Analysis and Modelling of Interfacial Phenomena in Carbon Fibre-Thermoset Composites

by

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A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the School of Physical Sciences

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December 1998
“The only certainty about the future is that it will surprise even those who think they have looked farthest into it”

Eric John Earnest Hobsbawm
ABSTRACT

Throughout the materials community, there exists extensive literature on carbon fibre chemical, physical and mechanical properties, and the effect of these on composite performance. To date, however, the atomistic chemical nature of the changing carbon fibre surface when surface treatments are applied has been a very difficult area to study using experimental measurements alone. This study shows the potential of molecular simulation methods to be applied to real engineering materials, and the chemical insight that can be gained in using them.

Inverse gas chromatography experiments show how the dispersive and acid-base nature of the carbon fibre surface changes as a function of surface treatment. In combination with these experimental measurements, the SORPTION™ molecular modelling algorithm is used to develop models that provide a representation of the surfaces of these materials in terms of specific chemical functional groups. These models are compared with separate experimental data, and used to predict and describe aspects of the adhesion in the interfacial region of a carbon fibre-thermoset matrix resin composite.
ACKNOWLEDGEMENTS

For their assistance throughout the course of this Ph.D. research, I should like to thank my industrial supervisors David Attwood and Paul Marshall and others at BAe Sowerby who helped me during my work there.

Aside from their enormous guidance as my supervisors in the Department of Chemistry, I should like to thank John Hay for his assistance in improving my golf game, Ian Hamerton for selecting me as a demonstrator for SBS101, and Brendan Howlin for the frequent meetings in Chancellors and discussions on current affairs.

At the University of Surrey, I am grateful to Phil Vickers in the Department of Materials Science & Engineering for the XPS analyses of the carbon fibres, and the staff and students of the Department of Chemistry and comrades in the Cecil Davies’ Laboratory for making my Ph.D. so eventful. Specifically, Vic Zettel has been of great assistance in the chromatography work.

Although many people have influenced my work over the past years, through my undergraduate and postgraduate degrees, my family deserves the largest recognition for their support and motivation. A special mention goes to Alex for her encouragement throughout the last three years.
This thesis is dedicated to my family.
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Chapter 1: Introduction to Composite Materials

In order to provide an insight into the class of materials used for this study, this section discusses the origins of composite materials and how their technological aspects have been exploited for use in modern applications. The Oxford English Dictionary entry for composite is as follows:

| composite. A. adj. 1. a. Made up of various parts or elements; compound; not simple in structure........2. b. A material made from two or more physically different constituents, each of which largely retains its original structure and identity. 1967 Times Rev. Industry June 68/1 Upgrading of the physical properties has......been achieved by the production of composites, materials in which physical deficiencies in the plastics are compensated by the addition of reinforcing materials. |

Thus, a composite consists of at least two phases, in the case under study a matrix and the reinforcement. The reinforcing phase will usually provide the stiffness and strength, while the matrix phase is designed not only to hold the composite together, but distribute the applied stresses over the component when it is in use. The aim of the design is that the mechanical response of the composite should be improved over that of the individual constituents and available isotropic materials. This can only be achieved if there is a mechanism by which the external load can be transferred through the matrix to the reinforcement. The interfacial region between the two components is therefore of great importance in determining the mechanical response of the material.

Different types, or classes, of composite materials can be defined in relation to the type of reinforcement used, i.e. particulate or fibre. Fibre-reinforced composites cover a wide range of reinforcing materials (carbon, glass and aramid) in a variety of matrices (polymeric, metal and ceramic). A very good historical perspective of composite use in aircraft structures is given by McMullen.
Early studies showed that composites manufactured from carbon fibres and epoxy resins had poor mechanical properties, particularly their interlaminar shear strength (ILSS). This test is used extensively to compare the effect of different surface treatments on the level of fibre/resin adhesion, although it does not provide a direct measure of interfacial strength. The poor performance recorded was due to low adhesion between the fibres and the matrix resin. In the absence of sufficient interaction across the fibre/matrix interface, stress transfer will not be effective and the full strength of the fibres will not be realised. A weak interface will also lead to a low transverse tensile strength (at 90° to the fibres’ longitudinal axis). The problem of a low level of interaction was overcome by the application of various surface treatments to the fibres to increase the adhesion between the two components.

In continuous fibre composites, if the fibres are aligned parallel to each other and packed densely, they are most likely to be arranged in a hexagonal or square lattice. The hexagonal arrangement leads to the greatest possible volume fraction \( V_f \) of the fibres in the composite, as defined,

\[
V_f = \frac{w_f \rho_f}{w_f \rho_f + w_m \rho_m}
\]

Equation 1.1

where \( w_f \) and \( w_m \) are the mass fractions of the fibre and matrix phases respectively and \( \rho_f \) and \( \rho_m \) are the densities of the fibre and matrix phases respectively. The volume fraction of the matrix is defined similarly, with the subscripts \( f \) and \( m \) interchanged.

A section of the material with the fibres embedded in the solidified matrix is known as a lamina; a unidirectional lamina is often termed a ply. These laminae are of the order of 100\( \mu \)m thick. The distribution of fibres in a ply is not as regular as the hexagonal or square lattice arrangement, leading to a decrease in \( V_f \). For a perfect hexagonal array \( V_f \) is 0.907, and 0.785 for a square lattice array. The lack of these perfect arrangements means that laminae cannot be regarded as microstructurally homogeneous and a fibre volume fraction of 0.7 is the practical limit. The advantage of (or perhaps reason for) a lower \( V_f \) and thus greater spacing between the fibres, is
that the penetration of the matrix between the fibres does not require such high applied pressures, and the probability of voids between both phases is reduced.

Figure 1.1 Schematic of a single lamina of unidirectional fibres in a matrix.

High performance polymer composites usually consist of laminae stacked in a predetermined arrangement to form a laminate. External loading of the laminate produces complex stress distributions in the individual laminae and between laminae. These may cause shape distortions of the laminate and local microstructural damage and failure. To reduce the anisotropic elastic properties of individual laminae, different orientations of the plies may be used in forming the laminate. The stacking arrangement of the laminae is represented by the orientations of their fibre longitudinal axes, e.g. a $0^\circ/90^\circ/0^\circ$ laminate would be a sandwich of two plies aligned in the same direction, separated by a middle ply with the fibre orientation at $90^\circ$ to the outer two. The exact construction of the laminate depends on the end application.

Figure 1.2 Schematic of a $0^\circ/90^\circ/0^\circ$ laminate of three unidirectional laminae. The interlaminar spacing is given for clarity, in the actual component the three plies are pressed together then heated to form one structure.
1.1 Carbon Fibre Technology

The use of carbon fibres in composites used for structural applications only became possible with the development of strong fibres formed under controlled carbonisation conditions in the 1960’s. Rayon and poly(acrylonitrile) (PAN) polymer fibres were the most frequently used precursors due to a relatively high carbon yield, and the improvements in carbon fibre strength which could be brought about by stretching the fibres before and during carbonisation.

1.1.1 The PAN Process

PAN was the original precursor for high strength carbon fibres and is still the most important. Typically, PAN is a co-polymer of acrylonitrile and methyl acrylate with itaconic acid, prepared by polymerisation in aqueous sodium thiocyanate solution. Bulk PAN is drawn down into a fibre form and stretched to induce alignment of the molecular chains. This stretched PAN is then heated, causing the nitrile groups to react in an intramolecular cyclisation reaction (the itaconic acid acting as an initiator), forming a ladder polymer consisting of a row of aromatic rings of pyridine-like structure.

The fibres pass through carbonisation furnaces where both the temperature profiles and the degree of stretch (or shrinkage) of the fibres are closely controlled. While maintaining the fibre under tension, it is heated in an oxygen-containing environment. This initiates reaction between the ladder polymer segments. In this stage up to 50% of the mass of the fibre is lost as volatile gases (water and hydrogen cyanide, etc.) as the graphitic crystallites (extended planes of almost pure graphite) begin to form.

These crystallites pack in a random fashion, having no orientational order between the planes, and are described as turbostratic. Marshall and Price have used scanning tunneling microscopy (STM) to show that a high proportion of the crystallites do not lie parallel to the fibre longitudinal axis. Bennett and Johnson suggest that the

---

1 The term crystallites is preferred in the current context as sheets would give an impression of two-dimensional planes with ordered stacking in the third dimension.
random crystallites occur in the fibre core, whereas they are more ordered at the surface. It is due to this random structure that PAN-based carbon fibres have more flexibility and less brittleness than the more sheet-like structures of mesophase pitch-based fibres.

![Schematic of the PAN process of carbon fibre manufacture.](image)

The carbon fibres can be characterised in terms of their mechanical properties. The three main classes of carbon fibre have tensile modulus ($E$) and tensile strength ($\sigma$) values as given in table 1.1. The carbon fibres used in this study are high strength (type II), manufactured by Akzo as the TENAX® HTA range.

<table>
<thead>
<tr>
<th>Fibre Type</th>
<th>Tensile Modulus (GPa)</th>
<th>Tensile Strength (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High modulus</td>
<td>I</td>
<td>350-600</td>
</tr>
<tr>
<td>High strength</td>
<td>II</td>
<td>200-250</td>
</tr>
<tr>
<td>Intermediate modulus</td>
<td>IM</td>
<td>240-320</td>
</tr>
</tbody>
</table>
1.1.2 Fibre Surface Treatment

Following the formation of carbon fibre with this intrinsic turbostratic structure (i.e. resembling graphite crystals, with irregular packing of the layer planes in the longitudinal axis), a surface treatment is applied to the fibres to improve their adhesive characteristics with respect to the particular matrix to be used in the composite component. Surface treatment could lead to a variety of effects, and change the level of adhesion between the fibre and the resin. Reactive functional groups could be introduced into the fibre surface region, which could form covalent bonds with the resin during cure. Alternatively, these groups could modify the surface energy of the fibres such that wetting and spreading by the resin is enhanced, giving rise to a more intimate contact between the two phases. It is also possible that topological changes in the fibre surface could be a significant factor in the improvement, either by the removal of weakly attached material, or by the development of pores and an increase in surface area.

The exact nature of the surface treatment applied to the fibres used in this study is proprietary information; however, other analyses have suggested that a solution of ammonium sulphate or ammonium bicarbonate is used as an electrolytic treatment. The different levels of surface treatment applied to the fibres used in this work represent the extent to which the treatment has been applied, 100% being the standard level, with 0% being untreated and 200% denoting an over-treatment. The percentages can be translated directly into treatment levels in W min g⁻¹, determining the rate at which the fibres pass through the electrolytic bath and the power supplied to the electrolyte solution during this stage.

Various methods for treating carbon fibre surfaces have been developed over the past few years. Waltersson has used a procedure involving refluxing the fibres in a mixture of nitric and sulphuric acids which increases the concentrations of both oxygen and nitrogen at the fibre surface. He also reports a concentration gradient of oxygen and carbon within the fibre sub-surface, which affects the constitution of the matrix in the interphase.
Plasma treatments are becoming increasingly popular as a means of introducing oxygen species into the fibre surface\textsuperscript{9,10,11,12}. Okhuysen \textit{et al.}\textsuperscript{13} use different acid (CO\textsubscript{2}) and base (NH\textsubscript{3}) discharge plasmas to tailor fibre surface chemistry, but this shows little effect on fibre-matrix adhesion, as determined by embedded fibre fracture measurements. Farrow \textit{et al.}\textsuperscript{14} employ a nitrogen plasma, which has no detrimental effect on fibre strength or diameter, to introduce nitrogen functionalities in the surface which could react and form covalent bonds with resin epoxy groups. This is reinforced by Bian \textit{et al.}\textsuperscript{15}, who report an increase in interfacial shear strength (IFSS) for carbon fibre-epoxy composites where the fibre has been treated with a nitrogen plasma.

1.1.3 \textit{Fibre Sizing}

The fibres are usually coated with an epoxy compatible \textit{size} or finish to enhance handling characteristics. This acts as a loose binder, minimising fibre damage during processing and ‘lubricating’ the passage of the fibre over rollers, bobbins, \textit{etc}. Standard sizes for TENAX\textsuperscript{®} HTA fibres are a monofunctional epoxy or polyester, although the exact formulations are proprietary information\textsuperscript{16}.

The effect of applying a size to the fibres, and the consequences for the interphase and composite as a whole, are not well understood. It can definitely act as a barrier against atmospheric contaminants such as moisture and particulates, which can adsorb onto the fibre surface and reduce the final composite properties. Drzal \textit{et al.}\textsuperscript{17} report that a size of approximately 100-200nm thickness has two effects. It creates a brittle interphase between the fibre and matrix, leading to an increase in IFSS, yet the mode of failure changes from interfacial debonding to matrix cracking which could have catastrophic consequences for the component. Using a computer lattice model, Termonia\textsuperscript{18} shows that following a fibre break, a region of size decreases the stress concentration and thus improves the overall load carrying capabilities of the composite.
1.2 High Performance Polymer Resins

The matrix is a vital constituent of any composite material. The best fibre reinforcement is of little, or no, use unless there is a suitable matrix and resultant interphase to transfer stress, enhance transverse properties and improve impact or fracture performance.

1.2.1 Thermoplastic Matrices

Thermoplastic resins differ from thermosetting ones in that they do not undergo a chemical reaction on processing but merely melt and flow when heat is applied, and re-solidify upon cooling. They are used as matrix materials, albeit in the minority of aerospace composites with respect to thermosets, but because the temperatures at which these polymers have a sufficiently low viscosity to infiltrate the fibres are relatively high, problems arise in composite manufacture due to poor infiltration and wetting. Furthermore, the resistance to solvents of thermoplastic matrix composites is generally poorer than for thermosets\(^19\).

Three of the most successful thermoplastic matrices for continuous fibre composites are poly(methylmethacrylate), poly(sulphone), and poly(ethersulphone). Work at the Royal Aerospace Establishment (RAE) suggested that these matrices were even comparable with an epoxy resin in terms of final composite properties, but severe buckling of the fibres occurred when specimens were deformed parallel to the fibre direction\(^19\). Poly(etheretherketone), more commonly known as PEEK, is an example of a relatively recently developed thermoplastic which is being investigated for use in aircraft surfaces\(^21\).

The advantage of using thermoplastic matrices for continuous fibre composites is that they have the potential to be moulded into shape repeatedly (by applying heat) without a loss of properties. Using carbon fibres in thermoplastic matrices offers the potential for an increase in thermal and possibly electrical conductivity.
1.2.2 Thermoset Matrices

The most convenient and widely used matrices in aerospace composites are thermosetting resins. On curing, the initially liquid resin passes through a gel stage, and finally becomes a three-dimensionally cross-linked solid. Cross-linking improves modulus and resistance to heat and chemicals. The main limitation of thermosets is that few are capable of maintaining their properties if continually exposed to high temperatures, but this is far outweighed by the ease of handling and processability compared to thermoplastic resins.

Epoxy resins are the most favoured matrices for use in carbon fibre-reinforced plastics (CFRP) and high performance applications because of their good mechanical properties, low shrinkage, good adhesion characteristics, and environmental stability, particularly in hot/wet conditions. Two of the most commonly used monomers are DGEBA (the diglycidyl ether of bisphenol-A) and TGDDM (tetruglycidyldiaminodiphenylmethane); their chemical structures are shown in figure 1.4. The strained three-membered epoxide ring functional group is highly reactive and opens when reacted with a curing agent (or hardener) to form a cross-linked network.

![Figure 1.4 Chemical structures of DGEBA (top) and TGDDM (bottom) monomers.](image)

Primary amine systems are commonly used as curing agents, reacting via nucleophilic attack on the epoxide group to form bis-\(\beta\)-hydroxyamines. A typical curing agent is diaminodiphenylsulphone (DDS) as shown in figure 1.5. The cure process involves the formation of an infusible, three-dimensional network through reaction of epoxide groups with amines and hydroxyl groups. To control final cured resin properties, the hardener is added at a stoichiometric concentration, dependent upon the epoxy
equivalent weight (molecular mass per functional group) and the molecular mass of the hardener, to allow for formation and reaction of hydroxyl groups.

Figure 1.5 Chemical structure of the DDS amine hardener used with epoxy resins.

Complete reaction of all epoxy groups is not normally achieved except after appropriate post-curing for long times at high temperature. The effect of this operation on mechanical properties can be generalised by the fact that heat distortion temperature (HDT), glass transition temperature (Tg), and Young's modulus increase with cross-link density.

Composite components made using bismaleimide (BMI) resins are generally more brittle than epoxy-based ones, although improvements have been made so that systems are available now that exhibit the same toughness as first generation epoxy systems without sacrificing their high temperature performance. In general, BMI glass transition temperatures are some 100°C higher than epoxies and they retain these properties much better under hot/wet conditions.

Figure 1.6 Chemical structures of a BMI resin (l.h.s.) and a poly(amide) (r.h.s.). The R groups are usually aromatic. The wavy line indicates cross-linking in the BMI. The curved parentheses indicate the (usually) aromatic dianhydride monomer backbone in the poly(amide).

Poly(amide) matrix systems are one of the best polymer systems available for high temperature applications, although the preparation of composites from these materials tends to be difficult due to the chemical reactions occurring. Prepregs are more difficult to handle than epoxy or BMI-based ones and they require long and extreme
cure cycles, evolving volatile by-products during processing. Operating temperatures of these composites are, however, in excess of epoxy and BMI systems, and they can be used in a variety of applications, such as jet engine ducts, where other resins are inadequate. 

A fourth, emerging, family of high performance polymers for use in structural composites is cyanate ester resins. These will be dealt with separately in chapter 3.

1.3 The Interphase and Associated Phenomena

The mechanical characteristics of a fibre-reinforced composite depend not only on the properties of the fibre, but also on the degree to which an applied load is transferred to the fibres by the matrix phase. A major parameter in the extent of this load transfer is the magnitude of the interfacial bond and the structure of the interphase between the fibre and matrix phases. Marshall and Price have studied the modes of fibre-matrix interfacial failure using a single-fibre pull-out method. They report simultaneous yielding of an interface with a high bond strength, whereas a low bond strength leads to crack propagation.

It is common to tailor the strength of an interface for the particular application in which the material is to be used. There can be disadvantages to 'optimising' the interface to maximum strength. When a large external force is experienced, the resultant stresses should be dissipated over the fibres in the entire component through the matrix and fibre-matrix interface. If the force is greater than the maximum that the component can withstand, then the interface (being the weakest factor) is designed to absorb the energy by failing (fracturing/micro-cracking), e.g. in the case of a motorcycle helmet the function is to absorb the impact of a crash, thus preventing head injuries. Were the interface too strong, then failure would occur in the matrix (being now the weakest phase) which could lead to the material falling apart - clearly not a desirable situation.
The concept of a three-dimensional interphase region rather than a two-dimensional interface has been extensively investigated for polymer composites. A summary of the effects involved has been presented by Hull\textsuperscript{24}, and they generally arise from microstructural modification of the matrix in the close vicinity of the fibres. This modification can induce changes in mechanical behaviour, \textit{i.e.} the interphase can have a strong effect on the properties of the composite. In the case of thermosetting matrices, Wright\textsuperscript{25} has shown that the nature of the fibre surface can affect the curing kinetics and crosslink density of nearby matrix.

The properties of the matrix in the interphase region are non-uniform as a function of position from the fibre surface, and mechanical models of the region have attempted to include these aspects\textsuperscript{26}. Some excellent reviews of research into the nature of the interphase region and its effect on properties are given by Hughes\textsuperscript{27}, Jones\textsuperscript{28}, and Scola\textsuperscript{29}.

1.3.1 \textit{Mechanisms of Fibre-Resin Bonding}

In order for two molecules to attract each other initially, and then remain in contact, physical interactions must be present to favour this process. In the case of molecules and surfaces, adsorption onto the surface must occur before any of the other bonding mechanisms can be considered. These types of interactions are governed by van der Waals forces.

Once intimate contact between fibre and resin has been achieved, chemical reaction, and the formation of chemical (covalent) bonds may occur at the interface; the bonds formed are much stronger than the purely physical interactions mentioned above. Carbon fibre surfaces in particular contain surface hydroxyl groups, which can react with epoxide functionalities to form ether linkages between the fibre and resin. The main problem in analysing the extent and nature of interfacial chemical bonds is to identify non-destructive techniques that can probe this region exclusively.

An analysis of the structure and topography of carbon fibres shows that pits and channels are present as defects in the surfaces. Some of these regions are large enough for polymer chains to penetrate and become entangled therein. Once
permanently hardened, it is impossible to withdraw these chains from the channels, thus any force applied to separate the matrix from the fibre would have to break the covalent bonds between the bulk matrix and the entangled chains. This phenomenon is known as mechanical keying and is often used to explain increases in adhesion with increased sample surface area. Direct evidence of this effect, however, is scarce, the best example of the theory being amalgam fillings used in dentistry 30.

1.3.2 The Critical Fibre Length

A critical fibre length is required for effective strengthening and stiffening of the composite material. This critical length \( l_c \) is dependent on the fibre diameter \( d \) and its tensile strength \( \sigma_f \), and (assuming no interfacial region influence) the shear yield strength of the matrix \( \tau_c \), given by the relationship,

\[
l_c = \frac{\sigma_f d}{\tau_c}
\]

Equation 1.2

Typically in CFRPs the critical length is of the order of 1 mm, corresponding to roughly 150 times the fibre diameter \((150d)\). When a stress equal to \( \sigma_f \) is applied to a fibre having just this critical length, the maximum fibre load is achieved only at the axial centre of the fibre. As the fibre length increases the reinforcement action becomes more effective, i.e. the 'zone' carrying the maximum fibre load is increased.

This study focuses on continuous carbon fibre, for which the average fibre length is greater than 15 times that of the critical fibre length. Discontinuous fibres have shorter lengths, and if these are shorter than the critical fibre length then the matrix deforms around the fibre so that there is virtually no stress transference and little reinforcement by the fibre (i.e. failure occurs in the matrix phase).

1.3.3 Fibre and Matrix Mechanical Property Considerations

Aside from the interfacial adhesion between the fibre and matrix phases, their individual mechanical characteristics have a significant influence on the component uses, in particular the brittle (low strain to failure) and ductile (high strain to failure)
properties. In the case of a brittle fibre and a ductile matrix, the fibre fails (breaks) at a lower strain than the matrix. Under uniaxial extension the fibres fail progressively, since not all fibres fail at the same strain. These fibres will be “contained” in the sense that the composite does not fail until a critical distribution of fibre breaks has occurred. This confers an important element of damage tolerance, exploited in polymer matrix composites where the principal purpose of reinforcement is to enhance stiffness.

If the fibre is ductile and surrounded by a brittle matrix, then the matrix will fail at a lower strain than the fibre. This is the common case in ceramic matrix composites. The unbroken fibres then bridge the cracks in the matrix conferring an added degree of integrity. Fibre reinforcements are used in this case to enhance the toughness of brittle matrix systems. Rao and Drzal have shown that there is a relationship between IFSS and both the matrix modulus and glass transition temperature, because of the stress transfer function of the matrix in the interphase. Using an embedded single-fibre fracture test they report a very good correlation of these parameters for DGEBA and TGDDM epoxy matrix-carbon fibre composites cured with a variety of amine hardeners.

1.4 Analysis of Bond Strength

Many simple methods to analyse fibre-matrix adhesion or bond strength involve the use of single fibre measurements. These can only give qualitative data as they most often involve shear debonding between the two phases and frictional sliding, with little or no attempt being made to change the normal stress across the interface (inherently complicated for single fibres). A further complication associated with single fibre measurements is the lack of constraints due to the absence of neighbouring fibres, and caution should be exercised in relating data from these test methods to the macroscopic behaviour of composites.
1.4.1 *Single Fibre Adhesion Measurements*

There are three simple methods for evaluating fibre/matrix bond strength by means of single fibre measurements: the pull-out, push-out, and push-down tests. In the pull-out test a single fibre, half embedded in a matrix, is extracted under tensile load. The results of load as a function of displacement can be interpreted using an adaptation of the shear-lag theory. A variant of this method is the microbond technique where a resin droplet is allowed to harden around a single fibre, the fibre loaded in one direction, and an object put in place to prevent the matrix from moving. There are three stages of pull-out, corresponding to elastic loading up to debonding; propagation of the debonding front; and subsequent pull-out by frictional sliding.

![Figure 1.7 Microdebond set-up of a resin bead around a single fibre, with knife edges to hold the bead as the fibre is drawn in the direction of the arrow.](image1)

The push-out and push-down tests can be applied to real composite specimens rather than a “microcomposite”. In the push-out test a specimen is cleaved normal to the fibre axis and a compressive axial load applied to the top surface of an embedded fibre until failure occurs. The fibre becomes displaced so that it protrudes from the bottom of the specimen. This test is easily applied to large diameter fibres (ca. 100-150μm, e.g. silicon carbide), but for finer and/or strongly bonded fibres there can be problems in the preparation and handling of the test specimens.

![Figure 1.8 The push-out/push-down method, the arrow indicating a force applied to the particular fibre which has begun to slide.](image2)

The push-down test is essentially an extension of the push-out test method, whereby debonding is followed by the fibre frictionally sliding downwards over a certain
distance, leaving a permanent displacement between the top of the fibre and the top of
the matrix when the applied load is removed.

1.4.2 Embedded Fibre Fracture Analysis

This method, which can involve either a single or multiple fibres, involves embedding
the fibre in the matrix and straining the matrix in tension parallel to the fibre
direction. The interfacial shear stress transfer mechanism is relied upon to transfer
tensile forces to the encapsulated fibre through the interface. The fibre tensile
strength is exceeded and the fibre fractures inside the matrix. This process is
repeated, producing shorter and shorter fragment lengths until the remaining
fragments are no longer sufficient in size to produce additional fracture through the
stress transfer mechanism. A shear-lag analysis is applied to the fragments in order
to calculate interfacial bond strength36.

![Figure 1.9 Fragmentation test applied to a sample (top) and after the test (bottom) with small lengths of fractured fibre.](image)

This technique affords a large amount of information for statistical sampling and
fewer parameters are involved in its characterisation than for the test in §1.4.1.
However, the pull-out, push-out and push-down tests can be applied to many
fibre/matrix combinations, whereas in the fracture test the matrix must have a strain-
to-failure at least three times that of the fibre. All of these tests produce values of
IFSS that are very similar to composite values37, yet none of the techniques offers a
complete and unambiguous method for measurement of bond strength.

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As an accompaniment to experimental measurements, finite element modelling (FEM) is becoming increasingly popular. This can be thought of as the engineering equivalent of molecular modelling. The prediction of properties is based on parameters of “elements” (e.g. moduli, Poisson’s ratio, etc.). It is frequently used to analyse processes involving complex shapes, and the stress field calculated for each element under the required conditions. Mitel and Chamis have used this approach to simulate the fibre push-down test and Hampe et al. report good agreement between a model of the pull-out process and experimental measurements.

It is a function of the work in this thesis to analyse the chemistry and chemical factors influencing the interfacial bond strength in carbon fibre-thermoset composites. The different scales of structure covered, from atomic level interactions to component failure, will all be used to this end.
Chapter 2: Theoretical Aspects of Experimental and Computational Work

2.1 Adsorption Phenomena

A molecule approaching a surface experiences an attractive potential due to a combination of dipole-dipole, dipole-induced dipole, and induced dipole-induced dipole forces. The process of molecules aggregating on a surface is called adsorption. The adsorbed molecule or atom is known as the adsorbate and the surface referred to as the substrate. Adsorption is always an exothermic process, i.e. it is thermodynamically favoured as both the enthalpy and the entropy of the system decrease.

The two types of adsorption are termed physisorption (physical adsorption) and chemisorption (chemical adsorption). In physisorption the attractive forces between the substrate and the adsorbate arise from van der Waals interactions. This process leads to a weak interaction between the adsorbate and the substrate; the strength of the substrate-adsorbate bond is typically less than 20 kJ mol\(^{-1}\). The adsorbate-substrate bond is long compared with the length of a covalent or ionic bond. The chemical nature of both adsorbate and substrate does not change through the process of physisorption.

In chemisorption the adsorbate is bound to the substrate by covalent or ionic forces, such as those which occur between atoms in a molecule. The process involves a molecular bond of one or both of the phases being broken and new chemical bonds forming between the molecular fragments and the substrate. Unlike physisorption, the strength of the substrate-adsorbate bond for a chemisorbed species is large; values between 250 and 500 kJ mol\(^{-1}\) are typical. Furthermore, the length of the substrate-adsorbate bond is shorter than for a physisorbed molecule. Because chemisorption involves the formation of chemical bonds to the surface, only a single layer (a monolayer) can chemisorb to the surface.
2.1.1 Interaction Forces Between Molecules

Intermolecular forces can be loosely classified into three categories. Firstly, those that are purely electrostatic in origin arising from the Coulombic force between molecules. Interactions between charges, permanent dipoles, etc. fall into this category. Secondly, there are polarisation forces that arise from dipole moments being induced in atoms and molecules by the electric fields of nearby charges and permanent dipoles; all interactions in a solvent medium involve polarisation effects. Thirdly, there are forces that are quantum mechanical in nature. Such forces give rise to covalent bonding and repulsive steric interactions that balance the attractive forces at very short distances.

2.1.2 Isotherms for Mono- and Multi-layer Adsorption

To display graphically the way in which a surface becomes covered by adsorbed molecules, an adsorption isotherm of the surface coverage is plotted as a function of gas pressure (at constant temperature). The simplest expression for an adsorption isotherm was derived by Langmuir. This model assumes that the adsorbed molecules do not interact with each other, that the enthalpy of adsorption is independent of the surface coverage and that there is a finite number of surface sites where a molecule can adsorb.

The process of adsorption and desorption for the adsorbate (A) and the substrate (S) is depicted by the reversible elementary process,

\[
A(g) + S(s) \xrightleftharpoons[k_a]{k_d} A-S(s)
\]

where \( k_a \) and \( k_d \) are the rate constants for adsorption and desorption respectively. The rate of adsorption (\( \nu_a \)) is proportional to the partial pressure (\( p \)) of A and the number of vacant sites, \( N(1-\theta) \),

\[
\nu_a = k_a p N(1-\theta)
\]

Equation 2.1

where \( N \) is the number of sites and \( \theta \) the fractional surface coverage,
The rate of desorption \( (\nu_d) \) is proportional to the number of adsorbed species,

\[
\nu_d = k_d N \theta
\]

Equation 2.2

At equilibrium the rates of adsorption and desorption are equal, hence,

\[
k_d \theta = k_a p (1 - \theta)
\]

Equation 2.3

or by rearrangement,

\[
\theta = \frac{Kp}{1 + Kp}
\]

Equation 2.4

where \( K \) is the equilibrium constant \((k_d/k_a)\).

