1 CHAPTER 1. INTRODUCTION

1-1 Project Aim

Thunderstorms and lightning strikes are naturally occurring phenomenon whose purpose is to maintain an electrical potential between the earth's surface and the ionosphere. Commercial aircraft generally experience a direct hit with lightning on average once a year. It is therefore important to ensure the protection of composite structures utilised on major aircraft fabrication. The main objective of this project is to explore the potential of creating an electrically conductive composite material through the incorporation of carbon nanographite, carbon nanotubes and other related electrically-conducting fillers. These fillers are to be used as a method of improving the electrical conductivity of a thermoplastic-toughened composite matrix material.

1-2 Background to Study[1-9]

The cure and physical properties of thermoplastic-modified epoxy resins was extensively studied approximately twenty years ago, at the University of Strathclyde, in collaboration with Dr Terry McGrail, recently retired from Cytec Engineered Materials.[1-6] The research led to the development of a range of thermoplastic-modified epoxy resins, which are currently utilised in major aircraft fabrication. They are used specifically in the horizontal tail section and the centre wing box of the Airbus A380 aircraft.[7] An important aspect of these studies is the recognition that the phase behaviour, which contributes to the attractive final properties, is due to the structure of the thermoplastic backbone, the molar mass, functionality and the method used in processing. Using these parameters, the morphology can be tailored by varying either, or both, of the thermoplastic and the epoxy matrix material, to produce molecular composites which have attractive characteristics for aerospace fabrication. The thermoplastic-modified epoxy resins have similar impact properties compared with that of the neat resin.[5,6]

The final composite structure has traditionally been manufactured from standard prepreg. The prepeg process involves combining a fibre reinforcement with a partly cured resin prior to moulding, with cure achieved by the application of heat. This has limitations with regards to the complexity of structure achievable, and is also expensive. A more cost effective alternative, such as Resin Transfer Moulding,[8] (RTM) was, until recently, not a viable alternative due to the high viscosity of the matrix resins prior to cure – caused by the dissolved thermoplastic. The process of RTM generally involves the resin being mixed with a catalyst and then injected into a mould that contains fibres. A static mixer regulates the ratio of resin to catalyst. The mixture is then injected at a low pressure, approximately 5 psi, into the mould, with the reaction time usually in terms of minutes.

Recently, there has been new technology developed by Cytec (PRIFORM™) which, by removing the viscosity constraint, would allow the more attractive RTM route to become more feasible.[7] This new technology is based on the thermoplastic toughening agent used in Cytec's CYCOM® 977-2 prepreg resin system. The technology involves the thermoplastic, rather than being initially dissolved in the epoxy resin, being incorporated into the prepreg in the form of a fibre, which would be co-woven into the carbon fibre preform. This particular resin lends itself to spinning and can be used to produce fibres, which have a controlled solubility within the injected thermosetting resin, see Figure 1-1 and Figure 1-2. It is noted that the process of spinning does not cause any chemical or physical change to the polymer. The process of co-weaving the structural carbon fibres and the soluble fibres can be carried out without any special treatment; moreover, varying the fibre count can create a range of different thermoplastic contents.

Figure 1-1 – Fibres wound on spools ready for weaving[7]

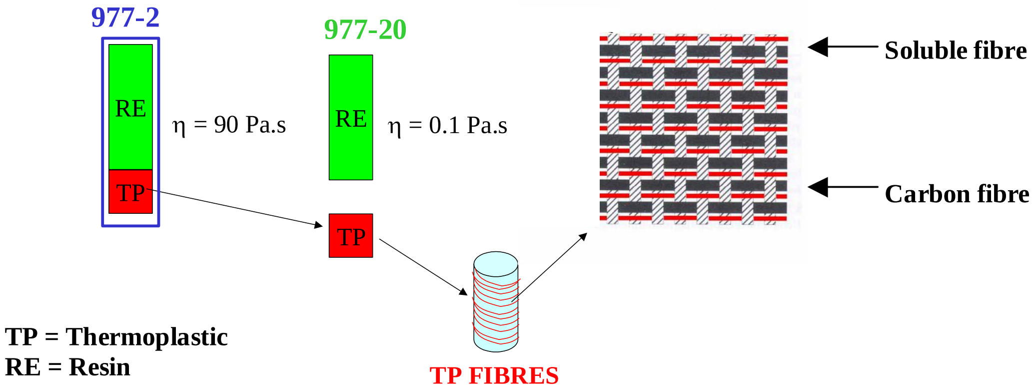


Figure 1-2 – Schematic representation of the soluble fibre technology[7]

During the time of resin infusion, which is carried out at about 60°C, the fibre is completely insoluble in the injected epoxy resin. It is important that the fibre should not be significantly soluble at the low injection temperature, as this would allow for the possibility of the injected resin to carry the polymer from the fibre to the exit port as it progressed through. In reality the fibres' solubility remains dormant until the initial injection of the resin has been completed and the mould's injection and exit ports have been closed.

As the temperature is increased through the cure cycle, the thermoplastic fibre should start to dissolve at about 90°C, and by the time the temperature reaches 120°C, the fibre should have fully dissolved. As the cure temperature is increased, typically to 180°C, the cross-linking reaction proceeds and the dissolved thermoplastic fibre should phase-separate from the epoxy resin, see Figure 1-3. The final matrix morphology and properties are identical to those obtained via the prepreg route.

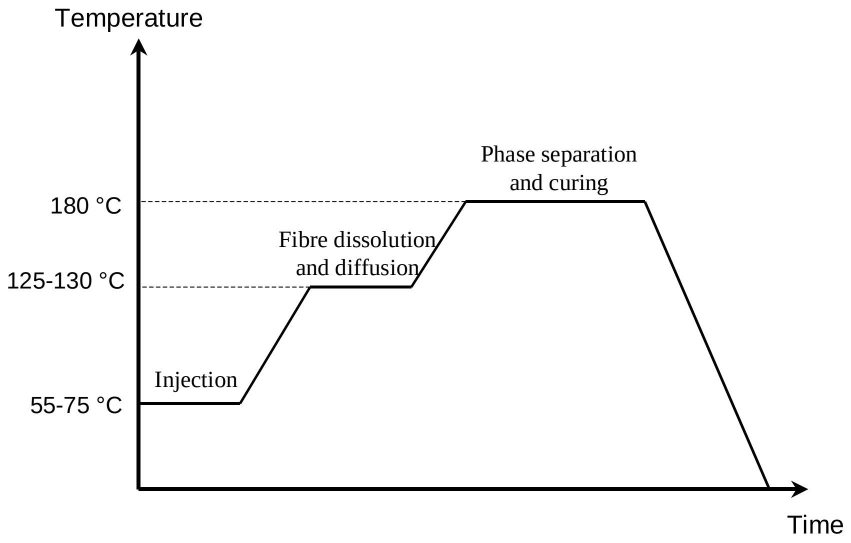


Figure 1-3 – Generic process cycle[7]

In order to explore the possible effects of the incorporation of the nanomaterial and related fillers, it has been proposed to introduce them to the system via their dispersion in the soluble thermoplastic fibres. It is anticipated that these nanomaterials will not only enhance the mechanical properties of the matrix, but also give the additional advantage of electrical conductivity, which is currently achieved in composites by the use of heavy metallic fillers incorporated in to the prepreg. At the moment Nanocyl[9] are manufacturing carbon nanotubes (trade name NC7000) with a view to imparting electrical conductivity to thermoplastics. In this project, the control of the electrical characteristics through the incorporation of conducting media at a nano level is a desirable objective, and forms the main thrust of the research.

