issues Related to the Increased Melt (or Solution) Viscosity due to Incorporation of CNTs

As CVD grown MWCNTs (unless aligned) are generally entangled in the form of curved agglomerates, only concentrations up to 30 wt% [62] have been realised in thermoplastic nanocomposites using melt compounding, because of rapidly increasing viscosity and subsequent processing difficulties, at higher loadings. However, in lower viscosity solvents even well dispersed CNTs can form a stiff gel due to their high aspect ratio and resulting network-forming ability; the large interaction volume may also increase the background viscosity of the solvent/matrix.

Most common approach being employed for dispersion of nanoreinforcements in polymers is melt compounding. Shaffer et al. [10] have shown well distributed carbon nanofibres in PEEK matrix as a result of twin screw extrusion at a nanofibre loading fraction of 15 wt%. In a recent study Chen et al. reported a simple mechanical strategy for dispersing carbon nanotubes efficiently in a PVDF matrix [61]. An ultra-high shear extruder containing feedback-type screw made the sample circulate in the extruder chamber during melt mixing [63]. PVDF/MWCNT composites were prepared using various screw rotation speeds to get the expected excellent dispersion of carbon nanotubes in the composites owing to the ultrahigh-shear processing. The linear viscoelastic properties of the PVDF/MWCNT

composites with various nanotube loadings showed that MWCNTs have a modest effect on the storage modulus whether processed in low or high shear rate. However, a higher shearing stress resulted in better nanotube dispersion and less alignment of the nanotubes [63].

2.4.1.2 Homogeneous Dispersion of CNTs in Polymer Matrices

For achieving optimal enhancement in the properties of polymer nanocomposites, one of the major issues which need to be resolved is to obtain homogeneous dispersion of CNTs in polymer matrices. The degree of nanotube dispersion depends on both the entanglement, state of the as-received material and the particular processing technology. A uniform reinforcement of the matrix with CNTs can bring improvement to the fracture strength of the composite by ensuring a shear stress transfer to the reinforcement [64]. The solution-cast nanocomposite thin films of PVDF/CNT reported by Levi et al. [65] were observed to have a well-dispersed nanophase within the fluoropolymer matrix which brought morphological changes in polymer crystallinity (confirmed through DSC and XRD) and caused enhancements in both the pyroelectric and mechanical properties. The presence of homogeneously distributed CNTs within a polymer matrix has shown improvements in nanocomposite properties.

Although carbon nanotubes are considered as desirable reinforcement to improve material properties of polymers, but when dispersed in polymer matrices they tend to entangle with each other because of the intermolecular Van der Waals force between their carbon atoms, leading to the agglomerate formation. In order to disperse them homogeneously these aggregated bundles must be broken to provide more interfacial area between the nanotube and the host polymer matrix. Otherwise the weak interfacial adhesion between carbon nanotubes and polymer leads to inefficient load transfer. A reduced cluster size not only makes more filler surface area available, but also prevents aggregation of the filler action such as stress concentrators as well as slippage of nanotube during nanocomposites loading, which all decrease the performance of the nanocomposites greatly. Due to the very high surface area of carbon nanotubes, only a few molecules of polymer can insert themselves between them. To distribute CNTs evenly in to the polymer matrix, a few challenges such as length of the CNTs, their entanglement, volume fraction and high viscosity of the melt (or solution) due to incorporation of CNTs need to be addressed. As a result, the mechanical performance of composites is not as good as envisaged [66]. Hence, aggregation issue encountered with the nanoreinforcements has become one of the major problems associated with all nanocomposites even at modest loading fractions.

This difficulty in dispersing the carbon nanotubes homogeneously in to the polymer matrices can be overcome by employing various methods. Mechanical stirring and ultra-sonication are the common agitating means which not only break the existing agglomerates of CNTs but also prevent the formation of any due to the application of shear forces. A reduction in the average cluster size of MWCNTs has shown improvements in the nanocomposite's tensile stiffness [67]. With the increase in the length of CNT, resulting interactive forces hinder the separation of the CNTs just like the influence of molecular weight (chain length). The sonication method is only suitable for very low viscous matrix materials and small volumes because ultrasonic devices have a high impact of energy, but introduce low portion of shear forces. The local introduction of energy, while sonicating leads to rupture and damage of CNTs reducing the overall aspect ratio and thus limiting the homogeneous distribution of CNTs in the polymer matrix. An accurate application of sonication techniques for producing polymer nanocomposites is to disperse CNTs in an appropriate solvent (i.e. ethanol, acetone, dimethyl formamide) first and allow it to sonicate, the agglomerates will be separated due to the vibrational energy. The suspension can later be mixed with either the polymer or the polymer solution in the same solvent, which can then be evaporated or filtered to obtain the nanocomposite material. Mechanical stirring, on the other hand, may result in CNT breakage as it involves high shear mixing, when used for dispersing MWNTs. It means CNT length decreases with energy input as there is some breakage involved. The rate at which mean CNT length is reduced diminishes as the material is dispersed and tube separation increases. As the tube breakage is not a serious problem, and the aspect ratio of the CNTs remain very high, reducing from 1000 to 250 [64], good dispersion can, therefore, be achieved at the expense of reduction in CNT length.

Another approach is to introduce a surfactant during mechanical agitation. Surfactants provide enhanced physical adhesion, which does not reduce the structural quality of the CNTs. Also, conjugated polymers such as poly(m-phenylenevinylene-co-2,5-dioctyloxy-p-phenylenevinylene) PmPV, just like surfactants, serve to enhance the physical bonding between the CNTs and the polymer matrix by improving the compatibility between them [68]. Nanocomposites containing as little as 1 wt% of surfactant dispersed MWCNTs show improved thermo mechanical behaviour, although the surfactant itself decreases the storage modulus of the matrix significantly. The combination of the MWCNTs and surfactant can increase the composite T_g , providing an indication for an enhanced interaction between reinforcement and matrix [67].

A third strategy for improved dispersion is to use chemical routes to directly functionalise the CNTs. Chemical functionalisation of CNTs enhances the compatibility of CNTs through covalent or ionic bonds to the polymeric matrix. These bonds (covalent or ionic) between carbon atoms of CNTs and the matrix improve the networking between them and enhance the degree of dispersion which in turn increases the interfacial area and provides homogeneous nanoreinforcement throughout the matrix. A reduction in the agglomerate size can be achieved via functionalisation process [64]. A combination of sonication and an oxidative process where the functional groups, which develop on the surfaces of the CNTs, leads to steric hindering and electrostatic interactions with the solvent, resulting in a better distribution of CNTs in the matrix.

Functionalisation involves an oxidative treatment of the CNTs to develop carboxylic groups, which enabled their direct bonding with the matrix via the functional group (e.g. amines in the case of epoxy matrix), at not only the CNT ends but the defects at the CNT side walls as well. For example, nitric acid treatment has been reported to oxidise successfully the surface of MWNTs [64, 69]. Finally, addition of the polymer and the CNTs lead to formation of equivalent bonds due to the reaction between the free functions on the surface of CNTs with the free molecules of the polymer matrix, thus ensuring an improved CNT-matrix bonding.

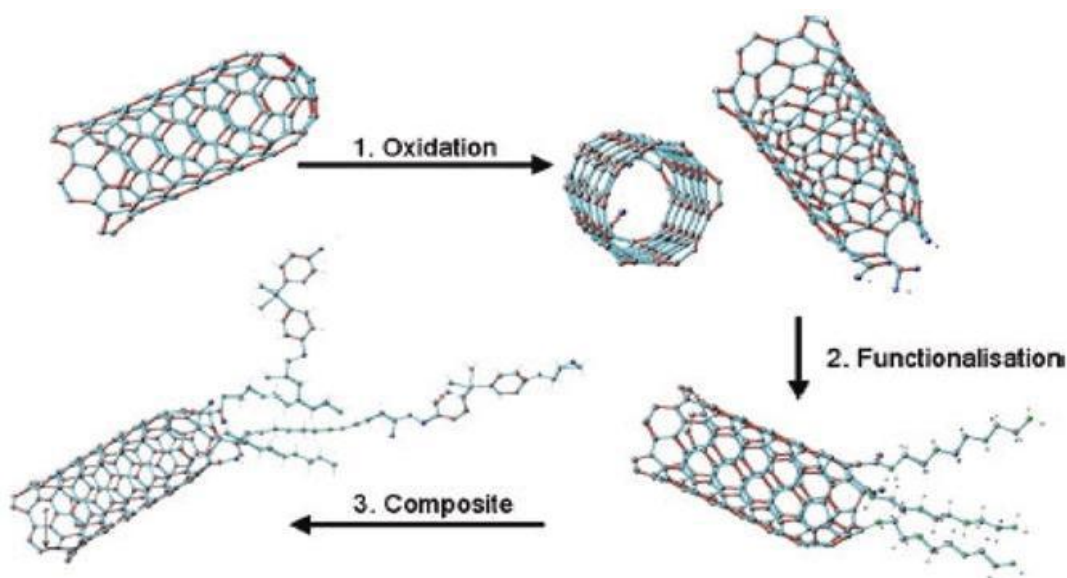


Figure 2-5: Schematic diagram of the functionalisation process of CNTs showing the steps involved from the oxidation to the nanocomposite manufacturing [64]

Various studies revealed that functionalisation of even less than 1% carbon atoms in the carbon nanotubes enhance the mechanical properties of the nanocomposites [64]. Oxidised

nanotubes show a better solubility and can form electrostatically stabilised colloidal dispersions in water as well as alcohols which in turns leads to improved dispersions in polymer matrices, a step forward in the development of carbon nanotube reinforced polymer composites could be made via chemical functionalisation of CNTs with various functional groups such as amines [70].

Other methods reported to aid nanotube dispersion include ultrasonication, polymer functionalised nanotubes and chemical treatment of the constituents [71, 72]. Ultrasonic treatment may also stabilise the dispersion by grafting polymer on to the CNT surface through trapping of radicals generated as a result of chain scission. With grafting modifications PMMA-g-MWCNTs showed improved dispersion in PMMA matrix as compared to MWCNTs [73].

2.4.1.3 Efficient Load Transfer from the Polymer Matrices to Reinforcements

Load transfer depends on the interfacial shear stress between the reinforcement and the matrix. A high interfacial shear stress will transfer the applied load to the fibre reinforcement over a short distance, and a low interfacial shear stress will require a long distance. There are three main mechanisms of load transfer from a matrix to reinforcement.

- The first is micromechanical interlocking; this could be difficult in nanotube composites due to their atomically smooth surface.
- The second is chemical bonding between the nanotubes and the matrix. Chemical bonding is not guaranteed, but a recent study by Wagner [74] indicates that the interfacial shear stress due to bonding could be as high as 500 MPa.
- The third mechanism is due to weak Van der Waals bonds between the fibre and the matrix.

In order to assess the success of CNTs when used as reinforcements for the improvement of mechanical performance of the nanocomposites, the issue of load transfer needs to be addressed. If load can be effectively transferred to CNTs, then the modulus of the nanocomposite should be similar to that of randomly oriented short fibre composites containing fibres of extremely high modulus and strength [57]. In addition, the high surface area of CNTs creates a large interfacial region which can have properties different from the

bulk matrix. The presence of a low mobility bound polymer layer has been reported in nanoparticulate polymer composites [58].

A very appealing approach used to improve the load transfer from the polymer matrices to CNTs is to graft polymer onto CNTs and employing this polymer grafted CNT as reinforcement in a polymer matrix [58]. It is well known that if polymer-grafted CNTs are to be used to reinforce a different polymer matrix, the two different types of polymers are required to be miscible with each other so that they mix thoroughly. Otherwise, the polymer–polymer interface with weak interfacial adhesion will compromise the load transfer. For example, a recent study of PMMA-*g*-MWNTs reinforced poly(styrene-*co*-acrylonitrile) (SAN), revealed that the composite exhibited much superior mechanical properties than SAN (without PMMA-*g*-MWNTs) because of the excellent dispersion of PMMA-*g*-MWNTs in SAN, owing to the fact that SAN is miscible with PMMA [58].

In industrial applications, PVDF is usually blended with acrylic polymers such as PMMA and PMMA is miscible with the amorphous region of PVDF. In a recent study, the grafting of PVDF onto MWNTs had not been proved successful so the advantage of the miscibility between PMMA and PVDF was availed, to thoroughly disperse the nanotubes in the PVDF matrix and to enhance the load transfer from the PVDF matrix to the nanotubes as well. PVDF/PMMA-*g*-MWNT composites were prepared by melt mixing. With only 1.93 wt% loading of PMMA-*g*-MWNTs in PVDF, storage modulus was increased by 100–150% over a wide range of temperatures [58]. None of the studies show the effect of CNT loadings higher than 2 wt% in PVDF nanocomposites. So it would be interesting to fabricate PVDF nanocomposites by melt mixing up to the loading fractions of 10 wt% and investigating their mechanical performance.

2.4.1.4 Alignment of CNTs during Nanocomposite Fabrication

CNT alignment is important because it is the only way to maximize the preferred anisotropic behaviour of a CNT nanocomposite. Because of their small size, it is exceedingly difficult to align CNTs in a polymeric matrix material in a manner accomplished in traditional short fibre composites. The lack of control of their orientation diminishes the effectiveness of CNT reinforcement in nanocomposites, whether for structural or functional performance. To date, various techniques such as carbon arc discharge [75], composite slicing [60], film rubbing [76], chemical vapour deposition [77], mechanical stretching of CNT-polymer composites

[78] and magnetic orientation [79] have been reported for aligning CNTs in composites [80]. Processing of compounds under conditions involving both shear and elongational flows, such as injection-moulding, can be used to induce alignment of the nanofiller [40]. Similarly, Kuriger et al. [81] showed that flow-induced nanofibre alignment occurred during extrusion; the degree of nanofibre alignment was improved by optimisation of the extruder die geometry. However, a decreasing degree of alignment with increasing nanofibre content was observed most likely as a result of nanofibre nanofibre interactions alternating the flow field [10, 81]. Similarly drawing of composite extrudates was shown to induce significant nanotube alignment [78]. In fact, approaches to achieve CNT alignment in composites are dependent on the process by which nanotubes are incorporated into polymer matrices. Furthermore, in order to realize the potential applications of nanocomposites some work has been done in improving the production techniques for CNTs with reasonable costs. For example, Iwasaki et al. [82] synthesized millimetre long aligned CNTs by an improved CVD technique, whereas, Mayya et al. [83] synthesized diameter controlled CNTs by modified CVD technique.

2.5 Hierarchical Fibre Reinforced Nanocomposites

2.5.1 Concept of Hierarchy in Composites

A large number of natural and synthetic materials exhibit structure in more than one dimension; sometimes elements assembling these materials themselves have structure. This structural hierarchy can help in understanding not only the physical properties but also pathways to improve mechanical properties of the materials. Natural examples include rock, wood and bone whereas; synthetic examples include hierarchical cellular material microstructures, polymers and multiscale composites etc.

Polymers can exhibit structural hierarchy on the molecular, ultra structural and microstructural levels. So it is instructive to consider a hierarchical organisation of structure in polymers at four successive levels the molecular, nano, micro, and macro levels. In semicrystalline polymers, there are spherulites on the scale of tens of micrometers, the spherulites themselves contain a lamellar texture and the molecules within the laminae contain structure [84]. Amorphous polymers have a structure on the molecular scale only. It is also important to examine how interactions at and between these various levels of structure are important and their specific influences. Fibrous composites normally have relatively low order hierarchy (in 10 μ m range instead of 10nm) in which fibres are set in a matrix to shape a

structural anisotropic sheet or ply (lamina), such laminae are bonded together to form a laminate [85, 86].

2.5.2 Hierarchical Fibre Reinforced Nanocomposites

Conventional composites can have remarkable in-plane mechanical properties but relatively weak transverse properties, due to polymer matrix being the only effective constituent holding the fibres together. Although, the mechanical properties of polymer matrix are relatively weak, not enough to provide the intense industrial requirements but, CNTs/CNFs reinforced polymer nanocomposites have been reported to reveal considerable enhancement in mechanical and physical properties as compared to neat polymer system. The motivation behind the fabrication of ultra-inert hierarchical nanocomposites is to enhance the performance of conventional fibre reinforced nanocomposites. The use of CNTs/CNFs as the nanoreinforcement in matrix of conventional composites would generate a hierarchical structure, containing multiple length scale reinforcement i.e. micro-fibre and nano-particles within a polymer matrix, which can improve the through thickness matrix dominated properties (shown in Figure 2-6).

The concept of incorporating nanoreinforcements in to a hierarchical continuous fibre reinforced system is a relatively novel idea. Due to intrinsically superior mechanical properties of nanoreinforcements, researchers have been motivated to improve conventional high performance carbon fibre reinforced composites by incorporating these nanoreinforcements either in matrices or carbon fibres for the development of hierarchical composite materials. This nanoreinforcement incorporation at the fibre/matrix interface is likely to improve the fibre/matrix interfacial strength, which enhances the adhesion and thus improves the composite delamination resistance. Researchers have also been working on improving the fibre/matrix adhesion for the past three decades, which is believed to enhance the matrix dominated properties by increasing the surface area provided by the nanoreinforcements in either of the phases of the composite. To date, there has been some research on carbon nanotube modification of thermosetting matrices, however; only rare research on hierarchical fibre reinforcement of thermoplastics has been reported. For example Vlasveld et al. [87] reported more than 40% improvement in compression strength of continuous glass fibre reinforced polyamide 6 composites containing mica layered silicate nanoparticles. However, nanoreinforced thermosetting matrices have been discussed as a potential hierarchical reinforcement scheme. Besides using the polymer matrices filled with

CNTs, CNFs and NC to make hierarchical composites, another interesting approach is to incorporate nanoreinforcements in the conventional composites by growing CNTs or CNFs either on one of their surfaces (matrix/fibre) or directly at the interface. Carbon fibres can be grafted with a higher loading of carbon nanotubes in a radial direction which can enhance the interlaminar properties due to the presence of through-thickness reinforcement by increasing the interfacial area. Some research has been focused on growing CNTs and CNFs onto the fibre surface using different catalyst systems and synthesis methods [88], and a variety of morphologies and distributions of CNTs and CNFs have been reported.

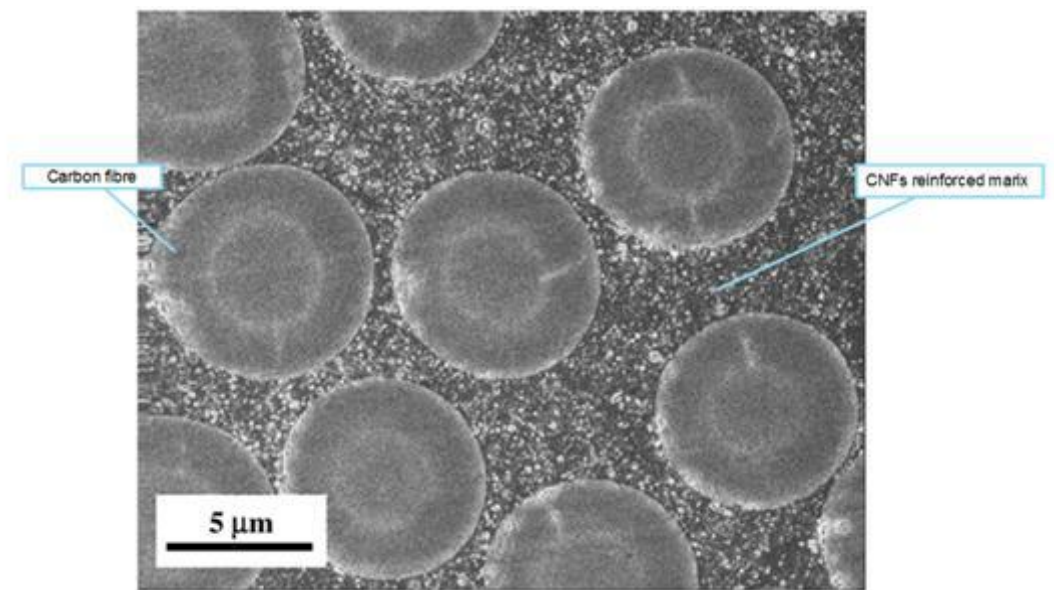


Figure 2-6 : Microscopic observations SEM of carbon nanofibre reinforced carbon fibre epoxy composites (5 wt%-CNFs) [89]

Based on the early studies, the CVD route is an effective and practical method. In CVD, CNTs and CNFs are grown using the catalytic decomposition of hydrocarbons over transition metal catalysts such as iron, cobalt and nickel at temperatures ranging from 550 to 1000°C. Moreover, plasma enhanced chemical vapour deposition (PECVD) is another effective way to grow CNTs and CNFs at much lower temperature and better control. Boskovic et al. [88] introduced this PECVD method for growing CNFs at a much lower temperature i.e. 120°C-250°C at the interface of carbon-carbon composites. This low temperature growth of nanoreinforcements achieved through PECVD is being considered suitable to use for temperature sensitive substrates like polymer matrices. Another similar approach has been employed for developing hierarchical carbon-carbon composites by growing carbon nanotubes directly on the surface of carbon cloth by catalytic pyrolysis of natural gas in a

CVD system [88]. Increased interlaminar shear strength due to good interfacial bonding was observed along with retardance in crack propagation in CNTs reinforced interface layer in carbon-carbon composites. Generally, there is a trade-off between superior interlaminar properties and in-plane properties due to the in-plane degradation of the carbon fibre surface when subjected to high temperature growth conditions for nanoreinforcements. This low temperature growth conditions for nanoreinforcements, thus make the composite able to retain superior interlaminar properties without considerable loss in their in-plane properties.

The first report on hierarchical reinforcement in thermosets was made by Downs et al. [90] and further refined by Thostenson et al. [91]. Downs et al. [90] studied the interfacial properties of the hierarchical composites based on CNFs grafted carbon fibres. The growth of CNFs on the surface of carbon fibres increased the interfacial shear strength by 4.75 times and surface area by around 300 times, providing a larger area over which to transfer load, which is a tremendous increase as compared to that obtained with conventional roughening or oxidation treatments of fibre surface. Thostenson et al. [91] investigated the interfacial properties of the single fibre model composites based on CNTs grafted carbon fibres through single-fibre fragmentation test. When these nanofibres (CNT grafted carbon fibres) were embedded in an epoxy matrix, the change in the length scale of carbon nanotubes relative to carbon fibres resulted in a multiscale hybrid composite, where individual carbon fibres were surrounded by a sheath of nanocomposite reinforcement. Interfacial shear strength of the composites was found to be improved owing to the presence of CNTs at the fibre/matrix interface as a consequence of increased shear modulus and yield strength of the nanotube reinforced polymer matrix surrounding the fibre/matrix interface. Interfacial properties might also be modified by forming CNTs reinforced interfacial layer.

A significant improvement, particularly, in transverse mechanical properties of hierarchical composites is expected due to the enhanced stiffness of the nanomatrix. Although limited concentration of CNTs can be incorporated in to the polymer matrix due to the resulting higher viscosity of CNT suspension and difficulty due to self-filtration during resin transfer, but still the presence of CNFs in the matrix has shown improvement in the longitudinal compression and interlaminar properties. For example, Sadeghian et al. [92] fabricated 1 wt% CNF toughened polyester/glass fibre composites using vacuum assisted resin transfer moulding which resulted in 100% enhancement in delamination resistance in addition to excellent in plane strength due to presence of longitudinal fibres in them. Wicks et al. [93]

fabricated fuzzy fibre plies for the FFRP (fuzzy fibre reinforced plastic laminate) containing a high-yield of grown aligned CNTs on alumina fibre woven cloth by a modified thermal CVD method at atmospheric pressure. The resulting three dimensional reinforced woven advanced epoxy composites containing aligned CNTs showed 76% improvement in toughness (more than 1.5 kJ/m^2) at steady state, and 19% and 5% improvement in stiffness and ultimate strength when tested in tension.

The aim of this project is to investigate the improvement in mechanical performance of carbon fibre reinforced thermoplastic nanocomposites by introducing the structural hierarchy in them, which is achieved via incorporation of carbon nanotubes in the PVDF matrix. Moreover, modifications of the PVDF matrix by adding various percentages of compatibiliser (e.g. PVDF with 25% MAH-g-PVDF) are also employed to study their effect on the mechanical performance of hierarchical composites. Another interesting approach which is investigated in this project is to produce PVDF nanocomposites containing PMMA grafted CNTs up to CNT loading fractions of 10 wt%. A thorough distribution of PMMA-g-CNTs in PVDF can be achieved, owing to the fact PMMA is miscible with the amorphous region of PVDF and possibly improve the load transfer from matrix to nanotubes which can improve mechanical performance of the nanocomposites fabricated. Moreover, none of the reports published the mechanical performance of PVDF and PEEK hierarchical carbon fibre reinforced composites with the loading fraction up to 5 wt% CNTs in past, which is represented in this thesis.

Chapter 3 - Experimental

This chapter presents the experimental procedures used for fabrication of PVDF nanocomposites, characterisation techniques and the test methods used to determine their mechanical performance. Furthermore, processing details for manufacturing hierarchical composites and the standard testing methods for their mechanical characterisation are also described in this chapter. Materials used along with their suppliers are provided.

3.1 Materials

3.1.1 Thermoplastic Matrices

Particular grades of two commercially available thermoplastic polymers, which are both chemical resistant coupled with high strength, were used for this research project: Vicote 150 and Kynar 711 which are powder forms for PEEK and PVDF homopolymers respectively. A modified PVDF (MPVDF) grade comprised of 75wt% Kynar 711 and 25 wt% Kynar ADX-121 was also used to alter the polymer formulation without losing the bulk characteristics of PVDF such as chemical resistance and mechanical strength. Where, Kynar ADX-121 is maleic anhydride grafted PVDF containing 5.0 ppm of grafted maleic anhydride. Both the grades PVDF (Kynar 711) and MAH-g-PVDF (Kynar ADX-121) were kindly supplied by Arkema (Serquigny, France).

3.1.2 Multi-walled Carbon Nanotubes

Commercially available, multi-walled carbon nanotubes (CNTs) were chosen for their high stiffness and strength [91], for preparing nanocomposites and carbon fibre reinforced hierarchical composites. Two types of CNTs were chosen for this project for consistency with previous research in the PaCE group. An industrial grade of CNTs (NC7000) supplied by Nanocyl (Sambreville, Belgium) was used for PEEK composites. NC7000 has a diameter range up to 10nm, an average length of 2 μ m (manufacturer's claim) and costs about €500 for 2kg. However, a commercially available grade of CNTs (Graphistrength® C100) supplied by (Arkema, Liverpool, UK) was used for PVDF composites. Graphistrength® C100 has a diameter range of approximately 10-20nm, a length of at least 5 μ m (manufacturer's claim) and costs £136 per kg. Both grades of CNTs were produced via catalytic chemical vapour deposition by their manufacturers and were used without any further purification. As received CNTs (AR-CNTs) were modified by grafting poly methyl methacrylate (PMMA) onto them, in order to characterise the mechanical performance of modified CNTs based nanocomposites.

3.1.3 Carbon Fibres

Two types of commercially available continuous, high strength and high strain, poly acrylonitrile (PAN) based carbon fibres were selected to manufacture unidirectional carbon fibre reinforced composites for this project, namely Hextow™ AS4 from Hexcel (Duxford, Cambridgeshire, UK) and T700 kindly supplied by Torayca® (Toray Industries, Tokyo, Japan). The properties of these fibres are summarised in the Table 3-1[94, 95].

Fibre	Torayca® T700SC	Hextow™ AS4
No of filaments	12000	12000
Tensile Strength (MPa)	4900	4475
Tensile Modulus (GPa)	230	231
Density (g/cm ³)	1.8	1.79
Elongation (%)	2.1	1.8

Table 3-1: Typical fibre properties of carbon fibres used in this research [95]

The choice of two types of fibres for specific polymers was based on the fact to make the results comparable to what others have done previously within the PaCE group. All the

formulations of PEEK and PVDF hierarchical composites with different loading fractions of CNTs were reinforced with T700 and AS4 respectively. Although, both the carbon fibres were industrially oxidised, the Hexcel AS4 fibres were available in an unsized form whereas the Torayca T700 fibres were only available with an applied epoxy sizing.

3.1.4 Other Materials

Dimethyl formamide (DMF, general purpose grade) and ethanol (+98%, general purpose grade) for washing the nanocomposite precipitate, were supplied by VWR, Poole, UK. The surfactant used for stabilising the nanocomposite particle dispersions was Cremophor A25 (polyethylene glycol 1100 mono(hexadecyl/octadecyl)ether), which was kindly supplied by BASF Ludwigshafen, Germany). A polyimide film (12.5 microns, Upilex UBE, Japan) was used as a starter crack insert for DCB specimens, whereas a relatively thicker film (25 microns, Upilex UBE, Japan) was used as a release film.

3.2 Experimental Procedures

3.2.1 Production of PVDF/CNT Nanocomposites

This section describes the whole manufacturing process for fabricating nanocomposites which includes dry blending of PVDF and CNTs, extruding the dry blend, chopping the resulting extrudate into pellets (1~3 mm in length), and finally injection moulding these pellets to prepare nanocomposite specimens. Three different formulations of PVDF nanocomposites were prepared: as received PVDF (AR-PVDF) and AR-CNT, MPVDF (mixture of 75 wt% PVDF and 25 wt% MAH-g-PVDF) with AR-CNTs and AR-PVDF with in-house modified PMMA grafted CNTs (PMMA-g-CNTs). Nanocomposites were manufactured with carbon nanotube loading fractions ranging from 0 to 10 wt%.

All materials were dried overnight in a vacuum oven at 50°C to ensure elimination of any remains of moisture. AR-CNTs were blended for 1 min using a stainless steel laboratory blender (Waring laboratory blender, UK) to allow breakage of bulk agglomerates in to fine powder. A 400g PVDF/CNT pre-mix was prepared in eight steps of adding 50g PVDF in to CNT powder and blending it for 10s followed by a 30s interval after each addition to cool down the mixture. The blended PVDF/CNT pre-mix was then blended again for 30s twice with a 30s break to ensure homogeneous blending. The PVDF/CNT blend was either force fed in to the extruder immediately after mixing or was placed in a vacuum oven at 50°C before

extruding. This ensures no moisture in the PVDF/CNT pre-mix and hence no bubble entrapment in the extrudate obtained.

3.2.2 Direct Mixing of CNTs with PVDF Powder by Twin Screw Laboratory Extruder

PVDF/CNT pre-mix was force fed in to a continuous twin-screw co-rotating extruder (PRISM TSE-16 TC laboratory extruder, Thermo Scientific Haake, UK) equipped with a barrel length to diameter ratio of 15:1 and a screw diameter of 16mm. A custom barrier screw design (Figure 3-1) was used to increase the shear mixing of CNT and PVDF within the twin screw extruder and to maximise the dispersion of carbon nanotubes within the polymer. The PVDF/CNT mixture was force fed in to the twin screw extruder at a rate of 1kg/h. An optimised speed of 80rpm was adopted for extruding PVDF/CNT blends with various CNT loadings after considering the influence of various processing factors on the final product such as shear forces generated due to screw design and viscosity of the mixture.

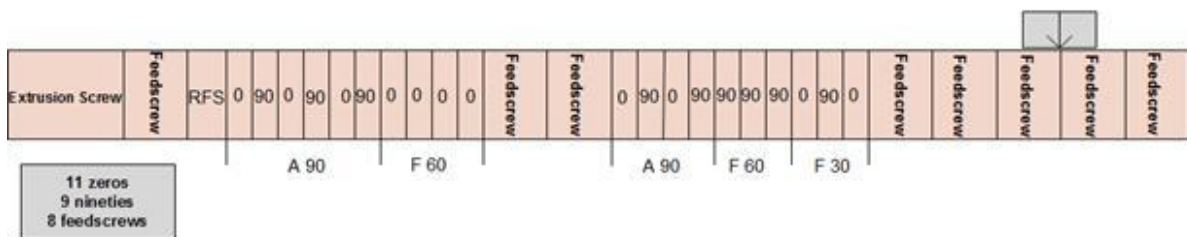


Figure 3-1: The barrier screw design

The rear, middle and front temperatures were set at 200°C, 210°C and 220°C respectively. The corresponding residence time within the extruder was approximately 40s. In order to ensure consistency of homogeneous dispersion of carbon nanotubes, the nanocomposite pellets were re-extruded twice under the same processing conditions. The continuous strands of PVDF/CNT nanocomposites leaving the extruder were quenched in a water bath, air dried and then pelletized around 3mm in length with a PRISM pelletiser unit.

3.2.3 Nanocomposite Specimen Preparation via Injection Moulding

The nanocomposite pellets produced from extrusion were dried in vacuum oven at 50°C for 24 hours and used to prepare nanocomposite specimens for mechanical testing via injection moulding in a laboratory injection moulder (Thermo Scientific Haake MiniJet, UK). Two kinds of mould were used to make the specimens for different mechanical tests. The mould dimensions for tensile test specimen were made according to the ASTM D638-03 Type V which is a dog bone shape mould. As for flexural and compression tests, the mould was a rectangular bar with dimensions of 80mm × 12.7mm × 3.2mm (length × width × thickness). For each batch, six specimens were made for each test. The parameters used for different CNT weight fraction were the same to ensure same thermal history is seen by all specimens and hence to minimise any effect on the mechanical performance of the nanocomposites. The dried pellets were fed in to the heated barrel at a temperature of 240 °C and were allowed to melt for 10 min before injection took place. The injection was conducted with a mould temperature of 90°C and an injection pressure of 600 bars held for 10 sec before being reduced to 300 bars and held at this pressure for 30 sec. This is to ensure a rapid filling of the mould cavity in the first step and the solidification of the melted polymer in to the mould shape in the second step. The injection moulded nanocomposite specimens were removed immediately from the mould after.

All test specimens (PEEK/PVDF) were annealed in order to release any residual stresses induced in the specimens during manufacturing process. PEEK composite specimens (injection and compression moulded), with various loading fractions of CNTs, were annealed in a programmable oven at 240°C for 4 h and cooled to 140°C at a rate of 10°C/h. On the other hand, PVDF and MPVDF composite specimens, fabricated via injection moulding, with various loading fractions of CNTs were annealed at 135°C for 6 hours before being cooled down to room temperature at the rate of 6 °C/hour. A 2kg weight was placed on top of each

specimen to ensure that they remained straight during the annealing process. Figure 3-2 shows the details of the annealing process for PVDF composites.

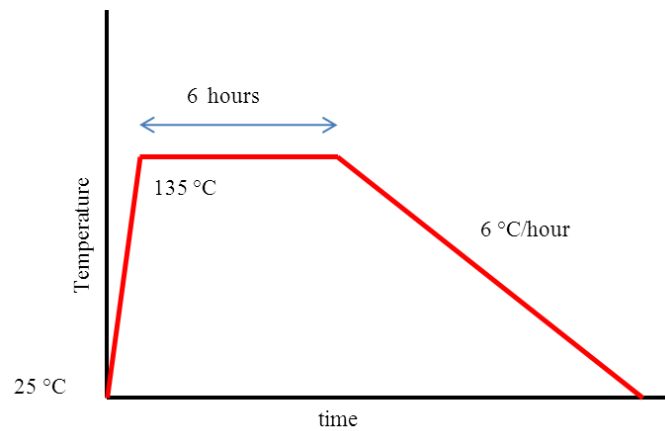


Figure 3-2: Figure representing the details of annealing process for all PVDF nanocomposites

3.2.4 Fabrication of Thermoplastic Hierarchical Carbon Fibre Reinforced Nanocomposites

PVDF and PEEK hierarchical composites were fabricated from thermoplastic nanocomposite powders impregnated and consolidated uniform carbon fibre tows to manufacture carbon fibre reinforced thermoplastic hierarchical composites. Three different formulations of hierarchical composites with CNT loadings ranging from 0 to 5% were fabricated: AS4/PVDF, AS4/MPVDF and T700/PEEK. T700/PEEK composite tapes were provided by Dr. Lamoriniere [14]. Unlike PVDF nanocomposite powders (prepared through a solution precipitation method), PEEK nanocomposite powders for T700/PEEK hierarchical composites were prepared by a temperature induced precipitation scheme using diphenylsulfone (DPS) as a solvent [14].

3.2.4.1 PVDF Nanocomposite Powder Preparation

The procedure for synthesising PVDF nanocomposite (NC) powder was adopted from Tran et al. [15]. The PVDF nanocomposite powder was prepared with a carbon nanotube loading of 2.5 and 5 wt%. The solutions of PVDF and the suspensions for carbon nanotubes were prepared separately. Pure PVDF and PVDF compatibilised with 25 wt% of maleic anhydride grafted PVDF were chosen polymers for preparing nanocomposite powder. DMF was used as a solvent to prepare PVDF and CNTs suspensions because of its suitability for both PVDF and carbon nanotubes. The solution for the matrix was prepared by dissolving 10 wt% of

PVDF in DMF using magnetic stirring. 0.2 wt% of carbon nanotubes in DMF suspension was prepared under ultrasonication for 3 h. The carbon nanotube suspension was added drop wise to the PVDF solution while stirring at 3000 rpm (L2H, Silverson, Chesham, UK). This drop wise addition of carbon nanotube suspension in to the polymer solution caused stabilisation of the mixture by inducing an adhering interaction between the carbon nanotubes and the matrix. After complete addition of the carbon nanotube suspension, the mixture was allowed to stir for an additional hour. The precipitation was induced by adding the non-solvent drop wise to reach a 1:1 wt ratio with the carbon nanotube/PVDF mixture while homogenisation was continued. The mixture was cooled to 0°C and filtered. The precipitated PVDF nanocomposite powder was washed with ethanol to remove residual DMF and filtered. And finally it was dried under vacuum at 50°C for 12 h and then at 120°C for 12 h. The PVDF nanocomposite matrix prepared via this solvent/nonsolvent precipitation scheme was a fine powder (Figure 3-3), which was believed to possess good dispersion of CNTs needed for mechanical reinforcement [5]. The product formed was an aggregated fine powder. Pure polymer (e.g. PVDF) was processed in a similar way to produce the reference material. DMF was added instead of adding the nanotube suspension in to the polymer to make up the difference in mixture volume. Additional distilled water (25 ml/min) was added to the mixture to make the total DMF to water content a 1:1 weight ratio.

Other samples of the matrix formulations were made in a similar fashion. Matrices with the following compositions were prepared: PVDF containing 0 wt%, 2.5 wt% and 5 wt% CNT loadings and MPVDF (i.e. PVDF with 25 wt% MAH-g- PVDF) containing 0 wt%, 2.5 wt%, and 5 wt% CNT loadings.

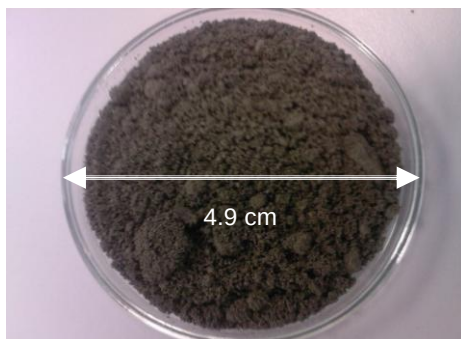


Figure 3-3: A photograph of in-house prepared PVDF nanocomposite powder via solution precipitation method

In the current precipitation scheme, the slow addition of the water/DMF non-solvent to the CNT/PVDF/DMF mixture induced phase separation and precipitation of the polymer from solution. Since the CNTs were wrapped with and stabilised by adsorbed polymer they co-precipitated with the PVDF, leading to a uniform nanocomposite (NC) powder as indicated by the uniform grey colour of the resulting composite.

3.2.4.2 Prepreg Fabrication via Continuous Composite Line Setup

A 10 wt% NC bath was prepared for the impregnation of continuous unsized carbon fibres in the continuous composite line. The surfactant (Cremophor-2 wt% with respect to the powder) was dissolved in water by agitation. The NC bath suspension was allowed to soak for about half an hour. Ethanol was added to break the surface tension of the water molecules to facilitate the water spreading and thus to improve the adsorption of water by the nanocomposite particles. Homogenisation of the suspension was carried out at 800 rpm for 30 minutes to obtain well-dispersed powder particles (determined to particle size distribution) for the suspension to be used as impregnation bath. In order to maintain a constant fibre volume fraction in the final composite tape, the concentration of the impregnation bath was kept constant by addition of specific amount of NC solution at regular intervals.

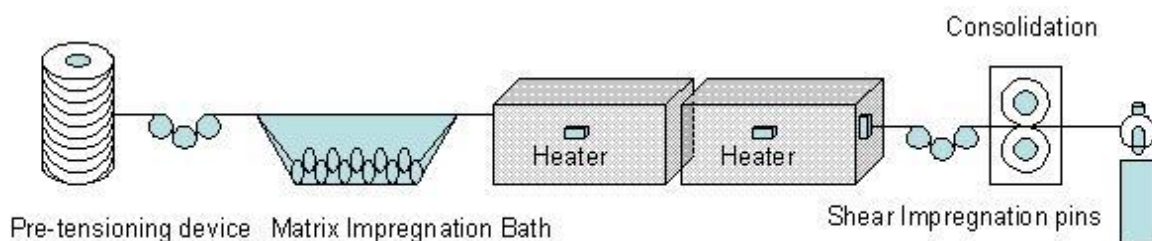


Figure 3-4: Schematic diagram of the continuous composite line

A schematic diagram of the continuous composite line is shown in Figure 3-4 which is used for powder impregnation technique for manufacturing thermoplastic composites [96]. The 12K carbon fibre roving was taken off from a tension controlled let-off unit (Izumi International, USA) and passed through a series of shear pins located in the matrix impregnation bath at specific positions to get required spreading and necessary tension in the fibres as shown in Figure 3-5. Moreover, shear pins helped in aligning the polymer impregnated fibre tow and ensuring no twists from the bobbin to the heaters, resulting in uniform distribution of carbon fibres and homogeneous impregnation of NC powder, all over

the straight fibres throughout the process. The first infrared heater served to dry off any water from the fibre tow coming out of the impregnation bath before leading to the second heater where NC powder was heated until it melt, which facilitated its impregnation on the carbon fibre. The three hot impregnation pins were adjusted with a suitable shear angle to ensure smooth enough resin/NC powder impregnation on the carbon fibre to produce composite tape as shown in Figure 3-6.

The three infra-red heaters controlled by a thermocouple were kept at an increasing order of 140°C, 180°C, and 220°C respectively, when pure PVDF was to be impregnated on carbon fibres. NCs typically require a slightly higher temperature owing to their high viscosity in order to get carbon fibres properly impregnated with them. So the temperatures of heaters were adjusted in increasing order of 170°C, 200°C and 220°C respectively while impregnating NCs. The hot carbon fibre reinforced NC tape was then passed through the heavy rolling die at room temperature exerting enough pressure for its consolidation. The consolidated NC tape/ prepreg was pulled through the line by the haul-off which consists of a pair of drive belts pressed together to grip the tape. The speed of the line was controlled by adjusting the speed of the belt drive motor (Model 110-3, RDN manufacturing Co., USA), which was fixed to 1.0 m min⁻¹ throughout this research project. The tape was then wrapped on a spool and collected. A single (NC) prepreg layer (tape) obtained via a continuous composite line setup was ranging in thickness from 0.125 mm to 0.25 mm containing continuous and unidirectional fibres.

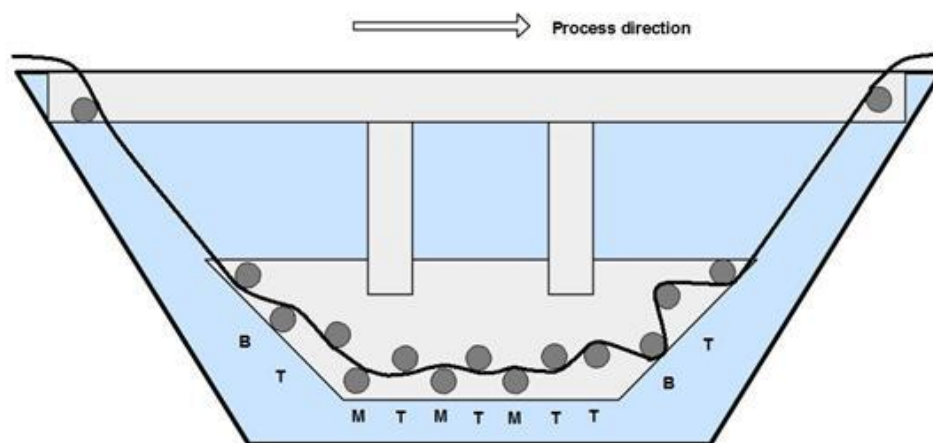


Figure 3-5: Schematic diagram of the pins guiding fibres inside the impregnation bath. The fibres were placed either at the bottom (B), middle (M), or top (T) of the pin slots within the guide frame of impregnation bath [97]

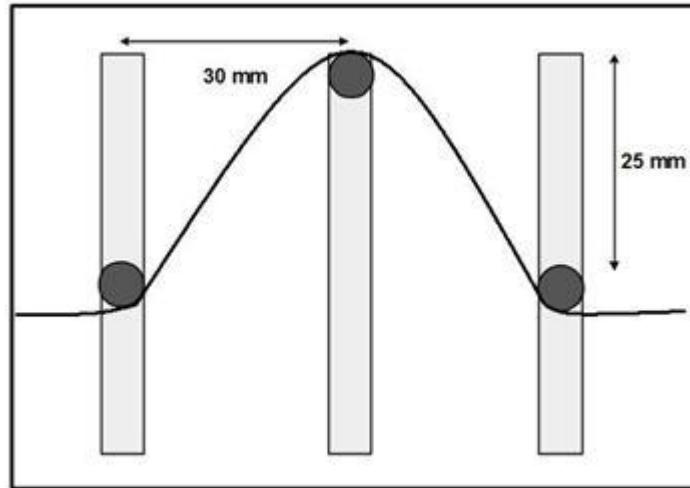


Figure 3-6 : Schematic diagram showing the position of shear pins and the path of the composite tape [97]

3.2.4.3 Fibre Volume Fraction Control of Prepregs (NC tapes)

For each matrix formulation, 250 m of the hierarchical composite tape was produced. The fibre volume fraction was maintained to be 0.57 ± 0.02 throughout the length of the hierarchical composite tape for each formulation. It was determined by gravimetric means based on Equation 3.1

$$V_f = \frac{\rho_m m_f}{\rho_f m_m + \rho_m m_f} \quad \text{Equation 3-1}$$

Where ρ and m are the density and the mass and the subscripts f and m correspond to the fibre and the matrix, respectively. For PVDF hierarchical composites based on AS4 carbon fibre, V_f from equation 1 can be rewritten as:

$$V_f = \frac{\rho_m m_f}{\rho_f (m_{Tape} - m_f) + \rho_m m_f} \quad \text{Equation 3-2}$$

where m_{Tape} is the mass of the hierarchical composite tape in g/m. Other parameters for this system are $\rho_m = 1.78 \text{ g/cm}^3$, $\rho_f = 1.79 \text{ g/cm}^3$, $m_f = 0.858 \text{ g/m}$ (1m of AS4 fibre). Thus, for every metre the mass of all the composite tape was kept at 1.5 g to maintain the constant fibre volume fraction value of 0.57.

3.2.4.4 Preparation of Hierarchical Composite Laminates

Preparation of laminates with thermoplastic matrices is a straightforward process, as polymer simply melts at a high temperature and solidifies when cooled [98]. The prepregs of carbon fibre reinforced PVDF/PEEK that measured 20 cm long were cut using a paper guillotine. Unidirectional carbon fibre reinforced PVDF/PEEK composite DCB test specimens were prepared by aligning layers of prepregs containing 0wt%, 1 wt%, 2.5 wt% and 5 wt% CNTs, with reference to a datum, on top of each other with the fibres in each layer oriented parallel relative to one another in a predetermined sequence. These aligned layers were carefully smoothed out while placing each layer over the previously laid one to prevent air entrapment. This avoids even a few degrees misalignment which can cause a dramatic effect on mechanical properties. The twisted fibre bundles or the prepreg areas containing gaps between bundles were not included in the laminate. Following completion of the layup, the stack of prepreg layers was prepared for consolidation of thermoplastics. A polyimide release film (Upilex 25S, UBE Europe GmbH, Dusseldorf, Germany) was used to wrap the prepreg layers in order to prevent laminate sticking to stainless steel frame mould (cavity dimensions: 200mm $\times$ 12mm $\times$ 5mm), which is also coated with a release agent (McLube 1862, Aston, PA, USA) during compression moulding. A hot press (P319, Moore, UK), capable of rapid cooling of its platens, was used for consolidating NC prepregs. The resultant composite bars (3.5 - 4mm thick) were cut and trimmed to remove the moulding errors. The edges were carefully handled during trimming to achieve correct (parallel) alignment with the fibres in the layers. The specimens were machined oversize and the final dimensions were achieved by grinding. The edges of composite specimens were trimmed using 220 grit sand papers.

For fabricating PVDF laminates, the mould was preheated at 220°C for 5 min before hot pressing which dwelled for 10 min at the pressure of 2 MPa. The mould was then cooled to 80°C for 10 min at 2 MPa. A total of 34 plies of PVDF prepreg layers were consolidated to fabricate a laminate for compression testing where as a total of 60 prepreg layers were consolidated for fabricating a double cantilever beam [99] to determine the fracture

toughness. Mix ply laminates were prepared by aligning alternate layers of prepregs of pure PVDF and of PVDF containing 2.5 wt% CNTs during compression moulding ensuring a total CNT content of 1.25 wt%. Laminates with 2.5 wt% CNTs were manufactured in a similar fashion i.e. piling up prepreg layers of PVDF and PVDF containing 5 wt% CNTs. PEEK composite laminates were prepared in a similar fashion (i.e. preheating the mould containing stacked carbon fibre tapes in hot press at 390°C for 10 min, followed by pressing at a pressure of 2MPa at the same temperature for 10 min, and finally cooling at 120°C for 10 min). A total of 30 and 25 plies were consolidated to fabricate a compression test bar for PEEK and APC-2 respectively, whereas DCB specimens were prepared with only 6 plies of the PEEK composite in the mid, making two thin face sheets, separated by a 60mm long insert, each of which (3 plies of T700/PEEK composite) was surrounded by doublers i.e. 26 plies of APC-2 at the other end.

3.3 Composites Characterisation

3.3.1 Scanning Electron Microscopy (SEM)

Electron microscopy was used extensively throughout this research project as a qualitative tool for analysing the dispersion of CNTs in nanocomposites as well as hierarchical composites. Fracture surfaces of failed specimens were also studied via SEM micrographs for both nanocomposites and hierarchical composites. SEM was performed using a Leo Gemini field emission gun electron microscope (Oberkochen, Germany) with an accelerating voltage of 5-10kV. Cryofracture surfaces were obtained by cutting cross sections of composites cooled in liquid nitrogen. Cross sections of the cryofracture surfaces for each specimen were attached directly to the SEM stubs with double-sided carbon tape. All composites to be examined under SEM were coated using chromium with a coating current of 50mA and coating time of 30s.

3.3.2 Differential Scanning Calorimetry (DSC)

Nanocomposites and hierarchical composites were examined using DSC (Q2000, TA Instruments, UK) in nitrogen environment to determine the influence of any modification (i.e. adding MPVDF or CNTs or PMMA-g-CNTs in PVDF) on the crystallinity of PVDF. All composites were provided the same thermal treatment before and during the characterisation process. The weight of each nanocomposite specimen was approximately 10mg, which were

cut from injection moulded bars. However, 40-45mg sample of carbon fibre reinforced hierarchical composite was taken from the laminates (57% fibre volume fraction) to ensure sufficient resin content available in them. The heat flow of samples was measured at a temperature varying rate of rate of 10°C/min, under nitrogen environment, for each specimen. The calorimetry experiments consisted of two steps i.e. a first heating step started at -100°C to 220°C and a second cooling step from 220°C to -100°C to allow full crystallization of samples in order to determine the influence of CNTs on crystallization temperature (T_m). The crystalline content, X_C , of the carbon nanotube-PVDF composites was estimated using the Equation 3.3

$$X_C = \frac{H_{f,nanocomp}}{H_{f,PVDF} W_{polymer}} \quad \text{Equation 3-3}$$

where $H_{f,nanocomp}$ is the heat of melting the crystalline portion of the PVDF within the nanocomposite sample, $W_{polymer}$ is the weight fraction of the polymer matrix and $H_{f,PVDF}$ is the standard enthalpy of melting PVDF. $H_{f,nanocomp}$ was determined through the integration of the endothermic heat of flow peak for the samples which was normalised to the samples mass. The value for $H_{f,PVDF}$ was 104.5J/g, as reported previously [100].

3.3.3 Fractography

Although fractographic assessment of failure in composites is often complicated because of the facts like; movement of the mating surfaces against each other during testing generates surface debris which masks many fractographic features, but still it helps considerably in understanding the cause of failure. Fractographic assessment of fracture surfaces of composites failed in compression and DCB testing was conducted in order to understand the mode of failure. Cross sections of the failed compression specimens were polished according to the standard procedure taken from Buehler's catalogue for materials preparation and analysed under optical microscope (see Table 3-2). The microscopic images obtained were adjusted to get an overall view of failed cross sections under compression. The basic modes of fracture under compressive loading include microbuckling and macro buckling. Whereas the crack tip of the DCB specimens was analysed under SEM to define the basic features that cause failure such as delaminations and fibre bridging.

3.3.4 Dynamic Mechanical Thermal Analysis (DMTA)

The mechanical performance of nanocomposites was measured by dynamic mechanical thermal analysis (DMTA). It can simply be described as applying an oscillating (sinusoidal) force to a sample and analyzing the material's response to that force. The resulting sinusoidal strain is then measured and used to calculate the tendency to flow (viscosity) from the phase lag and stiffness (modulus) from the sample recovery. The phase difference δ between the sinusoidal applied stress and measured strain provides information about the viscoelasticity of the material. The in-phase response ($\delta = 0^\circ$) is elastic, the out-of-phase response ($\delta = 90^\circ$) is viscous. As δ approaches 90° , the material behaves more viscous.

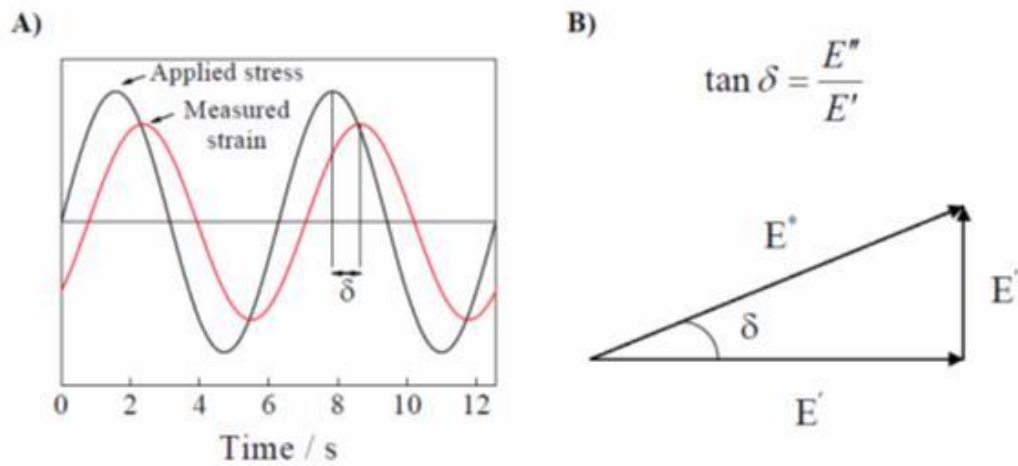


Figure 3-7: Schematic representation of A) the lag between the applied stress and the measured strain, B) the relation between the measured complex modulus and the storage and loss moduli [17]

The dynamic mechanical response of the material to the applied sinusoidal wave is defined as the complex modulus (E^*):

$$E^* = E' + iE'' \quad \text{Equation 3-3}$$

Complex Modulus E^* gives a contributed effect of E' (the storage (elastic) modulus or the in phase/elastic contribution) and E'' (the imaginary/loss modulus or the out of phase/viscous contribution) of a material subjected to an oscillatory force. These different moduli allow better characterisation of the material by providing an insight of its ability to return energy (E'), to lose energy (E''), and ratio of these effects ($\tan \delta$) which is called damping. This relationship of dampening factor ($\tan \delta$) is depicted in Figure 3-7.