It follows that the fractional coverage increases with increasing pressure and only approaches unity at very high pressures, when the gas molecules are forced into every available site on the surface. This isotherm however, is only valid for adsorption of a monolayer; to consider cases where molecules can adsorb on top of each other the Brunauer, Emmett and Teller (BET) isotherm \(^{42}\) is used. This is often written in the form:

\[
V \frac{p}{p^* - p} = \frac{1}{V_m c} \frac{(c - 1)p}{V_m c p^*}
\]

Equation 2.5

where \( p^* \) is the vapour pressure of the adsorbate at the experimental temperature, \( V_m \) is the volume corresponding to monolayer coverage on the surface, \( V \) is the total volume adsorbed at pressure \( p \), and \( c \) is a constant dependent upon both the adsorbate and substrate. This equation is normally rearranged so that \( V/V_m \) can be plotted as a
function of $p/p^*$. It has been extended to cover five separate types of isotherm\(^4\) and remains, arguably, the most popular isotherm used to interpret adsorption processes.

2.2 Methods of Surface Analysis

2.2.1 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS), also known as ESCA (electron spectroscopy for chemical analysis), involves placing a sample of the material to be analysed in a high vacuum chamber and irradiating it with soft (low frequency) X-rays. This bombardment causes electrons from atomic core-levels (i.e. those closer to the nucleus than electrons in the valence shell) to be ejected into the vacuum. Valence electrons are also emitted but their kinetic energies ($E_k$) are much weaker than those from the core levels, consequently interpretation does not usually focus on their spectral patterns. The kinetic energy of the emitted electrons is related to the binding energy ($E_b$) by equation 2.6, where $h\nu$ is the energy of the X-rays and $\psi$ is the work function of the spectrometer.

$$E_k = h\nu - E_b - \psi$$  \hspace{1cm} \text{Equation 2.6}

Although X-rays penetrate deep into the sample, only electrons generated close to the surface escape with their original energy intact. The sampling depth is roughly three times the mean free path of the electrons, e.g. 0.15-1.5 nm for polymers\(^4\). Surface sensitivity and depth profiling can be performed by altering the take-off angle for the electrons; that is the angle at which the X-rays are fired towards the sample, 90° being perpendicular and effecting the deepest penetration into the sample surface\(^4\).

X-ray sources are usually aluminium (AlK\(_\alpha\) of 1486.6 eV and linewidth 0.85 eV) or magnesium (MgK\(_\alpha\) of 1253.6 eV and linewidth 0.70 eV). The X-rays can damage the sample, thus the technique cannot be used \textit{in vivo}. All elements with the exception of hydrogen (which has no core electrons) can be detected. In general a
coarse survey spectrum of all elements is performed initially, followed by appropriate high-resolution examination of selected elements. In high-resolution spectra it can be seen that binding energies may vary with the nature of the bonding to the specific atom, e.g. different energies are observed for carbon atoms in a carbonyl (C=O) as opposed to a hydroxyl (C-OH) group. In the case of overlapping peaks, it is common practice to separate these using a computational curve-fitting procedure.

Peak heights or areas are proportional to the numbers of atoms in the sampling zone (typically a square of 50μm width), but a proportionality constant must be applied. This is empirical, the standard being fluorine 1s with a value of 1.00, and is known as the relative atomic sensitivity. The technique affords percentages of different atoms at the surface and, from curve-fitting and resolution, an indication as to the proportions of these atoms in different chemical environments. Coupled with other techniques, such as infra-red (IR) spectroscopy and secondary-ion mass spectrometry (SIMS), an intuitive prediction of the chemical groups present can be made.

2.2.2 Surface Energetics and Contact Angle Analysis

The extent to which a surface is covered by, and makes intimate contact with, a liquid, and thus the resulting possibilities for interfacial bonding, is dependent upon the surface energies of both components. Surface atoms are not bonded to the maximum number of nearest neighbours and are therefore in a higher energy state than the atoms in the bulk. The bonds of the surface atoms which are exposed to an external medium give rise to a surface energy. To reduce this energy, materials tend to adopt forms which minimise the total surface area, e.g. liquids form spherical droplets, yet for mechanically rigid solids this is not possible.

![Figure 2.1 Contact angles >90° (l.h.s) and <90° (r.h.s) of liquids on solid substrates.](image)

If a drop of liquid is placed on a solid substrate it will make a contact angle (θ) with the surface. Only in cases where the surface energy of the solid is greater than that
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of the liquid will the solid be completely wetted (covered) and a zero contact angle obtained. In cases where the contact angle is finite and greater than 90°, droplets are formed, whereas puddles result if the contact angle is less than 90° (figure 2.1).

The relationship between the surface energies of the solid-liquid interface (\(\gamma_{sl}\)), the liquid in equilibrium with its vapour (\(\gamma_{lv}\)) and the solid in equilibrium with the liquid vapour (\(\gamma_{sv}\)) is given by Young’s equation,

\[
\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta
\]

Equation 2.7

where \(\theta\) is the contact angle which the liquid forms when in contact with the solid. By separating the interactions between the solid and liquid phases into dispersive and polar components (equation 2.8, the superscripts \(d\) and \(p\) referring to the dispersive and polar components of the particular surface energy), and assuming that the forces can be treated independently, the geometric mean equation can be combined with equation 2.7 to yield equation 2.9, more often written as equation 2.10.

\[
\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2\sqrt{\gamma_{sl}^d \gamma_{lv}^d} - 2\sqrt{\gamma_{sv}^d \gamma_{lv}^d}
\]

Equation 2.8

\[
\gamma_{lv}(1 + \cos \theta) = 2\sqrt{\gamma_{sv}^d \gamma_{lv}^d} + 2\sqrt{\gamma_{sl}^d \gamma_{lv}^d}
\]

Equation 2.9

\[
\frac{\gamma_{lv}(1 + \cos \theta)}{2\sqrt{\gamma_{lv}^d}} = \sqrt{\gamma_{sv}^d} + \sqrt{\gamma_{sl}^d}
\]

Equation 2.10

By using a range of liquids with differing dispersive and polar surface energy components, the dispersive and polar energy characteristics of the solid substrate can be determined via measurement of the contact angle formed between the liquid and solid phases\(^{50,51,52,53}\).

Two common techniques used to measure solid surface energies by means of contact angles are the sessile drop and Wilhelmy plate methods. The first involves placing a drop of a liquid on the solid surface under analysis and measuring the contact angle formed through a microscope by visual inspection or projection onto a screen. In the second method the test sample (solid) is suspended from a microbalance with a vial of
test liquid underneath, supported by a motorised platform. The platform is set to rise a certain distance, and thus bring the liquid into contact with the suspended solid, then lower at a specified velocity. The force experienced by the microbalance as the solid is drawn into, and subsequently withdrawn from, the liquid is measured as a function of immersion depth.

Schultz et al.\textsuperscript{54} have used a novel two-liquid variant of the Wilhelmy plate method to study carbon fibres, although they note complications of the measurement of fibre surface energies due to surface heterogeneity which leads to preferential adsorption and surface energy gradients. Schreiber\textsuperscript{55} has used contact angle measurements in conjunction with donor and acceptor numbers from inverse gas chromatography experiments to evaluate specific interactions on polymer solids. He reports that acid-base interactions can lead to appreciable time-dependent variations in the contact angle. A comprehensive review of the rôle of molecular interactions in adhesion, adsorption, contact angle and wettability is given by Lee\textsuperscript{56}, and experimental procedures to characterise these forces are detailed by Lloyd\textsuperscript{57}.

2.2.3 The Work of Adhesion

The free energy change, or reversible work done, to separate unit areas of two different species 1 and 2 from contact to infinity in a vacuum is termed the work of adhesion ($W_a$). If the species are the same, the process is alternatively referred to as the work of cohesion. Since all media attract each other in a vacuum, $W_a$ is always positive.

![Figure 2.2 The work of adhesion ($W_a$) required to separate to species in contact.](image.png)

A good review of the relationships between surface energetics and adhesion is given by Smith\textsuperscript{58}, and the application of cohesive vs. adhesive parameters by Barton\textsuperscript{59}.

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Surface energies have also been used in the construction of a thermodynamic model of adhesive bonding by Gutowski\textsuperscript{60}, who defines conditions for zero bond strength, maximum bond strength, and durability.

The work of adhesion can be expressed in terms of surface energies of the two species using the Dupré equation,

\[ W_A = \gamma_1 + \gamma_2 - \gamma_{12} \quad \text{Equation 2.11} \]

\[ W_A = 2\sqrt{\gamma_1^d \gamma_2^d} + 2\sqrt{\gamma_1^p \gamma_2^p} \quad \text{Equation 2.12} \]

This equation indicates that a stronger bond will be obtained if both species are matched in their surface energy components, e.g. both having high dispersive and low polar character or \textit{vice versa}. Huntsberger\textsuperscript{61} shows that there are three cases when surface energies are related to bond strength: interfacial separation (\textit{i.e.} failure); non-complete wetting of a solid by a liquid; and when a third phase is present at the interface (\textit{e.g.}, adsorbed moisture or particles on a carbon fibre).

Fowkes\textsuperscript{62} dissects the work of adhesion into more than simply dispersive and polar components, suggesting also hydrogen bonding, acid-base, and dipole-induced dipole interactions. He proposes that for a solid-liquid interface, the hydrogen bonding component of the work of adhesion is directly related to the hydrogen bonding surface energy component of the liquid, and not the geometric mean-type relationship similar to that in equation 2.12. Hüttinger \textit{et al.}\textsuperscript{61}, however, use only two types of interactions: dispersive and acid-base. They use contact angle measurements of surfaces with a range of liquids of different pH values to characterise the components of the work of adhesion.
The reasons for adhesion between different species have been expressed by a range of theories, only some of which are applicable to this work. Physical adsorption of probe molecules onto the carbon fibre surfaces is relevant to both the chromatography experiments and the resulting computational study. Furthermore, such adsorption and the intermolecular forces involved are important in the wetting and spreading of the matrix resin upon the fibres in composite manufacture. Aside from physical interactions, the fibre-matrix adhesion is likely to be rationalised by a mixture of some other theories. In particular, chemical bonding (covalent and hydrogen) between both phases and mechanical interlocking of polymer chains into pores in the carbon fibre surfaces are strong factors.

Molecular theories of surface interactions involve such models as the hard/soft acid-base (HSAB) theory, the E and C equation and the use of donor and acceptor numbers. A comprehensive review is given by Jensen. Lee has analysed these models in terms of density functional theory (DFT) and quantum mechanical calculations. From these approaches he has defined a mechanism for solid adhesion based on molecular bonding. There are many components to the mechanism (e.g. polarisation, charge-transfer, etc.) and a simple theory such as the electrostatic double layer (adhesion purely as a result of two oppositely charged surfaces) is insufficient on its own to account for solid adhesion. The techniques used (in the latter sections of this thesis) to analyse model fibre-resin interactions will apply some of the aspects discussed here to the simulated interfaces.

2.3 Molecular Energy Calculations

The computational aspects of this thesis concern three main types of molecular energy calculations, namely *ab initio* quantum mechanics, semi-empirical quantum mechanics and molecular mechanics. This section provides a brief resumé of the background to these methods and their particular application in computational chemistry.
2.3.1 The Schrödinger Equation

In 1926 the Austrian physicist Erwin Schrödinger proposed his equation to describe a particle moving through space under the influence of an external field. This is applied computationally by considering the time independent form of the equation,

\[
-\frac{\hbar^2}{8\pi^2 m} \nabla^2 \psi + V \psi = E \psi \tag{Equation 2.13}
\]

where \( \hbar \) is Planck's constant, \( m \) is the mass of the particle, \( V \) is the potential energy of the particle, \( \psi \) is the wavefunction which characterises the particle's motion (it is from the wavefunction that various properties of the particle can be derived), \( E \) is the energy of the particle, and \( \nabla^2 \) is a partial differential in all three dimensions,

\[
\nabla^2 = \frac{\partial}{\partial x^2} + \frac{\partial}{\partial y^2} + \frac{\partial}{\partial z^2} \tag{Equation 2.14}
\]

To solve the Schrödinger equation it is necessary to find values of \( E \) and functions \( \psi \) such that when the wavefunction is operated upon, it returns the wavefunction multiplied by the energy.

2.3.2 The Hamiltonian Operator

Since the majority of interest in the quantum chemistry field is the calculation of energies (or energy levels to be more precise), the Hamiltonian operator is most often used in the Schrödinger equation. Equation 2.13 can be rewritten in the form,

\[
\left[ -\frac{\hbar^2}{8\pi^2 m} \nabla^2 + V \right] \psi = E \psi \tag{Equation 2.15}
\]

and further simplified to yield,

\[
H \psi = E \psi \tag{Equation 2.16}
\]
where $H$ is the Hamiltonian operator,

$$H = -\frac{\hbar^2}{8\pi^2m} \nabla^2 + V$$  \hspace{1cm} \text{Equation 2.17}$$

Thus, the Schrödinger equation has now been formulated as an eigenvalue problem, the wavefunction as an eigenfunction and the energy as an eigenvalue of the Hamiltonian operator.

Owing to the mathematics involved in solving the Schrödinger equation, there are three boundary conditions imposed on the wavefunctions: they must be continuous (i.e. have a continuous slope), single valued, and finite. Solutions of the Schrödinger equation yield quantised energy levels for the system being investigated, i.e. they are discrete values and do not occur arbitrarily.

2.3.3 Atomic Orbitals

The simplest (and only exact) solutions to the Schrödinger equation are obtained when considering hydrogenic atoms, that is atoms with a nucleus and single electron orbiting it e.g. H, He+, Li2+, etc.. The wavefunctions that satisfy the Schrödinger equation for these types of atoms are known as atomic orbitals. Thus, wavefunctions are merely three-dimensional mathematical functions from which properties of the system can be calculated.

The Born interpretation of the Schrödinger equation suggests that if the amplitude of the wavefunction of a particle is $\psi$ at some point $x$, then the probability of finding the particle between $x + dx$ is proportional to $\psi^*\psi dx$. This is known as a probability density and solutions for the hydrogen atom yield shapes recognised as the $s$-, $p$-, $d$-orbitals, etc.

To calculate the properties of polyelectronic systems, the Born-Oppenheimer approximation is invoked. This says that, as the mass of electrons is negligible compared to the mass of the nuclei they orbit, their motions can be treated separately.
Thus, the electronic energy of the system, with a given fixed internuclear distance, can be calculated and a nuclear-nuclear repulsion term added to yield the total energy.

2.3.4 Molecular Orbital Theory

The aim of most quantum chemical calculations is the production of a molecular wavefunction $\Psi$. This is found using a method known as the linear combination of atomic orbitals (LCAO). One first finds the wavefunctions for the individual electrons over the entire molecule by using a linear combination of (most often Slater or Gaussian) atomic wavefunctions. In the LCAO procedure each atomic orbital has a coefficient associated with it, indicating the 'proportion' that it contributes to the particular molecular orbital. The molecular wavefunction is then simply the product of all of these individual electron wavefunctions.

The atomic wavefunctions used in these types of calculations are grouped together into basis sets. For polyelectronic atoms a simple choice of basis set would comprise Slater functions (Slater-type orbitals or STO’s); however it is common in ab initio calculations to replace Slater orbitals by functions based upon Gaussians, because they are much simpler to solve for problems involving more than one nuclear centre. A Gaussian function has the form:

$$x^a y^b z^c \exp(-\alpha r^2)$$  \hspace{1cm} \text{Equation 2.18}

where $r$ is the atomic radius, and $\alpha$ is a measure of the radial spread of the function; a function with a large value of $\alpha$ does not spread very far whereas a small value of $\alpha$ gives a large spread.

Currently, the most popular basis sets include the fitting of Slater atomic orbitals by a number of Gaussian functions, the inclusion of orbital exponents ($\zeta$) in the generation of these atomic orbitals, and the separation of orbital descriptors for inner- and outer-shell electrons.
2.3.5 Quantum Mechanical Calculations – The Hartree-Fock Self-Consistent Field Method

The essence of the Hartree-Fock Self-Consistent Field (HF-SCF) procedure for calculating molecular orbitals is as follows. The initial basis set is used as a starting point for the electronic distribution in the molecule, and a series of molecular orbitals and their energies are calculated. The coefficients of the atomic orbitals (from the LCAO procedure) can then be recalculated from the energies of these molecular orbitals. The new coefficients are subsequently fed back into the calculation of the molecular orbitals and the process repeated. This 'recycling' continues until the changes in these coefficients are negligible between successive calculations. The results can then be described as being self-consistent.

The most significant drawback of Hartree-Fock theory is that it fails to represent electron correlation adequately. In the self-consistent field method the electrons are assumed to be moving in an average potential of the other electrons, and so the instantaneous position of an electron is not influenced by the presence of another electron. The correlation energy is defined as the difference between the Hartree-Fock energy and the exact energy. The inclusion of configuration interaction is a common procedure to incorporate correlation energy into the calculations, e.g. using perturbation theory.

2.3.6 Semi-Empirical Quantum Mechanics

As the name implies, calculations of this type are based upon quantum chemical methods but make a variety of approximations, giving rise to a decrease in time required for a particular calculation and an increase in the number of atoms which can be considered in the system.

All of the commonly used techniques are valence electron calculations; that is they neglect 1s electrons (the K shell), since they play little or no part in chemical behaviour, and define these as part of a 'core'. For heavier atoms the L shell electrons are also included in this core. The rationale behind this approximation is that the electrons involved in chemical bonding and other calculated phenomena are those in the valence shell.
In the neglect of differential overlap (NDO) approximation, the overlap between all pairs of orbitals centered around different nuclei is set equal to zero. In calculation terms, the overlap matrix is reduced to having non-zero values on the leading diagonal only, resulting in a massive increase in speed of calculation of polyatomic species. Complete neglect of this overlap is a major approximation, thus most semi-empirical methods incorporate NDO to an extent and modify other functions in a ‘parameterisation’ type procedure.

2.3.7 Molecular Mechanics

Molecular mechanics dissociates itself from its quantum relatives by ignoring all of the elemental particles, which make atoms distinct from each other, and instead treats them as “balls and springs”. The balls are distinct from each other in their atom type, that is to say (as opposed to QM methods) not all atomic species of the same element are equal. What this means practically is that the mathematical functions used in the energy calculation contain different parameters for the same element depending on its surroundings, i.e. hybridisation, valence bonding, neighbouring atoms, etc.

The molecular mechanics method assumes that the forces experienced by an atom can be calculated from a potential energy surface. This in turn is a summation of steric and non-bonded interactions, represented by empirical observations (e.g. spectroscopy) and are thus not ab initio. The potential energy of the molecule is represented as a function of geometrical variables, known as a force-field.

A typical energy expression would be,

$$ E_{total} = E_s + E_b + E_t + E_{nb} $$

Equation 2.19

where the subscripts $s$, $b$, $t$, and $nb$ indicate the energies due to bond stretching, bond angle bending, torsional rotations and non-bonded interactions respectively. The non-bonded interactions comprise van der Waals, electrostatic and hydrogen-bonding terms.
The typical vibrational behaviour of a bond (stretching) is near harmonic close to its equilibrium value, but shows dissociation at longer bond lengths. Rather than the most accurate description, the Morse equation, a more general harmonic expression is favoured in terms of computing time,

$$E_s = \sum k_s (l - l_0)^2$$  \hspace{1cm} \text{Equation 2.20}

where $k_s$ is the stretching force constant, $l$ the observed bond length (in metres) and $l_0$ the equilibrium bond length (in metres). Bond angle terms are also treated in a harmonic way, variations occurring depending upon which force-field is utilised. Typically,

$$E_\theta = \sum k_\theta (\theta - \theta_0)^2$$  \hspace{1cm} \text{Equation 2.21}

where $k_\theta$ is a force constant, $\theta$ is the angle of interest and $\theta_0$ is the equilibrium value for the bond angle. Dihedral (torsional) angles are more complicated in terms of the potential energies. They are frequently represented as a Fourier expansion, generally,

$$E_t = \sum \frac{V_n}{2} (1 \pm \cos n(\phi - \phi_0))$$  \hspace{1cm} \text{Equation 2.22}

where $V_n$ is the rotational barrier height, $n$ is the periodicity of rotation (e.g. 3 for an $sp^2$-hybridised carbon atom, 2 for an $sp^2$-hybridised carbon atom) and $\phi$ and $\phi_0$ are the dihedral angles under study and at equilibrium respectively.

Non-bonded forces denote interactions between closed shell molecules, including attractive interactions from partial electronic charges between polar molecules. These basically comprise dipole/dipole, dipole/induced dipole and instantaneous dipole/induced dipole interactions. The function of these interactions is to lower the potential energy of the pair of molecules. Assuming only dipolar interactions with a large average separation of the molecules, the average interaction energy can be expressed as,
where $C$ is a coefficient which depends on the identity of the molecules and $r$ is their internuclear separation. When molecules approach each other, the nuclear and electronic repulsions and the rising electronic kinetic energy begin to dominate the attractive forces. This short range repulsive potential energy can be expressed similarly to equation 2.23,

$$E = -\frac{C}{r^6} \quad \text{Equation 2.23}$$

Typically $n=12$, in which case the repulsion dominates the $1/r^6$ attractions strongly at short separations as $A/r^{12}$ is then much larger than $C/r^6$. The sum of equations 2.23 and 2.24, i.e. repulsive and attractive interactions, is given by the Lennard-Jones (12,6)-potential,

$$E_{\text{disp}} = \frac{A}{r_y^{12}} - \frac{C}{r_y^6} \quad \text{Equation 2.25}$$

in this case used to calculate the energy due to dispersive interactions ($E_{\text{disp}}$). The electrostatic energy component ($E_{\text{elec}}$) of the non-bonded interactions can be calculated as a Coulombic interaction,

$$E_{\text{elec}} = \sum \frac{q_i q_j}{Dr_y} \quad \text{Equation 2.26}$$

where $q_i$ and $q_j$ are partial charges of the nuclei involved, $r_y$ is their separation, and $D$ is the dielectric constant of the solvent medium. The charges of the nuclei are dependent upon the force-field and charge calculation method used.

The hydrogen bonding term is not always used explicitly and often no adjustments to the van der Waals and electrostatic terms are made. If, however, inter- or intra-
molecular hydrogen bonding is important, it is often included as a Lennard-Jones 12,10 potential.

\[ E_{H\text{-bond}} = \frac{A}{r_y^{12}} - \frac{C}{r_y^{10}} \]  
Equation 2.27

2.4 Molecular Simulation Techniques

Although the calculation of the energy of a system is an important aspect of computational modelling, the changes to the system under different simulation conditions can give a valuable insight into its properties. Simulations of thousands of atoms are now routine in molecular mechanics, and with the development of parallel processing the number will increase still further\(^7\). The scaling of atomic and molecular calculations to the macroscopic region, where engineering phenomena dominate, is a complicated procedure and no single method appears yet to be applicable over all materials. Some good reviews of the application, complication and limitation of this scaling procedure are given by Porter\(^7\).\(^7\)

2.4.1 Geometry Optimisation

In molecular mechanics methods, to calculate equilibrium structures it is necessary to find the set of geometrical variables for which the energy is a minimum. The potential energy surface in three-dimensional space can be complex, even for a molecule comprising only a few atoms. The condition for an energy minimum is that the derivative of the potential energy with respect to geometrical variables is equal to zero, \(i.e.\)

\[ \frac{dE}{dx} = 0 \]  
Equation 2.28

To locate the true minimum rather than a saddle-point (a maximum which would also have a zero derivative) one calculates the second derivatives as well.
The main goal of energy minimisation/geometry optimisation is to characterise a potential minimum, resulting in a new 'stable' structure (i.e. to examine the co-ordinates and energy). This new structure can be the starting point for quantum mechanics calculations and/or specific property simulations (e.g. molecular dynamics).

For polyatomic molecules where several minima occur on the potential energy surface, minimisation is required to locate the global minimum. This may be achieved by taking several different conformations for the starting geometry and/or systematically varying a dihedral angle \( \phi \). This type of procedure has been used to study the mechanical properties of different conformations of a linear epoxy system by Howlin et al.\textsuperscript{34}. However, for large molecules with many degrees of freedom this is difficult and impractical. Thus, molecular mechanics minimisation methods lead to local minima (inherent in most procedures).

Various minimisation methods (algorithms) can be employed to achieve convergence to the energy minimum. The efficiency of minimisation is judged by the time taken to reach the minimum (speed of convergence) and the number of structural adjustments (iterations) needed.

2.4.2 Steepest Descents

The simplest method uses the first derivative of the potential energy with respect to the cartesian co-ordinates. This is known as a 'first-order' minimiser. The starting geometry \( x_0 \) is chosen (for a molecule of \( N \) atoms, \( x_0 \) is a \( 3N \)-dimensional vector whose elements are the atomic co-ordinates) and the gradient at this point is calculated by evaluating the derivative, \( \nabla \), of the potential energy function. The direction of steepest descent is the negative of the gradient vector, \( g \).
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\[ g = -\nabla E = -\left( \frac{\partial E}{\partial x_1}, \frac{\partial E}{\partial x_2}, \ldots \right) \]  

Equation 2.30

where \( \partial E / \partial x_i \) indicates the derivative of atom \( i \) with respect to \( x \). This defines the direction in which the energy is changing most rapidly (i.e. it points downhill on the potential energy surface).

This procedure continues by the line search method, the new positions being found by,

\[ x_{i+1} = x_i - \lambda_i g \]

Equation 2.31

where \( x_{i+1} \) is the position at the next step size (iteration), \( x_i \) is the initial position (coordinates), and \( \lambda_i \) is the step size (a scalar quantity). If the energy goes down one stores the shift, if the energy goes up one stores zero. This iterative procedure continues until the minimum is reached.

The advantages of the steepest descents method are that it rapidly alleviates large (steric) forces on atoms, thus it is a good method to begin minimisation when the starting point is far from the minimum, and each step requires minimal computing time. However, it converges slowly near the minimum, especially on energy surfaces with narrow valleys. The method calculates first derivatives but does not look at how they are changing, i.e. it goes downhill on the potential energy surface to a local minimum, but this is not necessarily the global minimum.

2.4.3 Conjugate Gradients

This is also a first-order minimisation routine. As an improvement over the steepest descents method, it uses information or a history of first derivatives which allows a more intelligent search direction (i.e. it uses the current gradient and previous search direction). After defining the starting point, the initial conjugate direction \( (s) \) is chosen to be the steepest descent direction,
Chapter 2: Theoretical Aspects of Experimental and Computational Work

\[ h_i = g_i \]  \hspace{1cm} \text{Equation 2.32}

where \( g \) is the gradient vector (as defined for the steepest descents method). Minimisation along \( h_i \) proceeds until a minimum is found at a new point \( i+1 \). The gradient is re-evaluated as \( g_{i+1} \). The conjugate direction is updated according to,

\[ h_{i+1} = g_{i+1} + \gamma_i h_i \]  \hspace{1cm} \text{Equation 2.33}

where \( h_{i+1} \) is the new conjugate direction, \( g_{i+1} \) the new gradient and \( \gamma_i \) a coefficient calculated from both \( g_i \) and \( g_{i+1} \),

\[ \gamma_i = \frac{g_{i+1} \cdot g_{i+1}}{g_i \cdot g_i} \]  \hspace{1cm} \text{Equation 2.34}

This conjugate procedure allows a more efficient search direction. The conjugate gradients method is similar to steepest descents, but stores the direction of the shift and is better at getting out of local minima. This method is preferred for large molecules.

Molecular energy calculations, including molecular and quantum mechanics, consider static structures (calculations at 0 Kelvin), and as such, thermal or kinetic energy is not implicitly included. The study of molecular motion is important in areas where dynamic processes occur, e.g. for intermolecular interactions (particularly involving gaseous and/or liquid phases), diffusion in solids, chemical reactions and folding of large molecules (proteins). Two main approaches exist for simulating the dynamics of molecules, Molecular Dynamics (MD) and Monte Carlo (MC) methods.

2.4.4 Molecular Dynamics

In simple terms, MD uses Newton’s equations of motion to follow a time-evolution of molecular motions, i.e. a trajectory. This can be used to study time-dependent properties (e.g. diffusion and folding). This also allows molecules to cross energy maxima and thus explore their other stable conformations. The initial atom positions
(x) are obtained from crystallographic data or a molecular/quantum mechanics simulation, and the potential energy (E) and forces (F) calculated from the force-field chosen. Initial velocities are randomly assigned to the atoms, which is equivalent to supplying kinetic energy to the system. The new velocities and positions are calculated for a given ‘time-step’ (Δt) by solving Newton’s equations of motion, temperature being evaluated from the kinetic energy. The updating procedure continues in this way for the length of the simulation.

MD involves solutions of Newton’s equations of motion for atoms in a molecule. If the mass (m) of an atom is known, the acceleration (a) can be calculated using,

\[ F = ma \]  
Equation 2.35

F is known from the potential energy expression and equal to the negative gradient of the potential energy E,

\[ F = -\frac{\partial E}{\partial x} \]  
Equation 2.36

where x is the atom position. Velocity (v) and acceleration can be related to this by,

\[ v = \frac{\partial x}{\partial t} \]  
Equation 2.37

\[ a = \frac{\partial v}{\partial t} = \frac{\partial \left( \frac{\partial x}{\partial t} \right)}{\partial t} = \frac{\partial^2 x}{\partial t^2} \]  
Equation 2.38

Using equation 2.35 it can be seen that,

\[ -\frac{\partial E}{\partial x} = m\frac{\partial^2 x}{\partial t^2} \]  
Equation 2.39

Thus, it is now possible to solve this equation for future positions (x) in time (t), i.e. follow the molecule’s trajectory. The solution depends on knowledge of position,
velocity and acceleration. The initial velocities are assigned at random from a Maxwell-Boltzmann distribution, corresponding to the temperature of interest.

The Verlet algorithm is a method of updating new positions and velocities. If one considers the time step between $t$ and $t+\Delta t$ then the new position becomes,

$$x(t + \Delta t) = x(t) + v_{ave}\Delta t$$..........................................................Equation 2.40

where $x(t)$ is the initial position, $v_{ave}$ the average velocity and $\Delta t$ the time interval or 'time-step'. $v_{ave}$ can be expressed as,

$$v_{ave} = v \left( t + \frac{\Delta t}{2} \right)$$..........................................................Equation 2.41

leading to the equation,

$$x(t + \Delta t) = x(t) + v \left( t + \frac{\Delta t}{2} \right) \Delta t$$..........................................................Equation 2.42

The new velocity is calculated from the initial velocity ($u$),

$$v = u + at$$..........................................................Equation 2.43

$$v \left( t + \frac{\Delta t}{2} \right) = v \left( t - \frac{\Delta t}{2} \right) + a(t)\Delta t$$..........................................................Equation 2.44

where the average acceleration $a(t)$ is calculated from $(t-\Delta t/2)$ to $(t+\Delta t/2)$. The acceleration is determined and the cycle continued.