1-3 Introduction to Composite Materials[10]

The use of composite materials in structural aerospace applications has increased steadily over the last thirty years. Early usage included doors, control surfaces, and nose radomes. The key advantages of utilising composites include; improved corrosion and fatigue resistance, increased design flexibility, and perhaps most importantly, mass reduction, giving improved fuel efficiency. Another major advantage of composite materials usage is that it can overcome costly drawbacks associated with metallic designs, such as deleterious effects of fatigue and corrosion.

Early composite applications were mainly developed for military purposes, where maximum mechanical performance was the aim. In recent years though, the usage of composites in commercial applications has been, and continues to be, driven by affordability. As a result, product development strategies for use with composite materials, particularly in commercial aerospace applications, have shown a clear shift: from the attainment of mechanical performance at any cost, to the timely delivery of affordable composite manufacturing solutions.

1-4 Composite Concerns[10, 11]

The technological hurdles currently limiting the use of composite materials in commercial transport provides an insight into potential future research and development requirements. For example, components fabricated from composite materials can be costly to produce compared to traditional metallic structures. As cost is such an integral issue, reduced fabrication, tooling, inspection and capital requirements are essential to achieve the aggressive cost targets required for the increased utilisation of composites on future commercial airplanes. There is also a need for universal repair methods to be in place to give airlines the ability to use standard repairs at a variety of locations. These are the major concerns faced when designing composite materials for aerospace applications

1-5 Thermoplastic Usage[11]

Thermoplastic materials have the potential to significantly reduce the cost of composite structures. The benefits of thermoplastics are; indefinite shelf life, rapid non-autoclave processing, temperature resistance, impact resistance and melt fusibility. Continued research into the processing and joining of advanced thermoplastic materials is of course a necessary requirement.

1-6 Commercial PES-based Co-Polymer[12]

The thermoplastic material employed throughout this project is, essentially, a poly(ethersulfone) (PES) / poly(etherethersulfone) (PEES)-based co-polymer, which is end capped to varying extents with amine groups and hydroxyl groups.

Poly(ethersulfone) is a heat-resistant, non-crystalline engineering plastic, having the molecular structure shown in Figure 1-4.

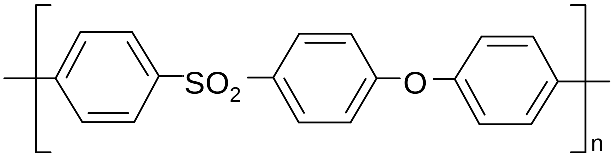


Figure 1-4 – Poly(ethersulfone) structure

It is a tough and rigid resin, similar, at room temperature, to conventional engineering plastics, such as polycarbonate. The greatest characteristic of PES is that it has, by far, better high-temperature properties than conventional engineering plastics. Specifically, PES can have a glass transition temperature (T_g) as high as 280°C, and therefore, it remains in satisfactory condition in long-term continuous use without causing any dimensional change or physical deterioration at temperatures as high as 250°C. It can also be easily processed at temperatures of 380-400°C. The downside is that composite parts based on PES do not have as good a solvent resistance as those based on a semicrystalline polymer such as poly(etheretherketone) (PEEK). That said, there is a downside to the use of PEEK, in that it has a lower T_g of 143°C, and therefore, due to the aerospace engineer's requirement of a minimum of about 30°C margin between the upper use temperature and the T_g, it is limited to a maximum use temperature of about 120°C.

1-7 Thermoplastic Dissolved Thermosets[1-7, 11]

Thermoplastic modification of thermoset resin material has been shown to lead to significant improvements in the impact and fracture properties of matrices used in composite manufacture. Highly cross-linked thermosets have a tendency towards embrittlement, which has restricted their use in applications requiring high strength or resistance to damage induced by thermal cycling – this has led to interest in toughening these materials. Figure 1-5 demonstrates the difference in viscosity between an epoxy system without added thermoplastic, and a standard toughened system used in aerospace primary structures.

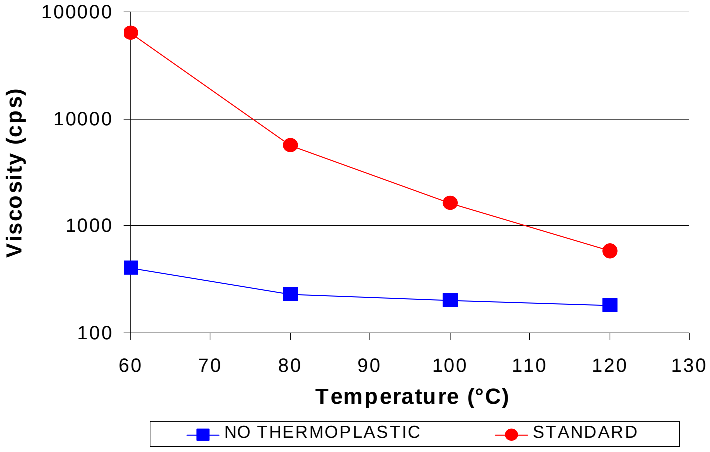


Figure 1-5 – Comparative viscosities of a resin system without thermoplastic with that of a standard thermoplastic toughened system[7]

Thermoset-based resins are, nonetheless, preferred for aerospace applications because of their ease of fabrication, low temperature cure, high tack and drape, which allows complex shapes to be readily fabricated.

Liquid carbonyl-terminated butadiene acrylonitrile copolymers (CTBN) are widely used with epoxy resins to generate rubber-toughened materials, but they are subject to degradation at relatively low temperatures. During the curing process, the CTBN rubber phase, which is initially compatible with the components of the resin, separates into micrometre-size domains. The CTBN composite materials have the disadvantage that small amounts of dissolved CTBN molecules reduce the glass transition temperature (T_g) and modulus of the matrix, which leads to poor performance in hot and wet conditions when compared to the unmodified resin.

In comparison, linear, high molecular mass thermoplastics are inherently tough and have been shown to reduce the brittleness of epoxy resins without degrading other properties. Thermosets and thermoplastics are generally chosen to be thermodynamically compatible, although increasing the molecular mass of the thermoset increases phase-separation during the curing process.

Whereas CTBN tends to form a relatively simple particulate morphology, the thermoplastic-modified epoxy resins may exist as homogeneous, particulate, co-continuous, or phase-inverted morphologies. The co-continuous phase is of particular interest because of its potential in property enhancement, barrier property improvement, static charge control, and also for applications containing moisture-sensitive products. Co-continuous polymers form what appears like a roadmap of many intertwining streets, where the streets represent one polymer and the areas other than streets represent one or more polymer(s). There are two basic definitions available to describe co-continuous polymers; the first explains the phenomenon as at least two continuous structures within the same volume that subsist with one another. The other definition describes the morphology as one in which at least a part of each phase forms a coherent continuous structure that permeates the whole volume. In the case of this project the thermoplastic-modified epoxy resin exists as a co-continuous phase.