Nanocomposites were produced via injection moulding (see section 3.2). The test samples were prepared by cutting the injection moulded bars (43 mm x 12.7 mm x 3.2 mm) with diamond saw (Diadisc 4200, Mutronic GmbH & Co, Rieden am Forggensee, Germany). The test was performed using a single cantilever beam configuration with a span of 15mm free length over a temperature range from -100°C to 120°C. Mechanical testing was performed at a frequency of 1 to 10 Hz.

3.3.5 X-Ray Diffraction (XRD) Analysis

The nanocomposites were analysed by XRD to determine the influence of any kind of modification (such as adding MPVDF, CNTs or PMMA-g-CNTs) on the crystallinity of PVDF. When a monochromatic X-ray beam with wavelength λ strikes the surface of a crystalline material at an angle θ , part of the beam is scattered by the layer of atoms at surface. The unscattered part of the beam penetrates to the second layer of atoms where again a fraction is scattered and the remainder passes on to the third layer and so on [101]. The direction of the diffracted beams depends on the size and shape of the repetitive unit of a crystal and the wavelength of the incident X-ray beam, whereas the intensities depend on the size of atoms in the crystal and the location of the atoms in the repetitive unit. A crystal lattice is a regular three-dimensional distribution (cubic, rhombic, etc.) of atoms in space. These are arranged so that they form a series of parallel planes separated from one another by a distance d , which varies according to the nature of the material. For any crystal, planes exist in a number of different orientations each with its own specific d -spacing. No two substances have absolutely identical diffraction patterns when one considers both the direction and intensity of all diffracted beams. However, some similar complex organic compounds may have almost identical patterns. The diffraction pattern is thus a fingerprint of a crystalline compound and the crystalline components of a mixture can be identified individually [102]. The requirements for X-ray diffraction are (1) the spacing between layers of atoms must be roughly the same as the wavelengths of the radiation and (2) the scattering centres must be spatially distributed in a highly regular way [101].

The information obtained in an XRD experiment is dominated by diffraction from the bulk of the sample to a depth of several micrometres. Nevertheless, the use of XRD in analysing surface structure in the hundred nanometre thickness range can be achieved via a technique known as *glancing angle X-ray diffraction*, in which the X-ray beam is incident on the surface at a very low angle, in order to maximise the distance travelled by the beam in transversing

the thin surface. However, note that the XRD analysis throughout this work was conducted in the wide angle X-ray scattering mode (WAXS).

The nanocomposite films were prepared by moulding extruded nanocomposite pellets in the form of a film following the procedure for preparing laminates of hierarchical composites (see 3.2.4). XRD analysis was undertaken using an automated powder diffractometer (PANalytical X'Pert 1, PANalytical Ltd, Cambridge, UK) with a secondary graphite crystal monochromator and nickel-filtered Cu-K α_1 radiation ($\lambda = 1.5406\text{\AA}$) source, operated at an acceleration voltage of 40 kV and 40mA. Samples were put on a spinner stage spinning at 1 rps and scanned over an angular range of 5-60° with a step size of 0.05° with count time of 2 seconds. The data was subsequently converted using PowDLL converter and analysed by calculating the area under the peak of the curves via Origin Software.

3.3.6 Density and Porosity Measurement

The density of each composite specimen was measured through helium pycnometry (a gas displacement technique for measurement) [103] using an AccuPyc 1330 (Micromeritics, USA). GeoPyc™ 1360 (Micromeritics, USA) was used to determine the envelope (bulk) density for composite specimens. Envelope density, is the mass of an object divided by its volume where the volume includes that of its pore and small cavities [104]. The GeoPyc determined the envelope density by a displacement measurement technique. The sample was placed in a bed of DryFlo, a quasi-fluid composed of small, rigid spheres having a high degree of flow ability, which was agitated and gently consolidated around the sample. The GeoPyc collected the displacement data, and determined the envelope density. It also provided percentage porosity and specific pore volume when absolute density information (density excluding pore and small cavity volume obtained from a Micromeritics AccuPyc helium pycnometer) was entered.

3.3.7 Laser Diffraction Particle Size Analysis

The nanocomposite powders for fabricating hierarchical composites, produced by the solution precipitation method, were analysed by laser diffraction particle sizing using a Malvern's Mastersizer 2000, UK. The principle of this technique is based on the scattering of a laser beam when particles pass through; the scattering angle is directly related to the particle size distribution. The observed scattering intensity is also dependent on particle's cross-sectional area and diminishes. Large particles therefore scatter light at narrow angles with high

intensity, whereas small particles scatter at wider angles but with low intensity [105]. The diffraction angle increases logarithmically with decreasing particle size. The average particle size (d_{50}) defines the diameter of the maximum volume (more than 50%) of the particles in the suspensions with an accuracy of $\pm 1\%$. Three 10 wt% nanocomposite solutions containing various CNT loadings were prepared containing 2 wt% surfactant in deionized water to analyse the particle sizes of the nanocomposite powder produced.

3.3.8 Fibre Volume Fraction

A major factor in determining the mechanical performance of any composite is its fibre to matrix ratio. Although the fibre volume fraction of the tape was controlled during production of the composite tape, the test specimens were analysed to confirm that control over the fibre volume content was maintained throughout the lay-up preparation procedure. The average fibre volume fraction values of the composites were calculated from the local fibre volume fraction values which were determined via microscopic images of the polished transverse sections of the composite laminates produced. The transverse sections of the composite specimens were embedded in polyester resin using a hardener (poly ether ether ketone oxide) (Kleer-set, Metprep, UK) and cured overnight at room temperature. Embedded specimens were then ground/polished using silicon carbide papers with increasing grit designation and final polishing using diamond based dispersions, details are provided in Table 3-2.

Sr.#		Time (min)	Pressure (kPa)	Speed (rpm)
<i>Grinding (using Water as medium)</i>				
1	220 grit SiC	3	207	220
<i>Polishing (using respective diamond suspensions as medium)</i>				
2	6 μ m diamond	2	207	220
3	3 μ m diamond	5	276	150
4	1 μ m diamond	5	276	150

Table 3-2: Polishing sequence and parameters followed for hierarchical composites

Polishing the hierarchical composite specimens based on pure PVDF or modified PVDF matrices was itself a major issue, as PVDF is a very soft thermoplastic ($T_g = -40^\circ\text{C}$) and polishing the specimens causes resin pull out. Buehler's polishing procedure for soft composites was adopted to get the optical micrographs of composite's transverse sections

showing fibre ends as circular regions in a matrix rich region (see Chapter 5). Four images were collected at different regions for each specimen, and the area fraction of carbon fibre was directly correlated to the volume fraction of the entire sample. The fibre area fraction in the image is calculated using the software ImageJ version 4.3 and is considered as corresponding fibre volume fraction. Details of the polishing are given in Table 3-2.

3.4 Mechanical Characterisation of Composites

All PVDF/PEEK nanocomposites and hierarchical composites were annealed prior to mechanical testing. The major prospective benefit of reinforcing thermoplastic polymer with CNTs is improvement which may be gained in matrix dominated properties such as stiffness and strength. Moreover, flexural modulus was chosen as a qualitative tool because it is often used as a design criterion for structural applications [98]. Also, short beam shear strength, and mode I fracture toughness were also determined.

3.4.1 Tensile Test

The tensile properties of nanocomposites were measured according to ASTM D 638-03. Six dog-bone shape specimens prepared via injection moulding were tested on an Instron 4505 universal testing machine with 1 kN load cell at crosshead rate of 1 mm/min. One strain gauge was attached to one side of the specimen in the middle of gauge section to measure longitudinal strain. Tensile strength was calculated from the maximum value on load displacement curve before the specimen's failure using Equation 3-5. For calculating tensile modulus of elasticity, tensile stress at each data point is calculated using Equation 3.6

$$F^{tu} = \frac{P^{max}}{A} \quad \text{Equation 3-5}$$

$$\sigma_i = \frac{P_i}{A} \quad \text{Equation 3-6}$$

where F^{tu} is the ultimate tensile strength (MPa), P^{max} is the maximum force before failure (N), σ_i is the tensile stress at the i th data point (MPa), P_i is force at the i th data point (N) and A is the average cross sectional area of specimen in the gauge section (mm²).

Tensile chord modulus of elasticity was calculated using the strains in the range of 1000 $\mu\epsilon$ to 3000 $\mu\epsilon$ obtained from strain gauge (FLA-2-11) using Equation 3.7

$$E^{chord} = \frac{\Delta\sigma}{\Delta\varepsilon} \quad \text{Equation 3-7}$$

where, E^{chord} is the tensile chord modulus of elasticity (GPa), $\Delta\sigma$ is the difference in applied tensile stress between the two strain points in the specified range and $\Delta\varepsilon$ is the difference between the two strain points.

3.4.2 Flexural Test

Due to the relative simplicity of the test method, instrumentation and equipment required, flexural tests are widely used to determine the mechanical properties of resins and laminated fibre composites. Flexural testing was conducted on both nanocomposites and hierarchical composites to measure the flexural properties in accordance to ASTM D790–03 [106]. Testing was performed with 16:1 span to thickness ratio on a three point bending jig. Instron 4505 universal testing machine at a crosshead motion of 1.4mm/min with 1 kN load cell was used for the testing both nanocomposites and hierarchical composites. Nanocomposite specimens with the dimensions of 80mm × 12.7mm × 3.2mm and hierarchical composites with the dimensions 75mm × 9.85mm × 3.85mm were tested. Each specimen was tested until the 5% strain achieved with the maximum deflection of 6.83mm. All measurements were repeated on six nominally identical specimens to obtain a statistical average. Schematic layout of the test is shown in Figure 3-8 shows the standard layout of the three point bending test.

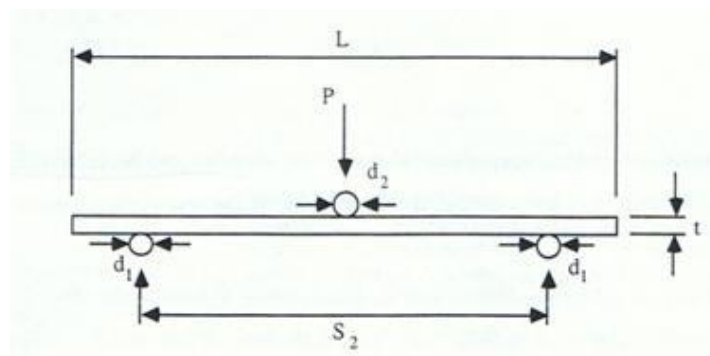


Figure 3-8: Three point bending arrangement

For the test, a load-displacement curve is plotted to get the elastic portion of the curve. The flexural modulus which is the ratio of stress with the corresponding strain was calculated using the following equation.

$$E_B = \frac{L^3 m}{4bd^3} \quad \text{Equation 3-4}$$

where, E_B is the modulus of elasticity in bending (MPa), L is the support span (mm), b is the width of beam tested (mm) and m is the slope of the initial straight line portion of the load-displacement curve. The strength of nanocomposite was determined at 5% strain on a stress-strain curve due to the fact that specimen does not break but yields. The flexural strength for hierarchical composites is the maximum stress in the outer fibre surface at mid-point of the test samples and was calculated using the following equation [106].

$$\sigma_f = \frac{3PL}{2bd^2} \quad \text{Equation 3-5}$$

where, σ is the stress at the outer fibre at midpoint of support span in MPa.

3.4.3 Compression Test

The compression test of nanocomposites was carried out in accordance to ASTM D 695 [107] (on an Instron 4505 machine equipped with 1 kN load cell, at a crosshead rate of 1 mm/min. Six specimens were tested with the dimensions of 80mm × 12.7mm × 3.2mm. The ends of each specimen were grit blasted and adhesively bonded with fibre glass composites end tabs, with the gauge length 10mm. Two strain gauges (FLA-2-11) were attached using superglue (Cyanoacrylate, RS components, UK) on each face of the bar to measure longitudinal strain as shown in Figure 3-9. Compression modulus was calculated using the strains in the range of 1000 $\mu\epsilon$ to 3000 $\mu\epsilon$ obtained from strain gauge. Whereas, compression strength was the taken at the intersection of the tangent to the initial stress-displacement curve and the tangent to the yielding behaviour of the same curve due to the fact that the specimens did not break but yielded.

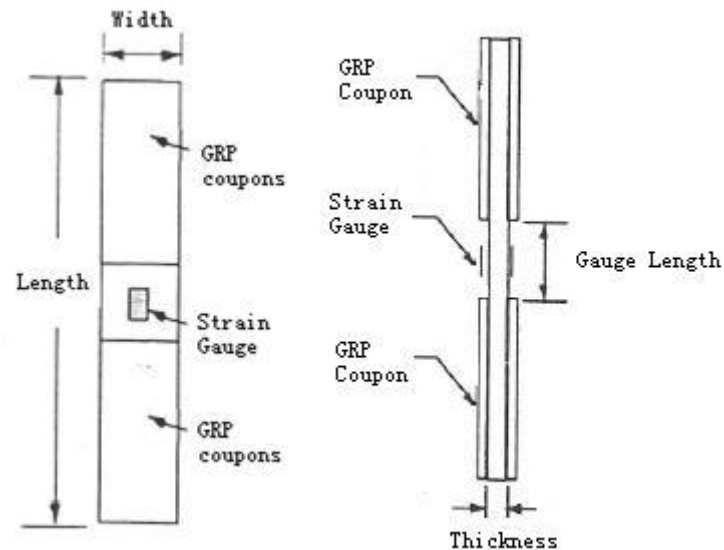


Figure 3-9: Typical compression test specimen

Machined hierarchical composite laminates, 2 mm thick with a short gauge length were tested using ICSTM method (The Imperial College Method for Testing Composite Materials in Compression), which gives the highest mean strengths, together with low scatter. Specimen configuration was similar to the modified ASTM D695 specimen where tabbed specimen is loaded purely on the ends. In the ICSTM, a portion of the load is transmitted by shear via the end tabs, thus lowering the average stresses at the end of the test piece [108] and avoid specimen failure due to buckling. Figure 3-10 shows details of the compression test specimen.

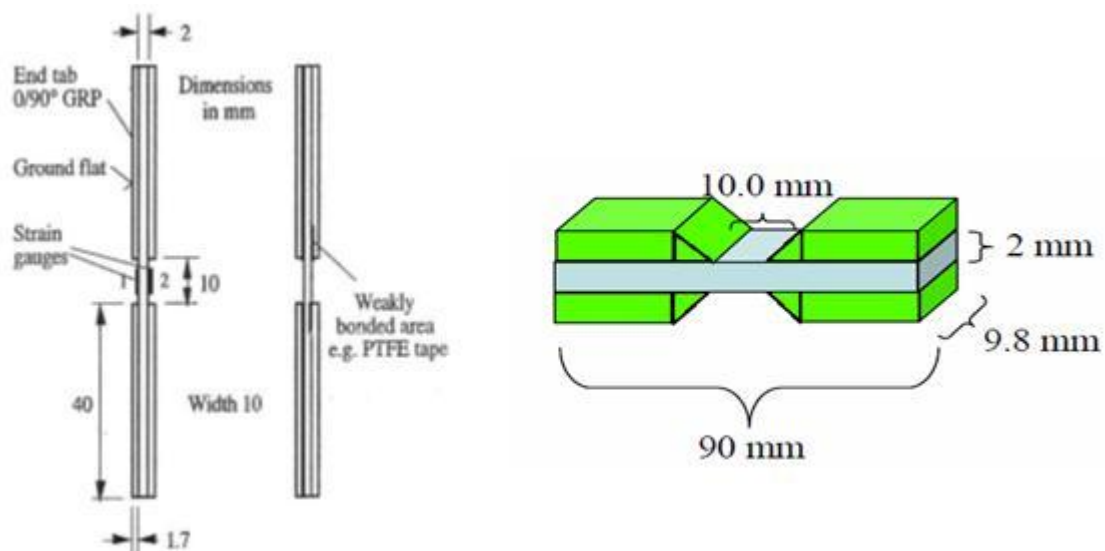


Figure 3-10: Details of a compression test specimen [17, 108]

Specimens were bonded with fibre glass end tabs (CROYLEK, F- glass sheet) either with a 45° chamfer towards the gauge section (Figure 3-10) or opposite to the gauge section (Figure 3-11) to prevent failure at the specimen ends and to diffuse the gripping loads. Surfaces to be bonded with end tabs were abraded, via sand blasting to remove surface contamination, whilst taking care not to damage the outermost fibres. Self-adhesive (masking) tape was applied to the surfaces not needed to be abraded. The dust left behind on the material after sand blasting was removed by flushing under running water (for PEEK composites). Following the drying of the little amount of water absorbed while removing dirt, surfaces were solvent (acetone) wiped and bonded. Reverse chamfered end tabs were consolidated in their place by placing a PTFE insert along with an adhesive filled between both of them as shown in Figure 3-11. PTFE insert was removed after curing the adhesive overnight.

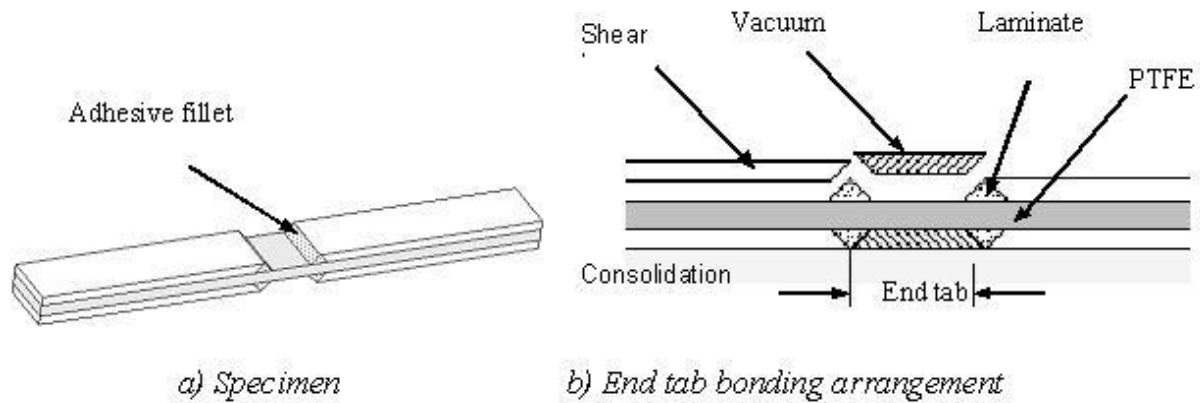


Figure 3-11: Reverse chamfered end tab specimen [109]

Like all mechanical tests, measurements of displacement or strains are also involved in compression testing. Strain gauges (Type: FLA-2-11, Tokyo Sokki Kenkyujo Co., Tokyo, Japan) on both front and back of the specimens were attached using an industrial grade cyanoacrylate glue (Kwik fix superglue, Chemence, Inc., Corby, UK) to record the measurement of displacement or strains, with precise alignment as defined in the standards, because errors of 15% can result from even a 2° misalignment [108]. The Imperial College compression test rig ensured good alignment of specimens as the fixture of blocks, where specimen was located, was placed in a four-pillar die set, which made the mounting and demounting of the specimen very simple. The specimen end was loaded directly and a certain amount of load was applied by shear through the end tabs, depending on the clamping force. The compression modulus was obtained from the slope of the stress- strain curve over a micro-strain range of 1000-3000 plotted from the data obtained.

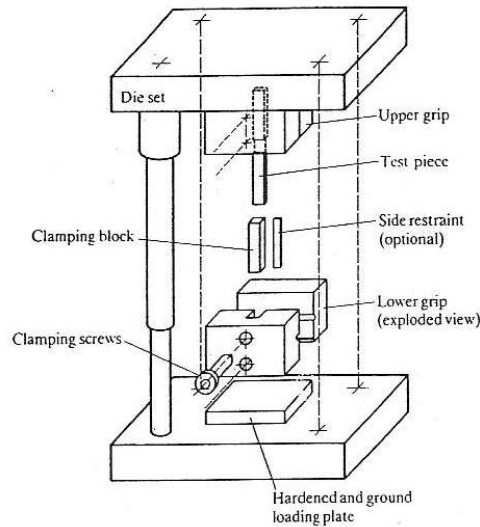


Figure 3-12: Imperial College compression test rig [108]

Six specimens of each formulation with the dimensions of $90\text{mm} \times 10\text{mm} \times 2.6\text{mm}$ were tested on a Zwick machine (1488, Zwick, Ulm, Germany), provided with a load cell of 200 kN, at a rate of 1 mm/min.

3.4.4 Short Beam Shear Test

The short beam shear (SBS) test was conducted for determining the interlaminar shear strength of hierarchical composites. It is a 3-point bending test which induces shear in the test specimen due to a small span-to-thickness ratio. This is a simple method based on classical beam theory and is very similar to flexural testing as shown in the schematic view of short beam shear loading Figure 3-13. SBS is not an ideal shear strength test, as the stresses induced are not pure shear and it is hard to fully remove flexural stresses as indicated in ASTM testing standard D2344 [110]. It allows maximum shear stresses to be introduced throughout the thickness of the specimen while reducing the tensile and compressive flexural stresses to a minimum by reducing the length of the test specimens, i.e. lowering the span to thickness ratio. During conventional SBS testing of unidirectional fibre reinforced thermoplastics, the stress that is induced in the specimen is neither a pure shear stress nor a pure flexural stress but is a mixture of both stresses so the stress calculated is apparent short beam shear strength. In areas away from the loading and support points, the shear stress induced in the specimen theoretically varies parabolically from zero on the specimen upper and lower surfaces, to a maximum value in the specimen mid-plane [110]. Correspondingly, the flexural tensile and compressive stresses are at a maximum on the specimen top and

bottom surface, varying linearly to zero at the mid-plane. Therefore, the undesired stress fields reduce to zero where the anticipated shear stress field is a maximum. However, a region of high shear stress exists along the mid-plane of the test piece and it is this stress which results in the failure of the tested specimens [110].

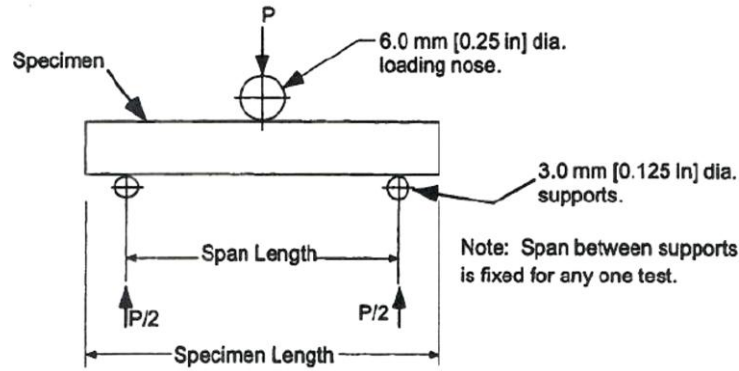


Figure 3-13: Schematic view for the short beam shear loading configuration [110]

The design of the test specimen allows reducing the tensile and compression flexural stresses but maximises through-thickness shear stresses in it. The compression moulded hierarchical composites of around 22mm × 10mm × 2.5mm were prepared and secured in to the test rig used for flexural test with a span to thickness ratio of 4:1 equipped with a 10 kN load cell. The short beam shear tests were carried out according to ASTM D2344/D2344M at a crosshead speed of 1mm/min until the failure occurred. The maximum load was recorded from the load-displacement curve. This data was then used to calculate the ultimate apparent shear stress according to Equation 3.11 [110].

$$F^{SBS} = \frac{0.75P_{max}}{bd} \quad \text{Equation 3-6}$$

where, F^{SBS} is apparent short beam shear strength (N/m²), P_{max} is force at the composite failure load (N), b is specimen width (m), and d is specimen thickness (m). All measurements were repeated on 6 different samples to obtain a mean value.

3.4.5 Measurement of Fracture Toughness/Delamination Resistance

Delamination, splitting or debonding of plies due to the interlaminar stresses in composite laminates is one of the major failure modes in composite laminates [98]. Laminated fibre reinforced composites made of high strength fibres in a relatively weak matrix material, are susceptible to delamination due to interlaminar stresses [98]. The subsequent propagation of

the delamination is, however, not controlled by the through thickness strength but by the interlaminar fracture toughness of the composite material in case of mode I (peel) loading and by interlaminar shear strength in case of mode II (shear) loading. So delamination is considered an important failure mode of composite structures and the resistance to delamination is normally characterised by fracture toughness [98]. Fracture toughness is actually defined as the resistance to delamination. Several approaches have been used by researchers to increase the resistance to delamination in unidirectional carbon fibre reinforced laminated composites. Also test standards have been developed to measure delamination fracture toughness under various modes of loading. Many current composites are made with brittle thermosets and have low interlaminar fracture toughness [111]. As a consequence of this, these laminates are easily damaged. So, recent work in composite science is aiming at producing a composite system with a much tougher matrix phase by employing tougher and more ductile thermoplastic matrices such as reinforced polyamides/imides, poly(ethylene terephthalate), poly(propylene), polyphenylene sulphide and poly ether ether ketone [112].

Interlaminar fracture toughness of laminated composites is normally expressed in terms of the critical strain energy release rate, which is represented by the symbol G_{IC} . The critical strain energy release rate is the energy consumed by the material as the delamination front advances to generate a unit area of fracture surface. Mathematically, G_{IC} is defined as the loss of energy, dU , in the test specimen per unit of specimen width, b , for an infinitesimal increase in delamination length, da , for a delamination growing under a constant displacement.

$$G_c = -\frac{1}{b} \left(\frac{dU}{da} \right) \quad \text{Equation 3-7}$$

where, U is the total elastic energy in the test specimen, ' b ' is the specimen width and ' a ' is the delamination/crack length. The units commonly used for G_{IC} are Joules per square metre. There are three different fracture modes of delamination including opening mode (mode-I), sliding shear mode (mode-II), and scissoring shear mode (mode-III). Interlaminar fracture toughness can be measured in each of the modes or in a combination of these modes. Mode I fracture toughness was measured by double cantilever beam testing developed exclusively for application to unidirectional laminates, with the delamination growth parallel to the direction

of fibres, to determine the influence of carbon nanotube reinforcement on delamination strength.

One of the major problems encountered during DCB Mode I testing is of translaminar failure at the surface of the specimen arms due to bending. The failure of these arms normally initiates on the external surface of the specimen where the maximum compressive stress under flexure occurs. The strength of a CFRP is significantly lower in compression than in tension [113] and the compression strength is particularly low at the surface of the material where the fibres have less support. The low compression strength of the composite material therefore leads to compression failure at the surface, as shown in Figure 3-14, before delamination extension occurs. This type of failure precludes a valid toughness measurement being obtained from the test.

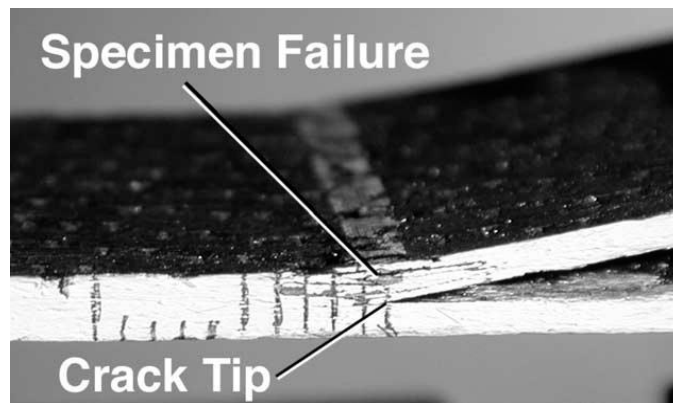


Figure 3-14: Failure of DCB test specimen at crack tip [113]

In mode-I, where tension is applied to the arms of the specimen, bonded doubler plates have been used to inhibit the bending failure in delamination toughness test specimen so that a measurement could be made. Bonded doubler plates were added to thin face sheet sandwich specimens so that the face sheet debond toughness could be determined [113]. The thin face sheets would otherwise have failed in bending in a manner similar to the premature bending failure shown in Figure 3-15. The doublers added thickness to the test specimen, which reduces bending stresses and thus critical bending stress, σ_c , in the composite (doubling the thickness reduces the stress by a factor 4) [113]. In most test configurations, the highest compressive stress occurs in the doubler plate, which can be made of a material that can tolerate higher compressive stresses than the composite. The effect of the doubler plate is shown schematically in Figure 3-15 for a DCB type test.

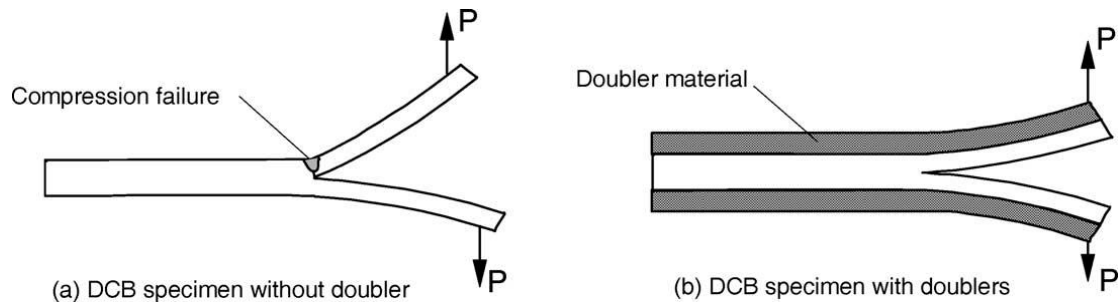


Figure 3-15: Schematic diagram showing the effect of doubler plates on a DCB test specimen [113]

3.4.5.1 Mode-I Double Cantilever Beam (DCB) Test

The DCB specimen was obtained by machining the laminate in to a beam of width 10 mm with the initial delamination extending a distance 60mm from the end of the beam. End blocks with an 8 mm hole which measured 20 mm long by 20 mm high by 10 mm wide were bonded to the specimens with cyanoacrylate glue. The specimen was painted with correction fluid on one side to facilitate crack length measurements. Lines were marked on that edge of the specimen to act as markers. The specimen was then attached to a tensile loading machine via pins through the end blocks and the beam was loaded at a constant displacement rate. Crack lengths were monitored using a travelling microscope provided with a video camera. Then, at each crack length, the load and displacement were recorded. Mode I fracture toughness was measured for six specimens for each formulation in accordance to ASTM D5528-01 at a test speed of 2 mm/min (1 kN load cell, 4502, Instron, Norwood, US). The steady state mode I fracture toughness was calculated by using modified beam method from the data recorded during the test for each composite formulation. The modified beam theory method for calculating G_{IC} is explained below:

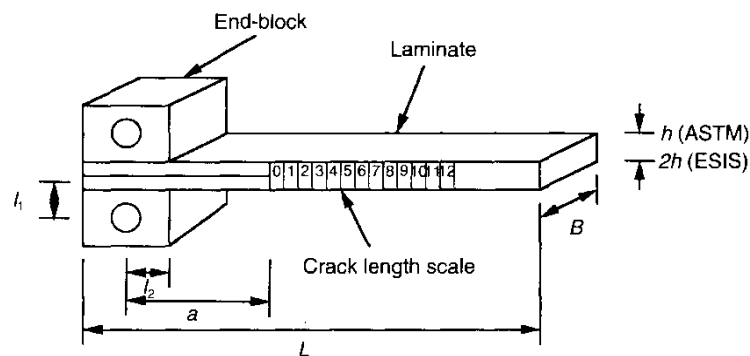


Figure 3-16: Double cantilever beam (DCB) specimen geometry with two end-blocks [98]

Modified Beam Theory (MBT) Method

The DCB test evaluates the critical energy release rate, G_{IC} , for delamination growth as a result of an opening load or displacement as arms are considered to be clamped at the delamination front with crack propagation perpendicular to the loads, which can be calculated based on the simple beam theory as

$$G_{IC} = \frac{3P\delta}{2Ba} \quad \text{Equation 3-8}$$

By inserting the values of load ' P ' and displacement ' δ ' associated with growth at a particular crack length ' a ' for a specimen width ' B ', the critical energy release rate ' G_{IC} ' at the crack length can be determined [98].

However, in practice, the arms are not perfectly built in and rotation may occur at the delamination front. This rotational effect may be accounted for by treating the DCB as if it contained a longer delamination at each length, $a + \Delta$, and so the mode I fracture toughness using this modified beam theory was calculated from equation given below:

$$G_{IC} = \frac{3P\delta}{2B(a + \Delta)} \quad \text{Equation 3-9}$$

The correction factor Δ is defined as the x-axis intercept on the plot of the cube root of the compliance, $C^{1/3}$, as a function of delamination or crack length ' a ', whereas compliance ' C ' is calculated as ratio of the displacement to the applied load i.e. $C = \delta/P$

This approach also allows the determination of flexural elastic modulus

$$E_{1f} = \frac{64(a+\Delta)^3 P}{\delta B h^3} \quad \text{Equation 3-10}$$

Chapter 4 - Nanocomposites

4.1 Introduction

Different formulations of nanocomposites consisting of modified PVDF and modified CNTs (PMMA-g-CNTs) were fabricated using extrusion and injection moulding up to a maximum CNT content of 10 wt%. The incorporation of CNTs into the matrix of conventional composites was expected to improve the matrix modulus, which should subsequently lead to hierarchical composites with much improved compression and other matrix dominated properties. This chapter provides details about the quality of the nanocomposites produced through density and porosity measurements as well as optical and electron microscopy. The effect of CNTs on storage modulus and crystallinity of nanocomposites was analysed via dynamic mechanical analysis and differential scanning calorimetry, respectively. The tensile, flexural and compression properties of the nanocomposite bars (80mm×12.7mm×3.2mm) prepared via extrusion and injection moulding (see Chapter 3) were measured as a function of CNT content and are explained in detail in this Chapter.

4.2 Characterisation of PVDF Nanocomposites

Since the mechanical properties of thermoplastic polymers such as PVDF are dictated by the degree of crystallinity, it is important to anneal the samples to minimise any variations that might suppress the effects of CNTs. It has been reported previously that degree of crystallinity for various annealed specimens of same formulation were within $\pm 2\%$ [14]. The annealing

process not only promotes crystallinity but also returns the materials to their relaxed and unloaded state after removing residual stresses induced during manufacturing process. All injection moulded nanocomposite test specimens were annealed prior to mechanical testing to ensure a high degree of crystallinity and the formation of small crystallites. These changes (if any) in the mechanical properties measured were due to the inclusion of CNTs and not because of a higher degree of crystallinity in the matrix caused by any nucleating effect of CNTs.

4.2.1 Quality of PVDF Nanocomposites

4.2.1.1 Density and Porosity of Nanocomposites

Voids are one of the defects which enhance the fracture process and they usually arise due to a number of factors such as poor packing during injection moulding or poor melt processing (such as higher screw speed, or lesser than required feed resulting in a partially filled barrel) during extrusion. Locally, failure initiates at a void, but usually voids need to be extensive or at a highly critical location to initiate global failure. The presence of voids promotes an early failure, and thus reduces strength. Pycnometry can determine the real density of the composites at room temperature so the instruments named “AccuPyc” and “GeoPyc” (based on Pycnometry) were used to determine the average density and percentage porosity values respectively for the nanocomposites fabricated.

	PVDF/ARCNTs Nanocomposites		MPVDF/ARCNTs Nanocomposites		PVDF/PMMA-g-CNTs Nanocomposites	
CNT Content [%]	ρ (g/cm ³)	P (%)	ρ (g/cm ³)	P (%)	ρ (g/cm ³)	P (%)
0	1.74	1.73	1.74	1.42	1.74	1.72
2.5	1.74	1.92	1.73	2.21	1.74	1.76
5	1.75	2.02	1.74	2.50	1.74	2.01
10	1.71	2.41	1.75	2.43	1.74	2.14

Table 4-1: Density and porosity values for PVDF nanocomposites

The density values for all PVDF nanocomposites were 1.74-1.75 g/cm³ which is almost the same as for PVDF i.e. 1.79g/cm³ as claimed by Arkema (manufacturers). True density for

Graphistrength[®] C100 multiwalled carbon nanotubes provided by Arkema is 2.1g/cm³. Density values suggest good compaction of nanocomposites. The porosity values (as determined from difference of true and envelope) density for the injection moulded nanocomposites lies in the range $1.7 \leq 2.4\%$, (Table 4-1) which indicates no failure has been promoted at lower loads due to the presence of voids. With the increase in CNT loadings, it becomes difficult to control the packing of the nanocomposite melt because of its higher viscosity. In order to include samples with good packing for mechanical analysis, all the samples were weighed and samples with weight lower than 5.25g for a bar (80mm×12.7mm×3.2mm) were discarded. Furthermore, care was taken not to include any mechanical testing results from the samples which showed voids/holes on the fracture surfaces.

4.2.1.2 CNT Distribution in PVDF Nanocomposites

For achieving optimal enhancement in the properties of polymer nanocomposites, one of the major issues which need to be resolved is “to obtain homogeneous dispersion of CNTs in polymer matrices” [114]. Optical and electron microscopy were used to view the CNT dispersion in the fabricated PVDF nanocomposites. The macro dispersion as observed by light microscopy is shown in the Figure 4-1, the majority of the agglomerates are smaller in size than 5µm. There are only very few agglomerates larger than 15µm. Whereas CNTs tend to form entangled agglomerates based on high van der Waals forces and these structures seem to need much lower shear forces to ensure dispersion and distribution in polymer melt.

Cryofracture surfaces of PVDF nanocomposites were prepared by cooling them in liquid nitrogen for ten minutes prior to cutting, which was carried out using a cold knife (cooled in liquid nitrogen for 10 min). Extra care was taken even during handling of the liquid nitrogen colded knife in order to maintain the temperature below T_g of PVDF (-45°C), by using cryogloves. These cryofracture surfaces of nanocomposites were observed to form a well-dispersed, structurally random nanophase within the fluoropolymer matrix as indicated in the scanning electron micrographs (Figure 4-2, Figure 4-3, Figure 4-4). Figure 4-2 represents SEM for PVDF composites with different CNT contents.

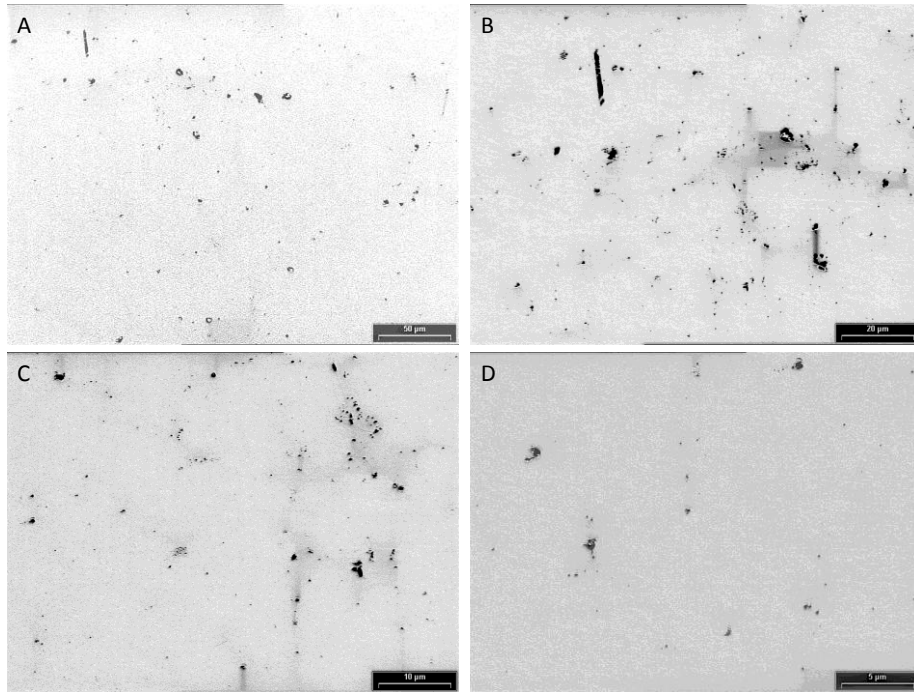


Figure 4-1: Optical micrograph showing CNT distribution in PVDF containing 2.5wt% CNTs at various magnifications A) 50 μ m, B) 20 μ m ,C) 10 μ m, D) 5 μ m

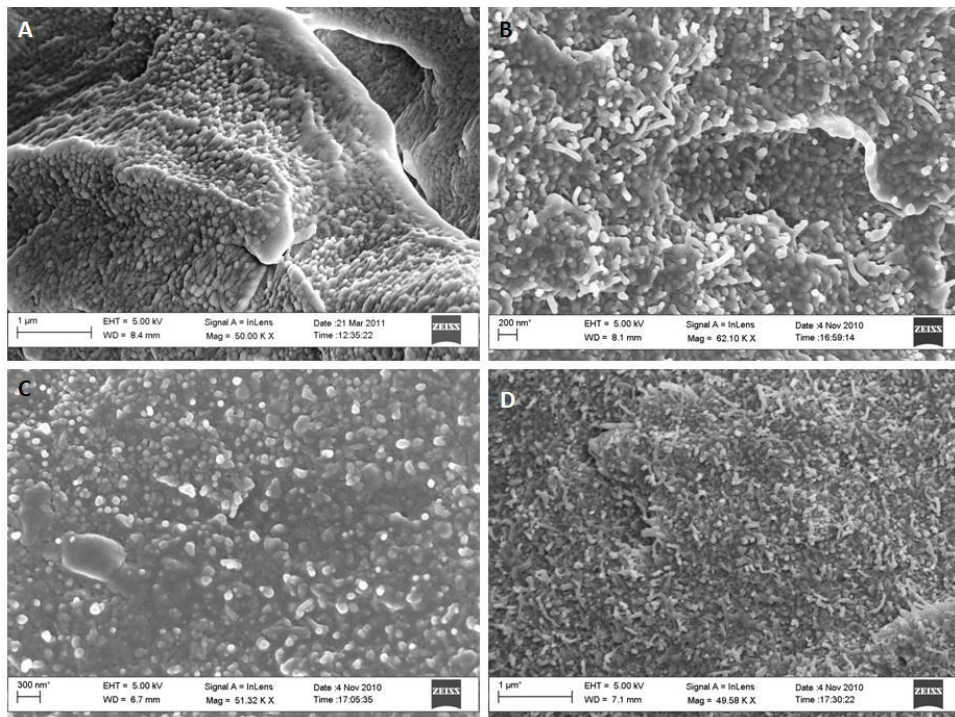


Figure 4-2: SEM micrograph showing CNT distribution in cryofracture surface of PVDF containing A) 0 wt% , B) 2.5 wt% , C) 5 wt% and D) 10 wt% CNTs (at $\sim \times 50k$)

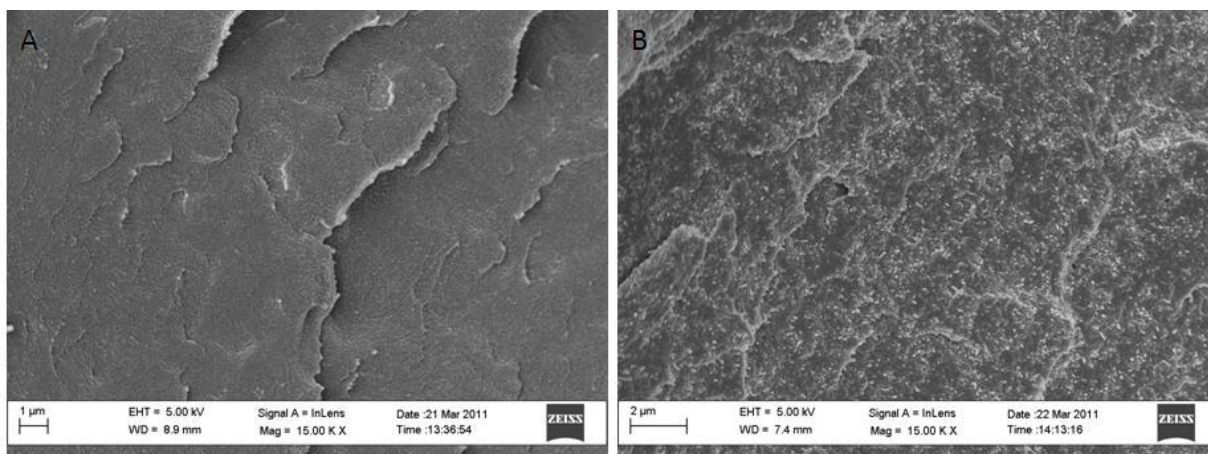


Figure 4-3: SEM micrograph showing CNT distribution in cryofracture surface of MPVDF containing
A) 0 wt% ($\times 15k$), B) 10 wt% CNTs ($\times 15k$)

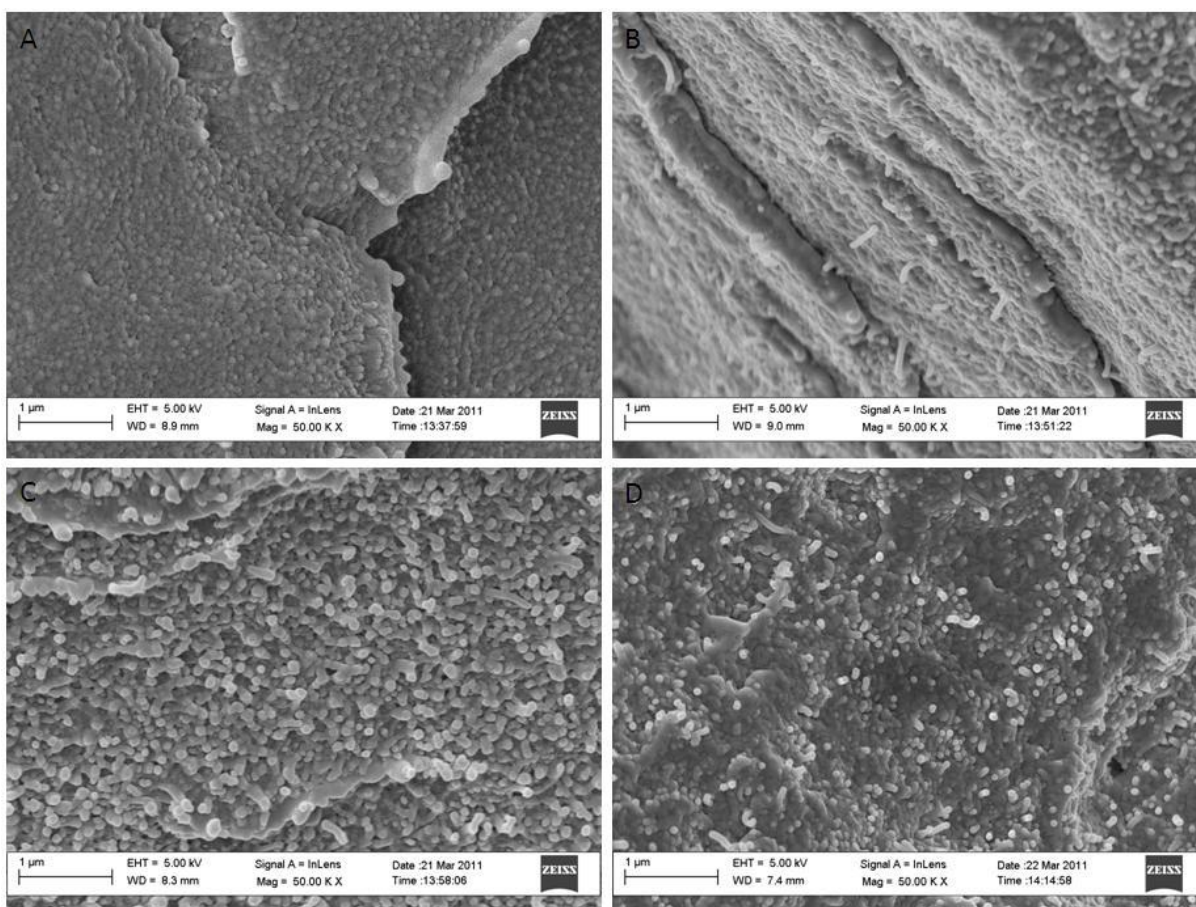


Figure 4-4: SEM micrograph showing CNT distribution in cryofracture surface of MPVDF containing
A) 0 wt% ($\times 50k$), B) 2.5 wt% ($\times 50k$), C) 5 wt% ($\times 50k$) and D) 10 wt% CNTs ($\times 50k$)

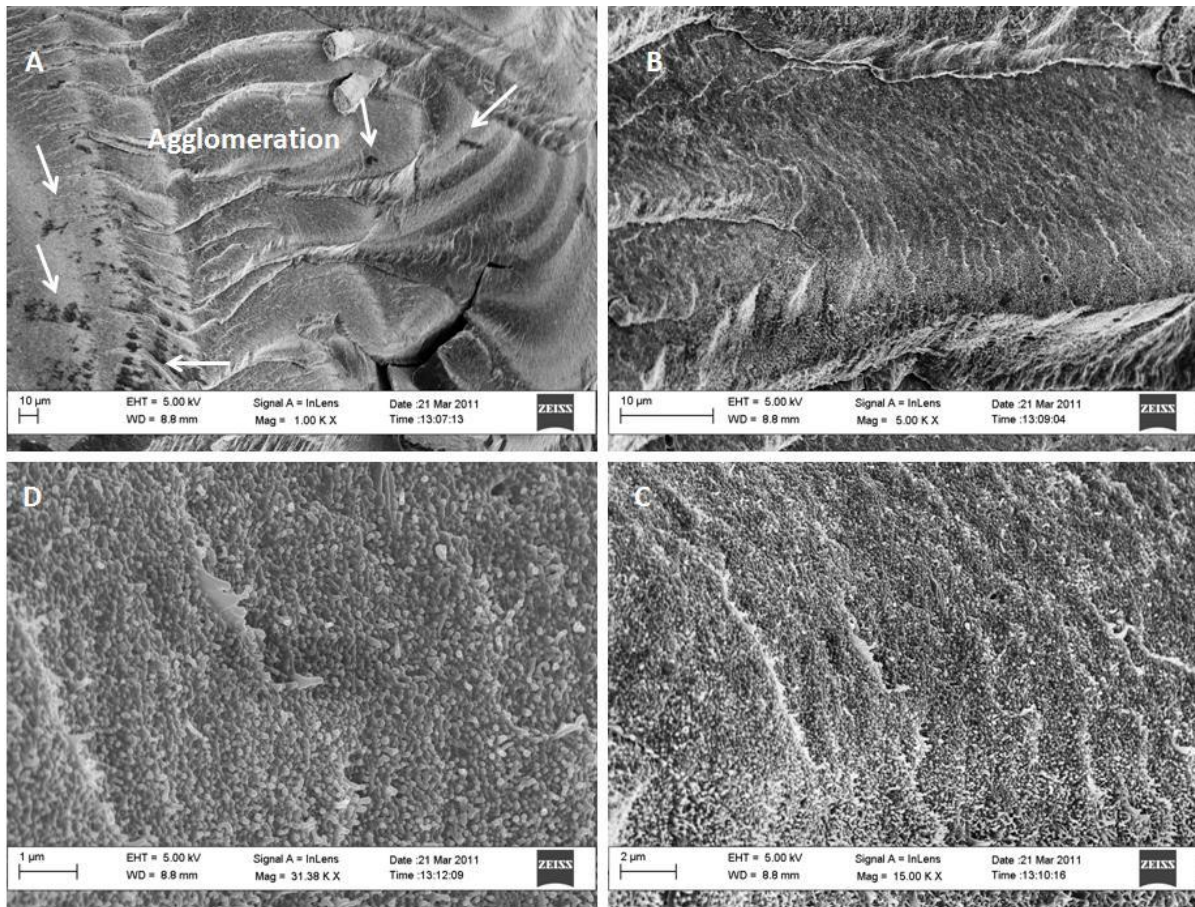


Figure 4-5: Cryofracture surface of PVDF nanocomposites containing 5% PMMA-g-CNTs at various magnifications A) ($\times 1k$) B) ($\times 5k$) C) ($\times 15k$) D) ($\times 31k$)

There is a significant difference in the appearance of a polymer and a nanocomposite containing CNTs as shown in the Figure 4-3. Polymer features are visible in samples containing 0 wt% CNTs (Figure 4-4-A, Figure 4-5-A), whereas CNTs are protruding out of the polymer particles in the nanocomposites (Figure 4-4-B, C, D, Figure 4-5-C, D). The entangled CNTs on the surface of PVDF can easily be seen in cryofracture surfaces of PVDF nanocomposite specimens as illustrated in Figure 4-5. The lower magnification SEM images A) shows the regions of local agglomeration (dark regions) as indicated by the arrows. Most likely, these small structures are never disentangled from their as produced state. However, higher magnifications (Figure 4-5 C, D) represent the protruding CNTs along with local areas of entangled CNTs or agglomerates within the nanocomposite.

4.2.2 Crystallinity of PVDF Nanocomposites

It has been reported that CNTs can affect crystallinity of polymers and specifically PVDF [115, 116] so a detailed DSC analysis was performed on heat treated samples in order to assess possible changes in the crystalline structures and overall degree of crystallinity of matrix. Approximately, 10 mg of each nanocomposite specimen (cut from injection moulded bars) was subjected to a heat flow at a temperature varying rate of 10°C/min, under nitrogen environment. The calorimetry experiments consisted of two steps i.e. a first heating step started at -100°C to 220°C and a second cooling step from 220°C to -100°C to allow full crystallization of samples in order to determine the influence of CNTs on crystallization temperature (T_C). The overall degree of crystallinity was measured by fitting each DSC curve with a baseline using the analytical software (TA Q Series Advantage) from the DSC machine and fitting all peaks. The peak enthalpies for nanocomposites were normalised to the actual weight fraction of polymer to determine the degree of crystallization.

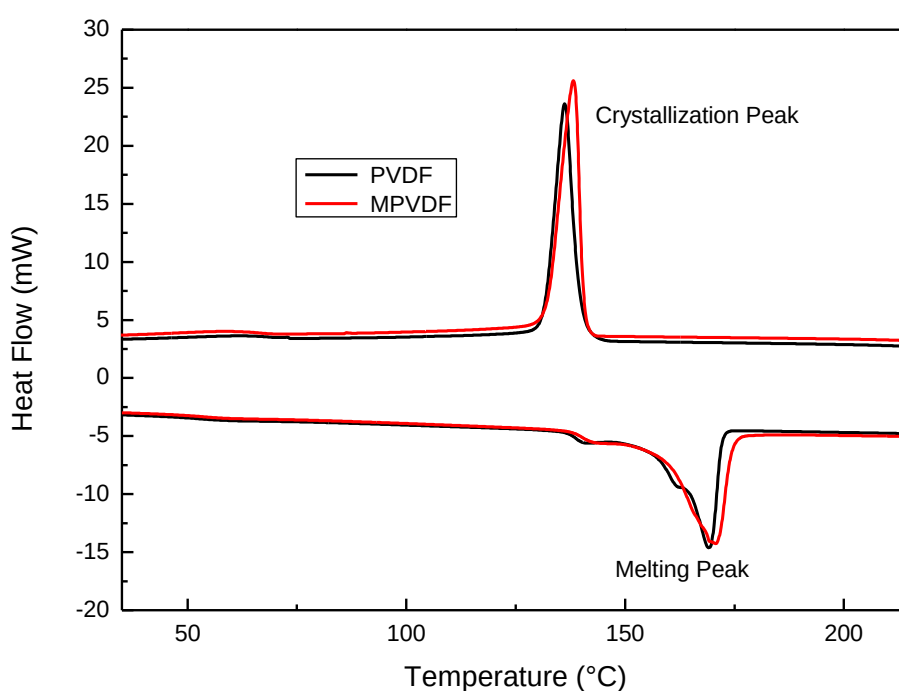


Figure 4-6: DSC thermogram of PVDF and modified PVDF showing melting and crystallisation peaks subjected to a temperature varying rate of 10°C/min

Thermograms of PVDF and MPVDF (Figure 4-6) show that there is negligible difference in melting and crystallisation temperature of the two polymer matrices. They exhibit the same degree of crystallinity as determined through the integration of the endothermic heat of flow peak for the samples which were normalised with respect to the samples mass (see Chapter 3).