This is often called the 'leapfrog' method because $v$ is out of step of $x$ by half a time-step. The resulting set of positions (and velocities) is the MD trajectory. Obviously to make best use of computer time a large time-step ($\Delta t$) should be used; however, there are fundamental limits. $\Delta t$ is restricted to a value smaller than the highest
frequency of molecular motion - fast vibrations imply rapidly changing $v$ and $a$. The fastest vibration is normally bond-stretching, e.g. for a C-H bond stretch whose period is $ca. 10^{-14}$ s this results in $\Delta t$ being of the order of $10^{-15}$ s (1 femtosecond). Fortunately, supercomputing facilities allow simulations greater than $10^6$ time steps to be performed and thus processes such as internal rotation can be studied.

MD is frequently applied to the calculation of polymer properties, in particular the glass transition temperature\textsuperscript{75}. Howlin et al.\textsuperscript{76} used this technique to analyse the changes in system volume vs. temperature (at constant pressure) and a good correlation was obtained with experimental values for poly(ethersulphone) (PES) systems.

2.4.5 Monte Carlo Methods

Monte Carlo techniques are essentially procedures for statistical sampling applied to numerical calculations. They are mainly used in the study of atomic interaction and diffusion processes\textsuperscript{77} (time-dependent properties), i.e. gas-surface interactions, fast-ion diffusion in solids, but they also find application in generating structures of polymer chains, using successive bond rotations as "moves"\textsuperscript{78}. The method consists of independently sampling points in $3N$ dimensional space. The system is described by periodic boundary conditions containing $N$ atoms/molecules.

The statistical thermodynamics involved in MC calculations is based on the principle that thermodynamic observables are averages of molecular properties. The system is defined by an ensemble $(N, T, P, V)$, which is related to the partition function $(Q)$,

$$Q = \sum_i \exp \left( \frac{-E_i}{kT} \right)$$  \hspace{1cm} \text{Equation 2.45}

where $E_i$ is the energy of the system in state $i$ (ground, first excited, etc.). One would typically sum over states of molecular energies. The proportion of molecules $(P_i)$ with energy $E_i$ could also be described,
where \( n_i \) is the number of molecules of energy state \( E_i \). Thus, the partition function gives an indication of the distribution of states.

The Metropolis MC method provides an estimation of 'canonical averages' by carrying out a random-walk in the configuration space of the system. For example, consider possible configuration states (atomic co-ordinates) represented by \( j \) and \( k \). \( p(j,k) \) is the probability if at time \( t \) the internal energy \( (U) \) is that of configuration \( j \), then at time \( t + 1 \) the internal energy will be that of configuration \( k \). The simulation is allowed to 'evolve' with time, noting that \( p(j,k) \) are independent of \( t \). For the desired averaging property the following conditions must be satisfied,

\[
\sum_k p(j,k) = 1 \quad \text{Equation 2.47}
\]

i.e. the total probability of transition is equal to 1, and one obtains,

\[
p(j,k) \exp \left( \frac{-U(j)}{kT} \right) = p(k,j) \exp \left( \frac{-U(k)}{kT} \right) \quad \text{Equation 2.48}
\]

For diffusion of molecules through porous solids the procedure typically involves construction of the solid framework (from crystal data or a molecular/quantum mechanics calculation) and the diffusing molecules. The probabilities of translation, rotation, creation and destruction are selected, along with the temperature, pressure, volume, \textit{etc}. depending on the ensemble used, and the simulation started. After a random assignment of the diffusing molecule's position the energy of the system is calculated. Based on the temperature input a random move of the molecule is made and the energy of the system recalculated. The probability of this move (proportional to the jump frequency \( W_i \)) is calculated and compared with a random number generated in the range 0-1. This procedure effectively 'weights' the probability of a jump according to its frequency,
\[ W_i \propto \exp \left( \frac{-\Delta E}{kT} \right) \]  

Equation 2.49

where \( \Delta E \) is the change in energy between successive moves.

If the probability is greater than the random number the move is deemed to be successful, it is accepted and the procedure continues. If the probability is less than the random number, however, the move is considered unsuccessful, it is rejected and the procedure continues from the original position.

MD and MC simulation methods differ in a variety of ways. The principal difference is that MD provides information about the time dependence of the properties of a system whereas there is no such relationship between successive MC configurations. In an MC simulation the outcome of each trial move depends only upon its immediate predecessor, whereas in MD it is possible to predict the configuration of the system at any time in the future. MD has a kinetic energy contribution to the total energy whereas in an MC simulation the total energy is determined directly from the potential energy function.

The two methods also sample from different ensembles or conditions for the simulation. MD is traditionally performed under conditions of constant number of particles \( (N) \), volume \( (V) \) and energy \( (E) \) (the microcanonical ensemble) whereas a traditional MC simulation samples from the canonical ensemble \( (\text{constant } N, V \text{ and } T) \). The simulations using the SORPTION™ algorithm have modified the MC method to sample from the isothermal-isobaric ensemble \( (\text{constant } N, P, T) \). The equilibrium state of this ensemble is characterised as the minimum Gibbs function.

2.4.6 The Periodic Boundary Condition

The number of atoms explicitly considered in an MD/MC simulation is typically 100-1000. This is a very small fraction of the \( 6.02 \times 10^{23} \) molecules present in one mole of the bulk system, but it is sufficient for most applications. In general, for computer simulations of bulk matter the aim is to calculate the properties of \( N \) molecules, which are taken to be 'representative' of the whole (macroscopic) system. The key word
here is 'representative' since $N$ must be large enough for the system to display all the phenomena of interest. To overcome this difficulty, periodic boundary conditions are imposed (figure 2.3).

Figure 2.3 Two- and three-dimensional representation of the periodic boundary condition.

The bulk system is imagined to be made up of an infinite number of identical cells that fill all space (similar to the unit cells of crystalline solids). These cells are 'equivalent' to each other, i.e. they have the same number of molecules and distribution.

The molecules may move freely between cells if the dynamics require it, but the equivalence preserves the $N$ in each cell. To prevent molecules 'feeling' effects of the periodic boundary, one uses an interaction cut-off of the energy potentials that must be less than half of the width of the shortest cell axis. This effectively ensures that no molecule can interact with its image in a neighbouring cell.
3.1 Cyanate Ester Resins

This class of high performance polymers comprises monomers with the cyanate functional group which undergo a cyclotrimerisation reaction to form poly(cyanurate)s (figure 3.1). The terms poly(cyanurate) and cyanate ester resin will be used interchangeably to indicate a cured thermoset network comprising the monomer backbone and cyanurate functionalities.

![Figure 3.1 Cyanate functionality (I.h.s.) and corresponding cyanurate (r.h.s.), where R is usually an aryl functionality (alkyl cyanurates are less common, and readily rearrange to form isocyanates).]

The most commonly used cyanate ester resins for aerospace applications are based on a bisphenol-A (\(p, p\)-isopropylidene diphenol) backbone structure.

![Figure 3.2 Bisphenol-A dicyanate (2,2'-bis(4-cyanatophenyl)propane).]

The bisphenol-A dicyanate product is a crystalline solid at room temperature, with a melting point of ca. 80°C. The resin is usually supplied as a pre-polymer in various stages of cure, e.g. 30% converted (AroCy® B30 by Ciba), 50% converted (AroCy® B50).
3.1.1 Applications

In the field of electronics, poly(cyanurate)s are used for manufacturing printed circuit boards. Their low dielectric constants enable the miniaturisation of the board size, as conducting units can be placed closer together, and thus an increase in its operating speed. Moreover their low dissipation factors aid in reducing the electromagnetic energy to heat output, which is significant if more devices are to be placed close to each other on the circuit board.

Cyanate ester resins are only just beginning to be employed as matrices in structural composites, e.g. in the aerospace industry, due to their competitiveness with conventional resins such as epoxies. When used in blends with thermoplastic tougheners, they show very good resistance to delamination upon impact. Their operating temperatures overlap those of toughened BMI composites and their lower dielectric constant provides an interesting opportunity for enhancing the stealth of military aircraft. The curing conditions and equipment are very similar to those used for traditional epoxy pre-pregs (sheets of fibres impregnated with resin).

Owing to the strength of the bond formed (as evidenced by shear strength and peel strength) between cyanate ester resins and a variety of metals used in aircraft alloys, these resins are increasingly finding application as adhesives. Many formulations of cyanate ester (particularly as copolymers) have been reported and patented. Other uses of these materials are as coatings, in which their mechanical and dielectric properties are exploited, e.g. as in foams and as cores for sandwich structures.

3.1.2 Mechanical and Physical Properties of Networks

Poly(cyanurate)s are thermoset materials: in contrast to thermoplastics, they become permanently hard when the monomers are heated above a critical temperature and will not soften again on reheating. The toughness of aryl poly(cyanurate)s is comparable with other high performance resins such as diepoxides and bismaleimides (BMIs). This is generally attributed to the rotational freedom of the ether linkages around the cyanurate ring, and the crosslink density which may be lower than that of comparable thermoset materials.
Glass transition temperatures ($T_g$) of bis-phenyl based poly(cyanurate)s lie in the range 250 to 290°C. The introduction of aryl or alkyl ring functionalities between the two aromatic rings in the monomer lengthens the backbone structure and thus the separation between reactive ends, and leads to a reduction in $T_g$. Thermal gravimetric analysis (TGA) of cured cyanate ester resins shows the onset of weight loss beginning in the range of ca. 380 to 430°C (measured under N$_2$), about 20°C higher than that of comparable BMIs.

3.2 The Origins of Force-Fields

As alluded to in §2.4.8, the potential energy of a molecule can be represented by molecular mechanics using a force-field of terms indicating equilibrium bond lengths, angles, dihedral angles, and the associated force constants for bond stretching, angle bending, and torsional rotation motions. These parameters are often determined from empirical observations such as crystallography and spectroscopic measurements.

Many different force-fields have been developed to cover a series of molecular species. These vary not only in the parameters chosen for the atomic equilibrium values and force constants, but also in some of the energy expressions used. In order to have a useful application over many different compounds a large sample set must be considered. The parameters should not be focused upon one particular term, rather they should all contribute to the conformational and intermolecular behaviour of the system.

3.2.1 Generation of Equilibrium Bonding Terms

A popular modern approach to the refinement of molecular mechanics force-field parameters is to perform quantum mechanical calculations on a series of “theoretical” molecules and use averages of the conformational data calculated. This is a very attractive proposition since no lengthy experimental work need be performed. It should not be forgotten however, that these ab initio methods contain an element of “parameterisation” themselves, e.g. in the choice of basis set used in the calculation.
In this chapter, data from X-ray crystal structure analyses have been used to generate new parameters for equilibrium bonding terms in describing the \textit{sym}-triazine molecular fragment. Alternative sources of data are gas phase structural studies such as microwave or electron diffraction. These have the advantage of being similar to \textit{in vacuo} molecular mechanics calculations as no significant intermolecular interactions affect the structure, whereas the X-ray crystal data are dependent upon not only molecular structure but the packing (hence, intermolecular forces/conformation) of the molecules as well.

The justification in using crystal structure data in the parameterisation procedure is that the ultimate aim of adjusting these values is to apply them to bulk systems of \textit{poly}-(cyanurate) networks. In this way the molecular packing interactions in the crystal structures should be representative (to an extent) of inter- or intra-molecular interactions present in the polymer network.

\textbf{3.2.2 Force Constant Calculation from Spectroscopic Analyses and Computer Simulation of Infra-Red Spectra}

The energy of most molecular vibrations corresponds to that of the infra-red (IR) region of the electromagnetic spectrum, having wavelengths between 1 and 25 \textmu m. Consequently, molecules exposed to a range of frequencies in this region will absorb energy corresponding to specific molecular oscillations of that compound. A conventional scan over the narrower range of the IR region (2.5-16 \textmu m) measures the intensity of radiation passing through the sample (\textit{i.e.} not absorbed by oscillation) and produces an IR spectrum of absorption 'peaks'. From this spectrum, functional groups present in the molecule can be determined and hence, from relative intensities and shifts in the peak locations from known compounds, the number and location of these functionalities.

The way in which a particular molecule vibrates is highly complicated. To simplify analysis of the vibrations, a group of vibrational modes can be described which, if combined in a suitably weighted fashion, will describe all possible vibrational modes for a given molecule. This group is referred to as the normal modes of vibration of the molecule.
For a hypothetical diatomic molecule, consisting of atoms with masses $m_1$ and $m_2$ and an equilibrium bond length $r_0$, the potential energy of the system can be described by simple harmonic oscillation,

$$V(r) = V_0 + \frac{1}{2}k(r-r_0)^2 \tag{Equation 3.1}$$

where $V(r)$ is the potential energy of the system, $V_0$ is the zero point energy, $k$ is the force constant for the bond stretch (in this case as only two atoms are present, connected by a bond) and $r$ is the bond length. A better description of this potential energy function is obtained if powers higher than 2 are considered, yet these complicate the calculations and so are generally neglected. This equation is, not surprisingly, of a very similar form to that used for the bond stretching term in typical molecular mechanics force-fields (§2.4.8, equation 2.20).

The frequency of this oscillation is characteristic of the force acting upon the atoms to return them to equilibrium, and is given by

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{ Hz} \tag{Equation 3.2}$$

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \text{ cm}^{-1} \tag{Equation 3.3}$$

where $\mu$ is the reduced mass of the system $(m_1m_2)/(m_1+m_2)$, i.e. the product of the masses divided by their sum (in units of the mass of a hydrogen atom, ca. $1.6\times10^{-4}$ g), and $c$ is the speed of light (ca. $3.0\times10^8$ m s$^{-1}$). Equation 3.3 expresses the oscillation in terms of a wavenumber, the conventional unit used in plotting IR spectra. Thus, by rearrangement of this equation, the force constant for the particular molecular oscillation can be calculated from the corresponding IR wavenumber of the absorption, assuming that the atoms are independent of each other (the normal mode approximation)$^{88,90}$. 

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3.2.3 United Atom Theory

A popular force-field is DREIDING2.21 of Goddard et al.\textsuperscript{91}. This incorporates United Atom Theory\textsuperscript{92} which is essentially a means of reducing the number of atoms in a calculation, and consequently the time and cost as well. When drawing organic structures it is common to use a series of lines to represent valence bonds (single, double, and triple) between atoms. Hydrogens are normally only drawn explicitly on polar atoms, \textit{e.g.} for an alcohol or amino functionality. United atom theory incorporates a similar approach to the treatment of such structures in molecular mechanics.

Molecular structures are constructed in a similar fashion to the shorthand notation when drawn on paper. Atom types are then assigned by the computer, depending on the particular atom’s environment, valence bonding, \textit{etc.} In a united atom force-field the (non-represented) hydrogen atoms are included as part of the carbon atom to which they would be directly bonded. This results in a greater mass and van der Waals radius for the atom, and a different set of equilibrium bond terms than if the hydrogens were considered explicitly.

There is a big advantage in using these force-fields when dealing with large organic systems, for example the \textit{poly}(carbonate) repeat unit (figure 3.3) is reduced from 33 atoms to just 19 atoms using this method, thus a simulation of the polymer would require much less computation time.

![Figure 3.3 United atom representation of bisphenol-A based \textit{poly}(carbonate) repeat unit.](image)

3.2.4 DREIDING2.21 Default Parameters

The force-field used for the molecular mechanics calculations in this study has been DREIDING2.21. This is supplied as an integral part of the Cerius\textsuperscript{2} software of
Molecular Simulations Incorporated (MSI), and has been used previously to study interaction phenomena between carbon fibres and high performance resins.93.

In assigning atom types, the carbon, nitrogen and oxygen atoms making up this functional group are treated as being in a resonance delocalised system. They are known as C_R, N_R and O_R respectively (figure 3.4), the R indicating that this atom is in a resonance delocalised state and the 1 indicating that united atom theory has been used to include a hydrogen atom implicitly in the associated carbon atom. The bond stretches of C_R-N_R and O_R-C_R are both represented as harmonic terms. The O_R-C_R bond stretch occurs not only between the carbon atom of the *sym*-triazine ring and propagating oxygen atoms, but, in the case of aryl cyanate-based *poly*(cyanurate) resins, for the bond between this oxygen atom and the carbon atom of the aromatic backbone structure.

Bond angle terms are also treated harmonically. There are essentially five that must be considered: the internal *sym*-triazine ring angles centred on carbon (N_R-C_R-N_R) and nitrogen (C_R-N_R-C_R), the angle at which the oxygen propagates from the *sym*-triazine ring (N_R-C_R-O_R), the angle between the R-group carbon atom and the *sym*-triazine ring carbon atom across the oxygen atom (C_R-O_R-C_R), and the angle between the oxygen and carbon atoms in the aryl R-group (O_R-C_R-C_R).

The angle bending terms use ‘dummy’ atoms either side of the central atom in the definition of the term to apply these values wherever the central atom forms a bond angle regardless of the other two atoms involved; the angle depends exclusively on
the central atom. In the three cases in table 3.1, each central atom has an \( sp^2 \) valence electron hybridisation configuration, with three trigonal planar orbitals, thus an angle of 120\(^\circ\) is the equilibrium value.

Table 3.1 DREIDING2.21 default values for bond stretch and angle bend terms for atom types in the cyanurate functional group (the X denotes a dummy atom).

<table>
<thead>
<tr>
<th>Energy term</th>
<th>Atom types involved</th>
<th>( r_0 ) (Å) or ( \theta_0 ) (°)</th>
<th>( k_{r,\phi} ) (kcal/mol Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bond stretch</td>
<td>C R–N R</td>
<td>1.34</td>
<td>1050</td>
</tr>
<tr>
<td>bond stretch</td>
<td>C R–O R</td>
<td>1.35</td>
<td>1050</td>
</tr>
<tr>
<td>bond angle bend</td>
<td>X–N R–X</td>
<td>120</td>
<td>100</td>
</tr>
<tr>
<td>bond angle bend</td>
<td>X–C R–X</td>
<td>120</td>
<td>100</td>
</tr>
<tr>
<td>bond angle bend</td>
<td>X–O R–X</td>
<td>120</td>
<td>100</td>
</tr>
</tbody>
</table>

The dihedral (torsion) terms are not considered for these atoms, rather an umbrella inversion motion is represented by a cosine term (equation 3.4) in the specific case for C_R, N_R and O_R where \( \omega_0 = 0^\circ \). The default force constants \( (k_{\omega}) \) are 40 kcal/mol for each atom. In this expression \( E_\omega \) is the dihedral energy, \( k_{\omega} \) is the dihedral force constant and \( \omega \) the dihedral angle of interest.

\[
E_\omega = k_\omega \left(1 - \cos \omega\right)
\]

Equation 3.4

3.3 Analysis of Triazine Crystal Structures

Searches of the Cambridge Crystallographic Structure Database (CCSD)\(^ {94} \) and literature for the \textit{sym}-triazine moiety produced a set of 12 structures, shown in figure 3.5. \( r \)-factors for the 12 crystal analyses range from 0.042 to 0.076. Of these 12, four can also be classed as cyanurates formed \textit{via} cyclotrimerisation of three identical monomers (molecules 1, 2, 9 and 11), having oxygen atoms bonded to the carbon atoms of the \textit{sym}-triazine ring, and identical ring substituents. By analysis of these structures, new terms to aid in the modelling of \textit{sym}-triazine compounds have been calculated and compared with those currently used by the DREIDING2.21 force-field.
Figure 3.5 Structures of molecules 1 to 12 (numbered left to right in rows)
3.3.1 Equilibrium Bonding Parameters for Triazine Ring Structures

Tables 3.2 and 3.3 list bond lengths and internal ring bond angles (respectively) of the 12 molecules containing the sym-triazine functionality. The mean values and percent standard deviations of these parameters are also included.

Table 3.2 Bond lengths (Å) in sym-triazine ring for the 12 crystal structures analysed.

<table>
<thead>
<tr>
<th></th>
<th>N1-C2</th>
<th>N1-C6</th>
<th>N3-C2</th>
<th>N3-C4</th>
<th>N5-C4</th>
<th>N5-C6</th>
<th>μ</th>
<th>σ (%)</th>
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<tr>
<td>1</td>
<td>1.317</td>
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<td>1.344</td>
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<td>1.341</td>
<td>1.330</td>
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</tr>
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<td>1.33</td>
<td>1.331</td>
<td>1.306</td>
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<td>1.510</td>
</tr>
<tr>
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<td>1.32</td>
<td>1.322</td>
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<td>1.321</td>
<td>1.329</td>
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</tr>
<tr>
<td>12</td>
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<td>1.319</td>
<td>1.319</td>
<td>1.319</td>
<td>1.319</td>
<td>1.319</td>
<td>1.319</td>
<td>0.000</td>
</tr>
</tbody>
</table>

Initially concentrating on the bond lengths, the mean values range from 1.317 to 1.336Å. In comparison, carbon-carbon bond lengths in an aromatic structure are of the order of 1.40Å, lying between values of single C–C bonds (1.54Å) and double C=C bonds (1.32Å) due to π-electron resonance delocalisation105. In pyridine and pyrimidine, both nitrogen-containing six-ring heteroatomic molecules, the mean carbon-nitrogen bond lengths are 1.338Å and 1.337Å respectively106. In these sym-triazine crystal structures the average C–N bond length is less than that for the
standard C=C double bond, and the reference C–N aromatic bond, and the C=N double bond in pyrazole of 1.331Å. Indeed the bond has the lowest value at 1.302Å. This has major consequences on the physical characteristics of these types of molecules.

As increasing numbers of electrons become involved in the bonding between two atoms, the length of the bond joining them decreases. This is shown in the C–C to C=C reduction of 0.21Å. What this implies for the sym-triazine moiety is that the lone pairs of electrons on the nitrogen atoms exhibit a donating effect towards the delocalised aromatic system, thereby reducing the C–N bond lengths. This also reduces the probability of the nitrogen lone pair electrons occurring outside the ring system. Thus, the tendency of these atoms to act as proton acceptors is greatly reduced, i.e. their basic character is reduced.

It should be particularly noted that the C–N bond length in sym-triazine itself is only 1.319Å, again less than the C–C aromatic bond length in benzene and the C–N aromatic bond lengths in pyridine and pyrimidine. When three electron donating groups are present, bonded to the ring carbon atoms, as in the case of trimethoxy-sym-triazine (molecule 9) the range of C–N bond lengths is only 1.315 to 1.344Å, the mean of these values being 1.330Å as for a C–C or C–N double bond.

The bond angle data show firstly that the triazine unit is not the expected hexagonal shape of benzene. The internal ring angles deviate from the expected 120° value alternately and oppositely, depending upon the central atom about which the angle is based. The values for the N–C–N bond angle range from 124.0° to 131.0° with a mean value of 127.4°. The C–N–C bond angle appears to balance this deviation from the hexagonal 120° value, having a range of values from 110.3° to 114.0° with a mean value of 112.6°. The percentage standard deviation is less for C–N–C than N–C–N, indicating that the angle centred on nitrogen is less prone to influence by R substituents than the angle at carbon.

The narrow bond angle at nitrogen (C–N–C) indicates either an external steric or electronic compression by the nitrogen atom itself, forcing its carbon neighbours
closer together, or compression of these carbon atoms by R groups attached to them (propagating from the ring), forcing a smaller internal C–N–C bond angle.

Considering the first case, nitrogen does not have any atoms bonded to it other than the two adjacent carbon atoms forming the ring structure. Thus, the nitrogen lone pair electrons are the sole source of any compression of this bond angle from the hexagonal 120° value. This is unlikely however, as the data for the C–N bond lengths suggest that these electrons are drawn into the delocalised ring (leading to the short C–N bond length) and therefore have a smaller probability of occurring in an $sp^2$ orbital exo to the ring. Such a case would, conversely, lead to a potential increase in the value of this bond angle, with a smaller external force exhibited by the lower lone pair electron density.

The second case requires compression of the ring carbon atoms by their R substituents, forcing a larger internal bond angle at carbon and smaller angle at nitrogen. The external bond angle at N–C–R would however decrease in such a case, thereby reducing the spatial distance between the substituent and the ring nitrogen atoms. This means that any reduction in steric strain on the R group, causing it to compress the sym-triazine ring, would be balanced against the interactions arising from the closer vicinity of the R group to the nitrogen atoms. In the case of sym-triazine itself (molecule 12) only a hydrogen atom is bonded to each of the ring carbon atoms. This surely would not experience any significant steric strain as in the case for a bulky substituent, yet the internal ring bond angles are 126.8° at carbon and 113.2° at nitrogen. These are still an appreciable deviation from the 120°, albeit being closer than the mean values of the 12 molecules.

This leaves the interactions between the R group and the nitrogen atoms as the only explanation for the bond angles found at nitrogen and carbon in the sym-triazine unit; both the electronic lone pair on nitrogen and steric R substituent effects would, on the contrary, suggest a larger internal bond angle at nitrogen and smaller angle at carbon. Owing to the partial delocalisation of the nitrogen lone pair electrons into the π-system or the ring, it exhibits an exocyclic attraction towards the electrons of the R substituents bonded to the ring carbon. Since the sym-triazine ring is relatively
symmetrical (although only exhibits a three-fold symmetry axis in molecules 1 and 12) the R group is drawn towards the ring by the nitrogen atoms on either side of the carbon to which it is bonded. This causes the puckering of the ring (by ca. 1°) from the conventional planar aromatic hexagonal structure of \( sp^2 \) hybridised atoms.

### 3.3.2 Improper Torsions of Cyanate Ring Substituents

As an investigation into the rotational freedom of aryl cyanate derived polymers, three of the crystal structures (1, 2 and 11) were analysed in terms of their improper torsion angles. These are the angles between the plane of the cyanurate ring moiety and the phenoxy substituent (figure 3.6).

![Figure 3.6 Improper torsion angle between planes (dashed triangles) of cyanurate unit and phenoxy substituent.](image)

<table>
<thead>
<tr>
<th>Improper Torsion (°)</th>
<th>1</th>
<th>2</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>74.6</td>
<td>74.6</td>
<td>74.6</td>
</tr>
<tr>
<td>2</td>
<td>69.6</td>
<td>67.7</td>
<td>84.9</td>
</tr>
<tr>
<td>11</td>
<td>34.7</td>
<td>73.8</td>
<td>68.6</td>
</tr>
</tbody>
</table>

Molecule 1 has a three-fold symmetry axis orthogonal to the plane of the ring, thus all values are the same. This is perhaps a consequence of the restricted rotation afforded by having the methyl groups ortho to the cyanurate ether linkage. Molecule 2 has no such bulky ortho group (only a hydrogen atom) thus more conformational freedom is allowed, shown in the greater variation of the improper torsion angle.

In molecule 11, two of the improper torsion angles are in the same region as those for 1 and 2, yet the third angle has a very low value, roughly half that of the other values. This molecule has no bis-phenyl monomer structure, rather a smaller \( p \)-tertiary-butyl
phenoxy substituent propagating from the sym-triazine centre. Furthermore, the
conformation of the phenyl rings about the sym-triazine centre in molecule 11 is not
as even as for molecules 1 or 2. The latter are arranged so that the three phenoxy
rings lie at roughly 120° to each other (using the centre of the sym-triazine ring as the
origin), i.e. the N–C–O–C torsions from one of the sym-triazine ring carbons to the
phenoxy carbon are all roughly 0°. Molecule 11 has a reversed conformation of one
of the phenoxy rings so that two of the p-tertiary-butyl substituents point in a similar
direction. It is the improper torsion angle about the oxygen atom of this phenoxy
group that has a value of 34.7°, presumably to avoid clashing with the other ring
(figure 3.7).

Figure 3.7 X-ray crystal structure of molecule 11 (original co-ordinates) showing uneven displacement
of (p-tertiary-butyl)phenoxy units about sym-triazine structure (grey = C, blue = N, red = O, hydrogens
not shown).

3.3.3 Calculation of Force Constants via Semi-Empirical Quantum Mechanics
The MOPAC semi-empirical quantum mechanics package was used to simulate the
normal vibrational modes of the individual molecules and from these calculate their
IR spectra. Very little work has been published previously on the specific
spectroscopic analyses of sym-triazine containing compounds, although these
methods have been applied to monitor the degree of conversion of cyanate monomers
to poly(cyanurate) resin by the loss of the –OCN IR doublet at 2230 and 2270 cm⁻¹. A paper of over 40 years ago
details ring stretching frequencies (C–N stretch) measured at 1556 and 1410 cm⁻¹ and calculated ring angle bending frequencies at 600
cm$^{-1}$; these were not observed in the calculations performed in this work. More recent work concerning calculations of vibrational frequencies of nitrogen heteroaromatics notes the large deviations in frequency values, in comparison with the other aromatic molecules studied$^{10}$.

The bond stretching, angle bending, and torsional twisting modes were selected via animation of the calculated absorption peaks. The MOPAC output files include the value of the reduced mass associated with a particular absorption, thus this was simply converted to the force constant using equation 3.3. Table 3.5 lists the calculated force constants for C–N bond stretching, ring bond angle bending, and torsional twisting for the 12 molecules used in the crystal structure analysis throughout this section. The X-ray crystal structures of these molecules were used as input for the calculations, the PM3 Hamiltonian$^{11}$ being applied as in a previous study it had been shown to reproduce the cyanurate ring structure of an AroCy® B-30 unit closest out of the available semi-empirical methods$^{112,113,114,115}$.

Table 3.5 Calculated force constants (kcal/mol \(\text{Å}^2\)) for C–N stretching \((k_s)\), C–N–C and N–C–N angle bending \((k_b)\) and C–N–C–N torsional twisting \((k_t)\) from normal modes simulations of 12 molecules using the PM3 Hamiltonian.

<table>
<thead>
<tr>
<th></th>
<th>(k_s)</th>
<th>(k_b)</th>
<th>(k_t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1501.98</td>
<td>184.60</td>
<td>278.16</td>
</tr>
<tr>
<td>2</td>
<td>1624.68</td>
<td>171.89</td>
<td>238.87</td>
</tr>
<tr>
<td>3</td>
<td>1488.01</td>
<td>203.75</td>
<td>287.50</td>
</tr>
<tr>
<td>4</td>
<td>1457.82</td>
<td>218.18</td>
<td>298.48</td>
</tr>
<tr>
<td>5</td>
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<td>1478.50</td>
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</tr>
<tr>
<td>8</td>
<td>1506.25</td>
<td>178.19</td>
<td>280.11</td>
</tr>
<tr>
<td>9</td>
<td>1509.03</td>
<td>199.54</td>
<td>284.19</td>
</tr>
<tr>
<td>10</td>
<td>1465.99</td>
<td>230.73</td>
<td>279.39</td>
</tr>
<tr>
<td>11</td>
<td>1504.76</td>
<td>191.33</td>
<td>279.48</td>
</tr>
<tr>
<td>12</td>
<td>1537.54</td>
<td>277.61</td>
<td>133.56</td>
</tr>
<tr>
<td>Mean</td>
<td>1502.33</td>
<td>193.04</td>
<td>267.99</td>
</tr>
<tr>
<td>S.D. %</td>
<td>2.86</td>
<td>18.33</td>
<td>15.98</td>
</tr>
</tbody>
</table>

The force constant for C–N bond stretching is clearly the largest of the three (stretch, bend, and twist) terms, indeed the mean value is some 7.8 times that of angle bending and 5.6 times that of torsional twisting. Thus, in terms of the computational molecular mechanics energy calculations, this is the most energetically expensive
motion. Torsional twisting has a higher force constant than angle bending, most likely attributed to the greater number of atoms involved in the motion and the tendency to remain in a planar aromatic conformation.