1-8 Lightning Strikes[13-17]

Thunderstorms and lightning are part of a global electric circuit; their purpose is to maintain an electric potential between the earth’s surface and the ionosphere, which is a band of charged particles 80 to 120 miles above the Earth's surface. The total number of thunderstorms occurring at any given time around the world is approximately 2000, with 40-100 discharges occurring each second; the number varies depending upon where in the world the measurement is taking place, being highest about the equatorial belt and decreasing towards the poles. To a passenger flying on an aircraft this can be a terrifying statistic, see Figure 1-6. Lightning-related fatality, injury, and damage reports in the United States were summarised for 36 years starting in 1959; it was found that there were 3239 deaths and 9818 injuries reportedly caused by lightning during this period.[15]

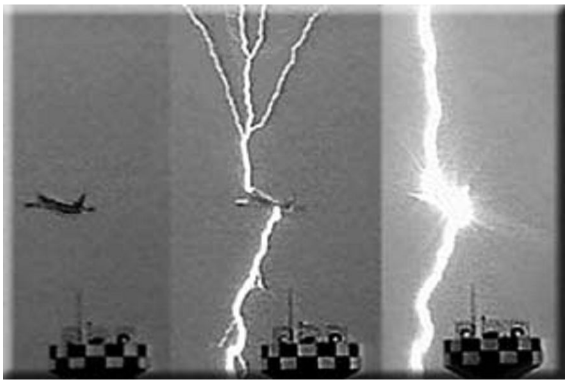


Figure 1-6 – Plane being struck by lightning[16]

Commercial aircraft experience a direct hit with lightning, on average, once a year.[17] The last confirmed commercial plane crash in America directly attributed to lightning occurred in 1967, when lightning caused a catastrophic fuel tank explosion.[17] What is more likely to happen is that the damage is confined to burn marks on the aircraft's skin, and to the trailing edges of wings or tail surfaces. This minimal damage experienced by most aircraft can be attributed to the widespread use of aluminium in construction; it is of course an excellent electrical conductor.

There is no doubt that lightning is hazardous for aircraft, and that their construction must include provisions for lightning protection. Although there is no known technique to prevent lightning strikes from occurring, lightning effects can be minimised with appropriate design technology.

When lightning first strikes a plane, it will initially attach to an extremity such as a nose or wing tip. As the aircraft flies through the lightning, the lightning reattaches itself to the fuselage at other locations while the plane is in the electric circuit between the regions of opposite polarity. Most of the current will pass through the conductive exterior skin, and then exit through an extremity, such as the tail. Lightning currents, therefore, do not usually enter critical systems inside the plane, such as in-flight computers, and travellers are protected by the conductive aluminium skin.

As previously mentioned, the expanding use of lightweight, performance-enhancing composite materials for aircraft structures have resulted in new challenges to ensure adequate lightning protection in the design of new airframes and control systems. This is of course in order to maintain today’s excellent lightning safety record. As composite materials are relatively poor electrical conductors, advanced techniques such as metallization of exterior surfaces or fine metal wires co-woven into carbon fibre composite skins, are required to provide adequate conductivity for lightning currents. The latter approach will increase the mass of the structure and decrease the mass advantage of using a fibre composite material.

1-9 Current Production[14, 18]

Composite aircraft structures are often designed with a series of outer conductive layers for protection in the event of a lightning strike. The idea is to provide a highly conductive path at the outermost surface of the structure, so that if hit, the high-voltage energy is quickly dissipated and routed overboard, rather than inboard into the structure.

Improper routing of this energy could result in the loss of flight-critical structures, or, in the worst-case scenario, ignition of the fuel onboard. For this reason, repairs to structures requiring lightning strike protection (LSP) must be done properly to ensure the conductive path over the repaired area is regained.

Common LSP materials include aluminium flame-sprayed surfaces, copper or aluminium mesh, or aluminium-coated glass or nickel-coated carbon fabric, laid-up as the outermost ply in the panel during manufacturing. Typically, conductive primer and paint products are used with the LSP layer to further enhance surface conductivity. The

LSP repair material may not be the same as the original material used, and usually a perforated/expanded foil or mesh is prescribed for the repair, even if the original material was a flame-sprayed metal or a metal-coated fabric layer. This will be an important area of future investigation with regard to the novel system being developed in this project.

1-10 Nanographite

1-10-1 Introduction[19-27]

Blending polymers with conducting fillers, such as natural graphite flake, carbon black and metal powders in order to prepare electrically conducting composites has been investigated over the past few decades.[19-21]

Among the various conducting fillers which are available, naturally abundant graphite, which possesses a good electrical conductivity of about 10^4 S/cm at ambient temperature, has been widely used.[22] In most cases, relatively large quantities of graphite were needed to reach the critical percolation value, as the graphite particle size is at micrometre and millimetre scales. Unfortunately, these very high loading levels – typically between 15 and 20 wt%[23] or more for fibres and platelets in the micrometre range – harm the composites' mechanical and thermal properties, and can make processing difficult. It therefore follows that in order to develop a conducting network within the polymer matrix with as small a concentration of filler as possible, one could consider the use of nanoscale fillers.

In contrast to traditional fillers, nanofillers i.e. exfoliated clays, are expected to be effective at a loading level of under 5 wt%, thereby introducing only a minor increase in the cost of the material.[24] Moreover, nanofillers provide significant improvement in modulus, thermal and dimensional stability, surface hardness and barrier properties. The majority of research on nanocomposites is focused around clay nanocomposites, which are produced by incorporating nanometer-sized clay particles into polymers. However, clay nanocomposites lack the electrical conductivity, which is imperative to this study.

When comparing graphite with clay it is seen that graphite has a much higher tensile strength of approximately 10-20 GPa, compared with approximately 1 GPa for exfoliated clay.[25] Graphite also has excellent electrical and thermal conductivity and when compared with clay, graphite has better mechanical and thermal properties. It also has a lower density. This led to the principles of the clay nano-reinforcement concept being applied to graphite – as it also has a similar layer structure – in order to produce graphite-polymer nanocomposites. Montmorillonite, once it is homogeneously dispersed in a polymer matrix greatly improves the properties of the polymer. If graphite could be dispersed in a polymer matrix, much like a layered silicate,[26] it would seem that a polymer-graphite composite with a high electrical conductivity at low graphite loadings could be prepared. However, although much success has been achieved in the polymer layered silicate nanocomposites, nanocomposites of polymer with graphite have rarely been reported. This is a result of the difficulty of preparing graphite nanosheets or nanoparticles.

