



Department of Mechanical, Industrial and Aeronautical Engineering
MSc (Mechanical Engineering)

**Electrospun Nano-mat Strengthened Aramid Fibre Hybrid Composites:
Improved Mechanical Properties by Continuous Nanofibres**

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Abstract

Aramid fibre reinforced epoxy composites were hybridised by the addition of electrospun PAN (polyacrylonitrile) and ECNF (electrospun carbon nanofibre) doped PAN nanomats. One of the major concerns in polymer composites is the effect of the interlaminar properties on the overall mechanical properties of the composite. Electrospun carbon nanofibres were used as doping agents within PAN nanofibres, and coated in between aramid epoxy laminates to improve the interlaminar properties. PAN nanomats and ECNF doped PAN nanomats were created by the use electrospinning on the surface of aramid fibre sheets. Multiscale hybrid aramid reinforced composites were then fabricated. Mechanical characterization was carried out to determine the effect of PAN and CNF doped PAN nanofibre mats on aramid fibre reinforced epoxy. It was found that PAN reinforced nanomats had improved the mechanical properties and more specifically, when doped by ECNFs, the volume fraction of ECNFs played a vital role. An addition of 1% vol. CNF doped 0.1% vol. PAN reinforcement within a 30% vol. aramid fibre composite (control composite), improved the tensile strength and elastic modulus by 17.3% and 730% respectively. The 0.5% vol. PAN reinforced AFC (aramid fibre composite) specimens revealed a major increase in the flexural strength by 9.67% and 12.1%, when doped by both 0.5% vol. ECNFs and 1% vol. ECNFs respectively. The 0.5% vol. CNF doped reinforcement increased the impact energy by over 40%, for both the 0.1% vol. and 0.2 % vol. PAN reinforced aramid hybrid specimens. The 0.5% vol. CNF doped 0.5% vol. PAN had increased by 30% when compared to a non-doped sample. Morphological studies indicated interlaminar shearing between plies was affected by CNF agglomerations. This was discovered when determining the impact properties of the multiscale doped hybrid composites. Electrospun nanofibres however, assisted in improving the interlaminar regions within aramid epoxy by mechanical locking within the epoxy, and creating an adhesive bond using Van der Waals forces and electrostatic charges between nanofibre and macro fibre. Hybridising aramid epoxy with the use of nanofibres assisted in improving various mechanical properties. Impact degradation was one disadvantage of hybridising using CNF doped PAN nanofibre reinforcements.

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Acronyms

AFC	-	Aramid Fibre Composite
PAN	-	Polyacrylonitrile
DMF	-	Dimethylformamide
CVD	-	Chemical Vapour Deposition
CNF	-	Carbon Nanofibre
ECNF	-	Electrospun Carbon Nanofibre
CNF-DP	-	Carbon Nanofibre Doped PAN
VGCNF	-	Vapour Grown Carbon Nanofibre
CNT	-	Carbon Nanotube
MWCNT	-	Multi-walled Carbon Nanotube
SWCNT	-	Single-walled Carbon Nanotube
PP	-	Polypropylene
AFRC	-	Aramid Fibre Reinforced Composite
TEM	-	Transmission Electron Microscopy
SEM	-	Scanning Electron Microscopy
ASTM	-	American Society of Testing Materials
HL	-	Hand Lay-up

1 Introduction

1.1 Background

A composite material is a multi-phase material in which the combination of the individual constituent properties will determine the overall properties [1]. A composite material consists of a matrix and a reinforcement. The matrix can be either polymer, ceramic or metal, depending on the application. Common polymer matrices are classified as thermoplastic such as polypropylene, polysulfone and polycarbonate or thermosetting consisting of epoxy, polyester and polyamide.

Reinforcements in polymer composite materials consist of fibres that can be either natural or synthetic. A combination of reinforcements or a singular reinforcement within a polymer matrix, allows various types of polymer composites. Fibre reinforcements can be randomly chopped and distributed or woven into mats. Woven fibre mats, regardless of orientation are used extensively as reinforcements, due to the combination of the strength of the individual fibres. Woven fibre mats are advantageous over randomly orientated chopped fibres as loads may be distributed evenly in both x and y directions [1]. Randomly chopped orientated fibre mats can act as separators when the load is normal to the direction of the fibre, therefore making the overall composite weak in specific directions. Common randomly orientated fibre mats consist of natural fibres such as coir, flax or hemp. Common woven synthetic fibres are carbon, glass and aramid fibres. Aramid has been extensively researched and used in various fields such as military, aerospace, automobile and sport. Aramid fibre can be woven into unidirectional mats therefore creating many opportunities for engineering applications. High impact, tensile and compressive strength as well as creep resistance are some of the properties of aramid fibres that provide an advantage over other existing reinforced fibres. They have a low weight to strength ratio and contain very good abrasive properties. Glass fibre and carbon fibre both have excellent compressive and tensile strength, however, poor stiffness in glass fibre, and the cost of carbon fibre, allow aramid fibre to be superior in applications where cost and weight are important. Aramid fibres are used primarily in applications where low density, high stiffness and high fracture strain are preferred [2].

Aramid fibre and other reinforced woven fibre mats alike are moulded into a polymer matrix producing a composite material by either coating, immersing or compressing the reinforced fibre into a matrix, depending on the method of composite processing. Old techniques such as hand lay-up are used to make aramid reinforced epoxy composites and consist of applying layers of epoxy resin in between the aramid fibre sheets. This creates resin thick region between mats. This region is known as the interlaminar region. Reinforced polymeric composites can have weak interlaminar regions that can negatively affect the overall mechanical properties [2]. Due to the weakness of the interlaminar region, external loads can result in delamination through the inter layer which then leads to catastrophic failure [3]. The interlaminar properties are affected by the fibre-matrix interfacial bond. In laminated composites, the fibre-matrix interfacial bond and the interlaminar region between plies (mats) are of concern. The interlaminar region within a composite material is the area where the

matrix is in contact with the fibre mats. If the fibre-matrix bond is strong, then the overall strength of the composite improves. The link between the fibre and matrix is known to affect the fibre matrix failure process [2]. This in turn affects the interlaminar properties.

One method to improve the interlaminar region of polymeric composite materials is hybridization. Hybridization can be carried out by either the inclusion of additional reinforced fibres, like glass and carbon or by the inclusion of nanoparticles. Hybridization by using two or more different fibres within a polymer matrix can be combined to utilise the optimum properties of the individual fibres. This is highly advantageous in improving the mechanical properties of the overall composite. The aim behind this process is to reduce the disadvantages of one fibre, by the addition of another. Glass laminates, for example, can be combined with carbon fibre laminates in a polymeric matrix to produce a hybrid composite. This reduces the overall cost, but maintains the flexural properties [4]. However, the interlaminar region is affected by the contact between the polymer matrix and the reinforced fibre, therefore regardless of the combination or number of reinforced fibres used, the interlaminar properties are not affected and no improvements occur. However, nanoparticles are small enough to improve the properties of the polymer matrix which affects the interlaminar region. Common nanoparticles such as CNTs (carbon nanotubes), CNFs (carbon nanofibres) or CNSs (carbon nanospheres) are generally added to the polymer matrix. There is research on the addition of nanoparticles within polymeric composites resulting in various disadvantages. Nanoparticles are random and discontinuous resulting in stress concentration, therefore creating crack propagation within the polymer matrix [5]. These short discontinuous nanoparticles are not evenly distributed and therefore create agglomerations which lead to matrix separation. Other major concerns with the inclusion of nanoparticles is the necessity to treat via functionalisation the nanoparticles before adding them into the polymer matrix. This treatment helps to improve the dispersion and adhesive bond between the polymer matrix and nanoparticle, but has been shown to reduce the strength of the nanoparticles therefore making the addition of nanoparticles within the matrix unfavourable [6].

Hybridization by the inclusion of nanofibre mats within reinforced fibre polymeric composites is advantageous over discontinuous nanoparticles as well as additional fibre reinforcements. The inclusion of nanofibre mats are highly advantageous as they are continuous and evenly distributed between layers. This is one method of improving the interlaminar properties of polymeric composite materials. Nanofibre mats can be coated on the surface of any material through the use of a method called electrospinning. Electrospinning is highly advantageous due to its ability to provide continuous and aligned nanomats. The nanomats can also be carbonized to produce CNF mats at a lower cost compared to existing methods such as CVD (chemical vapour deposition) in which CNTs and VGCNFs (vapour grown carbon nanofibres) are produced. Electrospinning is a method of producing nanofibres by controlling the flow rate of a liquid polymer through a charged capillary of a fixed diameter. Electrospinning has been applied in several fields from skin gauzes in biomedical application as well as water filtration [7]. The advantages of using electrospinning as opposed to other methods of nanofibre processing techniques such as CVD are, low cost and high production rate, ability to coat materials creating new layers, and the possibility of obtaining continuous nanofibres.

Polyacrylonitrile (PAN) which is a precursor polymer in the production of carbon fibres can be electrospun to produce continuous and evenly distributed nanofibre mats which provide an advantage over other nanoparticles such as CNT/VGCNF because electrospinning provides the ability to coat surfaces. Electrospinning is also highly advantageous as the process provides the ability to dope nanoparticles. Doping is a technique in which impurities are added to a material to improve its overall strength. Nanocomposites can be created using electrospinning by doping the polymer solution being electrospun, with CNTs and CNFs [8] [9]. The ability to produce nanofibres with improved mechanical properties is one major advantage of doping.

1.2 Problem Statement

One of the major concerns in polymer composites is the effect of the interlaminar (region between plies) properties on the overall mechanical properties. The region in which the polymer matrix and reinforced fibre are in contact, plays a huge role in the transfer of loads into the interlaminar region. Research has indicated attempts to improve the interlaminar properties. However, very few have provided a cost effective solution without the degradation of the fibre reinforcement and/or the degradation of the nanoparticles. Within any material design, the mechanical properties are a major concern, and hybridization through the addition of extra macro fibres can assist in reducing the negative properties of the initial fibre reinforcement. However the interlaminar properties can be further improved by any additional nanoparticle. This can then assist in improving the shear, tensile and bending properties of a polymeric composite material. Hybrid composites, through multiple macro fibre reinforcements, are also affected by the interlaminar region and hence increasing number of reinforcements will have no effect on the interlaminar properties. The interlaminar properties are known to be affected by the interfacial spacing between the reinforced fibre and the polymer matrix.

A major problem with nanoparticles such as CNFs and CNTs is the method of introducing them into the composite. Nanoparticles have indicated improvements towards the fibre-matrix interlayer region between the reinforced fibre and polymer matrix, however full potential of nanofibre properties are not utilised due to the damage of individual nanofibres as a result of nanofibre treatment techniques. Degradation of the individual nanofibres arise when various nanoparticle treatment techniques have been used. Another major concern with various nanoparticles is the method of production. CVD is the most common CNT and CNF production method but the cost of production is relatively high and there exists many difficulties in producing nanoparticles with continuity and even distribution.

1.3 Aim and Justification

The aim of this research was to determine the effect of electrospun nanofibre reinforcements on the mechanical properties of aramid reinforced epoxy. The interlaminar properties, more specifically, the interlaminar region, were examined to determine if nanofibres provided improvements in the epoxy and aramid fibre bonding. Nanofibre mat production and optimization was carried out to determine the effectiveness of nanofibres as potential fillers in aramid reinforced composites. The effect of hybridization using nanoparticles was carried out by using polyacrylonitrile (PAN) (polymer nanofibre), as well as CNF (carbon nanofibre) doped PAN.

Electrospinning is utilised as a cost effective method for producing continuous and evenly distributed nanofibres. Optimization of the electrospinning process was the first step in this research. Producing high quality and consistent PAN nanofibres was initially determined since the nanofibre mats affect the overall properties of the hybrid composite. Electrospinning as a nanofibre production technique allowed the aramid sheets to be coated with PAN nanofibre mats. Thereafter, carbonization of PAN nanofibres was carried out and since carbon based nanofibres are known to have a high tensile yield strength, the addition of CNFs as doping agents was determined to observe this effect.

1.3.1 Objectives

- Develop and optimize an electrospinning process to produce fibres on a nanoscale.
- Determine the effect of electrospun PAN nanofibre mats as a secondary reinforcement on the mechanical and interlaminar properties of aramid-epoxy hybrid composites.
- Determine the effect of CNF doped PAN electrospun nanofibre mats on the mechanical and interlaminar properties of aramid-epoxy multiscale hybrid composites.

1.4 Scope of work

The scope of this work is hybrid composite characterization. In order to characterize hybrid composites, research on basic understanding of composites was carried out. Mechanical characterization of composites was carried out using three mechanical tests as well as morphological studies. These methods provided an insight into the interlaminar properties as well as observation of the fibre matrix contact region. Research and design of the electrospinning set-up was carried out accordingly. A large portion of this research was dedicated to determining the optimal parameters for electrospinning and the breakdown is presented in Figure 1-1. This provided an insight to the nanofibre and strengthening techniques. Finally carbonization and doping were areas that were investigated to assist in understanding the effect of nanofibre reinforcements as a hybridization technique.

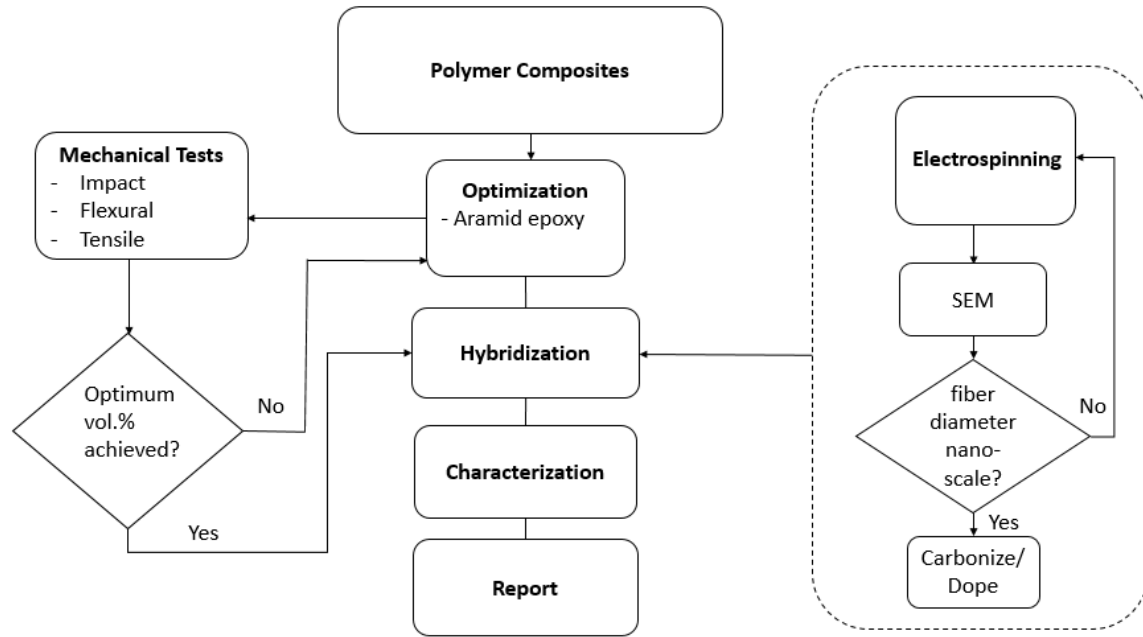


Figure 1-1: Project outline

1.5 Outline

This dissertation has 6 chapters. Chapter 2, discusses the relevant literature required to provide an in depth understanding of hybrid composites, aramid fibre, epoxy resin and electrospinning. Chapter 4 is the methodology for the experimental set up.

Optimization and design of the electrospinning set up was provided in chapter 3. This section of the research consumed most of the time as very little research on reinforced electrospun nanofibres had been published at the time. A project plan in Appendix A illustrates the breakdown of the time consumed to conduct the overall research.

Once the electrospinning phase had been conducted and optimal parameters were researched, the processing as well as the characterization of the hybrid composites followed. Hand laid neat aramid composite, PAN reinforced aramid hybrid composite and CNF doped PAN reinforced aramid composite specimens were produced. Testing was then conducted and morphological studies of nanofibres as well as failed samples were carried out. Chapter 3 discusses the detail of the morphological studies of the nanofibres. Chapter 5 shows the results and discussion of the effects of the PAN nanofibre reinforcements as well as the effect of CNF doped PAN nanofibre reinforcements on aramid fibre composites. Chapter 6 concludes this dissertation and the appendices provide the relevant data, images and the project plan.

2 Literature Review

2.1 Composites

2.1.1 Epoxy Resin

Polymer-matrix composites consist of two types of polymers; either a thermoplastic or a thermosetting polymer [10]. A thermoplastic polymer flows when the temperature of the thermoplastic is higher than its crystalline melting point. Once solidified, the thermoplastic polymer can be reheated and remoulded several times [11]. Thermosetting polymers cannot melt or flow upon reheating. This is due to the polymerization process in which strong cross-linking bonds are formed. Yielding and deformation of thermoplastics cause redistribution of the load at points of concentration but this is not possible for thermosetting plastics. Therefore thermosetting plastics tend to have a lower impact strength and toughness. The heat distortion temperature of thermosetting resins causes them to lose their stiffness but thus defines an effective upper limit for their use in structural components. However thermosetting plastics are considered to be more common than thermoplastic polymers. Epoxy and polyester have been the most widely used thermosetting resins since the discovery of plastics [12].

Epoxides have a three-membered ring structure, which consist of two carbon atoms and one oxygen atom as shown in Figure 2-1. Ethylene oxide is the simplest monomer. A monomer is a molecule that when combined with other monomers becomes a polymer.

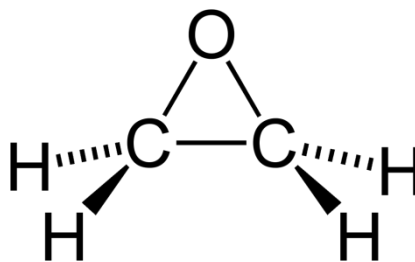


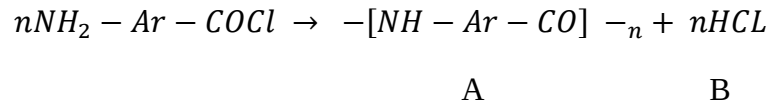
Figure 2-1: Ethylene oxide

Epoxide ring bonds have unfamiliar angles of 60° whereas the normal bond angle is a 109° . Due to this unusual trait, the structure contains internal ring strain and this strain equates to strain energy of approximately 60kJ/mol . This allows polymerization at a higher rate. Polymerization is the process used to produce various epoxies and this can be achieved by chain polymerization. This is achieved by activating the epoxide ring of a monomer by a catalyst so that it can react with a non-activated monomer [13].

2.1.2 Aramid Fibre

Aromatic polyamide fibres also known as Para-aramid fibres were first produced by DuPont in 1972. It was developed and named commercially as Kevlar-49 and similar aramid fibre patents such as Twaron were produced by Akzo in 1986 [14]. Since then, aramid fibre has been used in various industries within composite materials and its application has developed extensively.

Aramids are formed by a reaction between an amine group and a carboxylic acid halide group [15]. Syntheses of the AB homopolymers are carried out by the reaction below:



Interfacial polymerisation and low-temperature condensation are the methods applied to perform these reactions. AABB homopolymers are produced in the same way. Melt polymerisation as well as vapour-phase polymerisation similarly produces AABB homopolymers. Kevlar 49 which goes by the chemical name poly (p-phenyl terphthalamide) (PPTA) is the simplest form of AABB para-oriented polyamide. Its chemical formula is illustrated below in Figure 2-2.

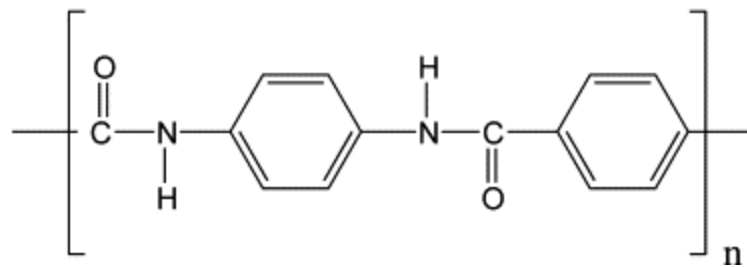


Figure 2-2: Chemical formula of Kevlar; poly (p-phenylene terephthalamide) (PPTA) [53]

Aramid fibres are produced by methods such as spinning. The polymer solutions are stretched across a small air gap when being extruded through spinning holes. The shear force created by these spinning holes is used to align the crystal domains towards the deformation [15]. Orientation is highly important when producing aramid fibres as this is directly related to the fibre modulus. In comparison to other fibre yarns, aramid fibre has a relatively high modulus. E-glass and Nylon-66 have a modulus 72.4 GPa and 5.5GPa respectively. Kevlar-49 has a modulus of 112.4 GPa. The spinning process allows various forms of aramid fibres. These fibres can be woven or aligned depending on required application. Aramid fibres have very advantageous mechanical properties over other organic fibres. They are used extensively in composite materials because they provide stiffness, strength, and durability as well as dielectric properties [15]. As aramid fibres are organic they exhibit typical properties. These are low density, fatigue and abrasion resistance and capable process ability. Apart from these properties, aramid fibres generally have a consistent modulus and therefore make it almost ideal for composite application.

2.1.3 Aramid Fibre Structure

As there are different types of aramid fibres on the market, the structural characteristics must be examined. *Dobb et al* [16] determined the structural characteristics of aramid fibre variants using tensile tests, electron microscopy and X-ray diffraction. It was noted that Twaron and Kevlar 29 were comparable but Twaron measured a higher strength [16]. A hydrogen sulphide gas and silver nitrate solution treatment allowed the detection of voids on the cross section of the aramid fibres as illustrated in Figure 2-3. Kevlar 981 was found to have the largest thickness at $2\mu\text{m}$ and Twaron was noted to be consistently $0.15\mu\text{m}$. Twaron was also found to have the second highest breaking stress after Kevlar 981 and the second lowest orientation after Kevlar 49 [16].

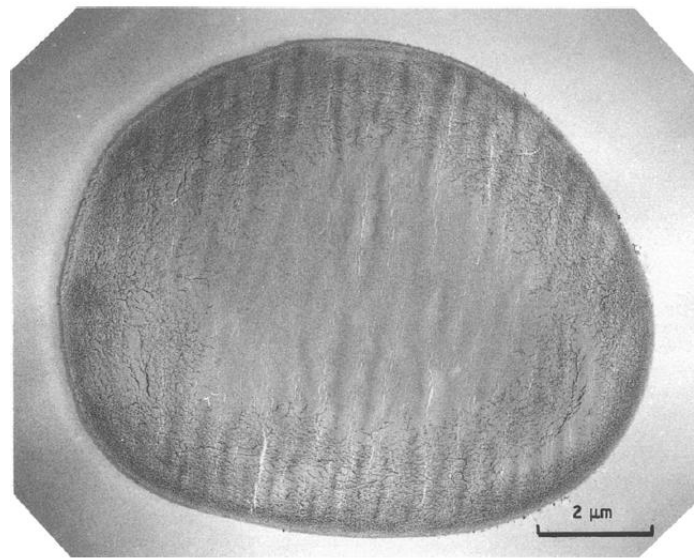


Figure 2-3: Cross section of individual aramid fibre

A comparison between Kevlar 29 and Twaron was carried out and differences in tensile properties were minimal, however skin core was examined and Twaron displayed a thinner skin region as well as more continuous core defects [16].

2.1.4 Epoxy and Aramid Interfacial Bond

For a composite to have an effective reinforcement, the fibre-matrix bonding strength is crucial. An ideal unidirectional composite is a composite that contains at least one continuous fibre all in the same direction. If the fibre in an ideal unidirectional composite has a higher modulus than that of the matrix, then the longitudinal tensile strength will be independent of the strength of the fibre-matrix bond. However, the effect the bonding strength has on the transverse and flexural tensile strength are positive. This means attention paid to increase the strength of the bond will naturally increase the flexural and transverse tensile strengths [10]. *Kalantar et al* [2] studied the bonding mechanism between aramid and epoxy. They concluded that the interphase of the composite can affect the overall mechanical and thermal properties of the composite [17]. An aramid to epoxy interphase is linked to the microstructural aspects of bond

forming between two polymers. The mechanical interlocking is caused by interpenetration at surface irregularities and molecular contact. The interactions may be observed to be weak however the irregularities act as anchors and this is because of the high strength bonds. Other forms of bonding include covalent bonding, where adsorption interactions take place. This is due to an attraction between molecules of phases.

Strengthening the bond however, will not necessarily result in a high strength material. It can cause brittle matrices to become even more brittle because the strengthened bond causes crack propagation perpendicular to the fibre-matrix interface. Brittle fibre prevents crack initiation within the interface for ductile matrices. Thus it is vital to reach an optimum balance with the fibre-matrix bonding in brittle matrices [10].

Mechanisms of fibre-matrix bonding are [10]:

- Chemical bonding
- Interdiffusion
- Van der Waals bonding
- Mechanical interlocking

Intimate contact between the fibres and the matrix will be needed in order for chemical bonding, Van der Waals bonding and Interdiffusion. This has an effect on the fibre-matrix strength. Van der Waals bonds are known as secondary bonds, however, the atoms or group of atoms are joined by strong covalent or ionic bonds [10]. An example of breaking a van der Waal bond is the breaking of bond when heating water to steam. Van der Waals forces are very important in determining surface tension as well as boiling points in liquids. Mechanical interlocking plays a role due to the frictional force between the fibre and matrix. The mechanical locking is affected by the wettability of the matrix and the surface of the fibre reinforcement.

The fibre matrix adhesion between aramid and epoxy is also affected by the mechanical interactions. On a micro scale, solid surfaces are known to be rough [17]. Molecular contact is limited to a few points between two surfaces when in contact. Limited interactions and weak adhesion are a result of a low contact area. A liquid to solid surface increases the contact area and increases the adhesion mechanisms. Interlaminar shear improvements of 20% was possible, however roughening the fibre decreases the fibre strength. A rupture of molecular bonds occurs during friction and takes place at 1nm. Deformation occurs at a micro scale usually at 1µm. Other areas that affect the adhesion is the wetting of fibres and the weak boundary layer in the interphase. The relationship of any 2 phase composite can be improved through methods such as hybridization. A hybrid composite is a composite material in which more than 2 phases exist.

Bonding mechanisms also apply to nanoparticles embedded in the matrix. If the surface of the nanoparticles are smooth, the mechanical interlocking has a negligible effect. The chemical bonding is caused by covalent bonding between the fibre and matrix. Amongst CNPs, chemical bonding is increased through functionalisation and surface modification. The improvement

and modification of nanofillers assists in improving interlaminar regions which in turn improves the interlaminar properties of the overall hybrid composite.

2.2 Hybrid Composites

Hybrid composite materials are generally defined as advanced composites. They consist of a range of reinforced fibres or particulates within a thermoset or thermosetting plastic [18] Hybrids can be processed in multiple ways. Aligned fibres may be sandwiched or nanoparticles may be combined with a polymer matrix and then combined with a woven fibre. These are just a few possible combinations out of the many in existence today. Reinforced fibres can be used in composites in multiple ways. Whether unidirectional, short, random, chopped or woven, fibres can alter properties in some way or another regardless of form.

Hybridization of a singular reinforced fibre composite allows alteration in other areas of the material that wouldn't have been possible without the addition of the hybridized material. For example, carbon is a material that can provide high strength but brittle properties within a matrix. Kevlar (aramid fibre) on the other hand, is a highly ductile fibre but has a low compression resistance [19]. Combining the two with a main goal of producing a composite for bone fixation is an application of hybrid composites that *Wan et al* [19] had investigated. They were able to combine Carbon fibre and Kevlar with bismaleimide resin as shown in the second sample in Figure 2-4 (a). These carbon and Kevlar fibres were woven together at various ratios as illustrated in Figure 2-4 (b).

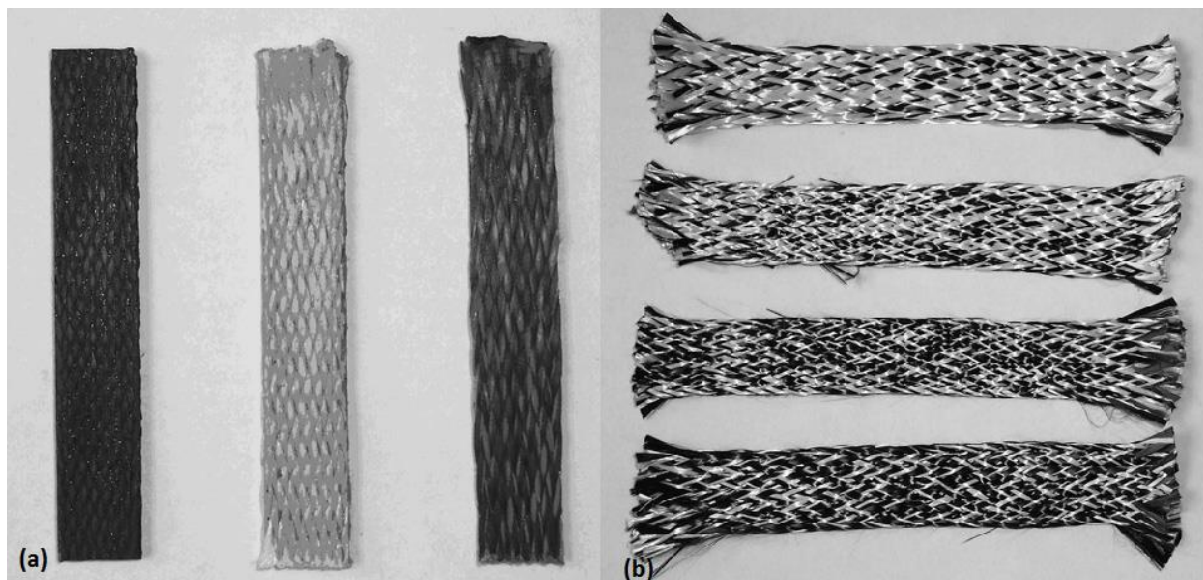


Figure 2-4: (a) carbon/ bismaleimide, carbon/Kevlar hybrid and Kevlar/ bismaleimide. (b) Woven Kevlar and carbon fibres at various ratios [19].

The results in this study indicated that the woven Kevlar/carbon hybrid increased in both modulus and flexural strength at a ratio of 3:2 Kevlar to carbon [19]. The residual flexural

strength was also improved amongst the hybrid composites. It was concluded that Kevlar/carbon hybrid are suitable for bone fixation.

Flexural strength of carbon/aramid hybrids was determined by *Marom et al* [20] and a high strength was observed for the carbon core between two aramid layers than the aramid core between two carbon layers. Hybridization can improve flexural properties and therefore improve interlaminar properties. It was concluded that the flexural strength is dependent on not only the compressive strength but the tensile strength equally. Carbon fibres tend to have a low compressive strength and this is due to yielding during bending. This is because a larger strain was observed at the compressive face than at the tensile face, therefore giving way to a shift in the neutral axis to the tensile face, while the yielding region increases in the compressive side [20].

Hybridization through randomly orientated fibres is another technique that can be carried out by the mixing of two different fibres and applying them as a reinforcement in a polymer matrix. Glass fibre was used to hybridize sisal-polypropylene composites by mixing chopped sisal and glass fibre together into PP (polypropylene), using an internal mixer [21]. It was observed that the influence of the glass fibre improved tensile, flexural and impact properties of the sisal-pp composite. The tensile modulus and flexural modulus were not affected however there were improvements in both the thermal and water resistance properties too.

Composites are mostly vulnerable to interlaminar failure because of the effects of laying mats ply by ply. This occurs between interlaminar planes. Free edges, joints, and out of plane loading within plies cause interlaminar stresses from the incompatibility of thermal and mechanical properties in between the plies [22]. Research has shown improvements of interlaminar strengthening through nanofibre plies. These plies generally have fibre diameters ranging in the hundreds of nanometres [22]. Other forms of hybridization include nanofillers within the polymer matrix and nanofibre coating of macro fibres. This process of adding nanoparticles into a single phase composite is known as multi-scale nano hybridization. One method of multi-scale nano hybridization is through a process called electrospinning. This is a method in which nanofibres are produced from a controlled flow polymer held through an electric potential.

2.3 Electrospinning Fundamentals

Electrospinning is not a new concept and has been in existence for more than 70 years. In 1934 it was *Formhals* [23] who published a series of patents that specified notions of polymer fibre production with the use of electrostatic force. It was only in 1994 where the term electrostatic spinning was used that eventually led to the use and research of electrospinning. Polymer filaments were produced when a polymer solution such as cellulose acetate was introduced in an electric field [7]. This paved a new way of producing polymer nanofibres.

This method of producing polymer fibres on the micro and nano scale is carried out by having a controlled electric potential between a needle and collector (see Figure 2-5). The needle is injected with a polymer at a controlled rate in which the surface tension of the droplet is

overcome by the electric field [24]. The polymer then becomes a jet that creates a whipping effect. This whipping jet creates what is known as a Taylor cone which results in fibrous material on a nano/micro scale that accumulates on the collector. This jet is dependent on several design parameters. The wider the diameter of the jet, the longer and thinner the fibres tend to be [24]. Design parameters also consist of polymer conductivity and molecular weight of polymer.

The basic apparatus for an electrospinning device consists of a capillary (needle) with nominal diameters ranging from 0.5mm to 1.5mm, a high voltage supply that produces an electric field in which the capillary is placed at the positive charge. This capillary is attached to a stored liquid polymer (syringe). The liquid polymer is then injected through the capillary at a controlled rate. Electrospinning uses electrostatic charge from the high voltage supply to draw the fibres onto the collector. When the high voltage supply is switched on, the charge creates a whipping effect of the liquid polymer jet. The nanofibres are then produced and collected randomly at the negative or grounded charge (the collector) (see Figure 2-5). This produces nonwoven nanofibrous mats.

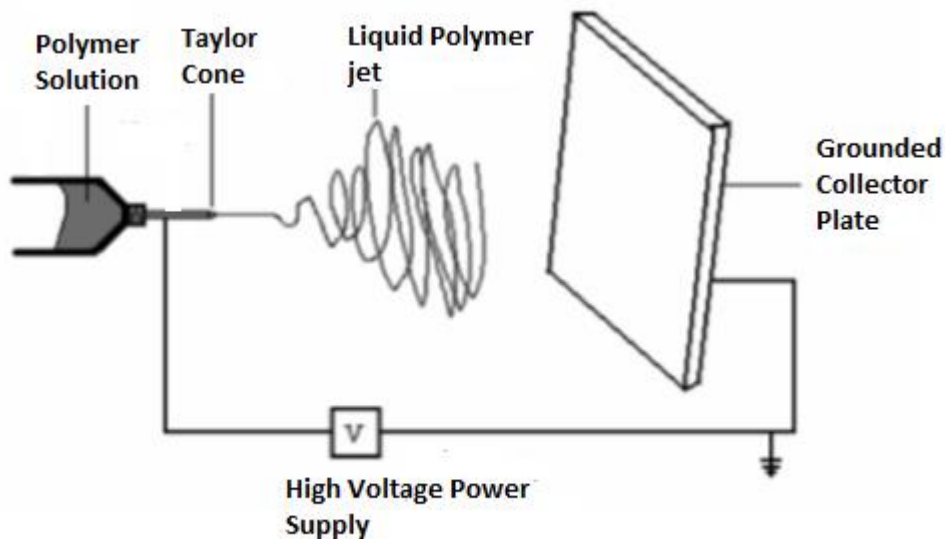


Figure 2-5: Electrospinning Apparatus [8]

Research in nanotechnology has increased exponentially recently and methods such as electrospinning are now being considered as economical alternatives to older methods such as drawing and template synthesis [7]. This has led to investigations and research of electrospun fibres and their effect in composite technology. The process parameters can easily be varied and provide diameters ranging from 50-100nm [25]. Electrospinning is a process used to provide nano fibrous mats that are applied in several industries such as membrane design, composite application and tissue engineering [24]. Methods other than electrospinning can only produce fibres with an average diameter of $2\mu\text{m}$ [26]. The fibres collect randomly and

produce nonwoven fibrous nano mats that can be used in composite materials. The lengths of these fibres are considered infinite in comparison to the diameter and because of this; the aspect ratio (L/D) is large and is highly advantageous.

2.3.1 Taylor cone

The electrospinning process occurs within three stages. These are seen in Figure 2-6. This image represents the tip of the needle to the base collector. In the first stage, A, the Taylor cone is initiated. This is where a smooth jet of polymer molecules is formed. This jet then becomes unstable in stage B when the whipping effect occurs. Then finally before the polymer molecules reach the collector they pass through a transition zone, phase C, and become nanofibres as evaporation takes place [27]. The Taylor cone is formed by electrostatic forces created from an even distribution of induced charges within tip of the needle.

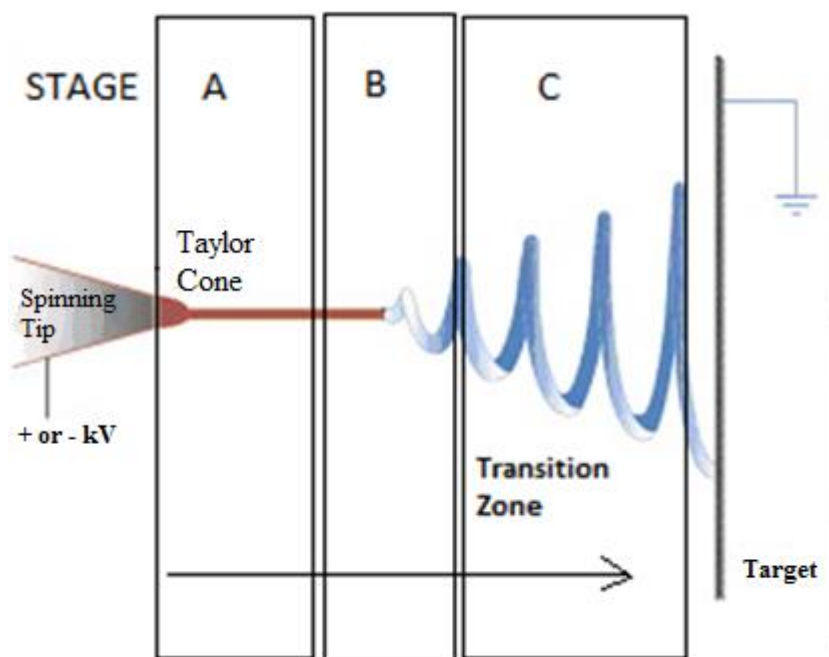


Figure 2-6: Movement of polymer solution jet stage-by-stage process during electrospinning [27].