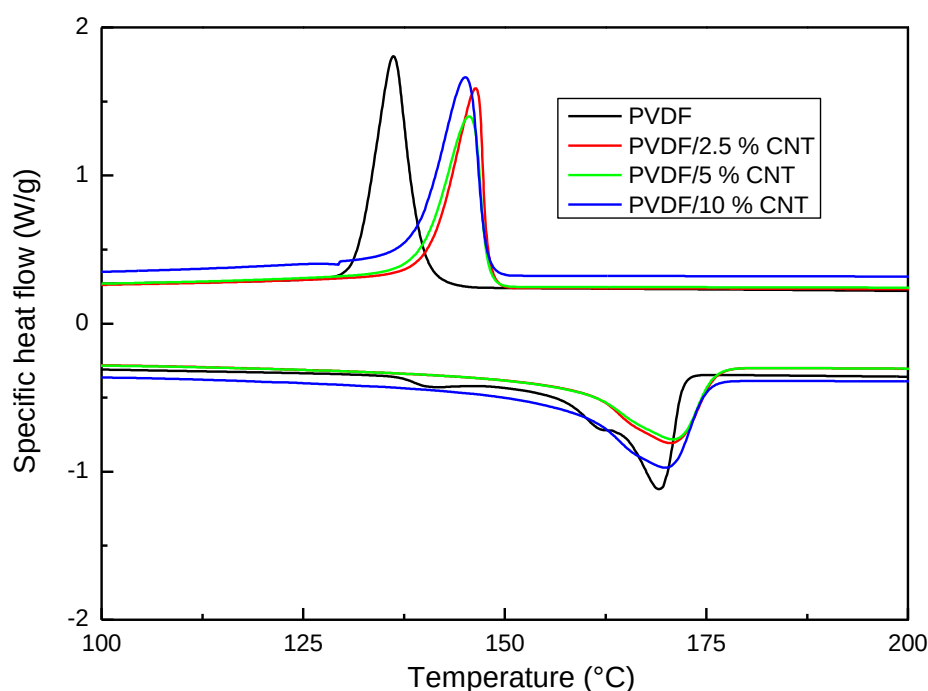


Figure 4-7: DSC thermograms for PVDF nanocomposites containing up to 10 wt% CNTs

PVDF had a lower and narrower melting peak (Figure 4-7) whereas PVDF nanocomposites with CNT loading of 2.5, 5 and 10 wt% show similar broadness in their melting peak with a shoulder starting at 159°C. This breadth of the melting peak for PVDF nanocomposites can be related to the presence of different spherulite sizes having melting point somewhere in range of $170^{\circ}\text{C} \pm 1$. The shallow peak at 160°C indicated some interaction at the molecular level took place. The cooling cycle provided information about the influence of carbon nanotubes on the crystallisation temperature of PVDF. On cooling, the crystallization temperature (T_C) for PVDF nanocomposites was higher than pure PVDF ($T_{C,\text{PVDF}} = 136^{\circ}\text{C} \pm 1$, $T_{C,\text{PVDF NC}} = 144^{\circ}\text{C}$) suggesting that the carbon nanotubes act as the nucleating agents

inducing crystallization. Also higher T_C for PVDF nanocomposites suggests an earlier spherulite formation/nucleation than pure PVDF.

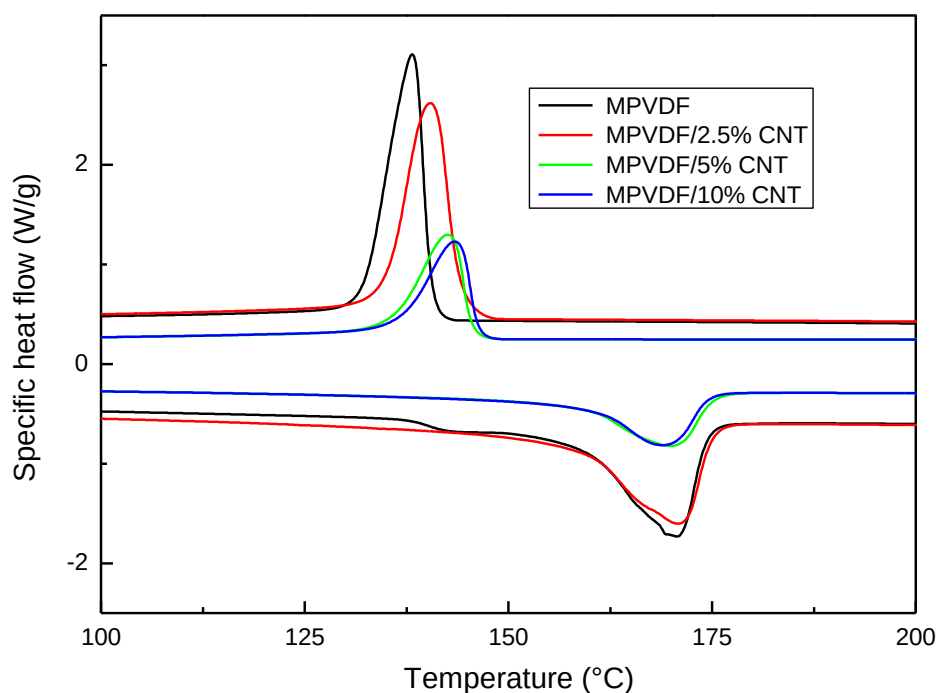


Figure 4-8: DSC thermograms for MPVDF nanocomposites containing up to 10 wt% CNTs

Figure 4-8 shows the thermal behaviour of MPVDF based nanocomposites. Similar nucleation effects were observed on cooling in pure polymer systems i.e. PVDF (Figure 4-7) and MPVDF (Figure 4-8). However, it was observed that the crystallisation temperatures for all the nanocomposite samples were slightly higher than that of the corresponding polymer samples regardless of type of CNTs employed in fabricating them (e.g. ARCNTs or PMMA-g-CNTs)(see Figure 4-7, Figure 4-8, Figure 4-9). It can be assumed that some crystallisation occurred during processing to a small effect due to nucleating effect of CNTs on the polymer matrix in all nanocomposites. The high and narrow melting peak for PVDF and MPVDF indicates the presence of crystallised material with a narrow spherulite size distribution. However, the lower and broader melting peak for nanocomposites can be attributed to the presence of different spherulite sizes.

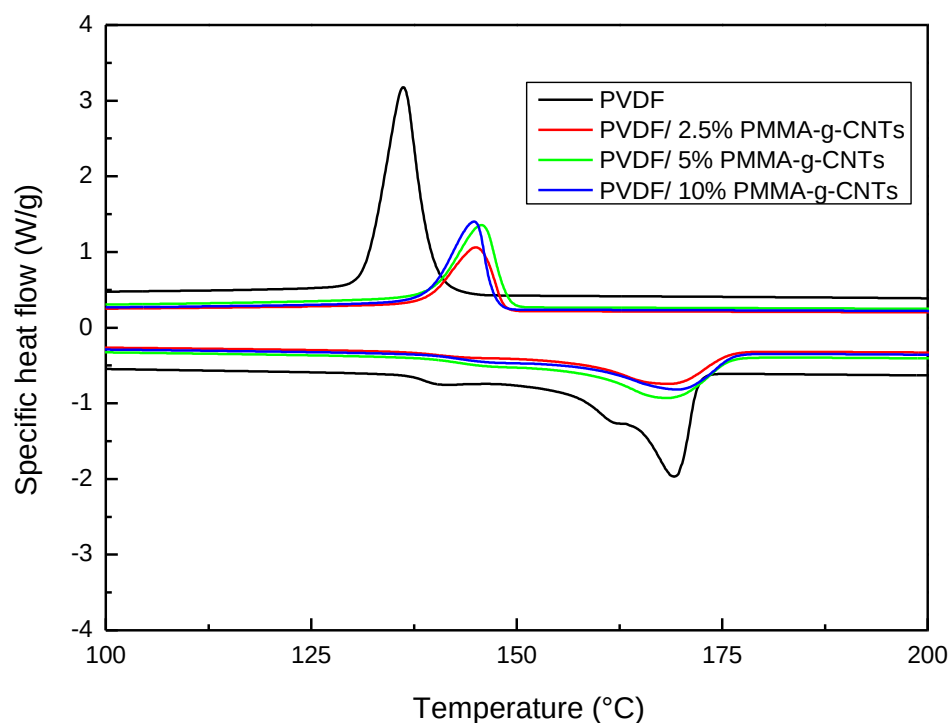


Figure 4-9: DSC thermograms for PVDF nanocomposites containing up to 10 wt% PMMA-g-CNTs

The presence of lower and broader peak in nanocomposites as compared to pure polymers can be either attributed to formation of different spherulite sizes (as explained earlier) or transformation of crystalline phase from α to β (as discussed in XRD results later). This led to the conclusion; CNTs nucleate crystallinity by giving rise to an early formation of spherulites in nanocomposites with no effect on melting temperature but a rise in crystallisation temperature of nanocomposites. However, this crystallinity is not significant enough to make considerable difference in mechanical properties. So it can be concluded from the first heating cycle, the crystallinity for the polymer and the corresponding nanocomposite samples were within 5% of one another as determined from the software “TA universal analysis” (based on integration of the endothermic heat of flow peak for the samples). The similarity in crystallinity between the polymers and nanocomposites supports the conclusion that matrix reinforcement was the main factor for the improvement of mechanical performance observed in nanocomposites.

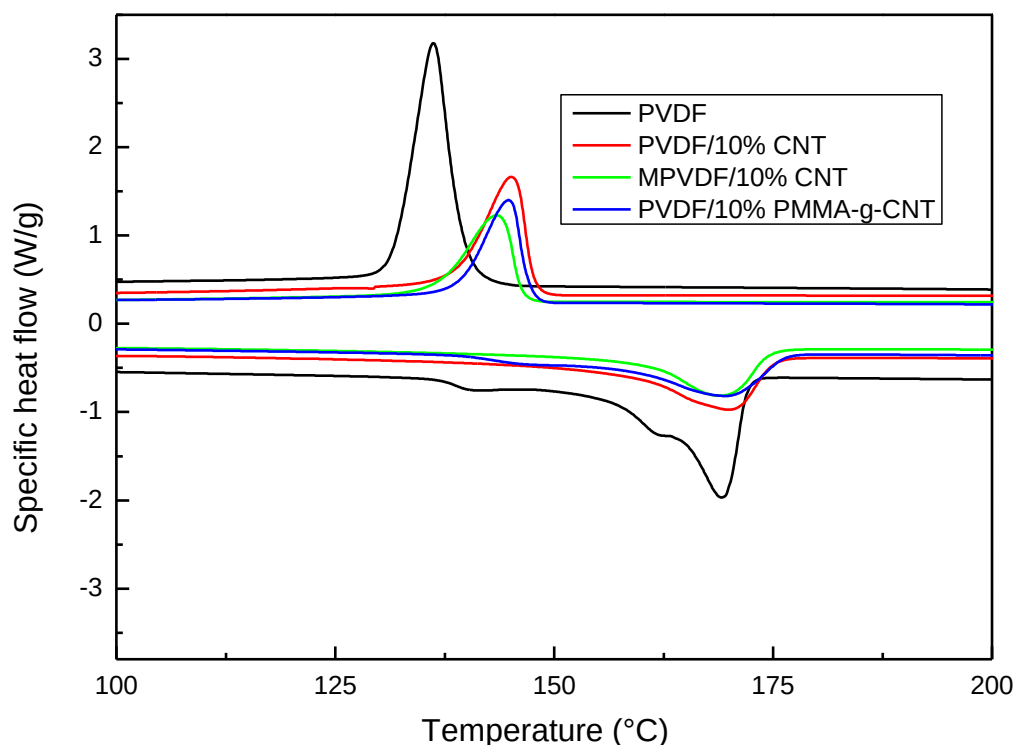


Figure 4-10: DSC thermograms showing comparison of PVDF nanocomposites containing 0 wt% and 10 wt% CNTs along with modified PVDF and modified CNTs

The second heating cycle was used to determine the maximum crystallinity for the polymer and nanocomposites after cooling the samples from melts at a slow and controlled rate. The second heating cycle provided an insight as to whether the sample production procedure allowed for the full crystallisation of the matrix to occur. The crystallinity measured from the first heating was only 4-5% higher for all the formulations than the second heating (Table 4-2). This implied the effect of annealing treatment almost fully erased the thermo-mechanical history of injection moulded samples and that all the samples prepared via injection moulding were fully crystallized before conducting any of the mechanical tests. The cooling cycle provided information about the influence of carbon nanotubes on the crystallisation temperature of PVDF/modified PVDF. The annealing process used throughout this study promoted spherulite growth within nanocomposites produced from the injection moulding process.

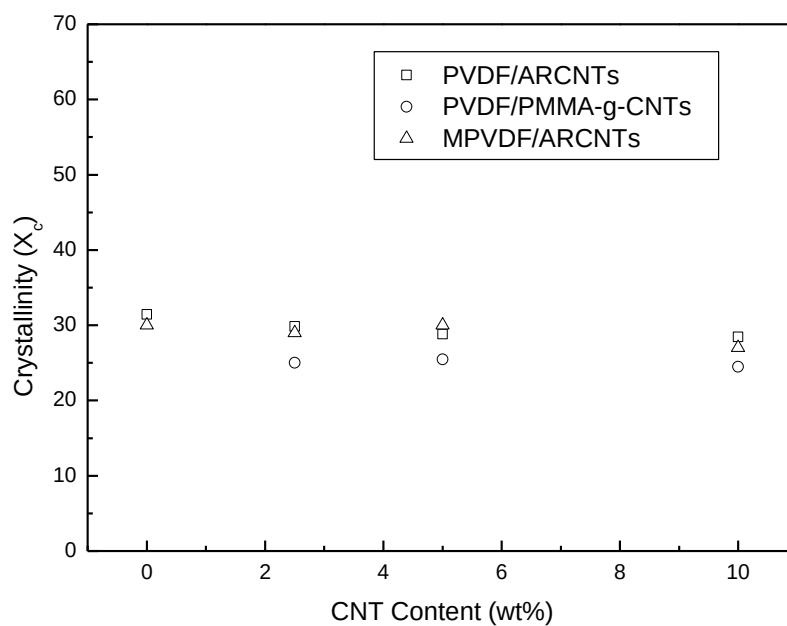


Figure 4-11: Degree of crystallinity determined via XRD on nanocomposite films containing up to 10 wt% CNTs

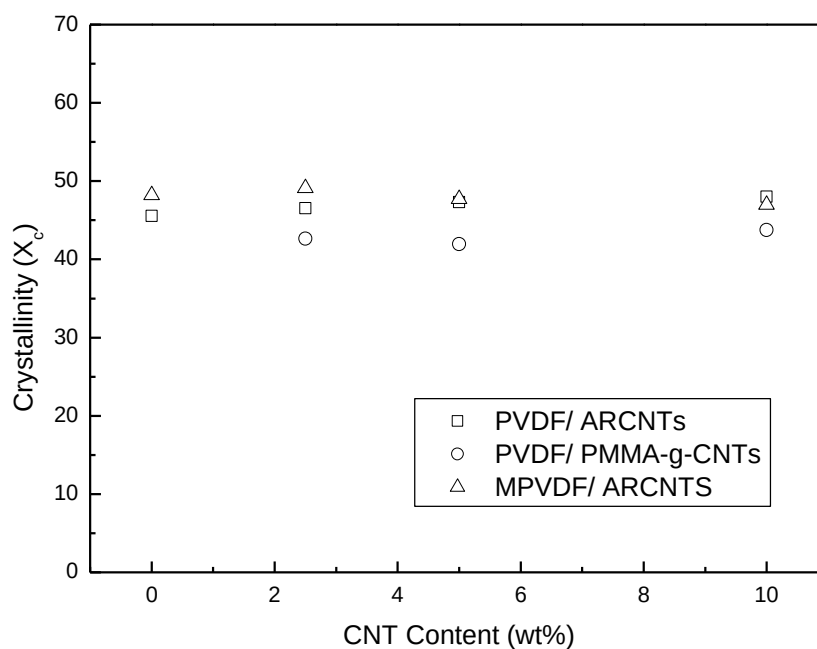


Figure 4-12: Degree of crystallinity of nanocomposites containing up to 10 wt% CNTs determined via DSC (1st heating cycle)

	PVDF/ARCNTs Nanocomposites		MPVDF/ARCNTs Nanocomposites		PVDF/PMMA-g-CNTs Nanocomposites	
CNT Content [%]	1st heating crystallinity (%)	2nd heating crystallinity (%)	1st heating crystallinity (%)	2nd heating crystallinity (%)	1st heating crystallinity (%)	2nd heating crystallinity (%)
0	45	43	48	45	45	43
2.5	46	45	49	43	42	45
5	47	44	47	44	41	42
10	48	46	47	45	43	41

Table 4-2: Crystallinity of PVDF nanocomposites containing different CNT weight fractions

X-Ray diffraction analysis was also conducted to get an insight of size and shape of crystals within nanocomposites and their crystallinity. A nanocomposite film was prepared by moulding extruded nanocomposite pellets following the procedure for preparing laminates of hierarchical composites including annealing (see Chapter 3 for processing details). The data was subsequently converted using PowDLL converter and analysed by calculating the area under the peak of the curves via Origin Software. The degree of crystallinity appear to be steady at $30\% \pm 2$ and $47\% \pm 2$ with increasing CNT weight fraction for PVDF and MPVDF nanocomposites as determined via XRD (Figure 4-11) and DSC (Figure 4-12) respectively. However, degree of crystallinity of PMMA-g-CNT based PVDF nanocomposites was lower as compared to PVDF/MPVDF nanocomposites. The lower degree of crystallinity for PMMA-g-CNT based PVDF nanocomposites could be because presence of amorphous PMMA has detrimental impact on the crystallization rates of α and β phases of PVDF [58]. PMMA has shown to vanish nucleating effect of sepiolite (a nucleating agent for PVDF) on PVDF crystallization [115]. The difference in the crystallinity values obtained from DSC and XRD could be due to the difference in the methods used to determine crystallinity. Moreover, DSC was conducted on the injection moulded nanocomposite specimens; whereas XRD was conducted on nanocomposite films (see Chapter 3 for details). The results obtained from X-ray diffraction of nanocomposites were probably compromised because of CNT agglomerates (if any) which could have affected the requirement of roughly same spacing between crystals and highly regular arrangements of scattering centres [101]. Given that degree of crystallinity variation was minimal, therefore, no conclusions should be drawn based on the weight fraction loading of CNTs and the crystallinity of PVDF.

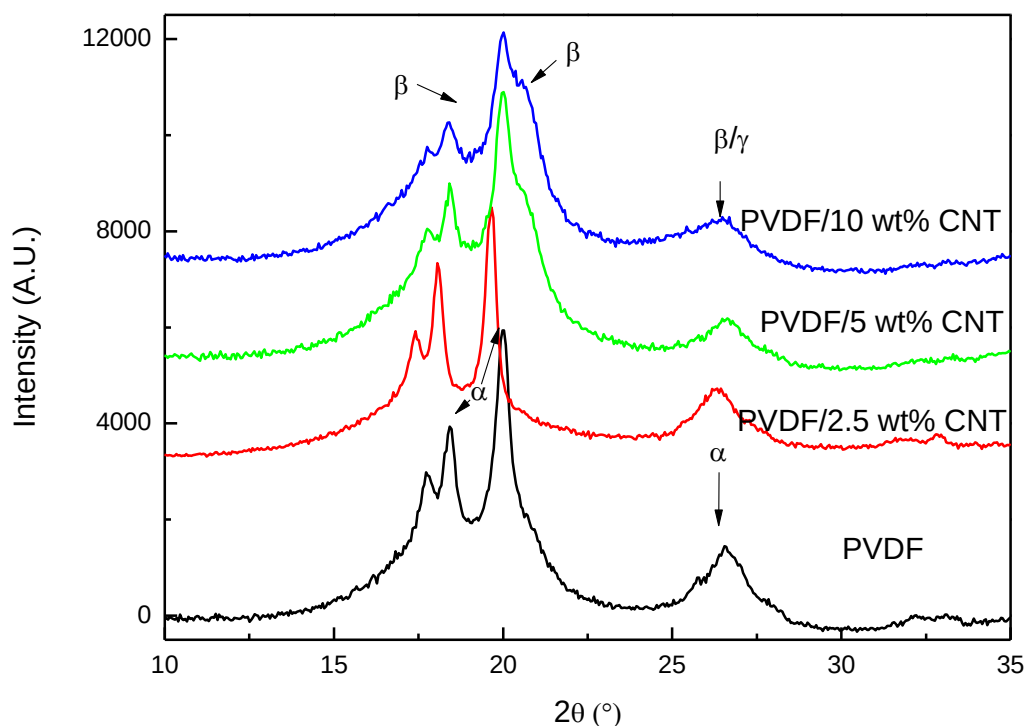


Figure 4-13: X-Ray diffractograms of PVDF nanocomposites containing A) 0 wt%, B) 2.5 wt%, C) 5 wt% and D) 10 wt% CNTs

Poly vinylidene fluoride is a semicrystalline thermoplastic polymer with five possible polymorphs [117]. XRD experiments were carried out in order to obtain information on the crystal structure. The spectra are arbitrarily shifted for clarity. X-Ray profiles of PVDF films (Figure 4-13) are in concordance with those of α -PVDF [118]. α -PVDF is the most energetically stable state (a planar zigzag structure and a monoclinic system) [119]. Two most intense peaks at 2θ values of 18° and 20° refer to (110) and (200) reflections in orthorhombic α -phase crystal (Figure 4-13). 2θ values of 26.6° correspond to (021) reflections in α -PVDF [58]. In order to improve performance and reduce costs, PVDF is often blended with miscible acrylic polymers. But the thermal history of PVDF/PMMA blends shows compatibility characteristics only if PVDF's crystalline phase is present. [119, 120] In contrast, compared with XRD scans of α -PVDF showing two distinctive peaks near 17° , two dull peaks are nearly attached with each other in case of 10wt% PMMA-g-CNTs loaded PVDF near 17° corresponding to (110) reflection in orthorhombic β crystal (Figure 4-15) [120]. Also the generation of new peak in 10% PMMA-g-CNT loaded PVDF at 2θ value of 20.6° can be

assigned to (200) reflection of β phase. Among these polymorphs, more attention has been paid to the β -phase due to its piezoelectric, ferroelectric, and pyroelectric properties. However, its crystal structure (TGTG' structure and a pseudo-orthorhombic system) is difficult to obtain. A variety of experimental techniques have been developed to induce β -phase formation in PVDF e.g crystallisation of the melt at pressure higher than 350 MPa by Matsushige and Takemura [118] which led to the formation of the β form of PVDF. However, the addition of MWNT (5 wt% in PVDF) have proved to promote the crystallization of PVDF in the β -polymorph [117]. Also, β and γ phase are similar to each other in 2θ values of X-ray reflections, the work of the identification of the crystal phase between β and γ is still in dispute.

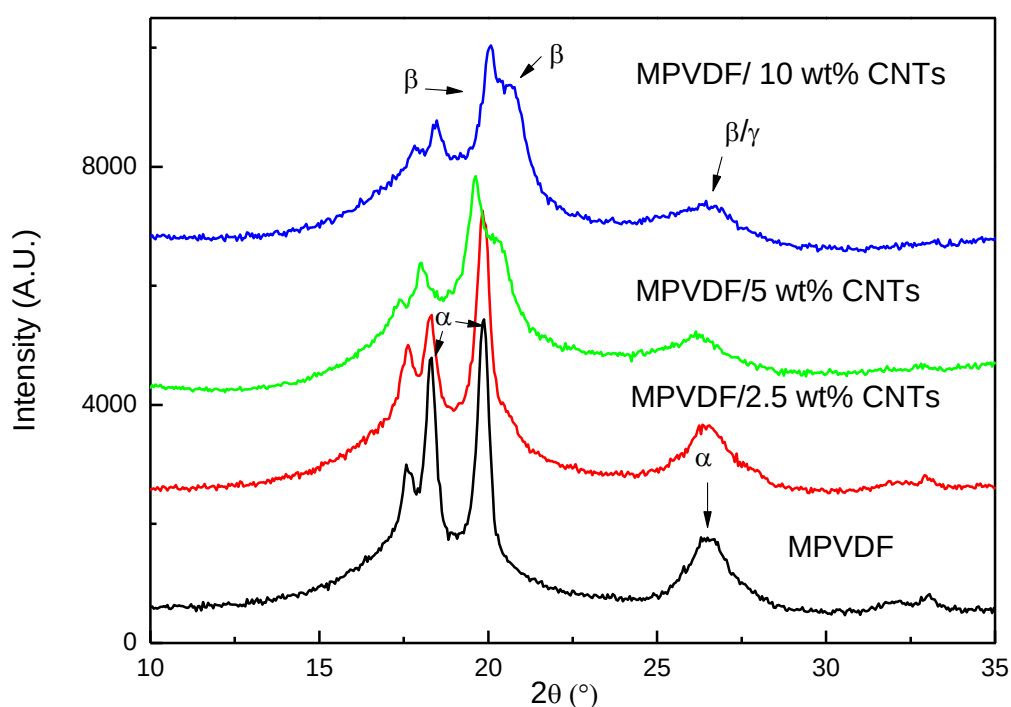


Figure 4-14: X-Ray diffractograms of MPVDF nanocomposites containing A) 0 wt%, B) 2.5 wt%, C) 5 wt% and D) 10 wt% CNTs

It was observed that addition of CNTs have suppressed and broadened the two sharp peaks (representative of α -polymorph) near 2θ value of 17° , which is indicative of the presence of either smaller crystallites or β -polymorphs in PVDF nanocomposites. Also, 10 wt% CNTs-PVDF nanocomposite samples exhibit large reductions in the areas under the peaks associated

with the α -polymorph whereas augmentation in the areas under the peak associated with β -polymorph that occur near 17° and 27° (Figure 4-16). So it can be concluded that presence of CNTs induced the β crystal formation in PVDF nanocomposites prepared via melt processing or solution processing (hierarchical composites) but this transformation of α -PVDF into β -PVDF is more prevalent in PMMA-g-CNT based PVDF nanocomposites as compared to PVDF nanocomposites containing as received CNTs (see Figure 4-13 and Figure 4-15). X-Ray profiles of MPVDF nanocomposites also showed the transitions in structure (Figure 4-14) but less prevalent than those observed in PMMA-g-CNT based nanocomposites. The difference obtained in crystal structure is because of the fact that higher polymer coagulation results in relatively fast rate of crystallization which should result in lower degree of crystallinity and vice versa [117]. On the other hand, the addition of a miscible polymer decreases the rate of crystallisation of a semi crystalline polymer as in the case of PVDF/PMMA blends [58]. It can be concluded that presence of PMMA in the CNTs suppresses the crystallization rate of PVDF and promotes crystallization in the β -phase resulting in the more desirable structure (close to β -polymorph) in PVDF. This also suggests that these nanocomposites should exhibit useful piezoelectric and pyroelectric properties.

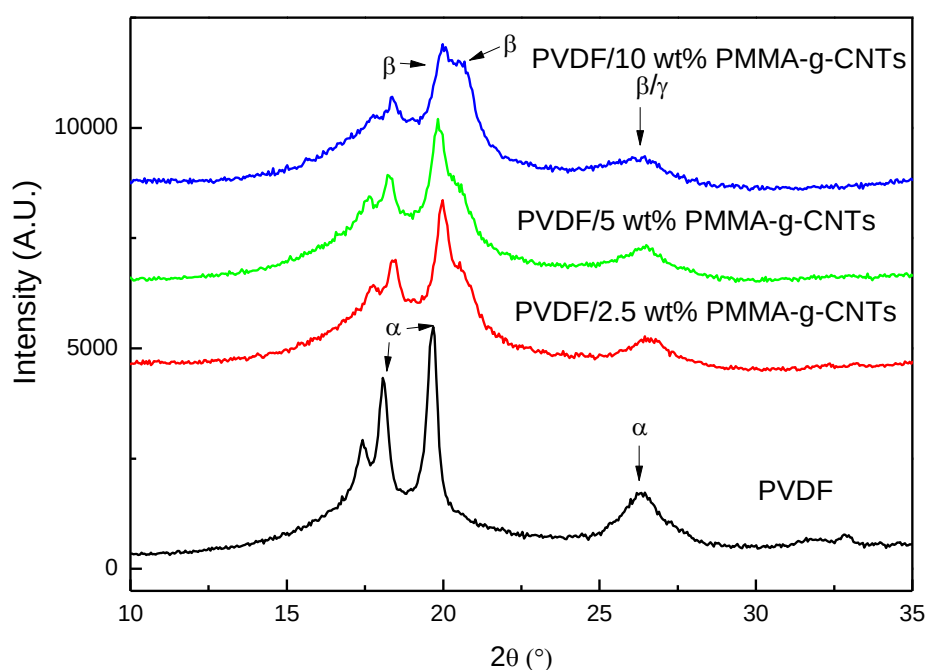


Figure 4-15: X-Ray diffractograms of PVDF nanocomposites containing up to 10 wt% PMMA-g-CNTs

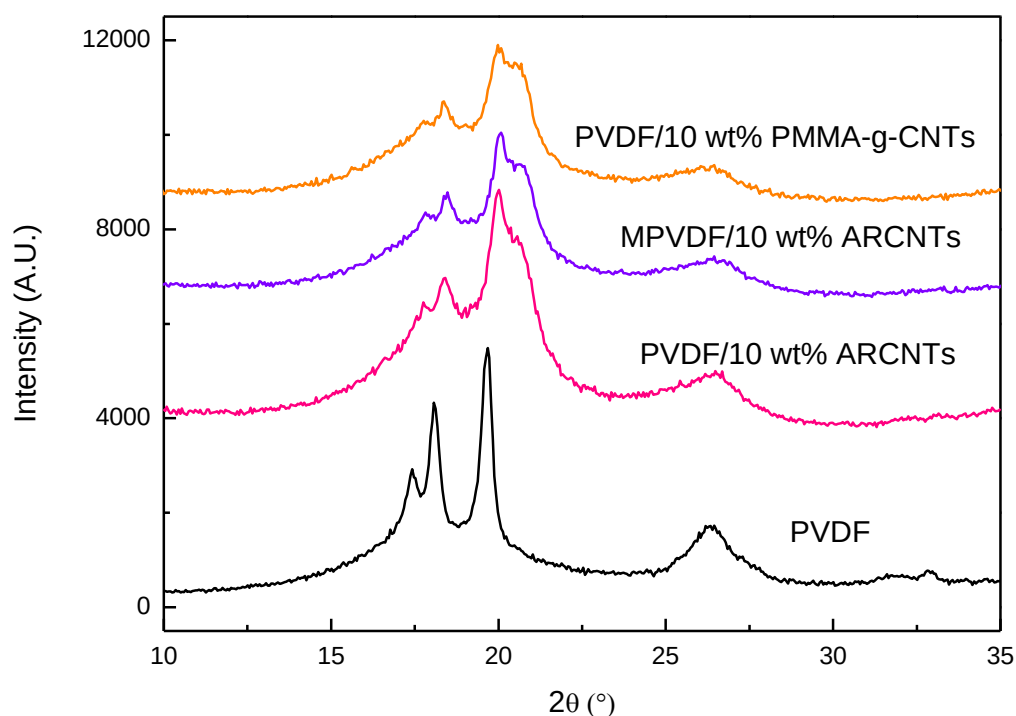


Figure 4-16: X-Ray diffractograms of PVDF nanocomposites containing A) 0 wt% ARCNTs B) 10 wt% ARCNTs C) 25 wt% MPVDF and 10wt% ARCNTs D) 10 wt% PMMA-g-CNTs

For polymer nanocomposites, the rate of crystallization of polymer increases due to the nucleation effect of CNTs. However, the effect of CNTs on the degree of crystallinity of the polymer is inconsistent. Both increases [115, 121], and decreases [58, 122] as well as no differences [123] in degree of crystallinity of polymers due to inclusion of CNTs have been reported. Moreover, annealing process has proved to change PVDF crystal structure (β -phase) in PVDF/ PMMA blends by slowing down the crystallization speed which effects its crystal structure [119]. The degree of crystallinity for various PVDF nanocomposite formulations calculated from DSC and XRD were in good agreement with each other. Although CNTs serve as nucleating agents for PVDF, they do not induce the formation of more crystallites [58]. However, the change in crystalline phase (α to β) has occurred and so far no literature has been reported regarding the influence of changed crystalline phase on mechanical performance of nanocomposites.

4.2.3 Mechanical Characterisation of PVDF Nanocomposites

4.2.3.1 Dynamic Mechanical Analysis

DMTA was chosen as the method for evaluating the mechanical performance of the nanocomposites because it has been shown to be sensitive to changes in interfacial adhesion of conventional filler systems [124]. It is a technique which supplies information about major transitions along with secondary and tertiary transitions. Moreover, it is often used as an evaluation tool for carbon nanotube based composites [49, 125]. The $\tan \delta$ and storage modulus “E'” from the DMTA analysis of the various PVDF nanocomposites samples are presented.

Dynamic mechanical measurements of the temperature dependence of the elastic moduli E' and loss moduli E'' were performed on PVDF nanocomposites with dynamic mechanical analyser in the rectangular bending mode. The transitions in E' are accompanied by peaks in $\tan \delta$, with α transition being the largest transition occurring at higher temperatures. α transition arises from the micro-Brownian motion of the main chain in the amorphous region and thus typically associated with glass transition temperature [126]. The location of the transitions, particularly the α transition, is very sensitive to frequency which was adjusted at 10 Hz in all tests to achieve consistent and reproducible results. The α transitions in the mechanical response were identified by the presence of peak in $\tan \delta$. The β transition is related to the hindered rotation of the side chain and a co-ordinated twisting motion of the main chain [127]. There were no β transitions observed in any of the PVDF nanocomposites because of the absence of side chains in PVDF [126].

Dynamic mechanical analysis experiments were performed on PVDF nanocomposites containing 0, 2.5, 5 and 10 wt% CNTs at a frequency of 10Hz and the results for E' and $\tan \delta$ are plotted as a function of temperature as shown in Figure 4-17.

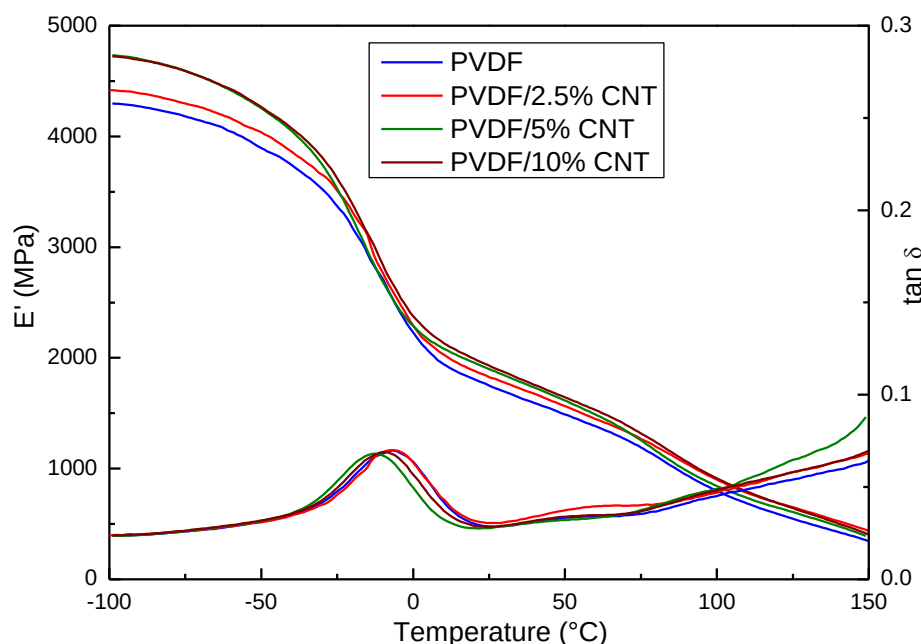


Figure 4-17: Temperature dependence of E' and $\tan \delta$ for PVDF nanocomposites at a frequency of 10Hz as determined by DMTA

It is apparent that higher loading of CNTs yield higher stiffness at all temperatures. This effect is greater below T_g , where the CNTs reinforce the glassy matrix. Although the curves are qualitatively similar, there are two quantitative differences. First, E' is appreciably larger for PVDF containing 10 wt% CNTs at the lowest temperatures. Second, at higher temperatures, in the vicinity of α transitions, the E' values for the samples containing different CNT content are reduced as compared to E' values at lower temperature and this indicates that PVDF nanocomposites containing different CNT content having slight shift in α transitions resulting in slightly different T_g 's which means that the amorphous regions with in the polymer bulk dominate mechanical T_g response in this temperature range. The convergence of E' at a higher temperature indicates that α transition, which is associated with translational dynamics of chains, dominates the mechanical response in this temperature range. The high stiffness of CNTs was expected to generate a relatively greater effect on a PVDF above T_g (when matrix is soft), but it appears that the flexibility of the matrix above T_g has reduced the reinforcing efficiency. This suggests that at higher temperatures, stress transfer at the CNT/PVDF interface is being compromised because of poor adhesion (reduced T_g), probably caused by less effective mechanical interlocking of PVDF with curly

nanotubes. The analysis of the $\tan \delta$ curves for PVDF nanocomposites did exhibit a small shift in α relaxation i.e. peak position of the nanocomposites, as compared to pure PVDF. At room temperature, the addition of 2.5 wt%, 5 wt%, and 10 wt% CNTs to pure PVDF led to 5%, 7% and 9 % increase respectively in the storage modulus. Wang [58] has shown previously a 10% increase in storage modulus of PVDF nanocomposites containing 1.6 wt% CNTs which is in close agreement with the 15% increase in storage modulus obtained between -100°C to 25°C .

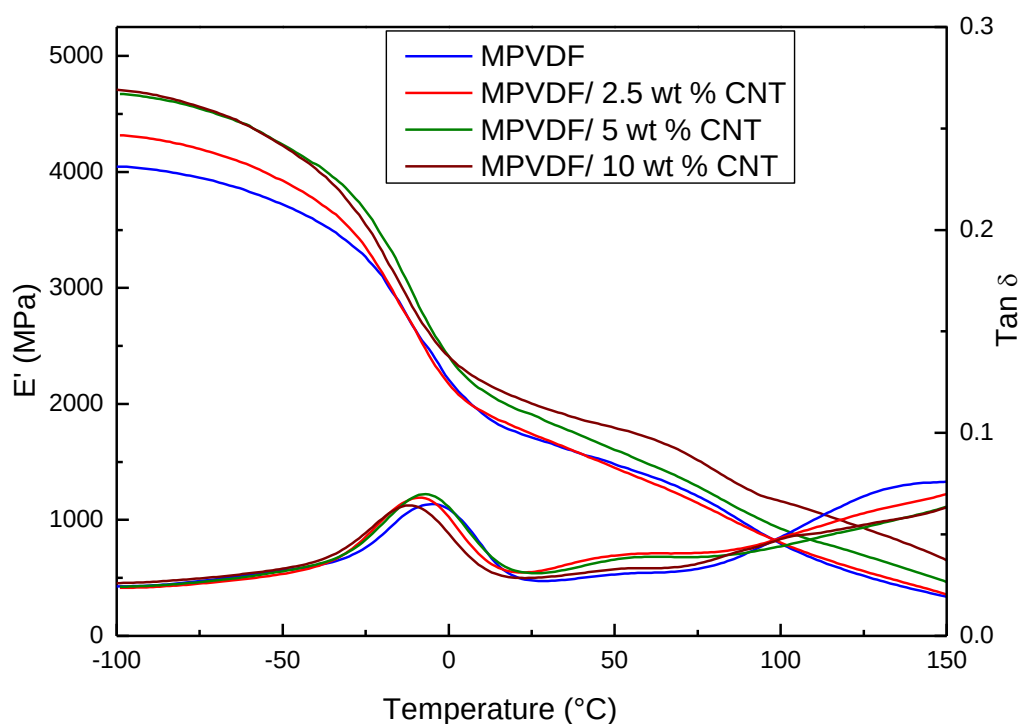


Figure 4-18: Temperature dependence of E' and $\tan \delta$ for MPVDF nanocomposites containing up to 10 wt% CNTs at a frequency of 10Hz as determined by DMTA

PVDF matrix modified with 25 wt% MAH-g-PVDF (MPVDF) exhibited a 2 % drop in E' as compared to PVDF matrix at room temperature, which lied within the uncertainty of the measurement and is not significant. However, the addition of CNTs to the MAH-g-PVDF modified matrices resulted in an increase in E' over the entire temperature range compared to pure PVDF and MPVDF (Figure 4-18). More specifically addition of up to 10 wt% CNTs raised the E' of MPVDF matrices by approximately 7% and 9% at room temperature as compared to PVDF and MPVDF respectively.

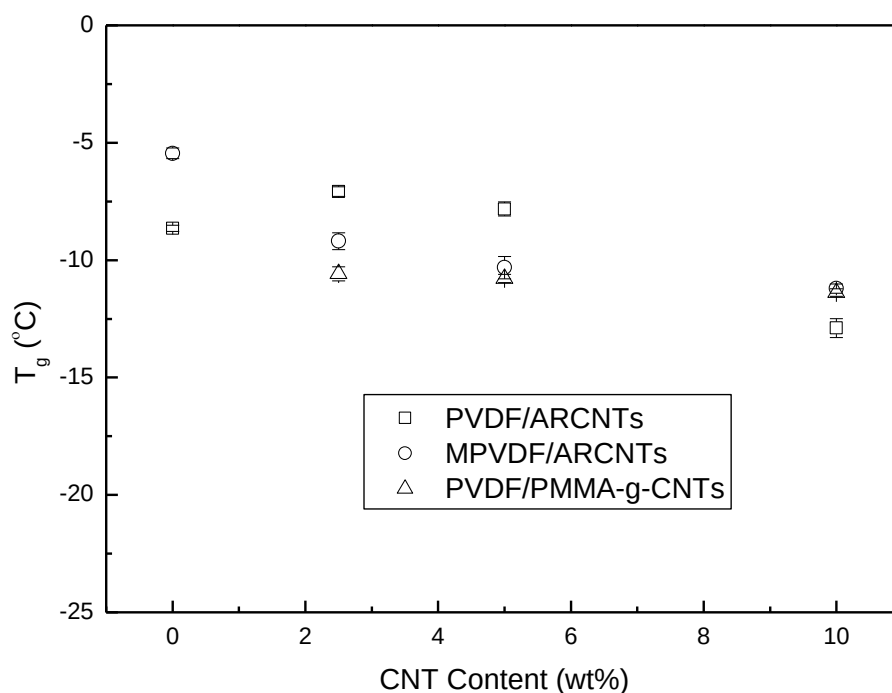


Figure 4-19: Glass transition temperature T_g for PVDF nanocomposites as a function of CNT loading

Glass transition temperature (T_g) was calculated from the peak of the $\tan \delta$ curves. It was observed that T_g 's of PVDF nanocomposites containing 10 wt% CNTs was lowered to -13°C from -8°C , T_g of MPVDF was lowered to -11°C from -5°C with 10 wt% CNT loading and T_g for PMMA-g-CNT based nanocomposites was -11°C irrespective of the CNT content as determined by the software "TA Q series advantage universal analysis". So it can be concluded that T_g of the PVDF nanocomposites is lowered with the addition of CNTs (Figure 4-19).

A modest linear drop in T_g 's of PVDF nanocomposites (Figure 4-19) with increase in CNT loading suggests that storage modulus is elevated due to stiffening effect of CNTs. Also, it suggests that there was no significant grafting between the surface of the carbon nanotubes and the maleic anhydride grafted into PVDF matrix or that the amorphous regions within the polymer bulk dominate mechanical T_g response.

The reason that the nanocomposite modulus is significantly higher than the modulus of pure PVDF and MPVDF is that the properties of these matrices themselves are changed in the vicinity of the nanotubes by the cohesive interaction.

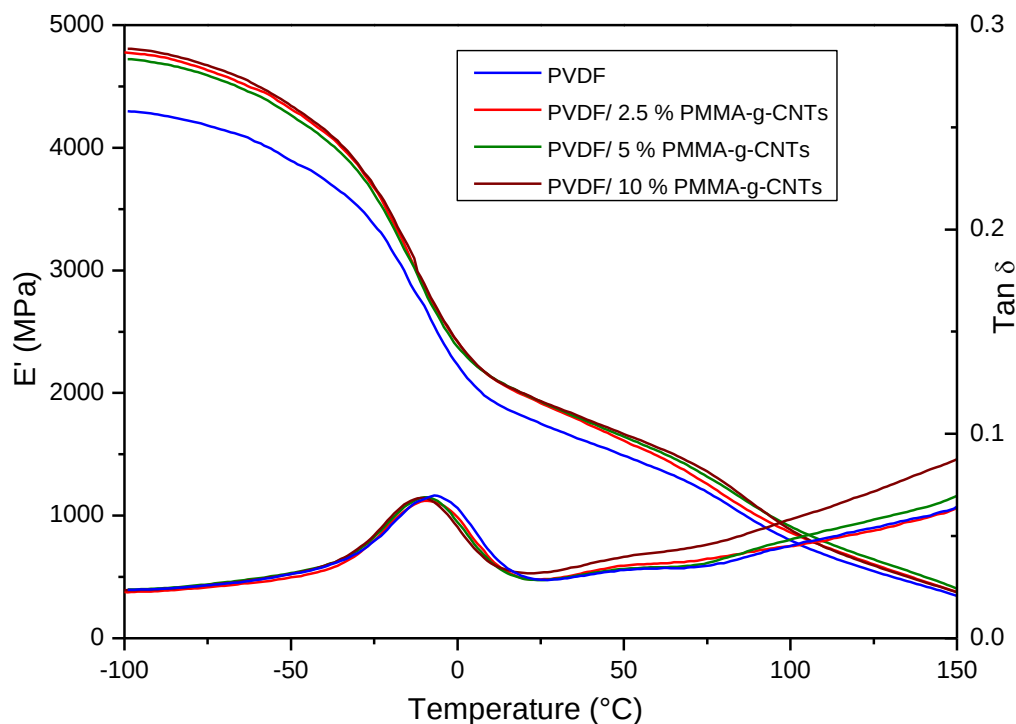


Figure 4-20: Temperature dependence of E' and $\tan \delta$ for PVDF nanocomposites containing modified CNTs (MDCNTs) at a frequency of 10Hz as determined by DMTA

PVDF matrix containing modified CNT loadings of 2.5 wt%, 5 wt% and 10 wt% exhibited an 8%, 9% and 10% increase (Figure 4-20), respectively in E' as compared to PVDF matrix in the low temperature range. At high temperature range, the relative increase in E' for the nanocomposites containing modified CNTs was similar for all CNT loadings (approximately 7-8%). Unlike PVDF nanocomposites containing as received CNTs, E' for PVDF nanocomposites containing PMMA-g-CNTs at a higher temperature was higher than pure PVDF. The analysis of the $\tan \delta$ curves did show a slight shift in α relaxation i.e. peak position of the nanocomposites, as compared to pure PVDF indicating slightly different T_g as compared to pure PVDF matrix (Figure 4-20). Overall, the thermo mechanical response of PVDF nanocomposites containing PMMA-g-CNTs showed superior stiffness than that of all PVDF nanocomposites containing either as received CNTs or MPVDF as shown in Figure

4-21. Wang [58] reported 150% improvement in storage modulus of PVDF containing 1.93 wt% PMMA-g-CNTs at 20°C when prepared by a melt mixing process. Miyagawa and Drzal [128] reported an increased storage modulus of epoxy based nanocomposites containing fluorinated SWCNTs. Also the storage modulus of PVDF/PMMA blend have been reported to be 25% greater than virgin PVDF at room temperature [129]. Since CNTs were grafted with PMMA, it may have contributed to the storage modulus PVDF/PMMA-g-CNT nanocomposites.

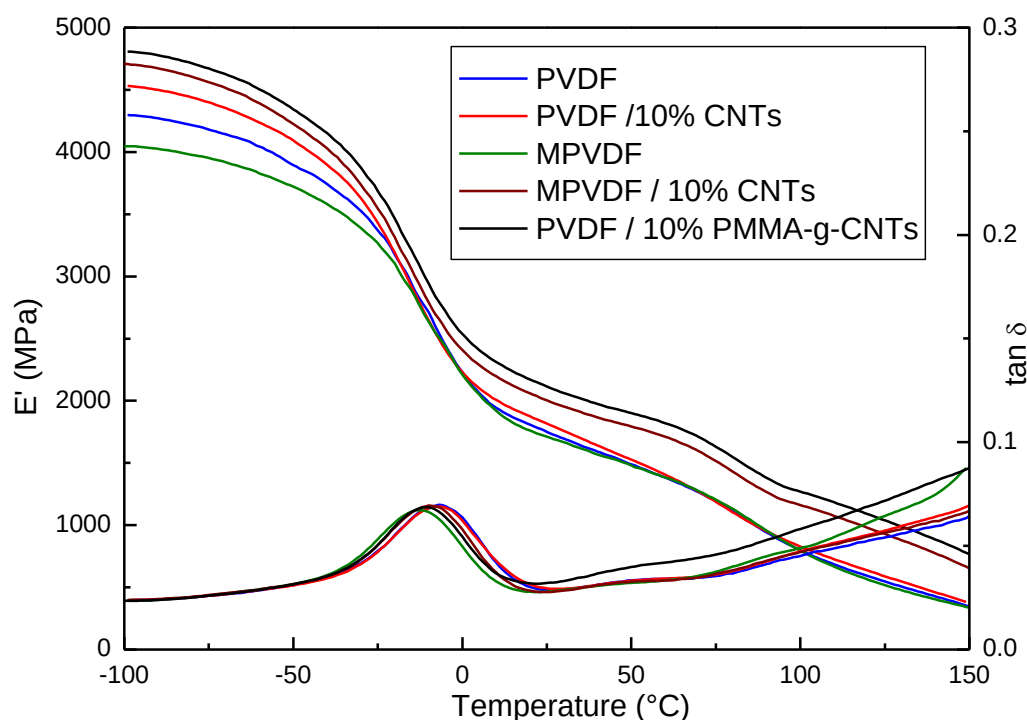


Figure 4-21: An overall comparison curve performance of PVDF nanocomposites containing either modified matrix or CNTs determined by DMTA in terms of temperature dependence of E' and $\tan \delta$

A comparison curve (Figure 4-21) will provide better understanding of the effect of maximum CNT loadings on stiffness and T_g of different systems. It is apparent that PVDF nanocomposites containing 10 wt% PMMA-g-CNTs depicted the highest storage modulus of 2142 MPa not only at room temperature but over the entire temperature range (4648 MPa @ $T = -80^\circ\text{C}$) as compared to PVDF nanocomposite containing 10 wt% CNTs (Figure 4-21). MPVDF nanocomposites showed a second highest storage modulus of 2000 MPa at room

temperature and 4615 MPa at -80°C as compared to PVDF nanocomposites containing 10 wt% CNT loading which has E' of 1805 MPa at room temperature and 4648 MPa at -80°C .

4.2.3.2 Tensile Properties of PVDF Nanocomposites

Tensile testing is a well-established method and is considered one of the main mechanical properties investigated by the research community studying nanocomposites. The tensile performance of the PVDF nanocomposites containing modified PVDF and modified CNTs were investigated (see details in Chapter 3) and the results are summarised in Table 4-3.

	PVDF/ARCNT Nanocomposites		MPVDF/ARCNT Nanocomposites		PVDF/PMMA-g-CNT Nanocomposites	
CNT Content [wt%]	Tensile Strength [MPa]	Tensile Modulus [GPa]	Tensile Strength [MPa]	Tensile Modulus [GPa]	Tensile Strength [MPa]	Tensile Modulus [GPa]
0	56.14 ± 1.2	2.49 ± 0.04	57.03 ± 0.75	2.62 ± 0.14	56.32 ± 1.02	2.49 ± 0.04
2.5	57.35 ± 0.6	2.54 ± 0.06	59.05 ± 1.20	2.74 ± 0.22	60.64 ± 0.37	2.88 ± 0.15
5	58.26 ± 0.7	2.65 ± 0.04	61.08 ± 1.06	2.78 ± 0.20	61.01 ± 0.64	2.95 ± 0.04
10	60.12 ± 0.2	2.68 ± 0.03	61.17 ± 1.03	2.94 ± 0.15	60.69 ± 0.45	3.14 ± 0.19

Table 4-3: Tensile performance of PVDF nanocomposites

The tensile testing was performed on three nanocomposite formulations defined on the basis of their contents which are PVDF/ARCNTs (PVDF reinforced with as received CNTs), MPVDF/ARCNTs (PVDF modified with 25 wt% maleic anhydride grafted PVDF reinforced with as received CNTs) and PVDF/PMMA-g-CNTs (PVDF reinforced with modified CNTs). The corresponding PVDF and MPVDF matrices were also tested (see Table 4-3). These three nanocomposite formulations were tested with CNT loading fractions of 0 wt%, 2.5 wt%, 5 wt% and 10 wt%. The MPVDF samples resulted, within error, in a slight increase of 5% and 2% (within scatter) in Young's modulus and in tensile strength respectively, as compared to pure PVDF. This suggests that the tensile performance of PVDF is not altered much with use of MAH-g-PVDF as the matrix.

The Young's modulus of the nanocomposites analysed followed the same trend that was observed in DMTA. All the nanocomposites exhibited a linear increase with CNT loading in both tensile strength and Young's modulus over pure PVDF (Figure 4-22). However, MPVDF

nanocomposites containing 10 wt% CNTs exhibited an 18% enhancement in Young's modulus over pure PVDF. On the other hand PVDF containing PMMA-g-CNTs depicted the highest improvement of 26% in Young's modulus as compared to pure PVDF. Overall, the Young's modulus of PVDF/PMMA-g-CNTs and MPVDF nanocomposites were 15-20% and 5-10% higher than that of PVDF nanocomposites (Table 4-3). This follows a rule of mixtures since it is stated when a matrix and reinforcement are blended together to obtain a composite, then the modulus of individual components are combined together based on the loading fraction. Given the superior Young's modulus of CNTs, even a low loading fraction would compensate for the decrease in volume fraction of the matrix and hence an overall increase in the Young's modulus. A similar trend i.e. a linear increase in Young's modulus with the increase in CNT loading fraction for PEEK nanocomposites has been reported [14] with an overall 48% improvement with 15 wt% CNT loading.