In addition, the lower cost of crystalline graphite (~ £1 per pound) and less than (~£4 per pound) for the graphite nanoplatelets, compared with other conductive fillers such as carbon nanotubes (~ £50 per gram for MWNT), vapour grown carbon fibres (~ £35 per pound) and carbon fibres (~ £3 per pound), makes graphite a more commercially viable alternative.[27]

Graphite also has superior mechanical properties when compared with a material such as carbon black. This makes graphite a more realistic choice for commercial applications requiring both mechanical strength and electrical conductivity in the final product. The key point in utilising the superior properties predicted is to achieve sufficient exfoliation, resulting in separation of the platelets into a single, or a few, layers of graphene sheet(s). It may also be beneficial to treat the surface in order to improve the adhesion between the graphite platelets and the polymer matrix, creating the desired result of strengthening the composite material.

1-10-2 Nanographite Structure[28]

Each carbon atom in graphite is covalently bonded to three other surrounding carbon atoms. The flat sheets of atoms are bonded into hexagonal structures. Carbon atoms within a particular layer are bonded covalently, while layers are bound by much weaker Van der Waal's forces. A graphite platelet has dimensions of ~ 1 nm x 100 nm.

The unit cell dimensions are a = 0.2456 nm and b = 0.6694 nm, see Figure 1-7. In the bulk form of carbon the C-C bond length is 0.1418 nm, and the interlayer spacing is $b/2$ = 0.3347 nm.

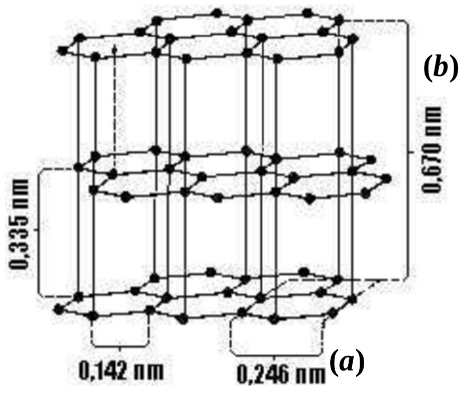


Figure 1-7 - graphite structure[28]

Each carbon atom possesses an sp^2 orbital hybridisation. The pi orbital electrons, which are delocalised across the hexagonal atomic sheets of carbon, contribute to the conductivity. In an oriented piece of graphite, conductivity parallel to the sheets is greater than the conductivity perpendicular.

1-10-3 Exfoliation of Graphite[29, 30]

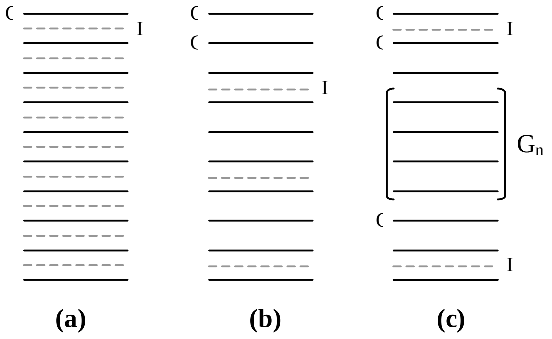
As previously discussed, graphite is a form of carbon where the carbon atoms are bonded in layers, with weaker Van der Waal's forces between the layers. These weak interplanar forces allow intercalation by the addition of atoms or molecules, which can occupy the spaces between the carbon layers. In doing this, the interplanar spacing is increased. To achieve intercalation it is usual to immerse the graphite flakes in concentrated nitric acid and sulfuric acid, which are used as chemical oxidisers, for a day or more.[29, 30] The reaction taking place can be seen in Figure 1-8.

$$n(\text{graphite}) + n\text{H}_2\text{SO}_4 + n/2[\text{O}] \rightarrow n[\text{graphite}^{\cdot}\text{HSO}_4] + n/2\text{H}_2\text{O}$$

$$([\text{O}] = \text{oxidant}; [\text{graphite}^{\cdot}\text{HSO}_4] = \text{GIC})$$

Figure 1-8 – Intercalation of acid groups into interplanar spacing of graphite

The resulting material, known as graphite intercalated compound (GIC) or intercalated graphite, consists of carbon layers and intercalated layers which are stacked on top of one another in a periodical fashion. This stacking can be in different forms; stage 1, (Figure 1-9(a)) stage 2, (Figure 1-9(b)) or stage n, (Figure 1-9(c)) the difference is essentially a random process dependent upon the ease of intercalation of the acid molecules.



(a) **(b)** **(c)**

Figure 1-9 – Schematic illustration of the stage of GIC: solid line – graphite layer; dotted line – intercalated compound

When the GIC is heated to a sufficiently high temperature – approximately 1050°C – this causes expansion to occur. The chemicals inside the graphite decompose forcing the graphite layers apart, see Figure 1-10. The exfoliation process will introduce into the graphite structure a small number of chemical functions. Sulfuric/Nitric acid mixes have the ability to oxidise the graphite and hence create OH and C=O functions, which will create points from which, and to which, charge migration can occur. The acid used in the intercalation process is lost during the high temperature thermal cycle.

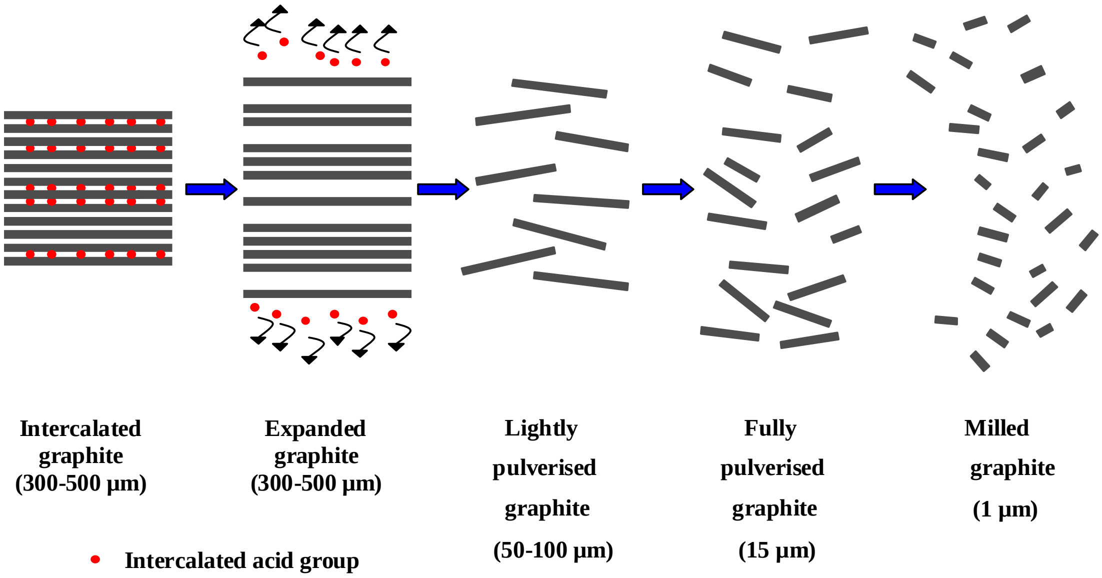


Figure 1-10 – Expansion, pulverisation and milling of graphite

This expansion means that there is a sudden increase in the dimension perpendicular to the carbon layers of the intercalated material. The graphite flakes are expanded up to hundreds of times along the c-axis, with the original graphite flake, of 20 μm thickness expanding up to 2,000-20,000 μm. The density is decreased significantly upon achieving expansion, and more significantly, perhaps, the electrical conductivity has been reported not to be significantly affected.[30]

The expanded graphite, which has a structure of parallel boards, collapses and deforms to form a vermicular or wormlike structure, which has many pores of different sizes ranging from 10 nm to 10 μm. The thickness of the graphite sheets at this stage has been reported to range from 100 to 400 nm.[30] According to the mechanism for the formation of the GIC and expanded graphite, the thickness of sheets in completely exfoliated graphite could, in principal, be equal in thickness to a single carbon layer, when the GIC precursor is in the form of stage 1 (Figure 1-9(a)).