The ratio of the surface tension within the solution, to the forces of electrostatic repulsion, as well as the field strength, directs the geometry of the cone [27]. This stable region is formed when the voltage supplied is approximately less than 6kV. This is known as the threshold voltage and beyond this voltage is where phase B occurs. The threshold voltage forming a Taylor cone occurs when the voltage is increased from 3.67kV/cm to 5.0kV/cm [28]. The flow rate in this instance was fixed and held at 0.5 ml/min. In the *Rutledge et al.* [28] study, glycerol was electrospun and analysis of the electro hydrodynamic behaviour was carried out. It was noted that characterization methods used to produce electrospun fibres are; solution properties, operating parameters, online processing monitoring and fibre characterization using scanning electron microscopy as well as optical microscopy.

2.3.2 Electrical Charge

Static electrical charges are induced on the molecules of the polymer solution at a density that causes self-repulsion of these charges, within the liquid, to stretch into a solid fibre when in the electric field [29]. Fibres are formed as the solvent evaporates. The high voltage causes the ohmic current, created from the resistance of the polymer, to distribute the charges throughout the molecules. When the solution has reached the capillary tip, a convective current is transited from the ohmic current. These charges are transferred from the tip to the collector with the fibre itself. A stabilisation of current oscillation occurs once the fibres have been deposited onto the collector. The charges can be positive or negative i.e. AC current.

The solution uniformity and direction is dependent on the curvature of the electric field [29]. Charges tend to concentrate in areas of higher curvature. A large curvature for the potential difference as well as the collector reaching a critical value causes the solution to accelerate towards the collector. The large charge density (electric charge per unit volume) is dependent on the voltage supplied. A very high charge density leads to an unstable jet and a very low charge density leads to dripping of the solution. A bending instability is caused when the charge density is high, this is because the self-repulsion of the charge exceeds the stabilizing tangential stress. This instability becomes highly disordered. This disordered instability causes loops of single jets to join into a cross linked network [29]. These loops constrain the motion of the electrospinning jet and form the nanofibres into a circular patch of a few centimetres.

2.3.3 Collector

The collector is generally used as the negative electrode. It is used to collect the nanofibres. It is electrically earthed. Deposited nanofibres are nonconductive so therefore residual charges build up as the nanofibre layer becomes thicker [29]. The side effect of this is a repulsive force that diverts the jet to other regions that are conductive. Another concern is non uniform packing density and adhesion between layers of nanofibres.

There are various collector designs to allow various alignment as well as reduction of layer stacking and adhesion. It plays an important role in the deposition of nanofibres [29]. Collectors used in previous research papers are knife-edge disk collector, grid collector, and parallel electrodes and a drum collector. Alignment is possible through parallel electrodes. A gap or insulating section allows the fibres to align themselves. The advantage of a drum collector is the possibility of producing continuous nanofibres.

2.3.4 Operating parameters

There are two sets of parameters that affect the overall quality of the electrospun fibres [30]. Solution parameters which consist of the following; concentration of polymer, ionic strength, solvent, temperature, viscosity. The other set of parameters are the process parameters; voltage, collector needle distance (drop height), flow rate.

The most important aspect of the electrospinning process is to provide fibres of very low diameters. It was found that the parameters that affect the diameter are the process flow rate and the polymer concentration [30]. These parameters all fall under the optimization phase of electrospinning. There are various amounts of research carried out on these parameters as well as alternative methods to improve properties such as alignment, quality, fibre diameter and

quantity. Some of the main areas in design and modification of electrospinning that still need a lot of work to be done on are; producing aligned fibres over a large area of thickness, fabrication of a 3D structure and form highly ordered structures at a large rate [31].

2.3.5 Optimization of Electrospinning

Electrospinning has several parameters that are applied to optimize the production of nanofibres. Alignment and continuity is achieved by the collector output however, quality and consistency of nanofibres are dependent on 9 variables. These are illustrated in table 2-1. The viscosity is dependent on the concentration of the liquid polymer within the syringe. *Martinez et al* [32] determined the effects of altering the concentration of PAN/DMF on the result of nanofibre.

Table 2-1: Processing parameters [32]

Process Parameter	Effect on fibre morphology
Viscosity/Concentration	Low concentrations/viscosities yielded defects in the form of beads and junctions; increasing concentration/viscosity reduced the defects
	Fibre diameters increased with increasing concentration/viscosity
Conductivity/solution charge density	Increasing the conductivity aided the production of uniform bead-free fibres
	Higher conductivities yielded smaller fibres in general (exceptions were PAA and polyamide-6)
Surface Tension	No conclusive link between surface tension and fibre morphology
Polymer molecular weight	Increasing molecular weight reduced the number of beads and droplets
Dipole moment and dielectric constant	Successful spinning occurred in solvents with high dielectric constant
Flow rate	Lower flow rates yield fibres with lower diameters
	High flow rates produced fibres that were not dry upon reaching the collector
Field strength/voltage	At too high voltage, beading was observed
	Correlation between voltage and fibre diameter was ambiguous
Distance between tip and collector	A minimum distance was required to obtain dried fibres
	At distances either too close or too far beading was observed
Needle tip design	Using co-axial, 2 capillary spinneret, hollow fibres were produced
	Multiple needle tips were employed to increase threshold
Collector composition and geometry	Smoother fibres resulted from metal collectors; more porous fibre structure was obtained using porous collectors
	Aligned fibres were obtained using a conductive frame, rotating drum or wheel-like bobbin collector
	Yarns and braided fibres were also obtained

Ambient parameters	Increased temperature caused a decrease in solution viscosity, resulting in smaller fibres
	Increasing humidity resulted in the appearance of circular pores on the fibres

The beading of the fibres is one of the physical instabilities within the electrospinning process. The concentration is required to be at an optimum value in correlation to the voltage. This instability is known as the Rayleigh instability and is axisymmetric [33]. The ideal parameters to reduce the Rayleigh instability is one in which both voltage and concentration are relatively high. The other two instabilities experienced during electrospinning are the bending and whipping instabilities. These are caused by the charge to charge repulsion between the excess charges in the jet [33]. When the voltage is increased the bending and whipping instabilities are in control therefore resulting in an inverse conical shape of jet. If the voltage is increased further then the Rayleigh and bending instabilities are suppressed and only the whipping instability has an effect.

Table 2-2: Fibre diameter concentration relationship [33]

PAN Concentration (w/w)	Range of variation of the diameters of the fibres (nm)
5%	109-260
4%	37-94
3%	35-88

A high voltage means a large electrostatic charge is induced into the polymer solution resulting in an accelerated drop from tip to collector. A small electrostatic charge induced in the polymer results in a lack of droplets thus creating difficulty in producing a Taylor cone as illustrated in Figure 2-7 [33]. When the electrostatic charged is increased at a slow rate a shear force is created within the liquid surface causing the charges to repel each other and in the direction opposite of the surface tension. This imitates the Taylor cone when the critical voltage is reached. This process as a whole produces nanofibres. Electrospinning polymers to produce nanofibres is the most common application used. The most common precursor to carbon fibres is PAN (polyacrylonitrile).

2.3.6 Polyacrylonitrile (PAN)

Acrylonitrile is a hard, rigid, fairly insoluble and high melting point material. It exists as a polymer known as polyacrylonitrile of which chains are formed through carbon bonds [34]. Acrylonitrile is produced by a reaction between propylene and ammonia in the presence of a catalyst [34]. Acrylonitrile monomers are suspended as droplets in water and are made to

polymerize to PAN through free radical initiators [34]. The structure of the repeating unit of the PAN has the structure shown in Figure 2-7.

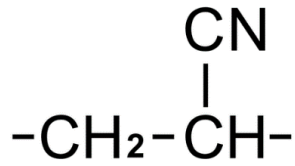


Figure 2-7: Chemical Structure of Acrylonitrile

The formation of the strong chemical bond between nitrile groups causes a resistance to a fairly large amount of organic solvents. This bond also disallows melting without decomposing. PAN is used to manufacture commercial acrylic fibres. These commercial acrylic fibres are identified as acrylic fibres if 85% or more of the fibre content is PAN. PAN is also difficult to dissolve and very resistant to dyeing and hence is produced as PAN alone.

PAN is an acrylic and the advantages of acrylics as opposed to natural fibres like wool are that they cost less, and are resistant to moths, mildew and sunlight. Application of PAN fibres apart from textiles and cloths are precursors to commercial carbon fibre, replacement material for asbestos in cement, industrial filters and battery separators [26]. When being used as a precursor for carbon fibre the PAN fibres go through a process of carbonization.

2.4 Multi-Scale Nano Hybrid Composites

Recently multi-scale hybrid composites have been produced with the application of nanoparticles as a secondary reinforcement. There are various methods to hybridizing a composite material. Multi-scale nanocomposites refers to composite materials that are reinforced with nano sized particles within macro sized reinforced matrices. *Taraghi et al* [35] determined the impact response of aramid reinforced epoxy with embedded MWCNTs. This inclusion of MWCNTs had resulted in an improvement of impact response. It was concluded that a 0.5% and 0.3% MWCNT addition resulted in a 35% and 34% energy absorption increase. *Gojny et al.* [36] determined the influence of nanoparticles on glass fibre reinforced epoxy and found that the interlaminar shear strength had improved with the addition of the nanoparticles but the tensile properties had not shown any improvements.

2.4.1 Electrospinning of PAN

PAN is ideally the most appropriate polymer to use in electrospinning. This is because of its carbonization ability and strength. Electrospinning of PAN must have ideal conditions depending on the requirements necessary to produce the required nanofibre quality length and diameter. Concentration is the most important parameter when electrospinning PAN. Lower concentrations tend to bead and higher concentrations tend to produce large diameters [37].

Kirecci et al [37] determined the effect of the viscosity and applied voltage on the uniformity and morphology of nanofibres. PAN solution from 6% to 16% concentrations were tested.

The reason for bead formation at lower concentrations is because of the high conductivity and low viscosity of the solution. The viscoelastic force is decreased and while the electrostatic force is increased, the fibre tends to bead and create a smaller diameter in between the beads. The diameter of the fibre increases as the concentration and voltage increases when the collector distance is 15cm. Concentrations lower than 8% are considered low concentrations where beading occurs. The lowest diameter achievable is carried out by using an 8% concentration at 35kV

This decrease is due to the increase of the electrostatic field and repulsion forces. Increasing the voltage reduces flight time and lowering the flight time stretches the fibres thus causing them to break and be discontinuous [37]. It was also noted that increasing the voltage above 34kV also creates a beading effect.

It was observed that a 15cm collector distance is ideal at large voltages to produce the lowest diameter without beading. Diameters were shown to decrease as the collector distance was increased to 15cm. The increase in flight time is the reason for the increase in diameter as the collector distance is increased further than 15cm regardless of the voltage supplied. A very low electrostatic force however with a large needle tip and collector distance tends to increase diameters too. A low collector distance creates beading due to less evaporation of solvent time. It was concluded that the optimum voltage and distance were 35kV and 15cm. The most appropriate concentration for the fixed distance and voltage was noted to be 10%.

2.4.2 Nanofibres

Nanofibres have diameters between 50-100nm whereas conventional macro fibres have diameters between 5-10 μ m. They are significantly smaller than conventional fibres but slightly larger than CNTs [38]. There are several advantages of obtaining fibres on a nano scale as oppose to micro and macro sized fibres. Micro and macro scale fibres have been applied comprehensively in the past and now, due to higher aspect ratios (length to diameter, L/D) of nanofibres, it is possible to have greater mechanical performance as well as superior flexibility. This is because a high aspect ratio provides a high surface to volume ratio [7]. This has led to research and focus on long and continuous fibres. It is well known that shorter fibres may cause stress concentrations due to the fibre edge, thus leading to crack initiation. The fibre edge has no effect on the matrix to fibre load transfer and a shorter fibre does not overlap thus adding no increase in strength [22]. The aspect ratio plays an important role therefore a long continuous and small diameter fibre will be advantageous in this characteristic. This is because a longer continuous fibre provides good adhesion too.

Nanofibres are applied in various industries for various applications. Apart from reinforcing material in composites, nanofibres are used in medical applications as well as electronics and environmental applications such as water filtration [39] [40]. Methods to produce fibres on a nano-scale are carried out using techniques such as template assisted synthesis, phase

separation, self-assembly, solvent evaporation, drawing process method and doctor blading method [39].

There are various advantages in applying nanofibres as reinforcements in composites. In laminate composites, more specifically when incorporating nanofibres for inter layers, strengthening has been observed. One example is Figure 2-8 in which nanofibres are located in between adjacent plies in the laminate [22].

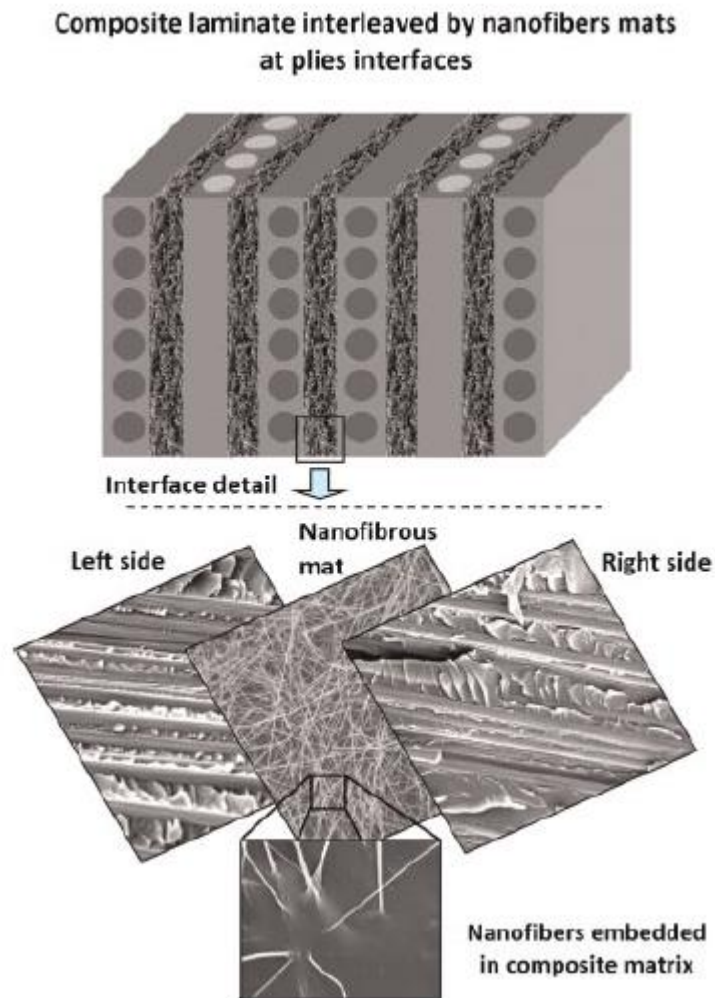


Figure 2-8: Multi-scale nano hybrid composite [22]

Nanofibre layers characterized by a combination of interlocked in-plane and out-of-plane nanofibres have been proposed to contribute to improvement of interlaminar fracture resistance similar too loops and hooks that function like Velcro [22]. Most research in composite strengthening entails CNFs and CNTs alike but very few works have been carried out on the potential of polymer nanofibre reinforcement. *Reneker et al* [41] were the first to propose the idea of embedding polymer matrices with polymer nanofibres. Polybenzimidazole (PBI) electrospun nanofibres (diameter of approximately 500nm) were moulded into an epoxy and rubber matrix. The fibre content played a huge role in the improvement of the bending modulus and the fracture toughness, with marginal increases on both composites [22]. Research on

electrospun nanofibres as interface reinforcement of composite laminates has also been conducted. Table 2-1 lists some of the research that has been conducted on the use of polymer nanofibres as secondary reinforcement. *Reneker et al* [41] used PBI nanofibres as a secondary reinforcement in graphite epoxy and it was concluded that an increase of 13% and 15% for critical energy and mode I/II interlaminar fracture respectively, occurred [41].

Three different polymer nanofibres, nylon-6, epoxy and polyurethane were electrospun onto glass fibre epoxy composites and the effect of the thickness was examined [22]. Flexural strength, modulus and the interlaminar shear strength were determined. A threshold thickness was found and it was concluded that properties under or equivalent to the threshold thickness of the nanofibre layers improved or had no effect at all. However, above the threshold thickness, properties were observed to decrease.

This is because a high thickness negates complete impregnation of the matrix. There exists many polymers that may be electrospun but only a few have been researched as possible composite reinforcements. PAN which is a carbon fibre and CNF precursor polymer is a highly conductive polymer that may be electrospun to form membranes alike.

Table 2-3: Polymer Nanofibres [22]

<i>Nanofibre (diameter)</i>	<i>Matrix/Laminate Type</i>	<i>Composite Characterization</i>
<i>Polybenzimidazole (300-500nm)</i>	Graphite/Epoxy Prepreg	Delamination in Mode I and Mode II
<i>Polycarbonate (200nm)</i>	Carbon/Epoxy Prepreg	Tensile stress-strain
<i>Nylon-6 (150-500nm)</i>	Glass/Fibre epoxy Composite	Three-point bending test (ASTM D790)
<i>Epoxy (EPO1691-410, Shell corp) (350-1200nm)</i>		Interlaminar shear test (ASTM D2344)
<i>TPU (300-600nm)</i>		
<i>Nylon-66 (75-200nm)</i>	Carbon/Epoxy Prepreg	DMA Tests Mode I DCB Mode I fatigue delamination
		Life test (ASTM D6115)

2.4.3 Carbonization

Carbonization is a process used to produce carbon materials through heat treatment. It is the main treatment process used in 90% of all commercial carbon fibre production through PAN as the precursor [34]. PAN carbonization has a three step process; stabilization, carbonization

and graphitization [42]. This treatment process converts PAN fibres into high strength and high modulus carbon fibres. PAN fibres are held in tension when stabilized in air at 200-300°C. Cyclization and dehydrogenation are processes that the PAN undergoes to make the carbon fibre dense and stable as a fibrous structure when being carbonized [42]. The carbonization of PAN occurs at 800°C or more in an inert atmosphere, giving way to an amorphous structure with limited crystallinity.

2.4.4 Carbon Nanofibres

Carbon nanofibres specifically, can produce mechanical characteristics of composites that conventional macro fibres fail to achieve. Characteristics such as fatigue and corrosion resistance are achieved through the reinforcement of CNFs [43]. This enables many applications such as super-capacitors, filters, nanocomposites, fuel cells and even optoelectronics [43]. Applying materials such as nanofibres in polymer composites have proven enhancement of strength, weight reduction, chemical resistance as well as good thermal properties [38]. These properties have provided a positive influence on fields such as aerospace, electronics and the automotive industry. This is due to the cost effective reliability of the weight, and the structural ability of carbon nanofibres [38]. *Zhou et al* [43] investigated the microstructure, electrical conductivity and mechanical properties of aligned individual CNFs. It was revealed that stabilization had a detrimental effect of the nanofibre diameter, however carbonization would reduce fibre diameter substantially. The results in their study determine that the tensile strength had improved by 67% and a 45% increase in Young's modulus when carbonization temperatures had been increased [43]. It was stated that the CNF bundles are linked to factors such as alignment and individual CNF properties.

The morphological studies determined by *Zhou et al* [43] demonstrated that ribbon shaped and stacking of graphene sheets were formed by a 2200°C carbonization temperature, and that a lower temperature such as 1000°C would produce a turbostratic structure with carbon stacks that were bundled and folded [43]. It was also stated that alignment had not shown absolute parallel fibres and that the fibres were inconsistent in terms of fibre relative to the fibre axis [43]. This was assumed to be because of two factors; Stretching of PAN nanofibres is vital in maintaining the alignment and orientation along fibre axis and was not conducted. Tension value needs to be optimised during stabilization. This value was smaller than that of conventional fibres.

Plasied et al [38] determined the effect of the CNF content on the mechanical properties of vinyl ester. It was found that an increase in fibre content would increase the brittleness of the vinyl ester composite. This was concluded to be caused by the agglomerations and clusters of the CNFs. These bundles were due to mechanical mixing with a 2% CNF content resulting in a high resin viscosity [38]. Improvements of modulus and yield strength were noted when a 0.5% CNF content was introduced. Increasing CNF content was proven to reduce UTS and elongation. Cluster build up was deduced as the reason for this decrease.

Difficulty in dispersion techniques due to entanglement and clustering of fibres is common problem in CNF reinforced composites. This has led to several works on dispersion techniques. These range from the dilution method and ultra-sonication, to high shear mixing and the use of

surfactant. These methods all fall in line with the need to improve the relationship between carbon and the polymer matrix. The carbon nano structure has been altered using two main methods to improve this relationship. These are through covalent functionalisation and non-covalent wrapping with surfactant, polymer coatings or polymers [44]. There are advantages and disadvantages to the process of functionalisation, as carbon degradation may occur when chemically bonding is carried out.

A bundle of electrospun CNFs were investigated under Raman spectroscopy [45]. The electrospun carbonized PAN Raman shift vs. counts graph is shown in Figure 2-9. The graph shows two broad overlapping peaks. These are D and G peaks according to Gaussian Lorentzian mixed shape, provide the order of atoms. The D represents the disordered carbon atom whereas the G represents the ordered carbon atoms. The integrated intensity ratio of the D versus the G provides this information.

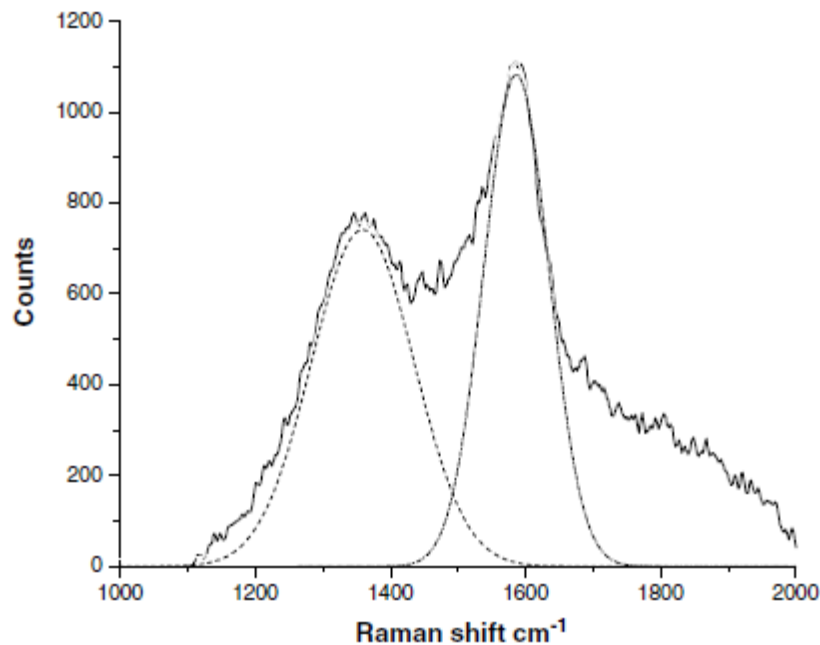


Figure 2-9: Raman Spectroscopy of carbonized PAN [50]

It was observed by *Zussman et al* [45] that the intensity ratio was lower for carbonized PAN than PAN at higher temperatures and therefore was indicative of more ordered fibres [45]. Improvements of hybrid composites has also been achieved with the inclusion of carbon nanotubes (hollow nanofibres) and nanofibres. *San-Bok Lee et al* [46] proved that the inclusion of MWCNTs and copper nanoparticles improved the electrical conductivity by 15%. The interlaminar shear strength was also increased by 13% in comparison to plain woven composites [46]. CNFs were also deposited onto carbon fibre using anodic and cathodic electrophoretic deposition (EPD). EPD is an industrial process in which charged particles are suspended and shifted towards electrodes and get deposited under an electric field [46].

The CNF deposited composites showed a 10% reduction in short beam strength. This was due to the effect of nitric acid treatment that caused structural defects on the CNFs [46]. This was because of poor interfacial bonding between CNFs and matrix resin thus weakening the strength of the composite.

Defect inducing failure and crack propagation was observed because the resin rich area crack propagates into the laminate [46]. The direction of propagation then changed direction along the carbon fibre bundle before transmitting into the laminate. This illustrates that the CNF did not prevent the crack propagation and therefore acted as a defect due to poor interfacial bonding. Furthermore, fibre pull out perpendicular to the crack plane and the need for improvement of interfacial bonding between CNFs and macro fibre reinforced polymer composites without the reduction of CNF strength. Electrical conductivity and interlaminar shear strength however were improved through hybridization of composites with CNFs. The interlaminar shear properties as well as the electrical properties of carbon nanofibre coated carbon fibre was also determined [46]. The test used to determine the interlaminar shear properties is the short beam shear test. The strength was shown to decrease through anodic EPD. The 10% short beam strength reduction was concluded to be caused by damage from nitric acid treatment resulting in structural defects. MWCNTs were noted to have good dispersion and uniform distribution on carbon fibres as well as a denser deposition than the CNFs. *Gojny et al.* [36] manually added CNTs and carbon black (CB) into epoxy resin with glass fibre used as the reinforcing macro fibre. The interlaminar shear strength was observed to have improved but the tensile strength was not affected. This was due to dictating effect of the macro fibres.

2.4.5 Doping

One method of improving the interlaminar properties of multi scale nano hybrid composites is by the improvement of the nanoparticles themselves. Doping is a technique in which nanocomposites are created in order to improve the properties of the individual nanoparticles themselves. These nanocomposites are created by adding impurities or any foreign material into a nanoscale material.

Li et al. [47] determined the effects of electrospun MWCNTs-EP/PSF (polysulfone) hybrid nanofibres on carbon fibre reinforced epoxy. The MWCNTs-EP were doped by adding the PSF into the electrospinning solution with the use of the solvent. The doped nanofibres were then spun onto the surface of carbon fibre mats and used as pre-pregs to create multiscale hybrid nanocomposites. Various properties were observed to have improved. The interlaminar shear strength results indicated an increase when loading of the doped nanofibres were increased. Fracture toughness had been observed to decrease when loading had increased of the 10%wt. Other advantages of using doped nanofibres is the ability to add ulterior properties such as electrical conductivity and thermal resistance. There are also applications such as in biomedical, where tissue engineering, wound dressing and drug delivery systems are improved through the use of doping.

2.5 Conclusion

This chapter concludes the relevant literature for this research report. Various research has shown the use of electrospinning as a method of doping, CNF (carbon nanofibre) production and hybridisation of polymer reinforced composites. Composites were initially discussed in detail. The mechanics and processing of epoxy and aramid fibre were researched. The relationship between epoxy and aramid fibre, and the development of hybrid composites was studied. The theory behind the electrospinning process was determined, as this was the method used to produce nanomats for coating and CNFs for the doping of PAN (polyacrylonitrile) nanofibres. Finally previous multi-scale nano hybrid composite research was carried out because of the use of nanoparticles within the aramid fibre composites for this report. The next chapter discusses the methodology used to fabricate the multiscale hybrid composites and the methods of mechanical characterization.

3 Methodology

Mechanical characterization was conducted by observing the effect of both the PAN nanofibres and CNF doped nanofibres on the tensile, flexural and impact properties of aramid fibre composite. The materials used, the procedure in which the aramid composite and hybrid composite samples were fabricated, as well as the testing procedure, is discussed in detail.

Initially the optimum volume fraction of aramid fibre within epoxy resin was determined. This was conducted by fabricating three different volume fractions, 10% 20% and 30%. Aramid reinforced fibre epoxy specimens were processed first and tested. Optimization of the volume fraction was then carried out by characterization of the aramid reinforced epoxy composites. The optimum volume fraction was found to be 30%. PAN coated aramid reinforced epoxy specimens were then fabricated and finally CNF doped PAN coated aramid reinforced epoxy composites. Specimens were then mechanically characterized and analysed.

3.1 Materials

3.1.1 Matrix

The matrix selected for the production of composites was Bisphenol-A epoxy resin. The epoxy resin and hardener was purchased from AMT composites Pty Ltd (South Africa). The product name of the epoxy resin and hardener was Ampreg 21 epoxy resin and Ampreg 21 hardener respectively. Ampreg 21 is known for the manufacturing of composite structures and is applied in both hand lay-up and vacuum bagging techniques. It has a low initial mixed viscosity and allows easy wetting with macro fibres.

Table 3-1: Mixing ratios of Ampreg-21

Hardener	Mix Ratio (resin: hardener)	
	By Weight	by Volume
Fast to Extra slow	100:33	100:38
High Tg	100:29	100:34

It was stated by the manufacturer that the mixing of the resin and hardener is very important. When measuring by weight, an accurate scale must be used. Thorough mixing is vital, especially when mixing by hand, therefore the sides and bottom must be observed carefully. The pot life is limited and a long duration within the mixing vessel may harden and heat excessively.

The minimum ambient curing temperature of Ampreg 21 is 18°C. Curing can be done at ambient temperature for 16 hours with a fast hardener or for 48 hours with a slow hardener. A temperature ramp rate of 10°C/hour when heating from ambient temperature to the post curing

temperature was recommended by the manufacturer. This allows thermal performance of the laminate to stay above the oven temperature so that no thermal shock effects would occur. The physical and mechanical properties of Ampreg 21 resin and hardener are indicated in Table 3-2 as per AMT composites ©.

Table 3-2: Ampreg 21 Epoxy resin and Hardener Properties (AMT)

Resin/Hardener (standard)						
Initial mixed viscosity (cP)	Gel Time (mins)	Demould Time (mins)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Cured Density (g/cc)	Linear Shrinkage (%)
1194	21	143	72.7	3.3	1.148	1.45

3.1.2 Fibres and Fillers

The macro fibre material used to produce all the composite samples was aramid fibre. The product name of the aramid fibre used was Twaron 2200 and was provided by AMT composites Pty Ltd (South Africa). Table 3-3 displays the physical and mechanical properties of Twaron 2200 as per Taijen ©.

Table 3-3: Physical and Mechanical Properties of Twaron 2200 (Taijen)

Property	Value	Unit
Specific Gravity	1.44-1.45	g/cm ³
Tensile Elongation	2.2-4.4	%
Young's Modulus	60-120	GPa
Tensile Strength	2.4-3.6	MPa

Twaron is produced by Teijin (Japan) and is a high performance synthetic fibre. It is highly advantageous due to its balanced performance in terms of mechanical properties, chemical resistance and thermal stability. It is a non-conductive material that has low flammability and no melting point [48].

The nanofillers used in this research were PAN nanofibres produced by electrospinning. The Polyacrylonitrile (PAN) granules and N, N Dimethylformamide (DMF) solvent were combined to produce an 8% conc. solution (details in section 4.2). Both were supplied by Sigma Aldrich Pty Ltd (South Africa). The fillers were electrospun into nanofibre mats and layered between sheets of Twaron. CNFs were fabricated using the electrospun PAN nanofibres and a tube furnace (details in section 4.3.2). The CNFs were used as doping agents within the PAN nanofibres and re-spun onto Twaron sheets.

3.2 Composite Fabrication Procedure

3.2.1 Aramid fibre composite (AFC)

The first phase of the methodology was to determine the optimum volume fraction for aramid fibre reinforced composites. Three volume fractions were initially selected and tested, 10%, 20% and 30%. To determine the number of aramid fibre sheets required to produce the three volume fractions, the volume (170 mm x 370 mm x 4mm) of the required mould was initially used to determine the mass of one aramid fibre sheet, before applying the following calculations:

The mass of a single layer was measured to be 10.92g:

$$\frac{10.92\text{g}}{17\text{cm} \times 37\text{cm}} = 0.017361\text{g/cm}^2$$

The number of aramid fibre layers required for the aramid volume fraction can be calculated using Equation (3.1) below:

$$n_{\text{layers}} = \frac{\rho_{\text{aramid}} \times t_{\text{mould}} \times V_{\text{aramid}}}{m_{\text{Area}}} \quad (3.1)$$

Where,

$\rho_{\text{aramid}} = 1.44\text{g/cm}^3$ Density of Aramid fibre

$t_{\text{mould}} = 0.45\text{cm}$ Thickness of Mould

$V_{\text{aramid}} = 0.1, 0.2 \text{ or } 0.3$ Volume of Aramid

$m_{\text{Area}} = 0.017361\text{g/cm}^2$ Mass per Area

Table 3-4 indicates the number layers and volume of resin needed for the production of aramid fibre composites. Appendix B contains a spreadsheet used to calculate all volume fractions.

Table 3-4: Number of layers and Resin volume required

Vol. Fraction	$n_{\text{karamid max}}$	$V_{\text{epoxy (L)}}$
10%	3	0.92
20%	7	0.81
30%	11	0.71

The next step was to fabricate the test samples. This was carried out using the hand lay-up technique. To produce a composite using the hand lay-up technique each layer should be immersed and rolled within a mould as seen in the schematic in Figure 3-1. For a 30% volume

fraction aramid composite, 11 aramid fibre sheets were used. The resin and hardener are measured according to the standard 100:38 ratio.

The first step was to coat 3 layers of Ramwax ® release agent onto the mould. Wooden stoppers were then placed at the ends of the mould to reduce resin leaks. A flat cover was placed to smoothen the resin and was coated with 3 layers of release agent prior to placement. Once the release agent was coated on all surfaces, the resin and hardener (catalyst) were mixed using a beaker and spatula.

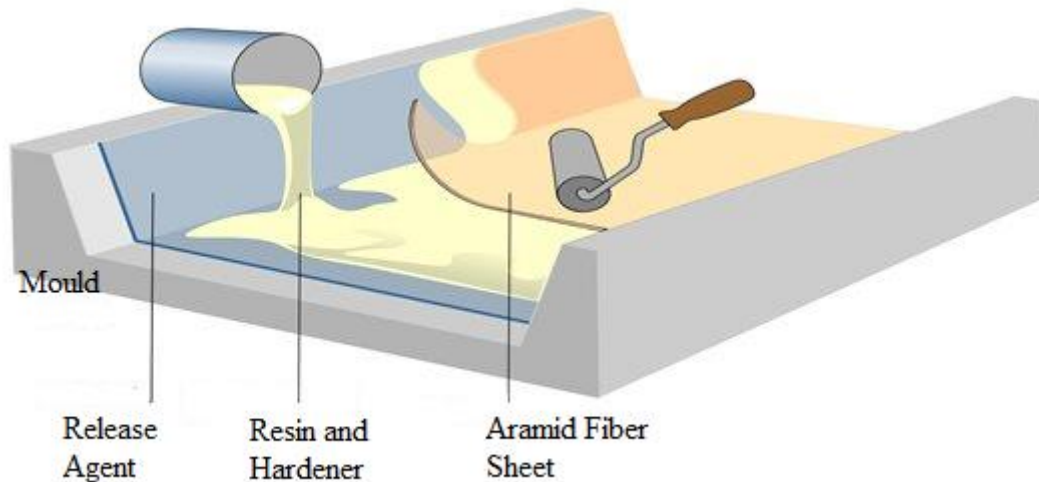


Figure 3-1: Schematic of Hand Lay-up Technique

The initial coat of resin was laid onto the mould using a paintbrush. An aramid fibre sheet was placed into the resin coated mould. The sheet was then pressed using a roller so that the whole sheet was immersed in the epoxy resin and done so to reduce air bubbles. A second sheet was then added. A brush and roller was used on the surface of the aramid fibre sheet with the epoxy resin. Rolling the surface for sets of 3 (10% vol.), 7 (20% vol.) and 11 (30% vol.) aramid fibre sheets was carried out repetitively to immerse the aramid fibre sheets as well as remove air bubbles. This was carried out until the total volume of epoxy resin was used and all sheets were immersed. This procedure can be seen in Figure 3-2. Finally a cover was placed on top of the mould with weights and left to cure.

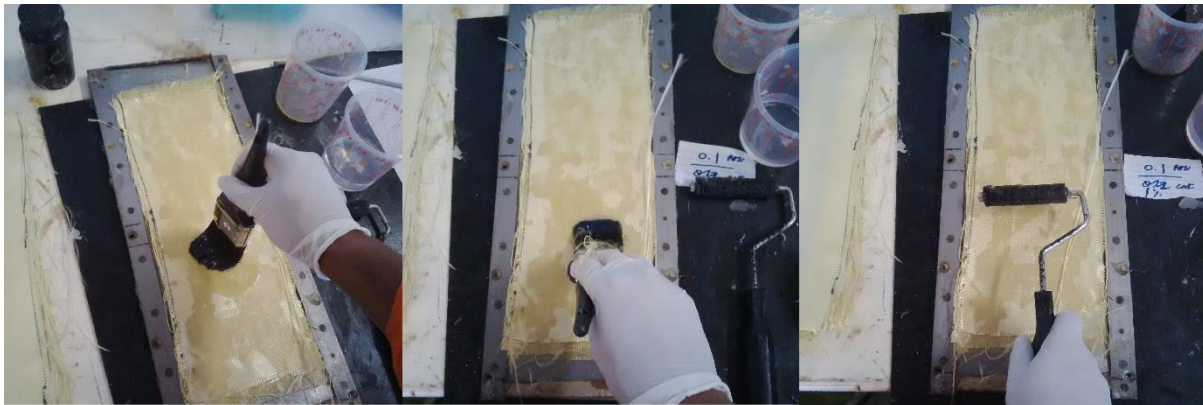


Figure 3-2: Hand lay-up of Aramid Epoxy

Once the mould had cured the panel was removed and cut into the desired shape as indicated in Figure 3-3.



Figure 3-3 Cured sample before cutting specimens

The tensile test, 3-point bending test and impact test specimens seen in Figure 3-4 (b) were prepared and cut using a band saw. A tensilKut rig as shown in Figure 3-4 (a) was used to shape the dog-bone specimens for the tensile test. Tensile test, 3-point bending test and impact test samples were cut according to ASTM D3039, D7264 and D256 respectively.

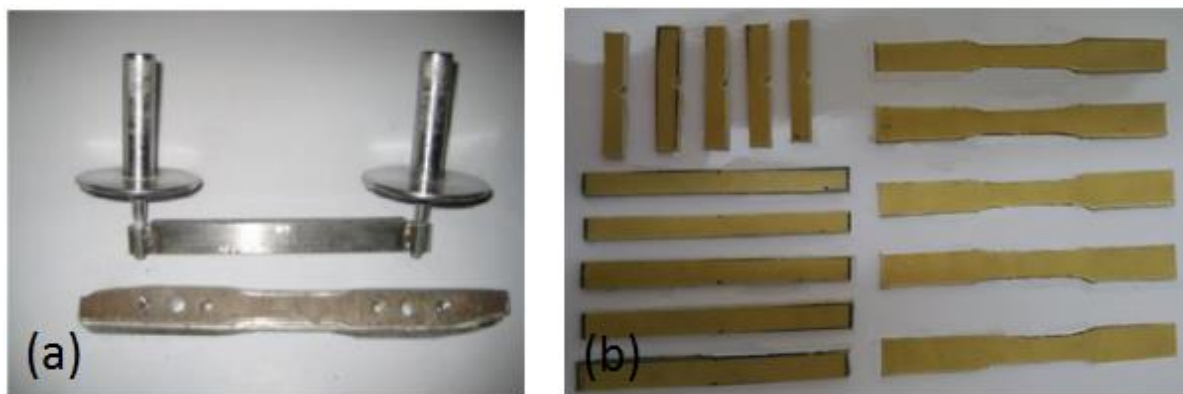


Figure 3-4: (a) TensilKut rig (b) ASTM specimens for mechanical characterization

Testing was carried out on the aramid reinforced composites to determine the optimum volume fraction.