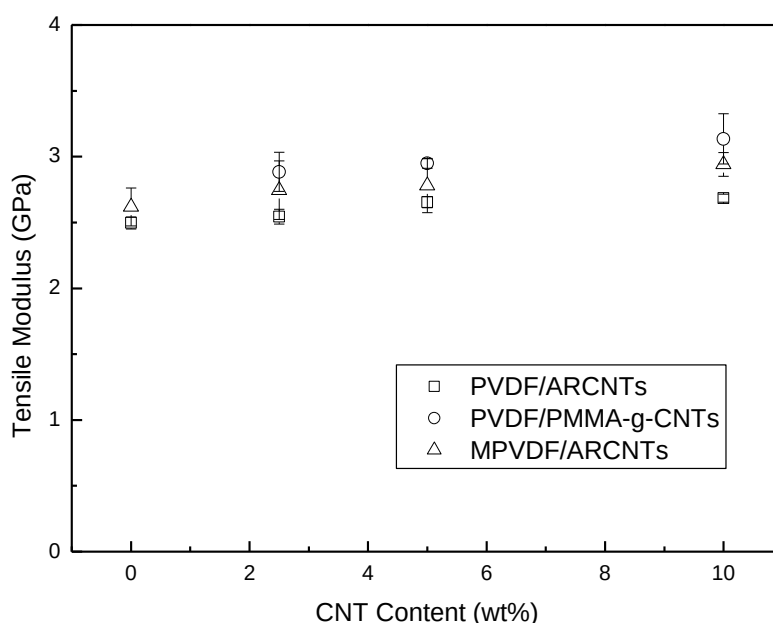


Figure 4-22: Tensile modulus of PVDF nanocomposites as a function of CNT loading

The PVDF nanocomposites reinforced with CNTs had higher performance than the baseline PVDF samples. The tensile strength of the specimens containing higher loading of CNTs shows higher material properties than pure PVDF samples. In addition, the material properties of PMMA-g-CNT nanocomposites are increased to a much higher value than the pure PVDF material itself.

Similarly, a linear improvement was observed in tensile strength for all PVDF nanocomposites. (Figure 4-23) PVDF nanocomposites containing 10 wt% CNTs exhibited a 6% enhancement in tensile strength over pure PVDF. However, the presence of 2.5 wt%, 5 wt% and 10 wt% PMMA-g-CNTs boosted the tensile strength by 8%, 9% and 10% respectively, in PVDF. Overall, the tensile strength of PVDF/PMMA-g-CNTs and MPVDF nanocomposites were 5-7% and 4-5% higher than that of PVDF nanocomposites (Table 4-3). This increase in mechanical performance was attributed to the improved dispersion and interaction between the CNTs (reinforcement) and PVDF (matrix) which was achieved by introducing modifications in either of them.

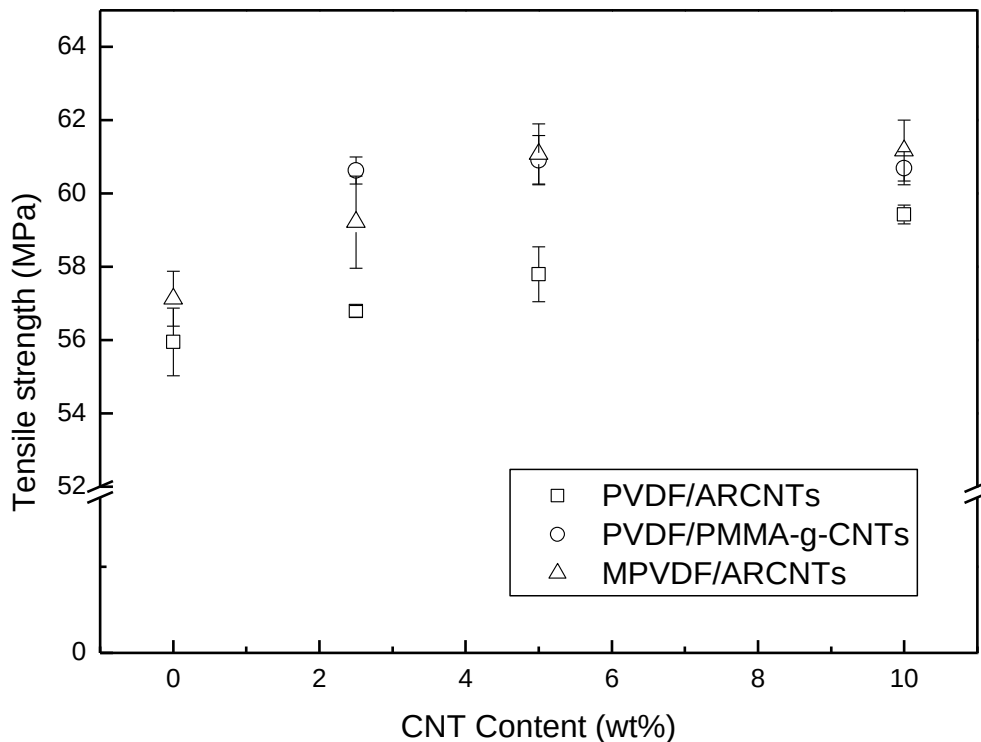


Figure 4-23: Tensile strength of PVDF nanocomposites as a function of CNT loading

Tensile strain at failure was determined from the maximum strain value taken right before the specimen failure for all nanocomposite formulations. It showed steady values in a range of 1700 to 2300 μ strain (Figure 4-24). Both PVDF and MPVDF nanocomposites depicted almost similar strain values for various loadings of CNTs (a negligible drop in strain is observed with increase in CNT loading). PVDF/PMMA-g-CNT nanocomposites however showed lower

strains than both PVDF and MPVDF NC's and a high scatter in strain values which suggests the presence of regions of varying crystallinity at the fracture plane as it tends to be located at the weakest site in the material and could indicate differences in the ductility of the matrix. This can be because of existence of two opposing factors affecting the crystallisation/melting behaviour of PVDF in composites. CNTs do serve as nucleation agents for PVDF, enabling PVDF to crystallize at a higher temperature upon cooling, whereas the melting temperature of PVDF is depressed upon the addition of PMMA. With increasing PMMA-g-CNT content in composite, the nucleation effect of CNTs is overshadowed by the suppression effect of PMMA [58]. All nanocomposite specimens underwent a brittle fracture compared to the PVDF specimens where plastic deformation occurred with necking and drawing of polymer prior to failure.

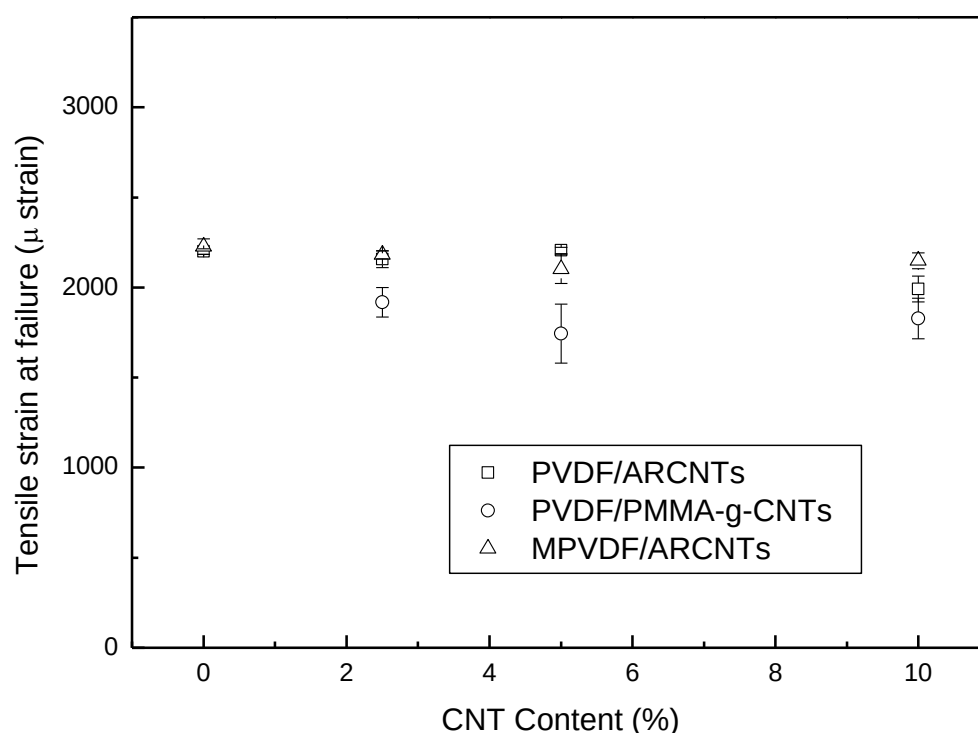


Figure 4-24: Tensile strain at failure for nanocomposites as a function of CNT loading

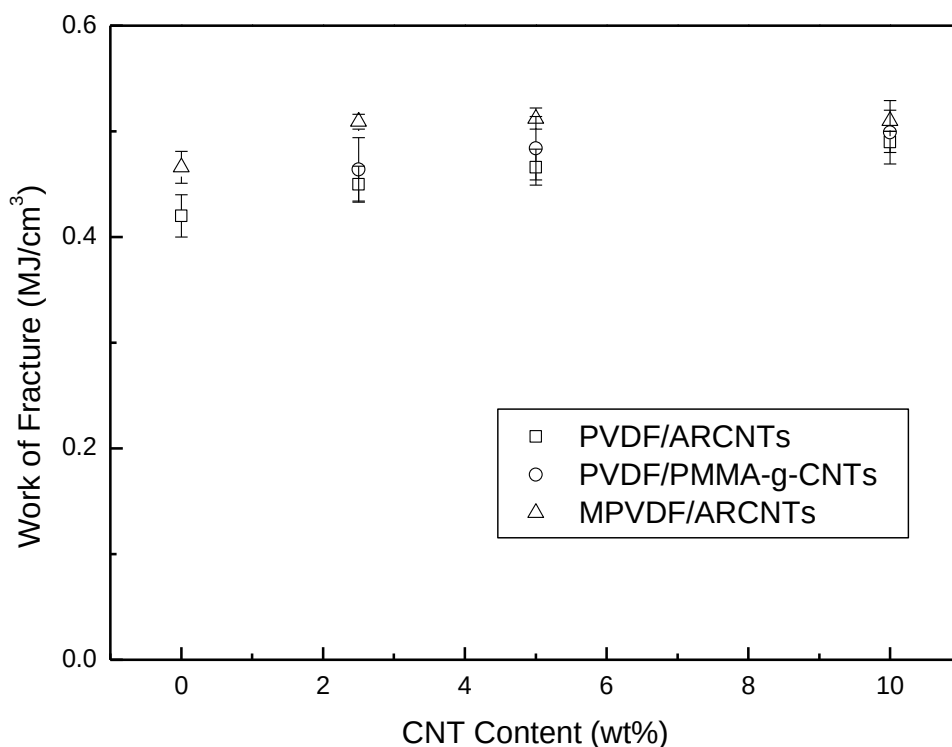


Figure 4-25: Work of fracture for nanocomposites as a function of CNT loading

Work of fracture was calculated from the area under the stress strain curves for tensile data. As concluded by Figure 4-25, it increased linearly for all nanocomposites with increased loading of CNTs. A 25% increase in work of fracture was observed for PVDF nanocomposite containing 10 wt% CNTs which indicates a reasonable improvement in toughness of the nanocomposites with an increase in CNT loading.

In conclusion, the increase in the tensile performance of nanocomposites based on CNTs and PVDF is due to reinforcing effect of CNTs and not from any increase in crystallinity. These PVDF nanocomposites depicted a linear increase in tensile strength, modulus and toughness (work of fracture) with increase in CNT loading in PVDF. PVDF/PMMA-g-CNTs nanocomposites showed the most superior material properties than the other NCs. These results are in agreement with the previous results reported by researchers. As for thermosets, Gojny et al. [130] reported an increased Young's modulus with the addition of double walled carbon nanotubes (DWNTs) into the epoxy resin. Moreover, additional improvement was observed when amino-functionalized DWNT was used, since the presence of polar amino-

groups helped improving dispersion of DWNTs developing stronger interfacial bonding which resulted in higher modulus. Furthermore, this improvement in stiffness depicted a linear relation to the DWNT-NH₂ loading. However the addition of DWNTs may sometimes reduce the tensile strength, which may be due to the effect of agglomeration of DWNTs and the weak interface between nanotubes and polymer. Nevertheless, the amino-functionalized DWNT can reduce the agglomeration and then got higher tensile strength, which may be due to better interface and better load transfer between DWNTs and epoxy resin. Similarly, Allaoui et al. [131] reported a significant increase in Young's modulus and strength with up to 4 wt% MWNT loading. As for functionalised CNTs, Zhu et al. [132, 133] also showed an increased tensile strength and Young's modulus by 1 wt% alkylamino functionalised SWNTs to an epoxy matrix.

4.2.3.3 Compressive Properties of PVDF Nanocomposites

Compressive mechanical properties are important for the matrix of any composite materials, indeed for composite materials the matrix governs the compression and shear properties. Compression test was carried out in accordance to ASTM D695 (see details in Chapter 3). Compressive strength at break could not be determined as all the specimens did not fracture but buckled across the width of the individual specimen. Instead the compressive offset yield stress at 0.2% strain was used for evaluation purposes of the compressive properties of the nanocomposite materials.

	PVDF/ARCNT Nanocomposites		MPVDF/ARCNT Nanocomposites		PVDF/PMMA-g-CNT Nanocomposites	
CNT Content [wt%]	Compressive Strength [MPa]	Compressive Modulus [GPa]	Compressive Strength [MPa]	Compressive Modulus [GPa]	Compressive Strength [MPa]	Compressive Modulus [GPa]
0	37.12 ± 1.16	2.37 ± 0.07	42.11 ± 1.02	2.72 ± 0.02	37.24 ± 1.25	2.37 ± 0.07
2.5	38.23 ± 0.72	2.39 ± 0.11	43.32 ± 0.64	2.74 ± 0.02	47.31 ± 0.36	3.01 ± 0.12
5	39.72 ± 0.75	2.49 ± 0.20	44.64 ± 0.23	2.84 ± 0.02	49.30 ± 0.41	3.29 ± 0.07
10	40.21 ± 0.21	2.67 ± 0.20	45.45 ± 1.77	3.08 ± 0.02	50.18 ± 0.64	3.51 ± 0.04

Table 4-4: Compression performance of PVDF nanocomposites

Compressive modulus was determined from slope of stress strain curve whereas strains were measured using strain gauges (FLA-2-11) as explained in Chapter 3. The compression testing

was performed on three nanocomposite formulations which are PVDF/ARCNTs, MPVDF/ARCNTs and PVDF/PMMA-g-CNTs for up to 10 wt% CNT loading. The corresponding PVDF and MPVDF matrices were also tested (see Table 4-4). The MPVDF samples resulted, within error, in a slight increase of 15% and 13% in Young's modulus and in tensile strength respectively, as compared to pure PVDF. This suggests that the compression performance of PVDF matrix is improved when modified with 25 wt% MAH-g-PVDF. The Young's modulus of the nanocomposites as determined from compression testing followed the same trend that was observed in DMTA and tensile properties. The PVDF nanocomposites displayed a linear increase in Young's modulus with increase in CNT loading corresponding to a maximum 13% increase with 10 wt% CNT loading in pure PVDF (Figure 4-26). Overall, the Young's modulus of PVDF/PMMA-g-CNTs and MPVDF nanocomposites were 26-32% and 14-15% higher than that of PVDF nanocomposites (Table 4-4).

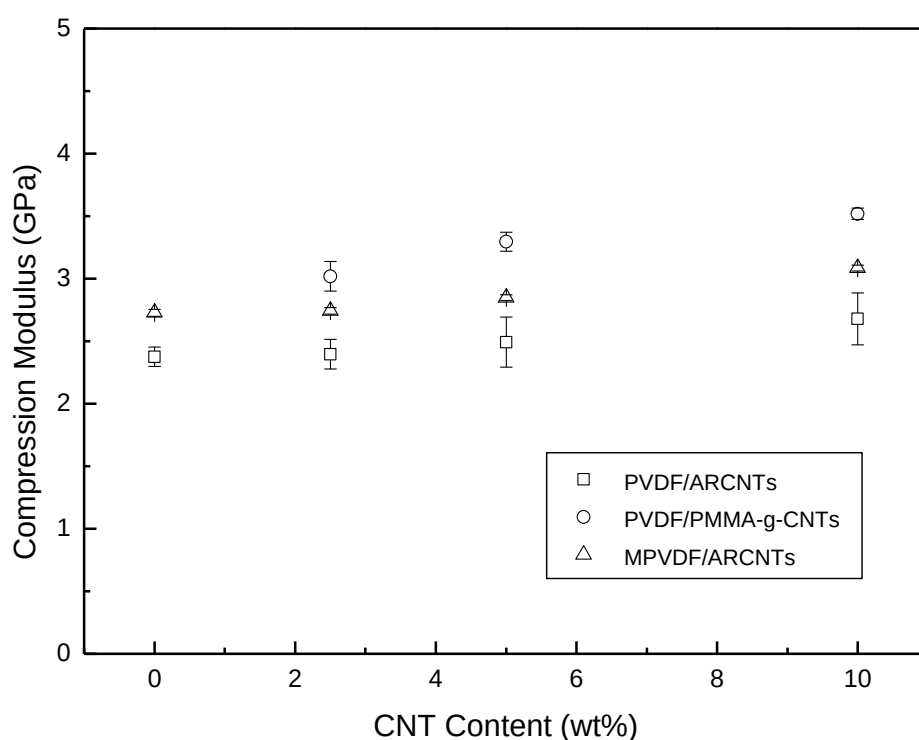


Figure 4-26: Compressive modulus of PVDF nanocomposites as a function of CNT loading

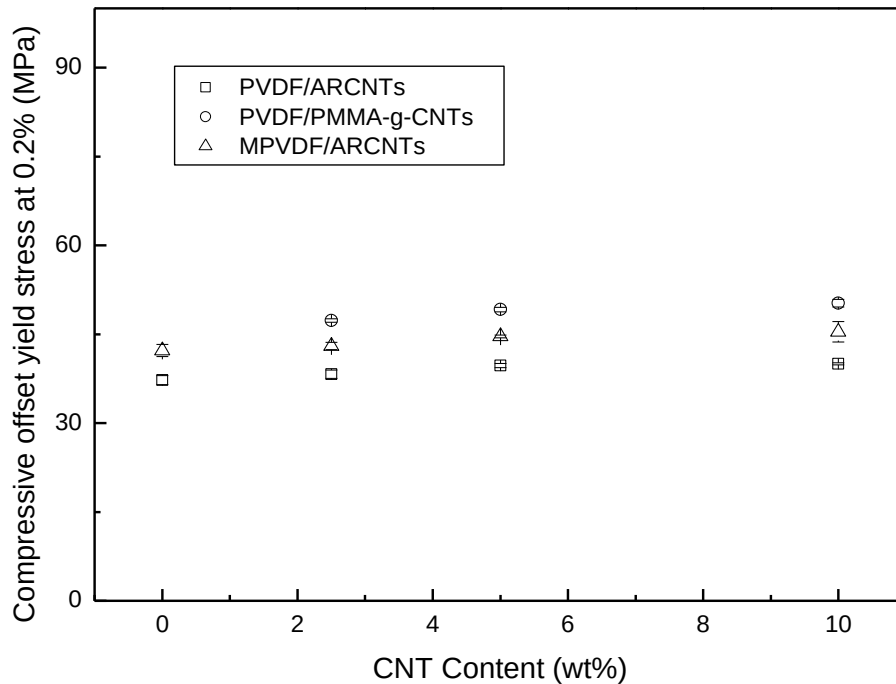


Figure 4-27: Compressive offset yield stress at 0.2% of PVDF nanocomposites as a function of CNT loading

Similarly, a linear improvement was observed in compressive offset yield stress (Figure 4-27) for all PVDF nanocomposites an 8% and 35% enhancement being the maximum for 10 wt% ARCNT and PMMA-g-CNT loading, respectively in pure PVDF (Table 4-4). Overall, the compressive offset yield stress of PVDF/PMMA-g-CNTs and MPVDF nanocomposites was 23-26% and 12-14% higher than that of PVDF nanocomposites. Although, compressive yield stress is not comparable to compression strength as it also takes in to account on going plastic deformation but still, it could be assumed that the results shown reflect an increase in stress of the nanocomposites before they fail in compression [14]. As is explained before, this increase in mechanical performance was attributed to the improved dispersion and interaction between the CNTs (reinforcement) and PVDF (matrix) which was achieved by introducing modifications in either of them. The difference between compression and tension could be explained by significant difference in stress transfer in nanotubes in compression and tension. This can be explained by the fact that load transfer in tension could be thought of as a hydrostatic pressure effect while load transfer in compression relies on matrix nanotube bond.

4.2.3.4 Flexural Properties of PVDF nanocomposites

Flexural testing is of importance for mechanical design purposes in industry as it shows the bending characteristics of materials, which is a common loading condition associated with components and structures. Flexural strength was measured at 5% strain value as the standard mentioned the validity of strength only up to this value. Flexural modulus was determined from the formula as defined in ASTM D790 (explained in Chapter 1). The flexural properties of PVDF nanocomposites are illustrated in Table 4-5. Failure within 5% strain was not observed for the nanocomposites so test was stopped when 5% strain was reached for these materials.

	PVDF/ARCNT Nanocomposites		MPVDF/ARCNT Nanocomposites		PVDF/PMMA-g-CNT Nanocomposites	
CNT Content [wt%]	Flexural Strength [MPa]	Flexural Modulus [GPa]	Flexural Strength [MPa]	Flexural Modulus [GPa]	Flexural Strength [MPa]	Flexural Modulus [GPa]
0	55.2 ± 1.7	1.54 ± 0.03	54.3 ± 3.2	2.12 ± 0.03	55.3 ± 1.7	1.54 ± 0.03
2.5	57.4 ± 1.6	1.67 ± 0.02	56.2 ± 2.4	2.19 ± 0.01	57.2 ± 1.5	2.52 ± 0.03
5	59.6 ± 1.8	1.75 ± 0.01	57.8 ± 3.1	2.28 ± 0.02	60.3 ± 2.0	2.65 ± 0.07
10	63.6 ± 2.5	1.84 ± 0.02	60.5 ± 3.3	2.72 ± 0.06	65.6 ± 3.0	2.98 ± 0.03

Table 4-5: Flexural properties of PVDF nanocomposites

PVDF nanocomposites depicted a linear increase in flexural modulus with increasing CNT weight fraction i.e. flexural modulus of PVDF improved from 1.54GPa to 1.84GPa with the addition of 10 wt% CNTs. PVDF nanocomposite containing 10 wt% as-received carbon nanotubes exhibited 20% improvement in flexural modulus over pure PVDF. The MPVDF nanocomposites containing 10 wt% AR-CNTs exhibited 28% enhancement in flexural modulus over pure PVDF (Table 4-5). However, PVDF containing 10 wt% PMMA-g-CNTs showed the highest improvement of 94% in flexural modulus as compared to pure PVDF (Figure 4-28). Overall, the flexural modulus of PVDF/PMMA-g-CNTs and MPVDF nanocomposites were 50-60% and 10-15% higher, respectively than that of PVDF nanocomposites.

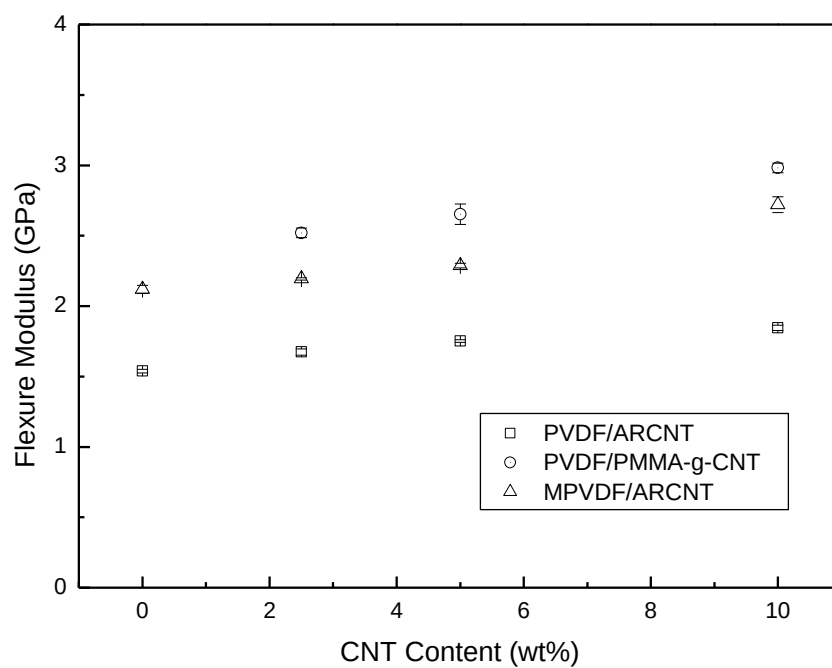


Figure 4-28: Flexural modulus of PVDF nanocomposites as a function of CNT loading

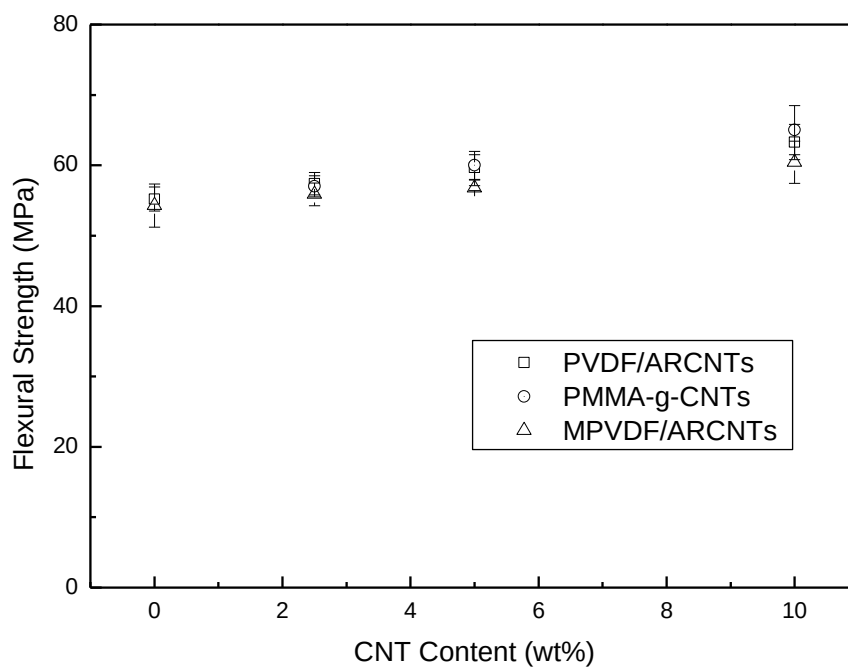


Figure 4-29: Flexural strength of PVDF nanocomposites as a function of CNT loading

Similarly, a linear improvement was observed in flexural strength (Figure 4-27) for all PVDF nanocomposites with maximum enhancement of 15% in flexural strength of PVDF containing 10 wt% CNTs as compared to PVDF. However, MPVDF nanocomposites containing 10 wt% as-received CNTs exhibited only 10% enhancement in flexural strength over pure PVDF which is 5% lower than PVDF with same CNT loading. On the contrary, the presence of 2.5 wt%, 5 wt% and 10 wt% PMMA-g-CNTs boosted the flexural strength by 4%, 9% and 18% respectively, in PVDF (Table 4-5). Overall, the flexural strength of PVDF/PMMA-g-CNTs and MPVDF nanocomposites was similar to that of PVDF nanocomposites for all CNT loadings except for PVDF/10 wt% PMMA-g-CNTs which showed a higher flexural strength of 65MPa but with an increased statistical scatter.

Higher scatter in data was seen with the increasing CNT weight fractions. The increase in scatter could indicate regions of varying crystallinity (crystalline phases) at the fracture plane and could indicate differences in the ductility of the matrix. Variations produced from the manufacturing process such as during extrusion or injection moulding could cause such discrepancies. From the results mentioned above, it is confirmed that CNTs are an effective reinforcement of the polymer composite.

4.2.4 Summary

CNTs in general exhibit a certain potential to improve the mechanical properties of various polymer matrices. The incorporation of CNTs into the matrix of conventional composites was expected to improve the matrix modulus, which should subsequently lead to hierarchical composites with much improved compression and other matrix dominated properties. It is imperative that high volume fraction composites with good dispersion can routinely be made. PVDF nanocomposites containing up to 10 wt% CNTs were successfully fabricated via extrusion and injection moulding. Constant density and negligible porosity values indicated nanocomposites fabricated possessed good quality. Optical and electron microscopy confirmed good CNT dispersion and absence of any CNT agglomerates greater than 15 μm . The nanocomposites were characterised for their mechanical properties to assess their potential as reinforcement for carbon fibre reinforced composites.

In summary, mechanical properties of PVDF nanocomposites (tension, compression and flexure) depicted a linear improvement with CNT loading irrespective of the modification in matrix or reinforcement. Both modified matrix (PVDF modified with 25 wt% maleic

anhydride grafted PVDF) and modified reinforcement (Poly methyl methacrylate grafted carbon nanotubes) depicted improvements in mechanical properties as compared to PVDF/ARCNT nanocomposites. PVDF/PMMA-g-CNTs nanocomposites depicted the most superior mechanical performance than the other NCs. PVDF nanocomposites containing 10 wt% PMMA-g-CNTs depicted the highest storage modulus value of 2142 MPa not only at room temperature but over the entire temperature range as compared to PVDF. Also, overall PVDF/PMMA-g-CNT nanocomposites showed an improvement of 60%, 48% and 26% in flexural, compression and tensile modulus respectively when loaded with 10% CNTs as compared to pure PVDF. Moreover, PMMA-g-CNTs promoted the β -phase crystals in PVDF (as investigated via DSC and XRD results) which is indicative of improved piezoelectric and pyroelectric properties [58].

PMMA-g-CNT based PVDF nanocomposites depicted the best mechanical performance. The presence of grafted PMMA or an MMA (methy methacrylate) functional group, because of its miscibility to PVDF, can improve the dispersibility and interfacial bonding of CNTs with PVDF, which are the key issues in the development of nanocomposites. A number of studies suggest that interfacial interactions with nanotubes result in an interfacial region of polymer with morphology and properties different to the bulk. This suggest that PMMA-g-CNTs developed an improved interfacial region in PVDF nanocomposites where external stresses applied to the composite as a whole were efficiently transferred to the nanotubes, allowing them to take a disproportionate share of the load which is the most important requirement for a nanotube reinforced composite. It was difficult for the strong nanotube-matrix interface to fail unless the matrix failed due to large shear stresses near the interface. The use of PMMA functional group enhanced CNT dispersion because of its compatibility with PVDF, optimised interfacial interactions and aided stress transfer.

In conclusion, the increase in the mechanical performance of nanocomposites based on CNTs and PVDF is due to reinforcing effect of CNTs and not from any increase in crystallinity. CNTs enabled the development of a new generation of materials with multifunctional properties, such as a combination interesting physical properties together with improved mechanical performance. CNTs (functionalised or non-functionalised) are a valuable chemical additive for the modification of polymers both thermoplastic and thermosets [128]. Choice of a compatible matrix (compatible with CNTs e.g. Polyamide, PMMA), or compatible functional group grafted on to CNTs (compatible with PVDF e.g. PMMA) can

improve the interfacial stress transfer at the nanotube matrix interface which is the most important requirement for effective reinforcement. Additionally, the combination of PVDF nanocomposites with conventional fibre reinforcements can be a promising approach for future perspectives in composite applications. Hierarchical composites of PVDF containing modified PVDF or modified CNTs would be an interesting idea to proceed on. Some of the work has already been done and is explained in next chapters.

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Chapter 5 - Carbon Fibre Reinforced PVDF Hierarchical Composites

5.1 Introduction

In this Chapter, the results obtained from mechanical characterisation of hierarchically reinforced PVDF composites are explained in detail. The objective of this study was to improve mechanical properties of carbon fibre reinforced PVDF (CF/PVDF) by introducing structural hierarchy, which is achieved by the incorporation of CNTs into the PVDF matrix. PVDF/CNT nanocomposite powder was prepared using a solution precipitation method [15] (see Chapter 3 for details) and subsequently reinforced with carbon fibres. Details about the particle sizes distribution of the PVDF nanocomposite powder will be reported in this chapter. The presence of nanotubes at the fibre/matrix interface is expected to improve matrix dominated properties of CFRPs. Composite prepregs were compression moulded into test specimens to study the influence of CNT loading on the matrix dominated mechanical properties of the composites. The consolidation parameters for compression moulding of hierarchically reinforced PVDF composites with a fibre volume content of 55 wt% were optimised based on the quality (as determined from density and porosity) of the composites produced using various processing conditions.

The major causes of the failure of unidirectional carbon fibre reinforced polymer composites (by brooming/end crushing or longitudinal splitting) are their poor transverse and interlaminar

properties. The interlaminar and mechanical properties of carbon fibre reinforced composites strongly depend on the fibre/matrix interface, which had been the area of interest for many researchers in the past (see Chapter 2). CNTs have been shown to introduce multifunctional properties, such as a combination of interesting physical properties together with improved mechanical performance in polymer matrices. PVDF has been shown to improve stiffness due to reinforcement effect of CNTs as shown in Chapter 4. Choice of a CNT reinforced PVDF nanocomposite, with improved matrix dominated properties can improve the interfacial stress transfer at the carbon fibre/matrix interface which is the most important requirement for effective reinforcement. The major objective of this research is to inhibit interlaminar failure in carbon fibre reinforced PVDF by enhancing the transverse and interlaminar properties which is achieved by introducing CNTs in the matrix. Additionally, the combination of PVDF nanocomposites with conventional fibre reinforcements can be a promising approach for future perspectives in composite applications. Unidirectional AS4/PVDF carbon fibre reinforced hierarchical composites with different CNT loadings were fabricated successfully using the continuous composite line as explained in Chapter 3. The mechanical performance of in-house manufactured AS4 carbon fibre reinforced PVDF with various CNT loadings of 0 wt%, 2.5 wt% and 5 wt% was investigated in compression and flexure. Furthermore, the interlaminar shear strength and delamination fracture toughness were also determined.

5.2 Production and Optimization of Processing

Hierarchically reinforced PVDF composites were manufactured using a laboratory scale continuous composite line, based on a powder impregnation technique (see Chapter 3 for details). Figure 5-1 shows the steps to fabricate hierarchical nanocomposites using pre-manufactured nanocomposite powder suspended in the impregnation bath. The carbon fibre reinforced PVDF tape manufactured from the composite line were cut in to equal lengths, laid up and consolidated under high temperature and pressure resulting in composite laminates. These composite laminates were characterised for fibre volume content (V_f), interlaminar shear strength, mode I fracture toughness, and compression as well as flexural properties.

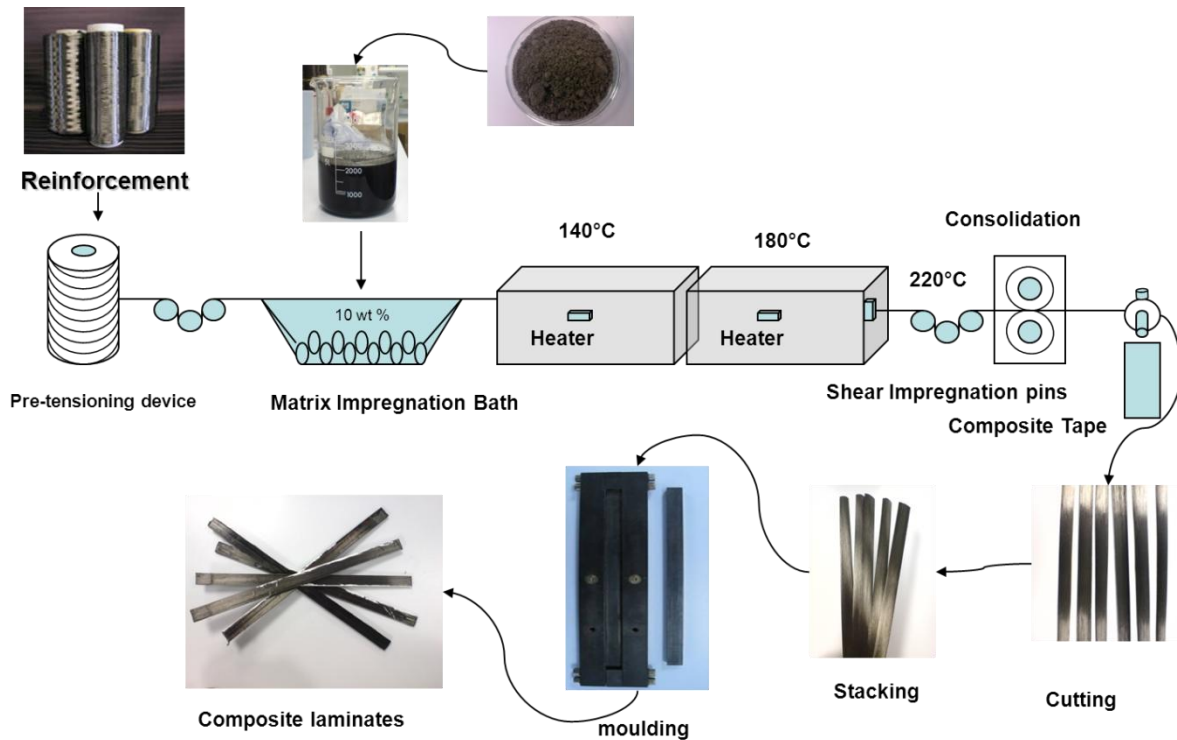


Figure 5-1: Schematic process diagram for fabrication of hierarchical nanocomposites

5.2.1 Size Distribution of Nanocomposite Powder

Three suspensions of 5 wt% nanocomposite powder containing up to 5 wt% CNTs in deionized water were prepared and stabilized by 2 wt% of Cremophor A25 with respect to polymer and the particle size distribution (PSD) was determined. During the operation of the line, samples were also taken from the impregnation bath at regular intervals. Particle size analysis was carried out using Malvern's Mastersizer 2000. The volume averaged diameter of the particles in the suspension is represented as d_{50} with an accuracy of $\pm 1\%$. Each reading obtained was an average of 6 values calculated by the Malvern Mastersizer 2000.

To manufacture hierarchical composites on the in-house continuous composite line setup, PVDF nanocomposites were manufactured into a powder form so that the material could be utilized in the powder impregnation process. The particle size of the nanocomposite powders is important because the powder should have particle sizes between 10-50 μm in order to be effectively picked up by the carbon fibres [14]. The particle size distribution of the PVDF nanocomposite powders can be seen in the Figure 5-2. It is clearly shown in Figure 5-2 that the average particle size (d_{50}) for nanocomposite powders increased with CNT content from 17 μm to 30 μm which is suitable for powder impregnation. Overall, nanocomposite powders

produced by solution precipitation method were less in size than $50\mu\text{m}$ presumably due to the relatively dilute solutions that were precipitated prevented extensive coalescence of the particles [17]. The increase in particle size is indicative of agglomerate formation at higher loading of CNTs.

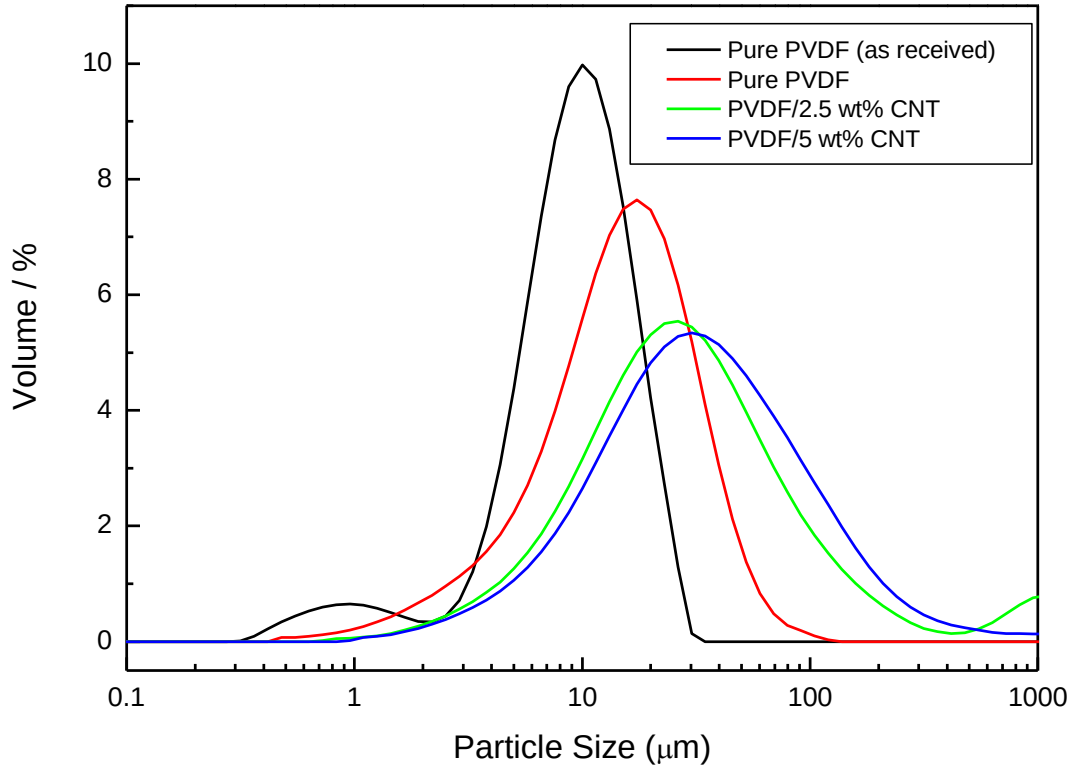


Figure 5-2: Particle size distribution of PVDF composite powder produced via the solution-precipitation scheme

Sample	Particle Size (μm)
PVDF (as received)	10 ± 1
PVDF	17 ± 2
PVDF with 2.5 wt% CNT	25 ± 3
PVDF with 5 wt% CNT	30 ± 2

Table 5-1: Volume averaged particle sizes for PVDF (Kynar 711) and its nanocomposite powders produced by the solution-precipitation method

CNT distribution in PVDF nanocomposites containing 5 wt% CNTs was investigated using the micrograph (Figure 5-3). Figure 5-3 (A) represents PVDF nanocomposite powder. Figure 5-3 (B) represents a higher magnification of the same. The presence of homogeneous pointed areas indicates that CNTs are well distributed within the nanocomposite matrix. It can be assumed that Figure 5-3 (C) represents higher magnification of PVDF nanocomposite powder particle containing CNT agglomerates (not greater than 1 micron). The protruding CNTs can still be seen in the agglomerate. These micrographs clearly show that particle size difference for formulations containing different CNT loadings has no major effect on CNT distribution. However, enhanced presence of agglomerates in PVDF nanocomposites by increasing CNT loadings was a common observation (Figure 5-3C).

At higher magnification it can be seen that the CNTs are not condensed on the surface of the matrix but evenly distributed in to the bulk of the matrix. This series of micrographs were taken to examine the morphology of PVDF. No agglomeration could be observed from the images which is encouraging.

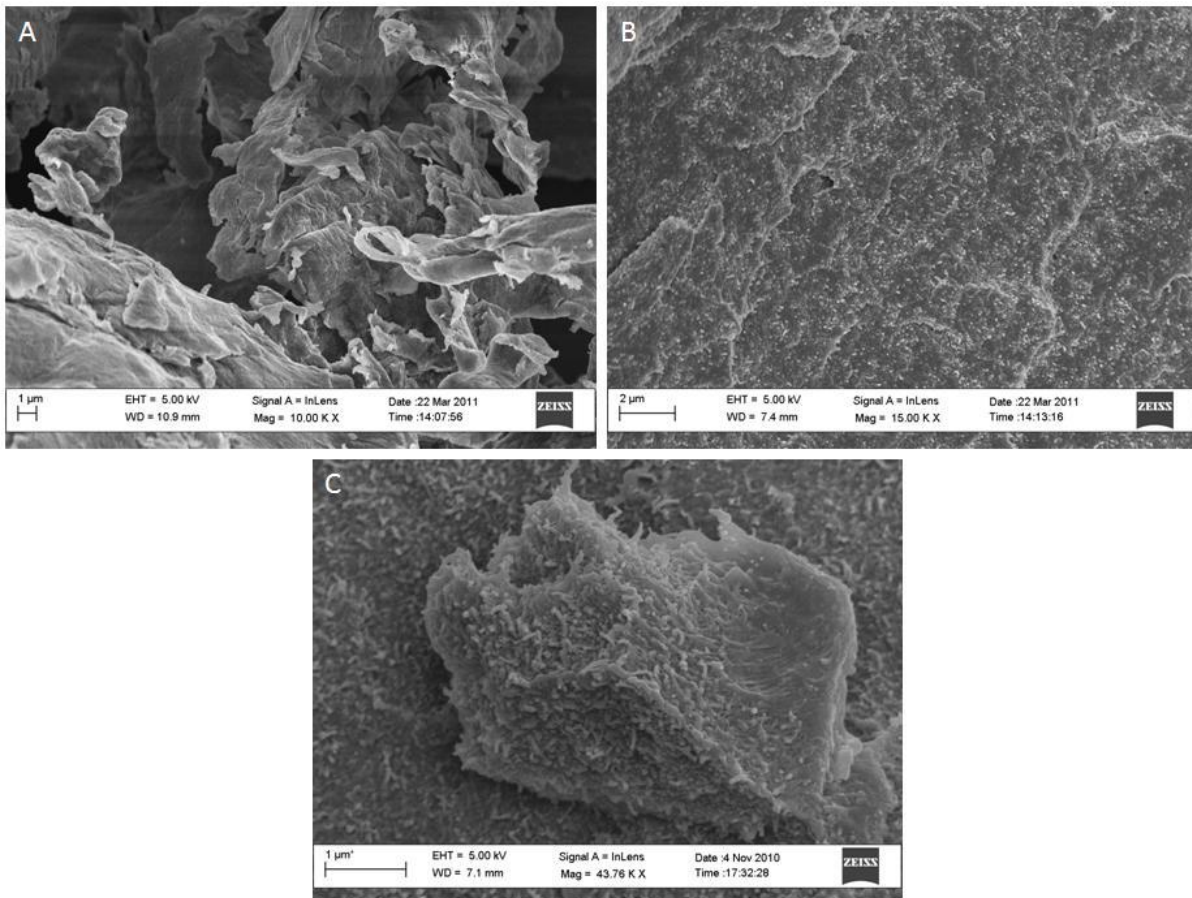


Figure 5-3: SEM micrograph representing a well dispersed region of PVDF nanocomposite powder containing 5 wt% CNTs at an increasing magnification clockwise A. ($\times 10\text{k}$), B. ($\times 15\text{k}$), C. ($\times 45\text{k}$)

5.2.1.1 Influence of powder impregnation bath concentration on composite tape quality

Powder impregnation consists of dispersing a fine powder ($<50\mu\text{m}$) of the polymer matrix throughout the carbon fibre tow [134]. The main disadvantage of this procedure is that a fine powder of the thermoplastic matrix is required which must be produced separately, often by grinding if not directly produced from polymer synthesis [134]. However, the distance that the polymer has to spread to wet and impregnate the fibres is very small which is beneficial for high viscosity polymer melts (such as nanocomposites), fibre volume content can be readily controlled and maintained. The polymer powder (PVDF/PVDF NC) concentration in the impregnation bath needed to be optimised to manufacture unidirectional carbon fibre reinforced PVDF composite tapes with consistent fibre volume content (FVC) was 55 %. The required bath concentration to produce a consistent CF/PVDF tape with a FVC of 55 % over 2 h of manufacturing time was identified to be 10 wt%. This was determined from the influence of impregnation bath concentration on the fibre volume content of the PEEK thermoplastic composites and little amendment would suffice for it to be used with other polymer matrices [14]. However, it is worth noting that this bath concentration was determined using the as received commercial available grade PVDF suspension whose particle size d_{50} was $10\mu\text{m}$, whereas the CNT/PVDF nanocomposite powder had a particle size d_{50} of $\sim 30\mu\text{m}$. Moreover, the average particle size of the PVDF NCs was slightly increased with the addition of CNTs. The concentration in the impregnation bath was maintained at 10 wt% for a PVDF powder with a d_{50} of $17\mu\text{m}$. However, the bath concentration needed for the PVDF nanocomposite powders (i.e. d_{50} up to $30\mu\text{m}$) was much lower i.e. a bath concentration of 5 wt% was used for PVDF containing 5 wt% CNTs to obtain a fibre volume content of 55%.

5.2.2 Fibre Volume Fraction

Although the fibre volume content of the tape was controlled during production of the composite tape (see Chapter 3), the test specimens were analysed to confirm that the fibre volume content was maintained throughout the production procedure. Optical micrographs of polished crosssections of hierarchical composites were taken (Figure 5-4) which were further analysed for fibre volume fraction by calculating the area of the fibres using the software “Image J”. Six Images of cross sections were taken for each composite formulation. The fibre volume content for each formulation was $57\% \pm 2$.

Matrix formulation	$\overline{V_{f,Geo}}$	$\overline{V_{f,Mass}}$
Pure PVDF	0.57 ± 0.01	0.57 ± 0.02
PVDF with 1.25 wt% CNTs (<i>mixed plies</i>)	0.57 ± 0.01	0.56 ± 0.02
PVDF with 2.5 wt% CNTs	0.56 ± 0.02	0.57 ± 0.02
PVDF with 5 wt% CNTs (<i>mixed plies</i>)	0.56 ± 0.02	0.57 ± 0.02
PVDF with 5 wt% CNTs	0.57 ± 0.02	0.56 ± 0.02

Table 5-2: Average fibre volume fractions of PVDF hierarchical composites determined geometrically and gravimetrically containing up to 5 wt% CNT content

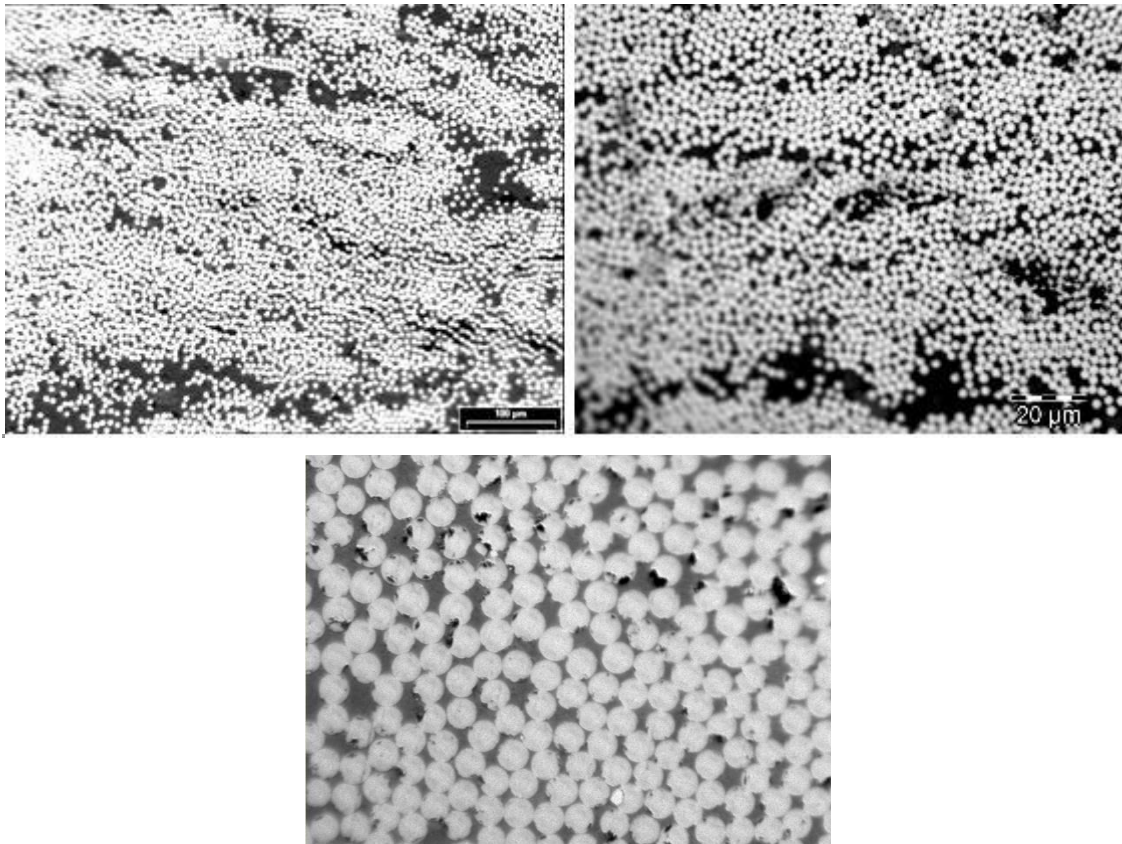


Figure 5-4: Optical micrographs showing the ends of fibres (rounded white area) impregnated with PVDF matrix (black area) in the transverse sections of the hierarchical composites at an increasing magnification from left to right (fibre diameter is 7 microns for the scale)

5.2.3 Crystallinity of PVDF Hierarchical Composites

The presence of CNTs can affect the processing, architecture and degree of crystallinity of the polymers. However, crystallinity of the polymer matrix can affect the toughness of the matrix and or the fibre/matrix interface is compromised. Differential scanning calorimetry (DSC)

was used to determine the crystallinity of the matrices with and without CNTs. It was observed that degree of crystallinity of PVDF and PVDF nanocomposites containing up to 5wt% CNTs were around $39 \pm 3\%$ which suggests that there was no effect of CNT loading on crystallinity of hierarchical composites. It implied that the mechanical performance of hierarchical nanocomposites was mainly due to the addition of reinforcement into the matrix and not because of any changes in the crystallinity caused by that reinforcement. Further to this, crystallinity values suggest that CNTs do not influence the architecture of the composite but still it was certainly thought that testing the hierarchical composites for interlaminar shear strength (ILSS) would help better understand any influences of CNTs on the composites' fibre/matrix interface and thus consolidation of prepreps to form laminates.

Hierarchical composites with the matrix formulation as	$\chi_c / (\%)$
Pure PVDF	38 ± 2
PVDF with 1.25 wt% CNTs (<i>mixed plies</i>)	39 ± 1
PVDF with 2.5 wt% CNTs	39 ± 3
PVDF with 2.5 wt% CNTs (<i>mixed plies</i>)	40 ± 1
PVDF with 5 wt% CNTs	39 ± 2

Table 5-3: Degree of crystallinity of PVDF matrix in hierarchical composites determined by DSC

5.2.4 Influence of Consolidation Pressure on Quality of Laminated Composites

Hierarchically reinforced PVDF containing 2.5 wt% CNTs were compression moulded in a hot press at various pressures to study the effect of consolidation pressure on the quality and mechanical performance of the composites. Composites were consolidated at a pressure range of 2-10MPa (extremes for the hot press in the laboratory), beyond which the excessive pressure resulted in a very thin composite bar with lots of flash. There was negligible flash observed in any of the moulded bars consolidated at pressure ranging 2-10MPa. The consolidation steps include 5 min preheating at 220°C, followed by 10 min loading at 220°C under pressure and finally cooling for 10 min at 80°C under pressure.

It was observed that all the samples of PVDF hierarchical composites containing 2.5 wt% CNTs consolidated at different pressures have an average absolute density of 1.77 g/cm^3 , as determined through AccuPyc, which suggests that a change in consolidation pressure did not

affect the compactness or quality of the hierarchical carbon fibre reinforced PVDF nanocomposites. The porosity of the unidirectional carbon fibre reinforced PVDF composites was also determined via GeoPyc to analyse the quality of consolidation. The optimised pressure chosen for pressing the hierarchical nanocomposites was 2 MPa.