By applying an ultrasonic bath, the expanded graphite worms, or rods, can be pulverized into flakes. The diameter of these flakes has been reported to be approximately 5-20 μm,[30] though it can be significantly reduced by ball-milling, which produces flakes with a length of less than 1μm.

1-10-4 Polymerisation[23, 31]

It is noted that there are few reactive ion groups on the graphite layers; it is therefore difficult to prepare the polymer/graphite nanocomposite via ion exchange reaction in order to intercalate the monomers into the graphite sub-layers. The expanded graphite does however contain abundant multi-pores, with the average pore size being approximately 2 μm. The monomer can therefore be introduced into these pores to be followed by polymerisation. This is a result of the multi-pores facilitating physical and chemical absorption between graphite and the polymer solution

It has been reported that low volume fractions of expanded graphite have been able to reach the percolation threshold of conductivity in nylon 6/graphite and PS/graphite. In these nanocomposites, the monomer was first introduced into the pores of the expanded graphite to be followed by polymerisation.[23, 31]

1-11 Carbon Nanotubes

1-11-1 Introduction

Since their ‘discovery’ in 1991 by Iijima,[32] carbon nanotubes have been of great interest, both from a fundamental point of view, and also for future applications. Progress in the chemistry and physics of carbon nanotubes has been explosive in recent years, with over 24,000 papers written on the subject (source – Sciencedirect), with more published each month. The most important features of the nanotube structures are their electronic, mechanical, magnetic, optical and chemical characteristics, which open ways to future applications. For commercial use though, large quantities of purified nanotubes are necessary.

1-11-2 Nanotube Structure[33-42]

Carbon nanotubes are generally considered to belong to the fullerine family, which also contains Buckminsterfullerine. Whereas Buckminsterfullerine is spherical in shape, a nanotube is cylindrical, with at least one end typically capped with a hemisphere of the buckyball structure. The caps are more reactive than the sidewalls and prone to oxidation and addition reactions. The sidewalls are a little less strained and more inert.

Their name is derived from their size, since the diameter of a single-walled carbon nanotube (SWNT) can be of the order of a few nanometres, while they can be up to several centimetres in length, although the length is more typically measured in terms of tens of micrometres. This gives them one of the highest aspect ratios known. Carbon nanotubes come in two classifications: single-walled and multi-walled. SWNTs consist of one cylinder, whereas multi-wall nanotubes (MWNT) comprise several (7 to 20 usually) concentric graphene cylinders, see Figure 1-11 and Figure 1-12. Each nanotube is a single molecule made up of a hexagonal array of covalently bonded carbon atoms.

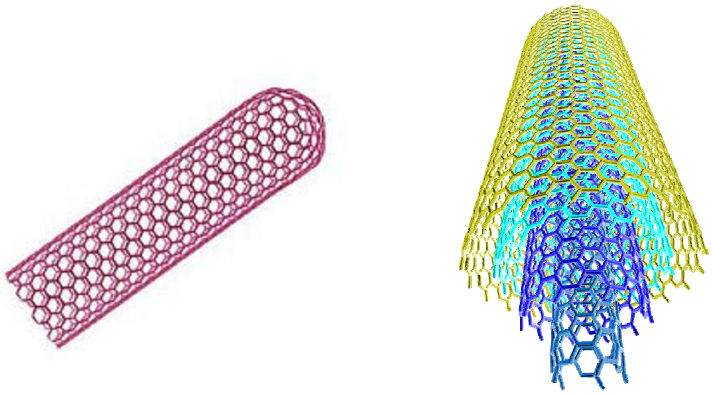


Figure 1-11 – Diagram of SWNT and MWNT[38,39]

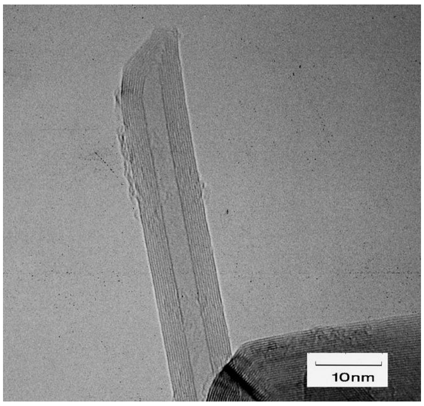


Figure 1-12 - TEM Image of MWNTs[40]

The structure of a SWNT can be conceptualized by rolling a one-atom-thick layer of graphite – known as graphene – into a seamless cylinder. The graphite sheet may be rolled up in many ways to form a SWNT, see Figure 1-13. This rolling breaks the symmetry of the planar system and imposes a distinct direction with respect to the hexagonal lattice, the axial direction. Depending on the relationship between this axial direction and the unit vectors describing the hexagonal lattice, the tube can be metallic, or semi-conducting. Looking to Figure 1-14, if the part of the graphene sheet between the two red lines were cut out and rolled into a cylinder**,** it can be seen that the vector v which maps an atom from the left hand border onto an atom on the right hand border line the result is an integer multiple of the 2 graphite basis vectors ***a1*** and ***a2***, therefore $v = n\text{a1} + m\boldsymbol{a2}$. The n and m terms are integers, and nanotubes which are constructed in this way are called (**n,m**) nanotubes.

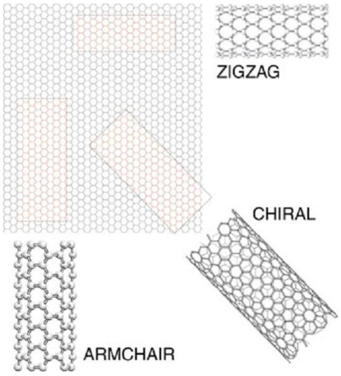


Figure 1-13 - Different types of possible nanotubes[41]

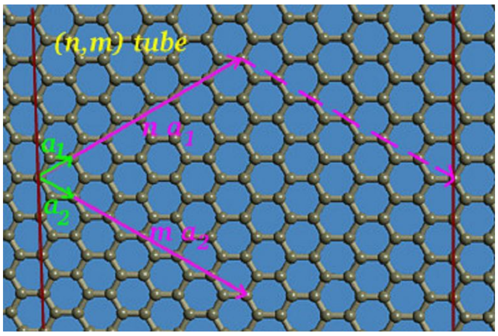


Figure 1-14 – Graphite planar structure[42]

Due to the unique structure and symmetry of the graphene sheet, the structure of a nanotube strongly affects its electrical properties. For a given (n,m) nanotube, if 2n +m =3q (where q is an integer), then the nanotube is metallic, otherwise the nanotube is a semi-conductor. Thus all armchair (n=m) nanotubes are metallic, and nanotubes (5,0), (6,4) etc. are semi-conducting. In theory, metallic nanotubes have the potential to achieve electrical current densities (defined as the current per unit area) of more than 1000 times that of metals such as silver and copper. Within a sample showing no preference for specific chiralities, one third of tubes are expected to be metallic, and the remaining two thirds are expected to be semi-conducting. Recent efforts have been made to separate conductive and semi-conducting nanotubes, but this process does not provide practical quantities of nanotubes for realistic studies of physical properties of composites.