3.2.2 PAN reinforced AFC hybrid composite

The electrospinning of PAN nanofibres onto aramid fibre sheets was carried out using the electrospinning set-up observed in Figure 3-5. Nanomats were created by coating the surface of each aramid fibre mat by attaching the mats onto the drum collector. The 6 syringes would then be filled and attached to the syringe pump. The syringe pump would be switched on and a high volume rate (~ 2 ml/min) would initially be selected to run the PAN solution through the tubes to the needle tips.



Figure 3-5: Electrospinning PAN onto aramid fibre

Once the solution had reached the needle tips, the pump would be switched off and the positive electrode crocodile clip and the grounded rod would be attached. The drum collector motor would be switched on and the flow rate adjusted to 1ml/hr where finally, the HV supply would be switched onto the desired voltage (13~15kV depending on Taylor cone).

It is important to maintain a Taylor cone during spinning. When the flow rate is too low the voltage tends to pull the solution out of the tube therefore breaking the fibre before reaching the drum. When the flow rate is too high, the PAN solution starts to drip, causing beading and waste. Using the ideal parameters are not enough to maintain a continuous nanofibrous mat. It is important to observe the process, so that clogging is prevented as well as coating of any

conductive material nearby. An ideal nanomat that was used as a coated interleaf on the aramid fibre can be seen in Figure 3-6. The nanomats are charged and therefore stick to the aramid fibre mats.

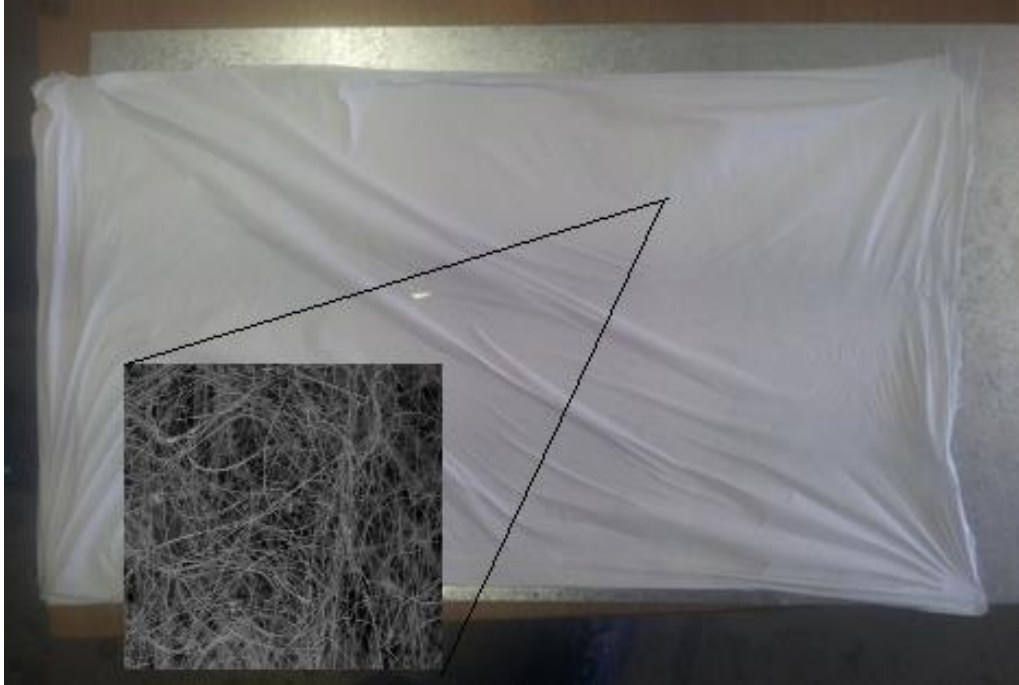


Figure 3-6: Electrospun PAN Nanomat

With the use of mechanical characterization, the optimum volume fraction for AFC was determined to be 30%. The coating of nanofibres was carried out on 11 sheets using the electrospinning process. Table 3-5 indicates the PAN volume fractions used as reinforcements within the AFC. Three different PAN volume fractions were used.

Table 3-5 Number of layers and volume of epoxy in hybrid samples

Vol. Fraction	n_{karamid} max	V_{epoxy} (L)
0.1%PAN	11	0.71
0.2%PAN	11	0.71
0.5%PAN	11	0.71

PAN reinforced aramid hybrid composites were fabricated using the same hand lay-up technique to that of the aramid fibre reinforced composite (section 3.2.1). The slight difference is that, every PAN nanofibre coated aramid layer was placed with the electrospun nanomat surface facing downwards. The initial mat was not coated and the aramid layers are placed in order as seen in Figure 3-7. This was prepared in order to roll and immerse the epoxy resin without damaging or shifting the nanofibre sheets. Nanofibre volume fibre calculations were used in adding the nanomats.

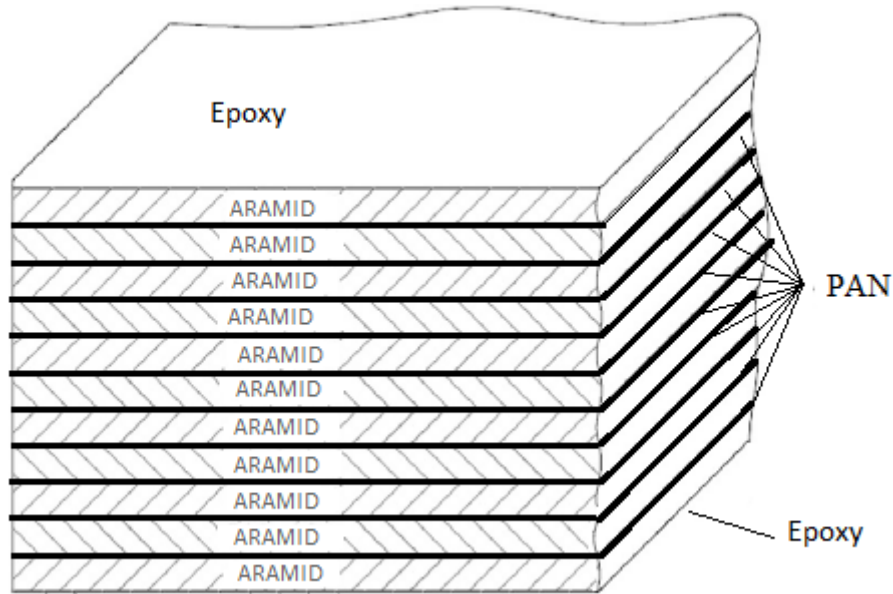


Figure 3-7: Layer arrangement with PAN nanofibres

3.2.3 PAN Volume Fraction Calculation

In order to determine the required PAN needed for a 30% vol. AFC, the density of the entire composite should be calculated. The rule of mixtures for a laminate composite was used to calculate the overall composite density as shown below in Equation (3.8). The density of PAN was found to be 1.184 g/cm³.

$$\rho_{comp} = V_{faramid}\rho_{aramid} + V_{fepoxy}\rho_{epoxy} + V_{PAN}\rho_{PAN} \quad (3.2)$$

Where,

$\rho_{aramid} = 1.44 \text{ g/cm}^3$	Density of Aramid Fibres
$V_{aramid} = 0.3$	Volume Fraction of Aramid Fibres
$\rho_{epoxy} = 1.14858 \text{ g/cm}^3$	Density of Epoxy
$V_{epoxy} = 1 - V_{aramid} - V_{PAN}$	Volume of Epoxy
$\rho_{PAN} = 1.184 \text{ g/cm}^3$	Density of PAN
$V_{PAN} = 0.01, 0.02 \text{ or } 0.05$	Volume of PAN

Using a 30% optimum aramid fibre volume fraction, it was found that the density of each volume fraction of PAN; 0.1%, 0.2% and 0.5% was 1.1340 g/cm³, 1.1357 g/cm³ and 1.1412 g/cm³ respectively.

With 1.137 g/cm³ selected as the average density and with the volume of the mould known, the mass of the composite was found to be 369.4g using Equation (3.9).

$$m_{comp} = \rho_{comp} \times V_{mould} \quad (3.3)$$

Where,

$$\begin{aligned} V_{mould} &= \text{width (19cm)} \times \text{length (38cm)} \times \text{thickness (0.45cm)} \\ &= 324.9 \text{ cm}^3 \end{aligned}$$

The next step required the calculation of weight fraction for the amount of PAN needed to be collected, which makes use of Equation (3.10).

$$\begin{aligned} W_{PAN} &= \frac{\rho_{PAN} \times V_{PAN}}{\rho_{comp}} \quad (3.4) \\ &= \frac{1.184 \text{ g/cm}^3 \times V_{PAN}}{1.137 \text{ g/cm}^3} \end{aligned}$$

Using equation 3.3 the W_{PAN} for the three volume fractions were 0.1 %, 0.2 % and 0.5 %. This then led to the mass required for each PAN fraction. Substituting the results from Equation (3.9) and Equation (3.10) into Equation (3.11) below, results in the determination of the required mass of PAN needed to be collected on the plate to provide for the correct volume fractions of PAN.

$$m_{PAN} = W_{PAN} \times m_{comp} \quad (3.5)$$

Therefore the mass of each weight fraction 0.1%, 0.2% and 0.5% was 0.36g, 0.74g, 1.85g respectively. The next step was to convert the mass into the required volume. Equation 3.6 was used to determine the volume per fraction.

$$V_{pan} = \frac{m_{pan}}{\rho_{pan}} \quad (3.6)$$

Where,

$$\rho_{PAN} = 1.184 \text{ g/cm}^3$$

The volume for 0.1%, 0.2% and 0.5% was 0.3ml, 0.63ml and 1.56ml respectively. This allowed electrospinning of the PAN, however the PAN solution consisted of PAN and DMF and therefore to determine the volume required to spin, Equation 3.7 was applied.

$$V_{pan/dmf} = \frac{V_{pan}}{pan_{conc.}} \quad (3.7)$$

Where, $pan_{conc.} = 0.08$ (8% solution)

The PAN solution volume for spinning for each 0.1%, 0.2% and 0.5% were 3.75ml, 7.88ml and 19.5ml. This therefore lead to the volume dispensed at 1ml/hr with 6 syringes giving way to spinning times of 37.5mins, 78.8mins and 195mins for 0.1%, 0.2% and 0.5% respectively. This calculation is a total spinning time for the whole composite, and because an aramid 30% volume fraction has 11 sheets and only 10 sheets are coated (see section 4.2.2), electrospinning is carried out at 3.8 mins/sheet, 7.9 mins/sheet and 19.5 mins/sheet for each volume fraction respectively. The volume per sheet is therefore calculated by dividing the PAN solution volume by the number of sheets.

3.2.4 ECNF Doped PAN reinforced AFC hybrid composite

The chosen 8% wt. fraction PAN/DMF solution (see section 4.2.1) was unchanged for the electrospinning of the electrospun carbon nanofibre (ECNF) doped PAN nanofibres. Sonication was carried out on the DMF/CNF solution for 20mins to ensure even distribution of the ECNFs in the DMF. After sonication, the mixtures were visually black, as seen in Figure 3-8, which is an indication of good dispersion.



Figure 3-8: Sonicated ECNF/DMF solution.

The PAN was then added to the ECNF/DMF mixture and magnetically stirred for a further 24hrs to completely dissolve the PAN to evenly disperse the ECNFs in the solution. Subsequently, it was observed that the viscosity of the PAN/DMF solution did not noticeably vary from the addition of 0.5%wt. fraction ECNF to the PAN/DMF solution. The viscosity of

the PAN/DMF had increased from the addition of the 1%wt. fraction of ECNFs. Similar results were also observed by *Pilehrood et al.* [49] with the addition of 0.25% (no noticeable effect on viscosity) and 0.75%wt. fraction CNTs (dramatic rise in viscosity ≈ 200 times that of the PAN/DMF viscosity) to a 10%wt. fraction PAN/DMF solution. It was observed however, that the colours of the electrospun fibres were neither black nor white but rather an off-grey colour as shown in Figure 3-9.

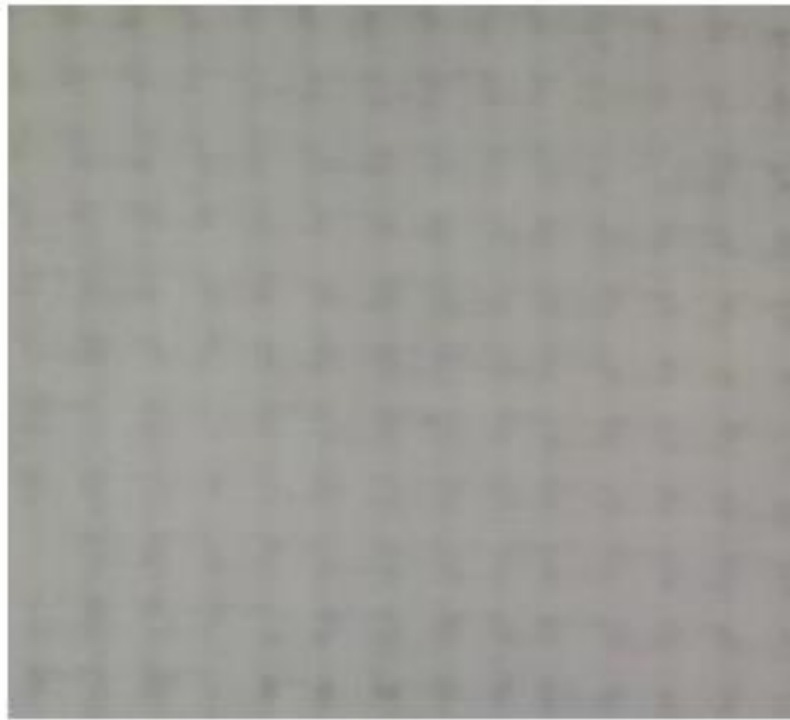


Figure 3-9: Dispersion of PAN nanofibres

The 0.5%wt. fraction ECNF/PAN/DMF mixtures were then electrospun in the exact method as that described in section 3.2.2. The 1% vol. fraction ECNF/PAN/DMF mixtures could not be electrospun using the same parameters due to the increased viscosity, therefore the applied voltage was decreased to 12kV and the distance between the electrodes was increased to 25cm, or until smooth fibre production was reached. Constant clogging of the needles was observed at the higher ECNF concentration which could have been caused by agglomeration of ECNFs into micro sized bundles as well as the increased viscosity. The final collection of the 1% vol. fraction ECNF embedded in 0.5% vol. fraction PAN nanofibres on an aramid fibre mat can be seen in Figure 3-10. From this image, it can be seen that there are in fact large agglomerations of ECNFs which were encapsulated in the PAN nanofibres during electrospinning. The uniformity and distribution of PAN is evident in Figure 3-10, however further analysis using SEM and TEM was required in order to characterise the distribution of ECNFs within the PAN nanofibre, which will be discussed further in section 4.4.

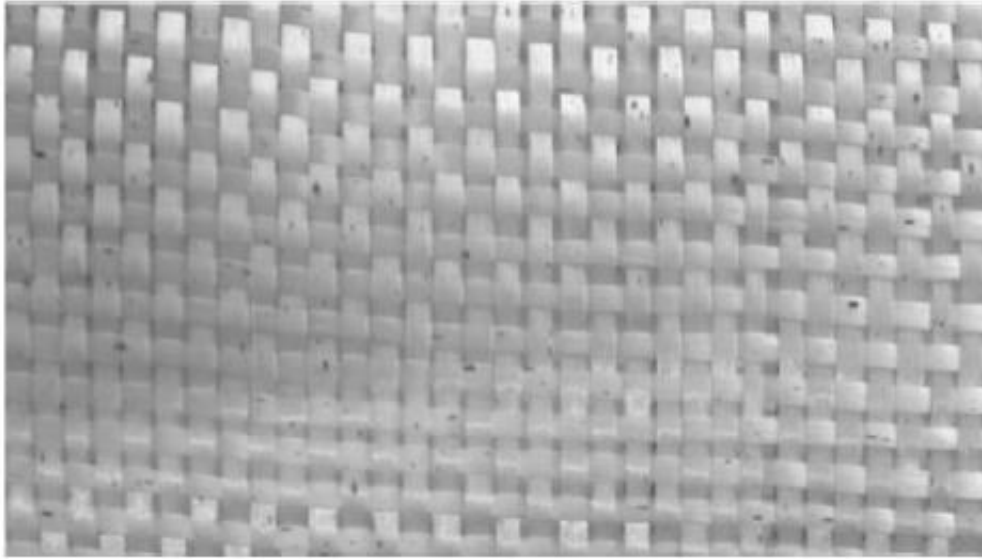


Figure 3-10: Image showing the macro-agglomerations of ECNFs imbedded in the PAN nanofibres.

Once ECNF doped PAN concentrations had been determined, electrospinning was carried out on all aramid fibre sheets using the procedure explained in section 3.2.2. Two different CNF doping volume fractions were applied to the three nanofibre PAN reinforcements and table 3-6 shows the number of layers and volume of epoxy required to produce CNF doped PAN nanofibre strengthened aramid hybrid composites. Using 11 layers for the optimum (30% vol.) aramid reinforcement, the nanomat coating was carried out by spinning onto 10 layers. This laminate order can be seen in the schematic in Figure 3-11. ECNF volume fraction calculations were used within the AFC.

Table 3-6: Number of layers and volume of epoxy per CNF-PAN volume fraction

Vol. Fraction	n_{karamid} max	V_{epoxy} (L)
0.1%PAN+0.5%CNF	11	0.7
0.2%PAN+0.5%CNF	11	0.7
0.5%PAN+0.5%CNF	11	0.7
0.1%PAN+1%CNF	11	0.69
0.2%PAN+1%CNF	11	0.69
0.5%PAN+1%CNF	11	0.69

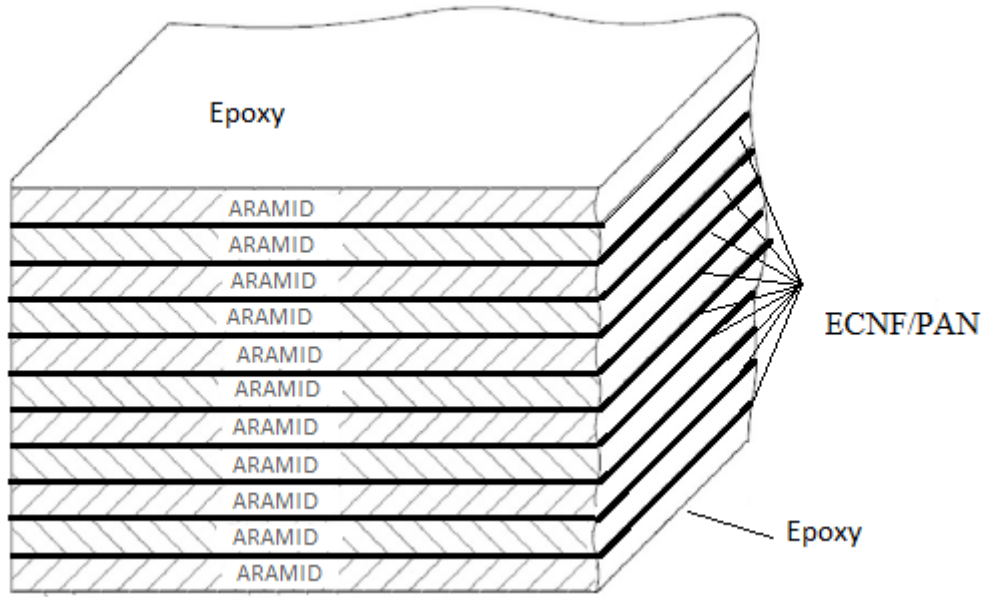


Figure 3-11: Layer arrangement with ECNF doped PAN nanofibres

3.2.5 ECNF doped PAN Volume Fraction Calculation

Rule of mixtures calculations were used to determine the required PAN/DMF volume to spin, and to attain the mass of CNF-DP to be collected on each aramid layer for each volume fraction of 0.1%, 0.2% and 0.5%. CNF weight fractions were determined by using a 0.5% and 1% volume fraction.

In order to achieve this, the density of the entire composite was calculated using rule of mixtures shown in Equation (3.8). The density of the final ECNFs was assumed to be 2.00g/cm³, according to Zussman *et al* [50].

$$\rho_{comp} = V_{faramid}\rho_{aramid} + V_{fepoxy}\rho_{epoxy} + V_{fcnf}\rho_{cnf} \quad (3.8)$$

Where,

$\rho_{aramid} = 1.44\text{g/cm}^3$ Density of Aramid Fibre

$\rho_{epoxy} = 1.14858\text{g/cm}^3$ Density of Epoxy

$V_{aramid} = 0.3$ Volume Fraction of Aramid

$V_{epoxy} = 1 - V_{aramid} - V_{fcnf}$ Volume of Epoxy

$\rho_{cnf} = 2.00\text{g/cm}^3$ Density of CNF

$V_{cnf} = 0.005 \text{ and } 0.01$ Volume of CNF

With the density of the entire composite and the volume of the mould known, the mass of the composite can be found using Equation (3.9).

$$m_{comp} = \rho_{comp} \times V_{mould} \quad (3.9)$$

Where, $V_{\text{mould}} = \text{width}(19\text{cm}) \times \text{length}(38\text{cm}) \times \text{thickness}(0.45\text{cm})$
 $= 324.9\text{cm}^3$

The next step requires the calculation of weight fraction for the amount of CNF needed, which makes use of Equation (3.10).

$$W_{fcnf} = \frac{\rho_{cnf} \times V_{fcnf}}{\rho_{comp}} \quad (3.10)$$

Now, substituting the results from Equation (3.9) and Equation (3.10) into Equation (3.11) below, results in the determination of the required mass of CNFs needed to be collected on the plate to provide for the correct weight fractions of CNFs.

$$m_{cnf} = W_{fcnf} \times m_{comp} \quad (3.11)$$

During stabilization and carbonization, the PAN nanofibres weight is reduced by between 45-55% depending on the heat treatment conditions used [51]. Therefore, a PAN mass degradation ratio of between 0.45 and 0.55 was chosen to apply to the PAN mass so as to account for mass losses during carbonization, as seen in Equation (3.12).

$$m_{pan} = (1 + m_{deg}) \times m_{cnf} \quad (3.12)$$

$$V_{pan} = \frac{m_{pan}}{\rho_{pan}}$$

Where,

m_{deg} = Between 0.45 and 0.55

$\rho_{pan} = 1.184 \text{ g/cm}^3$

With the mass of PAN needed to spin to obtain the required CNF volume fractions known, the volume of PAN/DMF needed, can be equated using Equation 3.13:

$$V_{pan/dmf} = \frac{V_{pan}}{pan_{conc.}} \quad (3.13)$$

Where, $pan_{conc.} = 0.08$ (8% solution)

Therefore, the amount of PAN/DMF solution needed to be spun for each layer can be calculated by dividing the $V_{pan/dmf}$ result calculated from Equation (3.13) by the number of layers

calculated using Equation 3.1. The CNF volume fractions were determined by using the $V_{\text{PAN/DMF}}$, and were added using the mass. The mass was calculated to be 0.28g and 0.57g for 0.5% and 1% CNF volume fractions respectively. A spreadsheet was used to calculate all the different volume fractions and is given in Appendix B.

3.3 Testing procedure

Three mechanical characterization techniques were conducted to determine various mechanical properties of the composites. Mechanical testing included the tensile test, 3-point bending test and the impact test. Testing was initially conducted on the aramid reinforced composites to determine the optimum volume fraction, which was found to be 30% vol. The 30% vol. aramid fibre with nanofibre (PAN and PAN/CNF) strengthened samples were then fabricated and tested. The data was gathered and the results interpreted.

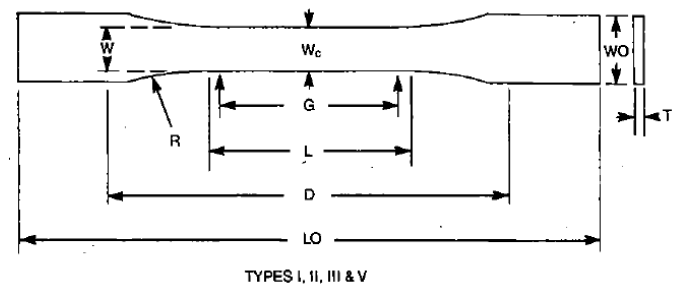
3.3.1 Tensile Testing

The tensile testing procedure was carried out according to ASTM D3039. A ruler and a marker were used to draw the dimensions of the required standard specimens as displayed in Figure 3-12 (b), and were cut to their desired shape using a band saw. The test specimens were mounted onto the tensile testing machine using the tightening grips seen in Figure 3-12 (a). A load rate of 1mm/min was set and a load cell of 20kN was used on the SHIMADZU AG-IS Tensile testing machine. The force was recorded by the on board computer software called Trapezium. The software recorded the stroke and the force of the individual specimens undergoing the test. Using a Vernier calliper the thickness and width of the gauge section were recorded onto the trapezium manually.

A laser extensometer was used to determine the extension of the specimens tested. The laser extensometer used was an LE-05 Epsilon Technology laser. The laser extensometer was linked to the DAQ (data acquisition) in which the extension from a fixed gauge length was recorded. The gauge length was fixed at an average distance of 50mm and was determined by the laser measuring the distance between the two pieces of reflective tape (Figure 3-12 (a)). This value could be seen on both the labview program linked to the DAQ, as well as the laser extensometer itself (see Figure 3-13). The extension is recorded by the laser sending a signal to the DAQ software when the two pieces of reflective tape separate on the specimen as it is elongated.



B	width of narrow section	$13 \pm 0.5 \text{ mm}$
L	Length of narrow section	$57 \pm 0.5 \text{ mm}$
WO	Width overall	$19 \pm 0.5 \text{ mm}$
LO	Length overall	165 mm
G	Gauge length	$50 \pm 0.25 \text{ mm}$
D	Distance between grips	$115 \pm 5 \text{ mm}$
R	Radius of fillet	$76 \pm 1 \text{ mm}$



T Thickness $3.2 \pm 0.4 \text{ mm}$ (b)

Figure 3-12: (a) Specimen gripped in tensile testing machine and (b) ASTM D3039 dimensions

Combined with the load cell and the 8-channel data acquisition tool, the laser extensometer then assists in recording the change in length. The data was recorded onto the computer notepad which was then transferred to a spreadsheet for processing.

The recording of data only occurred when the samples had failed in the appropriate region, which is in the gauge area. The number of specimens required by ASTM D3039 for an orthotropic material, was a minimum of 5.



Figure 3-13 Gauge length of sample using the laser extensometer

3.3.2 Flexural Testing

The testing procedure for the 3-point bending test was carried out using the ASTM D7264 standard. A ruler and a marker were used to measure the dimensions of the specimens. The samples were mounted onto the 3-point bending test rig. The rig was attached onto the Shimadzu AG-IS Tensile testing machine as shown in Figure 3-14 (b). The force arm was controlled and shifted downwards to the surface of the sample as indicated in Figure 3-14 (a). The trapezium, linked to the tensile testing machine, was converted to 3-point bending mode, where the top arm would move downwards. A load rate of 2 mm/min and a 20kN load cell were used for this test.

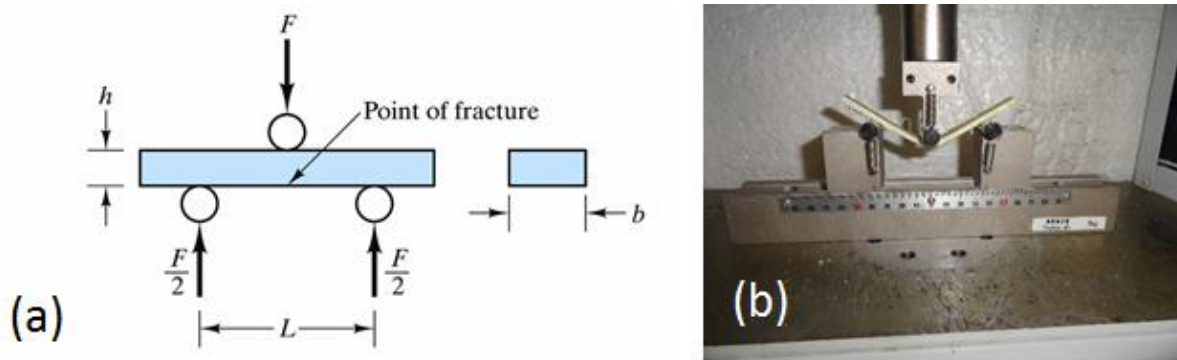


Figure 3-14: (a) Schematic of bending test (b) Actual bending sample in test rig

This test determines properties such as flexural strength, flexural modulus and flexural strain. Equation 3.13 was used to determine the flexural stress.

$$\sigma_f = \frac{3F_{max}L}{2bh^2} \quad (3.13)$$

Where:

- σ_f = Specimen flexural stress [MPa]
- F_{max} = Applied Load [N]
- L = Length between supports [mm]
- b = Width of specimen measured at its centre [mm]
- h = Thickness of specimen measured at its centre [mm]

Using the load rate as the deflection value the strain is calculated using equation y:

$$\varepsilon_f = \frac{6hD}{L^2} \quad (3.14)$$

Where:

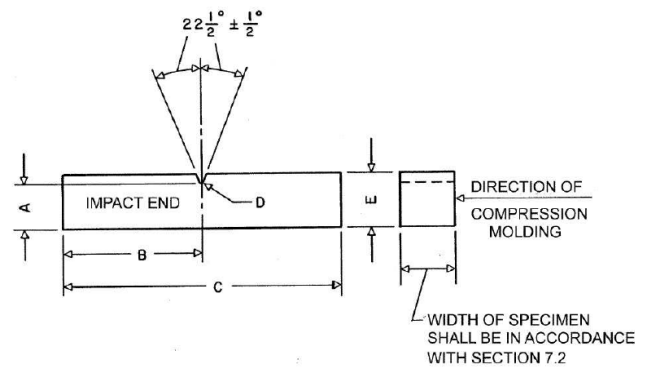
ε_f = Flexural strain of specimen [mm/mm]

D = Deflection of the specimen from point of load application [mm]

The modulus is measured by determining the rate of stress vs rate of strain.

3.3.3 Impact Testing

The impact test was carried out using the ASTM D256 Izod impact test. Dimensions were measured and cut using a ruler, a marker and a band saw. The Avery impact testing machine (Figure 3-15-A) was used to determine the impact energy. The Avery impact testing machine had a static dial arm pendulum which was shifted and locked before the testing of each specimen. The dial arm can be seen at the maximum 4.2 Joule mark when the arm is locked. Specimens were placed into the fitting and when the pendulum was released it resulted in the needle remaining stationary at a specific point on the dial gauge after fracture. The dial gauge readings were then used to determine the energy required to fracture the specimen. The machine ranges from 0-4.2 Joules with a resolution of 0.025 Joules.



Length (C) = 63.5±2mm

Width = 3-12.7mm

Thickness (E) = 12.7±0.2mm

A = 10.16±0.05mm

B = 31.8±1.0mm

D = 0.25±0.05mm

(b)

Figure 3-15: (a) - Avery Impact testing machine and (b) - Dimensions of specimen

The material sample is cut into a notched specimen with dimensions displayed in Figure 3-15 (b). The Izod impact test provides the necessary information to determine the impact resistance of a material. Impact properties are calculated through the energy absorbed when the pendulum impacts the specimen. This impact energy is used to determine the resistance of the material through the energy lost per unit cross sectional area. This energy is calculated using the following formula:

$$K_i = \frac{\nabla e_i}{A_i} \quad (3.15)$$

Where

- K_i = Impact resistance [J/mm²]
 ∇e_i = Energy lost by pendulum due to impact [J]
 A_i = Cross sectional area of impact specimen [mm²]

3.4 Morphological Characterization

Morphological characterization was carried out on PAN nanofibres and CNF doped PAN nanofibres. PAN nanofibres and fractured hybrid composite (PAN and CNF doped PAN) surfaces were observed using a SEM (Scanning Electron Microscope) instrument. Carbon based materials such as CNF and CNF doped PAN, were observed and analysed using the TEM and a Raman Spectroscope. The PAN and CNF doped PAN nanofibres had undergone a thermal analysis too, using TGA (thermogravimetric analysis). Finally an EDX (Energy-Dispersive X-ray Spectroscope) was used to analyse the PAN nanofibres only.

3.4.1 Microscopy

The scanning electron microscope (SEM) assists in observing failure modes on the surface of fractured specimens. This is advantageous when determining the effect that fillers have on the properties of the hybrid composite specimens as it produces images of the surface topography and the composition. The SEM operates by the use of an electron beam focused on a sample. The beam of electron scans over the sample surface and then scatters or reflects. The reflected electrons are collected by a cathode ray tube and then images are produced. The scanning electron microscope in this research was provided by the University of Witwatersrand, Microscopy and Microanalysis Unit (MMU). An FEI Quanta 400 FEG SEM instrument was provided to capture the images. The samples were cut and sprayed with a 15-30nm thick layer of gold palladium (Au, Pt) for 3 minutes using an Emitech coater. This was done to reduce charging effects caused by conductance of the material. This method is called sputter coating.

Samples examined were; PAN nanofibres, CNF doped PAN nanofibres, and failed hybrid samples.

The transmission electron microscope (TEM) works similar to SEM, in that electrons are beamed using a cathode tube into the specimen. The difference between the TEM as oppose to the SEM, is that the electrons are beamed through the specimen and are then reflected back through the same specimen, instead of from the specimen itself. This assists in observing the crystal structure, dislocations and the crystal boundaries. The TEM was used solely for the CNFs and the CNF doped PAN nanofibres. The imaging was carried out using the FEI TecnaiT12. It was performed at the MMU and used to observe the NC-graphitic carbon structure. Samples were prepared by placing the CNFs into an epoxy mould and once cured cut into 75-150nm sheets using a Reichert Ultra microtome. .

3.4.2 Thermogravimetric analysis

Thermogravimetric analysis is a process in which a material changes in physical and chemical properties are measured as a function of increasing temperature or a function of time. This tool is used to illustrate the thermal stability of a material. It can also be used to determine the oxidative stabilisation temperature as well as the carbonization temperature. In this research TGA was used to determine both stabilisation and carbonization temperatures of the PAN nanofibres. Analysis was conducted in air for both CNF and PAN nanofibres to find the oxidizing temperature and to understand the thermal transitional temperature.

3.4.3 Raman Spectroscopy

Raman spectroscopy is technique that uses the inelastic scattering of monochromatic light, mostly from a laser source. This means that when the light hits the sample, there is a frequency of photons that change upon interaction with the sample. The sample absorbs and then reemits the light, and the frequency of the photons shifts up or down when compared to the original monochromatic frequency, which is called the Raman Effect. Due to this shift, information such as vibrational, rotational, and low frequency transitions in molecules can be determined.

Raman spectroscopy was used on the CNFs to determine the quality of the carbon nanostructure and determination of the carbon content. The analysis was conducted using a Jobin-Yvon T64000 Raman Spectrograph. This was operated in a single spectrograph mode with an excitation source of 514.5nm line of an argon ion laser. An Olympus BX40 microscope attachment with a 20x magnification objective lens was used to observe the sample. A power of 1.2mW was used on the sample so that the laser does not cause localised heating on the sample. A 600 lines/mm grating on liquid-nitrogen cooled CCD detector was used for the backscattering of the light. Windows XP with LabSpec v4.18 software was utilised for the data acquisition.

3.4.4 Energy Dispersive X-ray Spectroscopy

EDX (Energy Dispersive X-ray spectroscopy) is a chemical characterization technique. It analyses the sample by determining the atomic structure by the use of an x-ray excitation source. An EDX can be carried out using the SEM. The backscattered electron images in an

SEM compositional contrast due to different atomic number elements and distribution allows for the on board EDS (Energy dispersive spectroscopy) to determine the elements and the proportions i.e. atomic %. In this research, the samples used in the SEM had undergone EDX and graphs were plotted.

3.5 Conclusion

This chapter discussed the methodology used for this research report. The materials used, and the composite fabrication procedure for the ASTM specimens were discussed. The testing methods used to determine the mechanical properties were followed by ASTM standards. Tensile, flexural and impact properties were determined. The morphological characterization was carried out by the use of the above mentioned microscopes. They were used to determine the quality and composition of PAN (polyacrylonitrile), ECNFs (electrospun carbon nanofibres) and ECNF doped PAN nanofibres. The next chapter discusses the development and characterization of the PAN and ECNF doped PAN nanofibres. The design and development of the electrospinning set up is discussed in detail and how the nanofibres were produced.

4 Development and Characterization of PAN and CNF doped PAN Nanofibres

In order to produce both PAN nanofibres and CNF-doped PAN nanofibres, an electrospinning device was designed and developed. PAN nanofibre and CNF-doped PAN (CNF-DP) nanofibre production was carried out using electrospinning. Individual components of the electrospinning set-up were either selected or designed. The methodology of the electrospinning process to produce PAN nanofibres to develop CNFs, and CNF-DP nanofibres is discussed.

4.1 Design and Development of Electrospinning Unit

In this research the aim of the electrospinning design was to produce continuous PAN nanofibre mats and CNF-DP nanofibre mats for reinforcement. The main concerns with electrospun nanofibres are the continuity, the alignment and the diameter of the individual nanofibres, which are dependent on the design of the electrospinning set-up. The continuity and alignment of the nanofibres are dependent on the collector design, and the diameter is dependent on the voltage, flow rate, needle diameter and collector distance. The three components that required designing were:

- The syringe pump
- The capillary and capillary attachment
- The collector

The syringe pump was developed to determine the flow rate and experimentally determine the appropriate operating parameters, such as the voltage and collector distance. The capillary and capillary attachments were developed to determine if the needle diameter plays a role in the quality and diameter of the individual nanofibres. Once parameters such as flow rate, collector distance, needle diameter and voltage were determined for the production of continuous nanofibre mats, a flow rate control component and capillary components were purchased. New Era syringe pumps were purchased from NNYG brands (South Africa) and the capillary and capillary attachments were purchased from Hamilton needles (Germany).