In *sym*-triazine (molecule 12) the bend and torsion values are roughly reversed in terms of magnitude, *i.e.* the angle bending force increases considerably whereas the torsional twisting force decreases. As force is the product of mass and acceleration (Newton's second law), the reduction in mass in changing from an R substituent to simply hydrogen bonded to the ring carbon atoms could account for the decrease in the torsional force constant. If this is true, then for the angle bending force, the velocity of movement would have to more than compensate for the reduction in mass to produce an increase in the force constant. This can be thought of as an increase in the frequency of the bending motion, which is highly likely as there is no bulky R group to be moved as the ring angle oscillates.

### 3.3.4 Definition of New Force-Field Parameters

After consideration of the 12 molecules analysed in terms of their crystal structures and calculated force constants, the data for molecule 12 (*sym*-triazine) have not been included in determining equilibrium bond stretch, bend, and torsion values and their associated force constants. The application of these new force-field terms will be exclusively towards *poly*(cyanurate)s as polymer matrix resins. These typically contain a *bis*-phenyl or similar units, linking between cyclotrimerised *sym*-triazine ring structures. Owing to the mass of these units compared with that of hydrogen in the case of *sym*-triazine itself, and the effect this showed in the bending and torsional force constants in the models compounds, only data for molecules 1 to 11 have been averaged.

The new force-field (RDA-DR2.21_Inv) has created three new atom types for the cyanurate moiety, namely C_Tr, N_Tr and O_Tr. These are applied instead of C_R, N_R and O_R assigned by the DREIDING2.21 force-field. Both the C_Tr–O_Tr and C_Tr–N_Tr bond lengths are shorter (1.337Å and 1.322Å respectively) and the stretching force constant greater (1499 kcal/mol Å²) than the DREIDING2.21 analogues. The O_Tr–C_R values are set equal to the DREIDING2.21 parameters.
In terms of bond angles, the new force constants for both the C-N-C and N-C-N bending motions are set at 185.4 kcal/mol Å². The internal ring angle at nitrogen is assigned the value of 112.252° and at carbon the value of 127.724°. The angle at which the ether oxygen propagates from the sym-triazine ring (in the cyanurate unit) remains unchanged from the DREIDING2.21 value of 120°, with a force constant of 100 kcal/mol Å². This implies however, that the angles about the C_Tr atom add up to 367.724°. This has the effect that the planarity of the ring is distorted slightly towards a chair-like conformation, such as that for the classical cyclohexane structure but to a smaller extent. This introduces a small torsion in the ring C–N–C–N angle which is also observed in the crystal structures.

Rather than use torsion terms, an umbrella inversion expression has been chosen for the C_Tr atoms, being bonded to a nitrogen atom either side in the triazine ring and an oxygen atom joining it to the backbone structure. The \( \omega_b \) parameter is set at 0° (i.e. a planar \( sp^2 \) geometry on the central carbon atom) with a force constant of 280.215 kcal/mol Å² as calculated from the ring torsional motion. This acts as a balance against the wide internal ring angle at carbon and, as shown in table 3.8, reduces the internal ring angle from the equilibrium value of 127.724°. In particular, the force constant is some seven times that assigned by the DREIDING2.21 force-field.

3.4 Comparison of Force-Fields by Molecular Mechanics

The majority of computational simulations (not simply energy calculations) in this thesis use molecular mechanics via the Cerius² interface. In order to perform calculations on the crystal structure data, it is preferred that the crystal symmetry is removed by conversion of the original cell to a “primitive superlattice” of P1 symmetry. This has the consequence that all atoms are now treated individually, not as molecular ‘images’ of one set of atomic co-ordinates. Thus, the symmetry of the experimental data is reduced without affecting the atomic positions or molecular structure, and symmetry constraints are removed.
3.4.1 DREIDING2.21 Energy Calculations of Crystal Structures

From the input crystal data, static (single point) energy calculations were performed to deduce the energy components of the molecules in their crystalline forms. The DREIDING2.21 force-field was applied with the QEq\textsuperscript{16} charge calculation. Unfortunately, the data file quoted for molecule 12 (sym-triazine) contained incorrect atomic positional data, and solution of this proved problematic. The structure was therefore not used in this analysis.

Table 3.6 Single point energy components (kcal/mol) and rank (1 = lowest energy, 12 = highest energy) of crystal structures using the DREIDING2.21 force-field and QEq charge calculation.

<table>
<thead>
<tr>
<th></th>
<th>Bonds</th>
<th>Angles</th>
<th>Torsions</th>
<th>Inversions</th>
<th>v.d.W.</th>
<th>Electrostatic</th>
<th>H-Bond</th>
<th>Total</th>
<th>Rank</th>
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<td>1230.52</td>
<td>-360.67</td>
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<td>-238.40</td>
<td>0</td>
<td>819.52</td>
<td>9</td>
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</tbody>
</table>

The data show that the majority of energy arises from the van der Waals and electrostatic components. The two largest molecules (1 and 2) not surprisingly also rank at the top of the total energy within the set. In particular, the van der Waals interactions are more than twice as large for molecule 2 than 1. This may be due to one of the phenylisopropylidene units being rotated 180° about the central isopropyl carbon atom and thus pointing back towards one of the other substituents.

Hydrogen bonding interactions are only found in those molecules in which hydrogens are represented explicitly (on hydroxyl and amino groups), united atoms are used for hydrogens bonded to carbon.

Two sets of data are given for the tertiary-butyl carbon atoms for one of the ring substituents (at the non-sterically crowded end of the molecule) of structure 11,
denoted 11 for the original data and 11(A) for the alternative positions of these three atoms. The relative abundance of these atomic positions is quoted as 0.78 for the original positions and 0.22 for the A positions. The molecular mechanics crystal energy calculations listed in table 3.6 confirm that the original atom positions are favoured in terms of energy. In particular, there is a small reduction in the bond stretching, angle bending and torsional energies, but the principal reduction is in the van der Waals non-bonding component. Since, in the molecular structure, these atoms are a considerable distance from the two relatively close p-tertiary-butyl phenoxy substituents, the van der Waals energy difference must occur in the intermolecular packing interactions of the crystal structure.

3.4.2 Molecular Mechanics Optimisations of Crystal Structures

Table 3.7 Mean bond lengths and internal bond angles of the \( \text{sym-triazine} \) ring unit for crystal structures, optimised using the DREIDING2.21 force-field and QEq charge calculation.

<table>
<thead>
<tr>
<th>( \text{C-N (Å)} )</th>
<th>( \text{N-C-N (°)} )</th>
<th>( \text{C-N-C (°)} )</th>
</tr>
</thead>
<tbody>
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<td>( \sigma (%) )</td>
<td>( \mu )</td>
</tr>
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<td>1.349</td>
<td>0.655</td>
</tr>
<tr>
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<td>0.292</td>
</tr>
<tr>
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<td>1.348</td>
<td>0.706</td>
</tr>
<tr>
<td>9</td>
<td>1.348</td>
<td>0.467</td>
</tr>
<tr>
<td>10</td>
<td>1.349</td>
<td>0.564</td>
</tr>
<tr>
<td>11</td>
<td>1.349</td>
<td>0.223</td>
</tr>
<tr>
<td>11(A)</td>
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<td>0.242</td>
</tr>
<tr>
<td>Total</td>
<td>1.349</td>
<td>0.425</td>
</tr>
</tbody>
</table>

The adapted force-field terms have been compared with the standard values to assess how both sets of parameters affect the optimisation process. From the crystal structure coordinates, geometry optimisation was performed, using the conjugate gradients routine until a difference of less than 0.01 kcal/mol was achieved between successive steps. The appropriate force-field terms were used in conjunction with the QEq charge calculation. Although the experimental crystal structures represent the observed conformation of the molecules and their packing, it is interesting to see how this changes when computational methods are employed.
The data in tables 3.7 and 3.8 show how the X-ray crystal structure co-ordinates are changed under the influence of different force-field parameters. Dealing with the DREIDING2.21 optimised data firstly, in terms of the sym-triazine unit the mean C–N bond length is overestimated in every case, indeed the bonds lengthen from the crystal co-ordinates to a mean value greater than the equilibrium ($r_0$) value of 1.34Å. The mean bond angles for the 12 structures deviate by as much as 0.8° from the equilibrium value of 120°, yet averaged over all of the crystal units the differences are only 0.1° from the equilibrium value. An inspection of the DREIDING2.21 parameters describing the cyanurate system shows that these are exactly the same as those used to describe a benzenoid sym-triphenoxy functionality.

Standard deviations in the bond lengths are lower in the DREIDING2.21 optimised data than the crystal data for all molecules. In the N–C–N bond angle measurements, standard deviations are higher for the DREIDING2.21 optimised cyanurates (molecules 1, 2, 9 and 11) but lower than the crystal data for all other molecules. These is no such trend in the C–N–C bond angles with roughly half of the simulated angle standard deviations being higher than experiment.

Table 3.8 Mean bond lengths and internal bond angles of sym-triazine ring for crystal structures containing the cyanurate unit, optimised using the RDA-DR2.21_inv force-field and QEq charge calculation.

<table>
<thead>
<tr>
<th></th>
<th>C-N (Å)</th>
<th>N-C-N (°)</th>
<th>C-N-C (°)</th>
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</thead>
<tbody>
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<td>$\sigma$ (%)</td>
<td>$\mu$</td>
</tr>
<tr>
<td>1</td>
<td>1.335</td>
<td>0.239</td>
<td>125.8</td>
</tr>
<tr>
<td>2</td>
<td>1.335</td>
<td>0.191</td>
<td>125.9</td>
</tr>
<tr>
<td>9</td>
<td>1.336</td>
<td>0.336</td>
<td>125.6</td>
</tr>
<tr>
<td>11</td>
<td>1.336</td>
<td>0.226</td>
<td>125.7</td>
</tr>
<tr>
<td>11(Δ)</td>
<td>1.336</td>
<td>0.249</td>
<td>125.5</td>
</tr>
<tr>
<td>Total</td>
<td>1.335</td>
<td>0.248</td>
<td>125.7</td>
</tr>
</tbody>
</table>

For comparison with the DREIDING2.21 optimisations, only the four cyanurate species, molecules 1, 2, 9 and 11 (both conformations), have been considered. New force-field parameters have not been set for all possible R groups, e.g. no specific C_Tr–Cl term has been added, as the end application of the force-field is for poly(cyanurate) systems.
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The optimisations using the RDA-DR2.21 Inv force-field show an improvement over the DREIDING2.21 calculations in all aspects of the $\text{sym}$-triazine ring structure. The mean C–N bond lengths of 1.335-1.336Å are closer to the crystal data than the DREIDING2.21 values, lying roughly equidistant from both sets of data. Other energy terms, particularly non-bonded electrostatic and dispersion (Lennard-Jones 12,6) interactions are believed to prevent the C–N bond lengths being closer to their $r_0$ value of 1.322Å. The standard deviations in the bond lengths are lower for molecules 1, 2 and 9 and comparable with 11 (both conformations) optimised using DREIDING2.21. This is a result of the larger force constant assigned to the new bond stretching term.

The internal ring bond angles at both carbon and nitrogen are clearly much closer to the crystal structures than using DREIDING2.21. Whereas the calculated angles at C–N–C fall within experimental error, the N–C–N angles are a slight underestimate of those found experimentally. This is due to the coupling of this term with the umbrella inversion also centred on this carbon atom. Standard deviations are lower than those for the corresponding DREIDING2.21 parameter for structures 2, 9 and 11 (both cases), yet greater than found in the crystal structure data. This can be attributed to the removal of the symmetry constraints in treating each molecule in the crystal cell as distinct in itself.

3.4.3 Molecular Mechanics Optimisations of Disordered Crystal Co-ordinates

To probe further the efficiency of geometry optimisation using both adapted and original force-field terms, an analogous series of optimisations was performed using the same criteria as in §3.4.2, but introducing positional disorder to all of the atoms in the crystal cell. The atomic positions were ‘disordered’ simultaneously by 0.1Å in a random direction (assigned as part of a computational routine). This procedure was performed five times. It was an initial aim of this section to calculate route mean square (RMS) displacements of each atom from the original coordinates (pre-disordered). During the optimisation routine however, the P1 crystal cell appears to translate in space and thus displaces all atomic positions. This would lead to greater RMS values than actually occur, thus the models have instead been analysed in terms
of their *sym*-triazine bond lengths and internal bond angles in a similar fashion to that in §3.4.2.

Table 3.9 Mean bond lengths and internal bond angles of *sym*-triazine ring for crystal structures, optimised from disordered atom positions using the DREEDING2.21 force-field and QEq charge calculation.

<table>
<thead>
<tr>
<th></th>
<th>C-N (Å)</th>
<th>N-C-N (°)</th>
<th>C-N-C (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>µ</td>
<td>σ (%)</td>
<td>µ</td>
</tr>
<tr>
<td>1</td>
<td>1.348</td>
<td>0.282</td>
<td>120.6</td>
</tr>
<tr>
<td>2</td>
<td>1.346</td>
<td>0.431</td>
<td>120.3</td>
</tr>
<tr>
<td>3</td>
<td>1.350</td>
<td>0.550</td>
<td>118.8</td>
</tr>
<tr>
<td>4</td>
<td>1.352</td>
<td>0.390</td>
<td>119.7</td>
</tr>
<tr>
<td>5</td>
<td>1.352</td>
<td>0.563</td>
<td>119.4</td>
</tr>
<tr>
<td>6</td>
<td>1.349</td>
<td>0.517</td>
<td>120.4</td>
</tr>
<tr>
<td>7</td>
<td>1.350</td>
<td>0.349</td>
<td>120.3</td>
</tr>
<tr>
<td>8</td>
<td>1.347</td>
<td>0.670</td>
<td>121.0</td>
</tr>
<tr>
<td>9</td>
<td>1.352</td>
<td>0.592</td>
<td>118.7</td>
</tr>
<tr>
<td>10</td>
<td>1.349</td>
<td>0.532</td>
<td>119.1</td>
</tr>
<tr>
<td>11</td>
<td>1.349</td>
<td>0.222</td>
<td>119.7</td>
</tr>
<tr>
<td>11(Å)</td>
<td>1.349</td>
<td>0.242</td>
<td>119.6</td>
</tr>
<tr>
<td>Total</td>
<td>1.349</td>
<td>0.445</td>
<td>119.8</td>
</tr>
</tbody>
</table>

Even after the molecular structures have been considerably perturbed, the optimisation routine returns the *sym*-triazine unit to a geometry very similar to that produced when starting from the crystal co-ordinates. For the DREIDING2.21 optimised structures both the mean C–N bond lengths and their standard deviations are comparable with those given in table 3.7. For the N–C–N bond angle, although the range of mean values for the DREIDING2.21-optimised disordered data is greater than that for the non-disordered optimisations (118.8 to 121.0° vs. 119.2 to 120.7°), the averages of these two sets of data differ by only 0.1°. The same applies to the C–N–C bond angle data in tables 3.7 and 3.9. The standard deviation of the ring angle data for the optimised disordered structures is comparable with that of the optimised crystal structures, indicating a good efficiency of the optimisation routine when applied to these disordered co-ordinates (albeit with inaccurate bond length and angle parameters).

Using the new force-field parameters in optimising the disordered cyanurate crystal structures, the mean C–N bond lengths and standard deviations are comparable with
those listed in table 3.8. The bond angle data for both C–N–C and N–C–N also shows the effectiveness of the optimisation routine on the disordered co-ordinates.

Table 3.10 Mean bond lengths and internal bond angles of sym-triazine ring for crystal structures containing the cyanurate unit, optimised from disordered atom positions using the RDA-DR2.21_Inv force-field and QEq charge calculation.

<table>
<thead>
<tr>
<th></th>
<th>C-N (Å)</th>
<th>N-C-N (°)</th>
<th>C-N-C (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>μ</td>
<td>σ (%)</td>
<td>μ</td>
<td>σ (%)</td>
</tr>
<tr>
<td>1</td>
<td>1.333</td>
<td>0.253</td>
<td>125.8</td>
</tr>
<tr>
<td>2</td>
<td>1.335</td>
<td>0.191</td>
<td>125.9</td>
</tr>
<tr>
<td>9</td>
<td>1.336</td>
<td>0.354</td>
<td>125.7</td>
</tr>
<tr>
<td>11</td>
<td>1.335</td>
<td>0.186</td>
<td>125.7</td>
</tr>
<tr>
<td>11(A)</td>
<td>1.336</td>
<td>0.249</td>
<td>125.5</td>
</tr>
<tr>
<td>Total</td>
<td>1.335</td>
<td>0.247</td>
<td>125.7</td>
</tr>
</tbody>
</table>

3.4.4 Conclusions Regarding Molecular Energies and Structures

New parameters to describe the conformation of sym-triazine units have been generated from analysis of X-ray crystal structures and applied to computational molecular mechanics force-field calculations on systems containing this moiety. They are found to be an improvement over existing force-field data when used in optimisations of these structures. The efficiency of the optimisation of a randomly disordered structure has also been analysed and is found to be good for all the cases studied.

With respect to the crystal data upon which they are based, the new force-field values do tend to overestimate the C–N bond lengths, probably arising from the conflict between the short bond length and the repulsive force of two atomic centres approaching each other (represented by a Lennard-Jones 12,6 potential). The internal ring angle at carbon is also underestimated by ca. 2°, being offset by an umbrella inversion term about this carbon atom with a relatively large force constant trying to maintain a planar geometry (analogous to $sp^2$ hybridisation of the carbon atom).
3.5 Quantum Mechanical Structure Optimisations

As outlined previously, molecular mechanics calculations do not include any subatomic detail and apply a simple ‘ball and spring’ treatment to atomic motion. For comparison with the (adapted and original parameter) molecular mechanics calculations, semi-empirical and ab initio quantum mechanical structure optimisations have been performed. These methods may be considered as a level of theory higher than molecular mechanics and take account of atomic and molecular electronic structure.

The molecules from the crystal data series were initially geometry optimised using the DREIDING2.21 force-field and QEq charge assignment by the conjugate gradients method until the energy between successive steps fell below 0.01 kcal/mol. In this way the improvement of the quantum mechanical methods on the original DREIDING2.21 parameters could be analysed. The datafiles for the quantum mechanical structure optimisations were generated from these structures, with the inclusion of explicit hydrogen atoms. No distinction was made between the original and “A” values for structure 11; the original atomic positions were used, then refined using molecular mechanics before creation of the datafile for the quantum mechanics calculation.

3.5.1 Semi-Empirical Structure Optimisations

The DREIDING2.21-refined structures were further optimised using the PM3 Hamiltonian within the MOPAC package. The optimised bond lengths and bond angles for the sym-triazine units are given in table 3.11.

Using this semi-empirical quantum mechanical method the C–N bond lengths are overestimated by ca. 3% compared with the crystal structure data, indeed they are even further adrift than the DREIDING2.21-optimised values. The standard deviations in the C–N bond lengths are lower than in the crystal data for all molecules except number 1. It must be noted however, that these calculations have been performed on single molecules in vacuo, whereas the molecular mechanics force-field
calculations used units of the crystal cells thereby including intermolecular interactions.

Table 3.11 Mean bond lengths and internal bond angles of the sym-triazine ring moiety for single molecules used in the set of crystal structures, optimised from DREIDING2.21-refined atom positions using the PM3 Hamiltonian.

<table>
<thead>
<tr>
<th></th>
<th>C-N (Å)</th>
<th>N-C-N (°)</th>
<th>C-N-C (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>μ</td>
<td>σ (%)</td>
<td>μ</td>
</tr>
<tr>
<td>1</td>
<td>1.369</td>
<td>0.590</td>
<td>123.0</td>
</tr>
<tr>
<td>2</td>
<td>1.370</td>
<td>0.368</td>
<td>124.0</td>
</tr>
<tr>
<td>3</td>
<td>1.372</td>
<td>0.489</td>
<td>124.3</td>
</tr>
<tr>
<td>4</td>
<td>1.374</td>
<td>0.601</td>
<td>124.6</td>
</tr>
<tr>
<td>5</td>
<td>1.370</td>
<td>0.629</td>
<td>123.6</td>
</tr>
<tr>
<td>6</td>
<td>1.370</td>
<td>0.763</td>
<td>123.6</td>
</tr>
<tr>
<td>7</td>
<td>1.372</td>
<td>0.504</td>
<td>124.4</td>
</tr>
<tr>
<td>8</td>
<td>1.370</td>
<td>0.391</td>
<td>125.0</td>
</tr>
<tr>
<td>9</td>
<td>1.371</td>
<td>0.000</td>
<td>125.1</td>
</tr>
<tr>
<td>10</td>
<td>1.373</td>
<td>0.604</td>
<td>124.3</td>
</tr>
<tr>
<td>11</td>
<td>1.370</td>
<td>0.080</td>
<td>125.1</td>
</tr>
<tr>
<td>12</td>
<td>1.358</td>
<td>0.000</td>
<td>126.1</td>
</tr>
<tr>
<td>Total</td>
<td>1.370</td>
<td>0.419</td>
<td>124.4</td>
</tr>
</tbody>
</table>

The mean C–N value of 1.370 Å lies above both the C–N double and aromatic bond lengths of 1.331 Å and 1.338 Å respectively, yet below the standard C–N single bond length of 1.468 Å. This implies that the PM3 method recognises these bonds have a greater electron density than a single σ bond but less than aromatic character. The shortest calculated mean C–N bond length is found for the sym-triazine molecule (number 12). Thus, the computational treatment of substituents bonded to the ring carbon atoms results in a withdrawal of electron density from the aromatic triazine π-system, resulting in a longer mean C–N bond length for these molecules (numbers 1 to 11).

The N–C–N and C–N–C internal ring bond angles depart from the hexagonal 120° values in the correct directions, i.e. the angle at carbon increases and that at nitrogen decreases, but not to the extent of the experimental measurements. This is an improvement over the DREIDING2.21 molecular mechanics calculations but not as accurate as the optimisations with the new force-field parameters.
The standard deviations in the internal bond angles are generally lower than in the crystal data, the exceptions being molecules 1 and 2 for N–C–N and 1, 2 and 10 for C–N–C. Molecules 9 and 12 are calculated as having a three-fold symmetry axis, thus their standard deviations are zero for the ring bond and angle data. Although molecules 1 and 2 also have the potential to exhibit three-fold symmetry, this was not shown using this method. This may be due to the greater number of atoms involved, resulting in a significant increase in the number of degrees of freedom and therefore a more complex potential energy surface.

3.5.2 Quantum Mechanical Structure Optimisations

Structures 3 to 12 were optimised using the 6-31G* basis set in the GAUSSIAN94 package. Owing to the number of atoms involved, and thus long calculation time required, molecules 1 and 2 were optimised using the 3-21G basis set.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>C-N (Å)</th>
<th>C-N-C (°)</th>
<th>N-C-N (°)</th>
<th>C-N-C (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.323</td>
<td>0.225</td>
<td>124.2</td>
<td>0.007</td>
</tr>
<tr>
<td>2</td>
<td>1.325</td>
<td>0.794</td>
<td>123.8</td>
<td>0.006</td>
</tr>
<tr>
<td>3</td>
<td>1.318</td>
<td>0.759</td>
<td>126.2</td>
<td>0.910</td>
</tr>
<tr>
<td>4</td>
<td>1.321</td>
<td>0.920</td>
<td>125.9</td>
<td>0.632</td>
</tr>
<tr>
<td>5</td>
<td>1.320</td>
<td>1.108</td>
<td>126.3</td>
<td>1.416</td>
</tr>
<tr>
<td>6</td>
<td>1.327</td>
<td>1.852</td>
<td>124.3</td>
<td>2.359</td>
</tr>
<tr>
<td>7</td>
<td>1.322</td>
<td>0.752</td>
<td>125.8</td>
<td>1.139</td>
</tr>
<tr>
<td>8</td>
<td>1.316</td>
<td>0.750</td>
<td>126.8</td>
<td>0.752</td>
</tr>
<tr>
<td>9</td>
<td>1.319</td>
<td>0.710</td>
<td>126.1</td>
<td>0.001</td>
</tr>
<tr>
<td>10</td>
<td>1.319</td>
<td>0.944</td>
<td>126.1</td>
<td>0.889</td>
</tr>
<tr>
<td>11</td>
<td>1.316</td>
<td>0.499</td>
<td>126.4</td>
<td>0.019</td>
</tr>
<tr>
<td>12</td>
<td>1.318</td>
<td>0.002</td>
<td>125.6</td>
<td>0.000</td>
</tr>
<tr>
<td>Total</td>
<td>1.320</td>
<td>0.777</td>
<td>125.6</td>
<td>0.678</td>
</tr>
</tbody>
</table>

The optimisations of the 12 molecules using ab initio methods show an improvement over the semi-empirical QM calculations in terms of structural ring parameters. C–N bond lengths are comparable with those of the original crystal data, although in general the mean bond length is slightly underestimated. Standard deviations in the calculated bond length data are lower than experiment except for molecules 4, 6, 11.
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and 12, although the difference in the standard deviations of molecule 12 is negligible.

The mean internal ring bond angles at carbon are generally closer to experiment than those of the semi-empirical calculations, the exceptions being molecules 2 and 12. All N–C–N angles still lie ca. 2° below the crystal data values, however, with standard deviations less than found in the crystal data. The mean bond angles at C–N–C conversely are all wider than found experimentally, by as much as 3.6° in the case of molecule 1. The overall mean value of 114.4° lies 1.8° above that of the crystal data. Standard deviations in the calculated C–N–C bond angles are lower in all cases than the corresponding experimental values, probably arising from a lack of intermolecular interactions.

The closeness of the C–N bond lengths to the observed values shows that this is calculated more accurately using a full electron treatment than the semi-empirical valence electron calculations. It is possible that the ‘closed shell’ radius used in PM3 is too large, thus the ring atom centres do not approach each other due to repulsive interactions. The inclusion of all electrons explicitly, and polarisation functions in particular to permit off-centre bonding, allows for perturbation to counter this effect and thus leads to a shorter C–N bond length than the semi-empirical treatment. As found in the crystal data, the mean ab initio calculated bond length is less than for a standard carbon-carbon aromatic or double bond, showing the bond order of the C–N bonds to be greater than the aromatic bonds in benzene. The values are also lower than the carbon-nitrogen aromatic or double bonds observed in pyridine and pyrazole respectively.

3.5.3 Comparison of Molecular and Quantum Mechanical Structure Optimisations

The different methods of energy calculation, and structure optimisation resulting from this, reveal how the various treatments interpret and deal with the aromatic nature of the sym-triazine unit by analysis of the molecular conformation. The simple molecular mechanics “ball and spring” approach can be refined by altering parameters in the force-field, as has been shown in this chapter.
When electrons are considered, in the semi-empirical and \textit{ab initio} quantum mechanical methods, conclusions can be drawn as to their distribution and resulting molecular physical properties. In terms of aromaticity, the \textit{sym}-triazine moiety conforms to the standard rules: it has a (roughly) planar conformation, contains $2n+2$ \pi electrons; a $p$ orbital on every atom on the ring; and a structure of conjugated double bonds. The conformation of the ring is not absolutely planar, however, rather there is a slight torsion angle of ca. 1° found experimentally. This may be due to the short C–N bond length observed and the bond angle behaviour about the carbon atoms in the ring.

The effect of ring substituents on the aromatic nature and bond lengths of the ring can be explained by considering quantum mechanically calculated electron densities at specific atomic positions in the set of molecules. In \textit{sym}-triazine (molecule 12) the partial charges on the carbon atoms are calculated as 0.0134 (PM3) and 0.2775 (GAUSSIAN 6-31G*), whereas those on the nitrogen atoms are -0.1572 (PM3) and -0.5079 (GAUSSIAN 6-31G*). The sum of all six (carbon and nitrogen) atoms is therefore -0.4318 (PM3) and -0.6913 (GAUSSIAN 6-31G*). This means that the six-membered ring is relatively electron rich, resulting in stronger and shorter bonds between the carbon and nitrogen atoms. This is observed experimentally in the mean C–N bond length being less than that for C–N aromatic or even double bonds.

Considering the trimethoxy-sym-triazine structure, this has three O–CH$_3$ groups evenly displaced around the triazine ring, bonded to the carbon atoms. In conventional aromatic chemistry the methoxy unit is one of the strongest electron donating activators (behind NH$_2$ and OH) and directs electrophilic substitution, and thus electron density, to the \textit{ortho} and \textit{para} positions\textsuperscript{118}. The activation arises from an electron donating resonance effect which more than outweighs the electron withdrawing inductive effect.

This theory suggests an increase in ring electron density, particularly on the nitrogen atoms, being in the \textit{ortho} and \textit{para} positions relative to the methoxy groups. The greater negative charge is reflected in the quantum mechanical calculations, the partial electronic charge at nitrogen increasing from -0.1572 to -0.2752 for PM3 and
from -0.5079 to -0.6838 for GAUSSIAN 6-31G*. The overall electron density of the ring system however is depleted for trimethoxy-\textit{sym}-triazine. The partial electron charge decreases to -0.1596 for the PM3 calculations and even becomes positive at 0.6782 for the GAUSSIAN 6-31G* calculations. This GAUSSIAN value suggests that, contrary to the theoretical electron donating activation of aromatic ring systems, the electron withdrawing inductive nature of this substituent outweighs the electron donating resonance effect.

Nevertheless, the ring electron density decreases upon addition of any of the substituents (other than hydrogen) studied in this work to the ring; they act as electron withdrawing groups. This is reflected in the increase in mean C–N bond lengths observed in the crystal structure analyses and GAUSSIAN 6-31G* (for all except molecule 11) and PM3 structure optimisations.

This suggests that, owing to the heteroatomic yet aromatic character of the \textit{sym}-triazine moiety, its electronic structure is more prone to influence by substituents than the monoatomic analogue benzene. Since in \textit{poly}(cyanurate) systems reaction proceeds by formation of these ring structures and it is not a structural unit of the monomer(s) used, inclusion of a functionalised co-monomer (\textit{e.g.} figure 3.8) could lead to a new generation of cyanate ester resins with novel electrical properties by the incorporation of an asymmetrically substituted \textit{sym}-triazine, as shown in figure 3.8, where the \textit{sym}-triazine ring electron density, and polymer conductivity, is influenced by the substituent (chlorine in this example).

![Figure 3.8 Hypothetical dicyanate monomer containing an asymmetrically substituted \textit{sym}-triazine functionality.](image-url)
3.6 Conclusions of the Adaptation of the Force-Field

These new terms change the characteristics of this sym-triazine/cyanurate unit markedly. In particular, the force constants for stretching, bending and inversion motions about the ring are much greater than those used in the DREIDING2.21 force-field. The flexibility of a poly(cyanurate) network would therefore have to rely much more on the backbone structure and ether oxygen linkages as their force constants are smaller in comparison.