Nanotubes are composed entirely of sp^2 bonds, very similar to graphite, and, as previously discussed, can be thought of as a single layer of graphite rolled-up into a cylinder. Sp^2 bonds are stronger than the sp^3 bonds found in diamond, and it is this bonding structure which provides them with their unique strength. In 2000, a single-wall nanotube rope was tested to have a tensile strength of 3.6 GPa**[33]** The author went one step further and surmised the strength of a SWNT to be 22.2 GPa, on the basis of the rules of mixtures. This led the author to conclude that the excellent mechanical properties of the tubes make them an ideal reinforcement agent for high performance composite material. In comparison, high carbon steel has a tensile strength of approximately 1 GPa.

Under excessive tensile strength, the tubes will undergo plastic deformation, which means a permanent deformation. A typical carbon nanotube begins to deform at strains of approximately 5 %, and can be typically stretched 15 % longer than its original length before breaking. A study carried out by Huang *et al*.**[34]** found that when a SWNT was heated to more than 1982°C, the tube was able to stretch to more than 280 % of its original length before breaking. This phenomenon of super-elongation was found to be due to full plastic deformation occurring. Obviously, this knowledge could prove useful in helping to strengthen nanocomposites performing at high temperatures. As an aside, CNTs are much less strong under compression, due to the fact that they are hollow and tend to undergo buckling when placed under compressive, torsional or bending stress.

Another reason why carbon nanotubes are ideal to be used as reinforcement for use in composites is due to their high Young's, or elastic, modulus (E). This value is normally taken as approximately 1 TPa, and this is applied to all CNTs. Their Young's modulus has been quoted as being five times that of steel, which makes them one of the strongest objects in nature. In 2005, Lukic *et al*.**[35]** further investigated this area and in doing so demonstrated that MWNTs produced by CVD have a much lower modulus, less than 100 GPa. They found this to be independent of growth conditions, and also found that additional high temperature annealing failed to improve the elastic property. The authors attributed the lack of performance to the presence of structural defects present as a result of the CVD method.

1-11-3 Nanotube Properties[36, 37]

Understanding the electronic properties of the graphene sheet helps to understand the electronic properties of carbon nanotubes. Graphene is a zero-gap semiconductor; for most directions in the graphene sheet, there is a bandgap, and electrons are not free to flow along these directions unless they are given extra energy. However, in certain special directions graphene is metallic, and electrons flow easily along those directions. This property is not obvious in bulk graphite, since there is always a conducting metallic path, which can connect any two points, and hence graphite conducts electricity.

However, when graphene is rolled up to make the nanotube, a special direction is selected, the direction along the axis of the nanotube. Sometimes this is a metallic direction, and sometimes it is semi-conducting, so some nanotubes are metals, and others are semi-conductors, with both types being made from the same all-carbon system.

A limitation of CNTs is that their electrical properties are sensitive to the surrounding environment, to the extent that their physical and chemical properties can be altered. The process of purification or functionalisation of the CNTs can lead to the introduction of defects, which can in turn lead to changes in the electronic properties of the tubes. A common result is lowered conductivity through the defected region of the tube.

1-11-4 Practical Considerations[43-45]

The inclusion of conducting nanoparticles in a host polymer matrix is expected to induce an electrical conductivity at very low filler contents. The electrical conductivity depends upon achieving percolated pathways of conductive particles, with an onset of conductivity occurring at a certain, critical filler level – termed the percolation threshold.

For spherical objects this has been quoted as ≈ 15 % volume.[43] To account for the high aspect ratios occurring in rod-shaped particles an advanced percolation theory has been developed. A percolation threshold of less than 0.005 wt% has been quoted for MWNTs, central to this low threshold is the ability to control the re-agglomeration of the CNTs.[44] Sandler *et al.*[45] found that aligned multi-wall nanotubes formed by an injection CVD process could be dispersed in an epoxy matrix and used as conductive fillers. They saw that sufficient conductivity for anti-static applications could be achieved at a loading level of ≈ 0.005 wt%.

MWNTs, rather than SWNTs have been used predominately due to their lower cost, better availability and easier dispersibility, though SWNTs do have a potentially higher intrinsic electrical and thermal conductivity which could potentially allow further reduction in the filler content required for property enhancement.

1-11-5 Synthesis[46]

Production of Buckminster fullerines and nanotubes does not only occur in high-tech laboratories – they can be formed in places such as candle flames. These naturally occurring varieties, due to the highly uncontrolled environment in which they are produced, are highly irregular in size and quality, lacking the high degree of uniformity necessary to meet the demands of both research and industry.

There are four main methods of manufacturing both SWNTs and MWNTs in sizeable quantities – arc-discharge, laser ablation, high-pressure carbon monoxide and chemical vapour deposition (CVD). All known preparations for nanotubes give mixtures of nanotube chiralities, diameters, and lengths. Of the techniques CVD is the most promising as it has the best price/unit ratio. The reaction generally involves reacting a carbon containing gas, such as acetylene, with a metal catalyst particle, such as iron, at temperatures in excess of 600°C. It is noted that this was the production method which was employed by the company (Swan), who supplied the nanotubes for this project.

1-11-6 Growth Mechanisms

Despite a large body of literature on the subject, no definitive model for the growth mechanism of carbon nanotubes has evolved, owing to a lack of consistent experimental data.[47-48] In order to achieve controllable growth of high quality CNTs with well-defined characteristics, it is imperative to understand their growth method, and in doing so also understand what controls their size, the number of shells formed (in the case of MWNTs), their helicity, and their structure during synthesis. This question, though, still remains open for discussion and there are several theories on the exact growth mechanism(s) of the tubes.

Firstly, there is a fundamental difference in the production of SWNTs and MWNTs, in that transition metal catalysts are necessary in order to produce SWNTs, but are not always required in order to produce MWNTs. This difference suggests that different growth mechanisms may be in operation for each type of CNT. Furthermore, the exact role of the catalyst in the growth remains unclear.[49] One could say that the role of the catalyst is to decompose the hydrogen molecules, which is surely true, although its role in decomposition is not responsible for the ability to form CNTs – it has been found that hydrocarbons can decompose without necessarily forming nanotubes. It therefore seems reasonable that the role of the catalyst could prove to be quite a complex one. A number of papers have been published in which the catalyst is seen as a growth point for the nanotubes and implies that the growth involves bonding between the metal and the nanotube.