Sample	P_{con} (MPa)	$\overline{\rho}_A$ (g/cm ³)	$\overline{\rho}_E$ (g/cm ³)	P (%)	Specific Pore Volume (cm ³ /g)	SBS (MPa)
1	2	1.77 ± 0.02	1.73 ± 0.02	1.41 ± 1.22	0.039 ± 0.002	39 ± 0.2
2	4	1.76 ± 0.03	1.71 ± 0.03	1.58 ± 0.75	0.043 ± 0.004	40 ± 0.4
3	6	1.75 ± 0.02	1.71 ± 0.02	1.47 ± 0.31	0.034 ± 0.005	40 ± 0.8
4	8	1.76 ± 0.02	1.72 ± 0.02	1.42 ± 1.05	0.027 ± 0.003	40 ± 0.7
5	10	1.76 ± 0.02	1.73 ± 0.03	1.35 ± 0.87	0.024 ± 0.004	40 ± 0.5

Table 5-4: Averaged absolute density, averaged envelope density, percentage porosity, specific pore volume and short beam shear strength for PVDF hierarchical nanocomposite bars containing 2.5 wt% CNTs (FVC- 63% ± 2) pressed at different consolidation pressures

Since consolidation process involves melting of the matrix polymer, it might cause settling of CNTs on the bottom of the resulting composite bar owing to the higher viscosity of nanocomposite melt. This could cause non homogeneous distribution of CNTs within carbon fibre reinforced PVDF nanocomposite bars and hence poor mechanical performance when tested. So, the influence of consolidation pressure on mechanical performance of composites was investigated by choosing short beam shear (SBS) test for the required purpose. Table 5-4 shows that there is no significant difference in SBS strength for PVDF hierarchical composites (containing 2.5 wt% CNTs) consolidated at various pressures i.e. 40 ± 2 MPa.

5.3 Mechanical Characterisation of Hierarchical Composites

The bond strength between reinforcing fibres and the surrounding PVDF matrix was inferred from macro mechanical tests. Flexural modulus was chosen as a qualification method because it is often used as component design criteria for structural applications. The compression strength and modulus were measured as a means to investigate matrix dominated composite properties. Mode I fracture toughness was measured by double cantilever beam testing to determine the influence of carbon nanotube reinforcement on delamination strength. Furthermore, although DSC crystallinity values suggested that CNTs do not influence the

architecture of the composite, interlaminar shear strength (ILSS) data would provide means to identify influences of CNTs on the composites' matrix dominated properties (load transfer at fibre/matrix interface) and thus mechanical performance.

AS4 carbon fibre reinforced with the matrix	$\overline{\rho_A}$ g/cm ³	$\overline{\rho_E}$ g/cm ³	P %	Specific Pore Volume (cm ³ /g)
Pure PVDF	1.76 ± 0.20	1.74 ± 0.25	1.22 ± 0.24	0.042 ± 0.002
PVDF/1.25 wt% CNTs (mixed plies)	1.78 ± 0.17	1.74 ± 0.62	1.23 ± 0.82	0.0340 ± 0.004
PVDF/2.5 wt% CNTs	1.76 ± 0.21	1.75 ± 0.38	1.11 ± 0.64	0.028 ± 0.003
PVDF/2.5 wt% CNTs (mixed plies)	1.76 ± 0.84	1.76 ± 1.22	1.02 ± 0.54	0.015 ± 0.004
PVDF/5 wt% CNTs	1.77 ± 0.86	1.75 ± 0.90	1.49 ± 0.76	0.049 ± 0.006

Table 5-5: The averaged absolute density, averaged envelope density, percentage porosity and specific pore volume for PVDF hierarchical composites (FVC-57 ± 2%) as determined via AccuPyc and GeoPyc

PVDF hierarchical composites with 0 wt%, 2.5 wt% and 5 wt% CNT loading were fabricated on the continuous composite line setup (see Chapter 3). However, alternate layers of 0 wt% and 2.5 wt% CNT reinforced PVDF composites were aligned with reference to a datum and consolidated to get an overall CNT content of 1.25 wt%. Similarly, PVDF composites with a CNT content of 2.5 wt% were also fabricated by mixing the alternate layers of 0 wt% and 5 wt% CNT PVDF composite plies. Table 5-5 shows the average density, percentage porosity and specific pore volume for PVDF hierarchical nanocomposites, which suggests the quality of the consolidation composites, was good enough to provide the true results from the mechanical testing.

5.3.1 Influence of CNT Content of PVDF Hierarchical Composites on Compression Properties

Details for compression strength determination of hierarchical composites are provided earlier in section 3.4.3. The Imperial College of Science, Technology and Medicine jig was used for testing composites in compression (ICSTM) [135]. Specimens, (90mm× 10mm × 2mm), were cut from the laminates using a diamond tipped saw (Diadisc 4200, Mutronic GmbH & Co, Germany). Specimens were bonded with end tabs (CROYLEK, F- glass sheet) to prevent failure at the specimen ends and to diffuse the gripping loads. Strain gauges (FLA-2-11, Tokyo Sokki Kenkyujo Co., Ltd.) on both front and back of the specimens were employed to determine strain, with precise alignment defined in the standard [135]. The compression modulus was obtained from the slope of the stress-strain curve plotted from the data obtained.

Sample	FVC $\overline{V_f}$	σ_c [MPa]	E_c [GPa]	Normalised Stiffness $\overline{E} = E \frac{0.55}{V_f}$ [GPa]	Strain $\mu\epsilon$
PVDF	0.57±0.01	523 ± 56	109 ± 3	105 ± 3	5307 ± 728
PVDF/1.25 wt% CNT (<i>mixed plies</i>)	0.57±0.02	623 ± 28	109 ± 2	105 ± 2	5732 ± 278
PVDF/2.5 wt% CNT	0.57±0.01	447 ± 53	113 ± 7	110 ± 7	4494 ± 607
PVDF/2.5 wt% CNT (<i>mixed plies</i>)	0.56±0.02	460 ± 24	111 ± 5	109 ± 5	4804± 503
PVDF/5 wt% CNT	0.57±0.02	362 ± 30	128 ± 8	123 ± 8	3266 ± 768

Table 5-6: Comparison of compressive strength, compressive modulus, and strain to failure values for PVDF hierarchical composites prepared with AS4 Fibre

The compression performance of all these formulations is provided in Table 5-6. Compression strength of hierarchical reinforced PVDF was increased by 20% with only the addition of 1.25 wt% CNTs but dropped by 14% and 45% when CNT content was further increased to 2.5 wt% and 5 wt% respectively (Table 5-6). The compression modulus (normalised to 55% V_f) is almost similar i.e. 106 ± 5 GPa for hierarchical composites containing 0 wt% and 1.25 wt% CNTs. However, there was a 4% and 17% enhancement observed in compressive modulus of hierarchically reinforced PVDF with the addition of 2.5 wt% and 5 wt% CNTs respectively (see Table 5-6). It was observed that the presence of low CNT content (1.25

wt%) influenced (perhaps stiffened) the matrix which improved its support for the fibres and enhanced the capability of matrix to transfer load to fibres. On the contrary, higher CNT loading, although stiffened the matrix, but affected its impregnation/infusion with fibres and hence reduced the consolidation efficiency of the final composites. It can be stated that there exists a competition in utilizing enhanced stiffness of CNT reinforced nanocomposite and its efficient impregnation with carbon fibres to consolidate composites with superior quality and mechanical performance. This suggests the presence of an optimum limit of CNT loading, where both above mentioned factors can be compromised to avail the requisite enhanced matrix dominated properties in hierarchical composites.

The hierarchical composites containing a nominal loading of 2.5 wt% CNTs were fabricated using two routes, all the plies containing 2.5 wt% CNTs and the composites containing mixed plies of pure CF/PVDF and CF/PVDF containing 5 wt% CNTs resulting in an average CNT content of 2.5 wt%. Both composites had the same modulus of 109 GPa, and the same compressive strength within error, respectively. The small difference in σ_c could be due to the small differences in fibre volume fraction of the composites. Based on these observations, it can be said that the overall CNT content in the composite is affecting the mechanical properties and not the use of similar or mixed plies.

5.3.2 Influence of CNT Content of PVDF Hierarchical Composites on Flexural Properties

Flexural properties give an insight in to mix of tension and compression failures of the unidirectional fibre reinforced composites and is dominated by fibre volume fraction [136]. A flexural strength of 336 MPa was obtained for AS4/PVDF composites, which increased by 56% to about 523 MPa by the incorporation of 1.25 wt% CNTs (mixed plies of AS4/PVDF and AS4/PVDF containing 2.5 wt% CNTs) which however, dropped by 8% when the CNT content was raised to 5 wt% (Figure 5-5). This suggests, in agreement with compression results, that CNTs enhance the matrix stiffness when introduced in PVDF matrix (see Chapter 4). Matrix with improved stiffness supports the fibres strongly which enhances its ability to transfer load from matrix to fibres and thus inhibits microbuckling. However, when CNTs are added beyond this limit, the higher viscosity of nanocomposite powder melt makes it difficult to contact to the carbon fibres sufficiently which caused poor fibre/matrix impregnation and reduced the flexural strength (see fractography). A 12% increase in the flexural modulus of PVDF composites was observed with the addition of 1.25 wt% CNTs which almost

diminished for 2.5 wt% CNT loading and was reduced by 29% for the composites containing 5 wt% CNTs, because of the poor fibre/matrix impregnation at higher contents of CNTs in the composite (Figure 5-6).

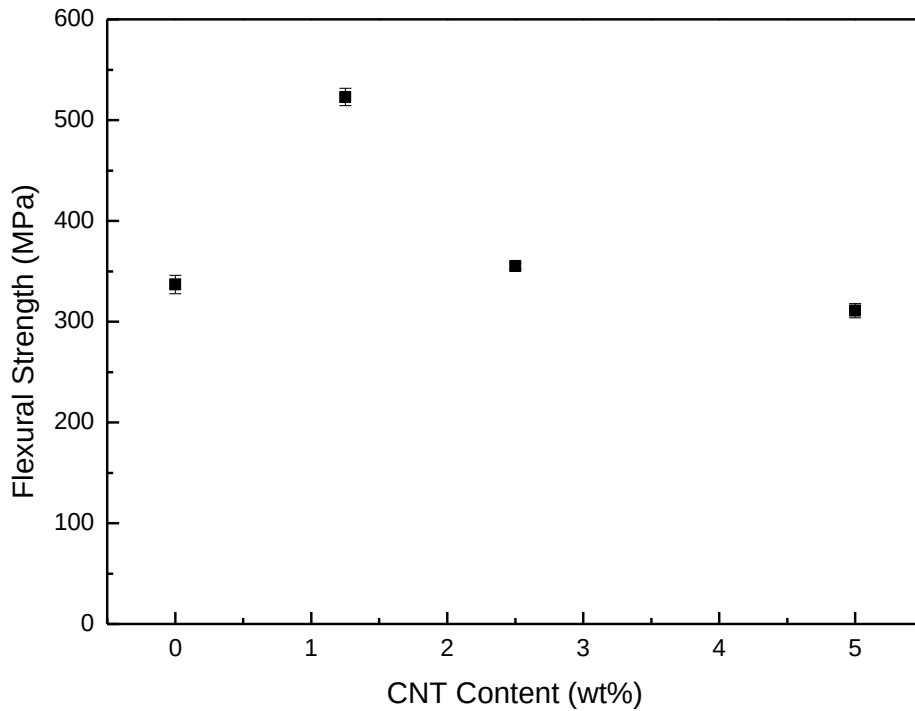


Figure 5-5: Flexural strength of AS4/PVDF composites as a function of CNT content (only AS4/PVDF composites containing 1.25 wt% CNTs are mixed ply composites)

In bending of a unidirectional carbon fibre reinforced composite a complex combination exists of tensile stresses on one face of the laminate (outside), compressive stresses on the other face (inside), and interlaminar shear stresses in the interior of the composites. The span to thickness ratio recommended by ASTM D790 ensured the interlaminar shear stresses are low enough to prevent shear failure. The flexural strength in this case is limited by the compressive strength. The compressive strength of the composite depends on the amount of buckling of the fibres, which depends on the lateral support provided by the matrix. The decrease in strength of hierarchical composites by increasing CNT loading can be explained by poor impregnation/infusion of CNT reinforced matrix in to fibres which adversely affects consolidation and hence decreases the lateral support of fibres at higher CNT loadings. It is likely that the increase in matrix modulus (see Chapter 4) with increase in CNT loading

should have increased the lateral support of the fibres. But with the introduction of CNTs in the polymer, firstly, the available polymer within a polymer nanomatrix, (which is basically an impregnation source between plies) is reduced causing premature failure due to fibre buckling and secondly the higher viscosity of nanocomposite melt make it difficult to impregnate to the carbon fibres completely causing the poor matrix infusion at fibre/matrix interface which is a compulsory requirement to avail the enhanced matrix dominated properties in hierarchical composites. Particularly when the matrix is PVDF, it is difficult to ensure good interfacial adhesion with reinforcing fibres because of the lack of compatibility between them. Carbon fibre composites seem to be more sensitive to this effect when impregnation is poor, probably because of the lower failure strain of carbon fibres [87]. Buckling of fibres with a lower failure strain will lead more quickly to fibre/matrix adhesion failure with in a ply and subsequent composite failure.

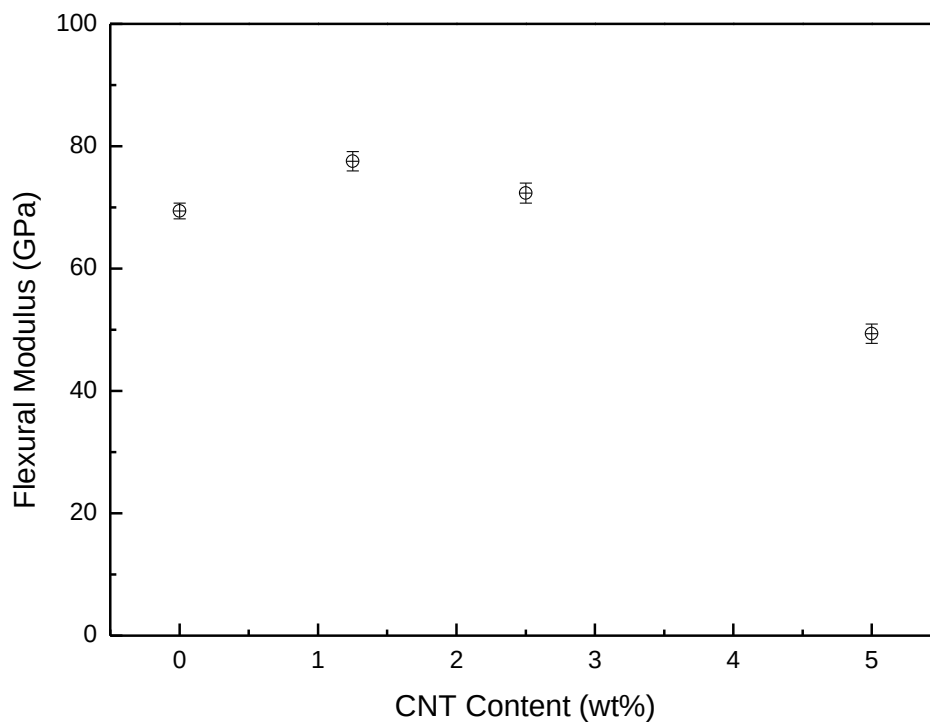


Figure 5-6: Flexural modulus of AS4/PVDF composites as a function of CNT content (only AS4/PVDF composites containing 1.25 wt% CNTs are mixed ply composites)

5.3.3 Influence of CNT Content of PVDF Hierarchical Composites on Short Beam Shear Strength

The short beam shear test is a three point bending test leading to through thickness shear and thus interlaminar shear strength of CFRPs without translaminar failure [14]. During the course of a SBS test, the three point bending load rises as a function of displacement until compressive failure of the upper surface occurs under the loading [110]. When the specimen was exposed to a steady state load, the load is conveyed from the matrix to the fibres via the interface and is in this case directly related to the shear stress producing interfacial failure [14]. In agreement with the standard, the steady state load was used for the calculations of the short beam shear strength.

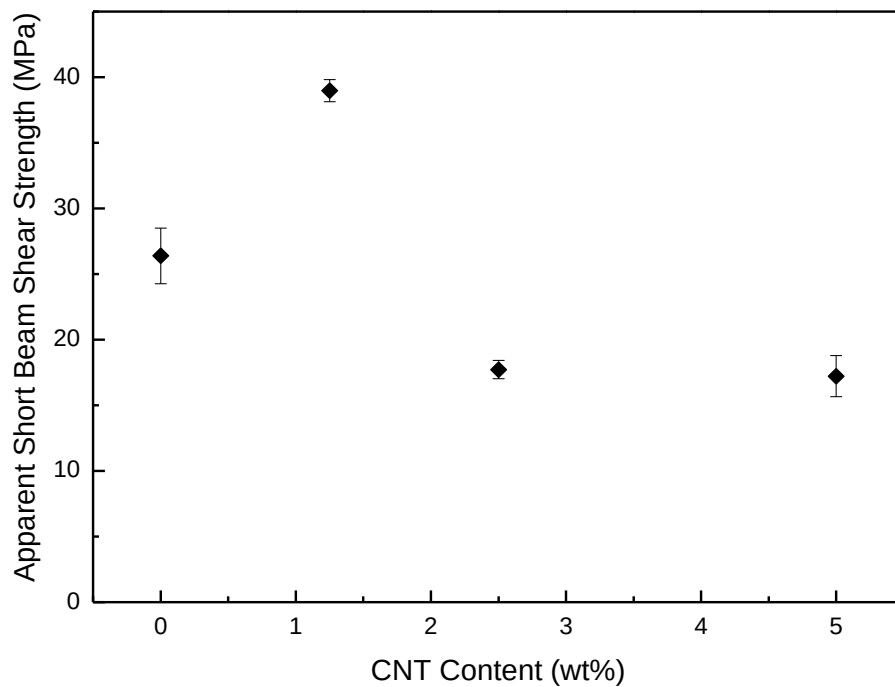


Figure 5-7: Apparent short beam shear strength of AS4/PVDF composites as a function of CNT content (only AS4/PVDF composites containing 1.25 wt% CNTs are mixed ply composites)

A 50% increment was observed of the apparent short beam shear strength (SBS) of carbon fibre reinforced PVDF/CNT nanocomposites by introducing only 1.25 wt% CNTs (mixed plies). However, on increasing CNT content up to 2.5 wt% and 5 wt%, a 49% and 53% drop

in SBS was observed respectively, as compared to AS4/PVDF composites. This suggests the presence of poor lateral support between the PVDF nanocomposite matrix and AS4 possibly due to poor impregnation of fibres by nanocomposite matrix. Furthermore, the addition of CNTs beyond a certain limit is probably, limiting the presence of polymer in nanocomposite matrix to take part in interfacial adhesion. One of the possible reasons could be the availability of more surface area of CNTs rather than PVDF to impregnate carbon fibre in the CFRP in addition to higher viscosity of nanocomposite melts which could adversely effect the impregnation/consolidation in hierarchical composites at higher loadings of CNTs. This suggests the existence of an optimum loading limit for CNTs around 1.25 wt%, at which fibre/matrix impregnation is not compromised and enhanced interlaminar shear strength is availed. However, the addition of CNTs beyond this limit, effects the consolidation in hierarchical composites which in turn effects fibre/matrix lateral support (which is responsible for load transfer from matrix to fibres) resulting in poor mechanical performance.

5.3.4 Influence of CNT Content of PVDF Hierarchical Composites on Fracture Toughness

DCB tests were performed on the carbon fibre reinforced composites; however, very little usable data ($G_{\text{propagation}}$) was obtained initially (three to ten data points for each specimen). The reason for the lack of usable data was the initiation of a number of secondary cracks away from the mid-plane caused by apparent delamination between the plies. The idea behind mode I fracture toughness measurements is to determine the energy release rate of a single crack [98], therefore the presence of multiple cracks/delamination failures invalidates the test. These additional cracks would result in an artificially high toughness because of fracture events away from the midplane contributing to the ‘toughening’ mechanism. The multiple delamination failures eventually led to the compressive failure of one of the arms of the DCB specimens. In order to avoid such failures, arm thickness of the DCB specimens was increased to 8 mm by adding further AS4/PVDF doublers, which resulted in the elimination of secondary cracks/delaminations.

Eventually, the steady state mode I fracture toughness of hierarchical reinforced PVDF composites could be measured using the DCB. The steady state energy release rate ($G_{\text{IC,ss}}$) was calculated using modified beam theory (see Chapter 3). Figure 5-8 represents load displacement curves from DCB tests of hierarchical reinforced PVDF composites containing

2.5 wt% CNTs. A mixture of stable and unstable crack propagation was observed in failed DCB specimens.

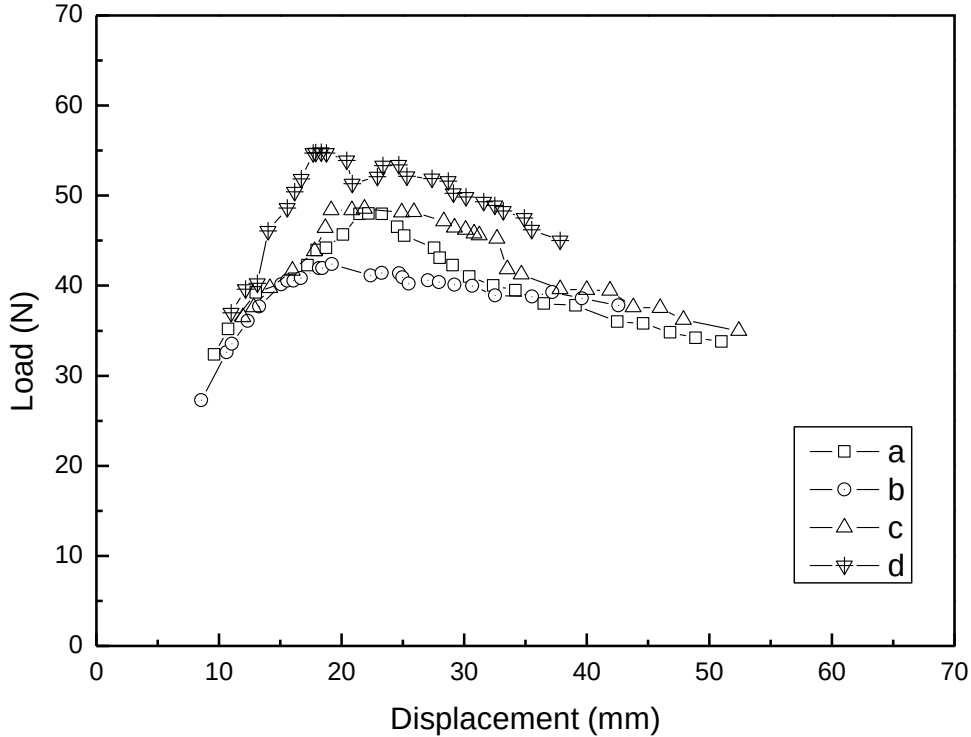


Figure 5-8: Load displacement curves from DCB testing of 4 nominally identical specimens (a-d) of hierarchical reinforced PVDF composites containing 2.5% CNTs

G_{IC} as a function of crack length (Figure 5-9) for PVDF hierarchical composites shows that the energy release rate stabilises rapidly and forms a steady state plateau with increasing crack length. Therefore, a crack length of 70 mm was chosen as the steady state propagation point where all the specimens presented steady state plateau of G_{IC} . The analysis of the results indicated that $G_{IC,ss}$ (i.e. G_{IC} at $a = 70$ mm) for PVDF composites without CNTs, was $2464 \pm 83 \text{ J/m}^2$, which was 45% higher than that of APC-2 ($G_{IC}: 1700 \text{ J/m}^2$) [36]. There was no significant difference in the steady state critical energy release rate, when the CNTs in the hierarchical composites were raised to 1.25 wt% (mixed plies) except for a larger scatter i.e. $2410 \pm 187 \text{ J/m}^2$. Conversely, Arai et al. [21] previously showed a 50% improvement in fracture toughness of carbon fibre-epoxy CFRPs toughened by a carbon nanofibre/epoxy interlayer. Also, cup stacked CNTs (CSCNT) dispersed CFRP laminates with thin epoxy interlayers containing 5 wt% short CSCNTs had shown a three times higher fracture

toughness than CFRP laminates without CSCNT [137]. However, the fracture toughness of PVDF hierarchical composites containing 2.5 wt% and 5 wt% CNTs decreased by 39% and 44% , respectively as compared to pure AS4/PVDF composites. This opposes the results obtained from a number of hierarchical polymer composites containing nanreinforcements showing significant improvement in fracture toughness [21, 92, 93, 137]. This explains how the poor impregnation of carbon fibres by PVDF nanocomposite matrix negatively affects the carbon fibre-PVDF interface and hence the fracture toughness of PVDF hierarchical composites.

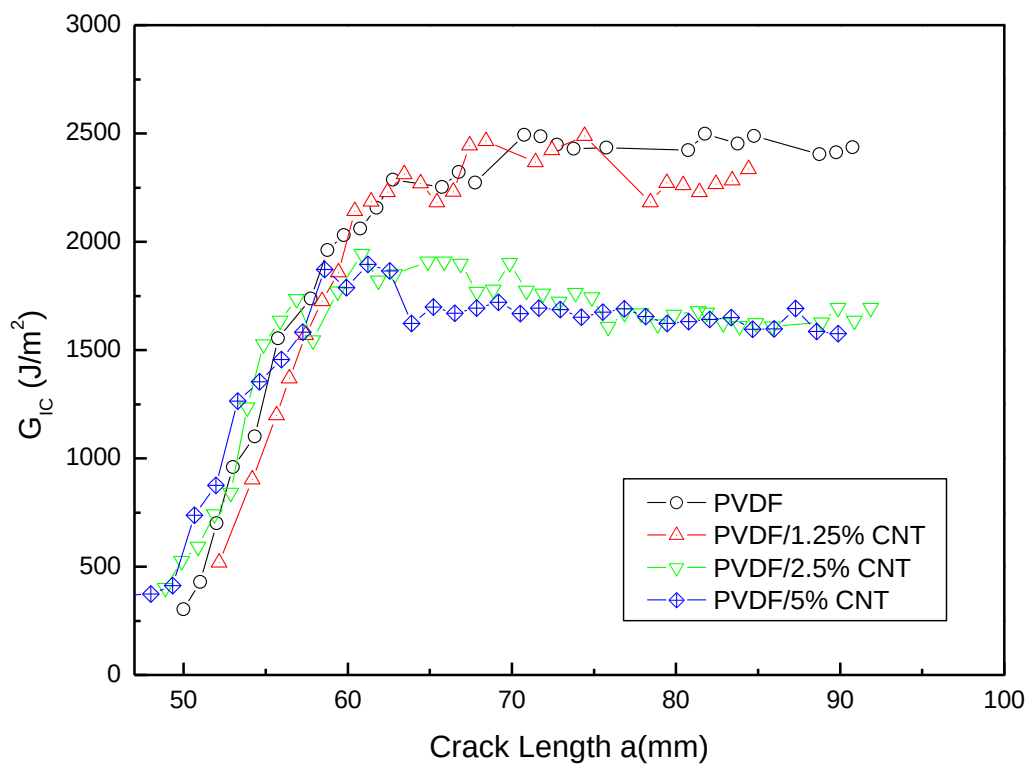


Figure 5-9: Delamination resistance curve for AS4/PVDF hierarchical composites containing A) 0 wt%, B) 1.25 wt% (mixed plies), C) 2.5 wt% and D) 5 wt% CNTs (one representative curve is plotted for each composite out of the six specimens tested)

Figure 5-10 presents the initiation and propagation values for the energy release rate for PVDF hierarchical composites. The initiation value provides a gauge of matrix dominated properties whereas propagation values provide information in to the quality of fibre/matrix interface. The higher $G_{initiation}$ value for PVDF containing 1.25 wt% CNTs indicated crack tip

blunting. An increased resin concentration around the crack tip could be the cause of this increased local toughness. The stored elastic energy had to build up until there was sufficient driving force to break the plastic zone at the crack tip for the crack to propagate further. This mechanism could take long and fibre breakage could have occurred during the process as well. The drop in $G_{\text{initiation}}$ values indicated either the poorer matrix dominated properties at higher loading of CNTs (which contradicts the findings mentioned in chapter 4, so could not be considered a valid option) or less amount of matrix at the crack tip (discussed later in the fractography section). The drop in the critical energy release rate at a crack length of 70 mm indicated the fact that quality of fibre/matrix interface is lowered due to poor impregnation of carbon fibre by nanocomposite matrix at higher CNT loading resulting in a decrease in fracture toughness of PVDF hierarchical composites. Fractographic analysis was conducted to get an insight in to the reason for this decrease.

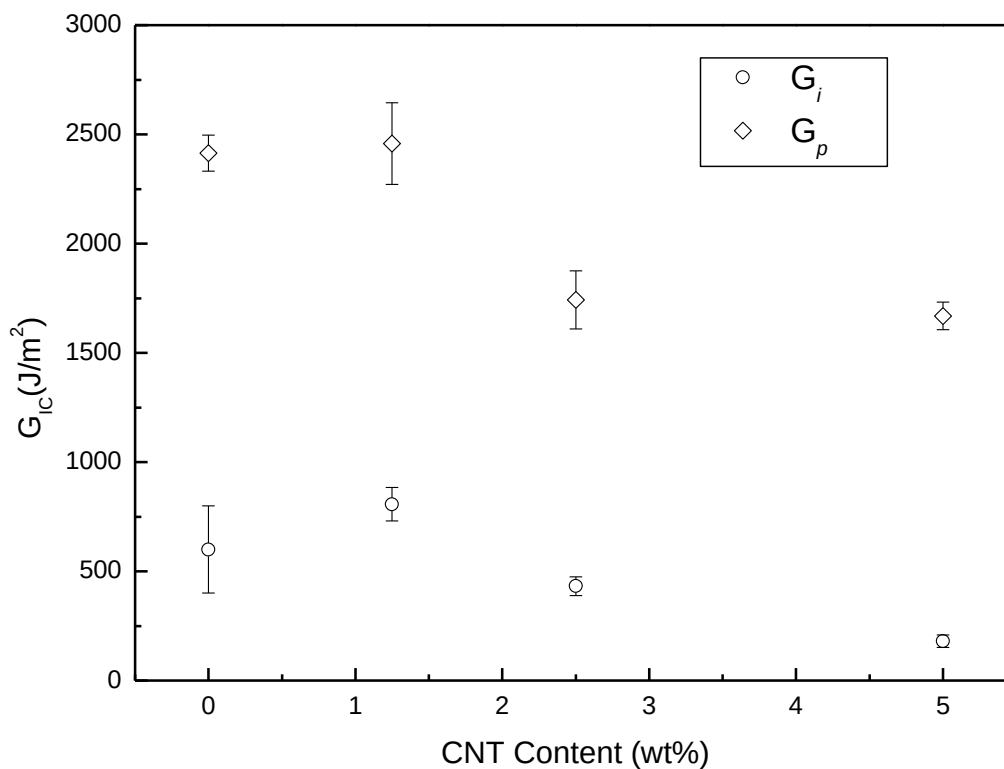


Figure 5-10: $G_{\text{initiation}}$ (G @ 50mm) and G_{plateau} (G @ 70mm) values for AS4/PVDF hierarchical composites as function of CNT loading (only AS4/PVDF composites containing 1.25 wt% CNTs were mixed ply composites)

5.4 Fractography of PVDF Composites

Fracture surfaces of compression and DCB failed specimens were analysed to understand the damage modes and failure mechanisms. Electron micrographs of three nominally identical specimens of each formulation were taken and compared to identify inherent differences.

5.4.1 Fractographic Analysis of Compression Failed PVDF Composites

Fractographic assessment of compression failures was conducted to understand the damage modes of failure. Crosssections of the failed compression specimens were prepared according to the Buehler's standard procedure for soft composites (see Chapter 3) and analysed using an optical microscope (BH2, Olympus, Tokyo, Japan). The basic modes of fracture under compressive loading include microbuckling and macrobuckling. (Figure 5-11) Macrobuckling (often called crippling) involves failure of the specimen structure in a combined flexural-compressive manner.

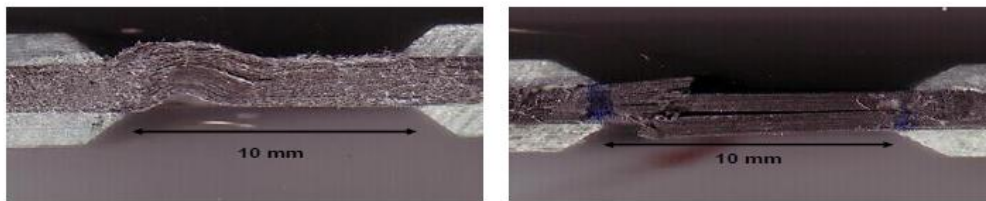


Figure 5-11: Photographs showing the cross sections (gauge regions) of failed compression specimens, (Left) macrobuckling, (Right) fracture after microbuckling [17]

Pure AS4/PVDF composites failed via classic kinkband formation, with a single band across the entire specimen (Figure 5-12 (A)). When the failure load was approached in the composite, the fibres began to buckle locally under the action of the compressive strain, taking on an S-shaped profile. Fracture occurred in the curved section of the fibres at the point of maximum flexure, resulting in a kinkband formation. Tensile and compressive fracture zones were separated by a neutral axis in the individual fibres. Large bundles of fibres were collapsed in the same direction resulting in successive rows of buckled fibres. Microbuckling occurred in several planes giving rise to a series of steps on the fracture surface, each step being a multiple of half the buckling wavelength. It can be said that the general axis of buckling exhibited the origin of the failure. The failure was due to shearing of fibres or microbuckling which suggests that the upper bound of the achievable compression strength was reached in these composites. There was negligible delamination and the kinkbands

extended across the entire specimen, suggesting that delamination resistance is not an issue for the pure AS4/PVDF composites.

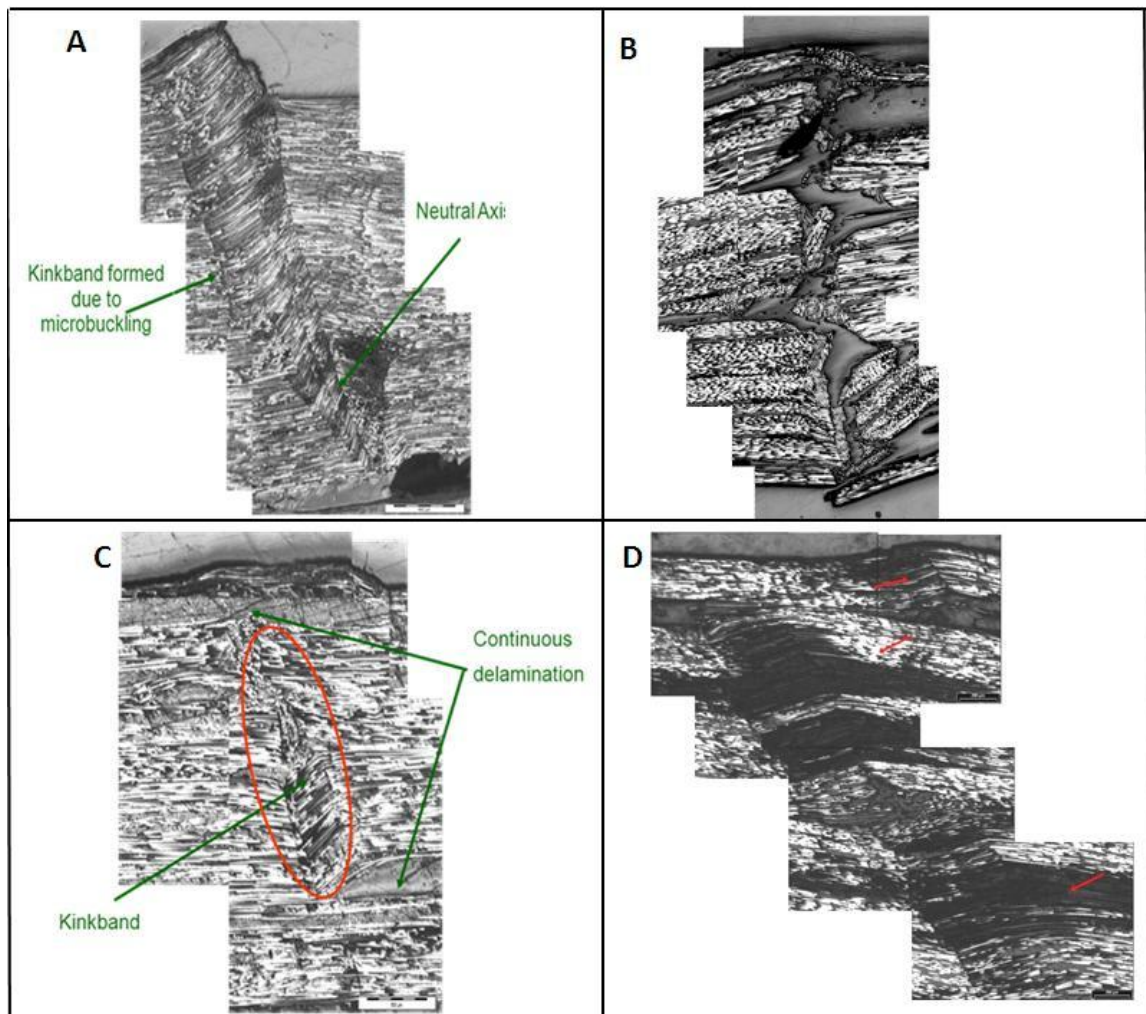


Figure 5-12: Typical crosssections (2 mm in thickness) of composite specimens failed in compression A) localised kinkband/translaminar fracture observed for AS4/PVDF composites (B) catastrophic failure after the formation of kinkband for AS4/(PVDF + 1.25wt% CNT) composites, C) continuous delaminations for AS4/(PVDF + 2.5wt% CNT) composites and D) delamination prevalent over kinkbands for AS4/(PVDF + 5 wt% CNT) composites

Hierarchical composites containing alternate plies of AS4/PVDF and AS4/ (PVDF + 2.5 wt% CNT) failed catastrophically as shown in Figure 5-12 (B) after the formation of a localised kinkband which suggests a true compressive failure caused by microbuckling (out of plane) or shearing of fibres. Such a catastrophic failure after an unstable microbuckling without any delamination suggests that the maximum compressive strength was reached. The presence of alternate AS4/PVDF plies between AS4/(PVDF + 2.5 wt% CNT) plies is thought to improve

ply-ply impregnation and an enhancement in quality of consolidation in PVDF hierarchical composites containing an overall CNT content of 1.25 wt%.

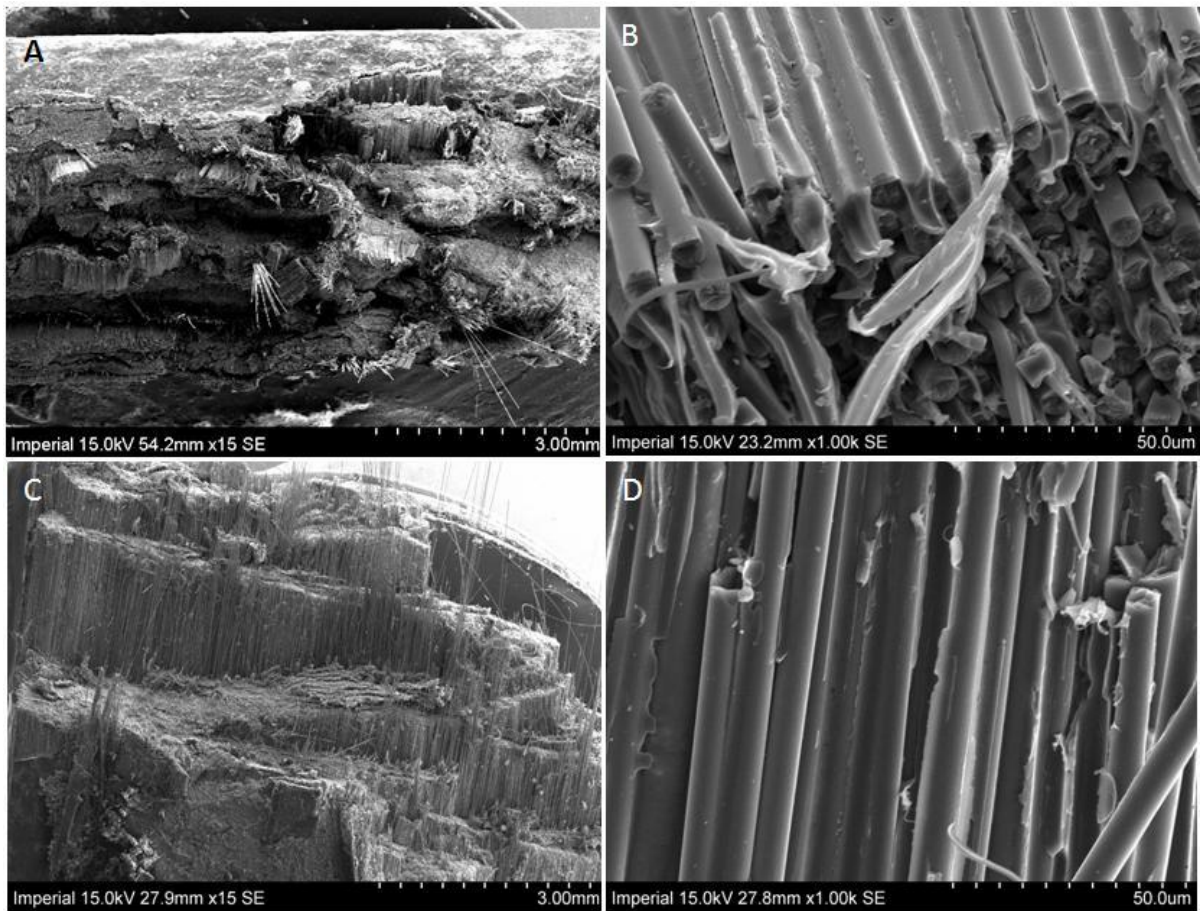


Figure 5-13: Typical SEM images of fracture surfaces of composites failed in compression at different magnifications: AS4/PVDF (A) $\times 15$, (B) $\times 1K$, AS4/PVDF + 2.5wt% CNT (C) $\times 15$ and (D) $\times 1K$

Hierarchical composites containing 2.5 wt% and 5 wt% CNTs in the PVDF matrix failed very differently; a deep kinkband formed in the middle of the crosssection with continuous delaminations at the both ends of the kinkband (Figure 5-12 C) in the area surrounding the middle crosssection of the compression specimen (edges). There was extensive delamination in between the plies (splitting) as well as between the consolidated tapes, which developed before compression failure occurred. There were numerous examples where delaminations were continuous across the end of a kinkband, as shown in Figure 5-12(C, D), implying that delamination was the first failure mode. The kinkbands were not very deep, again implying delamination was prevalent. This prevalent delamination might be due to poor impregnation of the fibres by such a viscous PVDF nanomatrix containing high CNT loadings of 2.5 wt% and 5 wt% when used in the hierarchical composites. As the delamination was the first failure

mode instead of kinkband formation, the maximum compression stress was not achieved. Thus hierarchical composites with PVDF nanocomposite matrices have the potential to achieve the upper bound of the compression strength if only full impregnation of the fibres could be achieved by such viscous nanomatrices. There was a lot more loose resin in hierarchical composites containing 2.5 wt% CNT, and some regions, particularly close to the specimen faces, seemed rather fibre rich indicating that the fibres were poorly bonded to/impregnated by the surrounding matrix (Figure 5-12). This can be clearly seen in Figure 5-13 (C, D) where loose dry fibres are visible in the hierarchical composite containing 2.5 wt% CNT when compared to well impregnated fibres in the pure AS4/PVDF composites (Figure 5-13 (A, B)).

5.4.2 Fractographic Analysis of Failed PVDF DCB Composites

The fracture surface of the DCB samples was investigated to determine the behaviour of the composites under mode I crack growth conditions. Visually, mode I fracture surfaces are rough in texture because of numerous broken fibre ends but flat, dark and spectrally reflective [138]. Visual inspection of cracks revealed that fibre bridging was very prevalent during crack growth. Considering the SEM micrographs of the fracture surfaces of failed DCB specimens of pure AS4/PVDF composites (no CNTs) shown in Figure 5-14, it is clear that no consistent resin rich layers existed and the carbon fibres from the neighbouring plies were nesting within each other. Fibre nesting is known to promote fibre bridging as a mode I toughening mechanism [138].

Also all the hierarchical composites exhibited extensive fibre bridging, the extent of which tended to increase with increasing crack length. It was clear from the SEM micrographs (see Figure 5-14, Figure 5-15 and Figure 5-16) that all hierarchical AS4/PVDF composites exhibited some ductile drawing of the matrix. A small amount of polymeric debris was also present on the fibre surfaces. This observation suggested that although the interface between PVDF and AS4 was thought to be relatively poor [139], matrix plastic deformation contributed, at least slightly, to the mode I fracture toughness and the fracture did not entirely occur at the carbon fibre-PVDF interface.

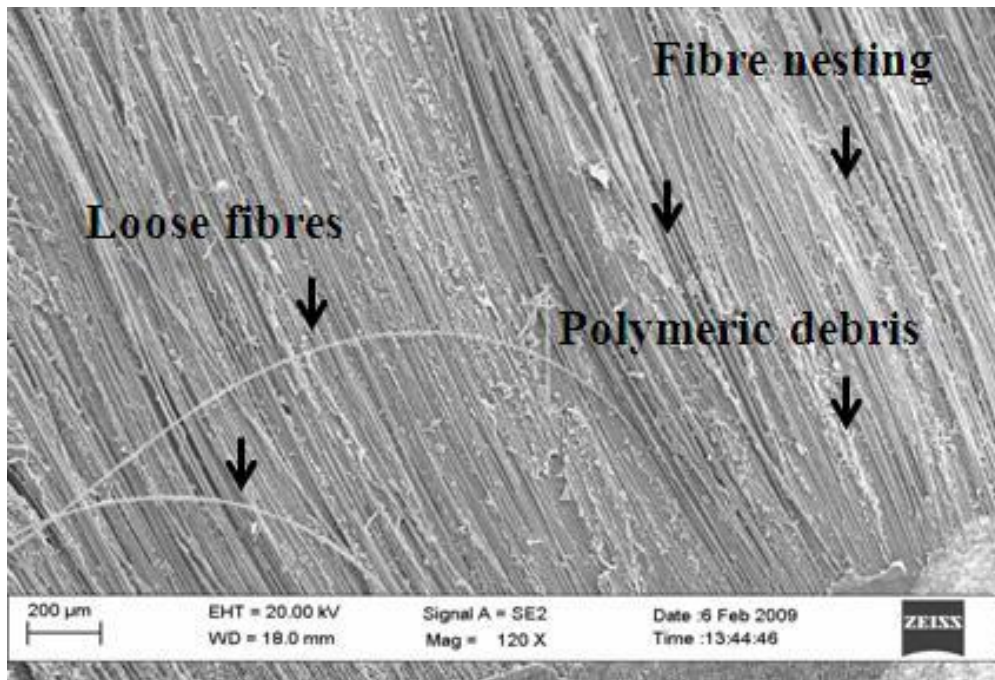


Figure 5-14: A typical SEM micrograph representing the fracture surface of a failed DCB specimen of AS4/PVDF composites ($\times 120$)

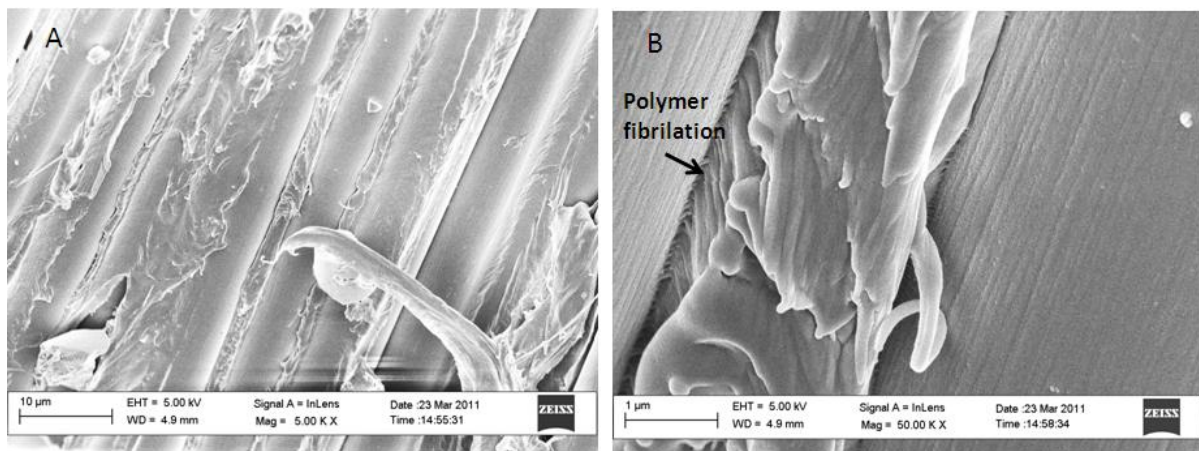


Figure 5-15: Characteristic SEM micrograph of a DCB fracture surface of carbon fibre reinforced PVDF showing PVDF fibrillation between AS4 carbon fibres at A) lower magnification ($\times 5k$) and B) higher magnification ($\times 50k$)

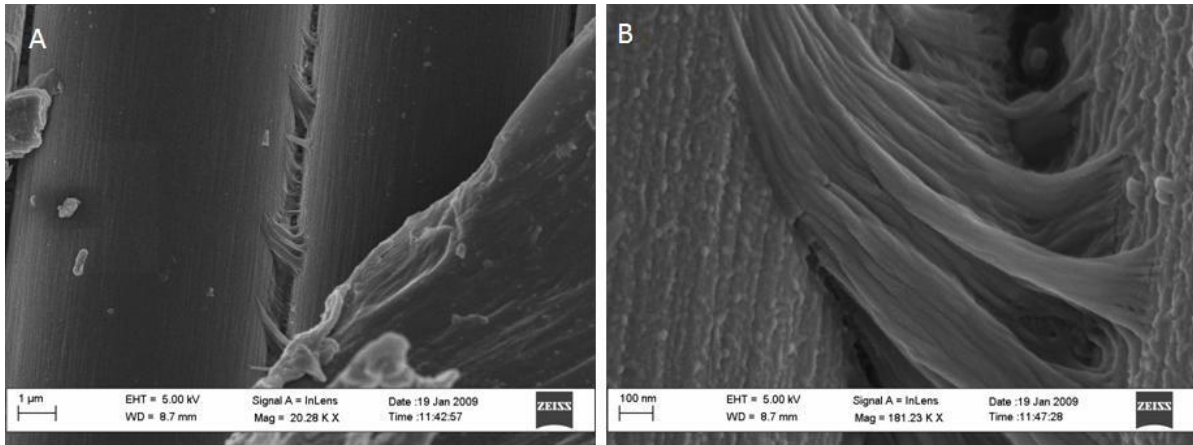


Figure 5-16: Characteristic SEM micrograph showing the polymer drawn between the fibres in hierarchical reinforced PVDF containing 2.5 wt% CNTs at A) lower magnification ($\times 20k$), B) higher magnification ($\times 181k$)

In general, for tough thermoplastic materials, the fracture energy is principally absorbed through void-coalescence, large scale ductile drawing and fibrillation [138]. The degree of drawing varies positionally with respect to the fibres and is at a maximum between the fibres where there is a minimum volume of matrix. In carbon fibre reinforced PVDF nanocomposite matrices, the matrix is drawn away from the interface, towards the mid plane, in places leaving the fibre surface appearing to be almost devoid of polymer, although closer inspection reveals fine polymer nodules remain on the surface (see Figure 5-16 and Figure 5-17).

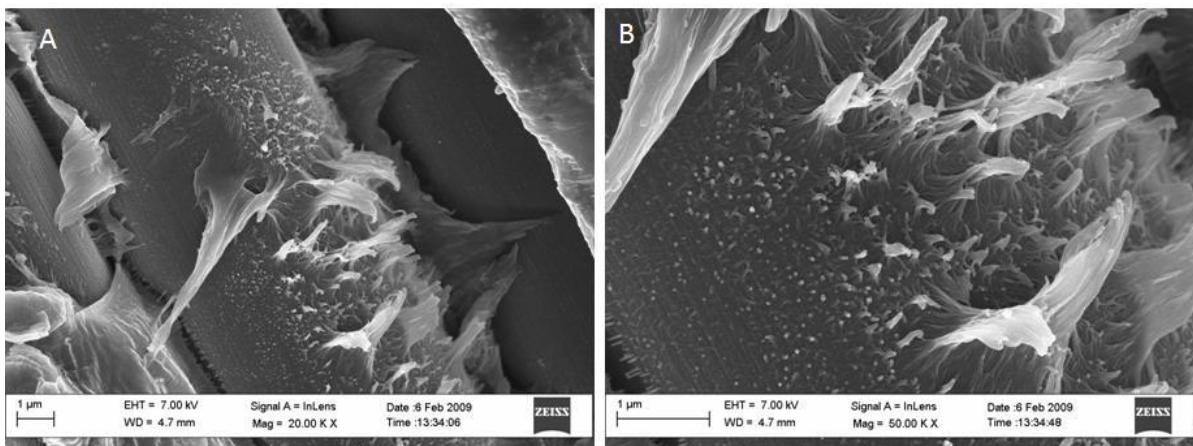


Figure 5-17: Characteristic SEM micrograph showing drawing of PVDF nanocomposite matrix containing 2.5 wt% CNT from fibre surface shown in the form of polymer nodules (during DCB fracture) at A) lower magnification ($\times 20k$) B) higher magnification ($\times 50k$)

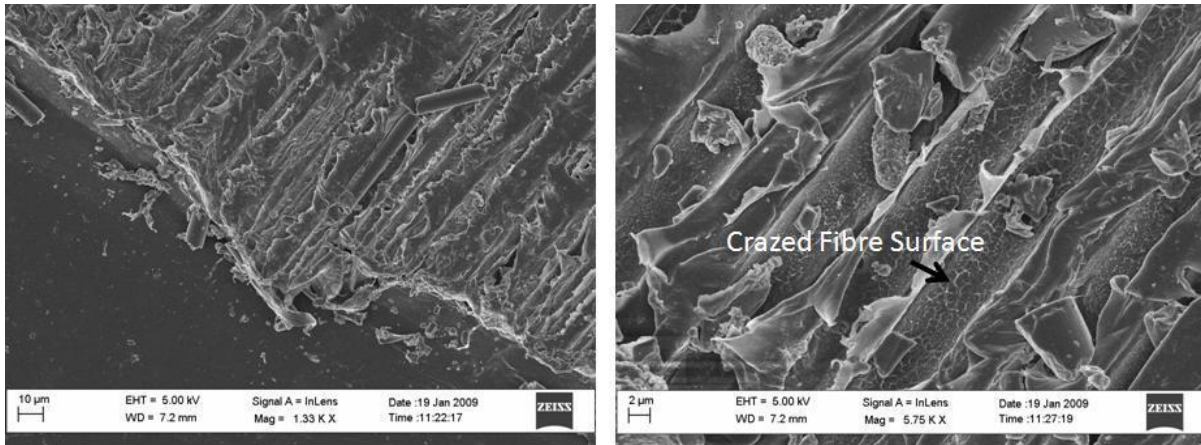


Figure 5-18: Typical fracture morphology of PVDF hierarchical composites containing 2.5 wt% CNTs shows brittle features caused by presence of CNTs i.e. the globules in the form of a filigree of star like patterns

It is clear from the SEM images (Figure 5-17, Figure 5-18) that the pure AS4/PVDF composites show continuous fibrillation between fibres, whereas hierarchical reinforced PVDF containing 2.5 wt% CNTs depicted fibrillation but at a lower level, which depended on the locations between fibres. This suggests there is a difference in the quality of the fibre/matrix interfaces in AS4/PVDF and AS4/(PVDF + 2.5 wt% CNT) probably caused by insufficient impregnation. The lower scale of fibrillation indicates that less energy was needed to carry out fracture and hence indicates a material with lower toughness.