4.1.1 Syringe Pump

The syringe pump controls the flow rate of the solution to the needle tip or capillary. Controlling the flow allows the flow rate of the solution to be altered according to the desired voltage and distance. Initially the syringe pump was designed using basic materials such as Perspex, a threaded rod, an Arduino chip and a bread board attached to a stepper motor shown in Figure 4-1. These parts were purchased from MicroRobotics (Pty. Ltd) and the design was used for the experimental phase of the electrospinning process. This experimental phase was carried out to determine the desired voltage and needle-to-collector distance required to produce fibres on a nanoscale.

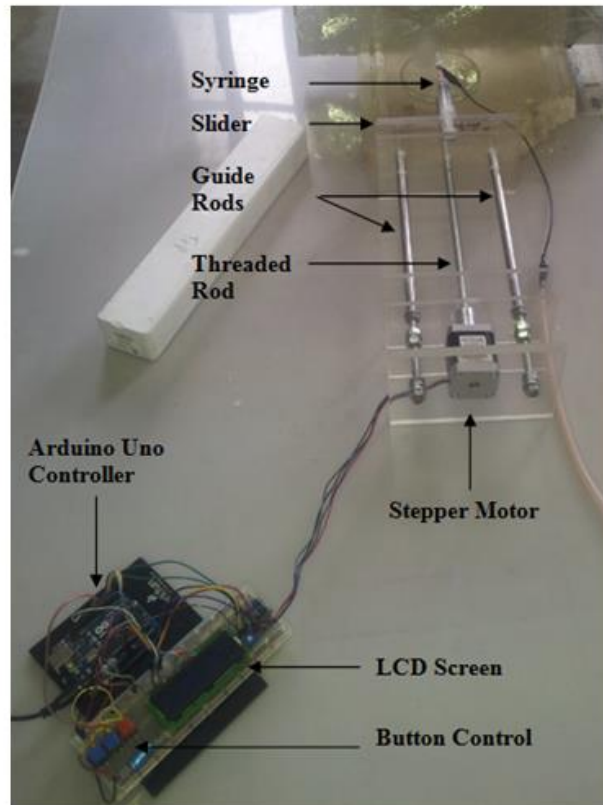


Figure 4-1: Syringe pump

The purpose of this syringe pump was to determine parameters that produce the lowest diameter of nanofibres possible. It was operated using a threaded rod in which Perspex sliders would thrust the syringe to produce droplets of solution at the needle tip. The self-designed syringe pump performed as required and was economical, however determining precise flow rates and volumes was not possible and therefore a commercial syringe pump was purchased.

A high precision NE-1000 syringe pump seen in Figure 4-2 was purchased from New Era Pump Systems Inc. The NE-1000 was used for a single syringe and assisted in determining an accurate flow rate as well as the most ideal collector-to-needle distance to produce nanofibres. Various syringes were experimented with and it was found that the Luer lock hub connector syringes were ideal because they did not possess any conductive material. The single syringe with a metal hub as observed in Figure 4-3 caused back current which restricted the voltage from increasing beyond 10kV.

Research indicates that a 1ml/min flow rate is the ideal flow rate to produce a Taylor cone and therefore was selected and used to determine the distance to the collector, as well as to determine the collector design. The NE 1000 pump (Figure 4-2) was used to test all the variable conditions prior to the purchase of the final electrospinning pump, which was the NE-1600 syringe pump (Figure 4-3). The NE-1600 was also purchased from New Era Pump Systems Inc.



Figure 4-2: NE 1000 syringe pump with metal hub syringe

The NE-1000 could only provide a circular nanofibre mat with a 50mm radius due to the single syringe and needle. This caused inconsistencies when coating the aramid fibre. A multiple syringe pump was purchased as to increase the surface area of spinning. A six syringe and needle system with the use of the NE-1600 was finally used to produce nanofibre mats.



Figure 4-3: NE 1600 Syringe Pump

4.1.2 Capillary and Capillary attachment

The capillary and capillary attachment is the component used in the electrospinning set up that allows the polymer solution to flow into the charged region. Needles were used as the capillary and were placed in Perspex blocks as the attachments. Designs and ideas were researched and various needle diameters were used. The needle sizes were selected according to *Heikilla et al.* [52]. As discussed by *Heikilla et al.* [52] the composition of the polymer solution is more influential than the actual needle diameter. A small needle diameter such as a 33G did not produce any nanofibres because of the pressure build-up of the solution within the needle and tubes. The 22G needle was selected according to the optimum solution concentration and voltage parameters. Three different needle diameter sizes were tested. Needle sizes were 17G, 22G and 33G.

A single needle in Figure 4-4 was first tested to determine the operating parameters required. The needle or capillary design was altered by introducing more needles to the electrospinning set up. This was carried out to produce nanofibre mats. The number of needles were increased to produce a nanofibre mat as wide as the aramid fibre mat. The number of needles were increased from three to six (Figure 4-4) which would eventually coat the whole surface of the aramid fibre mat.

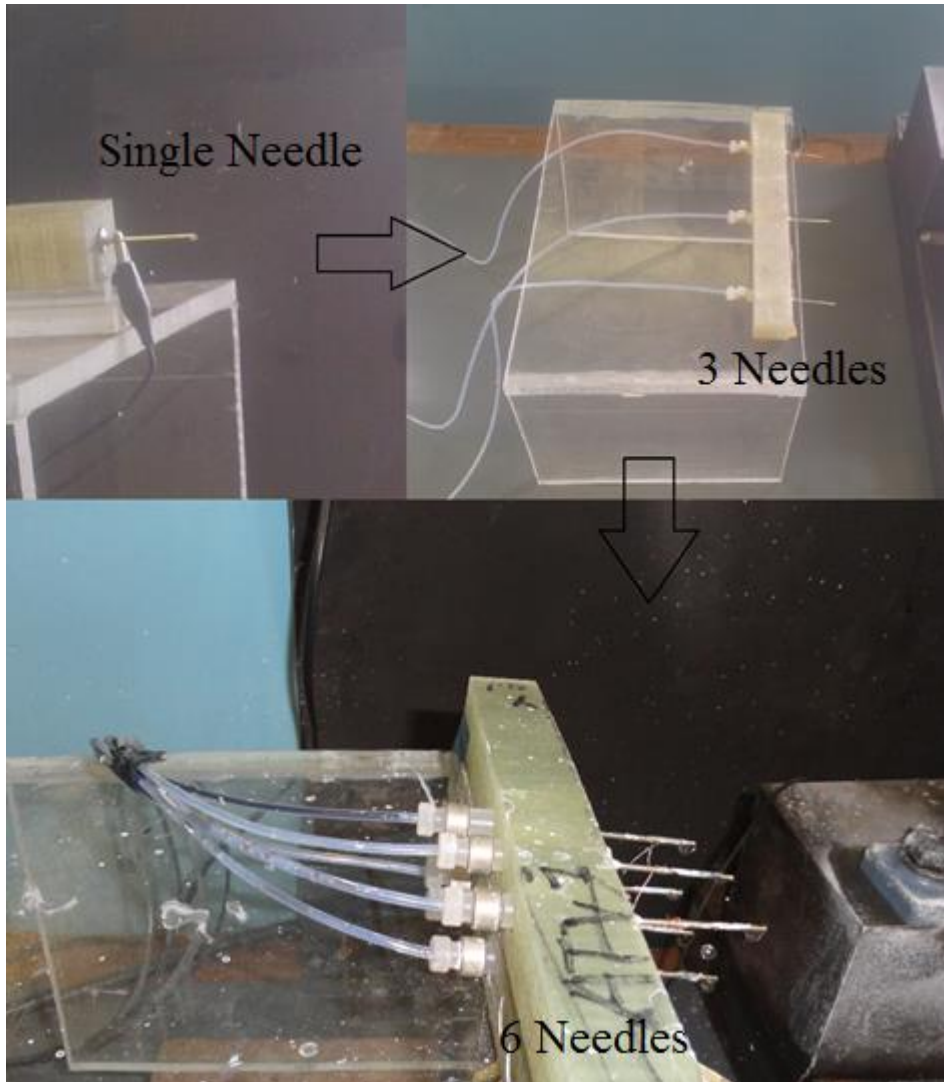


Figure 4-4: Development of capillary design

4.1.3 The Collector

The collector in an electrospinning set-up is the negative electrode. It was used to deposit the nanofibres onto the aramid fibre sheets. The design of the collector determines the formation of the nanofibres. A collector plate made from aluminium foil was initially used to determine the operating parameters and the outcome of the nanofibres. Randomly orientated nano fibrous mats on the surface was observed. The foil was then replaced with a square copper sheet which

was inserted into a Perspex fitting of which the negative electrode attached (Figure 4-5 B). The flat plate collector produced an evenly distributed mat when combined with the multiple needle capillary attachment.

To obtain aligned fibres, a collector with parallel plates was designed and used as displayed in Figure 4-5 A. The advantage of the parallel plate collector is the ability to produce aligned nanofibres. The alignment is caused by the air gap between the two plates. This allows the fibre length to be determined by the distance between the two plates.

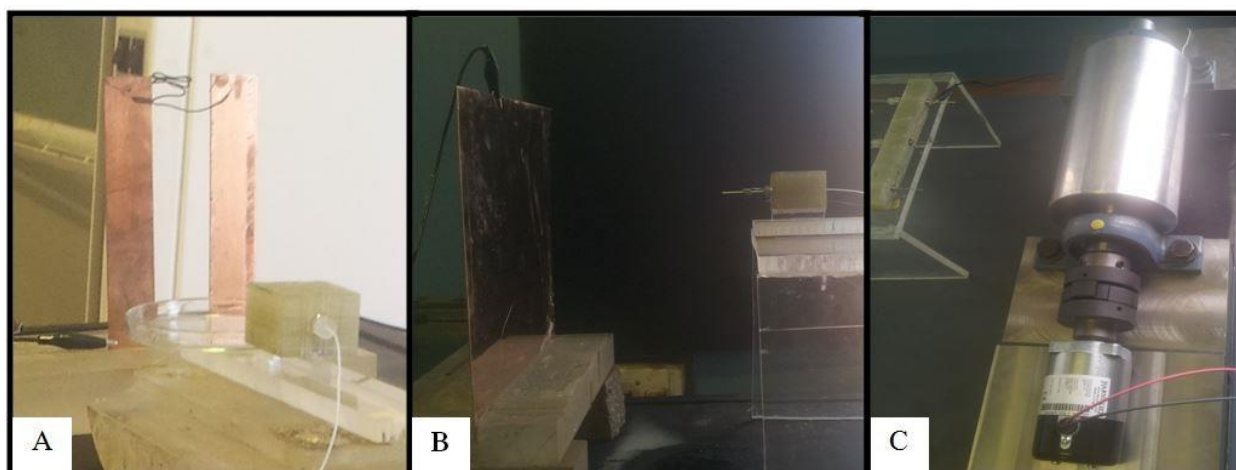


Figure 4-5: (a) Parallel plate (b) Flat late (c) Rotating drum

However, producing a continuous nanofibre mat was not achievable with the use of a parallel plate collector because the tension of the fibres would not allow the nanofibres to hold, resulting in a loss of nanofibres. The parallel plates were made conductive with a cable attached between the two plates. The plates were placed into a Perspex fitting where the negative electrode was attached.

The drum collector in Figure 4-5 C was machined in order to produce a continuous nanofibre mat. It was considered one of the better designs because it allowed the production of continuous nanofibres in the form of a mat. The drum collector size determines size of the nanofibre mat. The length of the drum was designed according to the width of the hand lay-up mould. The advantage of the drum collector was the ability to produce a continuous nanofibre mat onto the surface of the aramid fibre.

The drum collector was designed out of a lightweight and conductive material, such as aluminium, and isolated from the rest of the system in such a way that grounding was possible without having to ground any adjacent objects. This was achieved by placing the copper plate behind the drum and attaching the crocodile clip to act as the negative electrode. The copper plate would then act as a collector but the drum would collect the nanofibres. The drum collector was designed to rotate within the range of fibre take-up speeds for the polymer solutions. It was designed in such a way that the speed was controlled by an electric motor.

The motor to drive the drum was selected to achieve required rotating speeds as well as support bearings to allow for the rotation of the drum at these speeds.

The required RPM of the drum was calculated using equation 4.1 in Appendix B and therefore:

$$\begin{aligned} RPM_{REQ} &= \frac{60 \times 5m / s}{2\pi \times 0.0302m} \\ &= 1581rpm \end{aligned}$$

The required RPM for a drum shaft with a diameter of 60.46mm is 1581. However, because this is based on a minimum required radius from the mould dimensions, the radius of the drum could be increased so as to reduce the required RPM so that the drum collector could be operated under safer, lower RPM conditions. It was then decided to double the diameter of the drum to 120mm so as to reduce the RPM requirements:

$$\begin{aligned} RPM &= \frac{60 \times 5m / s}{2\pi \times 0.06m} \\ &= 796rpm \end{aligned}$$

The overall required RPM for the drum shaft was reduced to 796 RPM for a shaft diameter of 120mm. This resulted in a larger diameter but reduced the required RPM which led to safer operating conditions. The length of the drum was also specified to be slightly longer than the minimum requirement of 190mm and it was decided to be 220mm.

The next step of the collector design was to specify a motor that was capable of turning the drum at the required 796 RPM. A brushed DC motor was selected from RS Components' motor catalogue with the product code MPM10-0005/CONT and specifications as shown in Appendix A. The drum shafts diameters were specified at 30mm so as to stabilise the setup and the motor shaft diameter provided was 8mm. The motor shaft and drum shaft were then coupled and bolted to the frame. Pillow block bearings for the drum shafts were also specified to handle the 796 RPM required and bought from BMG Hydraulics with the product code UCP206D1.

The electrospinning unit consists of all components combined. Figure 4-6 the set-up consists of the HV power supply, the syringe pump, the capillary/needle and collector. The grounding rod was used to reduce any eddy current or back current and would protect the syringe pump power supply or any foreign conductive body. The unit consisted of three phases; design, experimentation and finally nanofibre production. Initially, due to budget constraints, the electrospinning unit had consisted of a foil collector and self-designed syringe pump shown in Figure 4-1. The second phase was achieved when a single syringe pump was purchased. This allowed more experimentation of various capillary and collector designs. Finally the drum and multiple syringe pump was used as it provided continuous nanofibre mats.



Figure 4-6: Collector design process

4.2 Development of PAN nanofibres

4.2.1 Solution Parameters

The solution used in the electrospinning process was a PAN solution. Solution parameters consisted of polymer concentration, viscosity surface tension, molecular weight and conductivity. The polymer concentration is directly related to the viscosity as well as the molecular weight of the solution. This plays a huge role in the quality and size of nanofibres spun. The ratio of solvent to polymer composition determines the surface tension of the solution. Polyacrylonitrile (PAN) has an average molecular weight of $M_w = 150,000$ g/mol (Sigma Aldrich) and was dissolved in *N,N* Dimethylformamide (DMF) for 24hrs, at room temperature, using a magnetic stirrer to yield an optimum of 8 wt.% concentration of PAN.

The PAN solution concentration was varied in order to determine the optimum concentration for smooth and uniform nanofibres. The concentrations used, ranged between 1 wt. % to 16wt. % concentration of PAN. This enabled a range of nanofibres analysed through morphological studies. It was observed that concentration between 1 wt. % and 8 wt. % yielded beads provided the diameter of the needle was small. The graph displayed in Figure 4-7 indicates the effect of low concentrations.

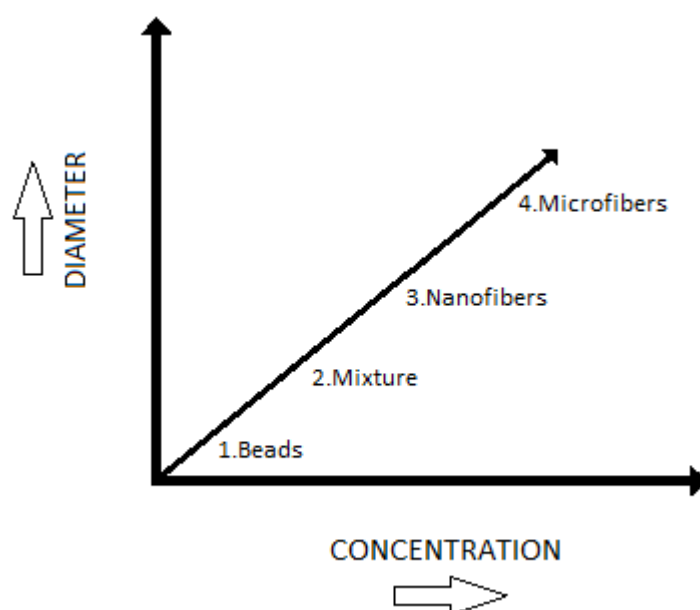


Figure 4-7 graph comparing needle diameter to polymer concentration

Very low concentrations did not produce any nanofibres and wastage of solution was observed. This was between 1 wt. % and 4 wt. %. Electrospinning was observed due to the low viscosity and high surface tension. When concentrations were increased from 4 wt. % to 8 wt. %, beads were observed but nanofibres had started to collect continuously (see Figure 4-8). Although nanofibres were continuous when observed under an SEM they were not uniform as can be seen in Figure 4-9 (a). Figure 4-9 (b) indicates the uneven distribution of fibres and clumping due to a higher concentration.

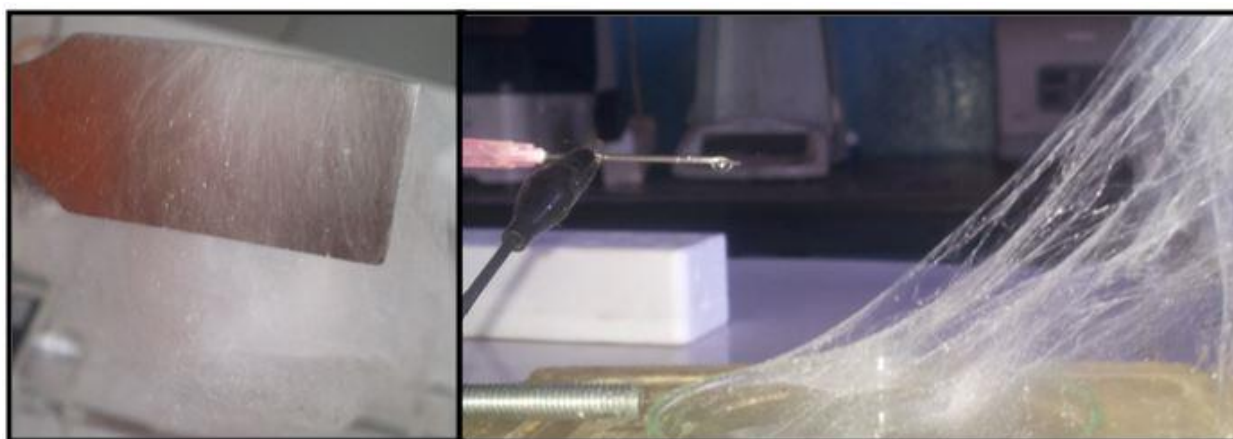


Figure 4-8: PAN nanofibres at low PAN concentration

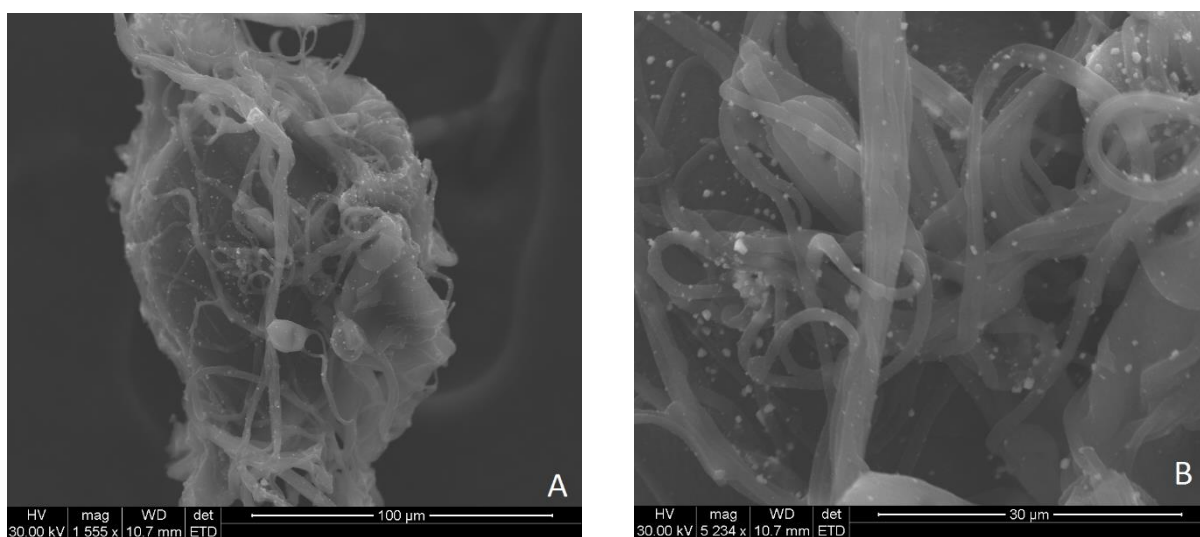


Figure 4-9: (a) Non uniform PAN nanofibres (b) Clumped PAN nanofibres at 5234 mag

When concentrations were increased from 8 wt. % to 12 wt. % smooth and uniform PAN nanofibres were observed as illustrated in Figure 4-10 (a). When the concentration was increased beyond 12% to 16% PAN nanofibres would be discontinuous as well as containing a poor surface morphology observed in Figure 4-10 (b). Based on the above observation, it was concluded that 8 wt. % would be selected and used for all spinning of nanofibres.

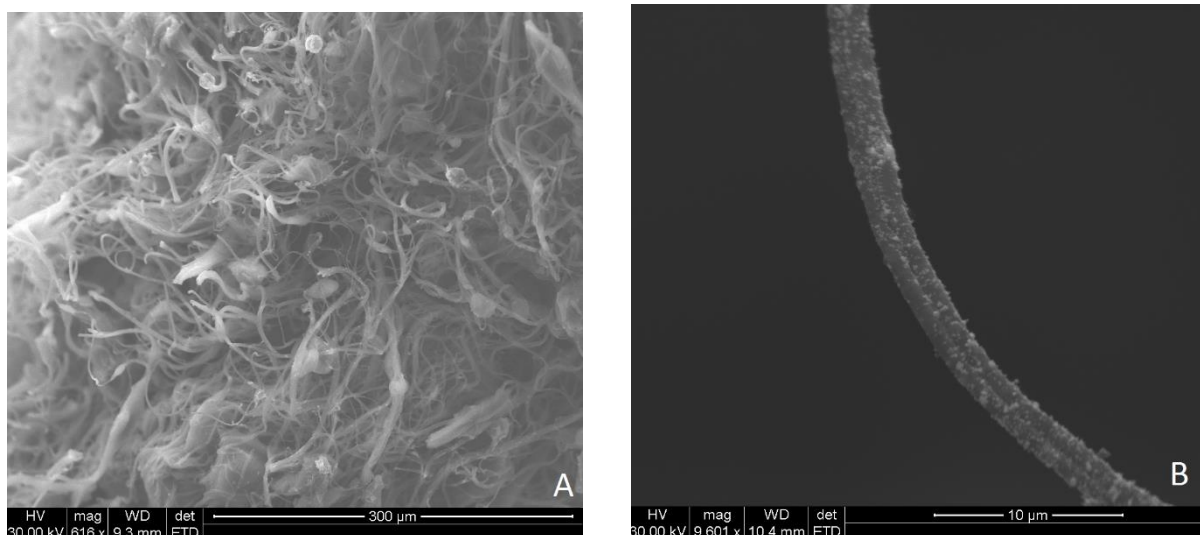


Figure 4-10: (a) Smooth PAN nanofibres at higher conc. (b) Individual PAN nanofibre

4.2.2 Operating Parameters

The operating parameters such as flow rate and electric field strength were investigated in the experimental phase of the electrospinning set-up. This assisted in determining the optimum parameters to produce smooth and continuous nanofibres. The flow rate was controlled by the pump and the electric field strength was controlled by the HV power supply. They were altered once the appropriate needle diameter and the needle-to-collector distance was determined. To locate the ideal collector needle distance as well as the appropriate capillary, trial and error methods were used when testing the self-designed syringe pump and foil seen in Figure 3-1.

A fixed distance of 15cm, a 17G needle size and a 13-15kV voltage was finally selected based on previous research and experimentation. This was tested using the electrospinning parameters used in Jones *et al* [53]. This distance and needle size provided the most uniform nanofibres. Scanning electron imaging was carried out for individual nanofibres to determine the quality and uniformity of the nanofibres. These samples were investigated using an *FEI Quanta 400 FEG*. Individual PAN nanofibre strands in Figures 4-11 (A) and 4-11 (B) have visual measured diameters ranging in the nanoscale. The consistency of the nanofibre diameter can be seen in Figure 4-11 (B). A measurement of 420.8nm and 420.9nm was observed. This shows an even distribution of fibre diameter. This was achievable because the collector distance was fixed at 15cm and an 8 wt. % PAN concentration was selected for the used voltage. This corresponded well with the 100-500nm required nanofibre diameter.

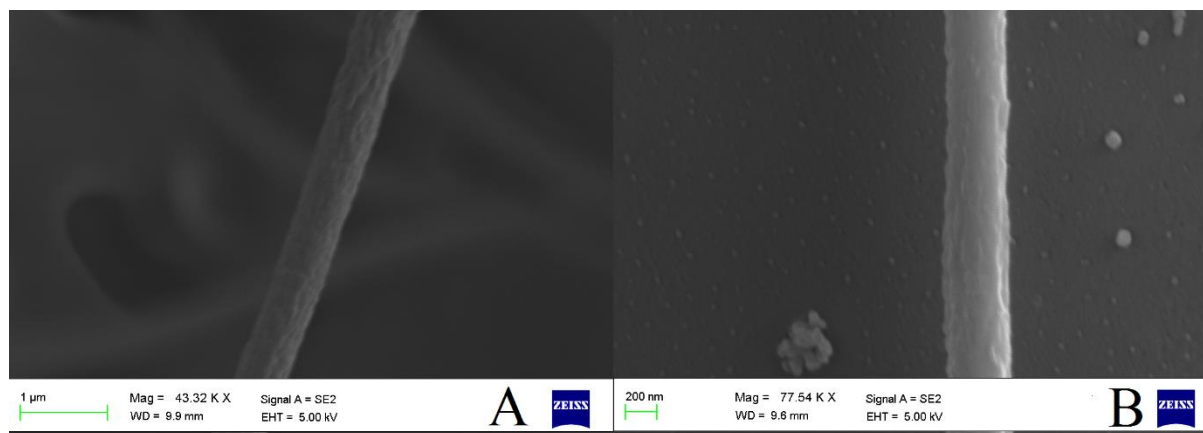


Figure 4-11: SEM images of individual PAN nanofibres (a) 551.1 nm diameter (b) 420nm diameter

Flow rates were tested ranging between 0.5ml/hr and 5ml/hr. This was done to determine the ideal flow rate for smooth uniform fibres. It was observed that at low flow rates the PAN/DMF solution would harden at the tips and within the tubing. A 1-2ml/hr flow rate was observed to be the model flow rate to produce nanofibres. This flow rate allowed the Taylor cone to form without wasting PAN solution or drying of the PAN droplet at the needle tip. Higher flow rates above 2ml/hr would produce beaded and wet nanofibres. This was due to a short drying time as well as low stretching forces. Pulsing is when the PAN solution is pulled back and forth at the needle tip and was seen when flow rates were increased.

Reduction of beading was seen when the collector distance and voltage were increased, however, a higher voltage led to a larger nanofibre diameter and PAN nanofibres were seen to have variable thicknesses as well as orientation. Figure 4-12 is an SEM image of electrospun PAN nanofibres. It was observed that at a low distance (5-10cm) between needle tip and collector, wet merged nano-fibrous moulded mats would form (Figure 4-12 (A)). Figure 4-12 (B) shows randomly orientated electrospun PAN nanofibres at 194X magnification. Nanofibres were observed to have uniform thickness and an even distribution with an 8 wt. % PAN concentration, 13kV, 15cm collector distance and a 1ml/hr flow rate. It was decided that these operating parameters would be used.

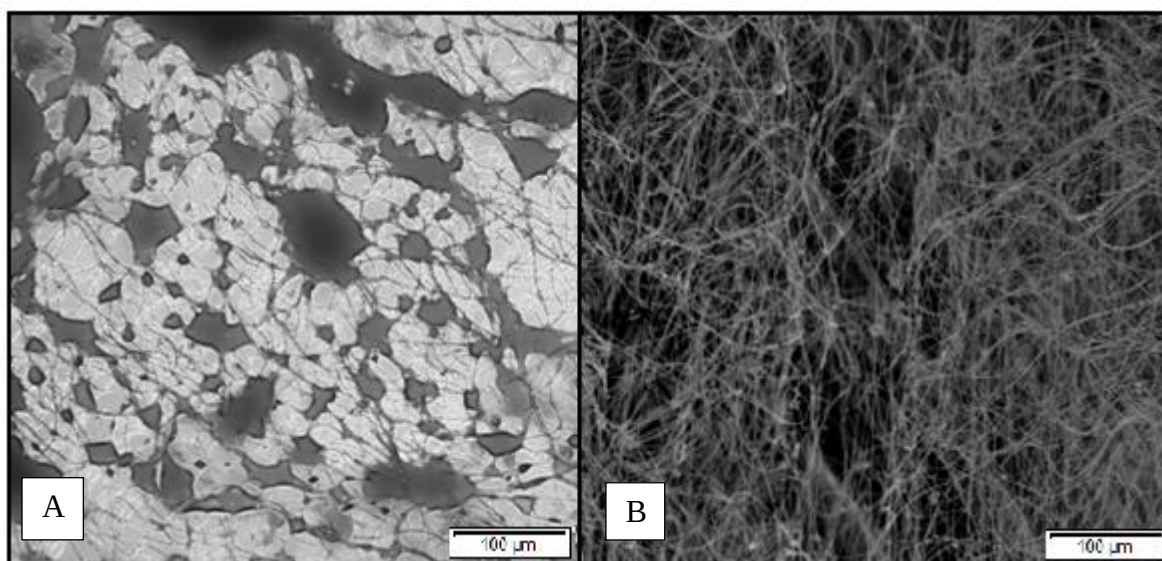


Figure 4-12: SEM Images of electrospun PAN (a) Beading (b) Uniform

4.2.3 Experimental Matrix

The operating parameters as well as the solution parameters are two major influences on the electrospinning process. They are however dependent on each other and both are needed to produce nanofibres. An experimental matrix was created in order to understand the relationship between the solution parameters and the operating parameters. As mentioned above the three main parameters that play a role in the production of electrospun nanofibres are the voltage, the distance between the electrodes (collector to needle) and the concentration of the solution being electrospun. The independent variables in this research were selected and used as the variables that were kept constant. This consisted of the needle diameter, syringes, collector design and the flow rate. The experimental matrix was designed as a 3D cube and can be seen in figure 4-13

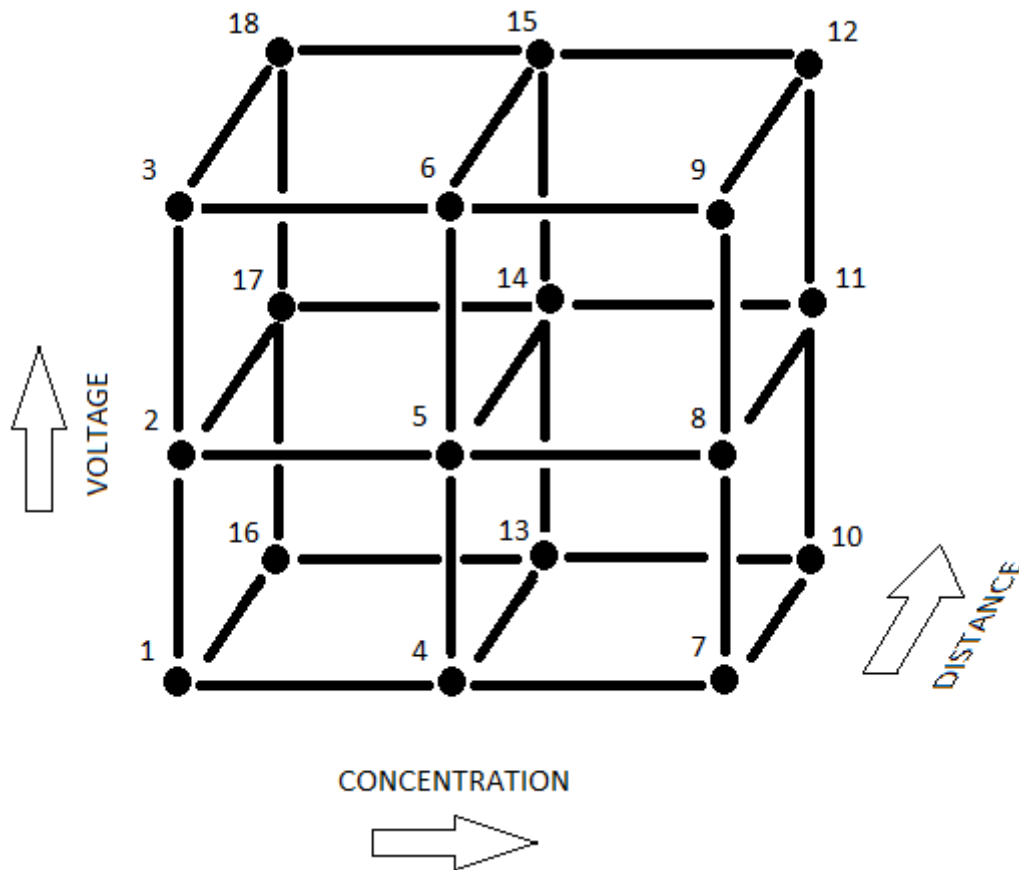


Figure 4-13: Experimental matrix of electrospinning parameters

The testing of the parameters that followed the experimental cube shown in Figure 4-13 was initiated by varying the parameters independently. The distance between the collector and needle was kept constant while the voltage was varied between 10kV and 15kV. Thereafter the distance between the collector and needle was varied between 15cm to 20cm while keeping the voltage at a constant value. Three PAN concentrations were tested; 6%, 8% and 10%. The concentrations were varied while keeping the voltage and collector distance constant. The results and findings are presented in Table 4-1.

Table 4-1: Observations and results of electrospinning experimental matrix

Experiment	PAN Conc. (%)	Applied Voltage (kV)	Distance (cm)	Comment
1	6	10	15	Beaded and broken fibres formed, distance was too far and surface charge was too large to maintain any consistency.
2	6	15	15	Beaded fibres formed, surface charge was high and caused irregular fibre morphology on collection of fibres.
3	6	20	15	No fibres formed, surface charge was too high which caused excessive dripping of solution at needle tips.
4	8	10	15	Broken fibres formed, surface charge was not high enough to form continuous collection.
5	8	15	15	Good fibres formed, Taylor cone was formed and showed consistent shape.
6	8	20	15	Good fibres formed, Taylor cone was formed and showed fairly consistent shape. Intermittent dripping occurrences.
7	10	10	15	Fairly good fibres formed, Taylor cone shape was consistent but was distorted and angled upwards from the droplets.
8	10	15	15	Fairly good fibres formed, some beading was observed but for the most part continuous fibres were formed.
9	10	20	15	Inconsistent fibres formed, the Taylor cone shape changed throughout spinning.
10	10	10	20	No fibres formed, surface charge was not sufficient to overcome surface tension.
11	10	15	20	Beaded and broken fibres formed, surface charge was barely able to overcome surface tension.
12	10	20	20	Fairly good fibres formed, some beading was observed but for the most part continuous fibres were formed.
13	8	10	20	Good fibres formed, Taylor cone was formed and showed fairly consistent shape. Intermittent dripping occurrences.
14	8	15	20	Good fibres formed, Taylor cone was formed and showed consistent shape. However, collection area was too large and difficult to control at this distance.
15	8	20	20	Beaded fibres formed, collection area was haphazard and difficult to control
16	6	10	20	No fibres formed, distance was too far away which meant that the fibres that did form never reached the collector.
17	6	15	20	No fibres formed, surface charge was too high and distance was too far away which caused spraying of solution.
18	6	20	20	No fibres formed, surface charge was too high and distance was too far away which caused spraying of solution.

4.3 Development of CNF-doped PAN nanofibres

4.3.1 Conversion of PAN nanofibres to CNFs

When converting PAN nanofibres to CNFs, the nanofibres needed to go through a process of carbonization. In order for nanofibres to be carbonized they need to be under extremely high temperatures (800°C-1200°C) that can only be reached in a furnace. Various furnaces were tested to determine the most appropriate and efficient manner of carbonizing PAN nanofibres. The capabilities of a variety of furnaces for the heat treatments of the PAN nanofibres were tested. This was carried out on three different types of furnaces; a muffle furnace, a box furnace and a tube furnace.

A muffle furnace (Figure 4-14 (B)) was tested and proved to be ineffective in producing CNFs. The PAN polymer reached stabilisation temperatures, however above 300°C during the carbonization phase, the nitrogen was observed to have leaked and therefore resulted in the presence of air inside the chamber. The presence of air increases the oxidation rate and therefore burns away the PAN nanofibres. The flow rate and the temperature were accurately controllable but the leakages were caused by the lack of a seal from the furnace door as well as the butterfly valve attachment for the nitrogen outlet.

The box furnace in Figure 4-14 (A), with a steel retort for environmental control, proved better at carbonization than the muffle furnace. However, due to a lack of accurate temperature control and inaccurate nitrogen flow rate control, the PAN nanofibre mats showed major cracking and wrinkling caused by the shrinkage of macro fibres.