It would be very interesting to assess the above comments by experimental analysis and computational simulation of a series of poly(cyanurate) networks with differing backbone structures. Such an investigation is unfortunately beyond the scope of this work, which is to improve modelling aspects of these resin systems for use in calculations of fibre/matrix interfacial interactions.

The optimisations on cyanurate systems using the new force-field parameters produce structures closer to those found in the crystal data than semi-empirical calculations and a better representation of internal ring bond angle data than *ab initio* quantum mechanical calculations. These quantum mechanical calculations have not only been used for comparison with the new force-field terms, but to explain some phenomena observed in the crystal structures, particularly substitution effects and C–N bond lengths.
Chapter 4: Inverse Gas Chromatography Characterisation of Carbon Fibre Surfaces

4.1 Chromatographic Techniques

4.1.1 Introduction

In 1993 the International Union of Pure and Applied Chemistry (IUPAC) defined chromatography as:\textsuperscript{119}

"... a physical method of separation in which the components to be separated are distributed between two phases, one of which is stationary while the other moves in a definite direction."

The underlying concept relies on the interaction between different species to afford a separation of the components. These interactions (only physisorption is considered here as chemisorption would change the chemical nature of the analytes and thus not belong to chromatography) are exactly the same as outlined previously (§2.1.1), comprising forces between permanent, induced and instantaneous dipoles in the molecules.

The most basic chromatographic system consists of two phases, known as stationary and mobile, and a means of detecting the result of the analysis. For example a separation of dye pigments by means of paper chromatography would use, say, water as the mobile phase to carry the dye mixture along the paper stationary phase. In the case of a coloured dye the analysis would be simply visual inspection of the dried paper to see the separation of colours. Many organic compounds, however, absorb practically no light in the visible region. For these compounds an alternative identification method could be by ultraviolet (UV) or infrared (IR) spectroscopy, resulting not only in a separation of compounds in the starting mixture but also a good indication of their molecular structure.
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The mobile phase is often known as the *eluant*, the component(s) that it carries across the stationary phase as the *solute(s)* and the process of this transportation from one end of the system to emerging at the other *elution*. The physical state of the mobile phase divides the types of chromatography quite neatly into gas and liquid methods, referred to simply as GC and LC (and modifications of these). The final, and arguably most important, component of a chromatographic system is the means of identification or *detection*. This really depends upon the type of information one wishes to obtain from the separation. If it is sufficient to measure only the elution times of the analyte(s) then a destructive system such as a *flame ionisation detector* (FID) or *flame photometric detector* (FPD) can be used. If, however, the sample is to be retained as its various components, then a non-destructive method must be used. The latter are typically spectroscopic analyses, UV, fluorescence, phosphorescence, *etc.*

A very popular destructive technique, which also allows a great deal of characterisation of the individual components of a sample, is the coupling of a gas chromatograph with a mass spectrometer (GC-MS). As the separated components elute they are fed directly into the mass spectrometer which provides chemical structure information from their molecular fragmentation patterns.

An FID has been used in the current work. This type of detector system consists of a hydrogen flame burning as a jet in a supply of filtered air. The jet acts as one electrode and a small wire ring of gauze above the flame as the other. Changes in ionisation current, due to components in the gas stream, are fed to an amplifier which converts the impedance to a value matching a 1mV recorder. A mixture of hydrogen and air is used for the flame, the flow rates of which must first be optimised for use. The flow rate of hydrogen should be close to that of the carrier gas, with the flow rate of air being of the order of ten times that of hydrogen. A low carrier gas flow rate will not be sufficient to light the flame while, conversely, a high flow rate will cause the flame to be extinguished. The temperature of the detector should be at least 125°C to prevent condensation of water formed from combustion of the hydrogen. This would lead to a noisy baseline and thus, problems in peak resolution.
4.1.2 Thin Layer Chromatography (TLC)

In this technique the stationary phase is normally coated on a glass slide or plate. The application of the analyte is in the form of a spot of the mixture dissolved in a volatile solvent, approximately 1-2 cm from the base of the plate. When the spot has dried the plate is placed vertically in a suitable tank with its lower edge immersed in a selected mobile phase. The solvent rises by capillary action (the liquid is drawn up the plate as a thin film in order to minimise surface energy) and an ascending chromatographic separation is obtained, resolving the sample mixture into discrete spots.

At the end of the run the solvent is allowed to evaporate from the plate and the separated spots are detected accordingly. After separation, detection and analysis it is relatively simple to recover an individual substance by scraping off and collecting the part of the layer on which the spot is adsorbed. The substance can then be extracted using a suitable solvent, prior to e.g. spectroscopic analysis.

Major features controlling the resolution capability of TLC are the ‘spot size’ and the physical dimensions of the plate. With a spot diameter of 0.5 cm and a plate length of typically 10 cm, a maximum of about 20 analytes could be resolved. The number of theoretical plates or separation steps indicates the efficiency of a column (its separation capabilities). In chromatographic methods where a chromatogram is produced, this is calculated from a ratio of the retention time to the peak width (at the baseline or at half-height). In TLC and other ‘planar’ chromatographic methods it is a function of the distance travelled by the spot divided by the width of the spot. Thus, ‘spot broadening’ must be minimised to effect a good separation.

The standard practice in reporting results using this separation technique are in terms of a migration value ‘relative to the solvent front’ \((R_f)\).

\[
R_f = \frac{\text{distance travelled by solute}}{\text{distance travelled by solvent front}}
\]

The variables which should be quoted are the identities of the stationary and mobile phases. The solvents used as mobile phases in TLC are usually ranked in order of
their dielectric constant and selected on the basis of the hypothetical polarities of the analyte mixture. There is a wide variety of stationary phases which can be used as well, depending on the compounds to be separated. The most common include silica gel, alumina (aluminium oxide), kieselguhr, cellulose powder and starch.

4.1.3 Liquid Chromatography (LC)

In the more conventional LC techniques, a column is packed or coated with the stationary phase, and the mobile phase transports the analyte mixture through it. As opposed to TLC, where in the mobile phase travels by capillary action alone, these methods require a force to move the mobile phase. In its simplest form a straight, cylindrical column is packed with the stationary phase and the mobile phase is added to the top if it. A separation of the sample mixture occurs as the mobile phase carries it through (down) the column by gravity and it is eluted at the bottom. The sample (or different sample components) would then be collected and analysed separately.

When pressurised, narrow bore cylindrical columns are used (as part of a chromatography instrument), a pump is required to elute the mobile phase but the principles remain unchanged. This technique has led to the term *high performance liquid chromatography* (HPLC), the previously explained gravity controlled method being referred to as *open column liquid chromatography*. The reasons behind the development of HPLC are manifold. Firstly, open columns are awkward to pack and generally only used once, making the technique very expensive. The efficiency achieved by these large particle packings is relatively low, the analysis time lengthy and the accuracy variable due to personal technique (*e.g.*, application of sample). Finally, the detection of the solute in the eluant is performed manually following collection of the individual fractions, again a lengthy process.

Modern instrumentation allows all of the variables (mobile phase flow rate, column temperature, detector parameters) to be adjusted quite easily, often as part of a computer interface. Autosamplers are commonplace, thus the operator need only make up the samples and input the parameters for the analysis. The interpretation of the results remains the only significant variable.
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The big advantage of HPLC over open column chromatography comes in the analysis of the results. As the mobile phase flows at a specific (either set or at least measurable) rate, a retention time \( t_R \) can be measured for the component to pass from injection to elution along the column. This retention time is a function of the interaction between the (solvated) component and the stationary phase. Differences in flow rate are normalised by multiplying the retention time by the mobile phase flow rate \( F_{col} \) to yield a retention volume \( V_n \),

\[
V_n = F_{col} t_R
\]

Equation 4.1

This is not really the entire picture as, owing to the column dimensions, it would take a certain amount of time for any non-interacting particle to flow through the column, known as the dead time \( t_M \). Thus, a corrected retention volume \( V_n' \) can be calculated,

\[
V_n' = F_{col} (t_R - t_M)
\]

Equation 4.2

Variations on this technique use different types of separation mechanisms for particular analyses. When dealing with polymer samples, size exclusion or gel permeation chromatography (GPC) is often employed. Exclusion chromatography utilises the selective diffusion of solute molecules within the solvent filled pores of a three-dimensional lattice. In general, two types of stationary phase are used for GPC, either macromolecular polymers (organic gels) or rigid inert porous silicas and glasses. Small molecules permeate the pores while large bulky molecules will be excluded, thus eluting first. In this way the separation is achieved on the basis of molecular hydrodynamic volume. In the case of polymer characterisation, GPC is used to calculate molecular mass distributions, calibrated by a series of standards of known molecular weight.

4.1.4 Gas Chromatography (GC)

The main difference here from liquid chromatography is that the mobile phase is gaseous, often referred to as the carrier gas, and transports the volatile sample
mixture through the column. The injection port of the machine is often heated to volatilise liquid samples as they enter the carrier gas stream at the column inlet. The stationary phase is usually solid, in the form of a packed or capillary column, although gas-liquid chromatography uses a liquid coated onto the inside of the column walls as the stationary phase.

As for liquid chromatography, a retention time can be measured and corrected by subtracting the column dead time. The flow rate of the carrier gas is used in place of a liquid flow rate. This can be measured and set using a soap bubble flowmeter.

![Soap bubble flowmeter](image)

**Figure 4.1** Soap bubble flowmeter used to measure gas flow rates.

Squeezing the teat (at the bottom in the diagram) forms a soap bubble and the time is measured for the carrier gas to propel the bubble a certain distance, calibrated in volume. Thus, the flow rate of the gas in the units volume/time is obtained. It is important to wet the walls of the flowmeter thoroughly before measurement as any dryness leads to irreproducible flow rate determinations because the gas in the meter is not saturated with water vapour.

Other important parameters to be taken into consideration are the inlet and outlet pressures. The pressure at the column outlet is simply that of the current atmospheric pressure and can be recorded using a conventional barometer. The inlet pressure, however, depends upon the force required to propel the carrier gas through the column at the required flow rate. This can be quite problematic to measure and regulate. The gas chromatograph used for the analyses of the carbon fibre surfaces
has been specifically adapted to constantly monitor the inlet pressure using a differential pressure gauge.

Figure 4.2 Schematic of the apparatus used to measure the pressure difference \( (P_{\text{diff}}) \) between the column inlet and outlet using a differential pressure gauge. The arrow depicts the flow of the carrier gas.

Before the injection port, where the sample is introduced into the carrier gas stream, a side junction connects the gas line to one side of the differential pressure gauge, the other side being open and thus, experiencing atmospheric pressure. Rather than recording the absolute value of the inlet pressure, a measure of the pressure difference between it and the atmospheric pressure is recorded. The inlet pressure is then the sum of both values. The measurement is actually performed across an electric gauge which records the difference in mV. This can be converted to mbar using the relation,

\[
1.000 \text{ mbar} = 0.0145 \text{ psi} = 0.0464 \text{ mV} \quad \text{Equation 4.3}
\]

Both the inlet and outlet pressures are used in the calculation of the \( j \)-value. For a given flow rate, this is dependent upon the column dimensions and packing.

\[
j = \frac{3}{2} \frac{\left( \frac{P_{\text{in}}}{P_{\text{out}}} \right)^2 - 1}{\left( \frac{P_{\text{in}}}{P_{\text{out}}} \right)^3 - 1} \quad \text{Equation 4.4}
\]

For calculating the sample retention volumes from their retention times, the corrected column flow rate \( (F_{\text{col}}) \) is used,
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\[ F_{col} = F_{fio} \times \frac{T_{col}}{T_{room}} \times j \times \left( \frac{P_{out} - P_{w}^{w}}{P_{out}} \right) \]  \hspace{1cm} \text{Equation 4.5}

This is a function of the carrier gas flow rate \((F_{fio})\), recorded using the soap bubble flowmeter, the column \((T_{col})\) and room \((T_{room})\) temperatures and the \(j\)-value. The final term is a correction for the vapour pressure of the water in the soap bubble flowmeter \((P_{w}^{w})\), inherent in using this method to measure the carrier gas flow rate.

4.2 Inverse Gas Chromatography (IGC)

The main difference between conventional gas chromatography and IGC is the rôle reversal of the stationary and mobile phases. The stationary phase becomes the unknown entity and a series of samples \((\text{probes})\) with defined physical interaction characteristics are used to quantify its surface by means of these interactions. Furthermore, the probes are generally injected individually into the column and not as mixtures, as separation is not the prime function of the stationary phase.

As for gas chromatography, the retention time is the fundamentally measured parameter and this is corrected for by the column dead time (the time which is required for the non-interacting carrier gas to pass through the column). This is usually determined using methane which is assumed to be non-interacting.

4.2.1 Dead Time Correction

At this point the procedure used in this work deviates from the norm, where it is standard practice to simply subtract the dead time from the retention time when calculating an adjusted corrected retention time\(^{122,123}\). This would be the correct procedure if a methane 'spike' was included in the sample and thus both values could be measured during the same run. The majority of samples used in this technique, however, are liquids and thus must be volatilised first before entering the carrier gas stream. The inclusion of a gaseous methane spike in a vial of liquid sample could
create problems in the mixing of the gaseous and liquid phases in this container. When drawn into a syringe for injection into the machine one could not be sure that there was a sufficient amount of methane to be detected.

Performing the dead time measurement separately from the measurements of the probes’ retention times requires normalisation by inclusion of changes in carrier gas flow rate, which is itself affected by temperature and pressure. Consequently, the dead time of the column has not been used to calculate corrected retention times, but used instead to calculate volume components in order to correct the retention volume term, normalising for pressure and temperature differences. Mathematically this means separation of the terms in equation 4.2 to yield equation 4.6, where the superscripts in the $F_{col}$ term indicate that the conditions (flow rate, j-value, temperature, pressure) are measured separately for the analyses of the probes ($R$) and dead time sample ($M$).

$$V'_N = (t_R F^R_{col}) - (t_M F^M_{col})$$  \hspace{1cm} \text{Equation 4.6}$$

Practically, this has allowed the column dead time measurement to be treated as a sample in its own right. It is one of the most important variables in the method of calculation, as any error in its measurement would, in turn, be magnified throughout the entire series of probe molecules used in the analysis.

4.2.2 Surface Thermodynamic Properties

From the retention volume ($V'_N$) and the determination of the surface area ($A$) of the stationary phase, a partition coefficient ($K_S$) can be calculated,

$$K_S = \frac{V'_N}{A}$$  \hspace{1cm} \text{Equation 4.7}$$

This is essentially a ratio of the concentration of the probe molecules retained on the stationary phase per unit area of the stationary phase. From $K_S$, and its temperature dependence, thermodynamic data describing the retention process can be derived. For example, the standard free energy change for the isothermal adsorption of one
mole of adsorbate, from the gaseous state to a standard state on the surface is given by,

\[ \Delta G_A^0 = -RT \ln \left( \frac{K_S P_{s,g}}{\pi_s} \right) \]  

Equation 4.8

where \( P_{s,g} \) is the adsorbate vapour pressure in the gaseous standard state, \( \pi_s \) is the vapour pressure in equilibrium with the standard adsorption state, \( R \) is the gas constant (8.315 J K\(^{-1}\) mol\(^{-1}\)) and \( T \) is the column temperature (Kelvin).

Two groups have presented different values for the \( P_{s,g} \) and \( \pi_s \) terms: de Boer\(^{24}\) proposed values of \( P_{s,g} = 101 \text{ kN m}^{-2} \) (1 atm) and \( \pi_s = 0.338 \text{ mN m}^{-1} \), while Kemball and Rideal\(^{25}\) alternatively proposed \( \pi_s = 0.0608 \text{ mN m}^{-1} \). The \( \pi_s \) value arbitrarily defines the surface pressure as the pressure at which the average distance of separation between the molecules in the adsorbed state equals that in the standard gas state.

If equation 4.1 is substituted into equation 4.2 and rearranged one obtains,

\[ -\Delta G_A^0 = RT \ln V'_N + C \]  

Equation 4.9

where \( C \) is a constant for a given column depending on the chosen reference states.

To a first approximation, \( \Delta G_A^0 \) is related to the energy of adhesion, \( W_A \), between the probe molecule and the solid, per unit surface area of the solid (\( Na \)) by,

\[ -\Delta G_A^0 = NaW_A \]  

Equation 4.10

where \( N \) is Avogadro’s number and \( a \) is the surface area (m\(^2\)) of the probe molecule. Combining equations 4.9 and 4.10 yields,

\[ RT \ln V'_N = NaW_A + C \]  

Equation 4.11
4.2.3 Calculation of Sample Dispersive Surface Energy

There are two general methods used in the calculation of a material’s dispersive surface energy component by IGC. Fowkes\textsuperscript{126} proposed that when only dispersion interactions are occurring, for example when performing measurements with $n$-alkane probes, the work of adhesion could be expressed in terms of the dispersive surface energy components of the solid ($\gamma_s^d$) and liquid ($\gamma_l^d$) phases,

$$W_A = 2\left(\gamma_s^d \gamma_l^d\right)^\frac{1}{2}$$ \hspace{1cm} \text{Equation 4.12}

In such a case equation 4.11 can be rewritten in the form

$$RT \ln V_N = 2N\left(\gamma_s^d\right)^\frac{1}{2} a \left(\gamma_l^d\right)^\frac{1}{2} + C$$ \hspace{1cm} \text{Equation 4.13}

This implies that $RT \ln V_N$ is a linear function of $a(\gamma_l^d)^{1/2}$. Thus, using such $n$-alkane probes, the dispersive component of a sample’s surface energy can be determined from a simple $y = mx + c$ relationship. This linear relationship is referred to the reference alkane line and defines the dispersive surface energy component of the probe-surface interaction.

The second method, formulated by Dorris and Gray\textsuperscript{127}, for calculating the dispersive surface energy component relies on analysis of the $n$-alkane probe measurements in terms of their increasing methylene (-CH$_2$-) backbone structure. A plot of $RT \ln V_N$ vs. the number of carbons in the $n$-alkane backbone allows an increment of the retention volume per methylene unit to be calculated. They then use the equation,

$$\gamma_s^d = \frac{RT \ln \left[ \frac{V_N^{(C_{\text{meth}}H_{10n})}}{V_N^{(C_{\text{meth}}H_{12m2})}} \right]}{4N^2 a_{CH_2} \gamma_{CH_2}^2}$$ \hspace{1cm} \text{Equation 4.14}

where $a_{CH_2}$ is the cross-sectional surface area of a methylene unit and $\gamma_{CH_2}$ is the surface energy of a surface constituted of close packed -CH$_2$- groups analogous to polyethylene which has a value of 35.6 mJ m$^{-2}$\textsuperscript{128}. 
The first approach was selected for a number of reasons. The plot of $RT\ln V_N^\prime$ vs. $\alpha(\gamma f)^{1/6}$ yields the information required to calculate the dispersive component of the fibre’s surface energy and provide the reference alkane line used in the analysis of the acid-base character by the donor-acceptor number approach. Furthermore, the sole consideration of a size parameter to reflect differences in the retention of $n$-alkanes of increasing carbon backbone seems an oversimplification. Although, e.g. $n$-heptane comprises one more methylene unit than $n$-hexane, owing to the larger number of atoms present in the molecule there is also a greater number of degrees of freedom ($x$), i.e. the molecule could exhibit a larger number of conformations. Not all of these conformations would lead to a greater external surface area to come into contact with the stationary phase. As the number of degrees of freedom increases as $x^3$, the methylene increment would seem non-linear. The analogy of the close packed $-\text{CH}_2-$surface with the polyethylene surface would appear unsatisfactory, and there are different reports in the literature as to the accuracy and source of the polyethylene surface energy measurement\textsuperscript{129}.

4.2.4 Calculation of Sample Acid-Base Character

For a full interpretation of the results obtained from use of the donor and acceptor probes, the reference alkane line, obtained by linear regression of the $n$-alkane data on the plot of $RT\ln V_N^\prime$ vs. $\alpha(\gamma f)^{1/6}$, is used. The displacement of the polar probe data from the reference alkane line is taken as an indication of the specific acid-base interaction of the particular probe. By calculating the retention volume of the reference alkane line at the same $\alpha(\gamma f)^{1/6}$ value the specific acid-base free energy component for the fibre-probe interaction can be determined using,

$$
\Delta G_f^{ab} = -RT \ln \left( \frac{V_N^\prime}{V_N^{ref}} \right)
$$

Equation 4.15

where $\Delta G_f^{ab}$ is the specific acid-base free energy component of fibre/probe interaction, $V_N^\prime$ is the retention volume of the probe molecule and $V_N^{ref}$ is the corresponding retention volume of the reference alkane line at the same $\alpha(\gamma f)^{1/6}$ value.
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The next stage involves calculation of the enthalpy of adsorption of the particular probes, $\Delta H_A$. Using equation 4.8 and Gibb's relation of free energy, enthalpy and entropy, one obtains\textsuperscript{130},

$$-RT \ln \left( \frac{K_p \rho}{\pi_s} \right) = \Delta H_A - T \Delta S_A$$

Equation 4.16

which rearranges to,

$$-R \ln \left( \frac{K_p \rho}{\pi_s} \right) = \frac{\Delta H_A}{T} - \Delta S_A$$

Equation 4.17

$K_s$ is dependent upon $V_N$ and not $A$ (assumed constant over all temperatures), thus if one plots $-R \ln(K_p \rho_s/\pi_s)$ vs. $1/T$ for each individual probe, the gradient should yield $\Delta H_A$ for the particular probe.

For the calculation of the specific enthalpy of adsorption ($\Delta H_{A \, ab}$) for the donor and acceptor probes, $\Delta H_A$ is plotted against $a(y^*)v^*$ (in a similar way to $RT \ln V_N$), and from the graph the equation,

$$\Delta H_{A \, ab} = \Delta H_A - \Delta H_A^{\text{ref}}$$

Equation 4.18

is used, $\Delta H_A^{\text{ref}}$ being calculated in a similar way to $V_N^{\text{ref}}$. The use of the donor and acceptor numbers comes in determining the donor and acceptor characteristics of the fibre under analysis. From the IGC results these are obtained using,

$$\Delta H_{A \, ab} = (K_A \times DN) + (K_D \times AN)$$

Equation 4.19

where $DN$ and $AN$ are the donor and acceptor numbers respectively for the particular probe and $K_A$ and $K_D$ represent the strength of electron-acceptor and -donor properties of the fibre. Amphoteric probes (finite donor \textit{and} acceptor numbers) will yield both $K$ values using,
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\[
\frac{\Delta H^{ab}_{A}}{AN} = \left( K_A \times \frac{DN}{AN} \right) + K_D \quad \text{Equation 4.20}
\]

i.e. a plot of \( \Delta H^{ab}_{A}/AN \) vs. \( DN/AN \) for different probes should provide a straight line with slope equal to \( K_A \) and intercept \( K_D \). A specific interaction term for fibre-matrix adhesion has been proposed,

\[
I_{sp} = \left( K_A^f \times K_D^m \right) + \left( K_D^f \times K_A^m \right) \quad \text{Equation 4.21}
\]

where the superscripts \( f \) and \( m \) refer to the fibre and matrix phases respectively. In order to verify this term, the task would be to establish a relationship between the interaction term for interfacial (fibre-matrix) adhesion and the strength of the interface as determined by mechanical testing. This remains an interesting prospect for future studies although no analyses of typical matrix resins were performed using this method.

Schultz, Lavielle and Martin\textsuperscript{132} have used this approach to study untreated, oxidised and coated carbon fibres with a DGEBA-DDS epoxy matrix. They reported a decrease in the dispersive component of the fibre's surface energy from untreated, through oxidised to coated fibres. In terms of acid-base interaction the untreated fibre had an average acidic and practically no basic character, the oxidised fibre had a strong acid character and rather low basic character and the coated fibre was considered amphoteric, possessing both strong acidic and basic character. The epoxy matrix analysed showed a dispersive surface energy component of the same order as those of the fibres (40 mJ m\(^{-2}\)) and relatively high acidic and basic character.

The specific interaction parameter was found to increase from the untreated to the oxidised and further to the coated fibre. The amphoteric nature of both this fibre type and the epoxy resin lead to the strongest acid-base interaction.

Fibre-matrix adhesion was further tested by using a fragmentation test, in which a fibre was embedded in the epoxy matrix and subjected to a uniaxial tensile stress in
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the direction of the fibre. The single fibre was broken into segments and the shear strength (τ) of the interface calculated using a Weibull analysis\textsuperscript{133}. In agreement with the IGC interpretation, the adhesion was found to increase from the untreated, through oxidised to the coated fibre. The adhesion of the coated fibre was roughly 30% greater than that of the untreated fibre. There was shown to be a strong correlation between the interfacial shear strength of the epoxy-embedded single fibre and the specific acid-base fibre/matrix interaction parameter. They concluded that the interfacial adhesion could result principally from acid-base or donor-acceptor interactions between the fibre and matrix, assuming that dispersive interactions are of the same order of magnitude in each substrate.

4.3 Assignment of Probe Characteristics

Table 4.1 Probe cross-sectional area (a), dispersive surface energy component (γ\text{d}), boiling point (b.pt.), donor number (DN) and acceptor number (AN).

<table>
<thead>
<tr>
<th>Probe</th>
<th>a (Å\textsuperscript{2})</th>
<th>γ\text{d} (mJ m\textsuperscript{-2})</th>
<th>a(γ\text{d})\textsuperscript{1/2} (Å\textsuperscript{2} mJ\textsuperscript{1/2} m\textsuperscript{-1})</th>
<th>b.pt. (°C)</th>
<th>DN</th>
<th>AN</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-hexane</td>
<td>51.0</td>
<td>17.91</td>
<td>215.8</td>
<td>69.0</td>
<td>19.2</td>
<td>3.9</td>
</tr>
<tr>
<td>n-heptane</td>
<td>57.0</td>
<td>19.80</td>
<td>253.6</td>
<td>98.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-octane</td>
<td>63.0</td>
<td>21.14</td>
<td>289.7</td>
<td>125.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>diethylether</td>
<td>42.1</td>
<td>17.00</td>
<td>173.6</td>
<td>34.6</td>
<td>17.7</td>
<td>12.5</td>
</tr>
<tr>
<td>acetone</td>
<td>33.1</td>
<td>18.50</td>
<td>134.5</td>
<td>56.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>36.6</td>
<td>19.20</td>
<td>160.4</td>
<td>66.0</td>
<td>20</td>
<td>8</td>
</tr>
<tr>
<td>benzene</td>
<td>37.0</td>
<td>26.70</td>
<td>191.2</td>
<td>80.0</td>
<td>0.1</td>
<td>8.2</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>39.5</td>
<td>33.50</td>
<td>228.6</td>
<td>101.3</td>
<td>14.8</td>
<td>10.8</td>
</tr>
</tbody>
</table>

The method of IGC relies to a large extent on the nature of the probe molecules used in the analysis. The parameters which characterise these probes are the assignment of donor and acceptor numbers, the calculation of their dispersive and polar surface energy components, and the calculation of their cross-sectional areas.

4.3.1 The Donor-Acceptor Number Classification

This empirical method has been introduced by Gutmann as a means of assigning values characteristic of a compound's electron-donor or -acceptor influence over an adjacent molecule. The method is based on a set of experimentally observed "bond
length variation rules", which describe the changes in intramolecular bond lengths as two molecules approach each other. Essentially this induced change in bond length is due to the transferal of charge from the Lewis base to Lewis acid species.

The donor number of a particular probe is defined as “the molar enthalpy value for the reaction of the donor (D) with SbCl₅ as a reference acceptor in a 10⁻³ molar solution of dichloroethane”¹³⁴. The molar enthalpy of 1:1 molecular adduct formation in 1,2-dichloroethane is taken as an approximate measure of the energy of the co-ordinate bond between donor atom and the Sb atom of SbCl₅.

The acceptor number of a particular probe is defined as “a dimensionless number related to the relative chemical shift of ³¹P in Et₃PO in the particular solvent, with n-hexane as the reference solvent on one hand and Et₃PO·SbCl₅ in 1,2-dichloroethane on the other, to which the acceptor numbers of 0 and 100 have been assigned respectively”.

In order to emphasise the relationship between acceptor properties and their conjugate donor properties, the same substance (SbCl₅) has been used as a standard for both parameters. It must be stressed, however, that donor numbers are distinct from acceptor numbers.

4.3.2 Dispersive and Polar Surface Energy Components

The routine method for determining energy components of a liquid sample is by contact angle analysis¹³⁵. The procedure measures the contact angle formed by a liquid sample on a solid surface. In the static form of the measurement, photographs of droplets on surfaces are taken and the angles at which the liquid and solid sample make contact recorded. The dynamic form involves the measurement of force on a solid sample as it enters, and is drawn out of, a liquid sample. Both methods rely on a knowledge of the surface energy components of the solid surface.
4.3.3 Probe Cross-Sectional Area Parameter

This is definitely the least well known of the three probe characteristics required in the IGC analysis. Values used in this thesis have been taken from the literature\textsuperscript{136}.

A question arising from this approach is the use of the cross-sectional area of a probe molecule rather than its surface area. This implies that the interactions (adsorption, desorption, etc.) are considered as two-dimensional processes only. It may be simpler by hand to calculate two-dimensional cross-sectional areas rather than three-dimensional van der Waals-type surface areas, yet current computational methods can determine these values with ease, for example by the method of Connolly et al.\textsuperscript{137,138} where a sphere of fixed radius is rolled over the surface of the molecule.

4.3.4 Other Methods of IGC Interpretation

There are several variations on the use of probe parameters for the calculation of $\Delta G^b_A$ values. Here $RT\ln V_N$ is considered as a function of probe cross-sectional area and dispersive surface energy, and analysed using donor and acceptor numbers. An alternative to this is the use of probe boiling point and work has also been published on this method\textsuperscript{139}. Figure 4.3 shows that there is little correlation between the two approaches\textsuperscript{129}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.3}
\caption{Correlation between different IGC probe parameters.}
\end{figure}
Others have explored the relationship between retention volumes and molar deformation polarisation\textsuperscript{140,141}. They conclude that the use of a particular method to interpret the results is dependent upon the type of material under analysis. Since previous work on carbon and glass fibres has used the probe cross-sectional area and dispersive surface energy approach\textsuperscript{142}, the data have been analysed using this method. This interpretation also has the advantage of splitting the surface energy of the adsorbates into dispersive and specific acid-base components, a routine procedure in the analysis of surface energies by contact angle measurements.

### 4.4 Surface Area Analysis

One of the important parameters in the characterisation of fibre surfaces by IGC is the total surface area of the sample under analysis. The dimensions of the chromatography column used allowed \textit{ca.} 5g of continuous fibre to be packed in each of the sample columns. Experimental apparatus to measure nitrogen adsorption at 77K, and from the resulting isotherms calculate the sample’s surface area, is well documented\textsuperscript{143,144}. Chromatographic methods have also been used to determine specific surface areas\textsuperscript{145}. A far simpler and more convenient approach was to use a Coulter SA3100 Surface Area Analyser, specifically designed for this type of measurement.