Looking to carbon fibres it is suggested that growth occurs via precipitation of dissolved carbon from a moving catalyst particle surface.[50] Termination occurs when the catalyst is poisoned by impurities, or after formation of a stable metal carbide. A notable difference with regard to carbon fibres and carbon nanotubes is that the tips of MWNTs are frequently observed to be closed, in contrast to the open, or metal particle terminated ends of catalyst grown carbon fibres. This leads into the question of whether CNTs are open or closed during growth. The first method assumes that the nanotubes are open during the growth process and that carbon atoms are added at the open ends of the nanotubes. A study carried out by Iijima,[47] who was experimenting with carbon arcs, found that in the absence of catalysts the tubes actually remained open during growth. The second method assumes that the nanotubes are always end capped and that growth occurs by C_2 absorption which is assisted by pentagonal defects on the caps. Molecular dynamics simulations have shown that nanotube closure is associated with the formation of curvature-inducing defects, such as adjacent pentagon pairs.[51] This curvature costs energy, and it has been suggested, by Maiti *et al.* [52] that it is therefore only favoured for narrow diameter tubes. This led the author to conclude that tubes of larger diameter should remain open during growth.

As the experimental conditions vary for forming nanotubes, the particulars of a growth method could depend on the method used to grow the tubes, and more than one growth method may be operative in the production of carbon nanotubes. This said, the generally accepted growth process for production of CNTs by CVD involves adsorption and decomposition of hydrocarbon gases containing carbon on metal surfaces, dissolution and diffusion of the released carbon atoms in the catalyst, and precipitation of the graphite-like layers.

1-11-7 Functionalisation[53-58]

Functionalisation of carbon nanotubes is an effective way to enhance the physical properties and improve the solubility and wettability of the tubes. The central problem in nanotube functionalisation is finding a method which modifies the tube, but which still preserves its strength and conductivity. Procedures for the synthesis of large quantities of nanotubes invariably deliver bundles, which are composed of potentially hundreds of single nanotubes; these bundles can entangle and lead to many defect sites in the resultant composite, limiting the efficiency. Breton *et al.*[53] studied the effect of dispersion of CNTs on the mechanical properties of polymer/CNT composites. It was found that poor dispersion and rope like entanglement of CNTs led to drastic weakening of the composite. Thus, alignment of CNTs has a predominant role on the mechanical and functional properties of the composites. It is very important to achieve both dispersion and alignment of CNTs in a polymer matrix.

Wichmann *et al.*[54] found that non-functionalised nanotubes (whether they are SWNT or MWNT) have a lower percolation threshold than functionalised tubes. They attributed this phenomenon to the process of functionalisation. They functionalised the tubes by introducing amino groups by the process of ball milling; this can rupture the tubes and in doing so reduce the aspect ratio. As the aspect ratio affects the percolation threshold, higher filler concentrations are required to reach the threshold. The authors also attributed the reduced conductivity of the functionalised tubes to the fact that introduction of functional groups into a conjugated π-electron system forms sp^3 carbons. These carbons interrupt the conjugation and can be regarded as defects, which can reduce the conductivity. The upside to the process of amino functionalisation is that it improves the affinity between the epoxy and the nanotube, although in this project dispersion is required in a thermoplastic polymer.

To enable easy access for chemical reagents however, it is obviously advantageous to have individually dispersed nanotubes. For this purpose, the first step in many chemical modifications is ultrasonic treatment of the CNTs in an aqueous surfactant solution. This has been shown to be effective, though experimental conditions have to be carefully controlled, since intensive untrasonication can cause damage to the tube walls and also affect the lengths of the tubes.[55] The use of surfactant molecules can lead to improved wettability and dispersion stability of nanotubes. Different surfactant molecules have been investigated for their suitability. There are ionic surfactants, such as sodium dodecyl sulfate (SDS), which can be used with hydrosoluble polymers, or alternatively, non-ionic surfactants have been proposed when organic solvents have to be used, as for epoxy resins.[56]

Potassium permanganate, traditionally used as an oxidising agent, has been employed in order to functionalise the nanotubes. Zhang *et al.*[57] used phase transfer catalysis. They found that the process increases the efficiency of the oxidation reaction and the yield is improved from ≈35-65 %. They confirmed that the functional groups are attached to the nanotube surface. Although the reaction is carried out under relatively mild conditions, no mention was made as to whether the process destroys the conductivity of the tubes.

It is normally necessary to purify the nanotubes in order to remove amorphous carbon and metal particles, as conductive impurities can affect the electrical properties of the tubes. Nitric and sulfuric acids are often used for this purpose, although they can destroy part of the nanotube. It has also been reported by Georgakilas *et al.*[58] that some of the electronic properties of the tubes were lost during the functionalisation process. For this reason it was decided to work with the nanotubes in an unfunctionalised state.

1-11-8 Nanotubes in Polymers

As previously discussed, carbon nanotubes have a high tensile strength, are lightweight and have a high thermal conductivity; they therefore make a good choice when creating composite materials. However, incorporating carbon nanotubes into other materials has been fundamentally inhibited due to the nature of their sidewalls, which are highly polarizable fullerine tubes, and readily form parallel bundles or ropes with Van der Waal’s interactions. This can lead to problems such as phase-separation, poor dispersion within the matrix – with the nanotubes remaining as aggregates in the host polymer – and also to poor adhesion to the host, see Figure 1-15. These problems have previously inhibited their adoption as a quality additive.

Aggregates of nanoropes **f ully exfoliated nanotubes**

Figure 1-15 – Dispersion of nanotubes

In conclusion, carbon nanotubes in principle have the capability of imparting a high electrical conductivity and improving the mechanical properties of a matrix. Whether the desired level of electrical conductivity can be achieved in practice depends upon the ease or difficulty of charge injection into the nanotubes. The study of this issue forms part of this project.

1-12 Polypyrrole: An Intrinsically-Conducting Polymer[59, 60]

Although polymers are more traditionally known as effective electrical insulators, with electrical wiring being contained in plastic sheeting, if an appropriate structure is designed it should be possible to obtain conductivity. Conductive polymers can be made by filling an insulating polymer matrix with conducting particles, such as nanographite or carbon nanotubes, or by chemical and electrochemical synthesis methods to produce intrinsically conducting polymers such as polypyrrole, Figure 1-16.

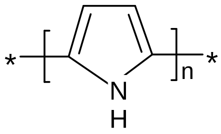


Figure 1-16 – Polypyrrole structure

In order for a molecule to conduct electricity the electrons have to be free to move. In an intrinsically conducting polymer it is a requirement that the electrons can flow down a backbone of alternating single and double bonds, termed conjugate bonds. Another requirement which has to be met in order that conductivity can be maximised, is to create a disturbance of the basic structure of the material by the addition or subtraction of electrons. This process is termed doping, Figure 1-17.