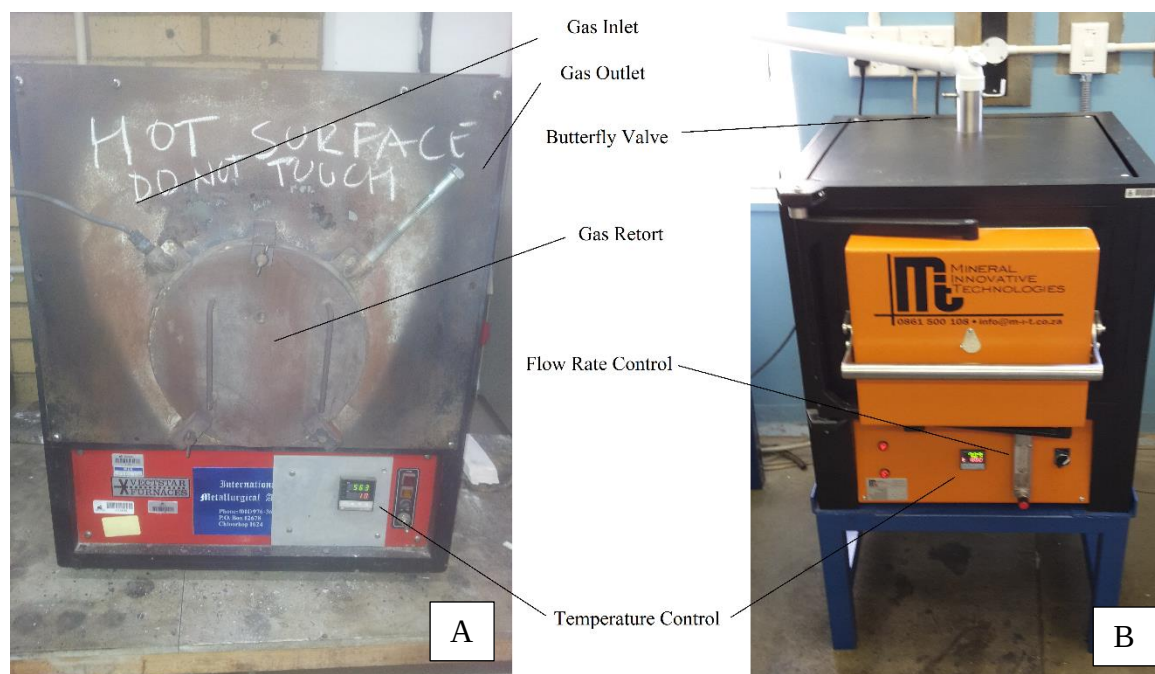


Figure 4-14: (A) Box furnace and (B) Muffle furnace

The tube furnace was found to be the most suitable for heat treatments of the PAN polymer, as the nitrogen environment, temperature and flow rate could be accurately controlled and sealed. Also the heating zone was found to be more uniform and as such, provided for more consistent diameter fibres. A major disadvantage of using the tube furnace, however, was the limited sample size of the ceramic boat. In order to make a substantial amount of ECNFs (electrospun carbon nanofibres), many runs were performed and the ECNFs were eventually used as a crushed fibre than a carbonized sheet as initially desired.

4.3.2 Carbonization Methodology

Carbonizing of electrospun PAN nanofibres was carried out using the Tube furnace displayed in Figure 4-15 A. Electrospun PAN nanofibres were collected in a vial as compressed clumps and placed into a ceramic boat using laboratory tongs (Figure 4-14 C). The boat was placed inside the tube and both the gas inlet and the outlet were sealed. The temperature control in Figure 4-15 B was set to 270°C at a ramping rate of 10°C per minute. The oxidizing temperature was then held at 270°C for approximately an hour before turning the nitrogen on. The carbonizing temperature was set at 800°C and was also held for an hour. The process took approximately 140 mins, however due to cooling time was found to be over 8 hours. The nitrogen was shut off once the temperature had dropped below ambient temperature.



Figure 4-15: (a) - Tube Furnace, (b) - Tube Furnace Temperature Control and (c) - Sample boat, Tongs and PAN nanofibre

Figure 4-16 shows 1g of the final ECNF produced in the tube furnace, after crushing with a pestle and mortar, which resulted in powdered texture ECNFs. The diameter and quality of the ECNF can be seen in Figure 4-16.

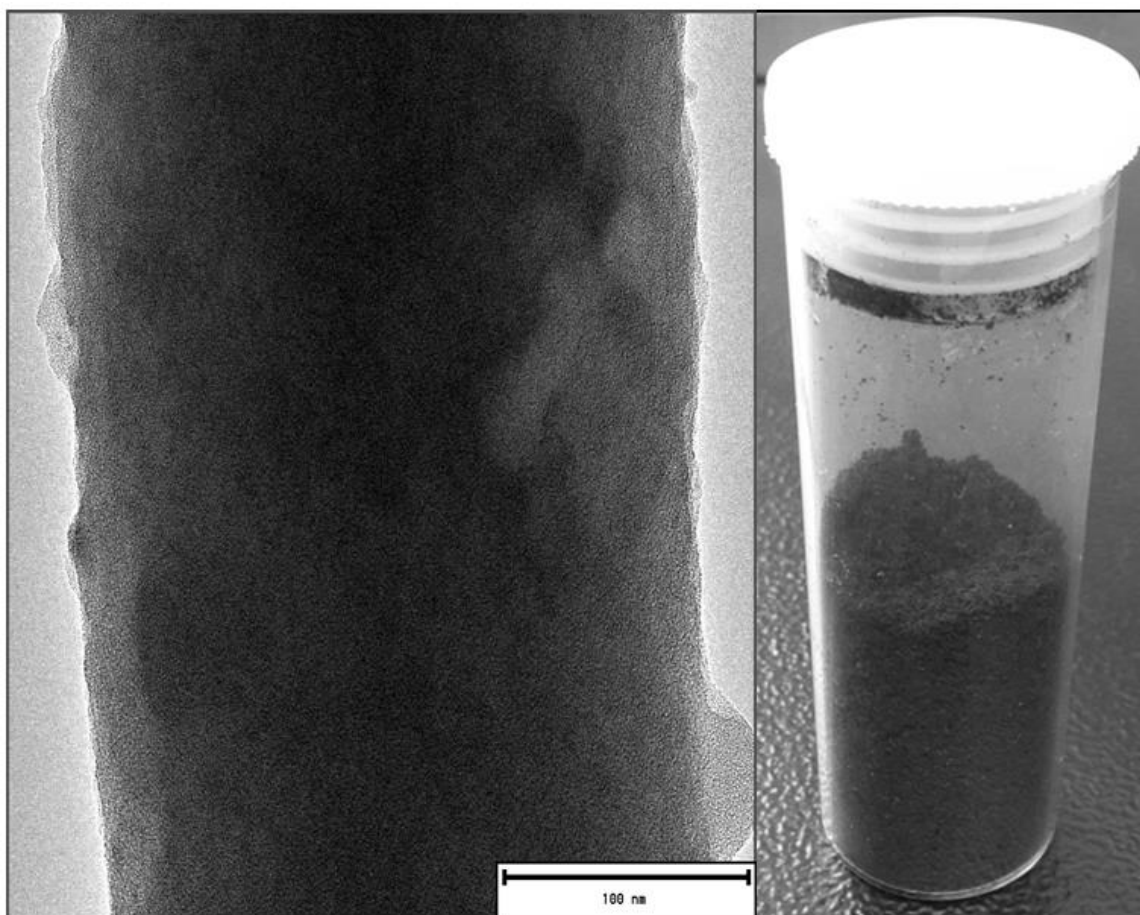


Figure 4-16: TEM image of the final ECNFs as produced by electrospinning and carbonisation of the PAN nanofibres.

Hybrid composites were fabricated using the same hand lay-up technique to that of the aramid fibre reinforced composite. The slight difference is that every nanomat coated aramid layer was placed with the electrospun nanomat surface facing downwards. The initial mat was not coated and the aramid layers are placed in order as seen in Figure 3-7. This was prepared in order to roll and immerse the epoxy resin without damaging or shifting the nanofibre sheets. Nanofibre volume fibre calculations were used in adding the nanomats.

4.4 Characterization of PAN and CNF Doped PAN Nanofibres

4.4.1 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried out on the PAN nanofibres as well as the CNFs. Weight reduction versus temperature was determined and a TG graph was plotted in Figure 4-17. A multi-stage decomposition with a resolved reaction is observed with the PAN TG analysis. This indicates that PAN has no thermal stability. PAN weight reduction started occurring at 130°C. This then led to a 30% reduction in weight between 300°C and 350°C. A steady decrease in weight percentage is then observed after 350°C to approximately 650°C. With this result, it can be concluded that the stabilisation temperature should not exceed 350°C, else there will be a loss of PAN nanofibres. This can safely justify the use of a 270°C stabilisation temperature which was used during oxidation.

The CNFs showed a more stable decline in weight % as temperature was increased. This indicates a good thermal stability. The CNFs indicated a steady weight percentage decrease between 0 and 500°C. A large reduction in weight percentage is indicated and a total loss at 600°C or more.

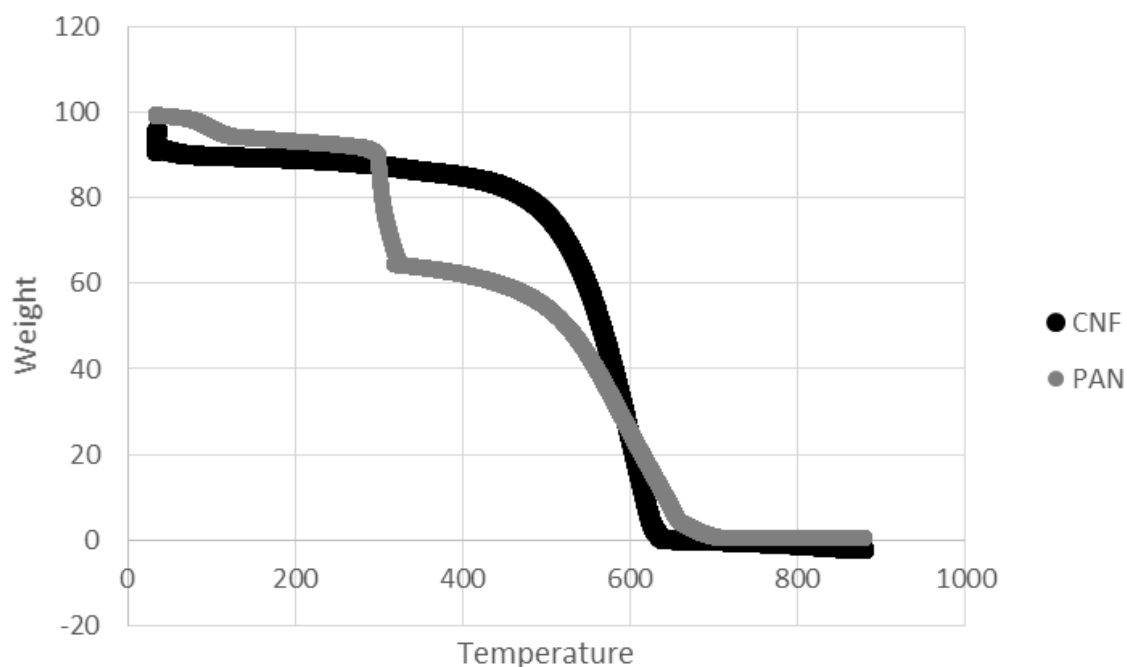


Figure 4-17: TGA of PAN nanofibre

4.4.2 Differential Scanning Calorimetry

The DSC (Differential Scanning Calorimetry) graph in Figure 4-18 provides an in depth understanding of the oxidative exothermic stabilisation process. The DSC shows a peak at 300°C for PAN nanofibres. This correlates with the TG analysis in terms of the stabilisation temperature and provides an accurate oxidation parameter. The area under the peak which represents the heat capacity of the sample, can provide the enthalpy. The heat flow for PAN was found to be 22W/g. Carbonisation effects are also observed when comparing the CNF values in the DSC analysis. This 600°C spike is a shift in the required temperature for crystallisation. It was observed that 8W/g was determined as the heat flow value for the CNF crystallization temperature.

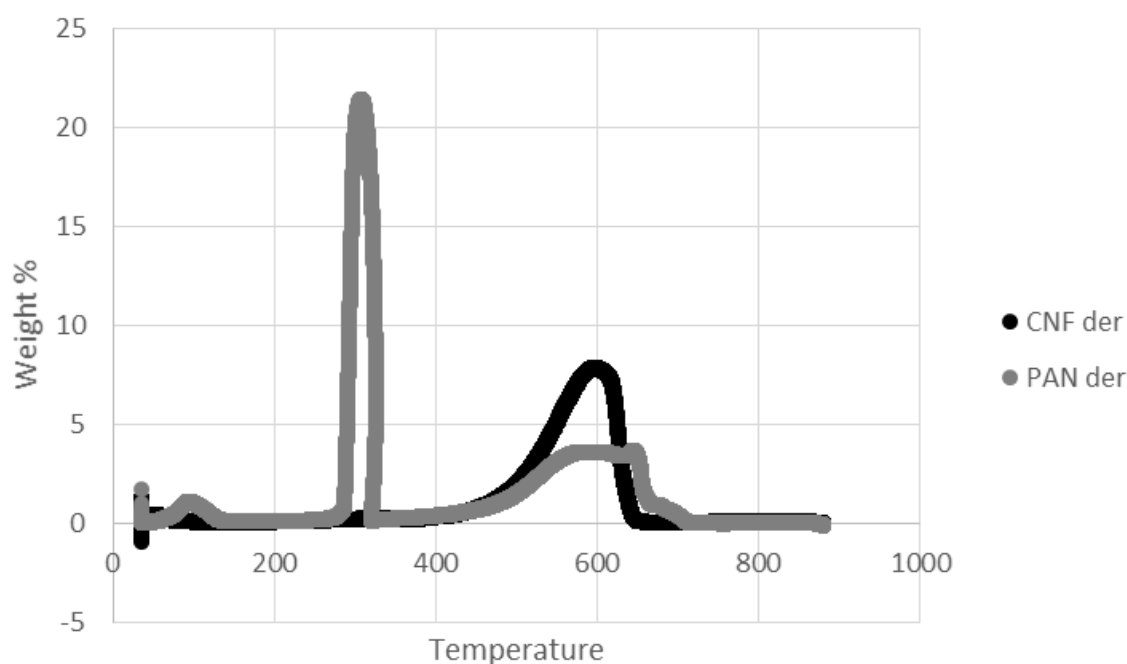


Figure 4-18 DSC analysis of electrospun nanofibres

4.4.3 Raman Spectroscopy

Raman spectroscopy was carried out on the CNF samples only. Carbonised samples were analysed to determine the quality of the carbon nanostructures. In Figure 4-19 the D band peak occurs at an intensity of 1300 au and a Raman shift of 1300 cm^{-1} . The G band also has an approximate 1300 au argon intensity at a shift of 1600 cm^{-1} . The Raman spectrograph of the CNF sample has a G/D band ratio (intensity ratio) of approximately 1:1 which indicates a disordered graphitic and crystalline structure. The D band represents the number of disordered atoms and the G band represents the number of ordered atoms [50]. This gives an idea of the localised defects within the carbon structure. A slightly higher G band means that there are more ordered atoms giving way to the possibility of having less defects and a highly graphitized structure.

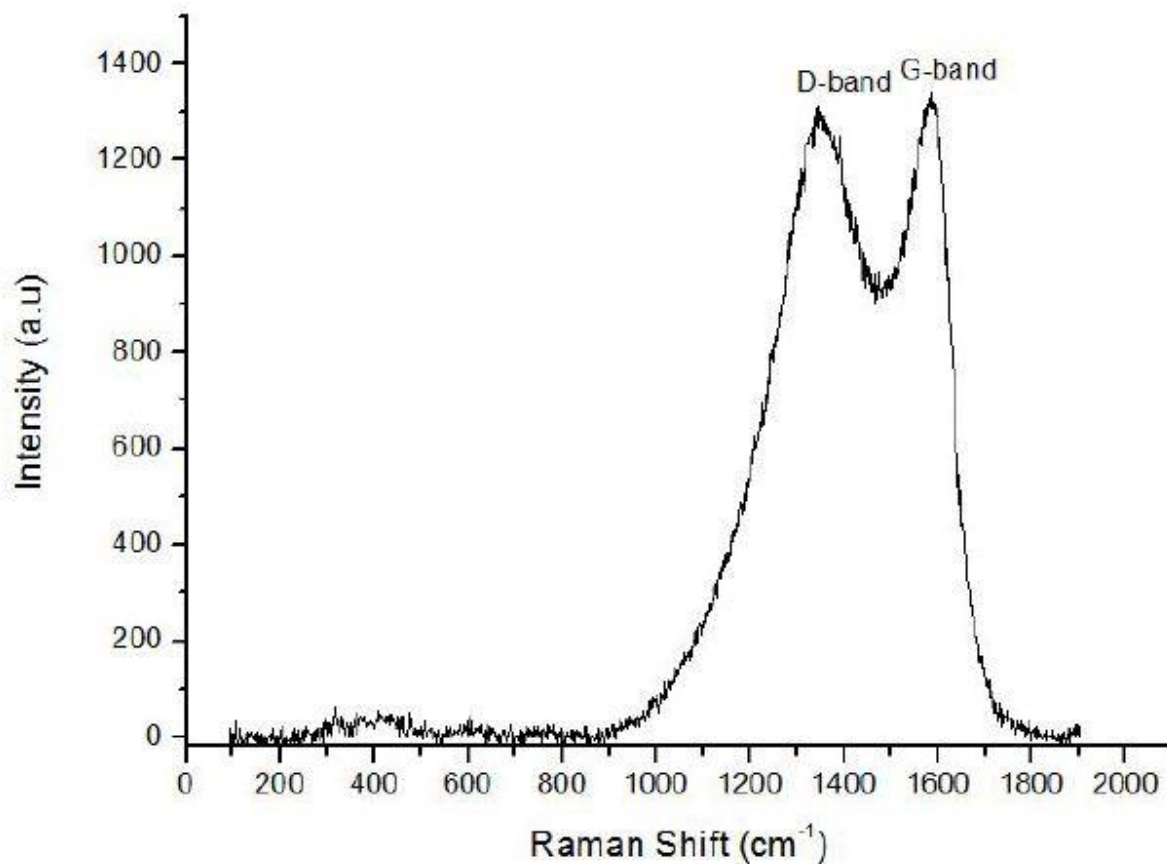


Figure 4-19 Raman Spectrograph of ECNF

4.4.4 Energy-Dispersive X-ray

EDX (Energy-Dispersive X-ray) spectroscopy was determined using the *FEI Quanta 400 FEG* SEM Instrument. EDX assisted in determining the quantifiable carbon content at the carbonised temperature used. A carbonisation temperature of 800°C was used to carbonize PAN nanofibres to convert them into CNFs. Figure 4-20 (A) and (C) indicate an approximate 83% carbon weight percentage and an atomic weight of 89.9%. This indicates a successful carbonisation procedure while maintaining semi-amorphous structure with partial crystallinity shown in Figure 4-20 (B).

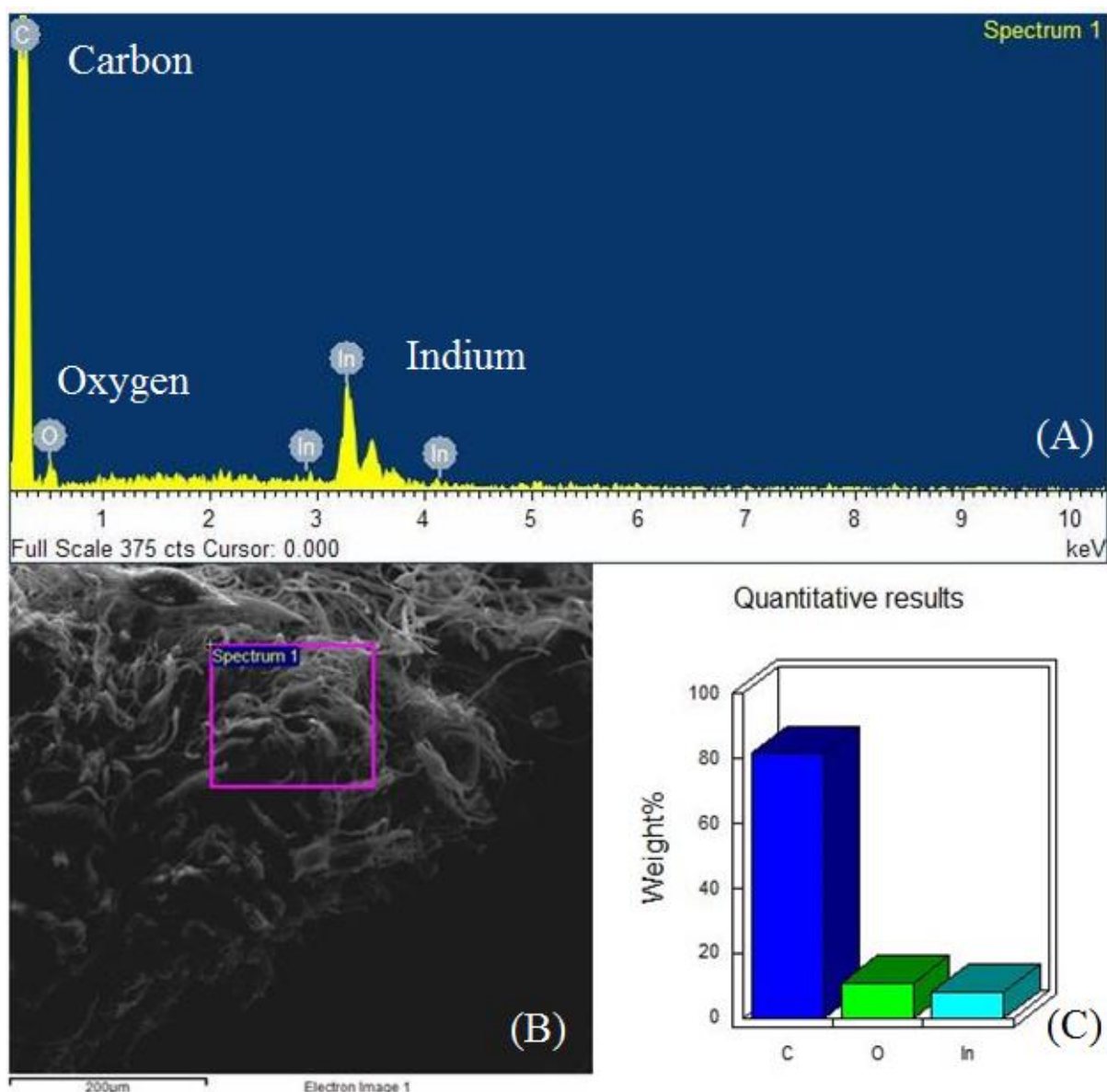


Figure 4-20 EDX analyses of ECNF (a) Chemical composition (b) SEM image and (c) Weight % of composition

4.4.5 TEM

Transmission electron imaging was carried out on the CNF doped PAN. They were placed in an epoxy resin mould and sheaved to have single layers for use of the microscope. The instrument used to produce these samples was the Reichert Ultra microtome. Samples ranged from 60nm to 80nm. Figure 4-21 is a TEM image of CNF doped PAN nanofibres embedded in epoxy resin

The dark patches in Figure 4-21 (a) indicate carbon based material and observing the size and occurrence it can be seen that CNFs were orientated at even spacing within the PAN nanofibre. In Figure 4-21 (b) a single nanofibre is observed and CNFs are positioned within the fibre. This indicates doping of the CNF within the PAN nanofibre.

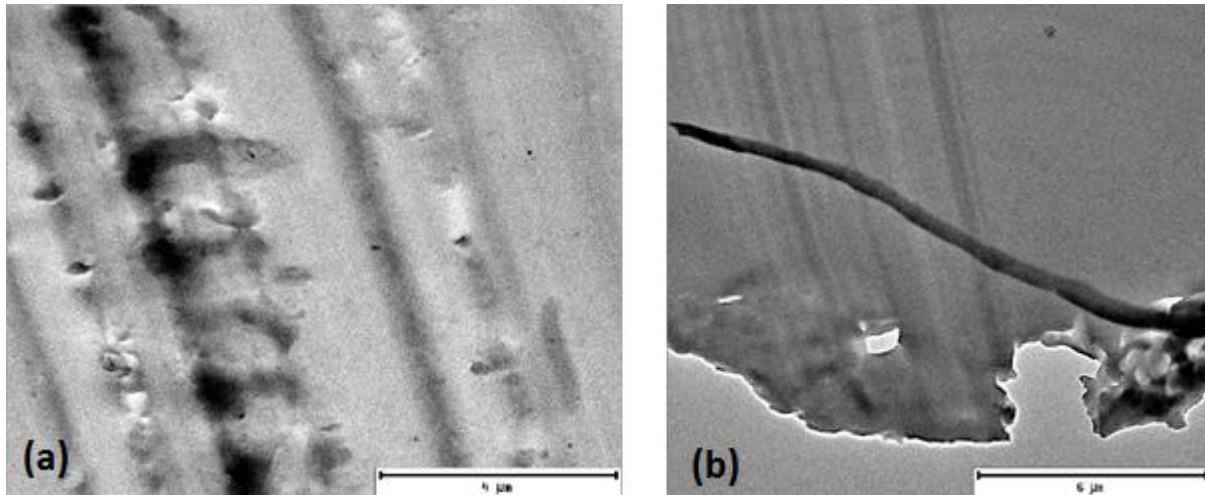


Figure 4-21: (a) Cross section of CNF embedded PAN (b) Individual CNF doped PAN

The fibre diameter can be observed in Figure 4-21 (a) to be that of a nano scale. The dark internal continuous fibre is an indication of the CNF. The transparent outline is an indication of the PAN nanofibre as the outer core of the CNF. This can be seen in Figure 4-21 (b). Figure 4-21 (a) has a cross sectional view of the PAN doped carbon nanofibres and Figure 4-22 (a) and (b) indicate the plane view of the individual nanofibres.

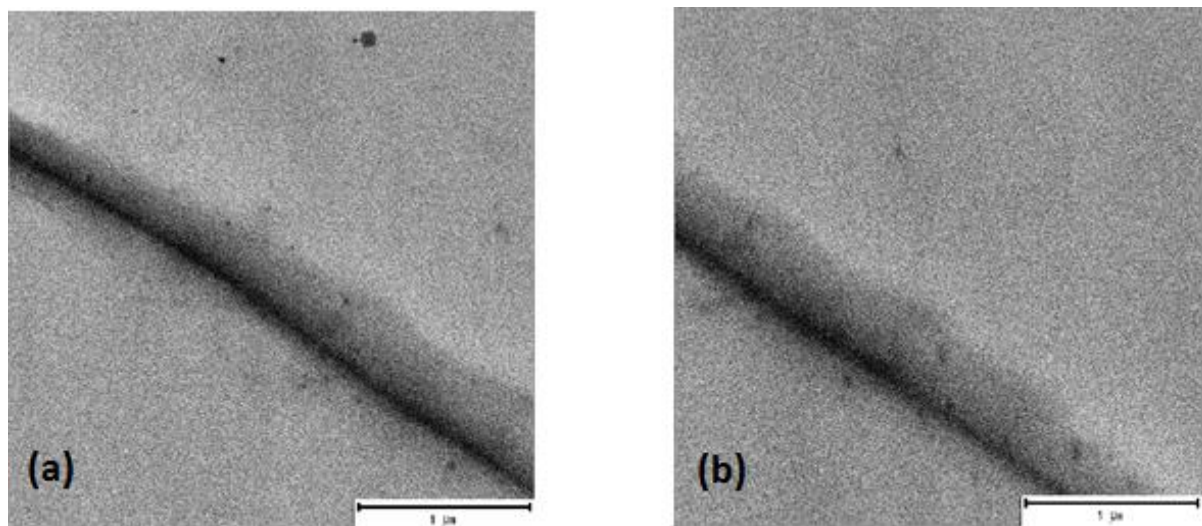


Figure 4-22: (a) Individual CNF doped PAN (b) Continuation of CNF doped PAN nanofibre

4.5 Conclusion

The electrospinning process used was determined to be sufficient for the production of PAN (polyacrylonitrile), ECNFs (electrospun carbon nanofibres) and ECNF doped PAN nanomats for coating aramid fibre sheets. The nanofibres; both PAN and ECNF, were found to have a diameter range between 200nm and 800nm. The PAN had shown good thermal stability for the carbonization process and the ECNFs were found to be of good quality due to very little disorder. TEM (transmission electron microscope) was used to determine if the ECNFs had been doped successfully and results indicated that ECNFs had randomly been dispersed within the PAN but signs of discontinuous spacing had been observed. The next chapter discusses the results of the mechanical tests.

5 Results and Discussion

This chapter discusses the experimental results associated with Aramid, PAN nanomats and CNF doped PAN nanomats strengthened hybrid composites. At first, the aramid composite specimens with the volume fraction of 10%, 20 % and 30 % were mechanically characterized. From the testing results, the optimum aramid volume fraction was obtained. Then the PAN nanomat and the CNF doped PAN (CNF-DP) nanomat strengthened multiscale hybrid composites were fabricated using the optimum aramid fibre volume fraction (30%). These hybrid composites specimens were then tested to understand the effect PAN and CNF doped PAN nanomats on the structural properties of the aramid composites. The morphological results were also analysed to discuss the effect of the nanomats on the hybrid composite failure mechanism.

5.1 Aramid Fibre Composites

5.1.1 Tensile Properties

Tensile properties of aramid fibre composites were measured and analysed. Three sets of samples of neat epoxy with 10%, 20% and 30% volume fractions, were tested and plotted in Figure 5-1, which shows the tensile strength and the elastic modulus. The tensile strength was observed to have increased linearly and evened out when reaching a 30% vol. aramid fibre reinforcement. There was an 8.4% increase in tensile stress from 20% vol. to 30% vol. aramid fibre reinforcement. The maximum tensile strength was measured to be 301.6MPa at 30% vol. aramid fibre reinforcement and the maximum elastic modulus was measured to be 66.5GPa at a 20% vol. aramid fibre reinforcement.

The elastic modulus increased as the volume fraction increased, which indicated an increase in stiffness. However, there was a decrease in elastic modulus from the 20% vol. to 30% vol. aramid fibre reinforcement. This result is not uncommon and research has shown an increase in volume fraction can reduce the elastic modulus. *Tarantili et al.* [58] found that unidirectional aramid reinforced epoxy had shown a decrease in elastic modulus when increasing a 35% volume fraction of aramid reinforcement to a 38% volume fraction of aramid reinforcement. This is an indication of a reduction in stiffness.

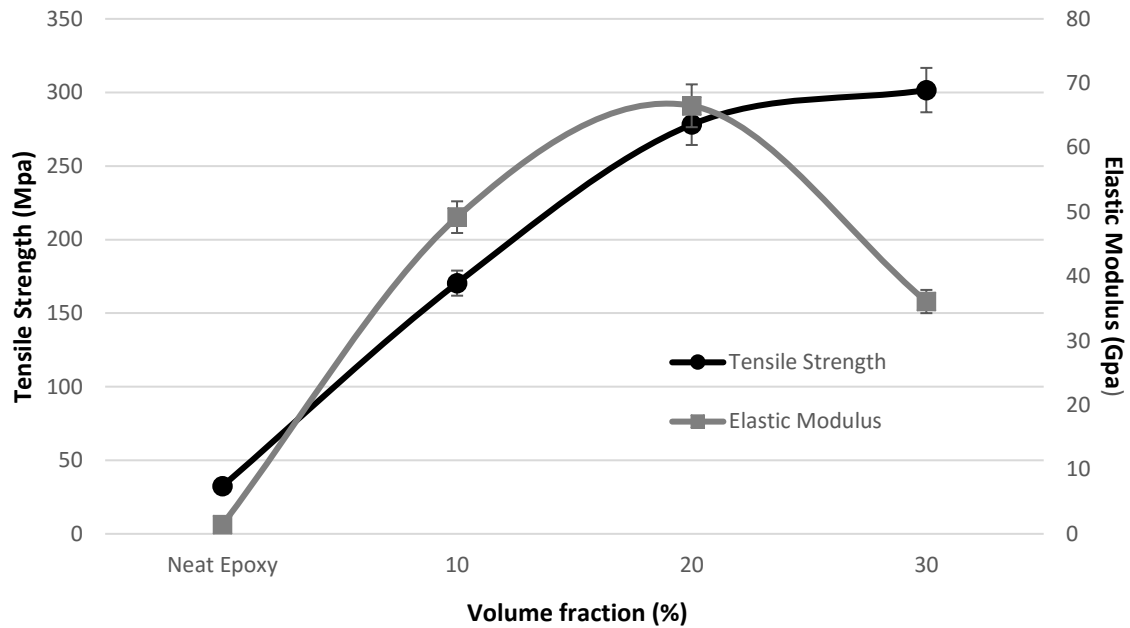


Figure 5-1: Tensile properties of aramid fibre reinforced composites

The fabricating method also played a huge role in the quality of fibre reinforced composites. One of the major problems with the hand lay-up method is the high possibility of resin coating inconsistency. Hand lay-up was done manually and therefore human error was likely to cause a build-up of resin within the composite. Figure 5-2 is an SEM image of a 30% vol. aramid reinforced failed tensile specimen. It can be seen on the surface of the individual aramid fibre the inconsistency of the epoxy. The resin build up created a weak zone when the composite experienced tensile loads. These tensile loads often result in fibre pull out, and when a larger volume of epoxy is built up in one area of the fibre, it creates a lower volume in another area on the surface of the fibre. This then leads to premature failure.

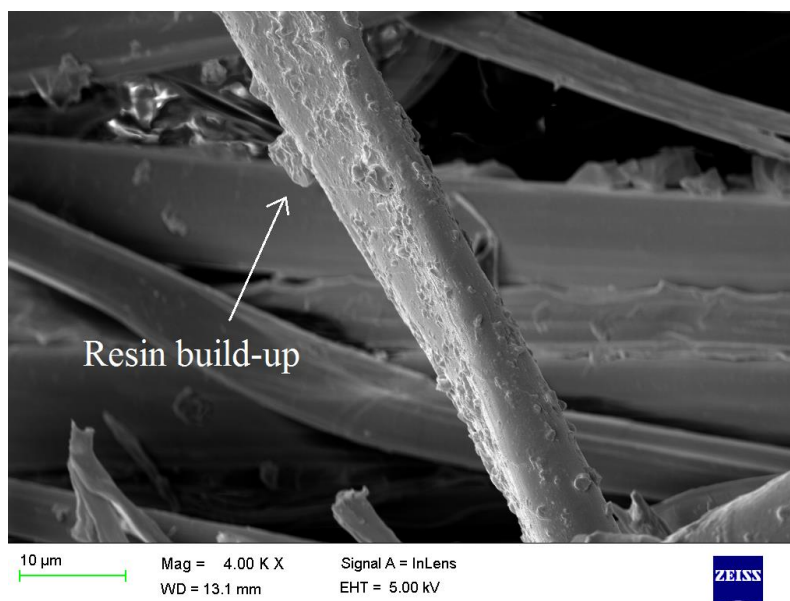


Figure 5-2: SEM image of a 30% aramid fibre reinforced composite

By observing the reduction in elasticity and stabilisation in strength, it would be justifiable to select 20% vol. aramid reinforcement as the optimum volume fraction for the control specimen, however, the results of the flexural test and the impact test were also taken into consideration to determine the most suitable volume fraction of aramid fibre reinforcement.

5.1.2 Flexural properties

Flexural tests were carried out on 10%, 20% and 30% volume fraction of aramid reinforced epoxy. Flexural properties were measured and analysed. The results of the flexural tests are plotted in Figure 5-3. The flexural modulus and the flexural strength, both followed a similar pattern demonstrating an increase, when the volume fraction of aramid fibre was increased. This assisted in justifying an optimum 30% vol. of aramid reinforcements for flexural properties. Higher volume fractions were not tested due to the degradation of the tensile properties observed in section 5.1.1 and previous research conducted by *Khalid* [56]. The maximum flexural strength and the flexural modulus was measured to be 174MPa and 1.96GPa respectively.

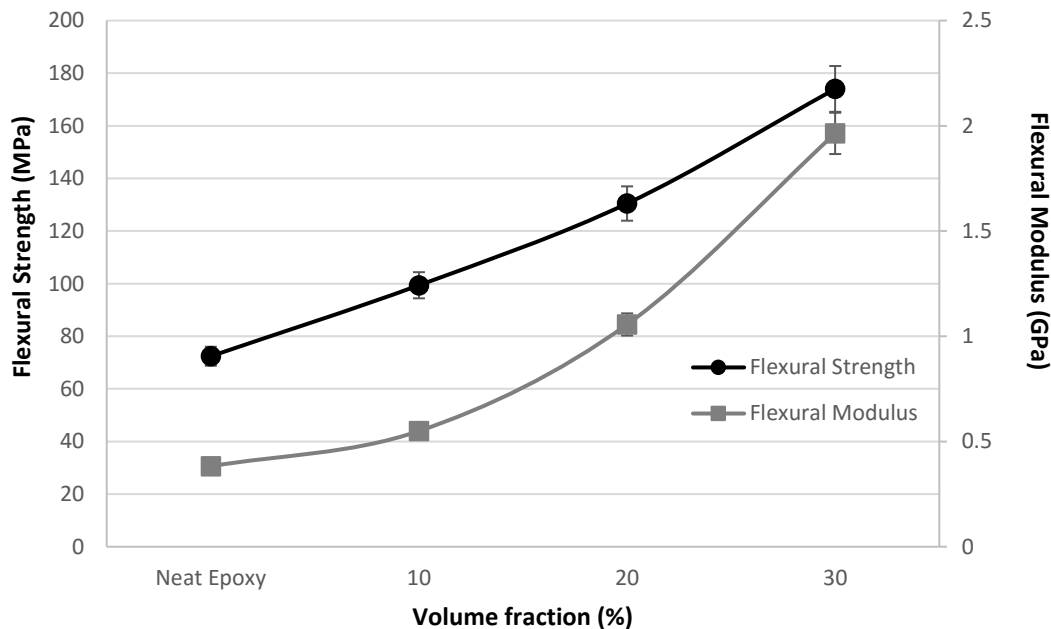


Figure 5-3: Flexural properties of aramid fibre reinforced composites

5.1.3 Impact Properties

The impact resistance of aramid fibre composites was determined. Figure 5-5 is a graph indicating the impact resistance of 10%, 20% and 30% volume fractions of aramid fibre reinforcements in epoxy. It was observed that neat epoxy has an impact resistance of 2.8 J/m² and the 20% vol. aramid reinforcement has an impact resistance of 42.8 J/m². The 30% vol. aramid reinforced composite has an impact resistance of 49.4 J/m², which is a 15.3% increase in impact resistance compared to the 20% vol. Fibre pull out and fibre breakage was observed in Figure 5-4. Fibre pull out is a good indication of load transfer from matrix to fibre.