#### 4.4.1 Procedure for Surface Area Measurement

A two-section sample tube was used to analyse the carbon fibre samples as the conventional tube facilitated packing only via a slender hole at the top of the tube neck. Although this is adequate for microporous powders and particulates, the continuous nature of the fibres required direct packing into the sample chamber. During analysis a glass rod was placed in this section of the tube to minimise the free volume, thereby increasing the accuracy of the measurement. The two sections of the tube were sealed with high vacuum silicone grease to eliminate leaks during the measurement.
Initially, the tube sections were cleaned in a hot water/teepol solution, rinsed with distilled water and then flushed with acetone to remove traces of water. They were then dried at 120°C overnight, allowed to cool and weighed prior to the sample packing for analysis. The mass was recorded to four decimal places on an enclosed microbalance to reduce air fluctuations.

A pre-analysis sample purification treatment (known as an outgas) was performed to remove contaminants adsorbed from the air such as dust particles and moisture. This was performed for 6 hours at 120°C under vacuum. The sample was re-weighed after outgas to monitor any changes in its mass and the new value used.

The machine was set up to record ten adsorption measurements on each sample and analyse the results using both the BET and Langmuir isotherms. The rôle of the Langmuir analysis was as a check of the accuracy of the results. As this method only considers monolayer adsorption, greater values of surface area are calculated than would be for multilayer adsorption, yet they should all lie roughly 10% above the BET results; this was indeed the case.

4.4.2 Limitations of the Technique with respect to Continuous Carbon Fibres

Owing to their relatively low surface areas, as much sample as possible should be packed into the sample chamber. It is recommended that a total surface area of at least 3m² be used, however "if the resulting volume is too large...the minimum total surface area can be reduced as low as 1m², although some accuracy will be sacrificed". In practical terms ca. 2.5-3g was the maximum amount possible to pack into the sample chamber because of its dimensions.
British Standard BS4359\textsuperscript{147} details recommendations for gas adsorption by BET methods. Although nitrogen is usually the most suitable adsorptive for the BET method, "...for powders with a low surface area an adsorptive with a low saturation vapour pressure at the temperature used, e.g. krypton, will reduce the dead space correction and increase the precision of the measurement."

It is worth noting that the customary value used for nitrogen cross-sectional area is 0.162 nm\textsuperscript{2}, yet quoted values range from 0.136 to 0.162 nm\textsuperscript{2}. Since the highest value is \textit{ca.} 20\% greater than the lowest, this is a significant factor in reporting results of surface area calculations measured in this way. Indeed, the difference in quoted values is even greater (in percentage terms) for argon, krypton and xenon adsorptives.

To this end, since the surface area of the carbon fibre samples is not the main focus of this study, but rather the values used in the analysis of the IGC results, with consideration of the instrument variables and the recommendations from BS4359, the procedure and sample mass used are adequate for the end result.

\subsection*{4.4.3 Results for Differently Surface Treated Carbon Fibres}

The measurements described above were performed on each fibre type five times and the results averaged. The isotherm data were analysed using the BET method for multilayer adsorption. Correlation coefficients for the BET analyses were 0.996 or greater. The results are listed in table 4.2.

\begin{table}[h]
\centering
\caption{Table 4.2 Results for 10 point surface area measurements analysed using the BET isotherm.}
\begin{tabular}{|c|c|c|}
\hline
Fibre Surface Treatment (\%) & BET Surface Area Determination & \\
& Mean (m\textsuperscript{2}g\textsuperscript{-1}) & Standard Deviation (\%) \\
\hline
0 & 0.323 & 4.5 \\
25 & 0.330 & 2.9 \\
50 & 0.335 & 2.0 \\
100 & 0.320 & 4.2 \\
200 & 0.327 & 1.1 \\
\hline
\end{tabular}
\end{table}

All of the averages lie within a range of 0.015 m\textsuperscript{2} g\textsuperscript{-1} of each other, just under 5\% of the mean values. This remarkably low deviation implies that the surface area and thus roughness of the fibre surfaces is not significantly modified by the surface
Inverse Gas Chromatography Characterisation of Carbon Fibre Surfaces

rather than using a single value, however, the IGC results for the various fibre types have been calculated using the corresponding surface area values given above.

These measurements compare favourably with literature data\textsuperscript{148} for similar analyses, which report values between 0.326 and 0.378 m\textsuperscript{2} g\textsuperscript{-1} and a small concentration of micropores (ca. 30 μg g\textsuperscript{-1}) for fibres with varying treatments. Pore blocking experiments suggested only limited accessibility arising from their small molecular dimensions and thus their ability to act as sites for mechanical keying of relatively large polymer matrix components was seen as "somewhat limited". A Ministry of Defence (M.o.D.) study\textsuperscript{149} into high temperature heat treatment effects on carbon fibre surface area and porosity also reported surface areas in the region of 0.298 to 0.364 m\textsuperscript{2} g\textsuperscript{-1}, although the study of the fibre treatment effects proved to be largely inconclusive.

4.4.4 Conclusions

The results for the surface area analyses of the differently treated carbon fibre samples indicate that the surface treatment does not significantly change the surface area. It is interesting to compare these values with calculated theoretical surface areas for cylinders. Assuming a density of 1.77 g cm\textsuperscript{-3}, as in the case of high strength carbon fibres\textsuperscript{150}, surface areas have been calculated for continuous cylinders with radii of the order of fibrous materials. The relationship between cylindrical radius and surface area is shown graphically in figure 4.5.

Comparing the surface area results for the surface treated carbon fibres with these "perfect" cylinders, the values would imply a fibre radius of ca. 3.5 μm. Experimentally, the radii are closer to 4 μm\textsuperscript{151}, corresponding to a cylindrical surface area in the region of 0.28 m\textsuperscript{2} g\textsuperscript{-1}. Thus, the geometry of the actual carbon fibres is more complex than a smooth cylinder; a degree of surface roughness also exists. This roughness, whilst having a possible contribution to interfacial adhesion, does not vary significantly with the application of the surface treatment. Hence, any observed changes in the interfacial properties of the differently treated fibres should be explained by mechanisms of adhesion other than mechanical keying.
Chapter 4: Inverse Gas Chromatography Characterisation of Carbon Fibre Surfaces

4.5 Practical Aspects of IGC including Setup

4.5.1 Instrument Parameters

High purity nitrogen was used as the inert carrier gas with a flow rate of 20 cm$^3$ min$^{-1}$. The FID required a mixture of hydrogen (20 cm$^3$ min$^{-1}$) and air (flow rate 200 cm$^3$ min$^{-1}$). All flow rates were set manually, the air and hydrogen at the start of each morning/afternoon and the nitrogen before each analysis as small changes in atmospheric temperature and/or pressure could lead to inaccuracies. The injection port temperature ($T_{inf}$) was maintained at 200°C to ensure flash vapourisation of the liquid probes as they were injected into the column. The detector temperature ($T_{det}$) was also maintained at 200°C. The operating temperatures for the fibre columns ($T_{col}$) varied from 60 - 175°C, depending on the probe elution time.

Integration of the chromatogram was performed automatically and the retention times determined from the peak maxima by the PU 1450 integrator. A limit to the accuracy of the retention data was the timebase, which was set at the maximum limit of resolution of 1/100 minute. This value, having a time interval of 0.6 seconds, is still more accurate than calculation of the distance between the injection marker and

Figure 4.5 Reciprocal relationship between surface area and cylinder radius (cylinder ends neglected).
peak maximum from a chromatogram using a ruler, and conversion to retention time with a knowledge of the chart speed. The integrator was started manually at the same time as the syringe was depressed and the sample introduced into the injection port.

4.5.2 Column Packing and Pre-analysis Conditioning

The continuous carbon fibre samples were packed into 1m long, \( \frac{1}{4}'' \) internal diameter glass columns to be subsequently fitted into the chromatography machine. The nature of the fibres meant that they had to be drawn through the column. This was achieved by tying an end to a length of copper wire which had been previously fed through the empty glass column. The wire was then drawn gently and the column rotated simultaneously to ensure even packing of the material with no voids. Care was taken to prevent surface damage of the material as it was drawn into the column.

Several attempts were made to determine the optimum quantity of fibre to use as the column packing. Obviously it is advantageous to have as much surface area (i.e. material) as possible in the column to afford the best possible separation of the probe molecules. Complications associated with the inlet pressure required for the carrier gas flow rate, lengthy retention times for densely-packed columns and column lay-up procedure restricted the packing to four fibre tows per column.

The \textit{conditioning} of the packed fibre samples can be considered to be analogous to the \textit{outgassing} procedure used in the surface area analysis (§4.4.1). Once the column was packed, it was connected to the inlet port and conditioned for 24 hours at a column temperature of 120°C under nitrogen flow.

4.5.3 Procedure for Sample Characterisation

Probe samples were analysed individually by injecting 0.02 \( \mu \text{l} \) into the carrier gas stream. A 1 \( \mu \text{l} \) Hamilton syringe was used to draw an amount of sample from a sealed vial, the plunger depressed to 0.02 \( \mu \text{l} \) and the needle wiped with a tissue before actual injection. Five injections were made for each probe sample at the specified \( T_{col} \) values and the results averaged. Upon changing the column oven temperature,
an equilibration period of five minutes was allowed. Atmospheric pressure and differential pressure readings were taken per set of 5 injections and changes allowed for in the calculations. The carrier gas flow rate was measured per sample series and changes adjusted for similarly. Owing to the large number of injections, the septum on the injection port was renewed per sample series to prevent leaks and fluctuation in the carrier gas flow rate and inlet pressure.

The volume of probe injected into the machine was extremely small to ensure infinite dilution of the sample. Using these volumes, the sample is so dilute that probe-probe interaction and association can be neglected, and solely probe-surface interactions measured. This exclusion of probe-probe interactions is evidenced by the gaussian shape of the elution peaks, as obtained in this work.

4.6 Measurement of Dispersive Surface Energies of Treated Fibres

The standard procedure for dispersive surface energy measurement involves determination of the retention volumes of a series of n-alkanes, typically from n-hexane ($C_6$) as far as n-decane ($C_{10}$). In this work a series comprising n-hexane to n-octane has been used because the high boiling points of n-nonane (ca. 150°C) and n-decane (ca. 175°C) would require maintaining the injection port above 225°C for flash vapourisation. This in turn might have damaged the fibre surface and thereby altered its chemical nature.

4.6.1 Temperature Dependence of $lnV_N$

From the calculated retention volumes over a series of column temperatures, a plot of the natural logarithm of the retention volume vs. the reciprocal of the temperature allows the extrapolation of these values to 298.15K. This not only normalises the retention volumes against each other in terms of temperature, but also for the probe dispersive surface energy measurement which was recorded at this temperature also.
4.6.2 Alkane Retention Behaviour Measured by C₆ - C₈ Probes

It is evident from figure 4.6 that the dispersive surface energy component decreases rapidly as the surface treatment is applied, yet levels off with further treatment. This is an indication that the nature of the fibre surface is becoming more polar/less dispersive. The standard treatment for these types of fibres is 100%, the sample of 200% represents an overtreatment. There is a slight rise in the dispersive surface energy of 200% over 100% which is within experimental error.

Table 4.3: Retention volumes (RTln Vᵣᵣ in kJ mol⁻¹) of n-alkanes on different surface treated carbon fibres (%).

<table>
<thead>
<tr>
<th>Fibre Surface Treatment (%)</th>
<th>0</th>
<th>25</th>
<th>50</th>
<th>100</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-hexane</td>
<td>1.395</td>
<td>1.375</td>
<td>0.789</td>
<td>0.943</td>
<td>0.787</td>
</tr>
<tr>
<td>n-heptane</td>
<td>2.572</td>
<td>2.475</td>
<td>1.768</td>
<td>1.494</td>
<td>1.542</td>
</tr>
<tr>
<td>n-octane</td>
<td>3.646</td>
<td>2.864</td>
<td>2.307</td>
<td>2.149</td>
<td>2.145</td>
</tr>
<tr>
<td>γₛ (mJ m⁻²)</td>
<td>39.39</td>
<td>17.35</td>
<td>17.99</td>
<td>11.27</td>
<td>14.36</td>
</tr>
</tbody>
</table>

Figure 4.6: Dispersive surface energy as a function of fibre surface treatment as determined by IGC.

The reduction in dispersive characteristics as surface treatment is applied compares well with XPS results of percentage C/N/O (§5.5.3) which shows a similar reduction in carbon at the fibre surface.
4.7 Calculation of Surface Acid-Base Characteristics

Once the retention volumes have been analysed and normalised for temperature, a plot of $RT \ln V_H$ as a function of the probe cross-sectional area and (liquid) dispersive surface energy is the standard interpretation. The "reference" dispersive interaction is obtained by the least squares linear regression of the $n$-hexane to $n$-octane points as shown. The gradient of this is then used to calculate the dispersive surface energy of the fibre (§4.6.2).

![Diagram showing the plot of retention volume as a function of probe cross-sectional area and dispersive surface energy for probes measured on 100% surface treated carbon fibre.]

From the gradient and intercept of this line, the dispersive interaction at the polar probe $\alpha (\gamma_d^l)^{\frac{1}{2}}$ ordinate can be calculated and thus the specific acid-base retention volume contribution determined. The free energy of acid-base interaction is calculated in this way (equation 4.15).
Chapter 4: Inverse Gas Chromatography Characterisation of Carbon Fibre Surfaces

4.7.1 Specific (Non-dispersive) Retention Volumes

Table 4.3 \( R\ln V_N \) retention volumes (kJ mol\(^{-1}\)) of probe molecules on different surface treated carbon fibres.

<table>
<thead>
<tr>
<th>Fibre Surface Treatment (%)</th>
<th>0</th>
<th>25</th>
<th>50</th>
<th>100</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>diethylether</td>
<td>0.363</td>
<td>1.036</td>
<td>0.840</td>
<td>0.804</td>
<td>0.928</td>
</tr>
<tr>
<td>acetone</td>
<td>0.108</td>
<td>1.037</td>
<td>0.931</td>
<td>1.230</td>
<td>0.978</td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>-0.333</td>
<td>1.949</td>
<td>1.107</td>
<td>2.244</td>
<td>1.538</td>
</tr>
<tr>
<td>benzene</td>
<td>1.120</td>
<td>1.513</td>
<td>1.086</td>
<td>0.981</td>
<td>0.808</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>0.236</td>
<td>1.560</td>
<td>1.640</td>
<td>1.271</td>
<td>1.807</td>
</tr>
</tbody>
</table>

Considering the absolute \( R\ln V_N \) values of the polar probe molecules, there is an initial increase as surface treatment is applied, followed by a levelling off upon further treatment. Significantly, tetrahydrofuran with its highly basic character is actually repelled by the untreated surface. This indicates that this surface also has strong basic character, traditionally attributed to a degree of surface nitrogen remaining from the \textit{poly}(acrylonitrile) precursor.
Table 4.4 Specific acid-base free energies of adsorption ($\Delta G_{A/B}$ in kJ mol$^{-1}$) of probe molecules on different surface treated carbon fibres.

<table>
<thead>
<tr>
<th>Fibre Surface Treatment (%)</th>
<th>0</th>
<th>25</th>
<th>50</th>
<th>100</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>diethylether</td>
<td>-0.249</td>
<td>-0.407</td>
<td>-0.857</td>
<td>-0.571</td>
<td>-0.900</td>
</tr>
<tr>
<td>acetone</td>
<td>-1.187</td>
<td>-1.199</td>
<td>-1.754</td>
<td>-1.636</td>
<td>-1.670</td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>0.0443</td>
<td>-1.587</td>
<td>-1.396</td>
<td>-2.227</td>
<td>-1.753</td>
</tr>
<tr>
<td>benzene</td>
<td>-0.470</td>
<td>-0.527</td>
<td>-0.740</td>
<td>-0.462</td>
<td>-0.456</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>1.557</td>
<td>0.184</td>
<td>-0.522</td>
<td>-0.141</td>
<td>-0.766</td>
</tr>
</tbody>
</table>

Table 4.4 shows the specific acid-base free energies of adsorption of the polar probes, calculated from their $RT\ln V_n$ plots using equation 4.15. Figure 4.9 shows these values as a function of fibre surface treatment. Whilst diethylether and benzene exhibit no strong trends over the fibre samples, the acid-base free energy becomes more favourable (more negative) for acetone as surface treatment is applied and markedly so for both tetrahydrofuran and 1,4-dioxane. This type of relationship is also observed in terms of the fibre dispersive surface energy, i.e. as the dispersive surface energy decreases with fibre surface treatment, the acid-base interactions become more favourable.

**Figure 4.9** Specific acid-base component of free energy of adsorption for polar probe molecules as a function of fibre surface treatment, diethylether (♦), acetone (■), tetrahydrofuran (▲), benzene (♦), 1,4-dioxane (♣).
It should be emphasised that although the trend is not identical for each probe analysed, the majority of published work in this field considers only two or three polar probes sufficient to characterise the surface acid-base nature.

4.7.2 Interpretation Using Donor and Acceptor Numbers

Specific acid-base enthalpies of adsorption have been calculated using equation 4.17 and are presented in table 4.5. Using the donor-acceptor number classification for the probe molecules, $K_A$ and $K_D$ values for the fibre samples have been calculated and are given in table 4.6 and figure 4.10.

Table 4.5 Specific acid-base enthalpies of adsorption ($\Delta H_{ab}$ in kJ mol$^{-1}$) of probe molecules on different surface treated carbon fibres.

<table>
<thead>
<tr>
<th>Fibre Surface Treatment (%)</th>
<th>0</th>
<th>25</th>
<th>50</th>
<th>100</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>diethylether</strong></td>
<td>0.18</td>
<td>0.03</td>
<td>-2.72</td>
<td>-0.99</td>
<td>-2.40</td>
</tr>
<tr>
<td><strong>acetone</strong></td>
<td>-0.75</td>
<td>-0.13</td>
<td>-4.37</td>
<td>-3.97</td>
<td>-3.42</td>
</tr>
<tr>
<td><strong>tetrahydrofuran</strong></td>
<td>4.71</td>
<td>-4.15</td>
<td>-3.21</td>
<td>-8.18</td>
<td>-4.24</td>
</tr>
<tr>
<td><strong>benzene</strong></td>
<td>0.08</td>
<td>0.12</td>
<td>-1.45</td>
<td>-0.35</td>
<td>-0.37</td>
</tr>
<tr>
<td><strong>1,4-dioxane</strong></td>
<td>6.72</td>
<td>2.14</td>
<td>-0.82</td>
<td>0.90</td>
<td>-1.23</td>
</tr>
</tbody>
</table>

Figure 4.10 Fibre acidic ($K_A$, *) and basic ($K_D$, *) character as a function of surface treatment.
Table 4.6 Electron acceptor ($K_A$) and donor ($K_D$) constants for different surface treated carbon fibres.

<table>
<thead>
<tr>
<th>Fibre Surface Treatment (%)</th>
<th>0</th>
<th>25</th>
<th>50</th>
<th>100</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_A \times 100$</td>
<td>2.490\times10^{-3}</td>
<td>2.75</td>
<td>11.58</td>
<td>7.17</td>
<td>12.41</td>
</tr>
<tr>
<td>$K_D \times 100$</td>
<td>24.14</td>
<td>0.545</td>
<td>10.34</td>
<td>16.40</td>
<td>6.18</td>
</tr>
<tr>
<td>$K_A/K_D$</td>
<td>1.032\times10^{-4}</td>
<td>5.056</td>
<td>1.120</td>
<td>0.437</td>
<td>2.009</td>
</tr>
</tbody>
</table>

The electron donor (basic) character decreases rapidly with initial surface treatment, appears to reach a minimum around 100% treatment and then rises again with overtreatment. The electron acceptor (acidic) character of the fibre also decreases from the untreated value but the trend is not as pronounced. Analysing the acidic vs. basic character ($K_A/K_D$) it appears that the surface changes rapidly from a strongly basic to a medium acidic nature, and remains relatively amphoteric with further treatment.

4.8 Conclusions of Experimental Fibre Surface Characterisation

The technique of inverse gas chromatography has been used to analyse the surface characteristics of carbon fibres with varying degrees of surface treatment. As a necessity for this analysis, surface area measurements by nitrogen adsorption have also been performed. The problem of regulation of the chromatography column inlet pressure has been overcome by the adaptation of the instrument and inclusion of a differential pressure gauge.

The surface area of the fibre does not change significantly as surface treatment is applied. The values are ca. 10% greater than for a geometrical cylindrical surface area, indicating that there is only a small degree of surface roughness. Thus, the number of sites available for a mechanical keying adhesion mechanism with a matrix resin is severely limited.

The dispersive component of the fibre surface energy decreases rapidly with initial surface treatment and levels off with higher treatments. Simultaneously, the acid-base interactions become more favourable as treatment is applied. By use of the donor-acceptor number classification and calculation of electron-acceptor and -donor
constants for the fibre types, it has been shown that the surface changes rapidly from very basic to acidic and becomes amphoteric at higher treatment levels. This change in basic nature may be due to the loss of nitrogen, inherent in the carbon fibre framework from its poly(acrylonitrile) precursor, or a large increase in acidic functionalities. The trends in $\gamma_d$ and $K_D$ vs. fibre surface treatment are very similar, indicating a breakdown in the graphitic nature of the surface, although not to the extent that the material becomes microporous.

Although, for confirmation of the aforementioned trends, it would have been desirable to perform measurements on, e.g. a sample treated to 150%, no fibres with treatments between 100-200% were available from the supplier.
Carbon fibres can undergo a surface treatment to promote or improve adhesion to the matrix phase used in the composite. This adhesion is believed to arise in a variety of ways, a change in the fibre surface chemistry and the introduction of roughness (as pores and channels in the surface) being two key aspects. This chapter focuses on the chemical functional groups that contribute to this adhesion. Computational modelling using the Cerius$^2$ and MOPAC packages has been employed to simulate the sorption interactions of small molecules at a range of functionalised surfaces. The results of these calculations are compared with the IGC data in Chapter 4, and models of the fibre surface chemistry with varying degrees of surface treatment are developed.

5.1 Construction of Two-Dimensional Fibre Planes

In the first instance, a surface can be thought of as a two-dimensional plane of atoms, but this is only the uppermost (exposed) layer. It is more common to define a “surface region”, as analysed by techniques such as XPS and SIMS which can probe up to 10nm below the surface. The non-destructive analysis methods of contact angle analysis and IGC measure the intermolecular forces between the surface and the liquid/gas being used in the analysis and can also give an indication of surface roughness. The surface region in these cases would be the depth at which intermolecular forces in the particular layer influence the adsorption process occurring in the exposed layer.

For the molecular mechanics non-bonded energy potentials, the Lennard-Jones 12,6 function (representing weak van der Waals interactions) does not exhibit any significant attraction or repulsion after ca. 6Å. Electrostatic forces, however, scale as the inverse of the interatomic separation distance and may still influence other
molecules or atoms in the region of 10Å distance. In terms of carbon fibres, this corresponds to roughly three layers, the spacing between successive fibre planes being of the order of 0.34nm. Sprague et al. have used experimentally determined physical properties of graphite to derive a force-field parameter set for use in molecular mechanics calculations of unsaturated hydrocarbons such as graphite and derivatives. The parameters are unfortunately not transferable to this work, due to the different energy expressions used.

The initial graphitic plane has been constructed from 216 carbon atoms, using the default benzene ring structure to build a sheet of aromatic carbons. The CRYSTAL BUILDER was used to apply a periodic cell to the structure. The dimensions of the cell are \( a=29.50\text{Å}, \, b=22.14\text{Å}, \, c=4.3\text{Å}, \, \alpha=90^\circ, \, \beta=90^\circ, \, \gamma=120^\circ \), the graphite sheet being aligned in the \( ab \) plane. The \( c \)-axis is adjusted for the different calculation types, e.g. for initial optimisation of the surface it is set so that the density of the cell is 1.77g cm\(^{-3}\) as determined experimentally for the particular brand of carbon fibre studied. After optimisation of the structure the \( c \)-axis is lengthened (depending on the model-type used) for use in the SORPTION™ calculations. This is to allow sufficient space within the cell for the small molecules to be created and undergo random motion without coinciding with the fibre framework.

### 5.1.1 Two-Dimensional Bonding Across the Periodic Boundary

For application of the periodic boundary conditions (the periodic cell) the dimensions were specifically chosen to facilitate automatic bond creation between the real fibre segment and its neighbours in the \( a \) and \( b \) directions. The principle is shown in figure 5.1. The central unit can be considered the “original” structure surrounded by images of itself.

The distance between adjacent real and neighbour atoms is exactly that of a carbon–carbon bond in benzene (1.40Å). The inclusion of the Auto-Bonding function when constructing the periodic cell causes the computer to search in the vicinity of the real atoms and assess whether any neighbouring atoms are within the region of a theoretical bond (typically < 1.6Å). Bonds are then formed, across the cell wall, between all atoms which fit this criterion, shown as the dashed lines in figure 5.1.
Chapter 5: Atomistic Modelling of Sorption Interactions at Carbon Fibre Surfaces

The model thus becomes an infinite fibre plane in the \( a \) and \( b \) directions, and loses the flexibility which a finite segment of this structure would otherwise possess.

![Figure 5.1 Central "real" segment of aromatic fibre structure (bold) surrounded by four neighbours showing automatically created bonds (dashed lines) and the periodic cell (solid line).](image)

5.1.2 Functional Groups Considered

To probe the surface chemistry of oxidatively treated carbon fibres, various functional groups have been considered (figure 5.2). These consist of a purely graphitic surface, a surface with inherent nitrogen, a surface with hydroxyl groups, a surface with carbonyl groups and a surface with carboxyl groups. These will be referred to as GR, N-N, COH, CO and COOH surfaces respectively throughout this chapter.

![Figure 5.2 The five types of functional group used in the modelling of the sorption interactions, referred to as GR, N-N, COH, CO and COOH surfaces.](image)

The N-N surface is representative of a degree of surface nitrogen remaining in the carbon fibre framework from the PAN precursor, as concluded by Reis et al.\(^{155} \)
oxygen-containing surfaces (COH, CO and COOH) represent functionalities introduced during the fibre surface treatment. The presence of these groups on surface treated carbon fibres has been well documented\textsuperscript{156-157,158,159,160,161}. Some workers suggest the presence of lactone, primary and secondary amine, and amide groups as well. These have not been used as model surfaces in this work.

The initial model surfaces consist of a plane of graphitic structure with (for the heteroatomic surfaces) 12 regularly spaced functional groups. The surfaces were constructed so that all functional groups were present on the same side of the fibre plane. For application of the periodic cell, dimensions of $a=29.50\,\text{Å}$, $b=22.14\,\text{Å}$, $\alpha=90^\circ$, $\beta=90^\circ$, $\gamma=120^\circ$ were used as in §5.1. This resulted in the bonding between real and neighbouring cells as described previously (§5.1.1). The $c$-axis was allowed to vary for density requirements; owing to the different chemical structures of the functional groups, the models had different masses. Consequently different cell volumes were required for geometry optimisation at the required density of $1.77\,\text{g cm}^{-3}$.

5.1.3 Complexity of Fibre Layers

The simplest representation of a surface as a single infinite two-dimensional plane has been used as a model along with other more complicated models. This has been termed the BROT model type\textsuperscript{2}. For this model-type, the oxygen-containing surfaces have all of their functional groups situated on one side of the plane, the opposite side being of graphitic character. The N-N surface incorporates the nitrogen atoms directly in the hexagonal aromatic framework. In this fashion, both sides of the fibre plane are identical, as in the case of the GR surface.

The next stage of complexity is to consider the SANDWICH model-type as shown in figure 5.3. In this series, two graphitic planes are used, spaced $3.4\,\text{Å}$ apart, with functional groups pointing in opposite directions in the $c$-axis. The construction of the fibre-types followed the same methodology as described in §5.1, \textit{i.e.} controlling the cell density during geometry optimisation by variation of the $c$-axis. In this

\footnote{\textsuperscript{2} After the German term for bread.}
model-type there is no bare graphitic underside to the oxygen-containing fibre-types. The surfaces exposed to the small molecules in the simulation therefore consist of purely the functionalised sides of the fibre planes. Were a molecule to be randomly created in between the two non-functionalised surfaces of the planes (i.e. in the area at the upper face of the cell shown in figure 5.3) it would be rejected on an energy basis, as the plane separation is so small that some of the atomic centres would coincide and thus lead to exceptionally high interaction energies.

![Figure 5.3 The SANDWICH model-type for the COOH fibre surface (white = H, grey = C, red = O).](image)

The most complicated model-type considered is known as the 5PLANE series shown in figure 5.4. This incorporated the SANDWICH model principle of having the surface layers all functionalised on one side and pointing in opposite directions in the c-axis. Three planes of graphite are included between the two functionalised surface layers, with 3.4 Å plane spacing. As mentioned previously (§5.1), electrostatic interactions may still be significant in the region of 10 Å distance. The inclusion of the underlying graphite planes separating the surface layers ensures that the functional groups do not influence the interactions of each other towards the probe molecules. The underlying graphite planes also act as a source of dispersive
interaction towards molecules close to the surface (due to the short range nature of this potential).

**Figure 5.4** The 5PLANE model-type for the COOH fibre surface (white = H, grey = C, red = O).

All five fibre-types (GR, N-N, COH, CO, COOH) have been used in the different model-type (BROT, SANDWICH, 5PLANE) simulations. The results of these different calculations, and models developed from IGC data to describe the interaction behaviour of surface treated carbon fibres, are compared in this chapter.

### 5.2 Assignment of Atomic Charges

A critical factor in calculating non-bonded interaction energies between the probe molecules and the fibre surfaces is the point charge assigned to a particular atomic
centre. This approach represents the charge as a value at the co-ordinate of the atom and not as electron density distributed in space. Whereas, in the Lennard-Jones 12,6 potential (equation 2.25) the energy only depends on the atoms involved, the Coulombic potential (equation 2.26) contains a product of the two partial charges assigned to the atoms under consideration. These charges can be calculated by empirical or quantum mechanical (semi-empirical or \textit{ab initio}) methods. The empirical charge assignment utilised here, the QEq method, is based on experimental ionisation potentials and electron affinities of the atoms involved in the system being simulated. The advantage of this method is that it is relatively quick to converge and can be performed many times during the course of a simulation. Thus, the charges can be updated according to the system's new conformation or environment.

A more theoretical treatment is to use quantum mechanically derived charges as these consider subatomic structure in the calculations. Owing to the time and resources required, however, it is not possible to update the charges during a simulation. Semi-empirical methods have been used here to assign charges to both probe molecules and fibre models. The number of atoms in even the simplest fibre model (216) makes the use of a full \textit{ab initio} treatment prohibitive.