Another example is shown in Figure 5-18 which shows a DCB fracture surface for AS4/PVDF composites, the regions of matrix between two close fibres experienced extensive plastic deformation forming fibrils. The areas indicating fibrils means fracture occurred slowly resulting in ductile drawing. However, crazed appearance of the fibres suggests that little plastic deformation had occurred giving rise to cleavage type morphology.

Toughened high performance thermoplastic materials exhibit a rate sensitivity in their toughness which is reflected in their fracture morphology [138]. At slower rates of crack propagation, the matrix has more time for plastic deformation and fibrillation. However, at higher rates, more brittle features and fracture planes tend to develop at the fibre/matrix interface. The embrittlement is characterised by the presence of uniformly distributed small globules over the fracture surface, produced through rapid drawing and ultimately fracture of polymer chains. As the test rate was fixed (2mm/min) for all composites/hierarchical composites, the occurrence of brittle features on the fracture surface of hierarchical

composites indicated the embrittling of the matrix caused by the presence of CNTs (see Figure 5-18).

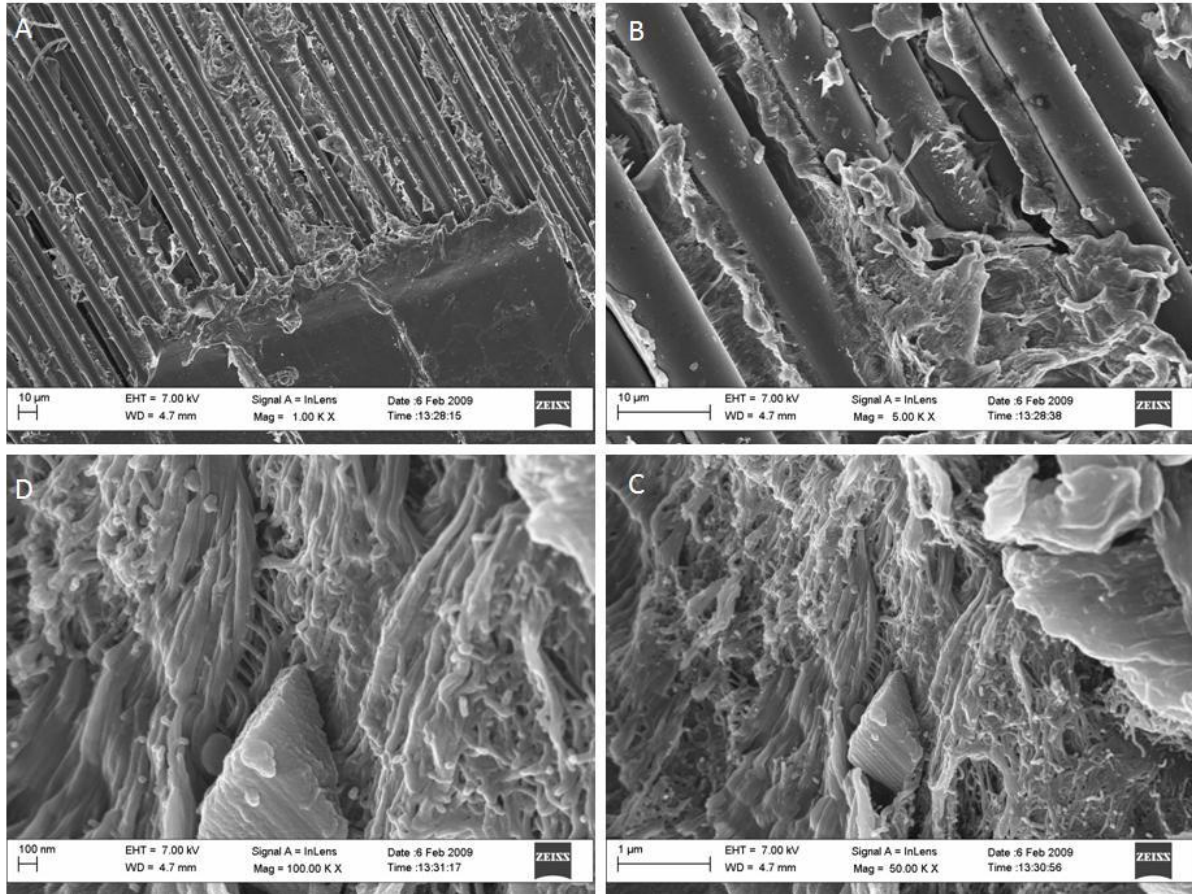


Figure 5-19: Characteristic DCB fracture surfaces of hierarchical reinforced PVDF containing 2.5 wt% CNT with increasing magnification clockwise from A to D

The extent of fibre/matrix interface strength can also be explained from the surfaces of the fibres and the fibre imprints in the resin. A cohesive failure of the matrix around the fibre leaving the fibre extensively covered with the matrix residue indicates an excellent fibre/matrix bond whereas adhesive failure along the fibre/matrix interface, leaving the fibre clean means poor fibre/matrix bonding. This also explains the fibre/matrix bond is getting adversely affected at higher CNT loading due to insufficient fibre/matrix impregnation. By comparing Figure 5-15 and Figure 5-19 it is clear that although there is still good fibrillation and matrix drawing involved in fracture mechanism for PVDF hierarchical composites containing CNTs, it is much lower than AS4/PVDF composites (no CNTs). Furthermore,

fibres look drier in PVDF hierarchical composites as compared to AS4/PVDF composites (no CNTs) possibly due to insufficient fibre/matrix impregnation.

5.5 Conclusion

PVDF nanocomposite powders were prepared using a solution precipitation method to be used for manufacturing hierarchical PVDF composites using the in-house continuous composite line. The average particle size (d_{50}) for nanocomposite powders increased with increased CNT content, from 17 μm for composites without CNTs to 30 μm for composites containing 5 wt% CNTs which lies in the appropriate range required for slurry impregnation of carbon fibres [17]. The increase in particle size was probably indicative of agglomerate formation at higher loading of CNTs. Fabrication of unidirectional carbon fibre reinforced PVDF hierarchical composites was optimised. The fibre volume content of AS4/PVDF composites was controlled to be $57\% \pm 2$ throughout the preparation procedure. The good quality of the final hierarchical composites fabricated at various consolidating pressures, from the as produced AS4/PVDF tapes, was confirmed from the constant density and negligible porosity values. The constant percentage crystallinity value ($39 \pm 3\%$) of all composites suggested that mechanical performance of composites can be totally attributed to the addition of nanoreinforcement.

Mechanical performance of pure CF/PVDF composites and hierarchical composites containing 1.25 wt% (mixed plies), 2.5 wt% and 5 wt% CNTs was investigated. Results from the mechanical testing of AS4/PVDF hierarchical composites show a 20% increase in compression strength, 56% increase in flexural strength and a 50% increase in apparent interlaminar short beam shear strength by the incorporation of 1.25 wt% CNTs, which indicates an improvement in interfacial adhesion i.e. fibre/matrix bonding. However a 14% and 45% drop in compression strength, negligible and 8% drop in flexural strength and 49% and 53% drop in short beam shear strength was observed by increasing of CNT content to 2.5 wt% and 5 wt% respectively. A negligible change was observed in compression modulus with CNT loading of 1.25 wt% but a 4% and 17% enhancement was observed by increasing the CNT loading to 2.5 wt% and 5 wt%. Correspondingly, an 11% increase in flexural modulus of PVDF composites was observed with the addition of 1.25 wt% CNTs but reduced by 29% for the composites containing 5 wt% CNTs because of the poor fibre/matrix bonding at higher contents of CNTs in the composite. These results indicate that quality of fibre/matrix interaction was improved with an optimum loading of CNTs at 1.25 wt% in

hierarchical composites. But beyond this limit, further addition of CNTs reduces the fibre/matrix adhesion which results in poor mechanical performance. The fracture toughness of AS4/PVDF hierarchical composites remained unaffected by increasing the CNT content up to 1.25 wt%. On the contrary, a 44% drop in the fracture toughness was observed at 5 wt% loading of CNTs.

Fractographic analysis was conducted to investigate the influence of CNT concentration on the fibre/matrix interface. The addition of CNTs to the composite matrix resulted in occurrence of brittle fracture features which suggests that CNTs have affected the rate sensitivity of the PVDF. As a result, hierarchical composites showed an adhesive failure at the junction between fibre and matrix, leaving the fibre clean meaning that fibre/matrix bonding/strength was decreased with increasing the CNT loading. In addition, the high number of twists in the tows of the AS4 fibres (AS4 fibres tows contain a twist every 1.1 m on average [14]) the PVDF hierarchical composites containing AS4 did exhibit improvement in flexural and short beam shear strength, which suggests that the influence of twists in the tow is marginal. In conclusion it can be said that the quality of the composites produced using our modular laboratory scale composite production line is improved with an optimum loading of CNTs.

Overall, PVDF hierarchical composites containing 1.25 wt% CNTs did exhibit the best mechanical performance over all composites. They were fabricated by consolidating a mixed ply setup containing alternate layers of AS4/PVDF and AS4/(PVDF +2.5 wt% CNT). The presence of AS4/PVDF plies in between the hierarchical PVDF composite plies actually provides the sufficient matrix which enhances fibre/matrix impregnation and binds the plies together. This suggests that, somehow by increasing the resin content between the hierarchical composite plies, adhesion in between them can be improved. However, the same architecture when employed for hierarchical composites containing 2.5 wt% CNTs obtained by consolidating alternate plies of AS4/PVDF and AS4/(PVDF composites containing 5 wt% CNTs) resulted in no improvement in mechanical properties (as explained in compression results). This might indicate that by increasing the CNT content, the polymer content available to impregnate itself on CF gets lowered. An interesting approach would be to increase the polymer content in the hierarchical composites i.e. either by decreasing the fibre volume fraction or by introducing polymer films in between hierarchical composite plies. This should provide the necessary adhesion required to explore beneficial CNT potential in

hierarchical composites at higher loadings. The mechanical performance of PVDF hierarchical composites can be improved by improving the wettability between PVDF and CF or by improving the dispersion even further. In future, the use of modified PVDF or modified CNTs potentially could improve the mechanical performance of PVDF hierarchical composites due to enhanced fibre/matrix wetting and improved fibre/matrix interface.

Chapter 6 - Carbon Fibre Reinforced Modified PVDF (25 wt% MAH-g-PVDF) Hierarchical Composites

6.1 Introduction

It is generally difficult to ensure good interfacial adhesion between thermoplastics, more specifically PVDF, and the reinforcing fibres because of the lack of compatibility between them [140]. This is because of the lack of reactive groups in PVDF (as compared to thermosetting systems and, indeed, other engineering thermoplastics) along with its inert nature which limits the level of interaction between the reinforcement and the matrix [140]. So far, there have been only a few studies investigating routes to improve the adhesion between fluoropolymers and carbon fibres, and these studies have focused just on the effect of fibre surface treatment [50, 54]. When considering the improvement in compatibility between carbon fibres and fluoropolymer matrices, two alternative methods have been employed in the past for modifying a matrix [17] which are either to introduce a miscible secondary polymer into the primary matrix [141] or modification of the homopolymer with moieties that promote adhesion [17, 142]. This chapter focuses on the use of a modified homopolymer matrix (MAH-g-PVDF) to interact and/or react with conventional carbon fibres as a source to enhance adhesion.

Surface composition of AS4 carbon fibres as determined via X-ray photoelectron spectroscopy (XPS) is reported to have a carbon, nitrogen and oxygen content of 88.5%, 2.4% and 10.6% respectively [139]. The presence of a variety of functional groups on the surface of the carbon fibres was not expected to result in any enhanced interaction with pure PVDF [54].

However, some of the functional groups existing on the carbon fibres especially oxygen containing ones should favourably interact or even react with the MAH in MAH-g-PVDF [139] which could address the weak interface in AS4/PVDF composites. PVDF (Kynar 711) was modified by the inclusion of 25 wt% maleic anhydride grafted PVDF (Kynar ADX-121) through a solution precipitation method (see Chapter 3) forming a modified PVDF blend (MPVDF). The quality of the interface between MPVDF and AS4 was already been analysed by direct contact angle measurements and single fibre pull out tests [124, 139]. The excellent wetting and adhesion between PVDF and epoxy sized carbon fibres (AS4-GP) could be attributed to a grafting reaction between the epoxide in the sizing on the surface of the AS4-GP and MAH in MAH-g-PVDF [28]. The addition of 25 wt% MAH-g-PVDF to PVDF was proven to increase the interfacial shear strength by 184% as compared to unmodified PVDF with unsized AS4 [28]. With the incorporation of maleic anhydride (oxygen) significant surface oxygen emerges in PVDF associated with carbonyl and ether moieties of the anhydride formed during processing [17]. Since MAH opens to a dicarboxylic acid, hydrogen-bonding may be the only mechanism for enhanced adhesion (as opposed to reactive grafting).

The objective of this study was to investigate the mechanical performance of MPVDF CFRPs by introducing structural hierarchy in them, which was achieved via incorporation of CNTs into the MPVDF matrix. The presence of nanotubes in the matrix interface was expected to improve matrix dominated properties of AS4/MPVDF composites. Matrices with 0 to 5 wt% CNT loading were fabricated through solution precipitation method and reinforced with unidirectional carbon fibres (AS4), to fabricate hierarchically-reinforced MPVDF composites (see chapter 3 for details). Moreover, details about particle size distribution of the MPVDF nanocomposite powder produced is also described in this chapter. Manufactured composite tapes were compression moulded into test specimens to study the influence of CNT content on the mechanical performance of the composites. The consolidation parameters for compression moulding of hierarchically reinforced MPVDF composites were optimised based on the quality of the composite obtained at various processing conditions. The mechanical performance of in-house manufactured AS4 carbon fibre reinforced MPVDF with various CNT loadings of 0 wt%, 1.25 wt%, 2.5 wt% and 5 wt% was investigated in compression and flexure. Furthermore, interlaminar shear strength and fracture toughness tests were also been conducted for MPVDF hierarchical composites and the results recorded were explained in detail in this chapter.

6.2 Production and Characterisation of MPVDF Composites

The approach to fabricate MPVDF hierarchical composites is identical to PVDF hierarchical composites (as explained earlier in Chapter 5). The optimised processing conditions chosen for PVDF hierarchical composites were used for fabricating hierarchically reinforced MPVDF. Although carbon nanotubes were well dispersed throughout the MPVDF hierarchical composites containing 5 wt% CNTs with a random orientation, there were also some regions containing CNT agglomerates which are shown in the SEM micrograph (Figure 6-1). Powder impregnation is a viable process which could homogeneously disperse carbon nanotubes in a PVDF composite, irrespective of matrix modification, while avoiding issues associated with self-filtration. Moreover, the random carbon nanotube orientation suggested that although the shear caused by the shear impregnation pins was parallel to the fibre axis, it did not cause change in carbon nanotube alignment which would allow nano scale reinforcement in hierarchical fibre reinforced MPVDF to spread in directions away from the fibre axis, where it is most needed to improve matrix dominated composite properties [17].

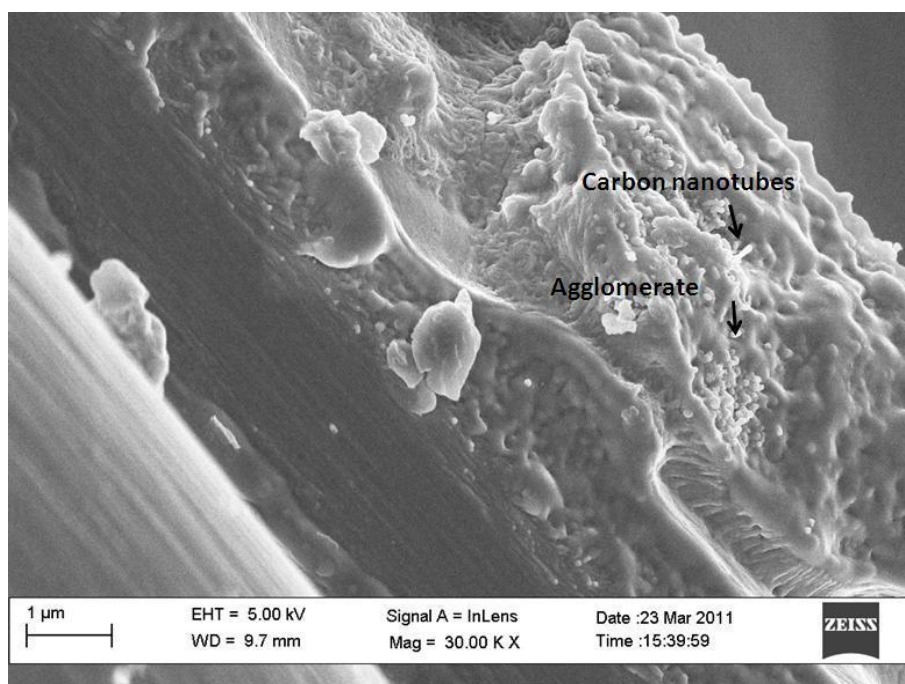


Figure 6-1: Characteristic SEM micrograph representing protruding CNTs in the polymer attached to a carbon fibre in AS4/MPVDF composite containing 5 wt% CNT

6.2.1 Size Distribution of MPVDF Nanocomposite Powder

Three suspensions of 5 wt% nanocomposite powder containing up to 5 wt% CNTs in deionized water were prepared and stabilized by 2 wt% of (Cremophor A25) with respect to polymer and the particle size distribution (PSD) was determined. Particle size analysis was carried out using Malvern's Mastersizer 2000. The volume averaged diameter of the particles in the suspension is represented as d_{50} with an accuracy of $\pm 1\%$. Each reading obtained was an average of 6 values calculated by the Malvern Mastersizer 2000. The average particle sizes of the MPVDF powder produced by the precipitation procedure were in the range of 16 μm to 30 μm in diameter for various CNT contents. Figure 6-2 shows particle size distribution of MPVDF nanocomposite powders produced via solution precipitation.

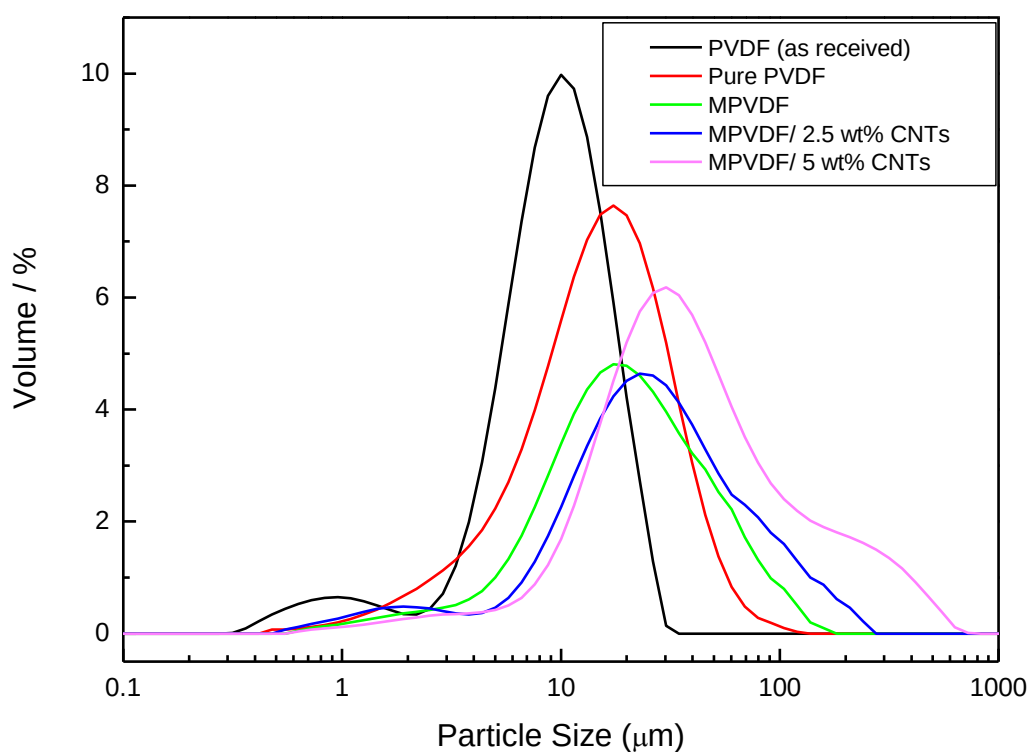


Figure 6-2: Particle size distribution of MPVDF composite powder containing 0-5 wt% CNTs produced via solution-precipitation

The MPVDF (75 wt% PVDF and 25 wt% maleic anhydride grafted PVDF) powders had an average particle size of 16 μm due to the controlled manufacturing method (solution

precipitation). The addition of the 2.5 wt% and 5 wt% carbon nanotubes to maleic anhydride modified PVDF caused the average particle size to increase to 23 μ m and 29 μ m respectively. The particle size gradually increased with the CNT loading in to the primary MPVDF particles. The broadening of peak shows clearly the fact that agglomerates were present in PVDF nanocomposites with increased CNT loading.

Matrix	Volume averaged particle size (μ m)
PVDF/25 wt% MAH-g-PVDF (MPVDF)	16 $\pm$ 2
PVDF/25 wt% MAH-g-PVDF with 2.5 wt% CNT	23 $\pm$ 3
PVDF/25 wt% MAH-g-PVDF with 5 wt% CNT	29 $\pm$ 2

Table 6-1: Volume averaged particle sizes for the MPVDF powders containing 0-5 wt% CNT content produced via solution-precipitation method

6.2.2 Fibre Volume Fraction

Although the fibre volume content of the tape was controlled during production of the composite tape (see Chapter 3), the test specimens were analysed to confirm that control over the fibre volume content was maintained throughout the process. Polished transverse sections of hierarchical composites were used to take optical micrographs, which were further analysed to determine the fibre volume fraction. Six images of crosssections were taken for each composite formulation. The fibre volume content for almost each formulation was 56% $\pm$ 1.

Matrix formulation	$\overline{V_{f,Geo}}$	$\overline{V_{f,Mass}}$
MPVDF	0.56 $\pm$ 0.02	0.57 $\pm$ 0.02
MPVDF/1.25 wt% CNTs (<i>mixed plies</i>)	0.55 $\pm$ 0.02	0.56 $\pm$ 0.02
MPVDF/2.5 wt% CNTs	0.57 $\pm$ 0.02	0.56 $\pm$ 0.02
MPVDF/2.5 wt% CNTs (<i>mixed plies</i>)	0.57 $\pm$ 0.02	0.56 $\pm$ 0.02
MPVDF/5 wt% CNTs	0.56 $\pm$ 0.02	0.56 $\pm$ 0.02

Table 6-2: Average fibre volume fractions of MPVDF hierarchical composites determined geometrically ($\overline{V_{f,Geo}}$) and gravimetrically ($\overline{V_{f,Mass}}$) containing up to 5 wt% CNT content

6.2.3 Crystallinity of MPVDF Hierarchical Composites

Differential scanning calorimetry (DSC) was used to determine the crystallinity of the matrices with CNT loadings of 0 wt% to 5 wt%. It was observed that crystallinity of 25 wt% MAH-g-PVDF was identical ($39\% \pm 2$) for all MPVDF hierarchical composites regardless of the CNT content as shown in Table 6-3. The degree of crystallinity of MPVDF hierarchical composites suggested that CNTs did not influence the crystalline content of the composite.

Hierarchical composites with the matrix formulation as	$\chi_c / (\%)$
MPVDF	39 ± 2
MPVDF/1.25 wt% CNTs (mixed plies)	38 ± 3
MPVDF/ 2.5 wt% CNTs	39 ± 1
MPVDF/ 2.5 wt% CNTs (mixed plies)	39 ± 2
MPVDF/5 wt% CNTs	39 ± 2

Table 6-3: Degree of crystallinity of MPVDF matrix in hierarchical composites determined by DSC

6.3 Mechanical Characterisation of MPVDF Hierarchical Composites

Carbon fibre reinforced composites of modified PVDF (75 wt% PVDF and 25 wt% MAH-g-PVDF) containing 0 wt%, 1.25 wt%, 2.5 wt% and 5 wt% carbon nanotubes were fabricated. The influence of CNT content on compression performance, flexural modulus, short beam shear strength and mode I fracture toughness are discussed below. Figure 6-3 summarises the average density, percentage porosity and specific pore volume for MPVDF hierarchical nanocomposites. The identical density (1.77 ± 0.18) and negligible porosity suggested that the quality of the consolidation composites was good enough to provide the true results from the mechanical testing.

AS4 carbon fibre reinforced with the matrix	$\overline{\rho_A}$ g/cm ³	$\overline{\rho_E}$ g/cm ³	P %	Specific Pore Volume (cm ³ /g)
MPVDF (75 wt% PVDF + 25 wt% MAH-g-PVDF)	1.77 ± 0.20	1.75 ± 0.25	1.32 ± 0.24	0.042± 0.002
MPVDF/1.25 wt% CNTs (mixed plies)	1.78 ± 0.18	1.75 ± 0.62	1.83 ± 0.82	0.074± 0.004
MPVDF/2.5 wt% CNTs	1.76 ± 0.21	1.75 ± 0.38	1.11 ± 0.64	0.038± 0.003
MPVDF/2.5 wt% CNTs (mixed plies)	1.77 ± 0.14	1.76 ± 1.22	1.32 ± 0.54	0.065± 0.004
MPVDF/5 wt% CNTs	1.77 ± 0.26	1.75 ± 0.90	1.67 ± 0.76	0.058± 0.006

Table 6-4: The averaged absolute density, averaged envelope density, percentage porosity and specific pore volume for MPVDF hierarchical composites (FVC-57 ± 2%) as determined via AccuPyc and GeoPyc

6.3.1 Influence of CNT Content of MPVDF Hierarchical Composites on Compression Properties

Compression strength was determined for mechanical characterisation of the hierarchical composites. There was an 18% drop observed in compressive strength of MPVDF composites as compared to PVDF composites (Table 6-5). The reason for this was not immediately clear as maleic anhydride exhibited improvement in interfacial shear strength with AS4 single carbon fibres as compared to PVDF [17]. This reduction in macromechanical performance of MPVDF composites as compared to PVDF composites also contradicts the wetting results obtained from contact angle measurements [28]. Later on it had been claimed through X-ray photoelectron spectroscopy (XPS) that the surface of MPVDF contained only 2.5% MAH, which was less than the 7% expected based on the simple two fold dilution of 100% MAH-g-PVDF (containing 14% MAH). This suggests that MPVDF is rather inhomogeneous with preferential surface segregation of PVDF. However, no major surface impurities were introduced by modifying PVDF by MAH [139]. Fractographic analysis was conducted to understand the reason and is explained later in this Chapter.

Sample	FVC $\overline{V_f}$	σ_c [MPa]	E_c [GPa]	$\overline{E} = E \frac{0.55}{V_f}$ [GPa]	Strain $\mu\epsilon$
PVDF	0.57±2	523 ± 56	109 ± 3	105 ± 3	5307 ± 728
MPVDF	0.57±2	443 ± 53	110 ± 6	106 ± 6	4249 ± 322
MPVDF/1.25 wt% CNTs (mix plies)	0.57±3	566 ± 26	106 ± 4	102 ± 4	5136 ± 397
MPVDF/2.5 wt% CNTs	0.57±3	417 ± 58	117 ± 6	110 ± 6	4979 ± 472
MPVDF/5 wt% CNTs	0.56±4	351 ± 6	110 ± 8	106 ± 8	5488 ± 171

Table 6-5: Comparison of compressive strength, compressive modulus, and strain to failure values for AS4/MPVDF hierarchical composites

Compression strength of hierarchically reinforced MPVDF increased by 28% with only the addition of 1.25 wt% CNTs (566 MPa which is 9% higher than compression strength of PVDF composites, 523 MPa). However, it dropped by 14% and 45% when CNT content was further increased to 2.5 wt% and 5 wt%, respectively (see Figure 6-3). The compression modulus, however, remained almost constant (normalised to 55% V_f) i.e. 106 ± 5 GPa for hierarchical composites irrespective of the amount of CNTs present (Figure 6-4). As explained before, the hierarchical composites were fabricated via two procedures. First one, where all plies containing the same CNT content, e.g. 2.5 wt% CNTs, were used and in the second procedure used alternate plies containing 0 wt% and 2.5 wt% CNTs resulting in an overall CNT content of 1.25 wt%. As previously shown, it was the overall CNT content in the composite that affected the mechanical properties and not the use of similar or mixed plies, so results from any of the specimens are comparable to each other.

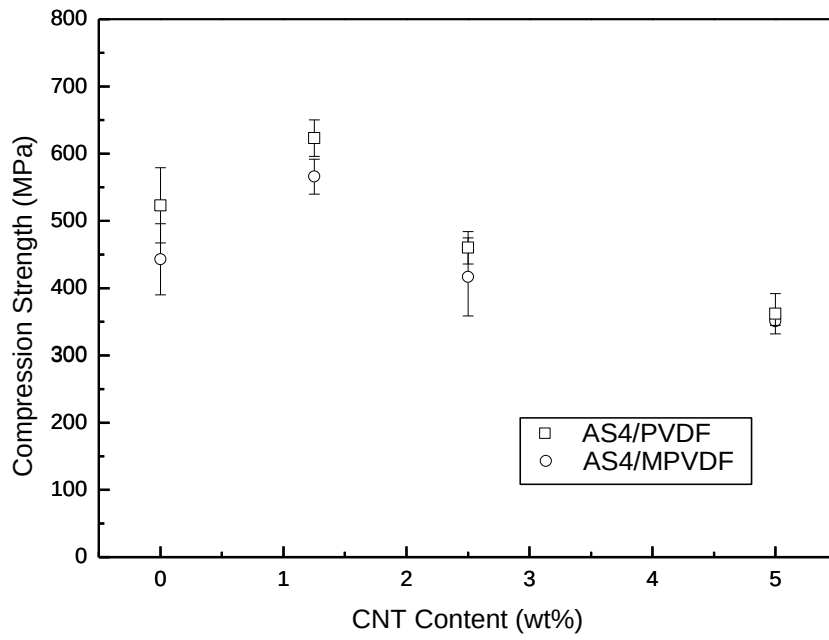


Figure 6-3: Compression strength of AS4/PVDF and AS4/MPVDF hierarchical composites as a function of CNT content

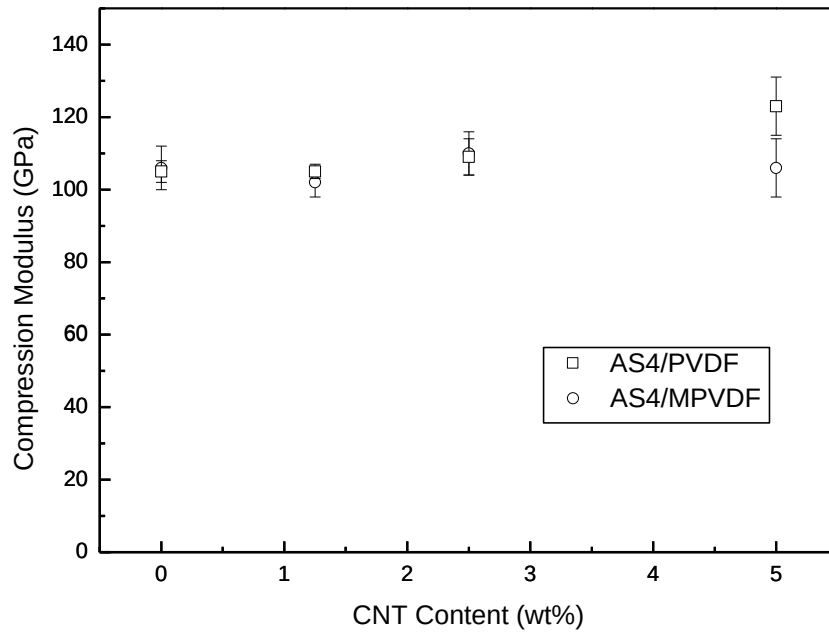


Figure 6-4: Compression modulus of AS4/PVDF and AS4/MPVDF hierarchical composites as a function of CNT content

6.3.2 Influence of CNT Content of MPVDF Hierarchical Composites on Flexural Properties

Flexure properties give an insight in to the fibre/matrix interface of the composites. A composite with poor fibre/matrix interface cannot bear load in flexure [136]. The flexural strength of MPVDF composites (336 MPa) increased by 18% as compared to PVDF composites. AS4/MPVDF composites presented a flexural strength of 395 MPa which increased further by 6% to about 418 MPa by the incorporation of 1.25 wt% CNTs (mix plies of AS4/MPVDF containing 0 and 2.5wt% CNTs). However, flexural strength of MPVDF hierarchical composites dropped by 20% and 158% when CNT content was raised to 2.5wt% and 5 wt%, respectively (Figure 6-5).

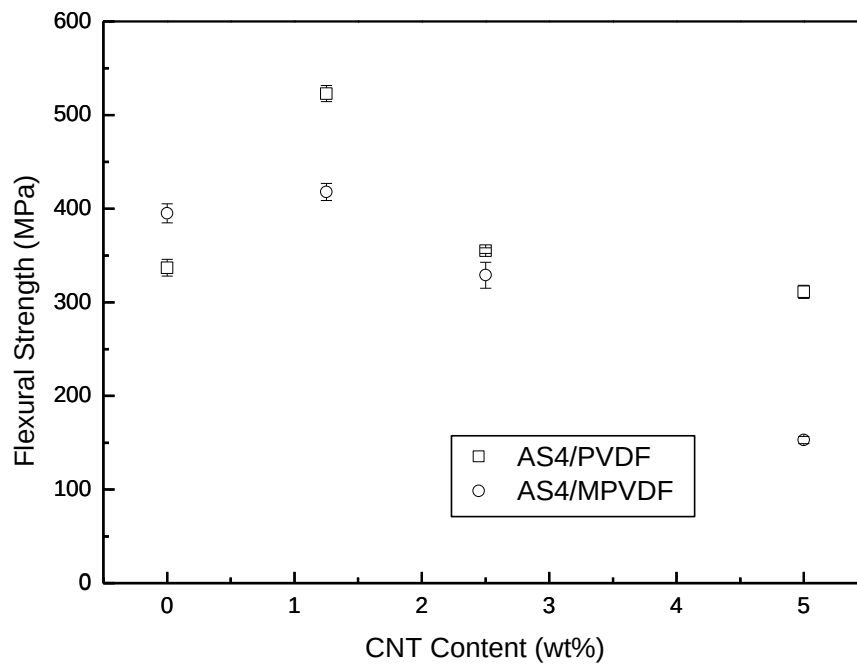


Figure 6-5: Flexural strength of AS4/PVDF and AS4/MPVDF hierarchical composites as a function of CNT content

Flexural modulus of AS4/MPVDF composites measured was 2% lower (within scatter) than that of AS4/PVDF composites. Whereas a 12% increase in flexural modulus of MPVDF composites was observed with the addition of 1.25 wt% CNTs which was reduced by 2% and 8%, respectively for the composites containing 2.5 wt% and 5 wt% CNTs (Figure 6-6). This suggests, in agreement with compression results, that CNTs enhance the matrix stiffness when

introduced up to an optimum limit in the matrix. Matrix with improved stiffness supports the fibres strongly which enhances its ability to transfer load from matrix to fibres and thus inhibits microbuckling. However, at CNT loadings higher than 1.25 wt%, it's either the higher viscosity of the nanocomposite suspensions, which is making it impossible/very difficult to impregnate the fibres completely or even if consolidated its limiting the surface area of MPVDF to bond to the carbon fibres which cause poor fibre/matrix impregnation and reduce the flexural strength (see fractography).

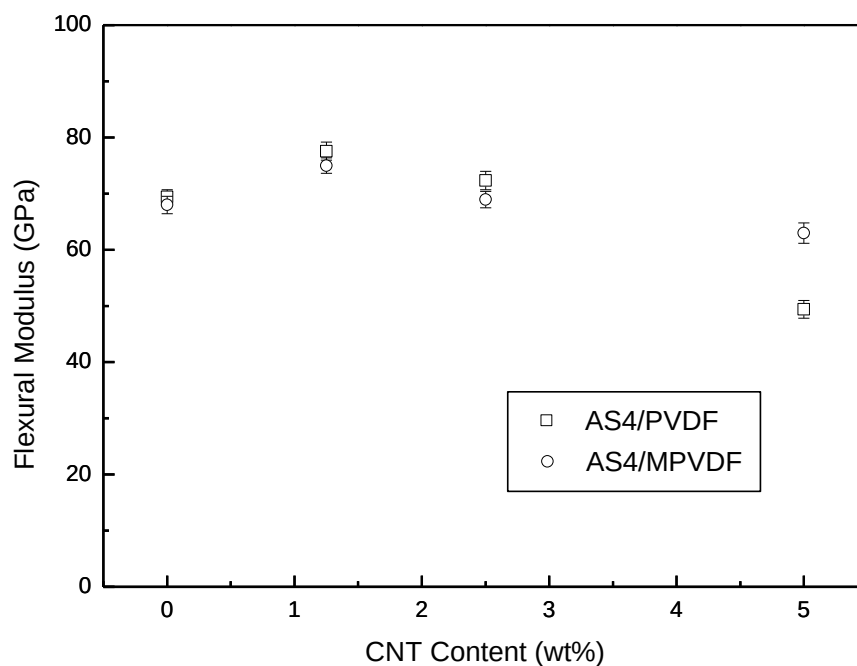


Figure 6-6: Flexural modulus of AS4/PVDF and AS4/MPVDF hierarchical composites as a function of CNT content

6.3.3 Influence of CNT Content of MPVDF Hierarchical Composite on Short Beam Shear Strength

Figure 6-7 shows the SBS strength for MPVDF hierarchical composites. The SBS strength determined for carbon fibre reinforced MPVDF composites was 19% lower than that of PVDF composites. However, with a total CNT content of 1.25 wt% in MPVDF (obtained through consolidating alternate plies of MPVDF containing 0 wt% and 2.5 wt% CNTs), a 51% improvement in SBS was observed. But when the CNT content was increased to 2.5

wt% and 5 wt% SBS was dropped by 4% and 118 %, respectively as compared to MPVDF composites.

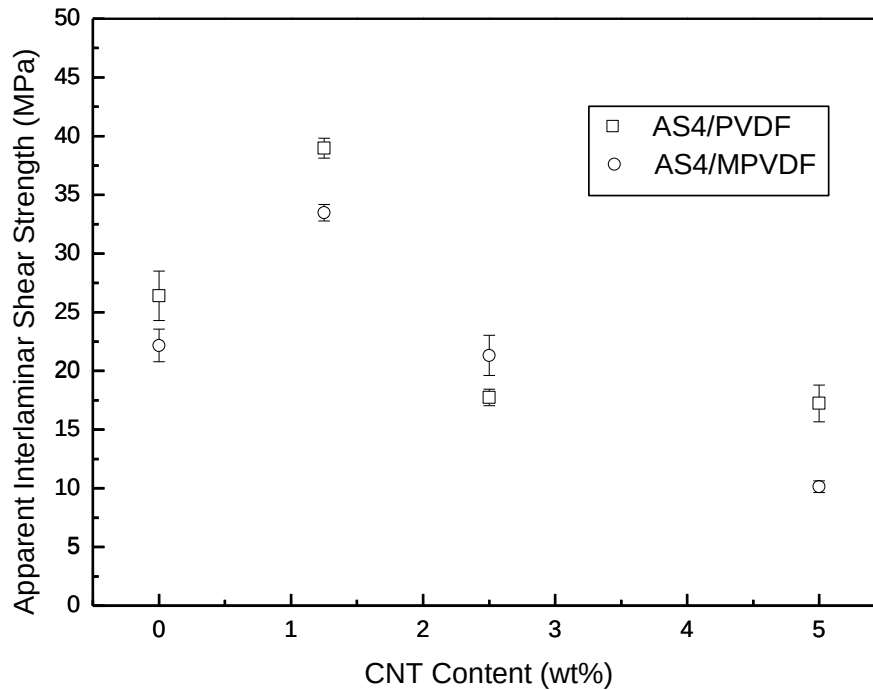


Figure 6-7: Apparent interlaminar shear strength of AS4/PVDF and AS4/MPVDF hierarchical composites as a function of CNT content

Comparing the macromechanical properties obtained from flexural and SBS tests, the results complement each other. The carbon fibre reinforced MPVDF composites exhibited a lower ILSS (22 MPa), as compared to the MPVDF hierarchical composites containing 1.25 wt% CNTs (34 MPa). Similarly the measured flexural strengths are also much lower (395 MPa) than of the hierarchical reinforced MPVDF composites (418 MPa).

The short beam shear strength, as measured by the SBS test, showed that the hierarchical reinforced MPVDF composites (containing 1.25 wt% CNTs) have improved the expected capability of transferring load from the nanocomposite matrix to fibres (or an improved interface due to improved matrix dominated properties (e.g stiffness)) by completely impregnating the fibres resulting in an efficiently consolidated composite, as compared to MPVDF composites containing no CNTs. However, at higher CNT loadings, the higher nanocomposite's viscosity is probably making it difficult for the nanocomposite matrix to

impregnate the carbon fibres completely in order to get efficiently consolidated. This suggests the existence of an optimal loading limit for CNTs where enhanced stiffness of nanocomposite matrix can be availed without compromising the interface dominated properties, beyond which either of these will have a trade-off which can adversely affect the overall mechanical performance of the hierarchical composites.

6.3.4 Influence of CNT Content of MPVDF Hierarchical Composites on Fracture Toughness

The steady state mode I fracture toughness of hierarchical reinforced MPVDF composites was measured using DCB. The steady state energy release rate ($G_{IC,ss}$) was calculated using the modified beam theory. A mixture of stable and unstable crack propagation was observed in failed DCB specimens.

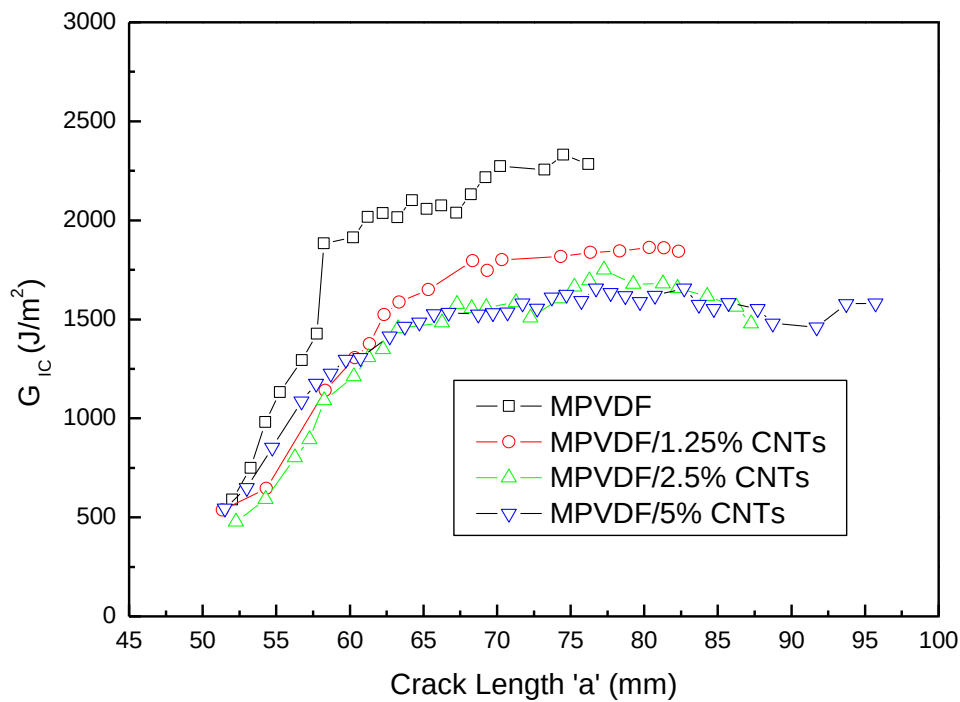


Figure 6-8: Delamination resistance curve for MPVDF hierarchical composites containing A) 0 wt%, B) 1.25 wt% (mixed plies), C) 2.5 wt%, and D) 5 wt% CNTs (one representative curve is plotted for each composite out of the six specimens tested)

A plot of G_{IC} as a function of crack length for MPVDF (75 wt% PVDF and 25 wt% maleic anhydride grafted PVDF) hierarchical composites can be seen in Figure 6-8. It is clear from these results that the energy release rate stabilises rapidly and forms a steady state plateau with crack growth. The crack length chosen as the steady state propagation point was 70 mm where all the specimens presented steady state plateau of G_{IC} . The analysis of the results indicated that $G_{IC,SS}$ (i.e. G at $a = 70\text{mm}$) for AS4/MPVDF composites, was $2272 \pm 152 \text{ J/m}^2$ which is 34% higher than that of APC-2 ($G_{IC}:1700 \text{ J/m}^2$) [36] but 8% lower than AS4/PVDF composites. A significant drop of 26% was observed in the steady state critical energy release rate, for AS4/MPVDF composites containing an overall CNT content of 1.25 wt% (mixed plies of AS4/MPVDF containing 0 and 2.5 wt% CNTs) except for a same scatter i.e. $1800 \pm 125 \text{ J/m}^2$ which is still 6% higher than APC-2. G_{IC} for MPVDF hierarchical composites containing 2.5 wt% and 5 wt% CNTs dropped further by a 45% and 48%, respectively as compared to AS4/MPVDF.

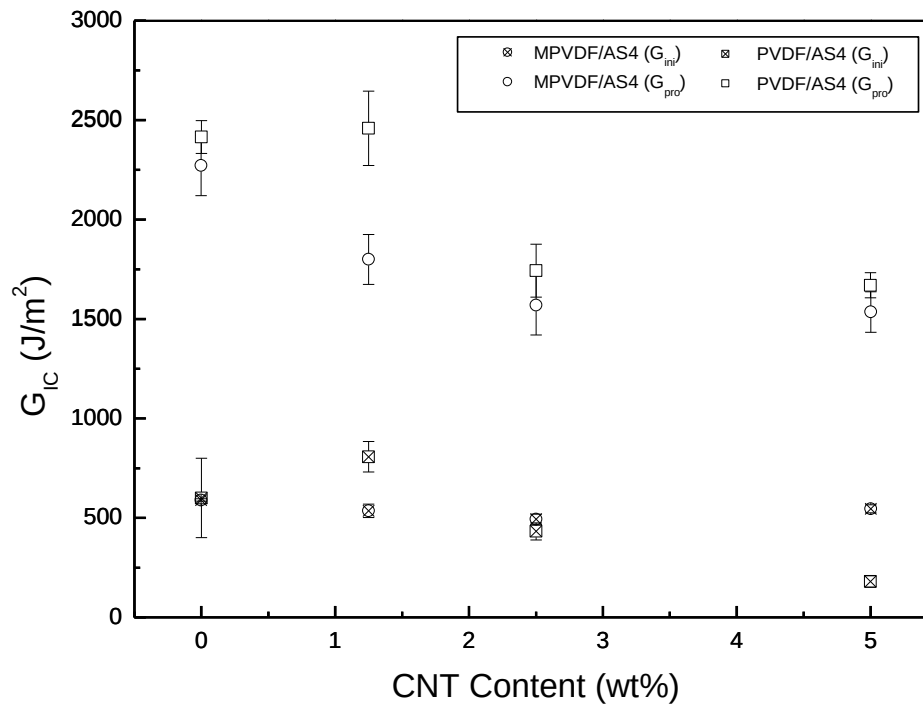


Figure 6-9: $G_{initiation}$ (G @ 50mm) and $G_{plateau}$ (G @ 70mm) for AS4/PVDF and AS4/MPVDF hierarchical composites as a function of CNT content

Figure 6-9 presents the initiation and propagation values for the energy release rate of MPVDF hierarchical composites. $G_{\text{initiation}}$ for MPVDF hierarchical composites dropped gradually with increase in CNT content. The drop in the critical energy release rate at $a = 70\text{mm}$ with the increase in CNT content indicated the fact that fracture toughness of MPVDF hierarchical composites decreased with increase in CNT content. This decrease in fracture toughness at higher CNT loading (explained in agreement with compression results) can be attributed to the fact that higher viscosity of nanocomposites at higher CNT loadings made it difficult for the matrix to impregnate fibres completely or matrix is not getting infused in to the fibres sufficiently to get consolidated properly in order to take advantage of enhanced nanocomposite matrix stiffness in hierarchical composites.

6.4 Fractography of MPVDF Composites

Fracture modes of compression and DCB failed specimens were analysed to understand the damage modes and failure mechanisms. SEM micrographs of three nominally identical specimens of each formulation were taken and compared to identify inherent differences.

6.4.1 Fractographic Analysis of Compression Failed MPVDF Composites

The hierarchical composites with a PVDF matrix containing 25 wt% MAH-g-PVDF (MPVDF) exhibited more delamination than those based on pure PVDF and perhaps as much as those based on 2.5 wt% CNT incorporated PVDF matrix (see Chapter 5) but it is apparent that most of these have occurred after kinkband formation as there is continuous kinkband formation but discontinuous delaminations. Hierarchical composites based on MPVDF as matrix material failed with kinkbands formed, segregated by discontinuous delaminations at various locations over the entire crosssection (Figure 6-10-A). MPVDF composites containing 1.25 wt% CNTs (alternate plies of AS4 MPVDF containing 0 and 2.5 wt% CNT were consolidated to fabricate them) failed catastrophically after the formation of a kinkband, but still there were regions around the plane of buckling showing delaminations. This observation suggests MPVDF based composites were more susceptible to delamination than not only pure PVDF but PVDF hierarchical composites as well (see Chapter 5).

Failed hierarchical composite specimens with an MPVDF matrix containing 2.5 wt% CNTs were heavily dominated by delamination, with extensive delamination of multiple planes before kinkband formation; they exhibited 'green-stick' fracture rather than localised kinkband/translaminar fracture (Figure 6-10C). There was a lot more loose resin in these

specimens, and some regions, particularly close to the specimen faces, seemed rather fibre rich indicating that the fibres were poorly impregnated by the surrounding matrix. The shiny and dark surface exhibited poor impregnation between matrix and fibre. Whereas the smooth and featureless appearance of the surface with the surrounding resin appeared to be raised like a lighter material, when observed under microscope, almost confirms the poor infusion of MPVDF nanocomposite in to carbon fibre.

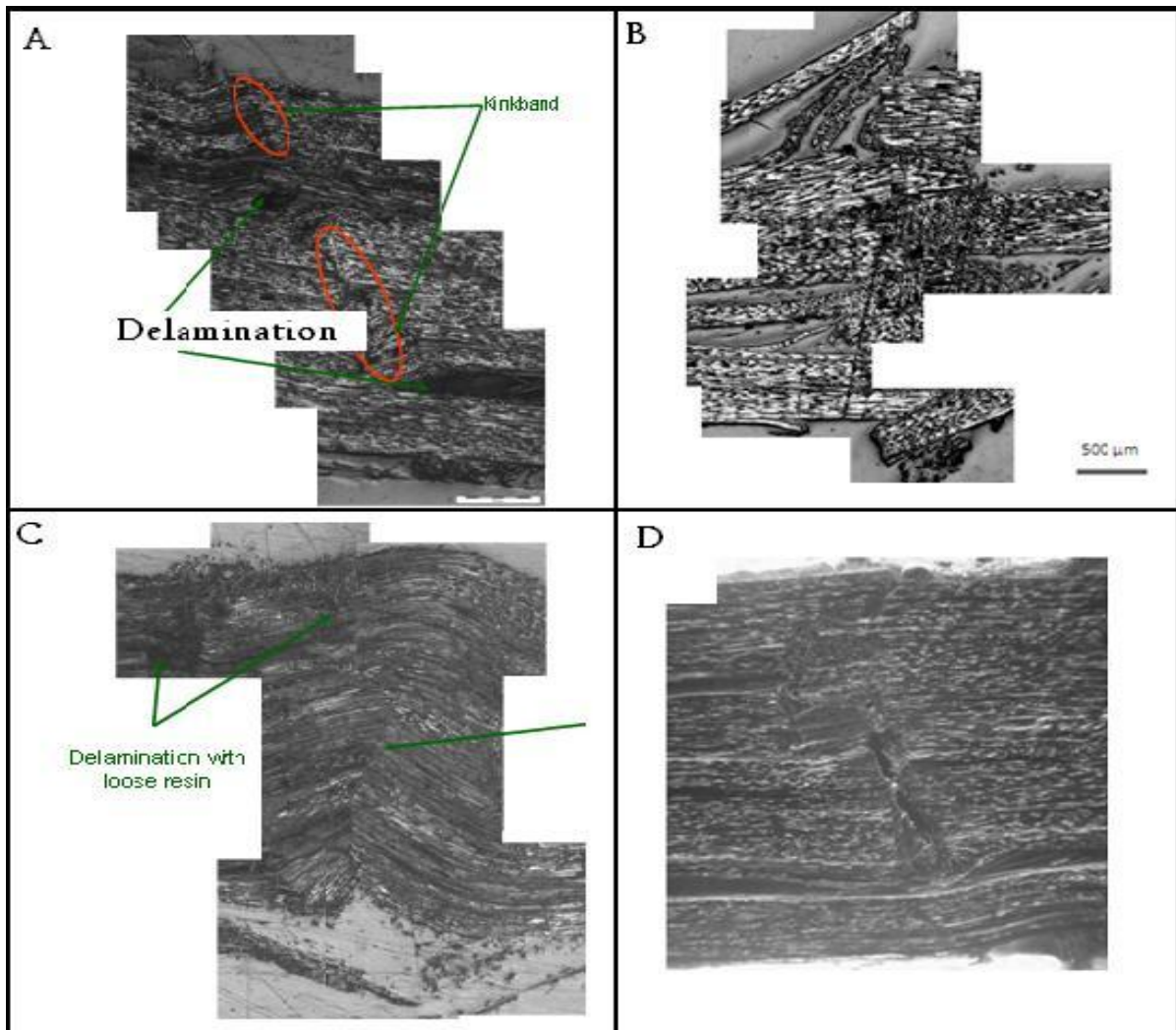


Figure 6-10: Typical SEM images of compression failure of hierarchical composite based on MPVDF with 25% MAH-g-PVDF containing A) 0 wt% CNT (localised delamination), B) 1.25 wt% CNT (localised delamination) C) 2.5 wt% CNT (globalised delamination) and D) 5 wt% CNT (globalised delamination)

Finally, hierarchical reinforced MPVDF containing 5 wt% CNTs showed a failure with dominant continuous multiplane delaminations followed by the formation of a kinkband. They also exhibited 'greenstick' failure, as it is akin to fracture of a freshly cut stick or twig.

The degree of delamination has a strong effect on the failure mode, as can be seen by comparing Figure 6-10 (A, B-Localised delamination) and Figure 6-10 (B, C-Globalised delamination). In Figure 6-10 A and B, the central region of the laminate containing 0 wt% and 1.25 wt% CNTs shows an angled crack, typical of in-plane compression failure. However the outer regions of the laminate exhibited multiplane delamination, These layers have failed independently in flexure. The laminates containing 2.5 wt% and 5 wt% CNTs exhibited considerable delamination (Figure 6-10 C and D), i.e. they delaminated on most of the planes through the thickness, but with little or no evidence of any fibre fracture in the laminate. In both these examples, the delamination occurred before any in-plane compressive fracture and is indicative of a poorer fibre/matrix interface than MPVDF composites containing 0 wt% and 1.25 wt% CNTs.