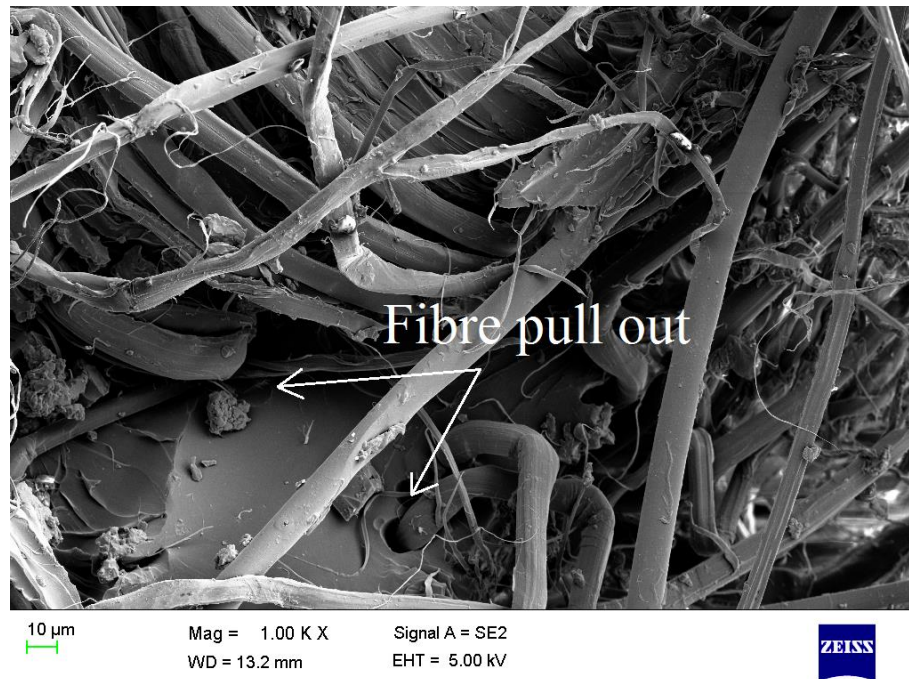


Figure 5-4: SEM image of 30% vol. aramid fibre composite

The tiny strands seen in Figure 5-4 are indications of fibre breakage. Fibre breakage was caused by the ability of the matrix to absorb the energy and transfer it to the aramid fibres.

This concludes that 30% vol. aramid fibre reinforcement was the optimum volume fraction for impact resistance. Higher volume fractions were not determined as the fabricating method allows a maximum thickness of 4mm for the testing samples. Previous research conducted by *Khalid* [56] also indicated a reduction in impact properties with higher volume fractions. Analysing the tensile, flexural and impact properties it was concluded that a 30% vol. aramid fibre reinforcement was used as the control specimen for the introduction of PAN and CNF doped PAN nanofibres as secondary reinforcements.

The minimum and maximum volume fraction for fibre reinforced composites, have previously been determined [54]. A very low volume fraction can create a very weak composite and a very high volume fraction can deteriorate the composite as the fibres become too close to each other. Another major factor that affects the volume fraction is the processing technique.

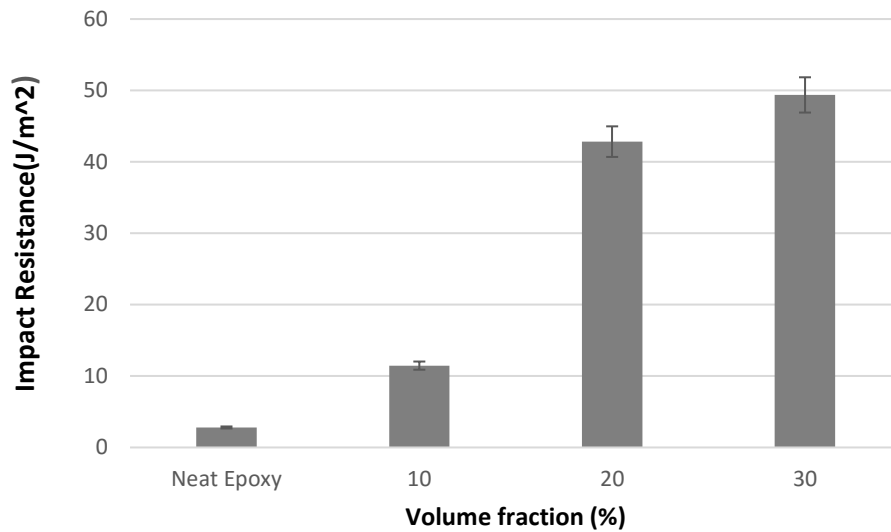


Figure 5-5: Impact properties of aramid fibre reinforced composites

The reasons behind the selection of the volume fraction for the control composite in this report are due to both the processing technique and previous studies. Three volume fractions were selected to provide evidence of optimal parameters for the selection of the control sample. Theoretically the assumption that all fibres have the same diameter and are perfectly parallel to each other, was concluded [55]. The theoretical maximum volume fraction is then determined by assuming that the packing of the fibres follows a hexagonal close packing arrangement seen in Figure 5-6.

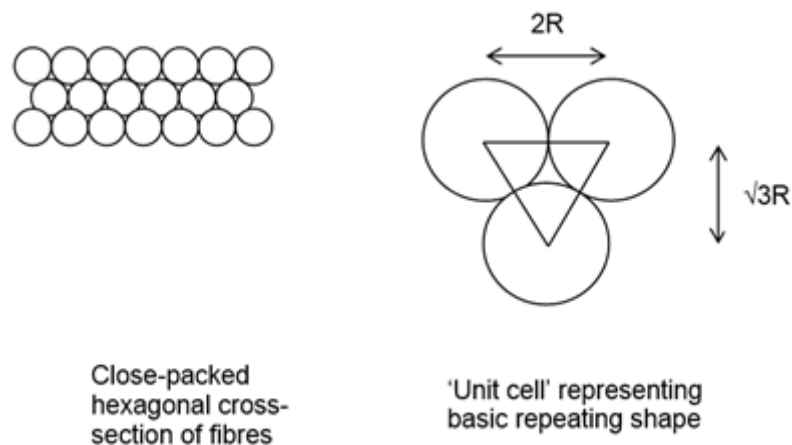


Figure 5-6: Fibre packing arrangement

As the alignment of the fibres was fixed, the volume fraction is the same as the ‘area fraction’. In the triangular unit cell in Figure 5-6, the total area occupied by fibre is equal to three 60° segments. The unit cell has area $\sqrt{3} R^2$, so that

$$V_f^{\max} = \frac{3 \times \pi R^2 / 6}{\sqrt{3} R^2} = \frac{\pi}{2\sqrt{3}} = 0.907 \approx 91\%$$

Such a high volume fraction is not practically possible. Even if such a high degree of fibre stacking was attainable, the fact that fibres are touching would cause an ineffective composite [55]. When fibres are arranged in a non-unidirectional system, like woven fibres, the orientation is proportionally out of plane. This then leads to a reduction in volume fraction as close packing is not achievable. Therefore the volume fractions selected for this study was based on table 5-1.

Table 5-1: Optimal volume fractions for polymer composites

Reinforcement form	Possible range of fibre volume fractions (%)	Typical value for fibre volume fraction (%)
unidirectional	40 – 60	50
woven	20 – 40	30
random mat	10 – 20	15

Previous studies have shown that a high volume fraction can result in a weaker composite. *Khalid* [55] determined the effect of temperature on high volume fraction aramid epoxy by determining the impact properties at various temperatures. It was found that an increase in volume fraction results in a decrease in impact energy regardless of the temperature [56]. Wear loss was determined by *Phitili et al.* [57] on both glass and aramid fibre composites and it was concluded that wear loss is affected by the polymer matrix than the reinforcement itself. A 40% vol. of aramid was used as a reinforcement for epoxy and it can be concluded that the volume fraction did not have an effect as the wear affected the epoxy only.

The processing method plays a role in the selection of the volume fraction. The mould used in this research for a hand lay-up only allowed a maximum thickness of 4mm which is the ASTM standard for tensile testing specimens. A higher volume fraction above 30% of aramid fibre would increase the thickness of the specimen and therefore 30% vol. aramid fibre (AFC) within epoxy resin was selected as the control sample.

5.2 PAN Nanofibre Reinforced Hybrid Composites

Hybridising composite materials with the use of nanofibres as secondary reinforcements has shown tremendous improvements in the mechanical and structural properties of polymer composite materials. Multi-scale hybrid composites are advantageous due to their ability to provide high strength with minimal increase in weight. The interlaminar region is an area that

is affected by the transfer of loads when a composite material experiences mechanical deformation. Strengthening the interlaminar region provides the composite an ability to withstand the transfer of load for a longer period without cracking, induced within the matrix rich zone. This can be advantageous as catastrophic failure can be prevented. PAN nanomats (nanofibre mats) placed in between the plies of conventional fibre reinforcements can assist in improving the interlaminar region. These nanomats act as bonding plies between the fibre and the matrix resulting in a stronger composite.

Continuous PAN nanomats were coated in between layers of aramid fibre sheets using electrospinning. Volume fractions of 0.1%, 0.2% and 0.5% PAN nanomats were tested. Various research on electrospun nanofibres have illustrated the use of nanofibres as secondary reinforcements in between plies. Table 5-2 shows research carried out that has covered secondary nanofibre reinforcement. *Molnar et al.* [59] did not exceed a 0.2% vol. PAN reinforcement and therefore it was decided in this research that the volume fraction of PAN nanomats would not exceed 0.5%.

Table 5-2: Previous Research on secondary nanofibre reinforcements

Research	Polymer nanofibre reinforcing material	Primary Composite	Optimum nanofibre volume fraction (%)
Zhang et al. [60]	Polyether ketone cardo (PEK-C)	Carbon fibre reinforced epoxy	0.4
Chen et al. [61]	Nylon 6	Poly(methyl methacrylate) PMMA	1.7
Neppalli et al. [62]	Nylon 6	Poly(e-caprolactone) (PCL)	2
Ozden et al. [63]	Poly(styrene-co-glycidylmethacrylate) P(S-co-GMA)	Araldite-epoxy	0.2
Molnar et al. [59]	PAN	Carbon fibre reinforced epoxy	0.2
Tian et al. [64]	Nylon 6	BIS-GMA/TEGDMA	1.5

The 30% volume fraction of aramid fibre reinforced composite was selected as the control specimen for the nanofibre reinforcement. Tensile, flexural and impact properties of PAN nanomat reinforced aramid hybrid composites were determined.

5.2.1 Tensile properties

The addition of PAN nanomats between layers of aramid fibre mats within epoxy indicated an increase in the tensile strength and an increase in elastic modulus. However, a 4.7% decrease in tensile strength was observed with the 0.1% PAN nanomat reinforcement compared to the 30% vol. (AFC) aramid fibre reinforced composite. This reduction in tensile strength is an indication of the effect of the low volume fraction of the nanofibre laminates when PAN nanomats are introduced. When low volume fractions of nanomats were introduced, the

distribution of the nanofibres were not consistent. This can be seen in Figure 5-7 where a low distribution of PAN nanofibres is observed. This created matrix rich zones (fractured epoxy) within the interlaminar region which resulted in a poor transfer of load. This caused the hybrid sample to fail prematurely. This is a result of the spaces created within the interlaminar regions between the PAN coated regions and non-coated regions. Stress concentration was created which led to weaker regions within the composite.

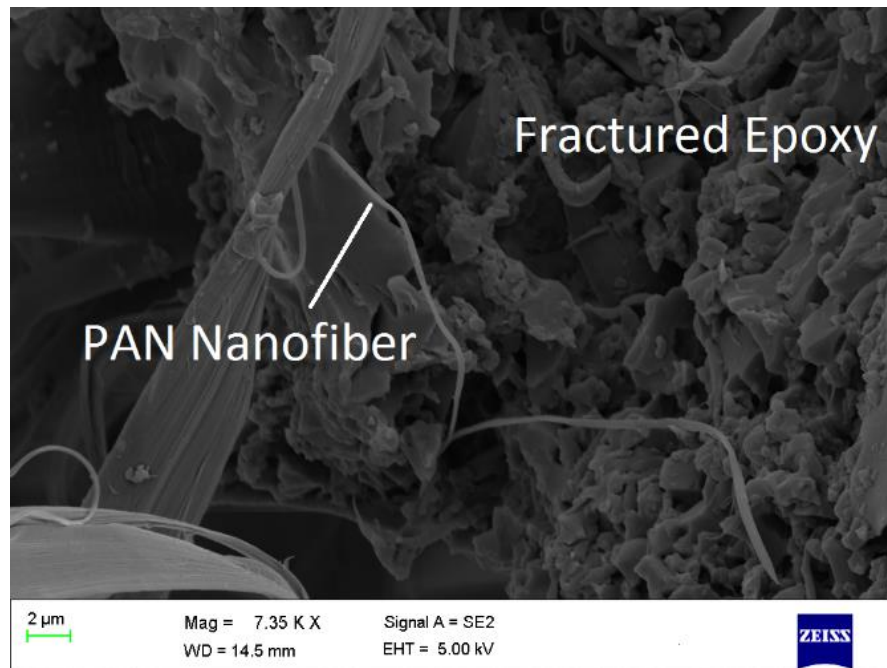


Figure 5-7: SEM image of a failed 0.1% PAN reinforced AFC

When 0.2% PAN nanofibre mats were added, the tensile strength of the PAN nanomat reinforced aramid hybrids was increased by 1.5% compared to the AFC. A 3% increase in tensile strength compared to the 30% AFC (Aramid fibre composite) occurred when 0.5% PAN nanomats were added. The 30% vol. AFC composite held a tensile strength of 301.6 MPa.

The elastic modulus of the AFC was measured to be 36.1 GPa. With an addition of the 0.2% PAN nanomat reinforcement, the elastic modulus increased by 140% deducing the ability of the PAN nanofibres to improve stiffness of the composite. The 0.1% PAN nanomat reinforcement also improved the elastic modulus of the hybrid specimen by 37%. The 0.5% vol. PAN nanomat inclusion indicated a 348% increase in elastic modulus. Figure 5-8 illustrates the noticeable improvement in tensile strength and an exponential increase in elastic modulus with a PAN nanomat addition.

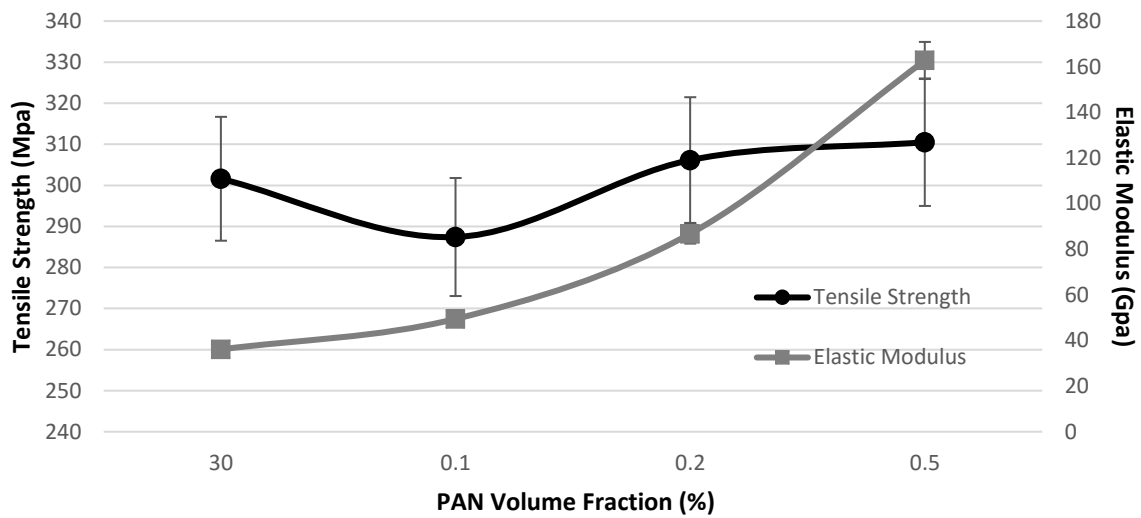


Figure 5-8: Tensile properties of PAN nanomat reinforced AFC

Improvements of tensile properties due to PAN nanomat addition can be attributed to the combination of interlaminar strengthening and prevention of fibre failure. This can be observed in Figure 5-9 in which a fractured tensile sample appeared to have nanofibres embedded in the matrix. This improvement of the interlaminar region allowed a transfer of loads from the aramid sheets onto the nanofibres increasing the stiffness of the overall composite.

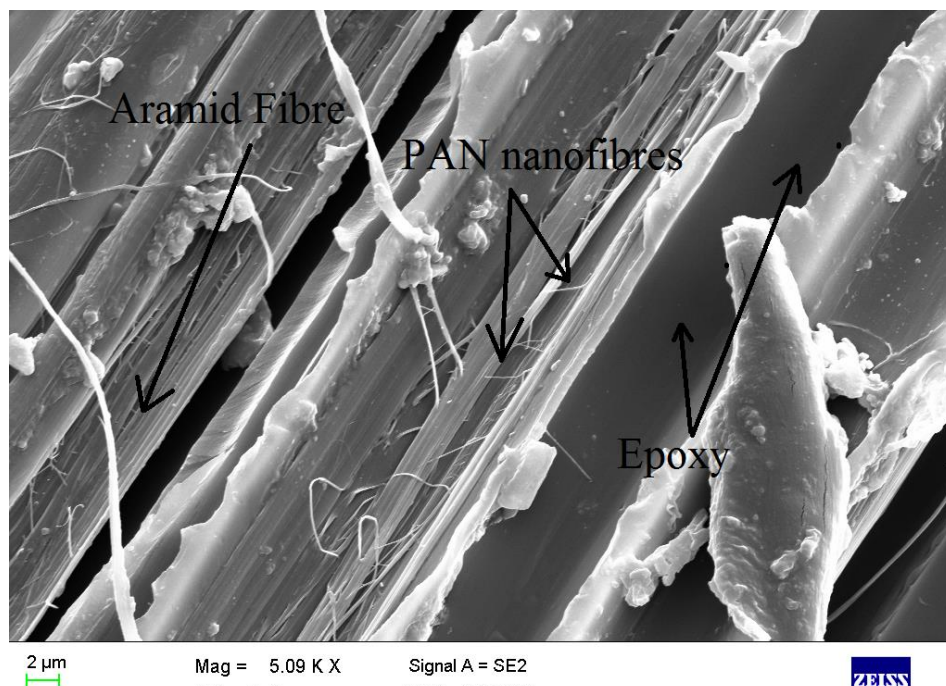


Figure 5-9: SEM image of interlaminar region of failed PAN reinforced hybrid composite

5.2.2 Flexural Properties

The influence of the PAN nanomats on the flexural properties of the aramid epoxy composites had also shown improvements. Figure 5-10 indicates a gradual increase in flexural strength of PAN nanomat addition. AFC measured a value of 174MPa for the flexural strength. With an addition of 0.1%PAN nanomats, an improvement of 5.2% was observed compared to the AFC. As the nanomat volume fraction was increased, the flexural strength increased at almost even increments, resulting in a 7.8% increase with the addition of 0.2% PAN nanomat reinforcement, and a 10.3% increase of flexural strength with a 0.5% PAN nanomat reinforcement, compared to the AFC.

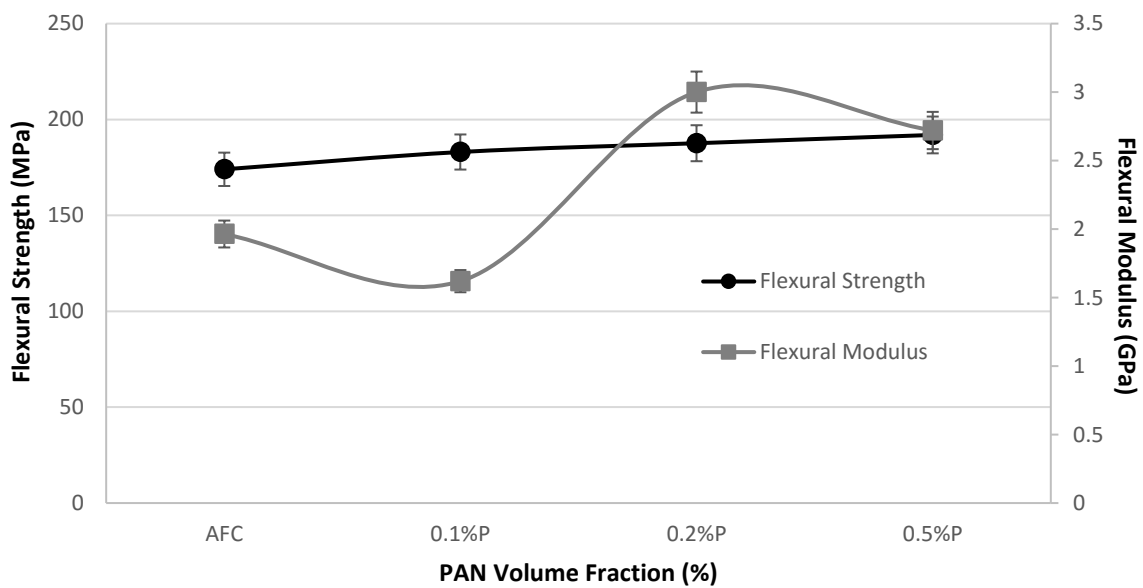


Figure 5-10: Flexural Properties of PAN reinforcement

Increase in flexural strength was indicative of improved fibre matrix interaction due to the nanofibres. Figure 5-11 is an SEM image of the internal fracture of a failed 0.2% PAN nanomat reinforced AFC flexural specimen. As a result, the contact between the PAN nanofibre and the aramid fibre was observed. PAN nanofibres provide an adhesive property when in contact with the macro fibres due to the electrostatic charge created when being electrospun [65]. The nanofibre mats, when electrospun onto the aramid fibre, created an electrostatic adhesive property. This contact indicated an improved interlaminar interaction because the PAN nanofibres had immersed within matrix. This caused a difficulty in fibre pull out which led to an improved stiffness.

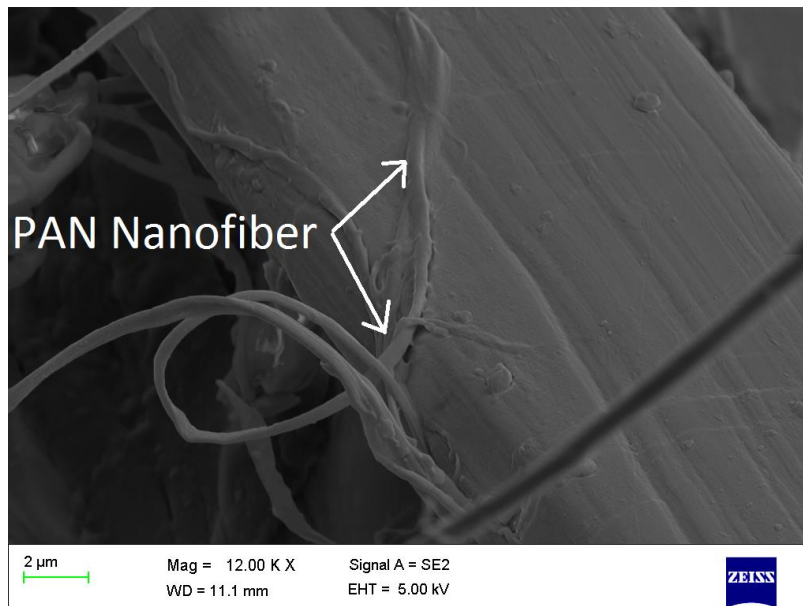


Figure 5-11: SEM image of PAN nanofibre on surface of Aramid fibre

The flexural modulus of PAN nanofibre reinforced hybrids however, did not show a gradual increase like the flexural strength. Figure 5-10 indicated that the AFC measured a modulus of 1.96GPa. The highest flexural modulus was observed at a 0.2% PAN nanomat coating. This was a 53% increase compared to the 30% vol. aramid fibre composite (AFC). Although not as good as the 0.2% PAN increase, the 0.5% PAN nanofibre reinforcement also showed an increase of flexural modulus. The influence of embedding 0.5% electrospun PAN nanomats between layers of aramid sheets was shown to improve the flexural modulus of AFC, with an increase of flexural modulus by 38.3%.

The out of plane properties are observed in Figure 5-12 to be affected by the nanofibres. The increased flexural strength and modulus from the addition of the PAN nanofibre reinforcement mats could be attributed to the prevention of the epoxy chains from moving in segmental motions, within the matrix when the nanofibres are well dispersed [66] [62]. The large surface areas and interconnected porosity of the PAN nanofibre mats provide an improved interfacial interaction with the epoxy matrix and the aramid fibres, resulting in improved strength and modulus. *Chen et al.* [66] indicated similar results by exhibiting an improved interfacial region, within the epoxy region strengthened by CNFs.

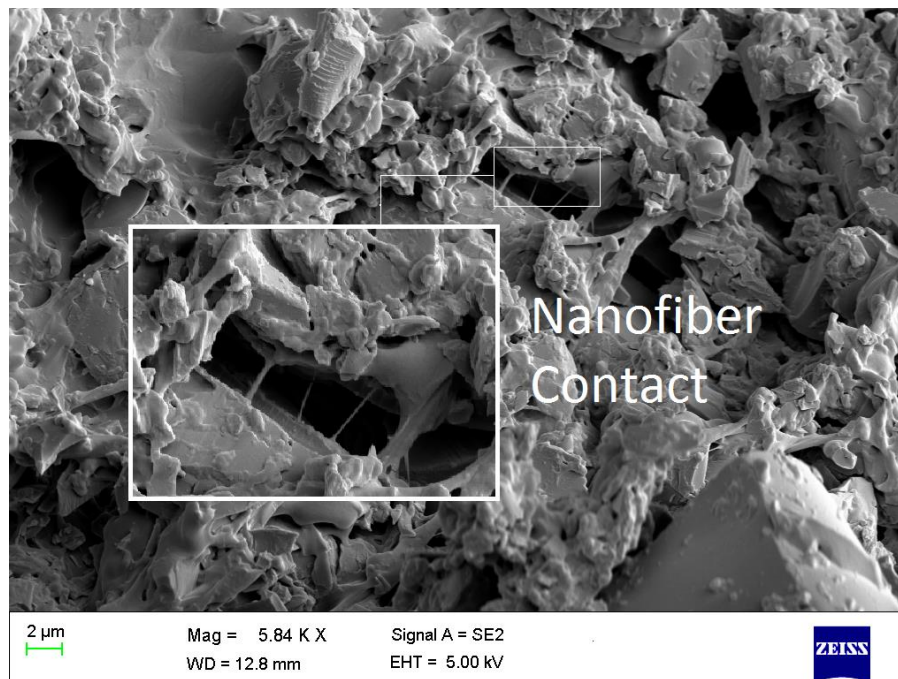


Figure 5-12: Fracture surface of PAN reinforced aramid fibre composite

5.2.3 Impact Properties

Poor impact resistance has been the major concern surrounding the long-term reliability of thermosetting matrices such as epoxy resin. However, with the interlayer toughening reinforcement of polymer nanofibres, the improvement of the impact resistance of composites was observed in Figure 5-13. A decrease in their in-plane mechanical properties was not evident for the aramid reinforced fibre composites (AFC). The PAN nanofibre reinforced AFC is observed to have reduced the separation between aramid fibres and matrix. It was noted that interactions between aramid fibre and epoxy are weak [17].

The influence of embedding electrospun PAN nanofibre sheets between layers of aramid fibre were shown in Figure 5-14 to improve the impact resistance of AFC. A 0.5% PAN nanofibre reinforcement measured a 58.1 J/m^2 impact resistance, this indicated a maximum increase of 18% relative to the AFC. PAN nanofibres demonstrated an adhesive bond induced by nanofibre reinforcement as was seen in Figure 5-11.

It is evident from Figure 5-12 that the PAN nanofibres have improved the load transfer between the aramid fibres and the epoxy matrix within the interlaminar region. The PAN nanofibres absorbed and distributed the maximum impact energy during loading to the stronger and higher moduli aramid fibres [66]. With a 0.7% increase in impact resistance from the AFC to the 0.1% vol. PAN reinforcement and a 3.3% increase from AFC to 0.2% vol. PAN reinforcement, the improvement was considered negligible as compared to 0.5% vol. PAN reinforcement.

The impact resistance continued to improve with the increased PAN nanofibre reinforcement. The relative increase in resistance was linear as the PAN nanofibre volume fraction increased for a 0.2% volume fraction of PAN reinforcement and a 0.5% volume fraction PAN reinforcement. This was recognised to a larger span of the distribution network of the interlaminar PAN nanomats on aramid fibre mats.

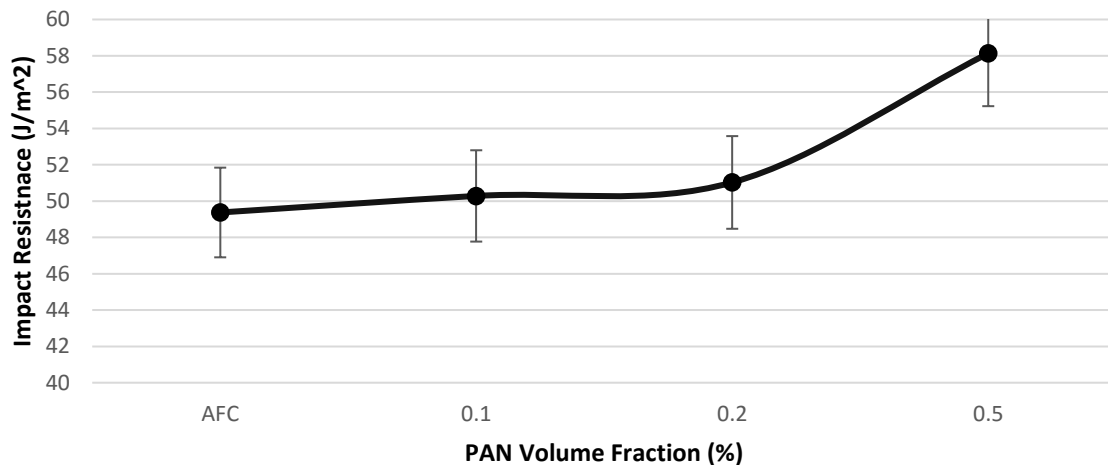


Figure 5-13: Impact properties of PAN nanofibre reinforcement

Figure 5-14 shows how the nanofibrous layer embedded in the matrix affected crack propagation during impact failure. When the cracks reached the nanofibrous band of the composite, the number of fracture fault lines increased and the surface plane became more ordered which is indicative of improved resistance. At the moment of impact when the sample was hit, parallel to the reinforcing plane of the aramid and PAN nanofibre layers, the PAN nanofibre layers absorbed and then instantaneously spread the applied load through the nanofibrous network to the adjacent aramid layers and throughout the entire shear plane, whilst deforming plastically.

Mechanical interlocking was also observed in Figure 5-15 by the ability of the PAN nanofibres to fill the voids within the epoxy matrix. This led to an improved interlaminar region. The impact resistance was affected by the shifting of the plies within the composite. PAN nanofibres acted as an inter-locking mechanism which improves the strength, demonstrating a prevention of ply shifting relative to one another.

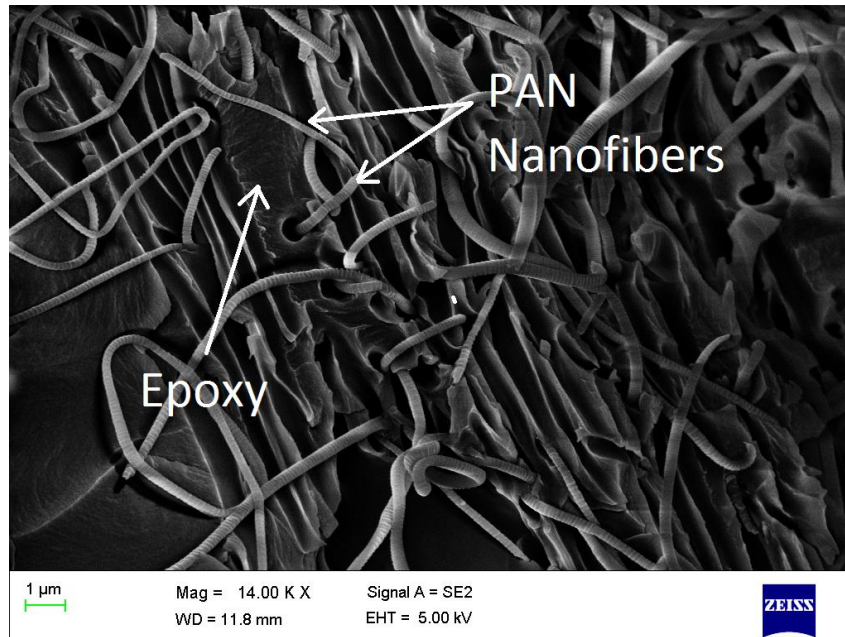


Figure 5-14: PAN nanofibre embedded in epoxy

It can also be seen in Figure 5-15 that there was an improvement of load transfer within the shear plane. This was due to the distribution of loads and bridging of cracks [62]. The fracture around the nanofibres indicated that the load was absorbed by the nanofibre and distributed throughout the matrix, resulting in the blockage of crack propagation. This was an indication of impact energy absorption through plastic deformation [59]. The continuity of the PAN nanofibres also assisted in micro-crack prevention and delamination by remaining intact across the crack plane [64]. This illustrates how the nanofibres acted like hook and loop fasteners similar to that of Velcro®, creating mechanical locks which resulted in a reduction of delamination.

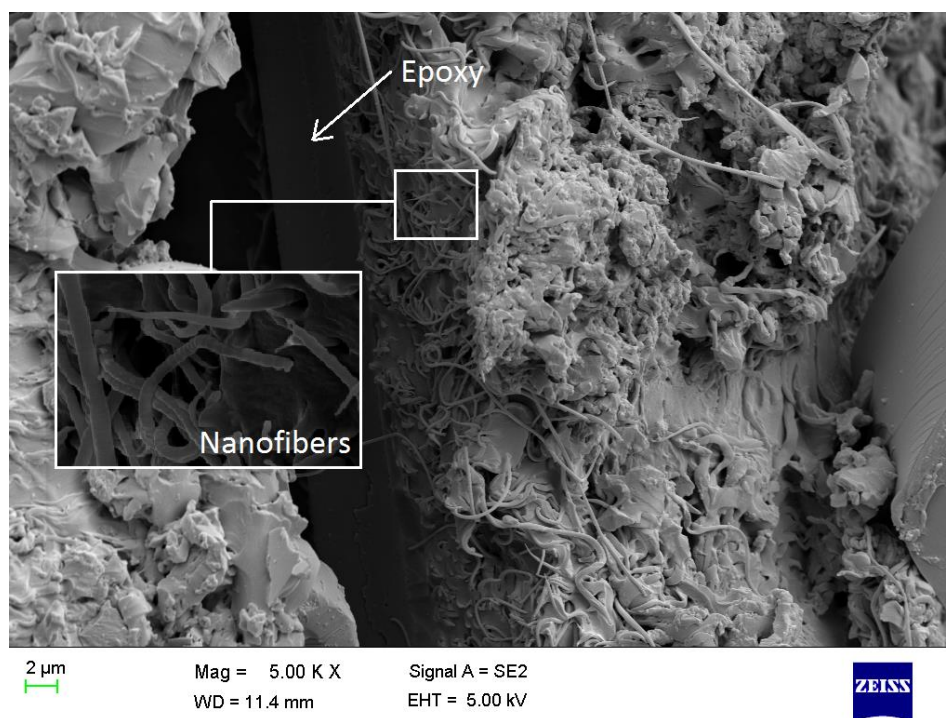


Figure 5-15: SEM image of PAN nanofibres embedded in epoxy resin

5.3 CNF Doped PAN Reinforced Aramid Fibre Hybrid Composites

Doping is a technique in which impurities or foreign material is added to another material in order to improve its properties. In this report, doping was carried out on electrospun PAN nanofibres. The PAN nanofibres were doped with ECNFs (electrospun carbon nanofibres) by adding the ECNFs into the DMF (Dimethylformamide), which was used as the solvent to produce the PAN solution, which was then electrospun. This nanocomposite (CNF doped PAN) was applied as an additional reinforcement within the controlled aramid reinforced epoxy (30% vol.) (AFC). Two doping volume fractions were used within the overall composite. A 0.5% and 1% volume fraction of ECNFs was doped into the three different PAN volume fractions, 0.1%, 0.2% and 0.5% as discussed in the previous section.

The 0.5% and 1% volume fraction of ECNFs were chosen due to the effect on the viscosity of the electrospinning solution. While observing the 1% volume fraction of ECNF within the three different PAN solutions, there was a noticeable increase in viscosity. The 0.5% volume fraction of CNF within in the PAN solution had not shown any changes in the PAN solution. The increase in viscosity prevented the ability to produce higher CNF doped PAN volume fraction. As by increasing the viscosity of the PAN solution, the concentration becomes very high. A high concentration leads to discontinuous and larger microfibrs. *Mcullen et al.* did not go beyond 3% MWCNT (multi-walled carbon nanotubes) within a 4% PEO (polyethylene oxide) electrospinning solution [8]. It was observed that 1% wt. of MWCNT doping within a 4% wt. of PEO produced optimum young's modulus. Further studies also found that very high concentrations of CNTs within PAN would cause crazing and fibre pull out [67]. *Chen et al.* found that doping PAN with glass fibres from 0-0.5 wt. % would improve the overall

mechanical properties and it was found that 0.25 wt. % of PAN produced the optimal mechanical properties.

5.3.1 Tensile Properties

A noticeable trend is observed with the increase of the tensile strength of CNF doped PAN (CNF-DP) hybrid samples seen in Figure 5-17. The addition of the CNF content does improve the tensile properties. It was found that the CNF-DP nanofibre reinforced aramid fibre composite (AFC) tensile properties was optimal at a 1% CNF doped 0.1% PAN nanofibre content with a 17.3 % increase compared to the AFC.

The decrease in tensile strength with the addition of the 1% CNF doped 0.2% PAN and 1% CNF doped 0.5% PAN nanofibre samples was attributed to the inconsistency of the distribution of the CNFs within the PAN nanofibres. The decrease in yield strength is a result of the inconsistency of distribution of the CNFs, as seen in Figure 5-16, as well as the distribution of the doped nanofibres within the inter-facial region. A 1% vol. of CNF content for increased amounts of PAN nanofibre content decreases the tensile properties due to the inconsistency of the CNF distribution within the PAN nanofibre. When doping low PAN vol. %, the distribution of CNF within the PAN nanofibres was considered more even at low PAN vol. %, whereas an increase in PAN volume allows the CNF to be unevenly distributed.

An uneven distribution of CNFs within PAN as observed in Figure 5-16 can decrease the strength of the individual nanofibres therefore affecting the overall tensile properties of the composite. If there is a weak nanofibre region, the transfer of energy from the aramid fibres onto the interlaminar region may cause cracking within the matrix therefore leading to premature failure.