\textbf{5.2.1 Probe Molecule Charge Assignment}

As a comparison of the available semi-empirical methods, dipole moment calculations have been performed on a range of probe molecules typically used in IGC and adsorption studies. Calculations using the MNDO, MINDO/3, AM1 and PM3 hamiltonians have been performed using the MOPAC package. The molecular structures were sketched using the Cerius$^2$ interface and refined to an extent using the \textit{CLEAN} function. This is not as comprehensive as a molecular mechanics optimisation routine, the geometry of the structure is simply organised based on the atomic environment, \textit{e.g.} the number of neighbouring atoms is taken as a measure of the hybridisation, there is a default bond length which is not atom specific, \textit{etc.}

These structures were used as the starting geometries for the MOPAC calculations. Semi-empirical geometry optimisation and charge assignment using the different
Hamiltonians was performed, and from the resulting structure the dipole moment calculated. The results are given in table 5.1 along with literature values.\(^{162}\)

<table>
<thead>
<tr>
<th>Probe</th>
<th>Literature</th>
<th>MNDO</th>
<th>MINDO/3</th>
<th>AM1</th>
<th>PM3</th>
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</thead>
<tbody>
<tr>
<td>acetic anhydride</td>
<td>2.82</td>
<td>3.60</td>
<td>4.90</td>
<td>4.02</td>
<td>3.40</td>
</tr>
<tr>
<td>acetone</td>
<td>2.69</td>
<td>2.51</td>
<td>3.19</td>
<td>2.92</td>
<td>2.78</td>
</tr>
<tr>
<td>chloroform</td>
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<td>1.39</td>
<td>1.13</td>
<td>1.16</td>
<td>1.02</td>
</tr>
<tr>
<td>dichloromethane</td>
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<td>1.90</td>
<td>1.54</td>
<td>1.50</td>
<td>1.36</td>
</tr>
<tr>
<td>diethylether</td>
<td>1.15</td>
<td>1.10</td>
<td>0.40</td>
<td>1.25</td>
<td>1.15</td>
</tr>
<tr>
<td>dimethylformamide</td>
<td>3.86</td>
<td>3.18</td>
<td>3.38</td>
<td>3.56</td>
<td>3.06</td>
</tr>
<tr>
<td>dimethylsulphoxide</td>
<td>3.90</td>
<td>4.63</td>
<td>4.15</td>
<td>3.95</td>
<td>4.49</td>
</tr>
<tr>
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<td>3.36</td>
<td>1.87</td>
<td>3.70</td>
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<td>iso-propanol</td>
<td>1.66</td>
<td>1.43</td>
<td>1.48</td>
<td>1.62</td>
<td>1.53</td>
</tr>
<tr>
<td>nitrobenzene</td>
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<td>5.00</td>
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<td>5.24</td>
<td>5.25</td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>1.75</td>
<td>1.77</td>
<td>1.80</td>
<td>1.92</td>
<td>1.67</td>
</tr>
</tbody>
</table>

Some of the calculated values are very close or identical to those of the corresponding literature values, e.g. MINDO/3 and AM1 for chloroform, PM3 for diethylether, AM1 for dimethylsulphoxide, MNDO for formamide, AM1 for iso-propanol, and MNDO for tetrahydrofuran. Unfortunately, there is no one method which stands out as being obviously suitable above the others. The calculated values have thus been analysed in terms of their percentage difference from the literature values. When averaged over all of the molecules, the PM3 method gives the smallest percentage difference and standard deviation (12.39 ± 77%), with the other methods AM1 13.93 ± 100%, MINDO/3 25.80 ± 98% and MNDO 18.36 ± 100%. The PM3 method has thus been used as a semi-empirical alternative source of charge assignment to the empirical QEq routine.

5.2.2 Route to Semi-Empirical Fibre Charges

To create a balanced energy expression when calculating SORPTION\(\text{TM}\) energies of interaction, it is essential that the same method of charge calculation be used for both the probe molecules and the fibre models. The magnitude of charges assigned by semi-empirical quantum mechanics methods is generally lower than that calculated by the QEq method. Using PM3-charged probes and a QEq charged fibre framework would create an imbalance in the Coulombic (electrostatic) energy term, due to the domination of the fibre partial charges. The use of semi-empirically-charged probe
molecules thus requires a means of applying the same calculation of charges to the various fibre-types and model-types.

As mentioned previously (§5.1.2) the functionalised fibre-types (N-N, COH, CO, COOH) are represented as 12 evenly spaced groups within a general graphitic structure. These were constructed by considering one small unit initially, altering the hexagonal graphitic structure to include the functional group, and enlargement of this unit into a \(4\times3\) array in the \(a\) and \(b\) directions. The periodic cell was then set to include this array as a single cell, not as 12 images of the same unit, thereby reducing symmetry constraints on the functional groups (figure 5.5). This new cell of (what was previously) 12 images of the same unit is then termed the fibre-type. The same methodology has been applied to all model-types (BROT, SANDWICH, 5PLANE) with the units including a different number of graphitic layers in each case.

Unfortunately, the MOPAC program, used for the calculation of semi-empirical charges, has a limit of 200 atoms for any one structure. Even for the simplest model fibre-type (BROT-GR) the number of atoms considered in the periodic cell is 216. A further complication in assignment of the PM3 charges to the simulated fibre surfaces is that the program is unable to cope with periodic boundary conditions (periodic cells), thus only discrete systems \textit{in vacuo} may be considered.

Both of these factors have been overcome by the use of the unit structure (\(\frac{1}{12}\) of the model cell) in the PM3 calculations. Explicit hydrogen atoms must be added to the units, for example at the edges of the graphite structure where the periodic boundary would cause automatic bond creation between the real and neighbouring cells. The semi-empirical treatment requires that each atom present be represented individually, \textit{i.e.} there is no facility for united atom theory. Using these structures, \textit{single point} calculations have been performed to assign partial charges to the atoms by the PM3 method, yet leave the structure unchanged. Following these calculations, the edge hydrogen atoms have been removed and the periodic cell for the unit re-applied. The model fibre-type has then been reconstructed by enlargement of the periodic cell to the \(4\times3\) array.
Figure 5.5 The unit of GR surface (l.h.s.) and 3x4 array as the model fibre-type with periodic cell added (r.h.s, projection down c-axis).

For use in the simulations, it is required that the framework (model) has overall neutral charge. This has been applied to the model fibre-types containing PM3-derived point charges through the Cerius² interface by averaging the total charge to zero. The effect of this is to scale all charges present based on the lack of edge hydrogen atoms which are required for use in the MOPAC calculations. With these averaged PM3 charges the model fibre-types are geometry optimised using the DREIDING2.21 force-field before being saved for use as the frameworks in the SORPTION™ calculations. By this method the models are a combination of PM3 semi-empirical quantum mechanics-derived point charges and molecular mechanics optimised structures.

5.2.3 Comparison of Fibre Functional Group Charges

<table>
<thead>
<tr>
<th>Model</th>
<th>C=O-H</th>
<th>C=O</th>
<th>C=O-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>BROT-COH</td>
<td>-0.3534</td>
<td>0.2060</td>
<td></td>
</tr>
<tr>
<td>BROT-CO</td>
<td>-0.3106</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BROT-COOH</td>
<td>-0.2969</td>
<td>0.3619</td>
<td>0.2414</td>
</tr>
<tr>
<td>SANDWICH-COH</td>
<td>-0.3527</td>
<td></td>
<td>0.2054</td>
</tr>
<tr>
<td>SANDWICH-CO</td>
<td>-0.3221</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SANDWICH-COOH</td>
<td>-0.2923</td>
<td>-0.3572</td>
<td>0.2252</td>
</tr>
<tr>
<td>5PLANE-COH</td>
<td>-0.3152</td>
<td>0.2236</td>
<td></td>
</tr>
<tr>
<td>5PLANE-CO</td>
<td></td>
<td>-0.3264</td>
<td></td>
</tr>
<tr>
<td>5PLANE-COOH</td>
<td>-0.2886</td>
<td>-0.3534</td>
<td>0.2210</td>
</tr>
</tbody>
</table>
Chapter 5: Atomistic Modelling of Sorption Interactions at Carbon Fibre Surfaces

The PM3 method calculates a withdrawal of electron density from the nitrogen atoms in the N-N fibre-types. The point charges on the nitrogen atoms are 0.1782 electron units (e.u.) in the BROT model, 0.2584 e.u. in the SANDWICH model and 0.2287 e.u. in the 5PLANE model. The greatest electropositive centre thus occurs in the SANDWICH model having the highest positive charge on the nitrogen atoms and a relatively short distance between both fibre planes.

In the COH fibre-types, the acidity of the hydroxyl hydrogen atom is represented as a positive charge, being greater than 0.2 e.u. in all three model-types. The hydroxyl oxygen atom is very electron rich, withdrawing electron density from both the hydrogen and carbon atoms to which it is bonded. The magnitude of the charge on this oxygen is least in the 5PLANE model-type, showing that its electronegativity is reduced with the underlying graphitic planes. However, in this model the acidity of the hydrogen is strongest, thus the oxygen atom must withdraw less electron density from the graphitic structure within which it is incorporated. The effect of the three graphite planes separating the two functionalised hydroxyl surfaces is to reduce the magnitude of the charge differences between the carbon and oxygen atoms in the surface layer.

The partial negative charge of the carbonyl oxygen in the CO fibre-type increases as the number of fibre layers in the model-type also increases. The basic character is thus highest in the 5PLANE model and lowest in the BROT model. Conversely, the partial negative charge on the carbonyl oxygen in the COOH fibre-type reduces in the order BROT, SANDWICH and 5PLANE models. Furthermore, the magnitudes of the negative charges on the hydroxyl oxygen and the positive charge on the hydroxyl hydrogen in the COOH models also decrease, thus the polarity of the COOH group as a whole is reduced as more fibre layers are included.

Separately, in the COH and CO fibre-types, the charges on the oxygen atoms are of roughly the same magnitude, however the difference between the charges varies in the different model-types. In the BROT model the charge on the hydroxyl oxygen is greater than that on the carbonyl, the difference is less pronounced in the SANDWICH model and the magnitude of negative charge is reversed in the 5PLANE
model. For the COOH group, the carbonyl-type oxygen has a greater negative charge than the hydroxyl-type oxygen for all three model-types.

5.3 SORPTION™ Algorithm

The SORPTION™ algorithm has been used to simulate the motion of probe molecules at surfaces with varying functional groups and fibre layers. The routine consists of a Monte Carlo statistical mechanics treatment for the transport of the small molecules. Within the periodic fibre cell a single adsorbate molecule is created at a random position and the energy of the system calculated. The molecule is then randomly translated or rotated and the energy of the system recalculated. If the energy of this new configuration is lower than that of its predecessor then the move is accepted. If the energy of this new configuration is greater than its predecessor however, the Boltzmann probability of the move is calculated and compared with a randomly generated number between 0 and 1. If the probability is greater than the random number then this move is also accepted. If not, then the move is rejected, the molecule destroyed and another created at a new random position. By repeating this process over a large number of moves, the phase space of the system can be sampled without having to overcome potential energy barriers as in the case of molecular dynamics calculations.

Figure 5.6 shows hexane molecules interacting with a hypothetical carbon fibre surface. The hexane molecule could be randomly created on the left hand side of the cell, the energy of the system calculated, then randomly moved to one of the configurations on the right hand side of the cell. Were this move rejected, the other configuration on the right hand side of the cell may be sampled etc. and this type of process repeated for the number of moves specified in the simulation.
Figure 5.6 Hexane molecules interacting on a hypothetical carbon fibre surface (white = H, grey = C, blue = N, red = O).

5.3.1 Mathematical Treatment

The particular Monte Carlo routine utilised in the SORPTION™ algorithm uses the Metropolis method which biases the generation of configurations towards those that make the most significant contribution (i.e. are the most probable or favourable). Specifically this method generates states with a probability \( \exp[-V(r)/k_BT] \) and counts them equally. The simple Monte Carlo method on the other hand generates states with equal probability (both low and high energy) and then assigns them a weight \( \exp[-V(r)/k_BT] \).

The mean value of the potential energy is calculated from,

\[
\langle V(r^N) \rangle = \frac{\sum_{i=1}^{N_{eq}} V_i(r^N) \exp[-V_i(r^N)/k_BT]}{\sum_{i=1}^{N_{eq}} \exp[-V_i(r^N)/k_BT]}
\]

Equation 5.1

where \( V(r^N) \) is the potential energy of the configuration and \( \exp(-V(r^N)/k_BT) \) is the Boltzmann factor. The progression of sampling in the Metropolis algorithm generates a Markov chain of states. This satisfies the conditions that, the outcome of each trial (move) depends only upon the preceding trial and not upon any previous trials, and each trial belongs to a finite set of possible outcomes.
5.3.2 Simulation Variables

Constant pressure and temperature simulations have been performed using the Grand Canonical ensemble. The default pressure of 10kPa was used and a simulation temperature of 298.2K selected, against which the IGC results could be compared. The temperature component only contributes to the probability of moves being accepted or rejected; at higher temperatures the randomness of motion increases and thus the probability of the move occurring.

The maximum step sizes for the probe moves were maintained at 1Å for translation and 50° for rotation at the start of the simulation and allowed to be automatically rescaled after every 1000 moves. This adjusts these parameters if too few or too many configurations are being rejected or accepted. Each simulation was allowed to sample for 500,000 moves in total, including rejections, creations and destructions.

The three model-types (BROT, SANDWICH and 5PLANE) used different dimensions in their c-axes, due to the number of fibre layers considered and non-occupied space required for diffusion of the sorbate molecules. For the BROT models the c-axis was set at 10Å, the SANDWICH models had a c-axis of 25Å, and 35Å was used for the 5PLANE models. One of the advantages of the SANDWICH and 5PLANE models over the BROT model-type was the use of a longer interaction cut-off due to the larger cell dimensions.

A cut-off is introduced to reduce the calculation of interatomic energies between atoms separated by more than a specified distance, and thus speed up the computation time. The minimum image convention restricts the interaction cut-off to no more than half the length of the shortest cell axis (for an orthorhombic system), in order than an atom exerts no forces upon its image in a neighbouring cell. In the case of the fibre model-types, the cut-offs were restricted to 4.9Å for the BROT models and 9.49Å for both the SANDWICH and 5PLANE models due to their cell dimensions and geometry.
5.4 Composition of Model Fibre Surfaces

Simulations were performed on each of the different model fibre types. In each case, the same series of probe molecules as used in the IGC analysis was allowed to diffuse individually within the periodic cell. Average energies of interaction were obtained as the mean value of all accepted moves. For comparison purposes, simulations involving the BROT fibre-types were performed using the QEq empirical charge assignment as well as the PM3 semi-empirical method.

5.4.1 Calculated Energies of Fibre/Probe Interaction

Table 5.3 lists the energies of interaction for the various probe molecules using the BROT fibre-types with the QEq charges applied. For the alkanes, hexane, heptane and octane, the interactions with all surfaces become progressively stronger with increasing methylene backbone structure. The interactions between the alkanes and the N-N surface are less than for the pure graphitic surface, yet in each case the most strongly interacting surface is that of carboxyl groups. This could be attributed to the atoms extending above the graphitic layer structure, thus their van der Waals and electrostatic forces would be experienced at a greater distance from the graphitic layer.

<table>
<thead>
<tr>
<th>-E\text{int} (kJ mol^{-1})</th>
<th>GR</th>
<th>N-N</th>
<th>COH</th>
<th>CO</th>
<th>COOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-hexane</td>
<td>27.33</td>
<td>26.16</td>
<td>26.14</td>
<td>26.63</td>
<td>29.64</td>
</tr>
<tr>
<td>n-heptane</td>
<td>36.90</td>
<td>35.94</td>
<td>32.58</td>
<td>30.62</td>
<td>38.06</td>
</tr>
<tr>
<td>n-octane</td>
<td>46.86</td>
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<td>45.69</td>
<td>44.94</td>
<td>51.76</td>
</tr>
<tr>
<td>acetone</td>
<td>16.94</td>
<td>16.92</td>
<td>30.17</td>
<td>29.98</td>
<td>41.63</td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>18.03</td>
<td>18.22</td>
<td>34.43</td>
<td>38.25</td>
<td>38.49</td>
</tr>
<tr>
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<td>18.66</td>
<td>18.60</td>
<td>23.66</td>
<td>23.82</td>
<td>25.34</td>
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<td>42.47</td>
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<tr>
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<td>19.87</td>
<td>24.79</td>
<td>44.22</td>
<td>42.51</td>
<td>58.79</td>
</tr>
</tbody>
</table>

In the case of the acid-base probes, the interactions with the GR or N-N surfaces is less than that calculated for the alkanes, with the exception of benzene. The highly aromatic nature of both of these surfaces and that of the benzene probe lead to an even stronger interaction than experienced by octane. In comparison with the
relatively low interactions with the GR and N-N surfaces (benzene excluded), the acid-base probes exhibit much greater relative interaction energies for the oxygen-containing fibre-types. Acetone, tetrahydrofuran, diethylether and 1,4-dioxane all show the strongest interaction for the carboxyl over the carbonyl and hydroxyl surfaces.

In comparison with the QEq data, the average energies of interaction using the PM3-charged BROT fibre-types are given in table 5.4. As for the QEq fibre-types, the alkane interactions are strongest for the octane probe molecule and weakest for hexane. The change in interaction energy between hexane, heptane and octane is more evenly spaced in the simulations using PM3 rather than QEq charges, e.g. for the COOH fibre-type, $\Delta E_{\text{int}}$ (in kJ mol$^{-1}$) between hexane-heptane and heptane-octane is 8.40 and 13.70 respectively for QEq, and 4.45 and 4.83 for PM3.

<table>
<thead>
<tr>
<th></th>
<th>GR</th>
<th>N-N</th>
<th>COH</th>
<th>CO</th>
<th>COOH</th>
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</thead>
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<tr>
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<td>25.37</td>
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<td>17.65</td>
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<td>23.38</td>
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<td>22.85</td>
<td>26.83</td>
</tr>
</tbody>
</table>

For the PM3-BROT fibre-types, the interaction energies for the GR and N-N surfaces are comparable for hexane and heptane, but there is a noticeably stronger interaction for the N-N surface in the case of octane. Whilst the carboxyl surface has the strongest interaction of all surfaces for hexane, as in the QEq-BROT model, this is not so for either heptane or octane, both having a greater interaction with the GR and N-N fibre-types. The incremental contribution of methylene group interaction is therefore greater for the GR and N-N than the COOH fibre-type. Of the three oxygen-containing surfaces, the interactions with the carboxyl groups are the strongest for the alkanes.
Similar to the simulations using the QEq charges, for the acid-base probes, the interactions with the oxygen-containing surfaces are greater than the GR or N-N surfaces, again with the exception of benzene. The benzene interactions with the GR and N-N fibre-types again lie above those of octane, in the case of the purely graphitic surface the interaction energy is 8.14 kJ mol$^{-1}$ greater, and 3.09 kJ mol$^{-1}$ greater for the N-N surface. This trend is the opposite to that observed in the QEq simulations, where the corresponding interaction energy differences are 0.71 kJ mol$^{-1}$ for GR and 6.36 kJ mol$^{-1}$ for the N-N surface.

Apart from the diethylether-COH and benzene-COOH interactions, all interaction energies involving the oxygen-containing surfaces are lower in the PM3-BROT than QEq-BROT model-types. Since the van der Waals interactions should be the same for both series as point charges are not included in the Lennard-Jones 12,6 energy term, the difference must arise in the electrostatic interactions. Specifically, the charges assigned by the QEq method are generally greater than those assigned by semi-empirical quantum mechanics calculations, thus there is a stronger charge-charge interaction resulting in a greater energy of interaction.

The basic probe molecules, tetrahydrofuran and diethylether, both exhibit stronger interactions towards the surfaces with acidic OH groups than towards either the N-N or CO basic surfaces. This phenomenon is an improvement over the QEq calculations, which for tetrahydrofuran show a stronger interaction for the carbonyl over the hydroxyl surface and negligible difference from the COOH value. For diethylether, the QEq calculations show that the interaction with the carbonyl surface is slightly greater than towards the hydroxyl surface, albeit less than that with the carboxyl surface.

As an example of the comparison between the simulated energies of fibre/probe interaction and the experimental IGC results, figure 5.7 shows some calculated values as a function of probe surface area and dispersive surface energy analogous to the type used in the IGC interpretation. The probe area and dispersive surface energy values are taken from table 4.1.
Figure 5.7 Calculated energies of interaction, using the SORPTION™ algorithm, between probe molecules and the PM3-BROT-CO model fibre-type.

The results of the simulations using the SANDWICH model fibre-types with applied PM3 charges are given in Table 5.5. The energies of interaction are greater in each case than those using the PM3-BROT model fibre-types and, with the exception of the acetone-COOH interaction, the QEq-BROT model fibre-types.

Table 5.5 Calculated energies of interaction between probe molecules and SANDWICH fibre-types using PM3-derived charges.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{int}$ (kJ mol$^{-1}$)</th>
<th>GR</th>
<th>N-N</th>
<th>COH</th>
<th>CO</th>
<th>COOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-hexane</td>
<td>64.35</td>
<td>64.35</td>
<td>60.00</td>
<td>60.42</td>
<td>48.12</td>
<td></td>
</tr>
<tr>
<td>$n$-heptane</td>
<td>72.80</td>
<td>74.77</td>
<td>65.69</td>
<td>71.09</td>
<td>60.38</td>
<td></td>
</tr>
<tr>
<td>$n$-octane</td>
<td>84.01</td>
<td>78.87</td>
<td>76.02</td>
<td>78.74</td>
<td>69.12</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>42.09</td>
<td>44.39</td>
<td>45.44</td>
<td>39.51</td>
<td>35.39</td>
<td></td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>53.56</td>
<td>51.38</td>
<td>51.00</td>
<td>49.20</td>
<td>43.26</td>
<td></td>
</tr>
<tr>
<td>Diethylether</td>
<td>51.38</td>
<td>48.95</td>
<td>56.36</td>
<td>47.95</td>
<td>44.06</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>61.46</td>
<td>63.39</td>
<td>60.67</td>
<td>59.75</td>
<td>57.66</td>
<td></td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>58.62</td>
<td>59.58</td>
<td>56.61</td>
<td>55.31</td>
<td>48.70</td>
<td></td>
</tr>
</tbody>
</table>

There is a large increase in the alkane energies of interaction for all five fibre-types over the corresponding PM3-BROT values. A longer interaction cut-off is used and two surface layers are represented, thus it might be expected that the SANDWICH energies of interaction are roughly twice as large as the values calculated for the PM3-BROT models. In the case of the oxygen-containing surfaces, however, all of the surface functional groups point towards the region generated into which the probe molecules may diffuse; there is no exposed graphitic underside to the layers as in the
single plane BROT models. The alkane interaction energies at the PM3-SANDWICH-COH and -CO surfaces are more than twice those in the BROT models indicating that, as well as dispersive interaction due to twice as many fibre atoms, electrostatic interactions must be stronger. This is not the case for the carboxyl surfaces. The greatest alkane interactions are still found for the planar GR and N-N surfaces.

For the specific acid-base probe molecules, the distinction between the oxygen-containing surfaces and the GR and N-N surfaces is not as clear-cut as previously. In particular, benzene, whilst still showing the strongest interaction with the N-N and GR surfaces respectively, has similar energies of interaction for all five fibre-types. For the oxygen-containing surfaces, all acid-base probes show the strongest interaction with the hydroxyl, followed by the carbonyl and carboxyl fibre-types.

The basic tetrahydrofuran and diethylether probes show a greater interaction with the purely graphitic SANDWICH model than either the N-N or CO surfaces. In the case of diethylether there is a significant attraction to the COH surface over that of pure graphite, yet for tetrahydrofuran the graphitic model has the strongest interaction and even the value for the N-N surface is greater than the models with oxygen-containing functional groups.

Table 5.6 lists the calculated energies of interaction between the simulated probe molecules and the SPLANE models. These consist of two functionalised surfaces separated by three layers of graphite to represent underlying structure and long-range forces (figure 5.4). The interaction energy cut-off is the same as for the

<table>
<thead>
<tr>
<th></th>
<th>GR</th>
<th>N-N</th>
<th>COH</th>
<th>CO</th>
<th>COOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-hexane</td>
<td>65.06</td>
<td>64.14</td>
<td>56.99</td>
<td>60.54</td>
<td>52.97</td>
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<td>40.66</td>
<td>39.46</td>
<td>35.32</td>
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<tr>
<td>tetrahydrofuran</td>
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<td>54.43</td>
<td>47.66</td>
<td>48.37</td>
<td>43.18</td>
</tr>
<tr>
<td>diethylether</td>
<td>52.76</td>
<td>52.43</td>
<td>50.12</td>
<td>46.94</td>
<td>42.89</td>
</tr>
<tr>
<td>benzene</td>
<td>60.58</td>
<td>65.35</td>
<td>60.84</td>
<td>60.67</td>
<td>54.89</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>58.28</td>
<td>61.21</td>
<td>54.60</td>
<td>57.32</td>
<td>52.09</td>
</tr>
</tbody>
</table>
SANDWICH models, although the cell c-axis is larger (35Å as opposed to 25Å) due to the depth of the five fibre layers.

For the alkane probe molecules the interaction energies with the graphitic surface are all greater, albeit to a small extent, than the corresponding SANDWICH model calculations. This is due to a combination of the cumulative dispersive interactions of the underlying graphite planes and the long-range nature of the electrostatic interactions. At the fibre surface these would also include two underlying graphite planes, although the charges associated with these atoms are small in comparison with the oxygen, nitrogen or hydrogen atoms in the functional groups. On the N-N surface the hexane and heptane interactions are comparable with those of the SANDWICH model-type, yet the octane interaction is greater. The incremental methylene interaction on the GR and N-N 5PLANE models is therefore greater than for the SANDWICH models.

The alkane interaction energies on the hydroxyl surface are all less than in the SANDWICH model type. On the carbonyl surface the interaction energy of hexane is comparable with that in the SANDWICH model, but for both heptane and octane the values are less. In the carboxyl fibre-type, the interaction energy with hexane is greater than calculated using the SANDWICH model-type. Similarly, the interaction energy with heptane is comparable for both fibre-types, and with octane the value in the 5PLANE calculations is less than that determined using the corresponding SANDWICH model-type. Thus, the methylene increment on the COOH surface is less in the 5PLANE than the SANDWICH model-type.

For the acid-base probes acetone, tetrahydrofuran, and diethylether, the interactions with the N-N surface are stronger and those with the COH surface weaker than the corresponding SANDWICH model values; the interaction energies of the other three surfaces are comparable between the two model-types. For benzene also, the interaction energy with the N-N surface is greater than in the SANDWICH model, yet for this probe it is the carboxyl surface which has a lower interaction energy than in the SANDWICH model. 1,4-dioxane exhibits a stronger interaction with the N-N,
CO and COOH surfaces and a weaker interaction towards the COH surface than in the SANDWICH models.

For every acid-base probe there is a greater energy of interaction with the N-N surface in the 5PLANE model than in the SANDWICH model, yet the charge on the nitrogen atoms is highest in the SANDWICH model (table 5.2). Thus, the stronger interaction is most likely a result of dispersive interactions due to the larger number of atoms in the 5PLANE models, and there may be less electrostatic repulsion as well due to the smaller atomic charges.

5.4.2 Methodology of Model Fibre Surface Construction

The calculated energies of interaction of the various SORPTION™ simulations have been compared with the absolute (specific and dispersive) free energies of adsorption ($\Delta G_a$) calculated in the IGC work. The relative magnitude that each simulated fibre-type contributes to the experimental probe adsorption is obtained by performing multiple linear regression on the computational $-E_{int}$ data using the five fibre-types as predictors.

This routine has been performed using the leastsqr s ($A, b$) ‘optimize’ function in the Maple4 mathematical package. Using the same data-set for the computational energies of interaction, the IGC adsorption free energies for the 0, 25, 50, 100, and 200% surface treated carbon fibres were used separately to calculate the proportions of the simulated fibre-types required to reproduce the adsorption trends by the modelling approach. This method also shows how the simulation represents changes in the characteristics of the differently surface treated carbon fibres using the five model surfaces. This procedure was performed for all four model-types considered here (QEq-BROT, PM3-BROT, PM3-SANDWICH and PM3-5PLANE).
5.5 Comparison of Fibre-Type-Charge Models

The surface proportions, calculated by multiple linear regression of the interaction energies with respect to the IGC free energies of adsorption, have been normalised by conversion to percentages of each fibre-type required to represent the surface treated carbon fibre characteristics. The magnitudes of the calculated proportions, for the different model types considered, are given in tables 5.7-5.10 as a percentage of the sum of all five fibre-type proportions for the particular surface treated carbon fibre.

5.5.1 Fibre-Type Contributions of Different Surface Models

In the case of the BROT model-type with the empirical QEq charges applied, the untreated (0%) carbon fibre surface comprises similar proportions of the GR, N-N and CO fibre-types, with a higher concentration of COH and a very low concentration of COOH. As surface treatment progresses, there is an undulating manner to the relative proportions of all five fibre-types. Noticeably the percentage of COOH always remains relatively low, whereas the amount of COH and CO groups are in general quite high yet reduce significantly upon over-treatment. The very low concentration of the N-N fibre-type calculated for the 25% treated carbon fibre model must be a result of the balancing required in the mathematical multiple linear regression calculation. It is very unlikely that the concentration of surface nitrogen would pass through such a deep trough when there is a contribution of greater than 20% before and after this treatment.

<table>
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<td>GR</td>
<td>22.74</td>
<td>11.75</td>
<td>20.3</td>
<td>12.1</td>
<td>29.9</td>
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<tr>
<td>N-N</td>
<td>23.97</td>
<td>0.15</td>
<td>20.8</td>
<td>9.78</td>
<td>34.24</td>
</tr>
<tr>
<td>COH</td>
<td>28.19</td>
<td>45.45</td>
<td>30.88</td>
<td>37.61</td>
<td>16.11</td>
</tr>
<tr>
<td>CO</td>
<td>22.21</td>
<td>28.99</td>
<td>25</td>
<td>32.44</td>
<td>8.71</td>
</tr>
<tr>
<td>COOH</td>
<td>2.89</td>
<td>13.66</td>
<td>3.03</td>
<td>8.06</td>
<td>11.05</td>
</tr>
</tbody>
</table>

Table 5.7 Calculated contributions (%) of fibre-types for differently surface treated fibres (%) using the QEq-BROT model.

In comparison with the QEq-BROT model, the calculated fibre-type contributions for the PM3-BROT model are given in table 5.8. The trends in the GR and N-N fibre-types are similar to those in the QEq model although the magnitude of the undulations
Chapter 5: Atomistic Modelling of Sorption Interactions at Carbon Fibre Surfaces

is, in general, greater. This oscillating trend of the surface treatment on the contribution is also present for the oxygen-containing groups. In particular, the COH surface proportion peaks for 25% treated carbon fibre whereas there are two maxima (25 and 100%) for the CO surface. The proportion of COOH groups is initially reduced to roughly half of the untreated value, then increases to 100% treatment before being removed upon over-treatment.

Table 5.8 Calculated contributions (%) of fibre-types for differently surface treated fibres (%) using the PM3-BROT model.