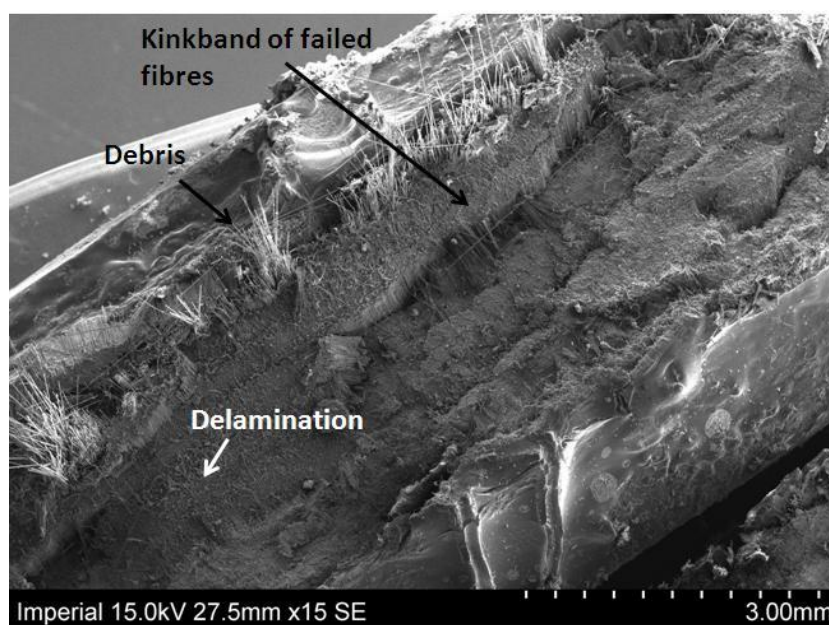


Figure 6-11: Characteristic fracture surface of compression failed MPVDF composites containing A) 0 wt% CNTs ($\times 15\text{SE}$)

So, it can be concluded that the failure of these specimens is a competition between kinkband formation (longitudinal microbuckling compression of the fibres) and of delaminations development. Hierarchical composites based on MPDVF matrix containing CNTs are more prone to delamination, particularly at higher loadings (> 1.25 wt%). In summary, it was observed that the hierarchical composites which are more susceptible to delamination did not exhibit the maximum upper bound of the compression strength they can actually achieve and by improving the quality of fibre/matrix interface somehow (probably by functionalising the

fibres), their potential can be achieved. It can be seen from the Figure 6-11 that the compression fracture surfaces of MPVDF composites were not normal to the loading direction but slightly angled. Also MPVDF nanocomposite matrix containing 2.5 wt% CNT (Figure 6-12) is shown not being infused in to fibres completely which is indicative of worst AS4/MPVDF nanocomposite adhesion. The poor fibre/matrix quality caused by insufficient fibre impregnation also tends to promote an increased prevalence of longitudinal splitting, leading to fibre separation along with transverse splitting (delamination) as depicted in Figure 6-12.

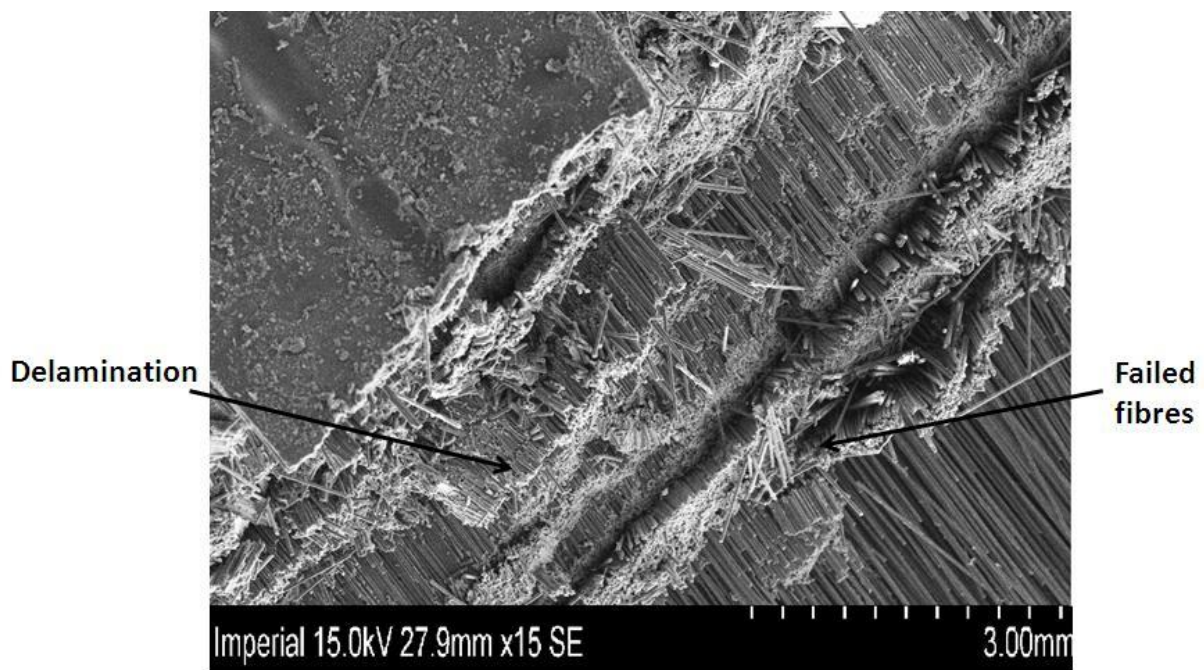


Figure 6-12: Characteristic fracture surface of compression failed MPVDF composites containing 2.5 wt% CNTs ($\times 15\text{SE}$)

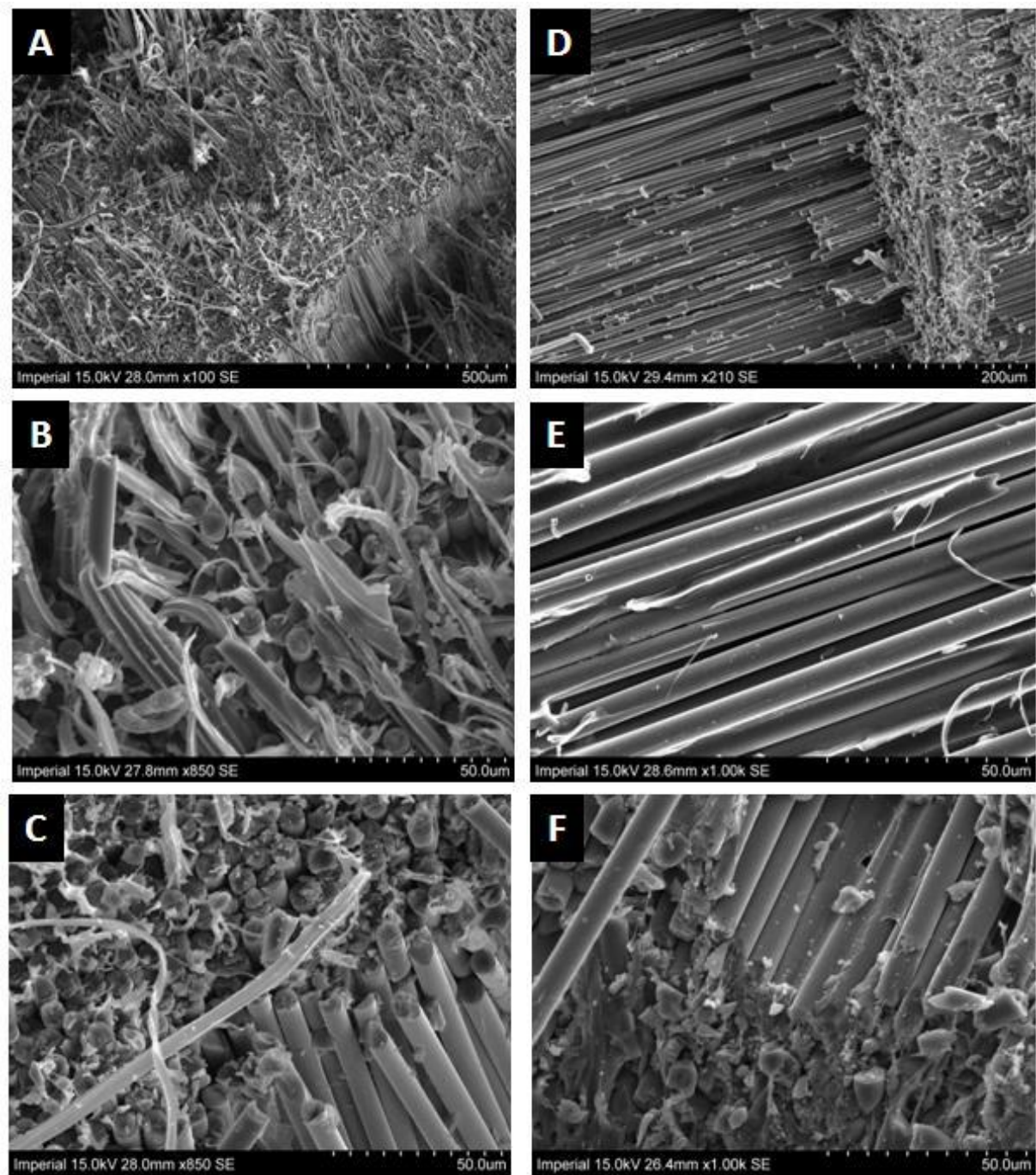


Figure 6-13: Typical SEM images of compression fracture surface of MPVDF composites containing 0 wt% CNTs at a magnification of A) $\times 100$ SE, B) $\times 850$, C) $\times 850$ and of MPVDF hierarchical composites containing 2.5 wt% at a magnification of CNTs D) $\times 210$, E) $\times 1k$, F) $\times 1k$

From Figure 6-13, it is apparent that the higher loadings of CNTs (> 1.25 wt%) had an adverse influence on fibre/matrix adhesion of AS4/MPVDF composites. In Figure 6-13 (A,B,C) compression fracture surface of MPVDF composites are shown. Many more matrix fibrils were observed on the fracture surface, as compared to PVDF composites. This suggests

that fibre/matrix adhesion in AS4/MPVDF is poorer than that of AS4/PVDF causing the matrix fibrils to leave the fibres and extend out of the fracture plane on application of compressive load. With the addition of CNTs, the insufficient impregnation of carbon fibres by the matrix causes the fibre/matrix interface to become even poorer as represented by presence of bare fibres at majority of places in the compression fracture surface of MPVDF hierarchical composites containing 2.5 wt% CNTs (Figure 6-13 D,E,F).

To summarise, the compression samples of AS4/PVDF composites typically exhibited translaminal failure (see Chapter 5) while the MPVDF samples reinforced with the carbon fibres failed through delamination and buckling of the plies (Figure 6-12). This type of failure resulted in low measured compressive strength and strain to failure and is likely the result of a poor fibre/matrix interface caused by poor infusion/insufficient impregnation of fibres with nanocomposite matrix probably due to its comparatively higher viscosity at higher CNT content [138]. The attempt to measure the mode I fracture toughness of the composites yielded further insight as to the mechanism behind the failure of the MPVDF composites containing carbon nanotubes.

6.4.2 Fractographic Analysis of Failed MPVDF DCB Composites

The fracture surface of the DCB samples was studied to determine the behaviour of the composites under mode I crack growth conditions. It was clear from the SEM micrographs (see Figure 6-14A) that the AS4/PVDF composite exhibited some ductile drawing of the matrix. AS4/PVDF composites exhibited a cohesive mode I fracture which indicates good fibre/matrix strength. The presence of small amount of polymeric debris left on the fibres also indicated a good fibre/matrix interface. Figure 6-14A shows fracture initially starting at fibre/matrix interface which also indicated a matrix with increased toughness. This suggested that although the interface between PVDF and AS4 was thought to be relatively poor, matrix deformation contributed, at least slightly, to the mode I fracture toughness and the fracture did not entirely occur at the carbon fibre-PVDF interface.

SEM micrographs of the mode I fracture surfaces of the AS4 reinforced with PVDF were compared to those of hierarchically reinforced PVDF and MPVDF composites. The influence of CNTs on the hierarchically reinforced MPVDF fracture behaviour (Figure 6-14D) can clearly be seen when compared to the AS4/MPVDF fracture surface (Figure 6-14C). The SEM micrographs of the hierarchically reinforced PVDF fracture surface showed very little

signs of ductile drawing or plastic deformation of the PVDF matrix. This indicated that the matrix did not contribute a lot to the mode I toughening mechanism. The weak fibre/matrix interface (as a result of poor fibre impregnation caused by high viscosity of nanocomposite matrix) and the ductile nature of the matrix limited the mode I fracture toughness of the hierarchically reinforced AS4/PVDF composites. Furthermore, reduced polymeric debris was observed on the fibre surfaces, which clearly shows that poor adhesion or interaction (caused by insufficient impregnation of fibres as explained earlier) existed between PVDF containing CNTs and AS4.

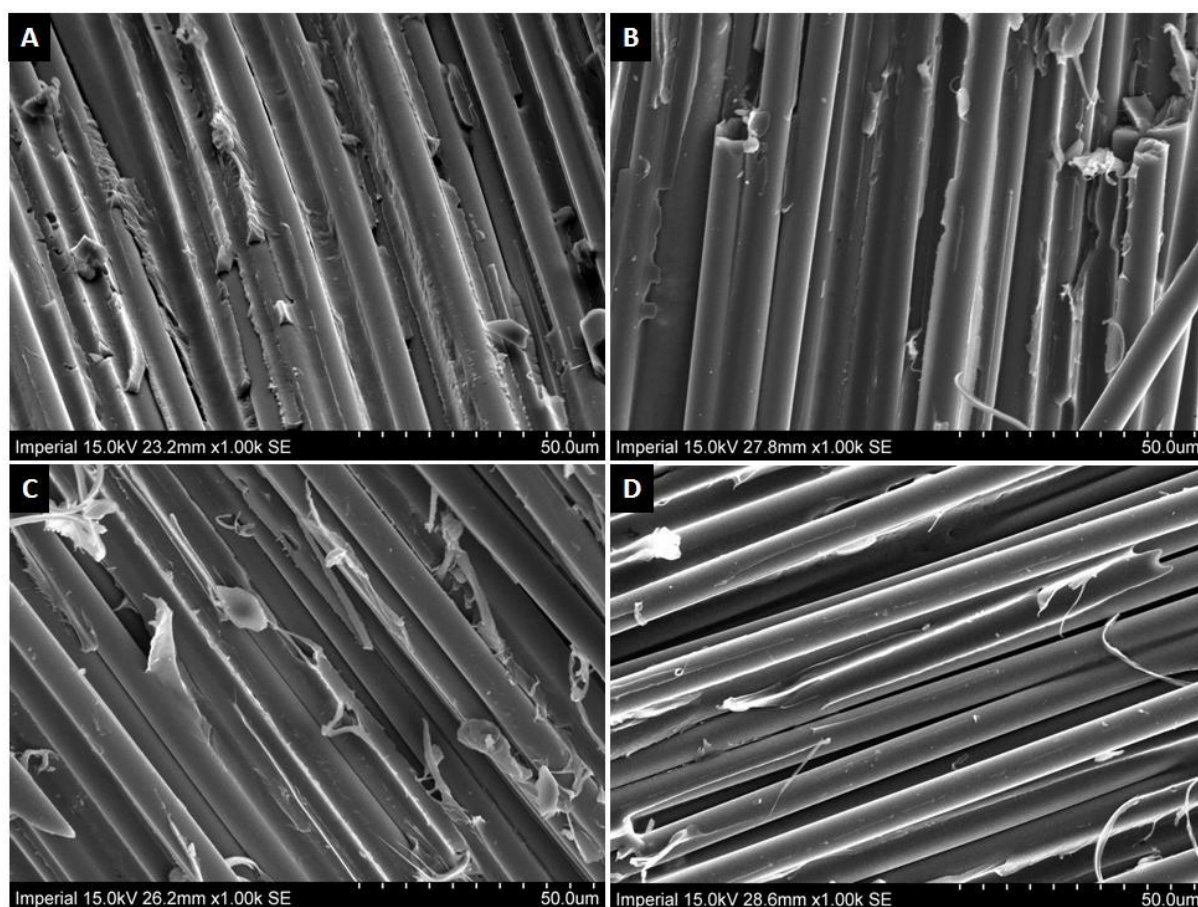


Figure 6-14: Typical DCB fracture surface of A) AS4/PVDF B) AS4/PVDF containing 2.5 wt% CNTs C) AS4/MPVDF D) AS4/MPVDF containing 2.5 wt% CNTs

The addition of maleic anhydride into the PVDF matrix and the hierarchical reinforcement changed the fracture behaviour between the carbon fibre and the matrix/nanocomposite. The limited ductile drawing observed in AS4/MPVDF became invisible in hierarchically reinforced MPVDF. Furthermore, no significant amount of polymeric debris was observed on fracture surfaces of AS4/MPVDF composites. Hierarchical reinforced MPVDF even exposed

bare fibres which suggest poor fibre/matrix interface caused by insufficient impregnation of fibres by nanocomposite matrix containing higher CNT content due to its higher viscosity. Therefore, the proposed mechanism for adhesion promotion (via ductile drawing/ matrix plastic deformation) would not be present. The analysis of the fracture surfaces of the hierarchical AS4/PVDF nanocomposites exhibited the same fibre/matrix adhesion failure as the conventional carbon fibre reinforced AS4/MPVDF composites (Figure 6-14). Figure 6-15 represents an even poorer fibre/matrix interface strength in hierarchically reinforced MPVDF containing 5 wt% CNTs indicated by exposed bare fibres. Under these conditions, a preferential fracture at the fibre/matrix interface would have also reduced the degree of matrix deformation. The mode I fracture toughness, of MPVDF hierarchical composites as determined by the steady state critical strain energy release rate, was higher than APC-2 (AS4/PEEK) which was attributed to fibre bridging as the predominant fracture toughening mechanism.

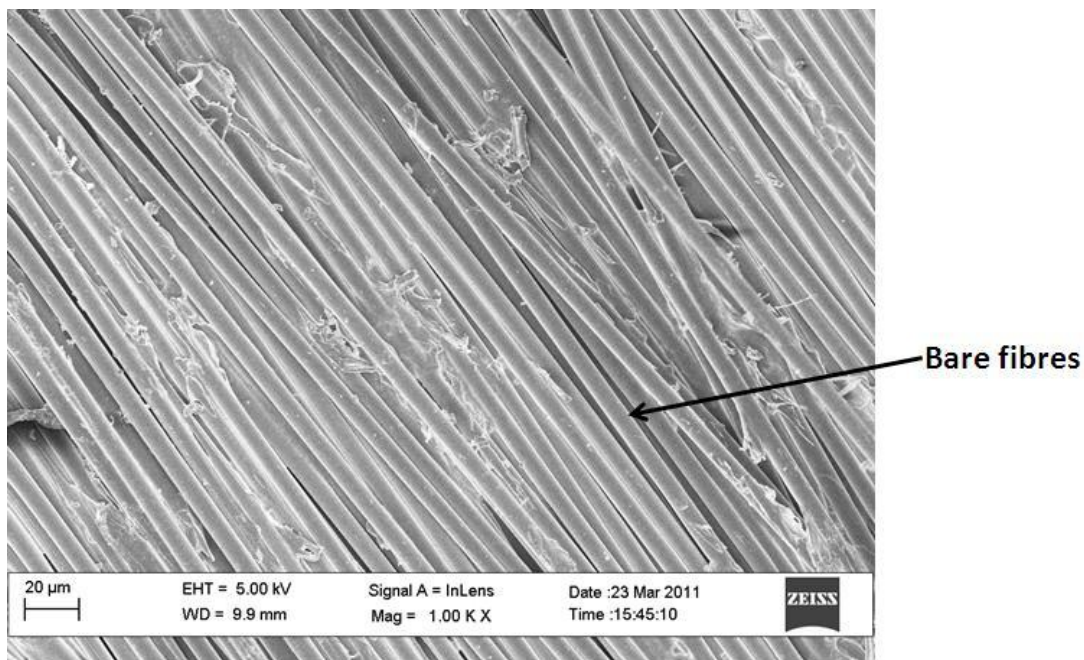


Figure 6-15: DCB fracture surface of MPVDF containing 5 wt% CNTs reinforced with AS4 carbon fibre

6.5 Summary

A method of improving the matrix dominated properties and hence fibre/matrix interface between carbon fibres and PVDF was investigated in CFRPs which is achieved by modifying

the matrix through addition of a compatibilising agent (MAH-g-PVDF). MPVDF (25 wt% MAH-g-PVDF/ 75 wt% PVDF) hierarchical composites (containing 0 wt%, 1.25 wt%, 2.5 wt% and 5 wt% CNTs) with a fibre volume content of $56\% \pm 2$ were successfully fabricated and investigated for their mechanical performance. It was observed that powder impregnation avoided self-filtration of the carbon nanotubes and the carbon nanotubes were randomly oriented throughout the composite.

Results from the mechanical testing of MPVDF composites showed a drop of 9% and 18% in compression and flexural strength, respectively, as compared to PVDF composites. However, a drop of 19% and 8% was observed in short beam shear strength and fracture toughness, respectively, in the same. This reduction in macromechanical performance of MPVDF composites as compared to PVDF composites contradicts the wetting results obtained from contact angle measurements [28]. Later on it had been claimed through X-ray photoelectron spectroscopy (XPS) that the surface of MPVDF contained only 2.5% MAH, which was less than the 7% expected based on the simple two fold dilution of 100% MAH-g-PVDF (containing 14% MAH). This suggests that MPVDF is rather inhomogeneous with preferential surface segregation of PVDF. However, no major surface impurities were introduced by modifying PVDF by MAH [139]. However, MPVDF hierarchical composites presented the same trend as PVDF i.e. showed a 28% increase in compression strength, 6% increase in flexural strength and a 51% increase in apparent short beam shear strength by the incorporation of 1.25 wt% CNTs, but a 14% and 45% drop in compression strength, 20% and 158% drop in flexural strength and 4% and 118% drop in short beam shear strength at higher CNT loading of 2.5 wt% and 5 wt%, respectively. This contradiction between mechanical performance and the quality assurance results of AS4/MPVDF is also verified by the fact that MAH is not homogeneously segregated on PVDF surface. On the other hand, 100% MAH-g-PVDF has shown extremely superb wetting with AS4. Polymer wets the fibres completely making it impossible to determine the contact angle (no discrete droplets of polymer melt formed) [17]. This can be verified by chemical pinning of 100% MAH-g-PVDF matrix droplet wetting front on the surface of carbon fibre. So, it is probably the solution precipitation method which did not introduce MAH moieties evenly throughout the polymer matrix so that the full potential could not be achieved. 100% MAH-g-PVDF should not have such kind of uneven segregation issues and should be capable of providing extraordinary macromechanical properties in addition to the superb quality assurance results. An interesting

approach would be to try various PVDF samples containing different MAH contents for improving the wetting and hence the interfacial adhesion of PVDF CFRPs.

Compression modulus was similar for all MPVDF hierarchical composites i.e. 106 ± 5 GPa irrespective of the CNT content. A negligible change was observed in flexural modulus of AS4/PVDF and AS4/MPVDF composites. However, a 12% increase in flexural modulus of MPVDF composites was observed with the addition of 1.25 wt% CNTs (when alternate plies of AS4/MPVDF containing 0 and 2.5 wt% CNTs were consolidated) which was reduced by 2% and 8% for the composites containing 2.5 wt% and 5 wt% CNTs because of the poor fibre impregnation probably due to higher viscosity of nanocomposite matrices containing higher CNT content. These results indicate that full potential of enhanced matrix dominated properties in hierarchical composites can only be achieved if matrix infuses/impregnates the fibres completely, than only quality interfacial adhesion is achieved and load can be transferred from the stiffened matrix to the fibres. AS4/MPVDF hierarchical composites showed an improvement in mechanical performance up to an optimum loading of CNTs i.e. 1.25 wt% (mixed plies), however, further addition of CNTs make it difficult for the fibres to impregnate completely by higher viscosity nanocomposite powders containing higher CNT content which results in poor mechanical performance. The fracture toughness of MPVDF hierarchical composites dropped by 8%, 45% and 48% with the addition of 1.25 wt%, 2.5 wt% and 5 wt% CNTs respectively. Compression gives an idea of matrix dominated properties, whereas flexure and short beam shear give an insight in to fibre/matrix interface. These results suggest an improvement in the fibre/matrix interface with the addition of 1.25 wt% CNTs (due to well impregnation) which became poor when CNT content was raised further to 5 wt% (due to poor impregnation at higher CNT content). Similarly, a poor interface at higher loadings of CNTs, because of the higher viscosities of nanocomposite matrices, resulted in a drop of the fracture toughness of MPVDF hierarchical composites.

Fractographic analysis was conducted to investigate the influence of CNT concentration on the fibre/matrix interface. MPVDF composites depicted a cohesive failure at the junction between fibre and matrix, but leaving the fibre clean means fibre/matrix bonding was decreased with the addition of MAH-g-PVDF in PVDF. Whereas, the addition of CNTs in the composites resulted in occurrence of bare fibres devoid of any polymer debris in the fracture surface which suggests CNTs are adversely affecting the interface. One of the possible reasons could be poor impregnation of fibres due to the higher viscosity nanocomposite

powders. In conclusion it can be said that although MPVDF did not exhibit the expected enhanced mechanical performance possibly due to the uneven distribution of MAH moieties on PVDF surface [139], the quality of the MPVDF composites produced using laboratory scale composite production line was still improved with an optimum loading of CNTs. Also fractographic analysis depicted that MPVDF nanomatrix showed poorer interfacial adhesion with AS4 as compared to PVDF nanomatrix which is indicative of poor wetting between CNTs and MPVDF.

Chapter 7 - Carbon Fibre Reinforced PEEK Hierarchical Composites

7.1 Introduction

In this section, results obtained from mechanical characterisation of PEEK hierarchical composites are explained in detail. A significant interest in the mechanical properties of poly ether ether ketone (PEEK) based CFRPs has already been reported. PEEK was chosen to follow on from Dr. Steven Lamoriniere's PhD [14] research on PEEK hierarchical composites, in polymer and composite engineering group (PaCE), Imperial College London and to assess whether the cause of reduction in mechanical performance of PVDF hierarchical composites at higher CNT loadings is poor wetting between PVDF and CNTs or the limited presence of PVDF (insufficient impregnation of fibres by PVDF nanocomposite matrices) at the fibre/matrix interface to provide necessary interfacial adhesion. Carbon fibre reinforced PEEK composites have the potential to facilitate improvements in material performance for use in aerospace applications as PEEK is also a high performance, semicrystalline thermoplastic. It would have high toughness (approximately 10 times higher than traditional carbon fibre reinforced thermosets composites). The high stiffness and low density of carbon fibre reinforced PEEK composites makes them a good choice for advanced designs that require the combination of non-metallic and metallic materials. On the other hand, despite the advantages offered by PEEK based CFRPs, they are relatively expensive and difficult to

process (need relatively higher processing temperature), when considered for oil field applications, as compared to PVDF when reinforced with carbon fibres to make high performance composites.

Unidirectional carbon fibre reinforced T700/PEEK hierarchical composites with different CNT loadings were fabricated successfully using the continuous composite line setup as explained in Chapter 3. SEM (Figure 7-1) shows a homogeneous distribution of CNTs in T700/PEEK hierarchical composite. The in-house manufactured T700 carbon fibre reinforced PEEK with various CNT loadings of 0 wt%, 1 wt%, 2.5 wt% and 5 wt% and commercially available APC-2 were characterised for their mechanical performance. Composites were tested under uniaxial compression, to characterise the compression strength and modulus and DCB to characterise mode I fracture toughness. The results recorded are explained in detail in this chapter.

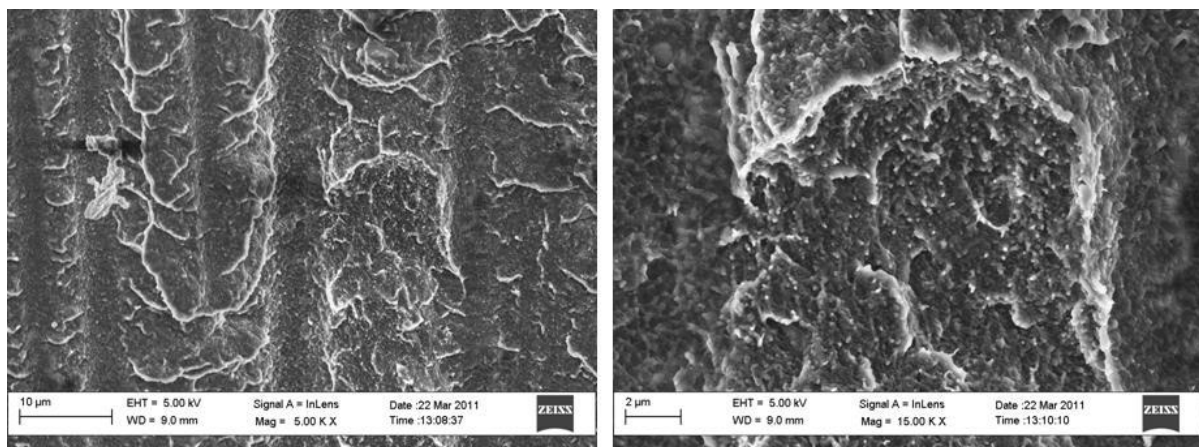


Figure 7-1: SEM micrograph of a typical DCB fracture surface of successfully fabricated unidirectional carbon fibre reinforced T700/PEEK composites containing 2.5wt% CNT (left) low magnification ($\times 5k$) (right) higher magnification ($\times 15k$)

7.2 Production and Characterisation of Carbon Fibre Reinforced PEEK Composites

The aim of this particular study was firstly to compare the quality of the in house manufactured T700/PEEK composites made from PEEK (PEEK-150, powder form) with commercially available AS4/PEEK APC-2 composite tapes and secondly to investigate the influence of CNTs on the mechanical performance of hierarchically reinforced T700/PEEK composites. The in-house manufactured CF/PEEK-150 composites contain T700 (epoxy

sized) carbon fibres whereas APC-2 contains AS4 which is an unsized carbon fibre. The surface chemistry of the two carbon fibres is very different; AS4 carbon fibres have a surface oxygen content, as determined by XPS, of 7 at.% [136] whereas T700 fibres contain 18 at.% surface oxygen [53]. T700 fibres have higher mechanical properties than AS4 fibres (see Table 3-1). Unfortunately, T700 is commercially only available with an epoxy sizing, which however, could be partially degraded during the production of composite tape as PEEK is processed at 390°C (above the degradation temperature of epoxy[14]). The idea was to take advantage of the higher mechanical properties of T700 and PEEK in fabricating hierarchical composites at a processing temperature of 390°C (during tape production and laminate fabrication) which partially burns off epoxy sizing [14]. The partially degraded epoxy sizing on the carbon fibres could potentially not only introduce defect sites but also possibly act as weak boundary layer [143] at the fibre/matrix interface. A fibre volume fraction of 60% is present in APC-2 however the in house manufactured T700/PEEK composite only had a fibre volume fraction of 55%. A higher fibre volume fraction (60%) of hierarchical composites resulted in bare fibres (possibly due to poor impregnation of fibres caused by insufficient matrix content) when fracture surfaces were analysed. So a lower fibre volume fraction (55%) was chosen for T700/PEEK hierarchical composites to avoid consolidation issues. This was targeted to avoid failing of in house manufactured consolidated composite tapes by splitting/delaminations because of absence of sufficient polymer in composites. Despite the consistency in samples preparation via compression moulding; the thickness of APC-2 (0.2 mm) was in fact double the thickness of the in house manufactured T700/PEEK composite tape. This would mean that to achieve the same specimen thickness, as specified in the standard for testing, the amount of manufactured composite tapes required was twice the amount of the hand cut APC-2 strips, i.e. the experimental error involved was higher.

7.3 Results and Discussion

7.3.1 Influence of CNT Loading on Compression Properties of PEEK Hierarchical Composites

Composites were tested under uniaxial compression to characterise the compression strength and modulus [98]. Details for compression strength determination of hierarchical composites are provided earlier in section 3.4.3. ICSTM was adopted to determine compression properties [135]. Specimens, (90 mm× 10 mm × 2 mm), were cut from the laminates using a diamond tipped saw (Diadisc 4200, Mutronic GmbH & Co, Germany). Specimens were bonded with

end tabs (CROYLEK, F-glass sheet) to prevent failure at the specimen ends and to diffuse the gripping loads. Strain gauges (FLA-2-11, Tokyo Sokki Kenkyujo Co., Ltd.) were attached to both front and back of the specimens to determine strain, with precise alignment as defined in the standard [135]. The compression modulus was obtained from the slope of the stress-strain curve plotted from the data obtained. Compression performance of carbon fibre reinforced PEEK composites is shown in Table 7-1.

It was observed that in house prepared T700/PEEK composites showed a 17% lower compressive strength than APC-2 when tested according to ICSTM whereas the strength reported for APC-2 by Cytec was 1360 MPa, which is 36% higher than that obtained in this study for the same material (998 MPa) (Figure 7-2). The possible reasons could be that a different standard was followed for testing materials in uniaxial compression or the misalignment of fibres in the composites, which has significant effect on both strength and stiffness of the material [98]. This (difference in results determined through different standards) was the motivation to use a different test method i.e. reverse chamfered end tabs (as explained in Chapter 3) were used. This resulted in a 6% increase in strength of APC-2 as compared to what was measured via ICSTM. But this is still 28% lower than the reported value of strength for APC-2 by Cytec.

Sample	Fibre	FVC $\bar{V}_f$	Testing details	E_c [GPa]	$\bar{E} = E \frac{0.6}{V_f}$	σ_c [MPa]	Strain $\mu\epsilon$
APC-2 (Literature)	AS4	0.60	Celanese Jig	124	124	1360	---
APC-2	AS4	0.60±0.01	ICSTM	122 ± 1	122 ± 1	998 ± 30	8712 ± 282
APC-2	AS4	0.60±0.02	Reverse Chamfered end tabs	126 ± 3	126 ± 3	1060 ± 9	8833 ± 316
PEEK	T700	0.55±0.03	ICSTM	114 ± 3	124 ± 3	853 ± 26	7995 ± 333
PEEK/1 wt% CNT	T700	0.55±0.02	ICSTM	107 ± 3	123 ± 3	945 ± 14	9930 ± 300
PEEK/2.5 wt% CNT	T700	0.55±0.02	ICSTM	112 ± 2	123 ± 2	811 ± 40	8236 ± 822
PEEK/5 wt% CNT	T700	0.55±0.02	ICSTM	115 ± 2	122 ± 2	778 ± 21	8422 ± 288

Table 7-1: Compression performance of carbon fibre reinforced PEEK hierarchical nanocomposites

Interestingly upon addition of 1 wt% CNTs, the compression strength increased by 11% for T700/PEEK hierarchical composites when measured via ICSTM. However, upon addition of 2.5 wt% and 5 wt% CNTs, the compression strength decreased by 5% and 9%, respectively. This finding would suggest that perhaps at very low CNTs loading, impregnation i.e. fibre/matrix contact can be improved and enhancement in matrix dominated properties of a hierarchical composite can be availed (see details in fractography later), but as the CNTs loading increased further then the enhancement would diminish. This reduction in mechanical performance could possibly be due to difficulty in maintaining few processing issues involved when processing CNTs particularly at higher loadings, i.e. their higher viscosity, homogeneous distribution, arrangement of the CNTs etc. (see Chapter 2).

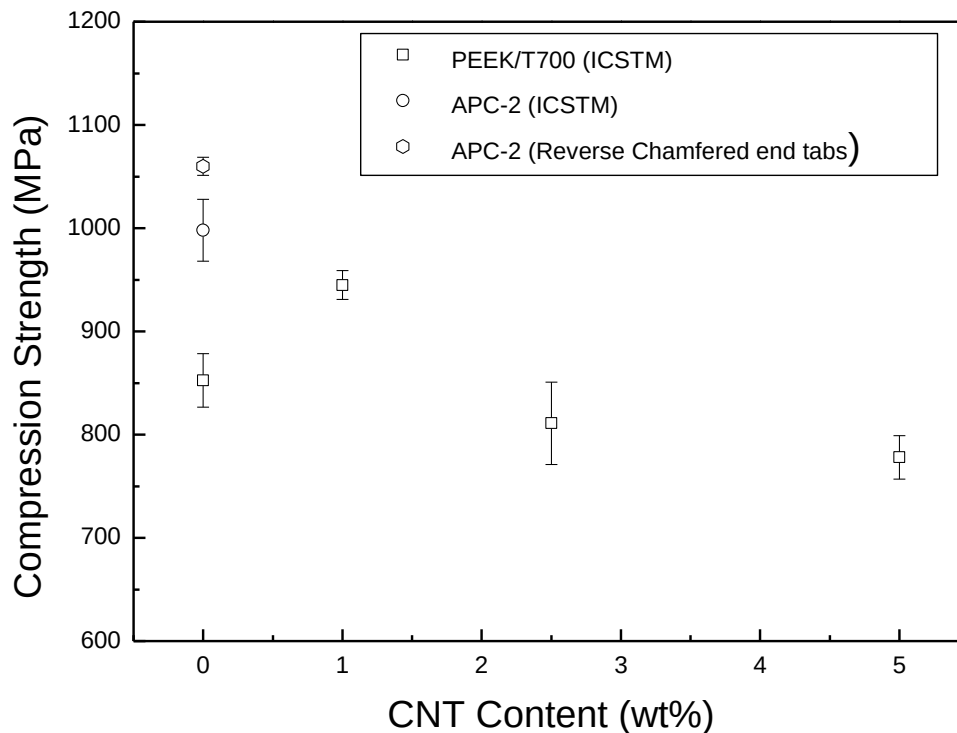


Figure 7-2: Compression strength of APC-2 and in-house prepared T700/PEEK-150 hierarchical composites as a function of CNT loading

It can be seen that (Figure 7-2) the in-house manufactured T700/PEEK composite specimens had a lower compressive strength compared to APC-2 (AS4/PEEK). However, the FVC of the T700/PEEK composites was only 55%. The lower mechanical properties are due to the fact

that fewer fibres are present to carry the applied load when the specimen was loaded under compression. One should not forget the aim of this research i.e. to modify the matrix within a fibre reinforced composite system by the incorporation of CNTs. If the matrix content in such system increases, then the effectiveness of matrix modification on the overall mechanical properties of the composite should be enhanced accordingly. Furthermore, its higher resin content in the middle region of in-house manufactured APC-2 specimens, where a higher out of plane load can be transferred (from glass end tabs to the specimens through shear via friction between specimen and grips) as compared to the T700/PEEK specimens which has lower resin content.

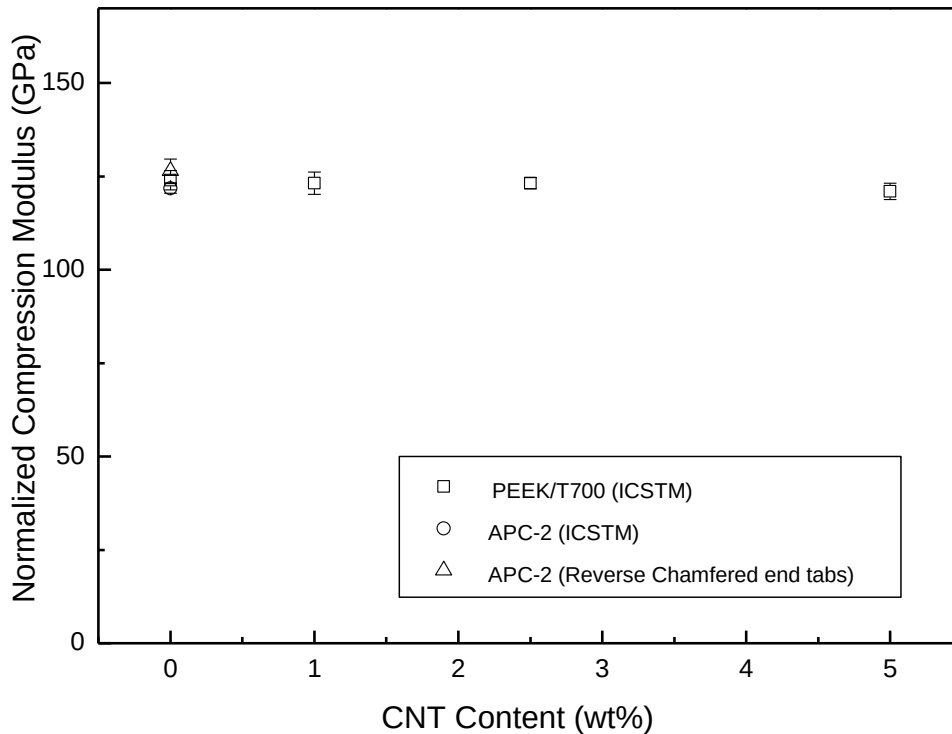


Figure 7-3: Normalised compression stiffness for APC-2 and T700/PEEK-150 hierarchical composites as a function of CNT loading

The measured compression modulus of the manufactured T700 carbon fibre reinforced PEEK composites was normalised to a fibre volume fraction of 60% which revealed similar compression stiffness of 124 ± 2 GPa for all T700/PEEK composites independent of CNT loading (Figure 7-3). This indicates that stiffness value for in house manufactured

T700/PEEK composites is identical to the reported stiffness value for APC-2 i.e. 124 GPa [36].

It was observed that the compression strength and modulus provided by Cytec i.e. 1360 MPa and 124 GPa, respectively, were higher than the those determined during this study using both the ICSTM standard with 45° chamfered end tabs as well as reverse chamfered end tabs (inwards opposite to the gauge area). A difference in specimen configuration or jig could be responsible for the different values obtained as is obvious in Figure 7-2. The compression modulus calculated via 45° chamfered end tabs as mentioned in ICSTM and reverse chamfered end tabs for modulus of APC-2 is 122 GPa and 126 GPa respectively. Whereas modulus obtained for APC-2 by Cytec using the different jig is 124 GPa (Figure 7-3).

The compression strength of T700/PEEK composites was found out to be 63% higher as compared to AS4/PVDF composites. The normalised moduli for a fibre volume content of 55% indicated an 8% higher value for T700/PEEK composites as compared to AS4/PVDF composites. Also, T700/PEEK hierarchical composites exhibited the same trend as PVDF and MPVDF hierarchical composites i.e. the compression strength increased by ~50% with 1/1.25 wt% CNTs but decreased with increasing CNT loading. However, there was no significant change in compression modulus due to CNT loading. So, this reduction in compression strength of hierarchical composites at higher CNT loadings could probably be due to the inclusion of voids caused by the high viscosity of nanocomposite matrix which leads to delaminations (see fractography).

7.3.2 Influence of CNT Loading of PEEK Hierarchical Composites on Fracture Toughness

Composites were tested for DCB to characterise mode I fracture toughness. Mode I fracture toughness as calculated from DCB tests provide matrix dominated properties at initiation whereas fibre/matrix interface dominated properties during propagation (if there is not much significant fibre bridging) and thus can provide an insight in to how CNTs are affecting the fibre/matrix contact in hierarchically reinforced PEEK composites. The mode I fracture toughness of commercially available APC-2 specimens and manufactured T700/PEEK composites with CNT loadings of 0%, 1%, 2.5% and 5% was measured using the DCB. The steady state energy release rate ($G_{IC,ss}$) was calculated using the modified beam theory and Berry's method of compliance calibration as explained in detail in Chapter 3. Resistance curves, or R curves, were generated for all PEEK composites by plotting the calculated ' G_{IC} '

values as a function of crack length ‘a’ to characterise the initiation and propagation of a delamination in a unidirectional composite. As the delamination started growing, the calculated G_{IC} first started increasing monotonically, and then stabilized with further delamination growth generating a steady state plateau. This steady state plateau was achieved at a crack length of 70 mm for all PEEK composites. So $G_{IC,ss}$ was taken as G_{IC} value at $a=70\text{mm}$. The initiation value gave an indication of matrix behaviour on its R-curve whereas the propagation values provide an insight in to the fibre/matrix interface of the composite.

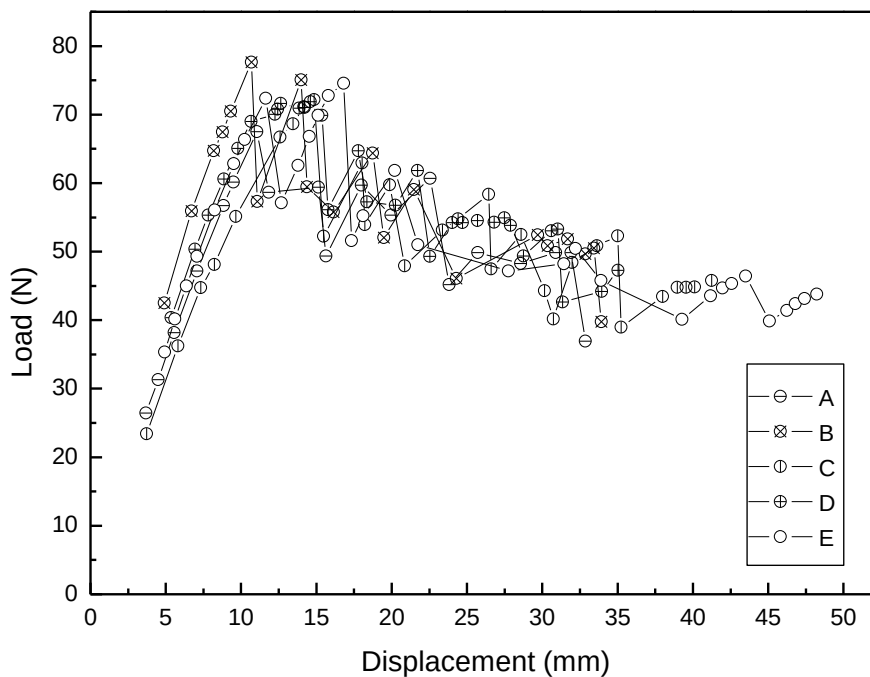


Figure 7-4: Load-displacement curves from DCB testing for five nominally identical (A-E) T700/PEEK composite specimens

Load displacement curves for T700/PEEK composites are shown in the Figure 7-4. Stable crack propagation but stick and slip behaviour was observed for all T700/PEEK and APC-2 composites. There were one or more regions of no, or very slow delamination growth followed by a delamination yielding sharp drops in load-displacement graphs with virtually infinite slope. Fibre bridging was more dominant in PEEK composites as compared to PVDF composites, probably because of the presence of a plastic zone at the crack tip which takes longer to open up resulting in breakage of fibres during the process shown by a peak in the

load value. Also, one of the reasons for fibre bridging being prevalent throughout the propagation could be the fibre misalignment caused by difference in viscosities of different grades of PEEK used as facesheets and doublers in DCB samples. This is shown by the arrest points (no delamination growth) and a reloading phase which results in a local peak load when delamination growth restarts. Such stick slip behaviour in the load-displacement curve was analysed by excluding the arrest points.

DCB specimens which failed by a mixture of stable and unstable crack propagation it is noticeable that the point of unstable crack initiation showed a higher toughness than all the previous values. This suggest that crack tip blunting was occurring, causing stored elastic energy in the sample to build up until there was sufficient driving force for unstable propagation. The mechanism for this blunting could be either local fibre bridging or an increase in the resin concentration around the crack tip, both of which would increase the local toughness and slow down the crack propagation and cause a build-up of strain energy until fast fracture initiated.

No flexural failure was observed in any of the DCB specimens of T700/PEEK or APC-2 and the arms recovered back to their original position which indicated that all the energy was utilized in the crack opening of the particular material. Doublers (see details in Chapter 3) helped in preventing the premature bending failure of the DCB specimen because the extra thickness, which reduced the bending stresses in the composite [113]. The highest compressive stress occurs in the doubler plate, i.e. APC-2 which can tolerate higher compressive stresses than the composite. The DCB specimen arms are not perfectly built and rotation may occur at the delamination front. In order to account for that rotational effect during DCB it was considered as if it contained a longer delamination at each length, i.e. $a+|\Delta|$, where $|\Delta|$ is the correction factor and was calculated as the x-axis intercept on the plot of the cube root of the compliance, $C^{1/3}$, as a function of delamination or crack length 'a'. The compliance 'C' is ratio of the displacement to the applied load i.e. $C = \delta/P$. For the calculation of G, only the specimens with a Δ value in the range of 2.8-5.1 were considered in the analysis as is recommended in literature [98]. A plot explaining the Δ determination is shown in Figure 7-5.

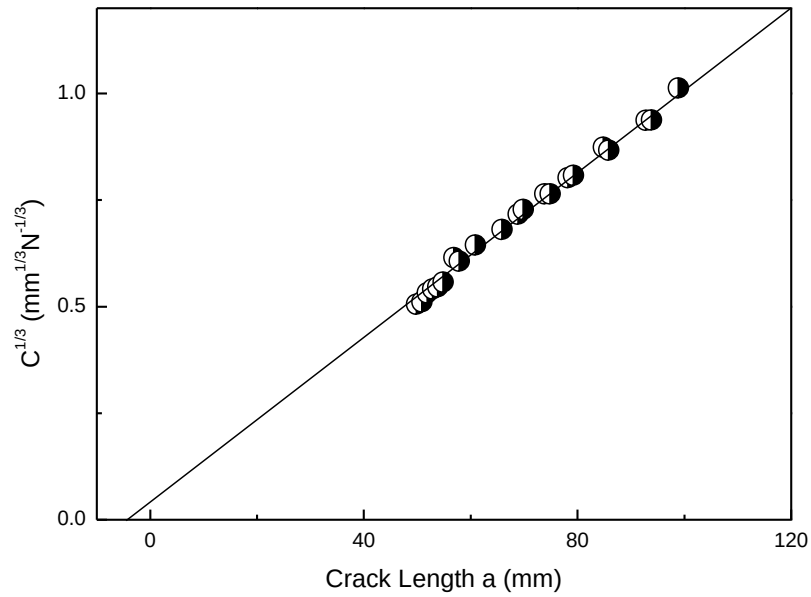


Figure 7-5: Determination of Δ (x-axis intercept on the plot of the cube root of the compliance, $C^{1/3}$, as a function of delamination or crack length 'a' using the modified beam theory, $|\Delta| = 4.40\text{mm}$

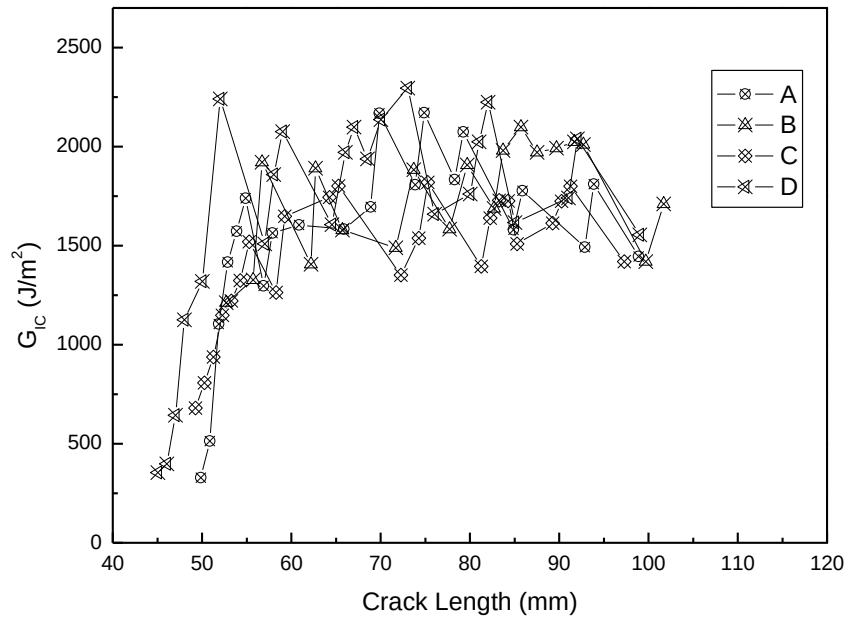


Figure 7-6: Delamination resistance curves (R-curves) for four nominally identical specimens (A-D) of T700/PEEK + 1 wt% CNT hierarchical composites

A plot of G_{IC} as a function of crack length (a) for T700/PEEK hierarchical composites containing 1wt% CNT can be seen in Figure 7-6. It is clear from these results that the energy release rate stabilises rapidly and the propagation values are well within the steady state crack growth regime, i.e. a steady state plateau is generated. The principal reason for the observed resistance to delamination is the development of fibre bridging. This fibre bridging mechanism results from growing the delamination between two 0° unidirectional plies. The specimens with arm thickness ' h ' different for two halves of the beam were excluded from the analysis to reduce the scatter. The analysis of the results showed that $G_{IC,ss}$ (i.e. G_{IC} @ $a = 70\text{mm}$) averaged for five specimens of T700/PEEK-150 hierarchical composites containing 1 wt% CNT was $2290 \pm 120 \text{ J/m}^2$ which was 35% higher than that of APC-2 (G_{IC} : 1700 J/m^2) [36].

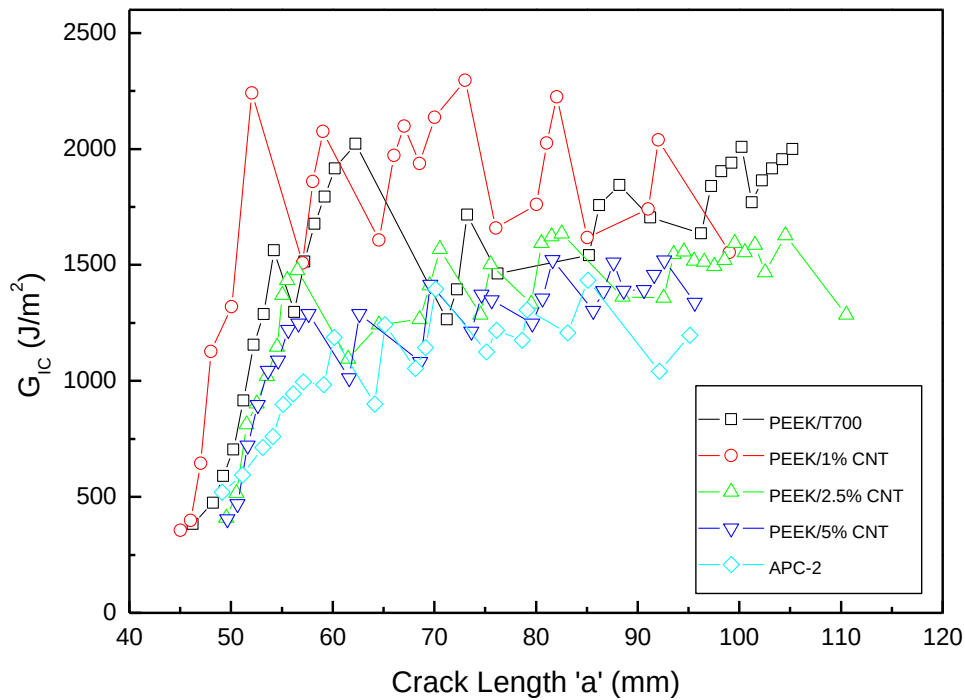


Figure 7-7: R-curves representing the fracture toughness of commercially available APC-2 and T700/PEEK hierarchical composites containing 0 wt%, 1 wt%, 2.5 wt%, and 5 wt% CNTs (one representative R-curve is drawn from nominally identical specimens for each formulation)

The values of flexural modulus (E_{1f}) provided in the Table 7-2 determined using the modified beam theory (see Chapter 3) were independent of delamination length, but 25% higher than

the those calculated from the 3 point bending flexure test because of the fibre misalignment [14]. It was observed that flexural modulus for T700/PEEK-150 composites was 11% higher than APC-2.