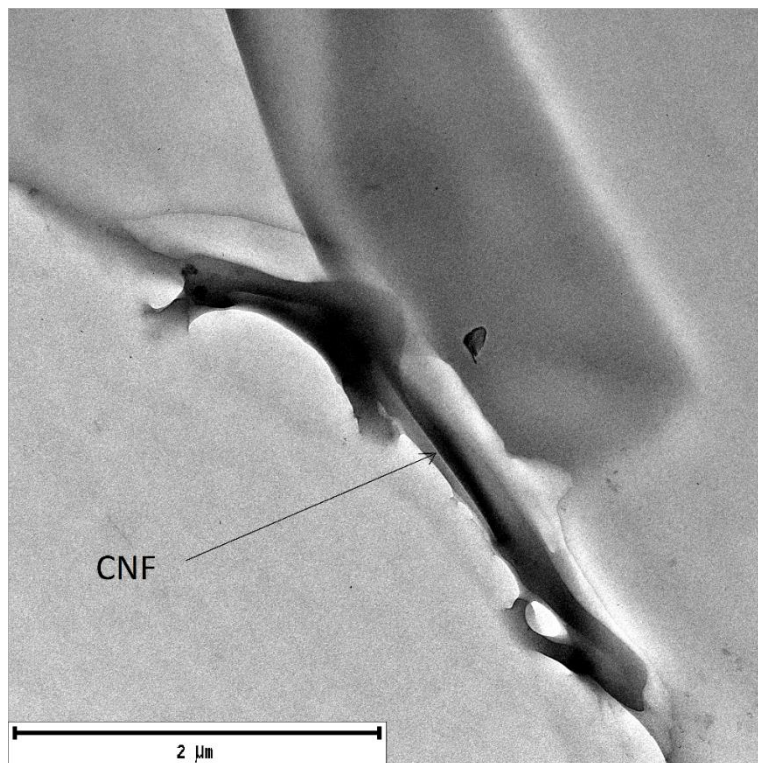


Figure 5-16: TEM image of CNF doped PAN

This then results in an uneven distribution of load. The loads would shift into the individual nanofibres and would break at weak regions caused by agglomerations of CNFs. The interfacial region may have improved by the load transfer in the out of plane region, however when reaching the CNF-DP the agglomerates would act as weak mechanical points or structural defects, leading to a lower tensile strength.

It is evident however, that doping of PAN does improve the overall tensile properties of the aramid fibre composite. When observing Figure 5-17, a 0.5% CNF addition to a 0.1% PAN reinforcement provides a UTS of 315.1MPa. That indicates a 9.64% increase in tensile yield compared to a non-doped 0.1% vol. PAN reinforced aramid fibre hybrid composite. The effects of doping with CNFs are visible for the other two PAN reinforcements as well. At a 0.2 % vol. PAN reinforcement and a 0.5% vol. PAN reinforcement, the addition of 0.5% vol. CNF shows an 8% increase in tensile strength for both.

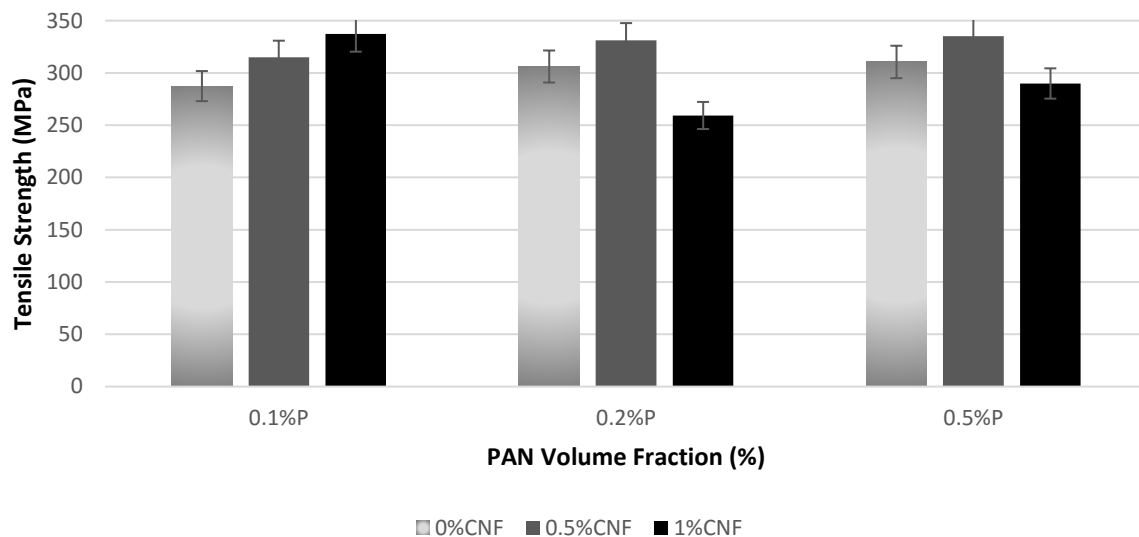


Figure 5-17: Tensile Strength of CNF Doped PAN Reinforced Hybrid Composites

The elastic modulus in Figure 5-18 follows a similar trend to that of the tensile strength for 0.5% CNF doped samples. A doped 0.5% vol. of CNF does increase the elastic modulus at 0.1% vol., 0.2% vol. and 0.5 % vol. of PAN reinforcements by 280%, 182.2% and 142% respectively, in comparison to the non-doped specimens. With a 730% increase from the 30 %vol. aramid fibre composite (AFC), the optimum modulus is at a 1% vol. CNF doped 0.1% vol. PAN reinforcement. It is however evident, that an increase in PAN nanofibre content with a 1% CNF doping content decreases the tensile strength at higher PAN volume fractions. This reduces the stiffness of the composite material resulting in early elastic deformation

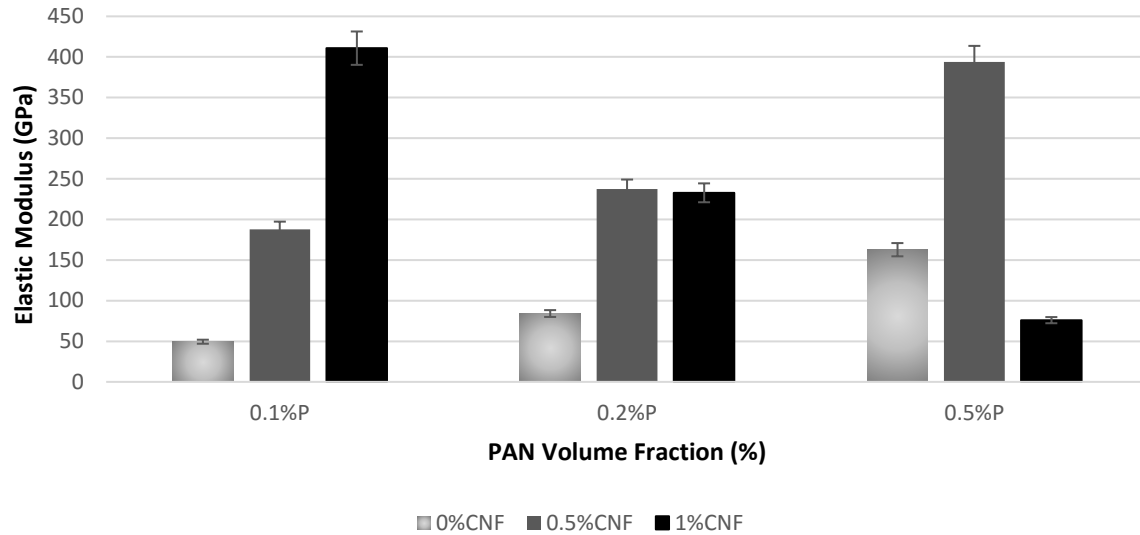


Figure 5-18: Elastic Modulus of CNF-DP Hybrid Composites

It is crucial for the interfacial bonding strength to be high between matrix and reinforcement as an even distribution of load is produced. If the interfacial strength between the matrix and reinforcement is low, then the fibre-matrix interface is the weakest part when a load is applied [66]. The reduction in stiffness from an increase of CNF content could be attributed to the weak spots or zones within the PAN nanofibre [66]. These weak spots or zones are created from agglomerations and are a result of poor dispersion within the PAN when mixing. The purpose of the nanofibres is to deflect propagating cracks and force the crack growth to shift from the out of plane region, so that the macro fibre reinforcement prevents the failure. However, if the nanofibres are weakened then the nanofibres tend to break prematurely and the aramid fibres are observed (Figure 5-19) to pull and slide out regardless of the nanofibre-matrix bond.

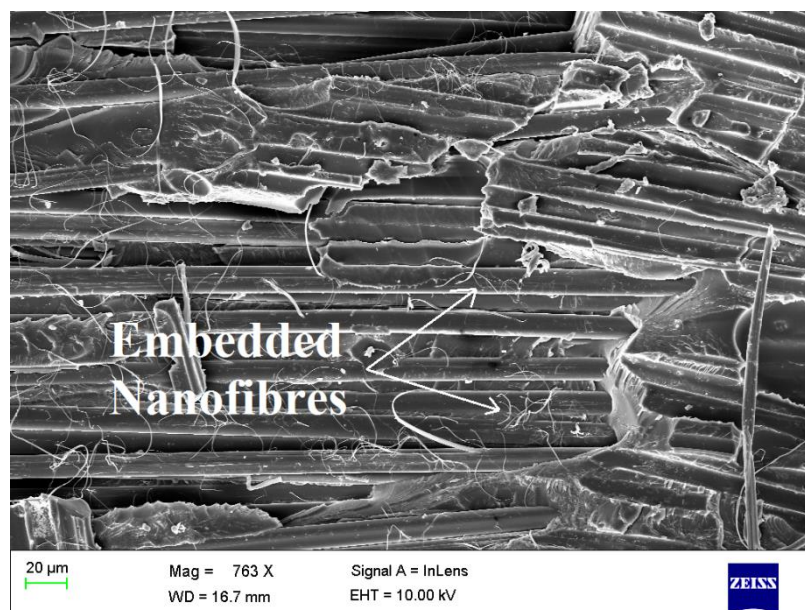


Figure 5-19: 0.5% vol. CNF doped 0.2% vol. PAN Reinforced Aramid Hybrid

5.3.2 Flexural Properties

3-point bending tests were carried out on CNF-DP aramid hybrid composites and flexural properties were determined. At 0.1% vol. PAN and 0.5% vol. PAN the flexural strength of the hybrid composites was observed (Figure 5-20) to increase as the CNF content within the PAN was increased. At a 0.2% vol. PAN, CNF doping decreases the flexural strength.

The 0.5% PAN reinforced AFC (aramid fibre composite) specimens revealed a major increase in the flexural strength by 9.67% and 12.1%, when doped by both 0.5% vol. CNF and 1% vol. CNF respectively. This is attributed to the increase in PAN nanofibre strength. The distribution of the nanofibres played a major role as they were spun directly onto the aramid fibre sheets using a drum collector. The drum collector method allows the nanofibres to be distributed across the face of each laminate. Continuous fibres were observed and therefore the continuity provides strength within the interlaminar region. It was observed that fractured bending samples were held together by the nanofibres within the interlaminar region and as a result, was seen to have improved the flexural strength. The distribution of CNFs within the PAN nanofibres with an additional even distribution within the fibre-matrix interphase had improved the flexural strength.

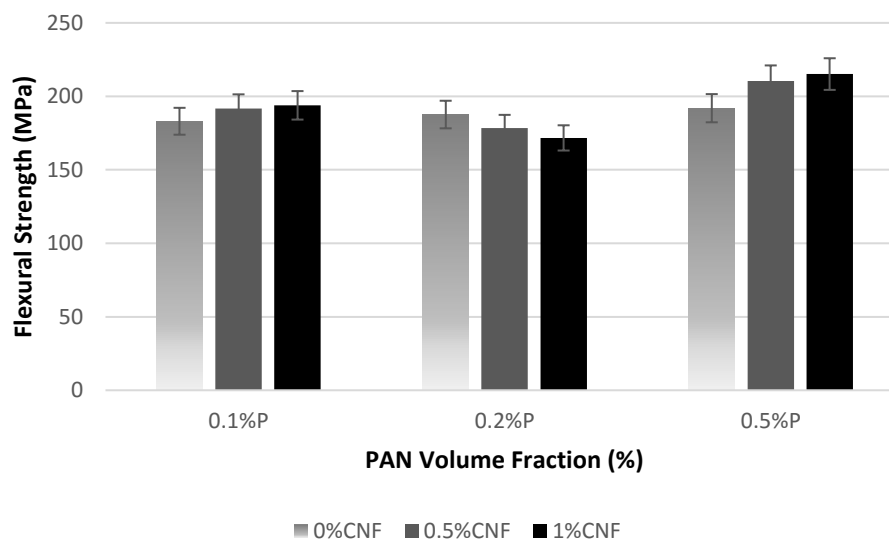


Figure 5-20: Flexural Strength of CNF doped PAN Aramid hybrid samples

Figure 5-21 is an SEM image of a 0.5 vol. % CNF doped 0.5% vol. PAN nanofibre fractured specimen. The ridges suggest brittle failure. When the nanofibre is held within the epoxy matrix, it disallows shifting of molecular chains within the interlaminar region and therefore withstands bending loads which increases the flexural strength of the overall composite. These bending loads create cracks and are prevalent within the out of plane region [66]. They are now transferred into the CNF-DP nanofibres which deflect the cracks. These micro cracks created from fibre-matrix separation (brittle fracture) observed in Figure 5-21, are deflected by the nanofibres.

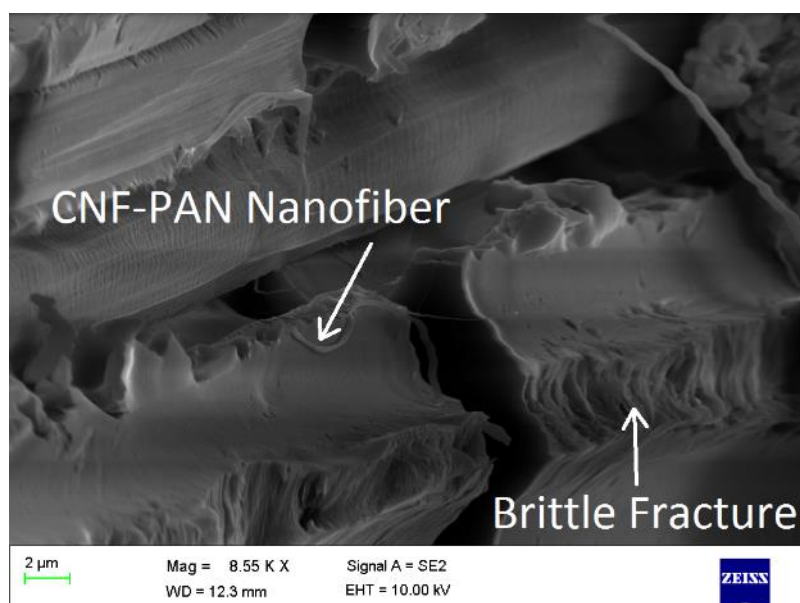


Figure 5-21: SEM image of a fractured 0.5 vol. % CNF doped 0.5 vol. % PAN bending specimen

It was observed in Figure 5-22 that with 0.5% vol. CNF doping, an increase of 4.8% and 9.7% in flexural modulus of 0.1% vol. and 0.2% vol. PAN occurred respectively. The flexural modulus of a 0.2% vol. PAN reinforced AFC was measured to be 3GPa. With the inclusion of a 0.5% vol. CNF and 1% vol. CNF the flexural modulus dropped to 1.2GPa and 0.9GPa respectively.

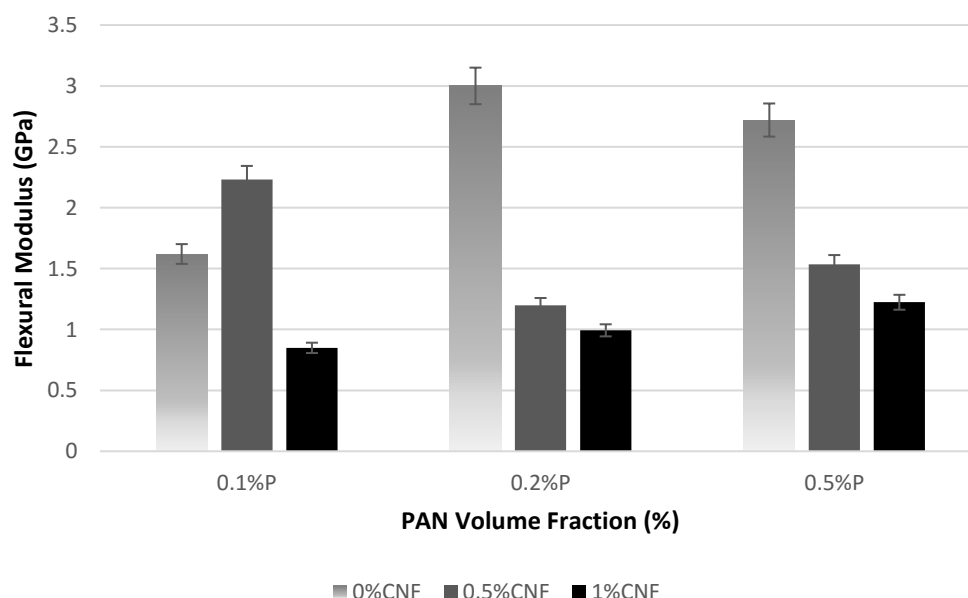


Figure 5-22: Flexural Modulus of CNF-DP Aramid Hybrid Composites

The flexural modulus of the 0.2% vol. PAN reinforcement was observed to decrease with the increase of CNFs. This could possibly be attributed to the distribution of CNFs within the PAN nanofibre resulting in weaker regions on the surface of the nanofibre. The elasticity of the individual nanofibre may have decreased, and therefore resulting in an add-on effect. The transfer of energy within the interlaminar regions was reduced because of the agglomeration of CNFs within the PAN nanofibre.

The spread and distribution of the doped PAN nanofibres was also observed to have been inconsistent therefore resulting in a low elastic modulus. The nanofibres agglomerate and create fracture points on the surface of the laminates therefore reducing the ability to withstand even load distribution. This can be observed in Figure 5-23 where brittle fracture was observed from the fracture ridges, caused by the inability to hold the aramid fibre, due to the nanofibre agglomeration.

These nanofibre clumps are caused by the inconsistency of the needle droplet rate. The droplets are formed at different rates due to the inaccuracy of volume within the syringes that contain the PAN/CNF solution. The volume is affected by the addition of air bubbles within the syringe and therefore the droplets are forced out at different times. One possible solution to the reduction of bubbles is a deoxidizing agent or an improved stirring method.

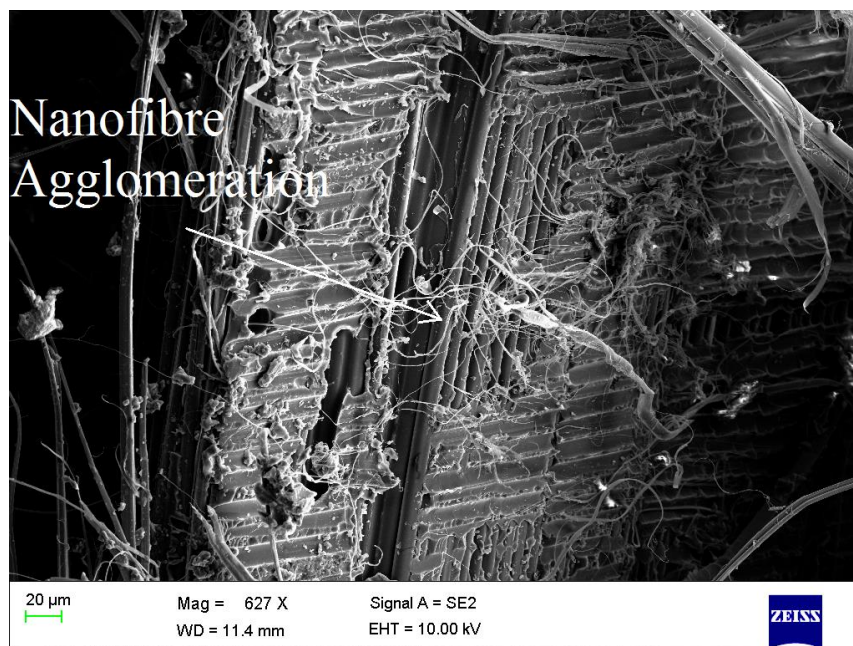


Figure 5-23: SEM image of failed 1%CNF doped PAN nanofibre hybrid composite

Flexural modulus represents the modulus of elasticity of a material when experiencing bending loads. Results showed a decrease in elastic modulus due to doping of PAN nanofibres, except at a 0.5% vol. CNF doped 0.1% vol. of PAN. This lack of increase was possibly due to the irregularity of the doped nanofibres observed in Figure 5-24 and discussed in section 4.45. An uneven distribution of CNFs within the nanofibres resulted in a distorted distribution of load and stress concentration. The stress concentration created weaker zones due to CNF agglomerations within the PAN nanofibre, and led to premature failure which affected the interlaminar regions.

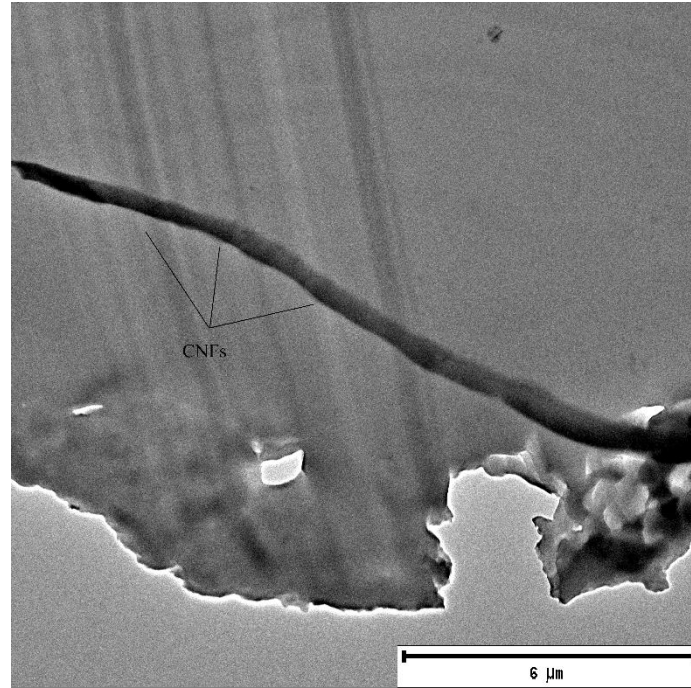


Figure 5-24: Individual CNF doped PAN Nanofibre

Coating of nanofibres onto the surface of the aramid fibre sheets do however, create a higher stiffness. This decreases the elasticity of the overall hybrid composite. It can be said that the interlaminar regions are in cohesion at a 0.5% vol. CNF doped 0.1% vol. PAN and shifting of the planes is reduced due to the nanofibre reinforcement.

5.3.3 Impact Properties

The impact properties were determined by the Izod impact test. The impact resistance of CNF doped PAN reinforced hybrid composites were measured and for all PAN volume fractions, the 0.5% vol. CNF doped reinforcement showed an increase in impact resistance (Figure 5-25). The 0.5% vol. CNF doped reinforcement increased the impact energy by over 40% for both the 0.1% vol. and 0.2 % vol. PAN reinforced aramid hybrid specimens. The 0.5% vol. CNF doped 0.5% vol. PAN had increased by 30% when compared to a non-doped sample.

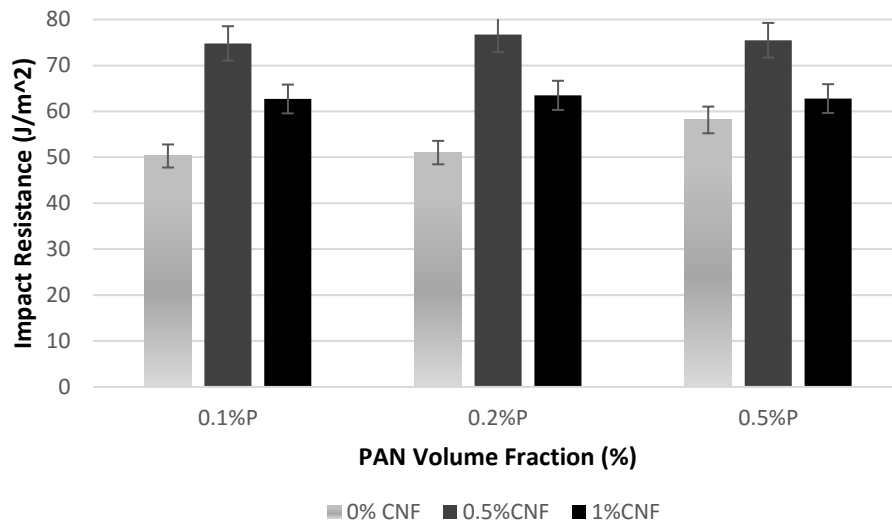


Figure 5-25: Impact Properties of CNF doped PAN Reinforced Aramid Fibre hybrid composites

A build-up of nanofibres was observed in Figure 5-26 which led to stress concentration. This stress concentration allowed the fracture rate of the specimen to increase and therefore reducing the impact energy. Nanofibre clumps or entanglement can create holes/void within the matrix therefore reducing the interlaminar properties [68]. This can be seen in Figure 5-26. This reduction in interfacial strength was due to the detachment of the nanofibres and the stress concentration from a strong interfacial bond (Van der Waals forces) in certain areas, and less in others [68] [22] [66]. This was due to agglomerations of CNFs within the PAN nanofibres that shift the distribution. The accumulation of these CNF areas created a point in which laminates may be separated therefore affecting the overall impact energy absorption.



Figure 5-26: SEM image of 0.5% CNF doped PAN

The optimum impact resistance 76.7 J/m^2 was measured for the 0.5% vol. CNF doped 0.2% vol. PAN reinforced AFC. A slight decrease in impact energy was observed as the PAN nanofibre composition was increased. A 0.5% PAN reinforcement is similar in impact resistance to a 1% CNF doped 0.1% PAN. The reason for the decrease in impact energy as the CNF content increased was possibly be due to the low shear property of the nanofibre, therefore decreasing the impact energy [66]. The agglomerations and distribution within the PAN nanofibre could possibly be the reason of degradation in holding the laminates together when under impact loads.

6 Conclusion

In this research paper multi scale hybrid composites were produced and tested. Electrospinning was used to provide a secondary reinforcement within the multiscale hybrid composite. Nanofibres were used and determining their effect on the mechanical properties as well as the interlaminar properties was carried out. Initially, aramid reinforced epoxy composites were hand laid, and the optimum volume fraction was determined. The optimum volume fraction was then used to determine the effect that PAN nanofibres have on the overall composite. PAN nanofibres were coated on aramid sheets as nanomats, then laid into epoxy resin and testing was conducted. Finally, doping of the PAN nanofibres with electrospun carbon nanofibres was carried out. CNFs were produced by carbonizing electrospun PAN nanofibres at 800°C. Doped samples were produced in a similar manner to the PAN reinforced specimens.

The average diameter of the nanofibres was found to be approximately 200nm. Electrospun nanofibres were discovered to be more cost effective than vapour grown CNFs and provided an advantage in coating without damaging the aramid, macro reinforcement. The optimum aramid reinforced epoxy composite was found to be 30% vol. and was increased with a 0.1% vol., 0.2% vol. and 0.5% vol. PAN and PAN/CNF nanofibre layers. Two sets of CNF doped nanofibre reinforcements used were; 0.5%vol. and 1%vol. These layers were implemented to determine the effect on the interlaminar properties.

The following points were drawn:

1. Interlaminar shearing between plies was affected by CNF agglomerations. This was discovered when determining the impact properties of the multiscale doped hybrid composites.
2. Continuous nanofibres with diameters of approximately 200nm were observed to be highly advantageous when producing hybrid composites and were discovered to improve the interlaminar region when experiencing bending loads.
3. Electrospun nanofibres assisted in improving the interlaminar regions within aramid epoxy by mechanical locking within the epoxy and creating an adhesive bond using Van der Waals forces and electrostatic charge between nanofibre and macro fibre.
4. The drum collector design was the most ideal form for coating of nanofibre mats onto surfaces of macro fibres such as aramid fibre.
5. The disadvantage of non-aligned nanofibres is their ability to separate laminates due to the horizontal position of random orientation.
6. Doping is useful in improving the strength of the individual nanofibres however CNFs within PAN nanofibres can agglomerate weakening the fibre as well as transferring energy to areas within the interlaminar region that weaken the overall composite.
7. Interfacial strength between CNF and PAN was important in load transfer. If weakened due to a poor bond, then it result in reduction of mechanical properties.

This research report illustrates the possibilities of electrospinning as a process for strengthening interlaminar regions of composite materials. Optimum volume fractions must be determined and discovering the balance of volume fraction is important depending on application. Hybridising aramid epoxy with the use of nanofibres assisted in improving various mechanical properties. Impact degradation is one major disadvantage of nanofibre hybridising and the use of doped nanofibres can be detrimental. However further research can be carried out on the individual nanofibres due to doping. Methods in improving the interfacial bonding strength between the CNF and PAN. Alternative tests can be carried out, such as determination of delamination and short beam shear strength. The effects of doped nanofibres could be rewarding due to the possibilities of ECNFs. The ECNFs are more conventional and cost effective due to its top down approach and low cost of production.

CNF doping using electrospinning is highly advantageous due to the low cost and high productivity rate. Alternative doping techniques are expensive and more time consuming. This research report provides evidence of the possibilities of electrospinning and doping as a strengthening technique in multiscale hybrid composites.

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8 Appendices

8.1 Appendix A

Drum collector size calculations

Equation (8.1) below was used to calculate the required RPM and diameter of the drum collector:

$$RPM = \frac{60 \times v}{2\pi \times r} \quad (8.1)$$

Where;

v = linear velocity (m/s)

r = radius (m)

RPM = revolutions per minute (rev/min)

The diameter and length of the drum were determined by the size of the mould as this determined the dimensions of the spun mat. The mould dimensions used, as described later, were 190mm x 190mm and as such the minimum required dimensions of the drum were calculated as using Equation (8.2) seen below so that the required RPM for the solution could also be calculated.

$$\begin{aligned} r &= \frac{D_c}{2\pi} \\ &= \frac{190}{2\pi} \\ &= 30.23mm \end{aligned} \quad (8.2)$$

Where;

D_c = Minimum drum circumference (mm)

r = radius (mm)

Therefore from Equation (8.2) it can be seen that the minimum required diameter for the drum collector is 60.46mm. Also from the given mould dimensions it can be seen that the minimum required length of the drum is 190mm.

Table A-1: Table showing the drum collector's motor specifications.

Motor Specifications	
Current Rating	2.7A
Maximum Output Torque	0.14 Nm
Output Speed	4000 RPM
Power Rating	60 W
Supply Voltage	24 V dc
Length	106.7mm
Shaft Diameter	7.927mm

8.2 Appendix B

Table B-2: Volume fraction spread sheet

P _{kevlar}	1.44	g/cm ³		W _{kevlar}	0.343651	34.36514	%		V _{kevlar}	0.3	30	%
P _{cnf}	2	g/cm ³		W _{cnf}	0.00162	0.161956	%		V _{cnf}	0.001	0.1	%
P _{epoxy}	1.148	g/cm ³		W _{epoxy}	0.654729	65.4729	%		V _{epoxy}	0.699	69.9	%
ρ _{composite}	1.234906	g/cm ³		m _{kevlar}	120.12	g	t _{composite}	0.45	cm			
V _{composite}	283.05	cm ³		m _{cnf}	0.5661	g	Areal m _{kevlar}	0.017361	cm ²			
m _{composite}	349.5402	g		m _{epoxy}	228.8541	g	n _{kevlar}	11.19758				
				V _{epoxy/hard}	199.3503	ml	m _{single kevlar}	10.92	g			
				V _{epoxy}	139.5452	ml	n _{kevlar max}	11	layers			
				V _{hardner}	59.80509	ml	V _{kevlar new}	0.294706				
DEGREDAATION RATIO	0			Epoxy/hard ratio	0.7		V _{epoxy new}	0.704294				
M _{pan}	0.5661	g										
V _{pan}	0.478125	ml										
V _{pan/DMF}	5.976563	ml										
V _{DMF}	5.498438	ml										
SPINNING TIME@1ml/hr	5.976563	mins										
PER LAYER												
M _{pan}	0.05661	g										
V _{pan}	0.047813	ml										
V _{pan/DMF}	0.597656	ml										
V _{DMF}	0.549844	ml										
SPINNING TIME@1ml/hr	35.85938	mins										
SPINNING TIME@6 syringes	5.976563											
M _{cnf}	0.05661	g										
M _{layer}	10.97661	g										

8.1 Appendix C

Table C1: Neat epoxy tensile and flexural sample data

Specimen Number	Dimensions		Tensile strength [MPa]	Tensile Modulus [MPa]	Flexural Strength [MPa]	Flexural Modulus [MPa]
	Tensile width [mm]	Flexural Width [mm]				
1	12.7	12.3	46.2	2715	78.2	2303.9
2	12.6	14	39.2	1550	74.6	2365.9
3	12	15.1	26.8	1044	66.9	1956.3
4	12.1	14.5	20.1	740.2	75.4	2199.3
5	12.5	14.7	29.7	1158	67.6	2395.8
Mean	12.4	14.1	32.4	1441.4	72.5	2244.2
SD	0.3	1.1	10.3	768.7	5.0	177.7

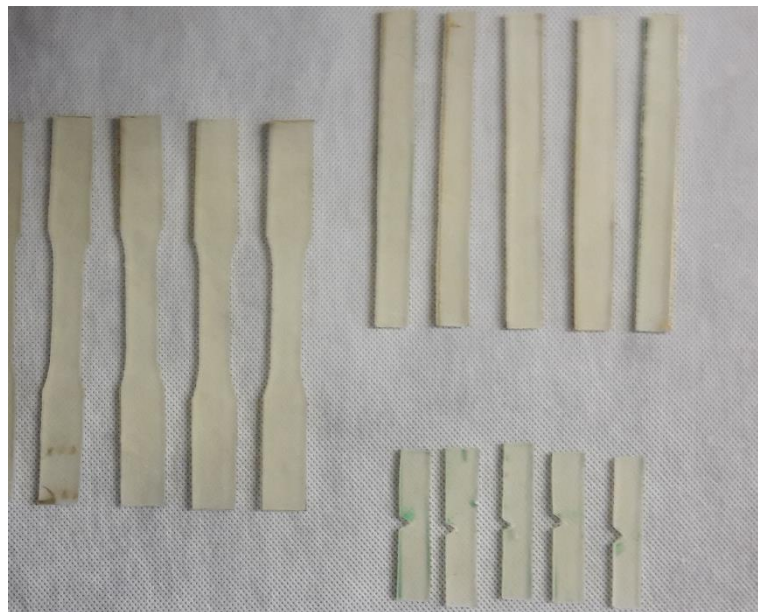


Figure C1: ASTM specimens for neat epoxy

Table C2: 10% Aramid reinforced fibre epoxy sample data

Specimen Number	Dimensions		Tensile strength [MPa]	Tensile Modulus [MPa]	Flexural Strength [MPa]	Flexural Modulus [MPa]
	Tensile width [mm]	Flexural Width [mm]				
1	12.5	12.8	165.4	66092.6	129.1	649823.0
2	12.6	11.4	169.7	22038.4	75.0	797731.9
3	12.6	12.9	157.8	76500.8	117.3	700425.0
4	12.6	12.0	174.5	16270.5	89.9	13262.9
5	12.6	13.9	184.6	65178.9	85.7	587178.2
Mean	12.6	12.6	170.4	49216.3	99.4	549684.2
SD	0.0	1.0	10.0	27875.3	22.8	309609.4

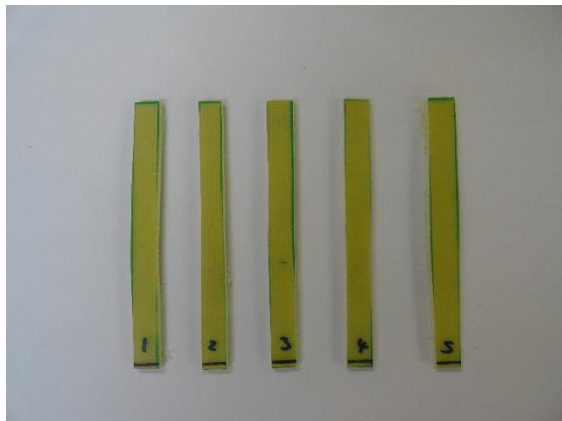


Figure C2: 10% AFC Flexural test specimens (before and after)

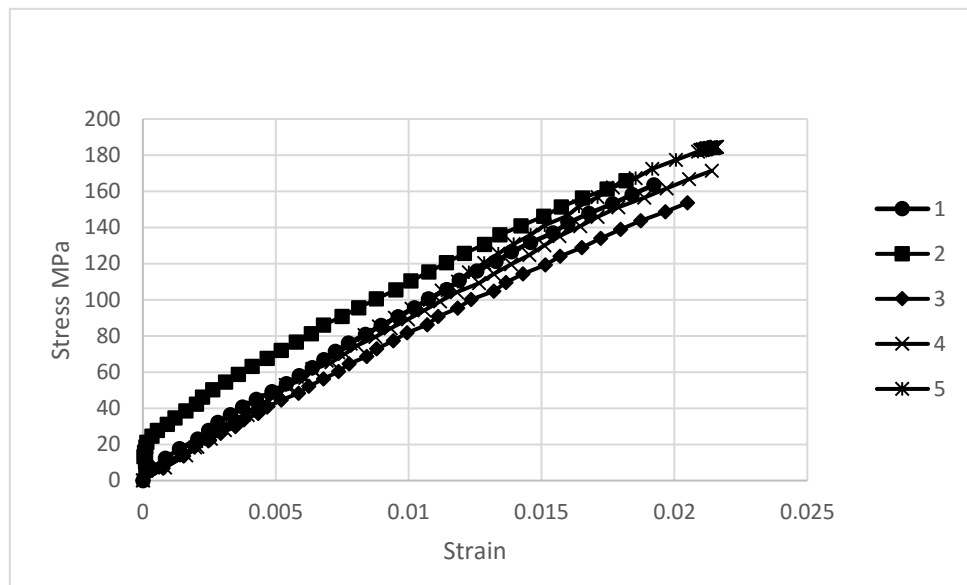


Figure C3: Stress vs Strain graph of 10% AFC

Table C3: 20% Aramid reinforced epoxy sample data

Specimen Number	Dimensions		Tensile strength [MPa]	Tensile Modulus [MPa]	Flexural Strength [MPa]	Flexural Modulus [MPa]
	Tensile width [mm]	Flexural Width [mm]				
1	12.7	12.7	294.3	108201.4	148.2	1060971.4
2	12.7	12.7	296.5	13787.5	121.7	1116923.2
3	13.0	13.0	261.3	145213.8	113.3	914186.0
4	13.0	13.0	272.5	12212.3	149.4	1198204.1
5	12.6	12.6	266.5	52854.3	130.5	990017.4
Mean	12.8	12.8	278.2	66453.9	132.6	1056060.4
SD	0.2	0.2	16.2	58836.3	16.0	110026.4