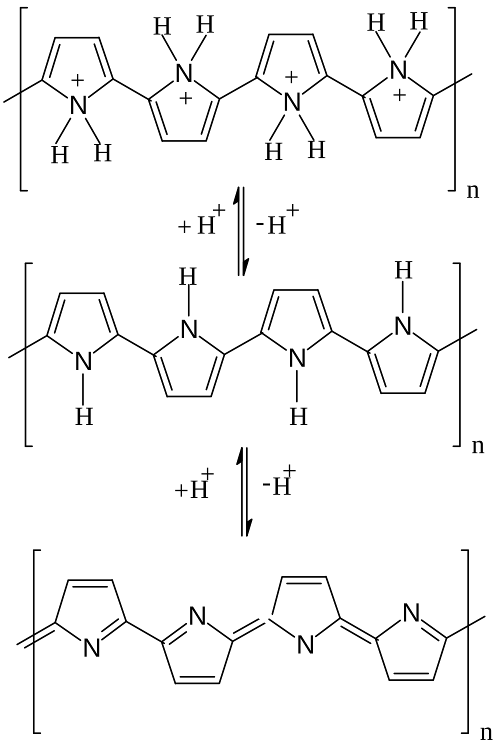


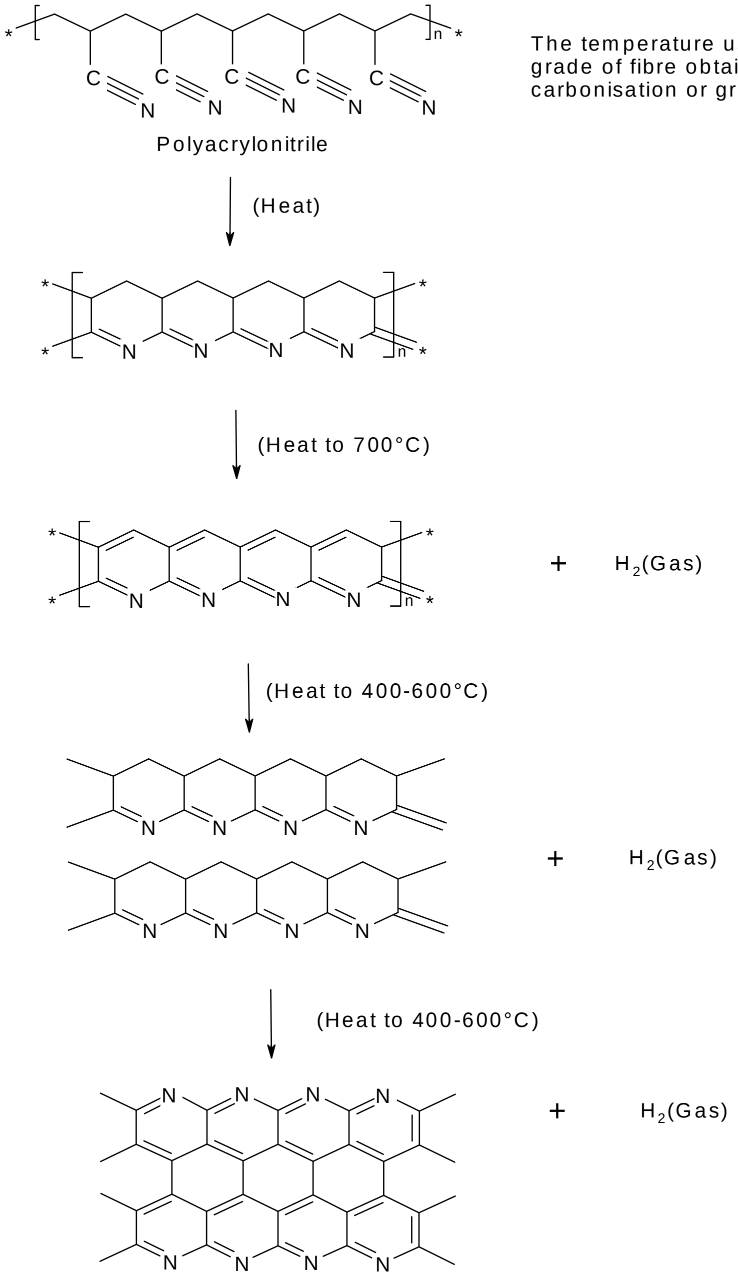
Figure 1-17– Deprotonation and reprotonation of polypyrrole

It was seen by Pethrick[59] that treatment of polypyrrole with acid and alkali induces changes in the conductivity. Treatment with alkali produced a significant reduction in the conductivity, which could be regained by subsequent treatment with acid. This is not surprising as increasing the number of quaternised nitrogens leads to better charge transfer and subsequently higher conductivity. Treatment with alkali causes the loss of this charge transfer and leads to significantly lower conductivity. Introducing small concentrations of the dopant anion results in semi conducting polymers with significant band gaps, whereas high dopant concentrations give rise to much more conductive polymers – these highly doped species are often referred to as “synthetic metals”.

1-13 Carbon Fibre[61]

Some polymer composites used for electrical purposes such as shielding, do not require significant structural strength. An attractive material for these applications is carbon fibre. Carbon fibre has a low density, and as such, finds applications in composite use in combination with a lightweight matrix, typically an epoxy resin. Most carbon fibres are derived from polyacrylonitrile (PAN), though for applications requiring high thermal conductivities, fibres derived from pitch can have three times the thermal conductivity of copper. There is, however, a trade-off to be made in that the lightness, mechanical properties and strength associated with the PAN fibres are lost, when compared to fibres derived from pitch**.** The exact chemistry of the PAN process remains unclear, although it is generally thought to proceed according to Figure 1-18.

In addition, as carbon fibre has available nitrogen atoms on the outside of the molecule, in this way similar to polypyrrole, it is theorised that it should be possible to dope the fibres in the same way, using acid to increase the conductivity.



The temperature used will determine the grade of fibre obtained i.e. degree of carbonisation or graphitization

The reaction continues by heating to higher temperatures, 600 to 1300°C, in order to obtain a higher degree of graphitisation. More H_2 is eliminated and the ribbons of carbon fibres are composed almost entirely of carbon, with some nitrogen functionalisation on the outside of the molecule

Figure 1-18 – Reaction scheme for production of carbon fibre

1-14 Project Objectives

As previously outlined the main objective of this project is to explore the potential benefits which can be achieved through the use of carbon nanotubes, and other related fillers, for the improved performance of thermoplastic-toughened composite matrix materials.

In practice this will involve the utilisation of a soluble fibre technology which has been developed by Cytec. The technology involves the thermoplastic polymer being incorporated into the prepreg in the form of a soluble fibre, which will be co-woven with the carbon fibre pre-form. At the resin injection temperature of 60°C, the fibre is initially insoluble. As the temperature is steadily increased through the cure cycle the fibre should have fully dissolved by 120°C and upon reaching 180°C the epoxy should have cross-linked and the dissolved fibre should phase-separate from the resin. The cure and physical properties of such thermoplastic-modified thermosets was extensively studied at the University of Strathclyde approximately twenty years ago.

It is proposed that nanotubes and related fillers could be introduced to the system via their dispersion in the soluble thermoplastic fibres, whereby it is anticipated that they will not only enhance the mechanical properties, but also introduce electrical conductivity.

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