Material	$G_{IC} @ a=50$ J/m ²	E_{1f} (GPa) [14]	E_f (GPa) (3 point bending)	$G_{IC} @ a=70$ J/m ²
APC-2-Literature	-	124	-	1700
APC-2	435 ± 18	130 ± 5	119 ± 2	1650±178
T700/PEEK	436 ± 26	144 ± 3	105 ± 3	2100±151
T700/(PEEK + 1 wt% CNT)	383 ± 23	145 ± 4	106 ± 3	2290±120
T700/(PEEK + 2.5 wt% CNT)	444 ± 26	148 ± 3	110 ± 3	2170±116
T700/(PEEK + 5 wt% CNT)	415 ± 18	137 ± 9	108 ± 4	2100±170

Table 7-2: $G_{initiation}$, $G_{propagation}$ and flexural moduli of APC-2 and T700/PEEK-150 hierarchical composites calculated via the modified beam theory method

The steady state critical energy release rate $G_{IC,SS}$ for APC-2 determined was 3% lower (which lies within error) than that reported by the manufacturers (Cytec) However, $G_{IC,SS}$ for T700/PEEK-150 composites was 27% higher than APC-2 and with only 1 wt% CNTs loading in T700/PEEK-150 composites the $G_{IC,SS}$ increased by 35% as compared to APC-2 and by 9% as compared to T700/PEEK-150 composites. These results contrast with the fracture toughness values for PVDF and MPVDF hierarchical composites explained earlier (Chapter 5 and 6) likely due to poor compatibility between PVDF and carbon fibres [28]. However, there was negligible increase in $G_{IC,SS}$ when CNT loading was further increased to 2.5 wt% and 5 wt%. The reason for higher flexural modulus and $G_{propagation}$ of T700/PEEK-150 composites as compared to APC-2 is probably the fact, that APC-2 still contains appreciable amounts of DiPhenyl Sulfone (DPS) [144] (as quantified by Bismarck et al.) [145]. The Cytec process is a melt impregnation process; PEEK is melted in DPS, which is a good solvent for PEEK but also acts as plasticizer for PEEK. One can therefore expect that the presence of DPS impacts on the mechanical properties of CF/PEEK. Moreover, the PEEK grade used to manufacture APC-2 is a well-guarded secret of the manufacturer Cytec, but it can be assumed that it is a low melt viscosity grade. The fibre (mis)alignment of the

laminated CF/PEEK tapes, caused by different melt viscosity of the matrix during compression moulding at conditions optimised for the in-house CF/PEEK tape, can also be a factor influencing the mechanical properties of the final composites [146].

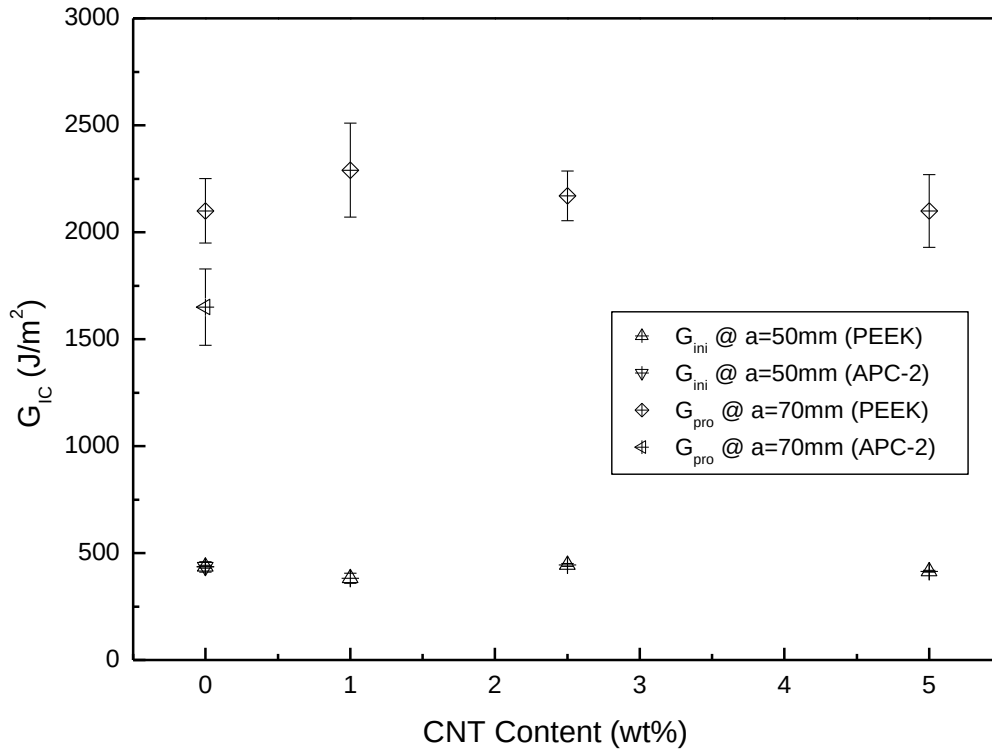


Figure 7-8: $G_{initiation}$ and $G_{propagation}$ for APC-2 and T700/PEEK-150 hierarchical composites as a function of CNT content.

However, in contrast to the compression results AS4/PVDF composites exhibited 18% and 45% higher $G_{IC,SS}$ values (fracture toughness) as compared to T700/PEEK-150 and APC-2 specimens respectively.

7.4 Fractography of PEEK Composites

Fracture surfaces of compression and DCB failed specimens were analysed to understand the damage modes and failure mechanisms. Electron micrographs of 3 nominally identical specimens of each composite formulation were taken and compared to see inherent differences.

7.4.1 Fractographic Analysis of Compression Failed PEEK Composites

Fractographic assessment of compression failures was conducted to understand the damage modes of failure. Polished cross sections of the failed compression specimens were analysed using optical microscope (BH2, Olympus, Tokyo, Japan). It was apparent from the micrograph (Figure 7-9) that the hierarchical composites containing different CNT contents failed in more or less the same way i.e. by a classic kinkband formation with a single localised band across the entire specimen

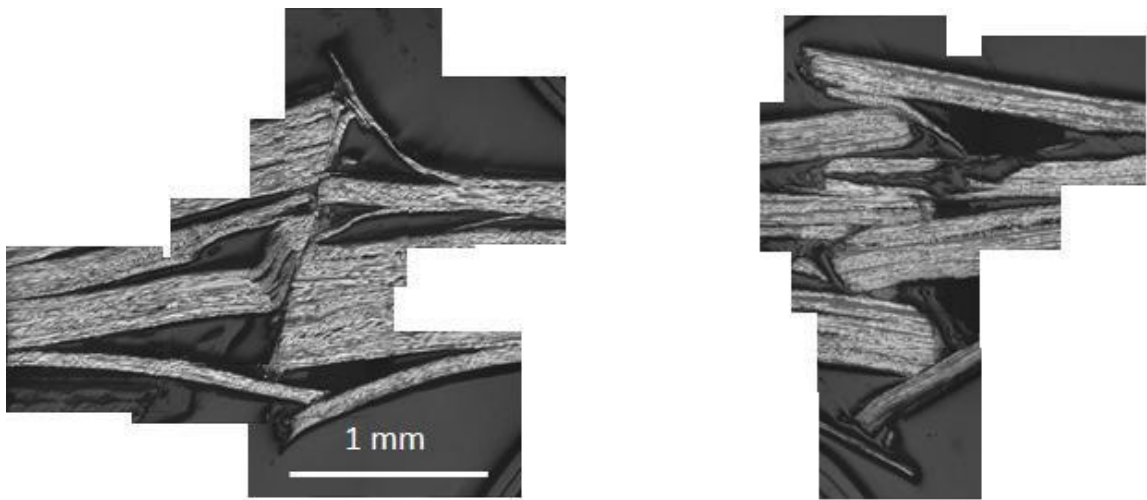


Figure 7-9: Micrograph showing the crosssections (gauge regions) of the failed compression specimens of T700/PEEK-150 composites (left) and T700/PEEK-150 hierarchical composites containing 5 wt% CNTs (right)

There were negligible delaminations, the prevalent kinkband extended across the entire specimen, ending in a catastrophic failure of the specimen leaving some polymer debris and broken fibres on the fracture surface as shown in the micrograph (Figure 7-10). As shown in Figure 7-10 (top), the composite failed in a classic kinkband formation leaving surface debris of failed matrix and broken fibres. The kinkbands were formed due to microbuckling of the fibres without any prior fracture process and then failed by fracture at the points of maximum flexural stress. There are limited delaminations seen at places showing the presence of a weak interaction (due to poor impregnation) between fibres and matrix.

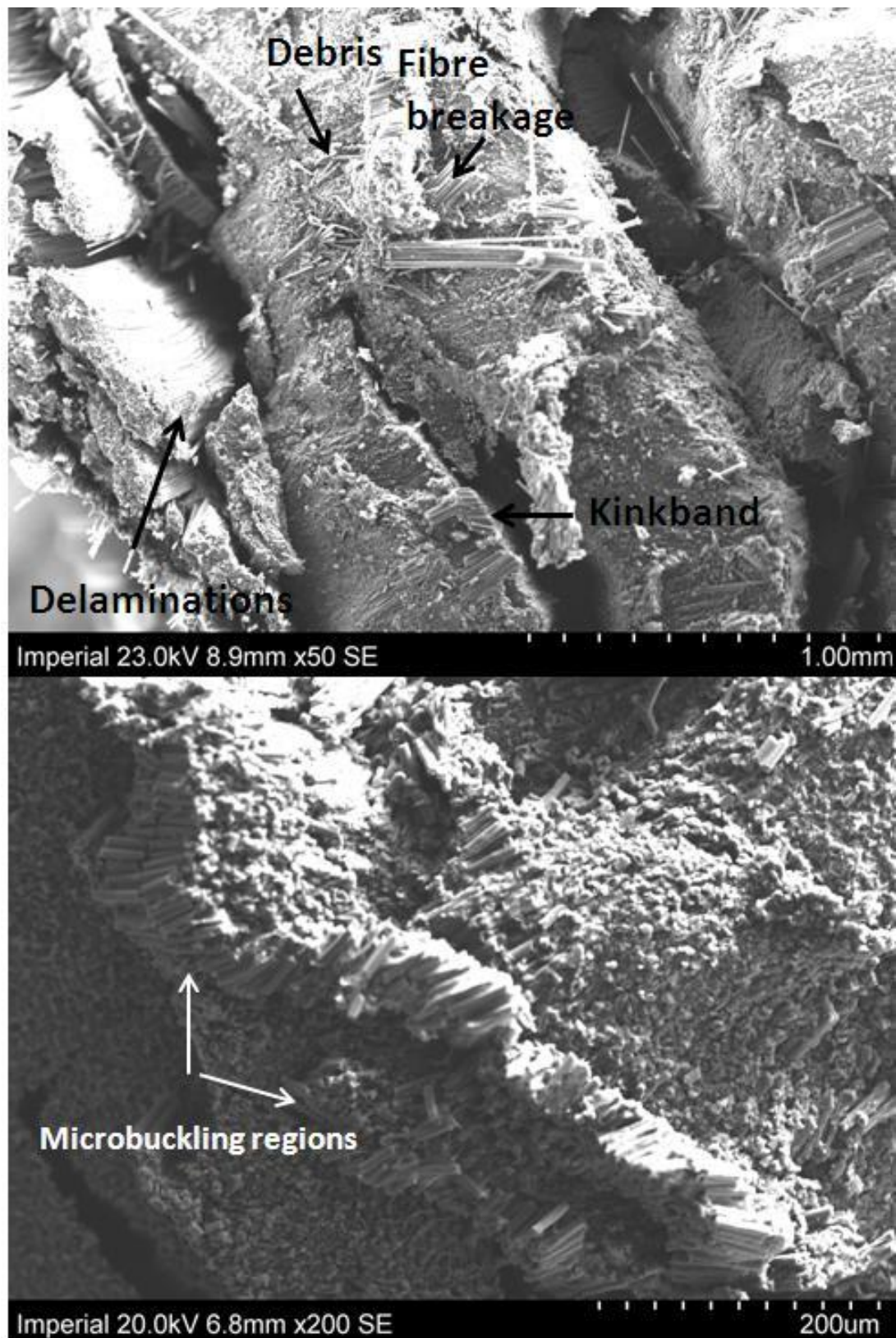


Figure 7-10: Compressive fracture surface of hierarchical carbon reinforced PEEK composites containing 2.5 wt% CNTs: at low magnification ($\times 50$) (top) at high magnification ($\times 200$) (bottom)

The detailed examination of the fibre ends of a compression fracture surface provides further evidence of the microbuckling failure mechanisms, seen in Figure 7-10 (bottom). The kinkband (microbuckling) formed due to a lack of or reduced lateral support of the fibres. The lack of support resulted from the splitting has induced localized microbuckling between fibres adjacent to the split. When the load increased, individual fibres microbuckled towards the split, leading to a band of microbuckled fibres [138]. Figure 7-11 shows the compression fracture surfaces of PEEK hierarchical composites containing 0-5 wt% CNTs. All composites failed more or less in the same way, i.e. catastrophically after the formation of a kinkband. There were delaminations observed in all specimens but kinkband formation was prevalent over delamination in all of them. A closer view of failed PEEK hierarchical composites is shown in Figure 7-12. It also shows the features of a classic kinkband failure due to microbuckling in both the composites containing 0 and 5 wt% CNTs.

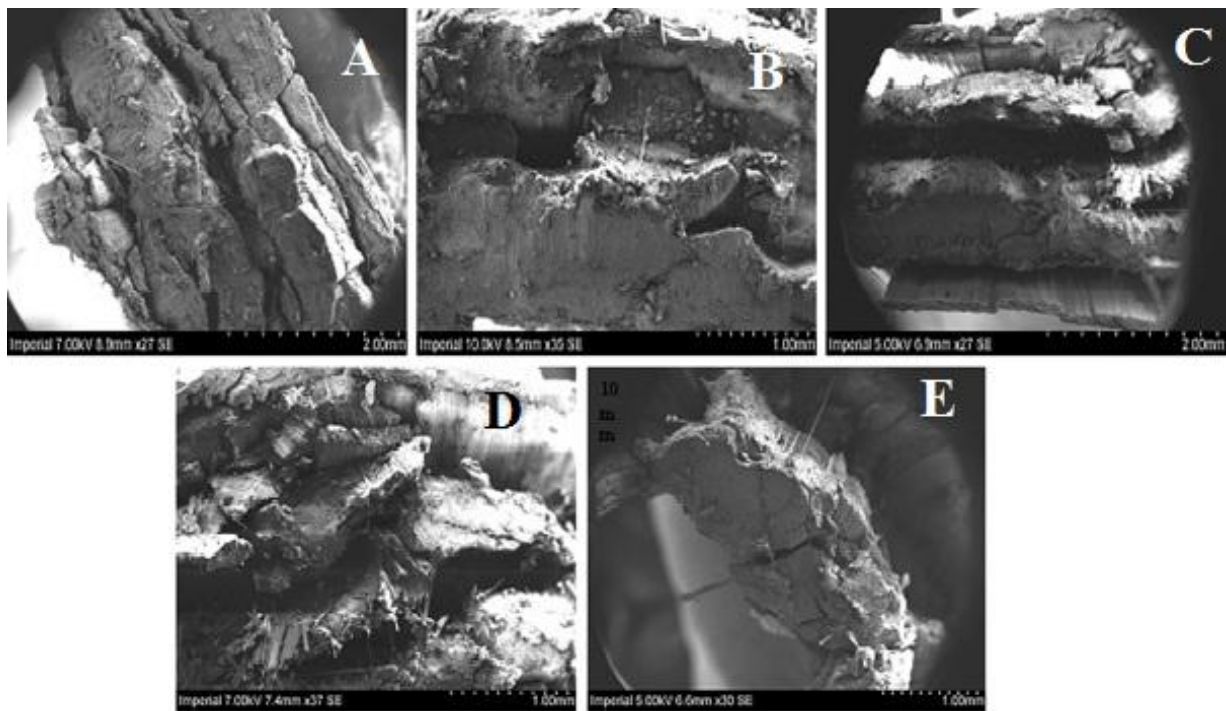


Figure 7-11: Typical SEM images for the compression fracture surfaces of carbon fibre reinforced composites A) APC-2, B) T700/PEEK-150, C) T700/PEEK-150 +1%CNT, D) T700/PEEK-150 + 2.5%CNT E) T700/PEEK-150+ 5%CNT

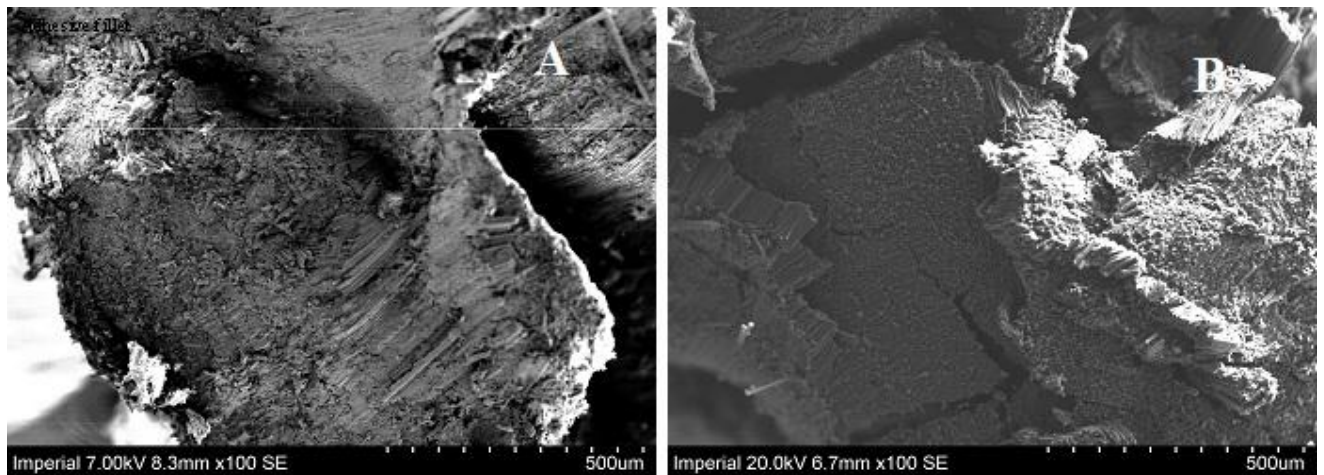


Figure 7-12: SEM images for the compression fracture surfaces of carbon fibre reinforced composites A) T700/PEEK-150, B) T700/PEEK-150 + 5%CNT

7.4.2 Fractographic Analysis of Failed PEEK DCB Composites

The fracture surface of the DCB samples was observed to determine the behaviour of the composites under mode I crack growth conditions.

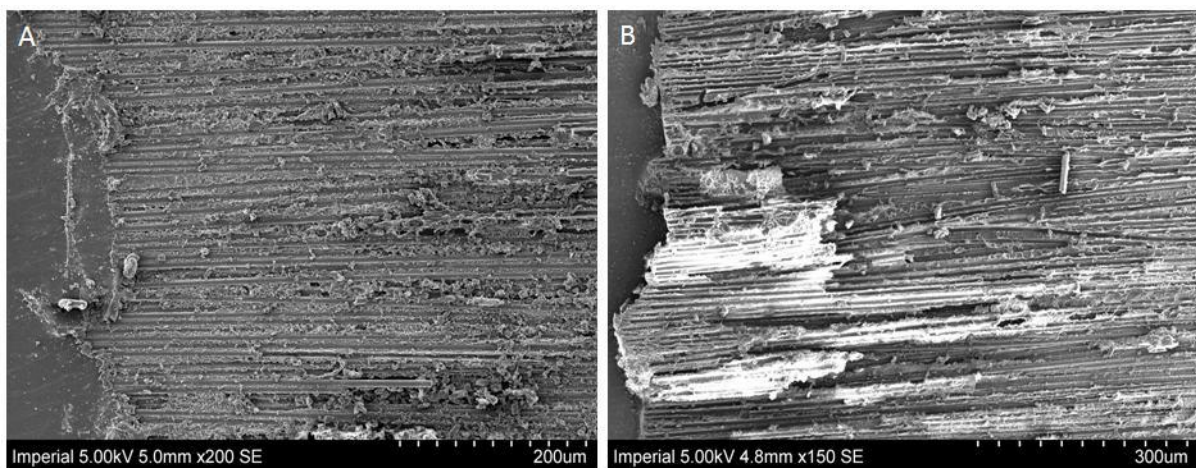


Figure 7-13: Typical SEM micrograph of a DCB Mode I fracture surface of A) T700/PEEK-150 composite B) commercially available APC-2

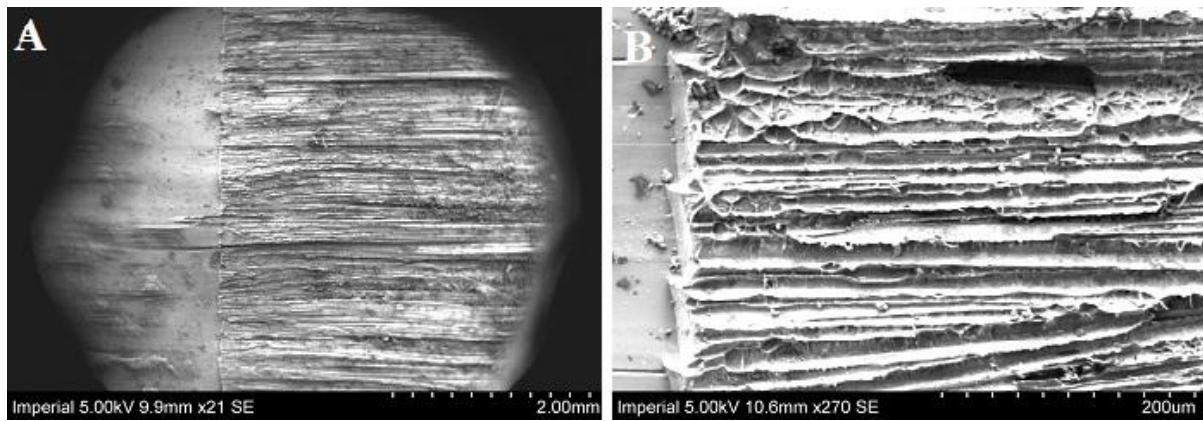


Figure 7-14: Typical SEM micrograph of a DCB Mode I fracture surface of T700/PEEK hierarchical composite containing 5 wt% CNTs at A) low magnification ($\times 21$) B) higher magnification ($\times 270$)

It was shown in Figure 7-13, that there was no ductile drawing observed in T700/PEEK-150 composites, which agrees with previous findings and is common observation for semicrystalline polymers [112]. That means with the addition of CNTs, the nanocomposite matrix actually started contributing and the fracture did not occur entirely at the interface which was observed in T700/PEEK composites. However, it was observed in the SEM micrographs (see Figure 7-14) that the T700/PEEK-150 composites containing 5 wt% CNT loading exhibited some ductile drawing of the matrix. A small amount of polymeric debris and fibre/matrix debonding was also apparent on the fibre surfaces of all PEEK composites. This suggested that matrix plastic deformation contributed to the mode I fracture toughness and the fracture did not entirely occur at the carbon fibre-PEEK interface. The higher magnification shows the surface is covered in tufted matrix (fibrils), which has undergone extensive and gross plastic deformation. This gross deformation forms fibrils of matrix, particularly in the regions of matrix between two close fibres. The normal orientation of the fibrils to the surface indicates the beam being loaded in peel, i.e. Mode I. These perpendicular matrix fibrils also indicated ductile drawing, which is a characteristic feature of a delamination failure in thermoplastic composites [147].

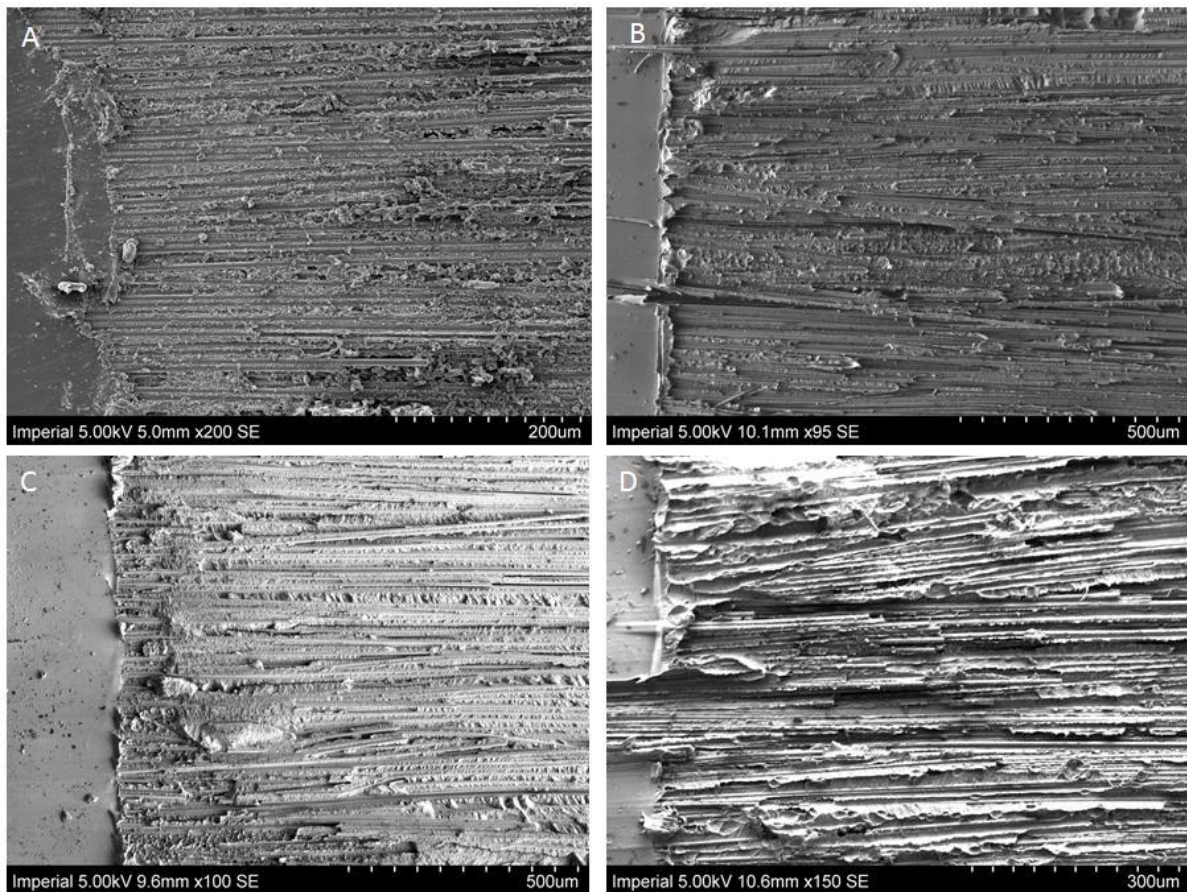


Figure 7-15: Typical SEM micrographs of a DCB fracture surface of A) T700/PEEK-150 and T700 reinforced, B) PEEK/1%CNT, C) PEEK/2.5%CNT and D) PEEK/5%CNT composites

The initiation point of crack growth shows a great amount of debris because of the contact of the fracture surfaces at this point during failure (Figure 7-15). Hine et al. [112] have shown the absence of plastic flow along with imprints of spherulitic textures in DCB fracture surfaces of AS4/PEEK composites, which is indicative of semicrystalline nature of PEEK. However, it is apparent that, with the increase in CNT loading, the contribution of matrix deformation is increased in fracture i.e. there is no plastic deformation in pure T700/PEEK-150 composites but maximum deformation in composites containing 5 wt% CNTs. So it can be concluded that, the matrix was improved upon addition of CNTs and is contributing in determining the fracture toughness, but still the fracture toughness decreased with a CNT loading of 2.5 and 5 wt%. This reduction in fracture toughness could be because of poor impregnation of T700 fibres by high viscosity PEEK nanocomposite powder melts at such high CNT loadings. As shown in the SEM micrograph (Figure 7-15) the wrinkling of the polymer film at the crack opening surface could be one of the reasons for the higher initiation values. For tougher polymers like PEEK, the plastic zone at crack tip is bigger [148] and on

the application of load before the polymer cracks actually a rise to fibre breaking occurs, which was the reason for the fibre bridging being prevalent throughout the opening of a DCB arm for carbon fibre reinforced PEEK composites. Also it is apparent from the SEM micrograph (Figure 7-15-D) that there were more voids in the hierarchical reinforced PEEK composites than that of pure T700/PEEK composites, which supports the fact that fibre impregnation became poor in composites by increasing CNT loading in nanocomposite matrices.

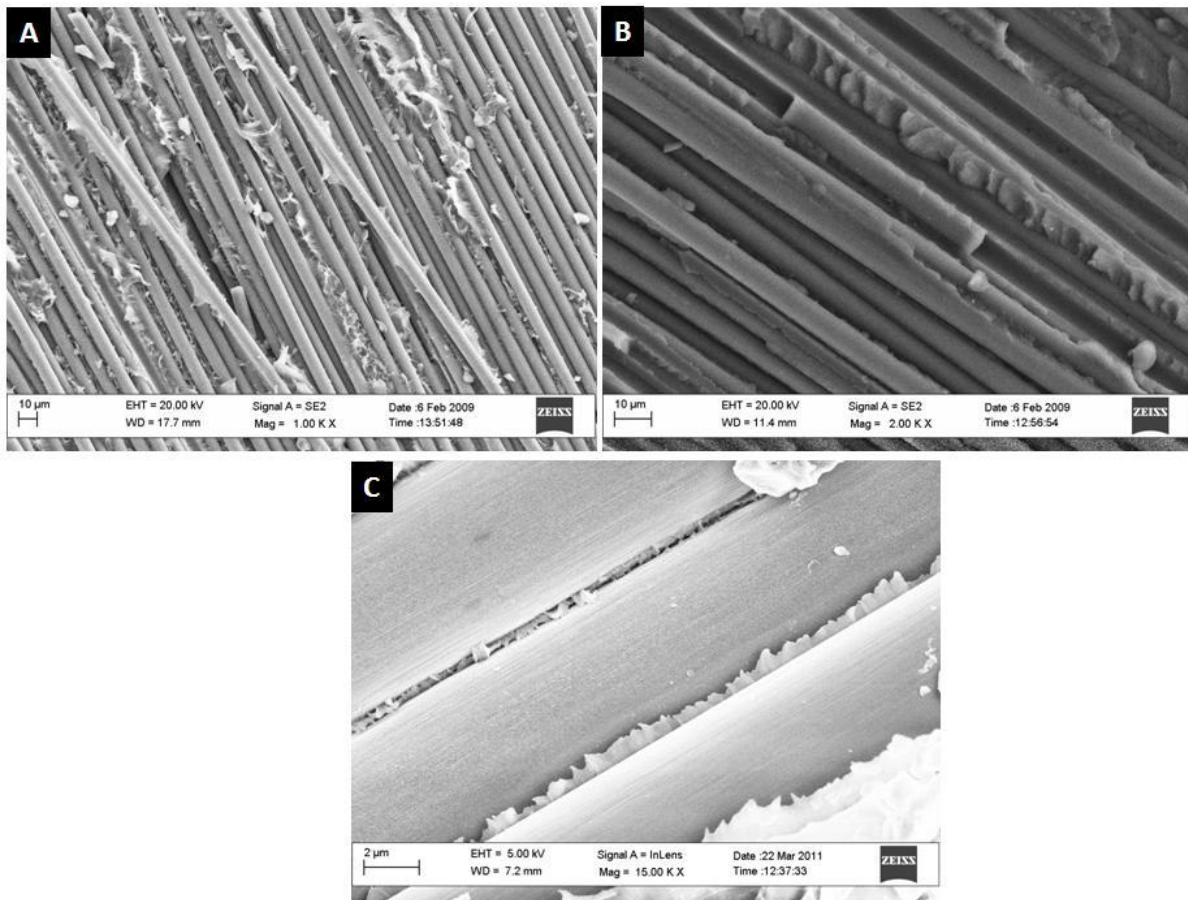


Figure 7-16: Typical DCB fracture surfaces of A) hierarchical PEEK composite containing 1 wt% CNTs, B) T700/PEEK containing 5 wt% CNTs and C) APC-2

Visual inspection of the crack revealed that fibre bridging was very prevalent during crack growth. Considering the SEM micrographs of the DCB Mode I fracture surfaces (Figure 7-15), it is clear that no consistent resin rich layer existed and the carbon fibres from the neighbouring plies were nesting within each other. Fibre nesting is known to promote fibre bridging as a mode I toughening mechanism [149]. The split/delamination initiation is dependent on a number of factors like the stiffness of matrix and fibre/matrix strength [138].

Hierarchical reinforced PEEK composites containing 1 wt% CNTs exhibited higher degree of ductile drawing as compared to rest of the PEEK matrices (i.e. APC-2 and PEEK nanocomposites containing 5wt% CNTs) as shown in Figure 7-16. A small amount of polymeric debris was also present on the fibre surfaces. This suggested that matrix plastic deformation contributed maximum in hierarchically reinforced PEEK containing 1 wt% CNTs to the mode I fracture toughness and the fracture did not entirely occur at the carbon fibre/matrix interface.

The extent of fibre/matrix strength may also be assessed from the surfaces of the fibres and the fibre imprints in the resin. A cohesive failure of the matrix around the fibre leaving the fibre extensively covered with the matrix residue indicates a good fibre/matrix bond whereas failure at the junction between fibre and matrix, leaving the fibre clean means poor fibre/matrix bonding. This also shows the fibre/matrix bond is being compromised at higher CNT loadings due to the processing difficulties associated with higher CNT loadings. For instance, higher viscosity of nanocomposite powders with increased CNT loadings makes it difficult/impossible to impregnate the carbon fibres completely and the benefit of enhanced matrix dominated properties in hierarchical composites can only be possible if it impregnates the carbon fibres well. It can be concluded from the fractographic analysis of T700/PEEK hierarchical composites that with the increase in the CNT loading in hierarchical composites of PEEK, matrix was improved and its contribution in determining the fracture toughness was improved, but strength of the fibre/matrix interface was compromised due to the processing issues related to CNTs at higher loadings in the PEEK hierarchical composites.

7.5 Summary

The aim of this particular study was firstly to compare the quality of the in-house manufactured CF/PEEK composites made from PEEK (PEEK-150, powder form) with commercially available CF/PEEK (APC-2) composite tapes and secondly to investigate the influence of CNTs on the mechanical performance of hierarchically reinforced PEEK composites. Carbon fibre reinforced PEEK composites were fabricated with CNT contents of 0 wt%, 1 wt%, 2.5 wt% and 5 wt% and characterised for compression strength, compression modulus and fracture toughness. Interestingly upon addition of 1 wt% CNTs, the compression strength increased by 11% for T700/PEEK hierarchical composites when measured via ICSTM. However, upon addition of 2.5 wt% and 5 wt% CNTs, the compression strength decreased by 5% and 9%, respectively. This finding would suggest that perhaps at very low

CNTs loading, impregnation i.e. fibre/matrix contact can be improved and enhancement in matrix dominated properties of a hierarchical composite can be availed, but as the CNTs loading increased further then the enhancement would diminish. This reduction in mechanical performance could possibly be due to difficulty in maintaining few processing issues involved when processing CNTs particularly at higher loadings, i.e. their higher viscosity, homogeneous distribution, arrangement of the CNTs etc. However, the measured compression modulus was 124 ± 2 GPa for all in house manufactured T700/PEEK-150 composites and T700/PEEK hierarchical composites containing various CNT loadings of 1 wt%, 2.5 wt% and 5 wt% as well as for the APC-2 specimens which is also identical to the reported compression stiffness value for APC-2 [36].

In comparison of AS4/PVDF and T700/PEEK composites, T700/PEEK composites exhibited better mechanical properties as compared to AS4/PVDF composites when tested in compression, flexure [14] and short beam shear strength [14]. On the contrary, fracture toughness of AS4/PVDF composites was 18% higher than T700/PEEK composites. Fracture toughness of both AS4/PVDF and T700/PEEK composites managed to maintain their fracture toughness up to 1/1.25 wt% CNT loading after which the enhancement diminished. These results are in agreement with interlaminar shear strength (SBS strength) results [14]. The short beam shear strength for T700/PEEK composites was 277% higher as compared to AS4/PVDF composites. Even when adding 1.25 wt% CNT in to AS4/PVDF showed a 50% improvement in SBS strength, (39MPa from 26MPa) it was still 150% lower than SBS strength for T700/PEEK composites (i.e.98MPa). Similarly, flexural modulus for T700/PEEK composites was 51% higher than AS4/PVDF composites.

The compression strength of T700/PEEK composites was found out to be 63% higher as compared to AS4/PVDF composites. The normalised moduli for a fibre volume content of 55% indicated that it was 8% higher for T700/PEEK composites as compared to AS4/PVDF composites. T700/PEEK hierarchical composites exhibited the same trend as PVDF and MPVDF hierarchical composites i.e. the compression strength increased by ~50% with 1/1.25 wt% CNT loading but decreased when the CNT content increased further but there was no significant change in compression modulus with increasing CNT loading. So, the limited/insufficient infusion of polymer matrix in to the carbon fibres at the interface of hierarchical composites caused by high viscosity of nanocomposite melts at higher CNT loadings could be considered the basic reason for this reduction in mechanical performance

which leads to delaminations. However, unlike for the compression results AS4/PVDF composites had 18% and 45% higher $G_{IC,SS}$ values (fracture toughness) as compared to T700/PEEK and APC-2 specimens, respectively. This improvement could be attributed to higher toughness of PVDF composites as compared to PEEK composites. The extraordinary potential of matrix dominated properties can only be utilized in carbon fibre reinforced hierarchical composites, if only the fibre/matrix impregnation is sufficient enough to provide an established interface.

Fracture toughness, determined from critical energy release rate during DCB ($G_{IC,SS}$), for T700/PEEK composites exhibited 9% improvement in $G_{IC,SS}$ upon addition of 1 wt% CNT loading. These results are completely in disagreement with the fracture toughness for PVDF and MPVDF hierarchical composites explained earlier (chapter 5 and 6) possibly because of the difference in fabrication i.e. PVDF and MPVDF composites containing 1.25 wt% CNTs were actually mixed ply composites (alternate plies of PVDF/MPVDF and PVDF/MPVDF containing 2.5 wt% CNT were arranged and consolidated). Another reason could be poor compatibility between PVDF and carbon fibres [28]. However, there was negligible increase in $G_{IC,SS}$ with further CNT loading of 2.5 wt% and 5 wt%. The reason for higher flexural modulus [14] and G plateau values of T700/PEEK composites (35% higher) as compared to APC-2 is probably the fact, that APC-2 still contains appreciable amounts of Diphenyl Sulphone (DPS) [144], [145]) which also acts as plasticizer for PEEK and therefore impact the mechanical properties of CF/PEEK. Moreover, the PEEK grade used to manufacture APC-2 is a well-guarded secret of the manufacturer Cytec, but it can be assumed that it is a low melt viscosity grade. The fibre (mis)alignment of the laminated CF/PEEK tapes, caused by different melt viscosity of the matrix during compression moulding at conditions optimised for the in-house CF/PEEK tape, is also a factor influencing the mechanical properties of the final composites.

Fractographic analysis was conducted to investigate the influence of CNT concentration on fibre/matrix interface. It is apparent that, with increasing CNT loading, the contribution of matrix deformation increased during fracture, i.e. there is no plastic deformation in 0 wt% CNT loading but maximum deformation in 5 wt% CNT loading. So it can be concluded that, matrix (stiffness) is improved with the addition of CNTs and is contributing in determining the fracture toughness, but still the fracture toughness decreased with a CNT loading of 2.5

and 5 wt%, that would be because of poor impregnation of carbon fibres by PEEK nanocomposite at higher CNT loadings.

Chapter 8 - Conclusions and Outlook

8.1 Summary of the Findings

This research involved the introduction of nanoscale reinforcements into matrices. The fabrication of such polymer nanocomposites posed major challenges involving the high viscosity of nanocomposite melt/suspension and its incorporation as a matrix in hierarchical composites. The incorporation of CNTs into the matrix of conventional composites improves the matrix modulus, which should subsequently lead to hierarchical composites with much improved compression and other matrix dominated properties.

High performance unidirectional carbon fibre reinforced thermoplastic nanocomposites were fabricated by combining a carbon nanotube reinforced polymer matrix with carbon fibres. Challenges such as attaining a good dispersion of CNTs within the matrix, producing micrometre scale nanocomposite powders and impregnating 12k carbon fibre rovings with a high viscosity nanocomposite melt were overcome. The major achievements include enhancement in matrix dominated properties upon addition of up to 1.25wt% carbon nanotubes and successful fabrication of hierarchical composites with enhanced mechanical performance. Unfortunately, the enhancement in mechanical performance of hierarchical composites due to matrix dominated properties was only obtained up to a CNT loading of 1.25 wt%. The processing issues associated with higher CNT loadings such as higher viscosity of nanocomposite melts made it difficult for nanocomposite matrix to

impregnate/infuse carbon fibres completely resulting in a lack of sufficient contact or poor quality fibre/matrix interfacial adhesion in hierarchical composites.

8.1.1 PVDF Nanocomposite Production and Mechanical Characterisation

Different formulations of nanocomposites consisting of modified PVDF (MPVDF) and modified CNTs (PMMA-g-CNTs) were fabricated using extrusion and injection moulding up to a maximum CNT content of 10 wt%. All the nanocomposites displayed well distributed nanotubes within the matrix which is a requirement to utilize the potential of nanoreinforcement to enhance composite performance. The nanocomposites were characterised for their mechanical properties to assess their potential as reinforcement for carbon fibre reinforced composites.

- Carbon nanotubes stiffened the matrix, but the stiffening effect of nanotubes was observed to be more prominent at a lower CNT loading which is a common observation for semicrystalline thermoplastics, possibly due to nucleation effects. However, a modest linear increasing trend was observed in composite stiffness with increased CNT loading which agrees well with literature.
- A linear improvement in mechanical performance of PVDF nanocomposites with CNT loading irrespective of the modification in matrix or reinforcement was observed.
- Work of fracture increased linearly for all nanocomposites with increased loading of CNTs. A linear increase in work of fracture was observed with increase in CNT loading for PVDF nanocomposites, which indicates that toughness of the nanocomposites was improved with an increase in CNT loading.
- In semicrystalline matrices the (often unanalysed) increases in crystallinity may be the source of non-linearity. In order to avoid any variations in matrix morphology or crystal structure, all nanocomposites were annealed prior to mechanical testing which helped in returning the materials to their unloaded state after removing residual stresses induced during manufacturing. However, presence of PMMA-g-CNTs promoted the β -phase crystals in PVDF (as investigated via DSC and XRD results) which is indicative of improved piezoelectric and pyroelectric properties. However, given that degree of crystallization was minimal and no literature was found stating an

influence of change in crystal structure on percentage crystallinity or mechanical performance, no conclusions were drawn based on CNT loading fractions and crystallinity of PVDF and the increase in the mechanical performance of nanocomposites was attributed to reinforcing effect of CNTs and not from any increase in crystallinity.

- The compatibility between MPVDF and CNTs enhanced CNT dispersion in PVDF, optimised interfacial interactions and aided stress transfer resulting in better mechanical performance as compared to nanocomposites containing pure PVDF.
- PMMA-g-CNT based PVDF nanocomposites displayed the best mechanical performance because of the miscibility of grafted PMMA or an MMA (methyl methacrylate) functional group to PVDF. It could have improved the dispersibility and interfacial bonding of CNTs with PVDF, which are the key issues in the development of nanocomposites resulting in enhanced mechanical performance. This suggests that PMMA-g-CNTs developed an improved interfacial region in PVDF nanocomposites where external stresses applied to the composite as a whole were efficiently transferred to the nanotubes, allowing them to take a disproportionate share of the load which is the most important requirement for a nanotube reinforced composite.

To sum up, it can be stated that CNTs enabled the development of a new generation of materials with multifunctional properties, such as a combination of interesting physical properties together with improved mechanical performance.

8.1.2 Hierarchically Reinforced AS4/PVDF Composite Production and Mechanical Characterisation

Conventional high performance AS4/PVDF hierarchical composites containing up to 5 wt% CNTs with enhanced mechanical properties have been developed within the scope of this research.

- The mechanical performance of successfully fabricated conventional high performance hierarchical composites showed an improvement in compressive, flexural, apparent short beam shear strength and fracture toughness for up to a CNT loading of 1.25 wt% CNTs. However, this improvement was diminished for a CNT loading of 2.5 wt% and 5 wt%, respectively. This is because of the poor quality

fibre/matrix adhesion caused by poor impregnation of carbon fibres by high viscosity nanocomposite melts at higher CNT loadings.

- The enhancement in matrix dominated properties can only be availed in hierarchical composites, without compromising the quality of fibre/matrix interface, for an optimum loading of CNTs. Beyond this limit, further addition of CNTs provoke processing issues like higher viscosity which could cause poor carbon fibre impregnation by the nanocomposite matrix and hence the fibre/matrix adhesion which results in poor mechanical performance as was shown for compression results. A 17% enhancement was observed in stiffness for a 5 wt% CNT loading in AS4/PVDF composites, which could not be availed in overall mechanical performance of hierarchical composites due to the processing discrepancies (confirmed via fractography).
- Fractographic analysis suggests that CNTs cause embrittlement of the matrix. Moreover, a cohesive failure at the junction between fibre and matrix, leaving the fibre clean was indicative of poor fibre/matrix infusion/impregnation at higher CNT loading. A possible reason could be the higher viscosity of nanocomposite melts at higher CNT loading.
- Furthermore, besides the high number of twists in the tows of the AS4 fibre, the PVDF hierarchical composites containing AS4 fibres did exhibit improvement in mechanical performance, which suggests that influence of twists in the tow is marginal.
- Hierarchical composites fabricated during this research had two kinds of architecture. They were either fabricated by consolidating a mixed ply setup containing alternate layers of CF/polymer and CF/NCs, or similar ply setup containing only the plies of CF/NCs. It was observed that the presence of CF/polymer plies in CF/NC plies actually provides the necessary impregnation to bind the CF/NC plies together. This suggests that, by increasing the resin content between the polymer nanocomposite plies, impregnation can be improved. However, the same architecture when employed for hierarchical composites containing 2.5 wt% CNTs (by consolidating alternate plies of PVDF and PVDF containing 5 wt% CNTs), no improvement in mechanical properties were observed (as explained in compression results). Also, PEEK

hierarchical composites showed decrease in mechanical performance at higher CNT loadings (Chapter 8). This indicates that it is not architecture (mix/similar ply) but overall CNT content in a hierarchical composite which affects the infusion of polymer matrix in to carbon fibres. An interesting approach would be to increase the polymer content in the hierarchical composites i.e. either by decreasing the fibre volume fraction or by introducing polymer films in between polymer nanocomposite plies. This would provide the necessary impregnation required to explore beneficial CNT reinforced matrix dominated properties' potential in hierarchical composites at higher loadings.

8.1.3 Hierarchically Reinforced AS4/MPVDF Composite (Mixture of 75 wt% PVDF and 25 wt% maleic anhydride grafted PVDF) Production and Mechanical Characterisation

It is well known that none of the variety of functional groups (carbon, nitrogen and oxygen) present on the surface of the carbon fibres are expected to bring any enhanced interaction with pure PVDF. In attempt to improve the interfacial adhesion between PVDF and the reinforcing fibres, PVDF was modified by introducing 25 wt% MAH-g-PVDF via solution precipitation method. The influence of a compatibilizing agent i.e. modified homopolymer matrix (MAH-g-PVDF) to interact and/or react with conventional carbon fibres as a source to stimulate adhesion between carbon fibres and PVDF was investigated. It was expected that some of the functional groups existing on the carbon fibres especially oxygen should favourably interact with the MAH in MAH-g-PVDF which could resolve the weak interface problem in AS4/PVDF composites.

- A reduction in macromechanical performance of AS4/MPVDF composites was observed as compared to AS4/PVDF composites. It was revealed through X-ray photoelectron spectroscopy (XPS) that the surface of MPVDF contained only 2.5% MAH, which was less than the 7% expected based on the simple two fold dilution of 100% MAH-g-PVDF (containing 14% MAH). This suggests that MPVDF is rather inhomogeneous with preferential surface segregation of PVDF. So, it is probably the solution precipitation method which did not introduce MAH moieties evenly throughout the polymer matrix and the improved potential could not be achieved. However, 100% MAH-g-PVDF should not have such kind of uneven segregation issues and should be capable of providing extraordinary macromechanical properties.

- Mechanical performance of AS4/MPVDF hierarchical composites presented the same trend as that of AS4/PVDF composites suggesting that matrix dominated properties can be availed in a hierarchical composite, only up to an optimum CNT loading, without compromising the quality of fibre/matrix adhesion. The increased CNT loading would reduce the nanocomposite infusion in to fibre and hence would cause an adverse effect on fibre/matrix adhesion resulting in poor mechanical performance.
- Fractographic analysis showed occurrence of bare fibres (devoid of any polymer debris in the fracture surface) at higher CNT loadings which suggests CNTs are reducing the impregnation of fibres by the nanocomposite matrix in hierarchical composites.
- In conclusion it can be said that although MPVDF did not exhibit the expected enhanced mechanical performance due to the uneven distribution of MAH moieties on PVDF surface, the quality of the MPVDF composites produced using laboratory scale composite production line was still improved with an optimum loading of CNTs.

8.1.4 Mechanical Characterisation of Hierarchically Reinforced T700/PEEK Composites

The aim of this particular study was firstly to compare the quality of the in-house manufactured T700/PEEK composites with commercially available PEEK composites (APC-2), secondly to investigate the influence of CNTs on the mechanical performance of hierarchically reinforced PEEK composites and finally to compare the mechanical performance of hierarchically reinforced PVDF and PEEK composites.

- Previous work had shown that in house prepared T700/PEEK composites showed higher flexural modulus and fracture toughness than APC-2. It is probably due to the fact, that APC-2 still contains appreciable amounts of DPS, which acts as plasticizer for PEEK and therefore impacts upon the mechanical properties of CF/PEEK. Moreover, it can be assumed that the PEEK grade used to manufacture APC-2 is a low melt viscosity grade. The fibre (mis)alignment of the laminated CF/PEEK tapes, caused by different melt viscosity of the matrix during compression moulding at conditions optimised for the in-house CF/PEEK tape, is also a factor influencing the

mechanical properties of the final composites. Also, fibre volume content is different for in-house PEEK composites and APC-2 i.e. 55% and 60% respectively. Furthermore, in-house manufactured PEEK composites contain epoxy sized T700 fibre whereas; APC-2 contains unsized AS4 fibre.

- T700/PEEK exhibited better mechanical properties compared to AS4/PVDF composites when tested in compression, flexure and short beam shear strength. However, AS4/PVDF composites showed 18% higher fracture toughness than T700/PEEK composites. This suggests that although the AS4/PVDF compatibility is poorer as compared to T700/PEEK composites, but still excellent toughness of PVDF can be availed in carbon fibre reinforced composites.
- T700/PEEK hierarchical composites also showed the same trend as AS4/PVDF composites i.e. enhancement in mechanical performance and fracture toughness was observed for a CNT loading of 1 wt% which diminished at higher CNT loadings. This is possibly due to existence of a poorer contact between PEEK nanocomposite and T700 in addition to a few traditional issues involved with processing of CNTs, i.e. alignment of the CNTs, arrangement of the CNTs etc. (Chapter 2). This finding would suggest that matrix dominated properties of a hierarchical composite could be improved but at very low CNT loadings.
- From fractographic analysis, it is apparent that, with the increase in CNT loading, the contribution of matrix deformation is increased in fracture i.e. there is no plastic deformation in 0 wt% CNT loading but maximum deformation in 5 wt% CNT loading. So it can be concluded that, matrix stiffness is improved with the addition of CNTs and contributes to the fracture toughness. However, fracture toughness decreased with a CNT loading of 2.5 and 5 wt%, due to poor infusion of PEEK nanocomposite in to T700 at higher loading fractions of CNTs.

8.2 Future Outlook

In on-going exploration in hierarchical fibre reinforced PVDF and PEEK nanocomposites, there are a number of practical issues which still persist. These issues mainly arise from the unexpectedly poor mechanical performance of the fabricated hierarchically reinforced composites at higher CNT loadings caused by poor fibre/matrix impregnation. The likely

causes for a poor fibre/matrix impregnation are incompatibility between the CNT reinforced nanomatrix and the carbon fibre, or the processing issues associated with higher CNT loadings such as viscosity. If the fibre/matrix impregnation is poor, the effective transfer of load from matrix to fibre is difficult to guarantee resulting in a poor composite performance. In future work, it would be interesting to enhance the fibre/matrix compatibility by utilizing both modified fibres and modified CNTs during fabrication of hierarchical composites. A few possible suggestions are explained below.

8.2.1 Introducing Atmospheric Plasma Fluorination in Hierarchical Composites

Atmospheric plasma fluorination of carbon fibres has proven effective in improving interfacial adhesion with PVDF. An interesting approach would be to produce the PVDF and PEEK hierarchical composites using atmospheric plasma treated carbon fibres. However, this method would require simultaneous control of both the bath concentration in the composite line and the atmospheric plasma treatment, which could make the running of the composite line difficult. This issue can be resolved by introducing an automatic dosing system to control the bath concentration of composite line, which in turn will control the fibre volume fraction of the composite. An expected good quality interface should result, which can enhance the overall composite performance.

8.2.2 Optimising the Carbon Nanotubes (Reinforcement) in PVDF Hierarchical Composites

One of the major obstacles for the advancement of carbon nanotube based nanocomposites is dispersion of the nano reinforcement within a polymer. The use of perfectly straight carbon nanotubes would significantly facilitate dispersion. Surface chemistry of carbon nanotubes plays an integral role in their interaction and adhesion to matrix. It has been shown in Chapter 4 that 10 wt% loading of PMMA-*g*-MWNTs in PVDF, storage modulus was increased by 14% over a wide range of temperatures. The miscibility between PVDF and PMMA helps improve the dispersion of PMMA-*g*-CNTs in the PVDF matrix and also the load transfer from the PVDF matrix to the nanotubes. The mechanical performance improvements observed with PMMA-*g*-CNTs clearly show the significance of tailoring the surface chemistry of carbon nanotubes for nanocomposite applications. PMMA-*g*-CNTs are expected to improve the interfacial interaction between the fibre and PVDF, because of their miscibility with PVDF. A

very appealing approach will be to fabricate hierarchical nanocomposites using PMMA-g-CNTs reinforced PVDF nanomatrix.

8.2.3 Introducing Sized Fibres (e.g. PMMA coated) in PVDF Hierarchical Composites

One of the significant routes to enhance interfacial interaction between fibre and matrix can be fibre sizing. Sizing, if strongly adhered to carbon fibre surface can improve the interfacial interaction by either getting miscible or reacting with the polymer matrix. PMMA, which concentrates preferably in PVDF rich phase, has shown a very beneficial effect in improving the interfacial adhesion of PVDF with its immiscible polymers (such as poly carbonate (PC)) by premixing it with PVDF. This suggests that PMMA can be used as an adhesion promoting agent in PVDF hierarchical composites. By introducing PMMA functionalities to carbon fibres, i.e. PMMA sized carbon fibres, the apparent interfacial shear strength between sized carbon fibres and PVDF can also be enhanced. These suggest that a good balance in the correct functionalities in both fibre and matrix can have a positive impact on the carbon fibre/polymer matrix interfacial properties. It would be interesting to further prove this assumption by expanding the study of carbon fibre reinforced PVDF composites to other thermoplastics such as PEEK and PPS.

The approach of using reactive compatibilisation between functionalised nanotubes, sized fibres and compatibilised polymers should be able to improve the fibre/matrix interfacial interaction which has been shown to correlate with interlaminar performance and fracture toughness of the unidirectional carbon fibre reinforced composite laminates.

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