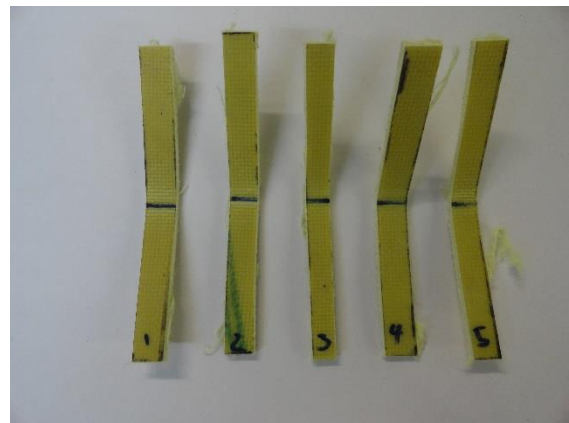


Figure C4: 20% AFC Flexural test specimens (before and after)

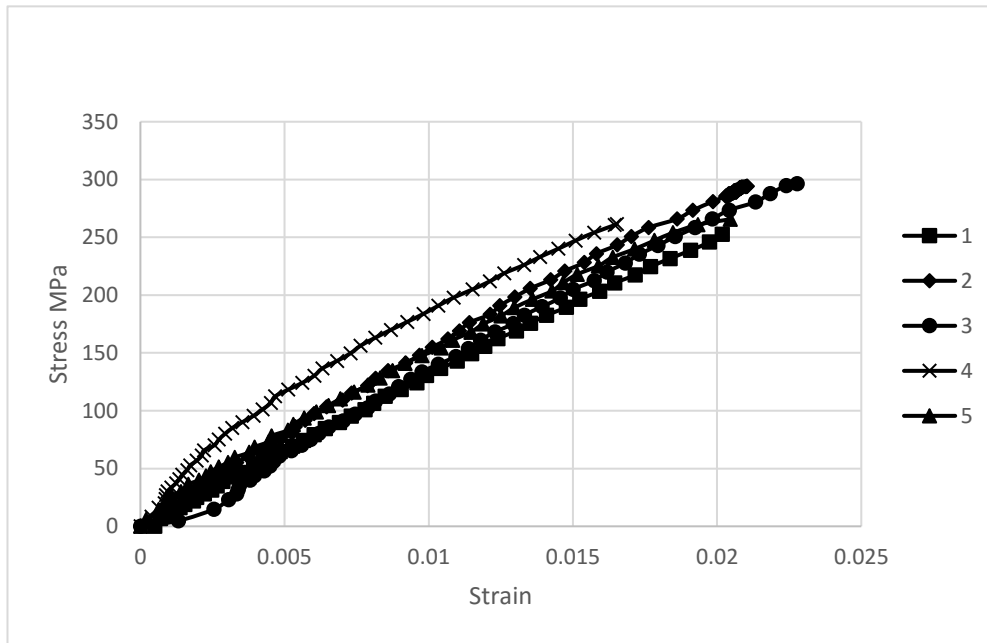


Figure C5: Stress vs Strain graph of 20% AFC

Table C4: 30% Aramid reinforced epoxy sample data

Specimen Number	Dimensions		Tensile strength [MPa]	Tensile Modulus [MPa]	Flexural Strength [MPa]	Flexural Modulus [MPa]
	Tensile width [mm]	Flexural Width [mm]				
1	13.3	12.2	312.9	18415.8	176.2	2052579.2
2	12.7	11.4	270.6	35271.8	176.3	2132862.9
3	13.2	13.8	293.2	24509.8	188.1	2053636.8
4	13.0	12.0	309.4	24313.8	164.1	1734495.3
5	12.8	12.0	322.0	45787.4	165.5	1846471.6
Mean	13.0	12.3	301.6	29659.7	174.0	1964009.1
SD	0.3	0.9	20.2	10875.7	9.7	166494.1



Figure C6: 30% AFC Flexural test specimens (before and after)

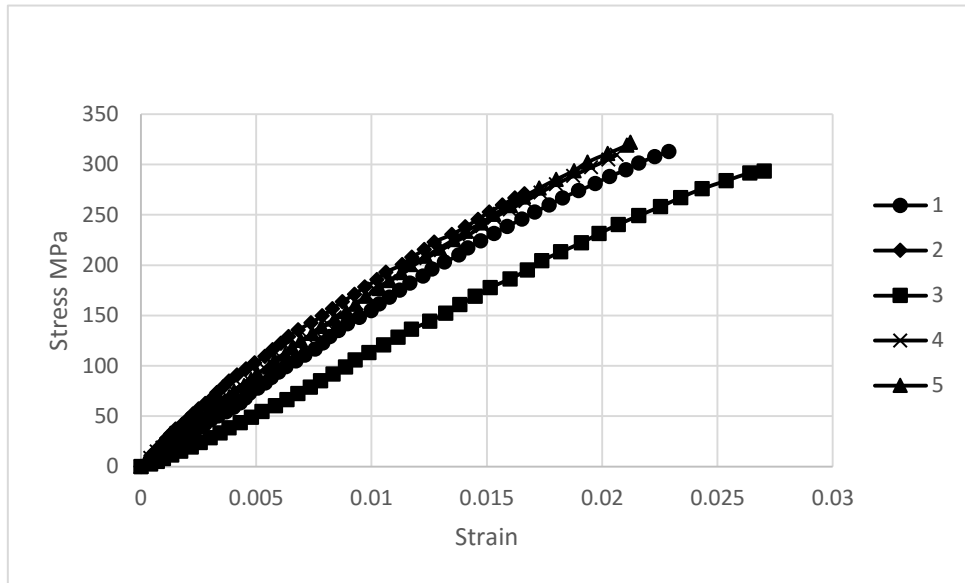


Figure C7: Stress vs Strain graph of 30% AFC

Table C5: 0.1% PAN Reinforced AFC sample data

<i>Specimen Number</i>	<i>Dimensions</i>		<i>Tensile strength [MPa]</i>	<i>Tensile Modulus [MPa]</i>	<i>Flexural Strength [MPa]</i>	<i>Flexural Modulus [MPa]</i>
	Tensile width [mm]	Flexural Width [mm]				
1	13.0	11.6	292.0	108947.9	190.3	1980741.6
2	12.6	13.3	311.8	17216.4	170.2	973338.3
3	13.1	12.6	258.1	22037.1	180.8	1478976.8
4	13.4	11.6	284.7	21754.0	196.6	2175544.6
5	13.1	11.8	290.4	77331.1	177.3	1490833.0
Mean	13.0	12.2	287.4	49457.3	183.1	1619886.9
SD	0.3	0.7	19.3	41457.5	10.5	472627.6



Figure C8: 0.1% PAN reinforced AFC Flexural test specimens (before and after)

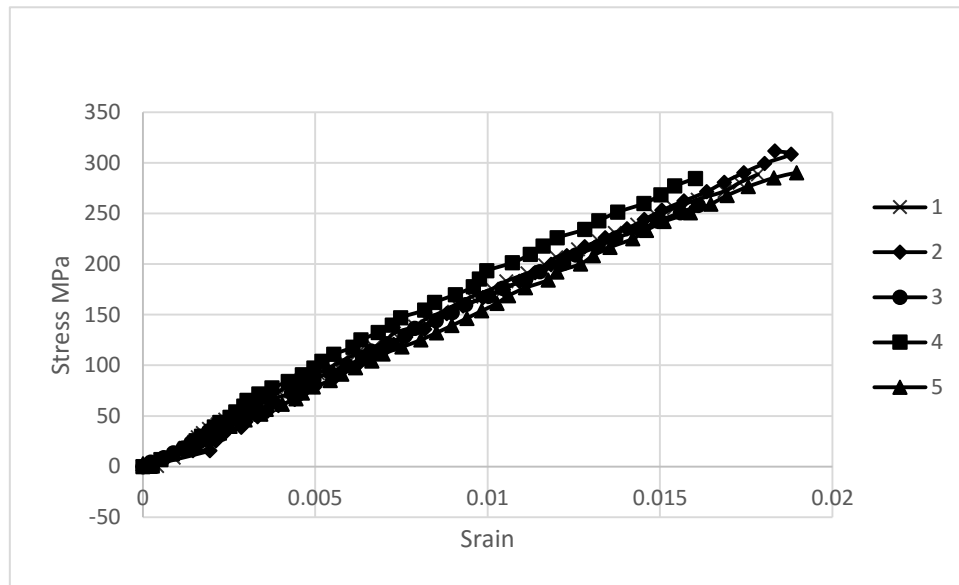


Figure C9: Stress vs Strain of 0.1% PAN reinforced AFC

Table C6: 0.2% PAN Reinforced AFC sample data

<i>Specimen Number</i>	<i>Dimensions</i>		<i>Tensile strength [MPa]</i>	<i>Tensile Modulus [MPa]</i>	<i>Flexural Strength [MPa]</i>	<i>Flexural Modulus [MPa]</i>
	Tensile width [mm]	Flexural Width [mm]				
1	13.7	12.1	307.3	17916.6	206.3	3482328.5
2	12.9	12.0	336.3	13709.2	209.6	3779063.4
3	13.0	11.7	301.0	14406.4	166.0	2386573.0
4	12.7	11.3	351.4	352629.8	183.8	2820346.3
5	13.0	13.4	234.8	35367.0	172.5	2531927.4
Mean	13.1	12.1	306.2	86805.8	187.6	3000047.7
SD	0.4	0.8	44.9	148861.4	19.6	605648.5

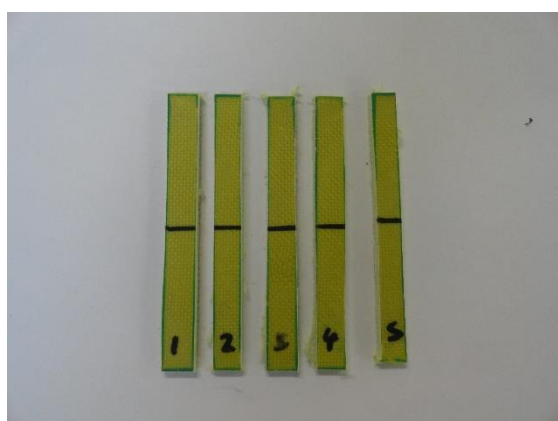


Figure C10: 0.2% PAN reinforced AFC Flexural test specimens (before and after)

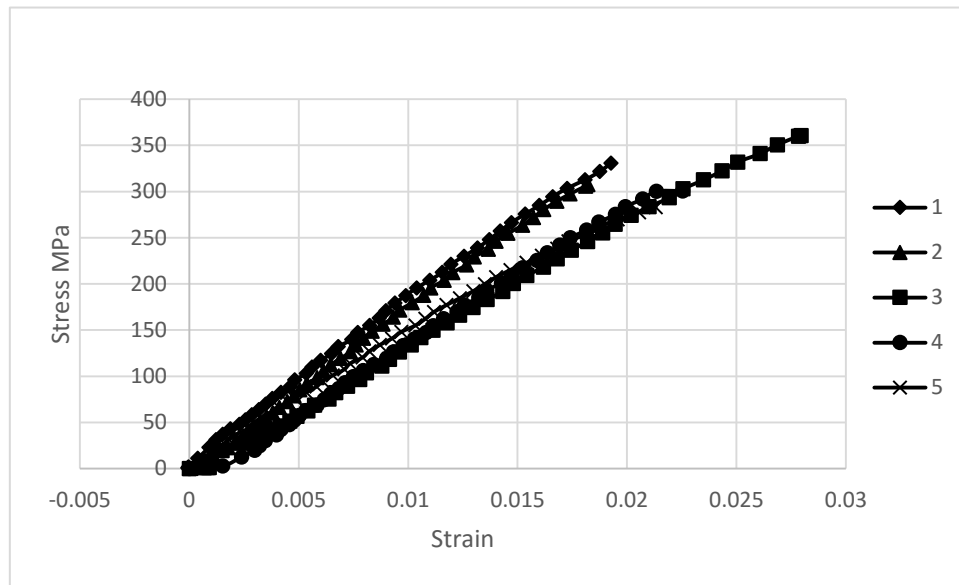


Figure C10: Stress vs Strain of 0.2% PAN reinforced AFC

Table C7: 0.5% PAN Reinforced AFC sample data

<i>Specimen Number</i>	Dimensions		Tensile strength [MPa]	Tensile Modulus [MPa]	Flexural Strength [MPa]	Flexural Modulus [MPa]
	Tensile width [mm]	Flexural Width [mm]				
1	14.8	13.6	328.0	69977.7	207.8	3374211.8
2	13.9	13.7	355.6	21749.5	183.5	1869648.6
3	13.7	13.4	269.6	26814.5	201.6	3073159.6
4	13.0	12.4	292.1	661297.3	178.7	2656853.1
5	12.6	13.5	307.3	33876.6	188.2	2625127.1
Mean	13.6	13.3	310.5	162743.1	191.9	2719800.1
SD	0.9	0.5	33.0	279340.3	12.3	567626.8



Figure C11: 0.5% PAN reinforced AFC Flexural test specimens (before and after)

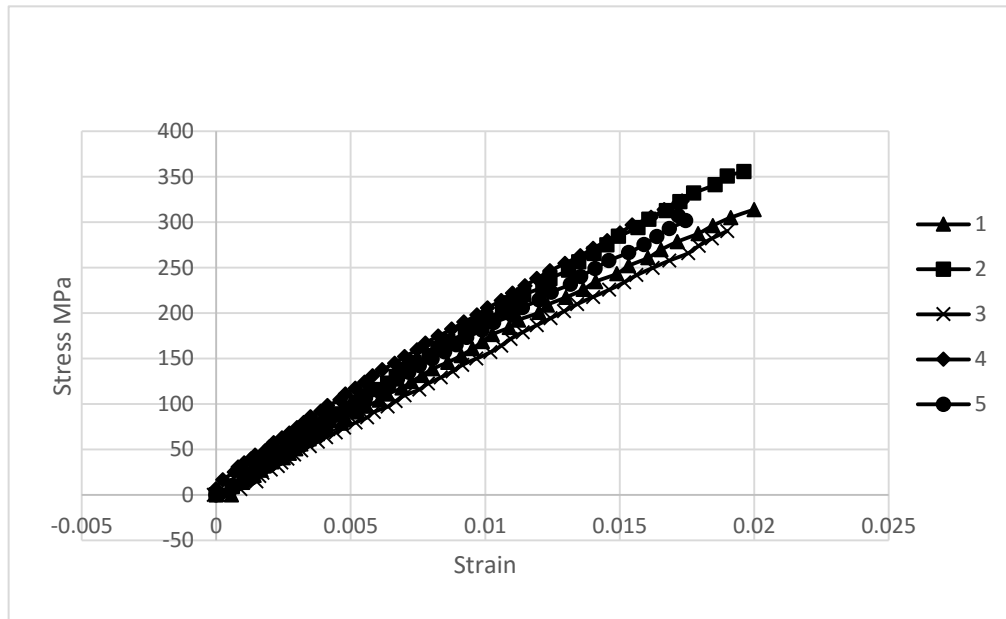


Figure C12: Stress vs Strain of 0.5% PAN reinforced AFC

Table C8: 0.5% CNF doped 0.1% PAN Reinforced AFC sample data

Specimen Number	Dimensions		Tensile strength [MPa]	Tensile Modulus [MPa]	Flexural Strength [MPa]	Flexural Modulus [MPa]
	Tensile width [mm]	Flexural Width [mm]				
1	13.0	12.5	321.7	112947.4	180.9	1849162.9
2	13.5	13.5	268.5	607990.8	245.7	2709245.8
3	12.0	10.8	332.1	10155.9	184.1	2406760.2
4	12.6	12.5	318.3	116145.0	183.8	1937514.6
5	12.8	10.0	335.0	92177.3	164.5	2254596.1
Mean	12.8	11.9	315.1	187883.3	191.8	2231455.9
SD	0.5	1.4	27.0	238746.0	31.2	350749.1



Figure C13: 0.5% CNF doped 0.1% PAN reinforced AFC Tensile test specimens (before and after)

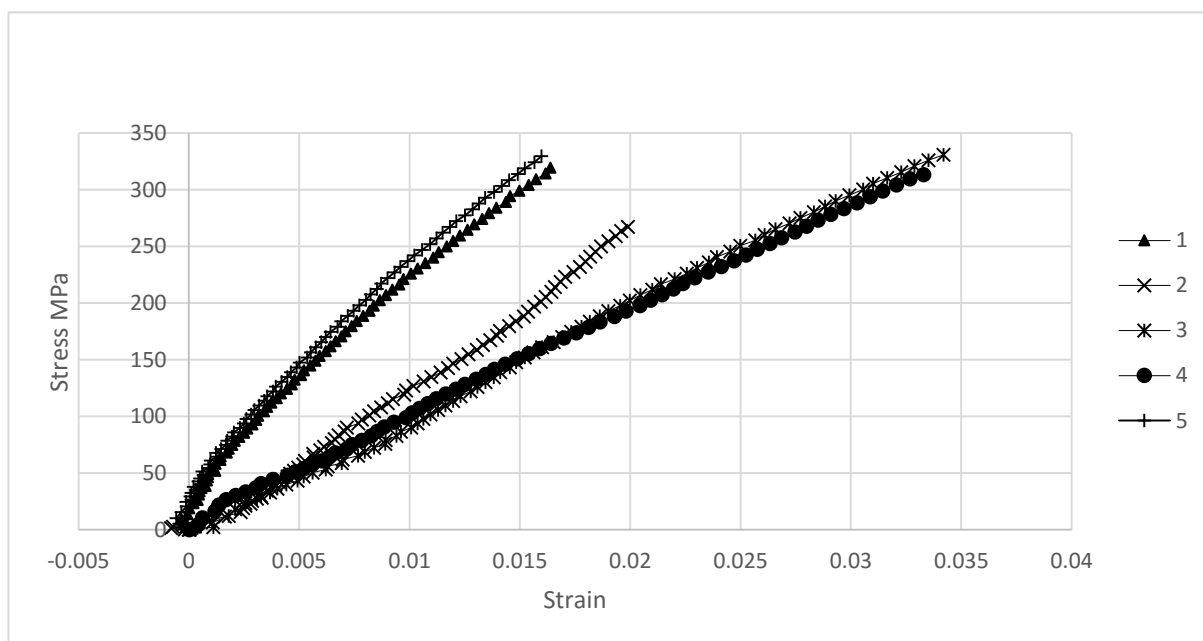


Figure C14: Stress vs Strain of 0.5% CNF doped 0.1% PAN reinforced AFC

Table C9: 0.5% CNF doped 0.2% PAN Reinforced AFC sample data

Specimen Number	Dimensions		Tensile strength [MPa]	Tensile Modulus [MPa]	Flexural Strength [MPa]	Flexural Modulus [MPa]
	Tensile width [mm]	Flexural Width [mm]				
1	13.2	11.3	337.0	318858.6	197.0	1940967.3
2	13.4	12.2	290.6	18408.0	156.8	1097904.3
3	13.1	11.5	307.9	710636.7	166.3	961694.4
4	13.3	12.0	377.2	108809.5	168.5	967013.5
5	13.5	13.0	343.0	29572.8	204.0	1317607.3
Mean	13.3	12.0	331.1	237257.1	178.5	1257037.4
SD	0.2	0.7	33.5	290806.4	20.7	408684.9

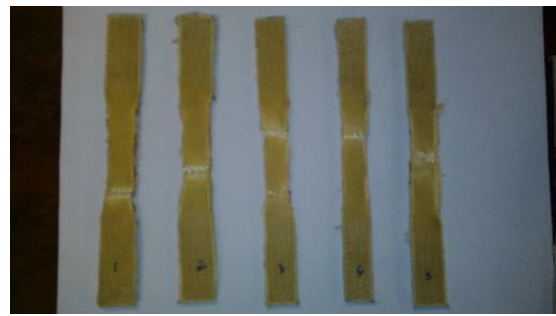


Figure C15: 0.5% CNF doped 0.2% PAN reinforced AFC Tensile test specimens (before and after)

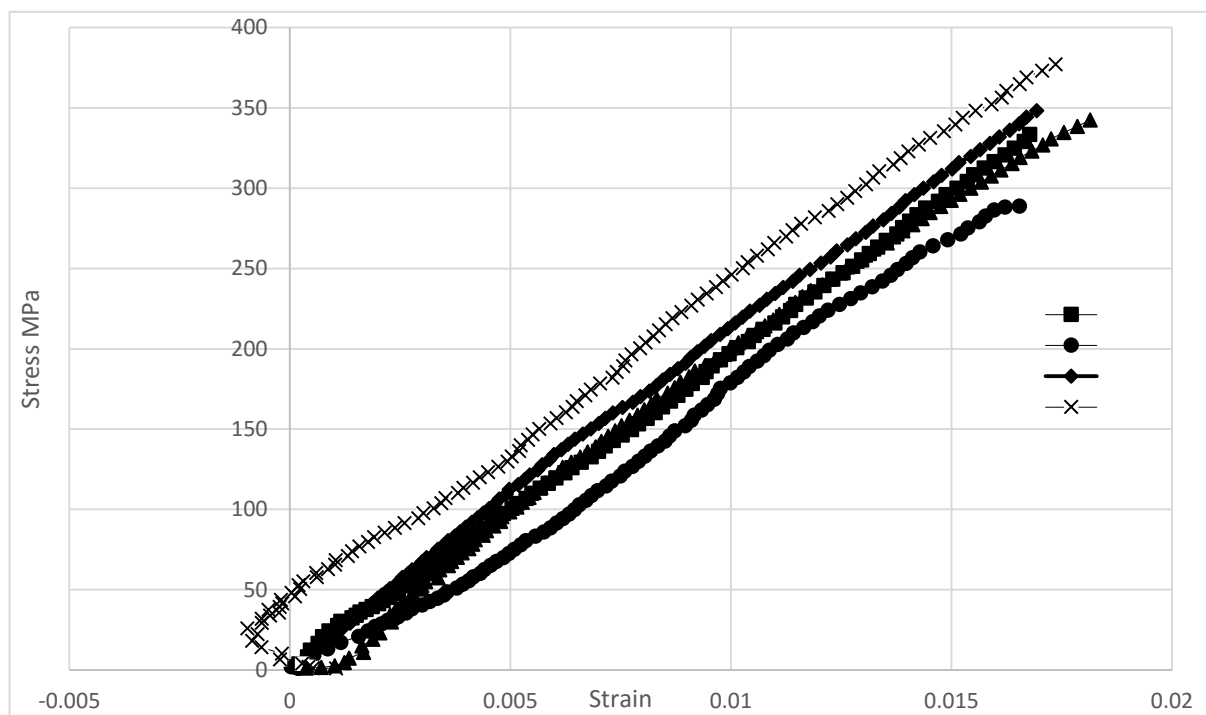


Figure C16: Stress vs Strain of 0.5% CNF doped 0.2% PAN reinforced AFC

Table C10: 0.5%CNF doped 0.5% PAN Reinforced AFC sample data

Specimen Number	Dimensions		Tensile strength [MPa]	Tensile Modulus [MPa]	Flexural Strength [MPa]	Flexural Modulus [MPa]
	Tensile width [mm]	Flexural Width [mm]				
1	14.5	11.3	329.0	78143.9	156.1	1129039.7
2	15.0	12.4	341.5	1607497.7	167.6	1693181.9
3	14.0	12.4	343.7	177523.0	222.6	1397180.9
4	14.4	11.5	351.7	69927.6	243.5	1523710.9
5	14.0	12.4	310.4	36707.3	262.8	1596622.4
Mean	14.4	12.0	335.2	393959.9	210.5	1467947.2
SD	0.4	0.6	16.1	680419.9	46.8	218096.1

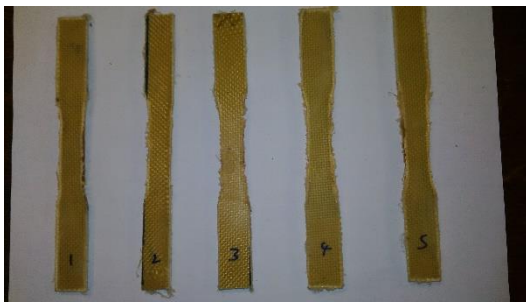


Figure C17: 0.5% CNF doped 0.5% PAN reinforced AFC Tensile test specimens (before and after)

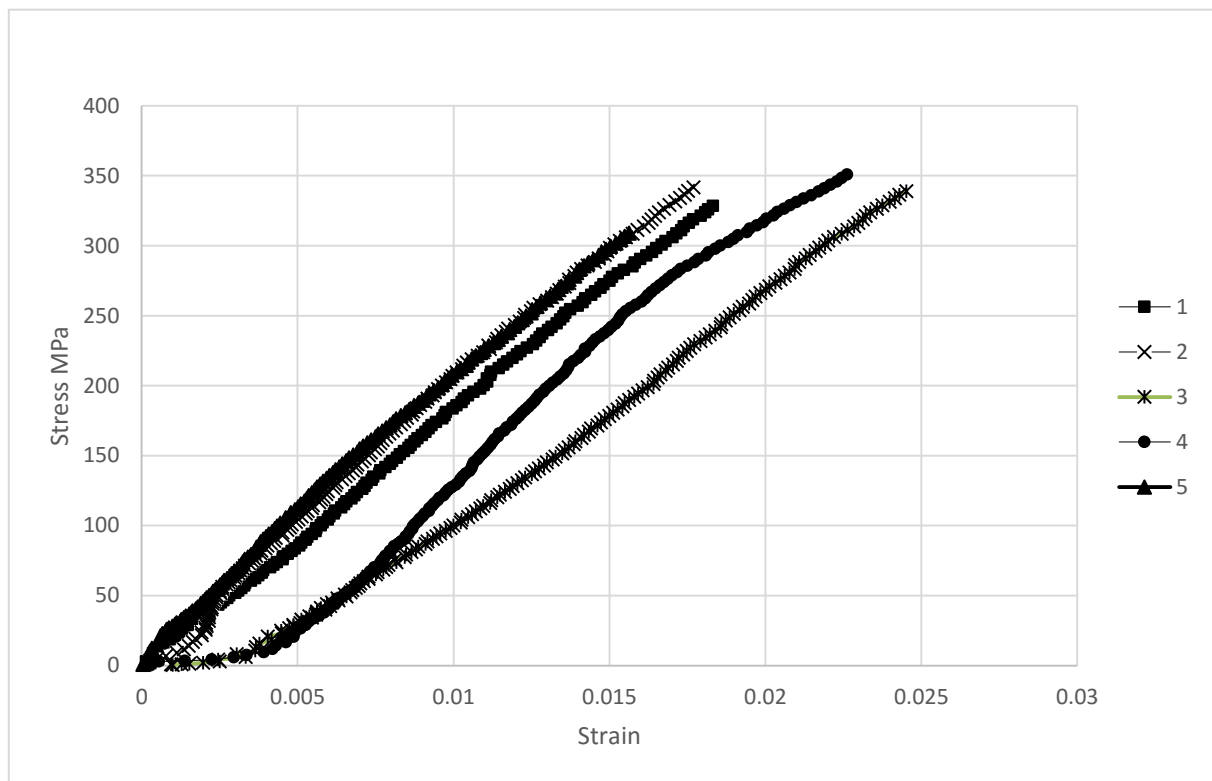


Figure C18: Stress vs Strain of 0.5% CNF doped 0.5% PAN reinforced AFC

Table C11: 1%CNF doped 0.1% PAN Reinforced AFC sample data

Specimen Number	Dimensions		Tensile strength [MPa]	Tensile Modulus [MPa]	Flexural Strength [MPa]	Flexural Modulus [MPa]
	Tensile width [mm]	Flexural Width [mm]				
1	13.0	12.6	345.5	927661.5	197.0	639050.6
2	13.2	11.0	336.0	423335.5	214.6	1350845.7
3	13.3	13.8	348.1	243053.6	195.0	647982.9
4	13.0	11.6	309.2	143897.5	197.8	937112.1
5	13.5	11.5	347.2	316266.8	165.0	670377.8
Mean	13.2	12.1	337.2	410843.0	193.9	849073.8
SD	0.2	1.1	16.4	306437.3	17.9	306596.4



Figure C19: 1% CNF doped 0.1% PAN reinforced AFC Tensile test specimens (before and after)

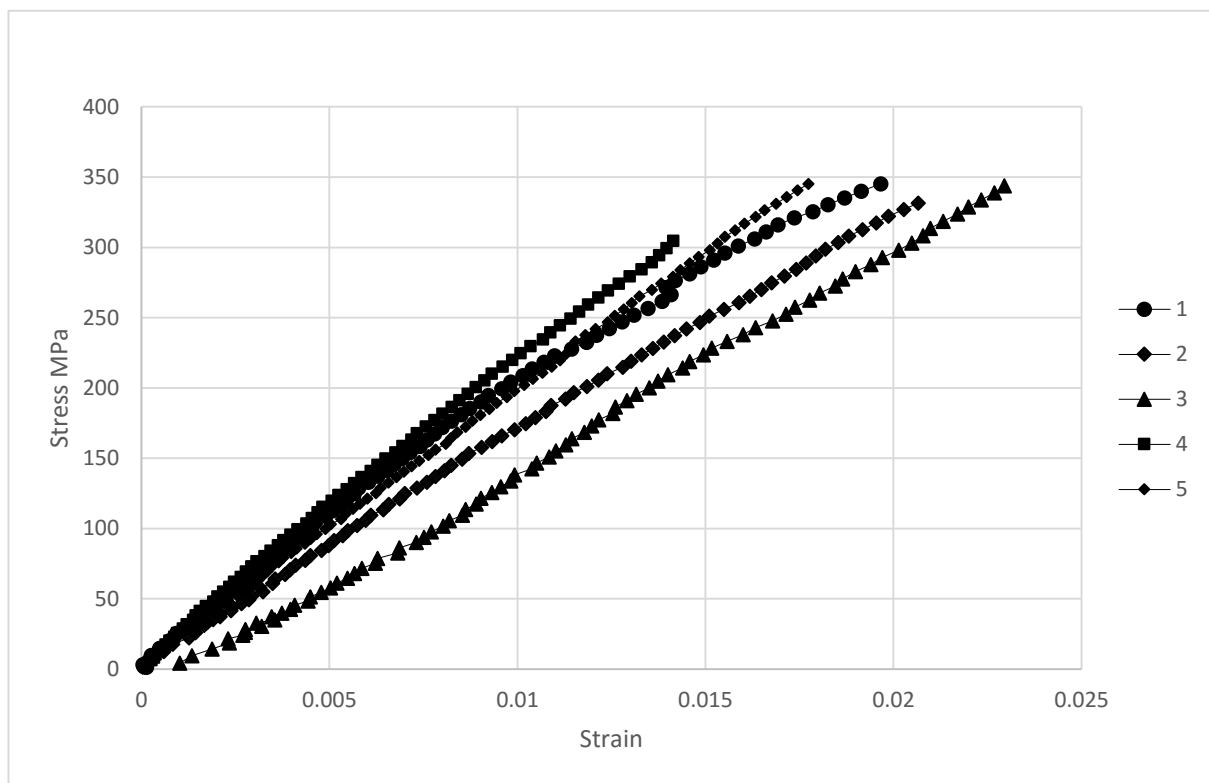


Figure C20: Stress vs Strain of 1% CNF doped 0.1% PAN reinforced AFC

Table C12: 1% CNF doped 0.2% PAN Reinforced AFC sample data

Specimen Number	Dimensions		Tensile strength [MPa]	Tensile Modulus [MPa]	Flexural Strength [MPa]	Flexural Modulus [MPa]
	Tensile width [mm]	Flexural Width [mm]				
1	13.2	13.6	280.4	983369.9	204.6	755257.0
2	13.4	11.7	243.5	29333.1	185.3	706460.9
3	13.0	11.6	317.9	125391.3	190.2	959880.1
4	13.2	12.5	219.3	13375.6	151.6	1351604.8
5	13.4	11.5	235.5	12289.3	126.9	1192332.8
Mean	13.2	12.2	259.3	232751.8	171.7	993107.1
SD	0.2	0.9	39.7	422215.2	31.7	277513.2



Figure C21: 1% CNF doped 0.2% PAN reinforced AFC Tensile test specimens (before and after)

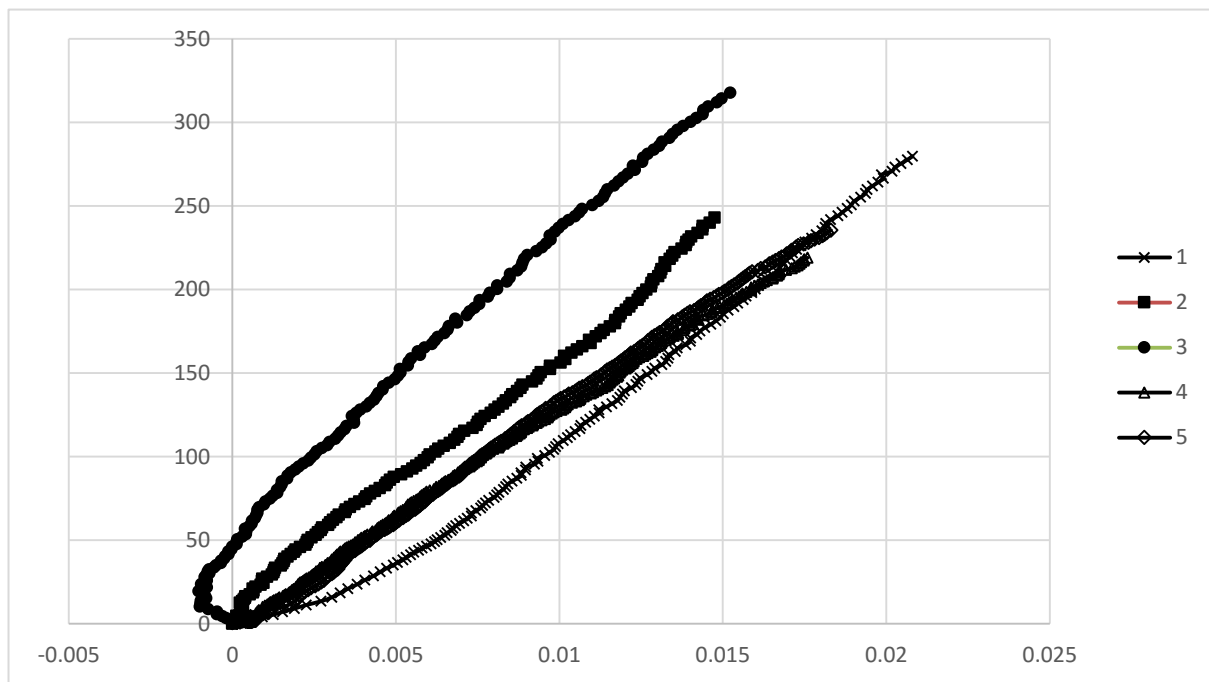


Figure C22: Stress vs Strain of 1% CNF doped 0.2% PAN reinforced AFC

Table C13: 1% CNF doped 0.5% PAN Reinforced AFC sample data

Specimen Number	Dimensions		Tensile strength [MPa]	Tensile Modulus [MPa]	Flexural Strength [MPa]	Flexural Modulus [MPa]
	Tensile width [mm]	Flexural Width [mm]				
1	13.4	11.7	282.7	192037.5	232.3	1436080.7
2	13.4	11.0	279.9	112417.1	199.4	1589623.0
3	14.0	10.7	297.5	23011.1	222.2	1253271.0
4	13.0	13.5	292.0	31400.4	213.7	1175439.4
5	14.0	12.5	297.6	21102.5	208.2	663540.9
Mean	13.6	11.9	289.9	75993.7	215.2	1223591.0
SD	0.4	1.1	8.3	75169.1	12.7	352131.7

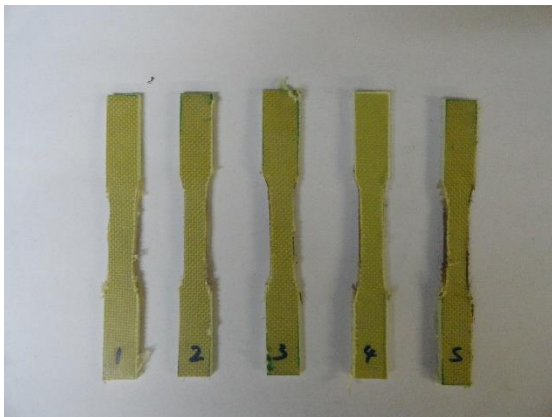


Figure C23: 1% CNF doped 0.5% PAN reinforced AFC Tensile test specimens (before and after)

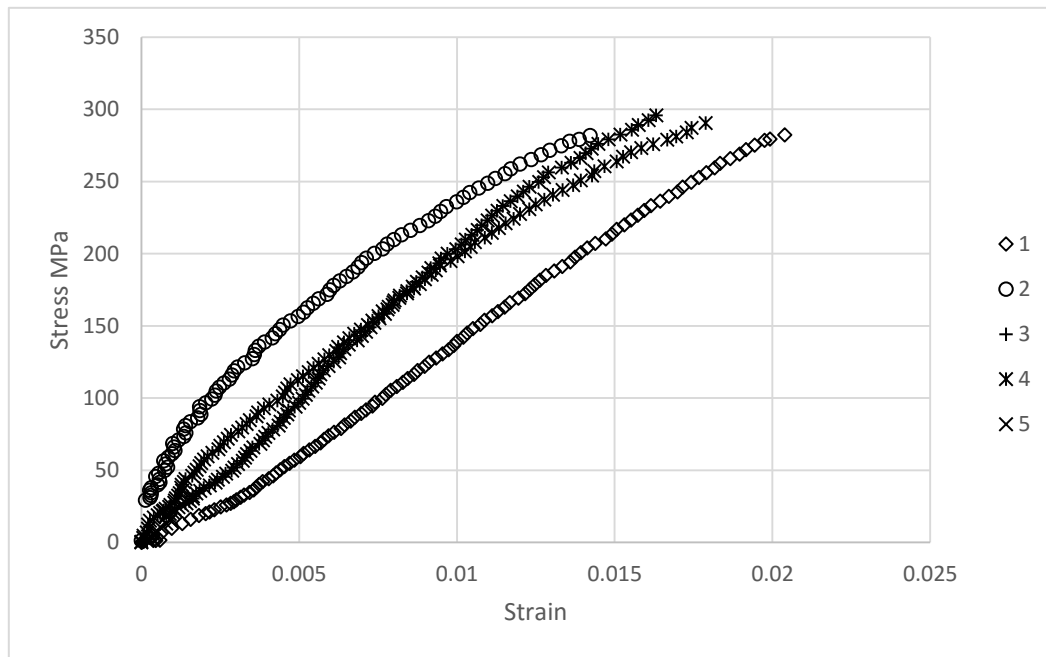


Figure C24: Stress vs Strain of 1% CNF doped 0.5% PAN reinforced AFC