<table>
<thead>
<tr>
<th></th>
<th>0</th>
<th>25</th>
<th>50</th>
<th>100</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>GR</td>
<td>25.30</td>
<td>11.11</td>
<td>27.87</td>
<td>6.91</td>
<td>41.22</td>
</tr>
<tr>
<td>N-N</td>
<td>29.40</td>
<td>1.68</td>
<td>30.04</td>
<td>14.81</td>
<td>35.75</td>
</tr>
<tr>
<td>COH</td>
<td>3.13</td>
<td>31.08</td>
<td>6.16</td>
<td>11.12</td>
<td>13.23</td>
</tr>
<tr>
<td>CO</td>
<td>22.29</td>
<td>45.67</td>
<td>20.40</td>
<td>46.85</td>
<td>7.51</td>
</tr>
<tr>
<td>COOH</td>
<td>19.87</td>
<td>10.46</td>
<td>15.54</td>
<td>20.32</td>
<td>2.30</td>
</tr>
</tbody>
</table>

The model suggests that the initial increase in the concentration of COH groups reduces later due to oxidation of these species to CO and COOH functionalities. The over-treatment (200%) removes the majority of the highly oxidised functional groups, perhaps cleaving the top surface layer/region. This leaves a surface of primarily GR and N-N fibre-type character with only a small contribution from surface oxides.

The data calculated using the PM3-SANDWICH model (table 5.9) suggest a quite different effect of surface treatment. The contribution from the GR fibre-type is low before treatment, yet increases sharply then levels off as treatment continues. The opposite trend from the PM3-BROT model is observed for the N-N surface, which decreases significantly from its initial value yet rises to a small extent at higher treatment levels. The relative proportion of the COH fibre-type does not rise greater than 20; it peaks at 25% surface treatment after a rise from the initial value, yet declines before reaching a plateau at higher treatment. A similar trend is evident for the COOH surface although the rise from the untreated value is greater and the maximum concentration occurs at 50% surface treatment.

In contrast to the hydroxyl-containing oxygen functionalities, the basic carbonyl fibre-type maintains a significant proportion in each of the fibre surface treated carbon fibre models. An initial halving of the proportion, coinciding with the
maximum in the COH contribution at 25% surface treatment, recovers to level off at 100 and 200% treatment. In general, the PM3-SANDWICH model implies that a rapid loss of surface nitrogen occurs, alongside an increase in graphitic structure. The oxidised (25-200%) fibre surfaces are predominantly of graphitic (GR) and basic (CO) character. The increase in both hydroxyl and later carboxyl groups reduces the carbonyl contribution to an extent, but it increases again as the COH and COOH proportions decrease.

### Table 5.9 Calculated contributions (%) of fibre-types for differently surface treated fibres (%) using the PM3-SANDWICH model.

<table>
<thead>
<tr>
<th></th>
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<th>25</th>
<th>50</th>
<th>100</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>GR</td>
<td>6.27</td>
<td>40.75</td>
<td>35.21</td>
<td>34.53</td>
<td>36.07</td>
</tr>
<tr>
<td>N-N</td>
<td>32.91</td>
<td>1.37</td>
<td>1.45</td>
<td>7.87</td>
<td>6.37</td>
</tr>
<tr>
<td>COH</td>
<td>7.03</td>
<td>19.23</td>
<td>15.72</td>
<td>7.26</td>
<td>8.08</td>
</tr>
<tr>
<td>CO</td>
<td>51.88</td>
<td>26.27</td>
<td>31.47</td>
<td>42.48</td>
<td>41.16</td>
</tr>
<tr>
<td>COOH</td>
<td>1.91</td>
<td>12.39</td>
<td>16.15</td>
<td>7.87</td>
<td>8.33</td>
</tr>
</tbody>
</table>

In the case of the PM3-5PLANE model (table 5.10) there is a reduction in the GR fibre-type proportion as surface treatment progresses. The initial largest contribution of the N-N surface also reduces initially, although it peaks again at 100% treatment before declining upon over-treatment. For the oxygen-containing surfaces, the hydroxyl fibre-type proportion doubles initially, then reduces and levels off, although it still maintains a contribution greater than for the untreated fibre. Coincident with the hydroxyl surface maximum, the carbonyl surface proportion reduces upon treatment then rises and levels off to greater than the initial value. The contribution of the COOH fibre-type increases and peaks at 50% treatment before decreasing to 100% treatment and increasing again upon over-treatment.

### Table 5.10 Calculated contributions (%) of fibre-types for differently surface treated fibres (%) using the PM3-5PLANE model.

<table>
<thead>
<tr>
<th></th>
<th>0</th>
<th>25</th>
<th>50</th>
<th>100</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>GR</td>
<td>12.54</td>
<td>11.61</td>
<td>7.12</td>
<td>5.79</td>
<td>5.78</td>
</tr>
<tr>
<td>N-N</td>
<td>32.18</td>
<td>17.30</td>
<td>7.91</td>
<td>20.17</td>
<td>10.96</td>
</tr>
<tr>
<td>COH</td>
<td>10.85</td>
<td>25.88</td>
<td>17.85</td>
<td>18.05</td>
<td>16.64</td>
</tr>
<tr>
<td>CO</td>
<td>27.41</td>
<td>22.08</td>
<td>30.04</td>
<td>31.16</td>
<td>31.79</td>
</tr>
<tr>
<td>COOH</td>
<td>17.02</td>
<td>23.14</td>
<td>37.08</td>
<td>24.83</td>
<td>34.83</td>
</tr>
</tbody>
</table>

Noticeably, the basic fibre-types N-N and CO dominate on the untreated surface, yet for the treated surfaces the oxygen-containing functional groups contribute most (with
the exception of N-N on the 100% treated surface). The model represents the
treatment process as initially the creation or introduction of hydroxyl groups, which
are oxidised to carbonyl and/or carboxyl functionalities at higher treatments.
Furthermore, surface nitrogen declines initially, the peak at 100% treated carbon fibre
perhaps indicating desheathing of the top fibre layer(s) to reveal underlying nitrogen
in the graphitic structure.

5.5.2 Selection of a Representative Model

Of the four model-types considered, the PM3-5PLANE representation has been
selected as the best model of the changing nature of the carbon fibre surfaces as
surface treatment is applied. The choice is based on the trends in the fibre-type
contribution data (tables 5.7-5.10) as well as the inclusion of depth (underlying
graphitic layers) below the functionalised surface layer. In particular, the
contribution data for the PM3-5PLANE fibre-types exhibits no excessively large
peaks or troughs as are present for the other model types. Furthermore, the PM3-
5PLANE data show a logical decrease in the dispersive GR fibre-type, a desheathing
effect in the N-N fibre-type and an oxidising trend of hydroxyl→carbonyl→carboxyl
functionalities.

The point charges applied to the atoms in the PM3-5PLANE model are more
“fundamental” than those generated by empirical methods. This model excludes the
possibility of conflicting, differently-natured surfaces which could act as substrates
for adsorption as in the oxygen-containing BROT fibre-types, having an oxygen-
functionalised side and a graphitic side. The long-range interactions of underlying
graphitic layers are also included, and any complication of functionalised surface-
surface interaction removed; this is an improvement over the SANDWICH model-
types.

The PM3-5PLANE model-types have been used hereafter, combined with the
calculated relative contributions (table 5.10), to represent the chemical and physical
nature of the differently surface treated carbon fibres.
5.5.3 Comparison of PM3-5PLANE Model with Experimental XPS Data

The fibre-type relative proportions calculated in the preceding section should not be mistaken for a percentage of functional groups present on the surface. Even in the case of the functionalised surfaces, the majority of the atoms in the fibre-types are carbon, firstly as there are three layers of graphite between the two surfaces and, secondly as the functional group is present as a unit covalently bonded within a graphitic layer.

By scaling the fibre-type proportions by the percentages of each atom present, the data can be compared against XPS measurements of atomic percentages at the fibre surfaces. The experimental XPS data (table 5.11) were collected after the fibres had been conditioned at 120°C for 12 hours to remove any adsorbed water and other contaminants. Aluminium Kα X-rays were used with a 50eV analyser and a step size of 1eV to detect the concentrations of carbon, nitrogen and oxygen in the surface region of the fibres.

| Table 5.11 XPS analyses (atom%) of differently surface treated carbon fibres. |
|-----------------|---|---|---|---|---|
|                | 0 | 25 | 50 | 100 | 200 |
| C1s             | 93.24 | 88.57 | 87.78 | 85.47 | 83.67 |
| O1s             | 3.32 | 7.71 | 8.69 | 10.79 | 12.50 |
| N1s             | 2.58 | 2.57 | 2.27 | 2.17 | 2.39 |

Figure 5.8 Atomic percentage of oxygen (♦) and nitrogen (■) (measured by XPS) as a function of fibre surface treatment.
The experimental data show that the atomic percentage of carbon is reduced and that of oxygen increased as surface treatment is applied. The concentration of nitrogen is only reduced at intermediate treatments (50 and 100%), by which time ca. 15% has been removed, but increases upon over-treatment, although not becoming as high as the untreated value. After initially more than doubling from 0-25% surface treatment, the atomic percentage of oxygen continues increasing throughout the range of treated fibres but at a lower rate than initially. The changes in O1s and N1s signals are shown graphically in figure 5.8.

In comparison with the XPS data, the calculated atomic percentages of carbon, nitrogen and oxygen from the PM3-5PLANE model fibre-types and relative contributions are listed in table 5.12. The concentrations of both oxygen and nitrogen in the model surface treated fibres are much less than detected in the XPS analyses, however the trends in the two sets of data are similar. In the model, the percentage nitrogen reduces initially, then peaks again before reducing upon over-treatment. The simulated oxygen atomic percentage rises steadily from the untreated model surface but dips at 100% treated carbon fibre then recovers to a relatively high concentration in the 200% treated surface.

Table 5.12 Calculated concentrations (%) of atoms in PM3-5PLANE models of differently surface treated carbon fibres.

<table>
<thead>
<tr>
<th></th>
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<th>25</th>
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<th>100</th>
<th>200</th>
</tr>
</thead>
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<td>91.62</td>
<td>92.43</td>
<td>91.76</td>
</tr>
<tr>
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<td>1.88</td>
<td>2.44</td>
<td>1.98</td>
<td>2.36</td>
</tr>
<tr>
<td>[N]</td>
<td>1.43</td>
<td>0.77</td>
<td>0.35</td>
<td>0.9</td>
<td>0.49</td>
</tr>
</tbody>
</table>

The XPS data suggest that a high percentage of the surface region consists of oxygen and nitrogen species, yet the model implies that much of this does not contribute to adsorption interactions with the small molecules used in the IGC analyses and computer simulations. Significantly the analysis depth of XPS can be between ca. 15 and 100Å, thus it is questionable whether XPS data should be used for comparison with adsorption interactions. Non-bonded atomic and molecular interactions have very little effect if the two centres are separated by more than 10Å, a feature utilised in the interaction cut-off used in the simulations. Thus, it is only the top one or two
surface layers that initially attract a molecule to the surface and the top four layers which interact to keep the molecule in the physically adsorbed state.

The number of layers analysed by XPS is greater than the number considered in the PM3-5PLANE model fibre-types. Furthermore, the model consists of two functionalised surfaces, with groups protruding in opposite directions in the periodic cell c-axis. As can be seen in the simulated energies of interaction for the PM3-BROT and PM3-SANDWICH models (tables 5.4 and 5.5), the two surfaces in the SANDWICH model result in significantly larger energies of interaction than the single (BROT) surface. Thus, the effect of the two surfaces in the 5PLANE model is to reduce the concentration of functional groups required to effect the same interaction as a single surface with continuous graphitic depth below and nothing above the functionalised layer.

The 5PLANE model approximates a real carbon fibre by, firstly, having only functionalised surfaces exposed to the external medium, whereas the BROT model comprises a functionalised surface and a purely graphitic surface within the same model fibre type. Furthermore, these functionalised layers are spaced far enough apart (separated by graphitic planes) so that their non-bonded interactions do not influence each other, whereas only ca. 3.4Å separates the two functionalised surfaces in the SANDWICH model. Thus, the 5PLANE model is a more realistic representation of an actual carbon fibre, with a graphitic “core” and a functionalised surface.

Considering the depth of the experimental analysis and the two surfaces used in the PM3-5PLANE model, the atomic percentages of oxygen and nitrogen in table 5.11 should be multiplied by a scalar between 4 and 5 to be a proper comparison. This raises the values much closer to those determined by XPS.
5.6 Conclusions

A computational model of the changing chemical nature of differently surface treated carbon fibres has been produced, using the SORPTION™ computer algorithm to simulate fibre/probe interactions and correlation of these data with experimental IGC fibre surface characterisation. The trends in calculated oxygen and nitrogen atomic percentages in the modelled surface treated fibres compare reasonably well with XPS data, although the absolute values differ as the model is based on intermolecular interactions as present in the IGC which do not have a significant effect beyond 10Å.

Five different surfaces (fibre-types) were considered in the computational model: a purely graphitic surface; a surface with nitrogen incorporated into the graphite framework; a surface with hydroxyl groups; a surface with carbonyl groups; and a surface with carboxyl groups. The model shows how the contribution of these surfaces varies through a range of surface treatments, shown in figure 5.9.

![Figure 5.9](image)

Figure 5.9 Relative contributions of PM3-5PLANE model fibre-types, GR (♦), N-N (●), COH (▲), CO (■), COOH (•), as a function of fibre surface treatment.

The contribution of the nitrogen-containing surface decreases sharply at first, before peaking and decreasing again upon over-treatment. Jones et al.\textsuperscript{167,168} report several different nitrogen species, concentrated at the fibre surface as amide, aza, imide and amine, although they conclude that only amine functionalities present from the PAN precursor are likely to react with an epoxy matrix. This leads to a higher interfacial
bond strength than composites with no nitrogen present. Other nitrogen functional groups are not expected to react with an epoxy matrix or contribute to interfacial bond strength.

A limitation in the model is the lack of surface roughness, aside from the topography of the functional groups themselves. The BET surface area data (table 4.2) show that surface treatment does not have a profound effect on total surface area of the carbon fibres. However, work has been published, using trichloromethane labelling and XPS analysis, which details an oxidation-dependent micropore volume of $2-13 \times 10^{-5}$ cm$^3$ g$^{-1}$ of fibre$^{169}$. The authors further propose that functional groups are bound to the edge carbon atoms in the micropores.

The changes in surface oxygen groups with fibre surface treatment correlate well with experimental heats of adsorption for acidic and basic probes$^{170}$. Farinato et al. generalise that adsorption isotherms are largest for bases over acids of comparable structure, and for probes with little steric hindrance. This implies that the surface of the fibres is predominantly acidic, and that specific adsorption sites are only accessible to molecules which are not sterically cumbersome. Adsorption methods have also been used in conjunction with functional group labelling to show an initial rise in acidity with surface treatment which plateaus at higher treatments$^{171}$. The same trends were observed in mechanical tests of carbon fibre/epoxy matrix composite bond strength$^{172,173}$.

Denison et al.$^{174}$ used a similar labelling technique with XPS analysis to show that there is no increase in the atomic percentage of surface oxygen above ca. 75% surface treatment. The chemisorptive characteristics of the fibre surface continue to increase however, at higher treatment levels, denoting that the chemical nature of the oxygen functional groups changes. It is reported, using an ammonium bicarbonate electrolytic treatment, that C=O species dominate at low treatment levels, whereas C–O groups increase with treatment$^{175}$. This is a similar effect to that shown in the computational model.
Chapter 5: Atomistic Modelling of Sorption Interactions at Carbon Fibre Surfaces

Contact angle analysis has been used to determine acid/base characteristics of surface treated carbon fibres\(^{176}\), and it is reported that interactions with model probe vapours (water, aniline and epoxystyrene) quantitatively increase in the same ratio as superficial oxidised sites\(^{177}\). Escoubes \emph{et al.} report an increase in total surface energy upon fibre treatment, and the accompanying rise in polar component (2.6 to 15.2 mJ m\(^{-2}\)) with reduction in dispersive component (42.9 to 35.1 mJ m\(^{-2}\)).

Hammer and Drzal\(^{178}\) performed the same measurements on these types of fibres, “as received” and after cleaning by means of a vacuum treatment, using eight different wetting liquids. They detail similar total surface energies to those in reference 177, yet their values of polar and dispersive components are of much the same magnitude as each other, \emph{e.g.} with surface treatment the polar surface energy component increases from 23.6 to 30.0 mJ m\(^{-2}\) and the dispersive component decreases from 27.4 to 26.4 mJ m\(^{-2}\). The same trends are observed for the cleaned carbon fibres although the change in surface energy upon surface treatment is not as great. They conclude that the surface treatment increases adhesion by increasing surface polarity as well as increasing the concentration of surface oxygen.

In comparison with these measurements, table 5.13 lists computational non-bonded energy components of the model surfaces developed in this chapter. It should be noted that these are internal energy components and not necessarily what would be experienced by an external medium. The van der Waals energy increases initially then dips for the 100\% treated surface before rising again upon over-treatment. The electrostatic energy decreases (becomes more negative) at first then appears to level off through 50-200\% treatment.

| Table 5.13 Energy components (kJ mol\(^{-1}\)) of the simulated surface treated carbon fibres using the relative contributions of the fibre PM3-SPLANE model fibre-types. |
|-------------------------------------------------|-----------|-----------|-----------|-----------|-----------|
| | 0 | 25 | 50 | 100 | 200 |
| van der Waals | 11940.83 | 12227.35 | 12660.59 | 12389.41 | 12632.30 |
| Electrostatic | -355.28 | -357.44 | -367.40 | -368.30 | -369.59 |

Although the van der Waals energy significantly outweighs the electrostatic energy component (being ca. 33\times greater), electrostatic interactions have a longer range and are thus more significant at long distances, \emph{i.e.} in the initial attraction of an adsorbate
molecule. When the molecule is close enough to absorb on the surface, the interaction forces are a combination of both energy components. Considering a decrease in energy as making the surface more attracting towards other species, the trends in the van der Waals and electrostatic energies with increasing fibre surface treatment are similar to those of dispersive and polar surface energy components as analysed by wetting measurements.

In terms of composite mechanical properties, correlations between surface chemistry and interfacial shear strength (IFSS, $\tau$) or interlaminar shear strength (ILSS) have been reported. Fukuda et al.\textsuperscript{179} derive relationships (equations 5.2 and 5.3) between IFSS and active surface area ratio ($R_{ao}$, defined as the surface area of oxygen chemisorption to that of krypton adsorption) as well as surface oxygen concentration ($C_{O/C}$, measured by XPS) with reasonable correlation coefficients.

\begin{align*}
\tau &= 13.01 \ln(R_{ao}) + 54.3 \quad \text{Equation 5.2} \\
\tau &= 18.3 \ln(C_{O/C}) + 58.3 \quad \text{Equation 5.3}
\end{align*}

Bogoeva-Gaceva et al.\textsuperscript{180} detail increased values of ILSS for composites containing oxidised carbon fibres "probably due to higher concentration of carboxyl groups at the interface". This view is reinforced by Hüttinger et al.\textsuperscript{181}, although they also note the strong differences in ILSS dependent upon the matrix used. In a thermoplastic poly(carbonate) matrix, surface treated fibres improved ILSS by 10% over untreated fibres, yet for a poly(ethersulphone) matrix the increase was 40%.

There is agreement that surface treatment of carbon fibres improves adhesion (IFSS and ILSS) and adsorption characteristics, yet the factors controlling this have still to be fully determined. The computational model developed in this chapter attempts to resolve the changes in fibre adsorption phenomena into contributions arising from specific surface oxygen and nitrogen functional groups. The general trend in surface concentration of these atoms is similar to XPS analyses of the surface treated carbon fibres and is in agreement with previously published work.
The benefits of the approach used in this work are that the experimental adsorption characteristics of differently surface treated carbon fibres can be qualitatively assigned to contributions from specific types of surface functional groups. The opportunity then arises to simulate the effects on fibre properties of varying the concentrations of these functional groups, with a view to tailoring fibre surface treatments for specific applications.
Chapter 6: Predictive Modelling of Fibre-Matrix Adhesion in CFRP

6.1 Representation of Crosslinked Polymer Networks

6.1.1 Polymer Crosslinking

Thermoset polymers react, or *cure*, to form highly intractable crosslinked resins which cannot be moulded by flow, thus components of these materials must be fabricated during the crosslinking process. This process involves reactions between polymer chains to form a three-dimensional network of covalently bonded polymeric units. Thermoplastic polymers do not form these type of crosslinked networks, however, semi-interpenetrating networks (semi-IPNs) can be formed between thermoplastics and thermosets, where the amorphous thermoplastic polymer chains become entangled within the thermoset crosslinked structure.

In the case of epoxy resin systems, the epoxide group can be cured with an amine hardener (a type of curing agent). The amine must be primary or secondary, *i.e.* have "active" hydrogen atoms. Reaction occurs *via* nucleophilic attack of the lone pair electrons of the amine nitrogen on the methylene (CH₂) group of the epoxide ring. The highly strained ring opens to form a β-hydroxyamine and covalently bond the two molecules.

![Figure 6.1 Nucleophilic attack of primary amine to open epoxide ring and form β-hydroxyamine.](image)

Using a primary amine for the first step, the possibility still exists for further reaction between the β-hydroxyamine and another epoxide group to form a bis-β-hydroxyamine. Such a primary amine group would be termed di-functional since it has the capability of reacting with two epoxy groups. Typically, for epoxy resin
systems in aerospace applications, one would use a tetra-functional amine such as DDS (figure 1.5) which could react with up to four epoxy groups. Catalytic curing agents are often included, albeit in small quantities, as well as amine hardeners in epoxy resin formulations. The hardener influences the cured resin properties as a result of its incorporation in the molecular structure of the network chains, whereas the catalytic curing agents promote etherification condensation reactions, via homopolymerisation of epoxy groups, and between hydroxyl groups formed in the epoxy-amine reaction\textsuperscript{182}.

The side reactions which occur during the curing process of an epoxy resin system are dependent on the epoxide and amine formulations used. The most widely-used epoxy system for aerospace composites comprises the TGDDM epoxy and DDS amine hardener and this been studied by Attias \textit{et al.}\textsuperscript{183}. Using model representative compounds they have found by-products of cyclic ethers, and quinoline structures arising from intramolecular cyclisation reactions. In a further study, using the actual resin components, the same authors report a predominance of intramolecular cyclisation of diglycidyl amine groups at the same amine (hardener) nitrogen atom\textsuperscript{184}; the resins were thus less crosslinked than expected. They compare the reactivity of DDS to another common hardener DDM (4,4'-diaminodiphenyl methane), and suggest that the low reactivity of DDS leads to a high proportion of residual unreacted secondary amines present after cure, as determined by $^{13}$C nuclear magnetic resonance (NMR) spectroscopy.

The small cyclic side products in the TGDDM-DDS resin system are also reported by Matejka \textit{et al.}\textsuperscript{185}, whereas no cyclisation is observed in the di-functional epoxy DGEBA-DDS resin system\textsuperscript{186}. Furthermore, in a study to determine the rate constants of different steps in the DGEBA-DDS reaction mechanism, Finzel \textit{et al.}\textsuperscript{187} report that etherification does not occur to any significant extent.

Many groups have produced models for the progression of the epoxy-amine reaction. An early statistical model by Dušek \textit{et al.}\textsuperscript{188}, which has recently been updated to incorporate kinetic aspects, has lead to an improvement in accuracy against experimental studies\textsuperscript{189,190,191}. Cheng and Chiu\textsuperscript{192} have incorporated the etherification
process, a reaction which results in lower critical epoxy conversion, into their kinetic model. A similar approach has been adopted by Tsou and Peppas\textsuperscript{193}, who report that the formation of these ether links occurs at the expense of secondary amine species remaining after reaction.

An emerging family of thermosetting polymers which shows potential for use in aerospace applications is cyanate ester resins. These molecules polymerise by cyclotrimerisation of three cyanate ester groups to form 1,3,5-triazines (or sym-triazines) shown in figure 6.2. The reaction is promoted by heat and a range of catalysts including protic acids, Lewis acids, bases and metal ions. The rate of cure (cyclotrimerisation) is catalyst dependent and may be controlled, considering the need to dissipate the high exothermic heat of the polymerisation reaction\textsuperscript{194}.

![Cyclotrimerisation of three cyanate ester groups to form a poly(cyanurate).](image)

The most common types of catalyst used to cure aryl cyanate esters are carboxylate salts and chelates of transition metal ions. The transition metal ion forms coordination complexes with the cyanate ester functionalities to facilitate the close interaction required for cyclotrimerisation. A co-catalyst is also added to act as a solvent for the transition metal catalyst and complete the cyclotrimerisation to a triazine ring. The most commonly used catalyst is an alkylphenol such as nonylphenol although alternatives include bisphenols, alcohols, imidazoles and aromatic amines\textsuperscript{195}.
Kasehagen and Macosko have analysed a cured, bisphenol-A based cyanate ester resin by a variety of methods to characterise side products of the polymerisation reaction. Possibly the most important side reaction involves the presence of water which reacts with the cyanate ester groups to form carbamates. These carbamates can then decompose into amine-terminated fragments and carbon dioxide. Internal cyclisation to form bicyclophane cage structures has also been postulated. These deviations from ideal behaviour consume functional groups at the expense of polymerisation, however intramolecular cycles, determined by GPC and HPLC, appear to be formed in quantities so small that they may be assumed to be insignificant in their effects on structure evolution of the polymer.

In terms of crosslink density, Georjon and Galy have synthesised poly(cyanurate) networks with different extents of reaction to study various bulk physical properties. As the conversion increases so does the glass transition temperature, but there is a decrease in van der Waals volume and packing density. Correspondingly, the concentration of free-volume ‘holes’ increases with conversion, attributed to bulky triazine crosslinks which do not provide a suitable environment for close packing. Georjon and Galy conclude that the free-volume controls the amount of water adsorbed, which also increases with the extent of reaction.

In terms of ultimate temperature properties, from their theoretical cure kinetics modelling, Stutz et al. conclude that the maximum available $T_g$ appears to be more a result of a competition between curing, side reactions and thermal degradation and is not a result of a topological limit for network formation.

6.1.2 Three-Dimensional Computational Network Considerations

Probably the most common epoxy resin system for advanced composites uses a tetra-functional glycidyl amine TGDDM (marketed commercially as MY720 by Ciba) with DDS as the hardener and a boron trifluoride monoethylamine accelerator ($\text{BF}_3\text{C}_2\text{H}_5\text{NH}_2$). Using such a system as this, with a tetra-functional epoxy monomer and tetra-functional amine hardener, creates problems when attempting to represent the polymer networks by relatively small-scale computer simulations.
To generate the minimum of six potential "bond-halves", in order to create across-cell bonds in the three \((a, b\) and \(c\)) cell dimensions, only one amine molecule need react with one epoxy molecule. This new amine-epoxy unit would still contain three active hydrogen atoms on the amine portion and three glycidyl amine groups on the epoxy portion which could react with each other, forming the bonds across each of the cell dimensions. Spatially, however, the constraints this bonding would impose in the network structure would be so great as to represent a very brittle material which is unrepresentative of this epoxy resin system.

In view of this, the consideration of a di-functional epoxy molecule, DGEBA, simplifies the problem to an extent and allows more molecules to be present in the minimum representation. Now to generate the minimum six bond-halves, at least two amine molecules must be used. An epoxy molecule bonds across the two amines so that there are six active amine hydrogen atoms. However, only epoxy molecules may react with the amines, but in the case of the di-functional DGEBA this does not complicate the representation; it merely reacts with an amine to leave an unreacted glycidyl ether group at the other end of the molecule (as opposed to three unreacted glycidyl amine groups in the case of TGDDM). Thus, the minimum representation requires three further epoxy molecules to react with the six active amine hydrogen atoms, leaving three epoxy chain ends and three active amine hydrogens. The minimum representation therefore involves two amine and four glycidyl ether molecules.
Chapter 6: Predictive Modelling of Fibre-Matrix Adhesion in CFRP

Figure 6.4 Schematic of the minimum DGEBA-DDS network. The A denotes a DDS molecule and the D a DGEBA molecule. Bonds are created in the three dimensions to join 1 to 1', etc.

For cyanate ester resins, the representation of their polymer network structures is simplified somewhat by the fact that (for the model case considered here) only one type of monomer is present. Possessing a functional group at either end of the molecules, the unit is di-functional. To generate the six bond-halves required for the minimum representation four cyanurate rings must be formed and six monomer molecules considered.

Figure 6.5 Schematic of the minimum bisphenol-A based cyanate ester network. The Tr denotes a sym-triazine ring structure with three network chains propagating from it. Bonds are created in the three dimensions to join 1 to 1', etc.

6.1.3 Construction of Computational Models of Three-Dimensional Polymer Networks

Many studies using "model" compounds, representative of a larger system, tend to focus on particular functional groups and therefore require that the remaining portion of the molecule does not affect the phenomena being studied. To consider a crosslinked thermoset network, however, it is important that covalent bonding of
polymer chains propagates in all three cell dimensions to add stiffness which discrete model compounds would not exhibit. To generate such infinite networks requires manipulation of the model unit and periodic boundary conditions to facilitate bond creation between real and simulated units. Work using previous versions of the computational software has utilised the facility to generate non-linear, i.e. branched or network, polymer models\textsuperscript{199}. Unfortunately, the current algorithms do not allow this, thus the method developed in this section has been employed.

In a similar procedure to that used in §5.1.1, the starting point for the thermoset models is consideration of the minimum representation required to allow bonding across all three dimensions. As mentioned previously, a minimum of six cyanate ester units (thus four sym-triazine rings) must be used in the case of the poly(cyanurate), and for the DGEBA-DDS epoxy resin system two DDS and four DGEBA molecules are required. For both cases, an orthorhombic cell with bonding in the \(a\) and \(b\) directions has been constructed initially, using the molecular structures

\[ \text{Figure 6.6 Minimum representations of poly(cyanurate) (top) and amine cured epoxy (bottom) required to construct the two-dimensional models with bonding across the periodic boundary of ends \(a\) to \(d\) and \(b\) to \(c\).} \]
shown in figure 6.6. A primitive cubic cell has been applied and the cell axes adjusted to create covalent bonds across the periodic boundary with application of the *Auto Bonding* function. The minimum two-dimensional cyanate ester network is shown in figure 6.7.

![Figure 6.7 United-atom poly(cyanurate) model with two-dimensional bonding across the periodic boundary of ends a to d and b to c (grey = C (implicit H), blue = N, red = O).](image)

From these two-dimensional models, the visualisation is then changed to show two adjacent cells in the *a* direction, with a bond across them. These two cells are then merged by creation of a *SUPERSTRUCTURE*, to leave a single bond across the cell *a* dimension and two bonds in the cell *b* dimension. One of these bonds in the *b* direction is then broken and the atoms translated in the *c* direction, such that a new bond is formed across this cell boundary *via* auto bonding. Once the model has this
three-dimensional structure, the cell axes are adjusted so that the correct density is specified (1.260 g cm$^{-3}$ for the cyanate ester resin$^{200}$ and 1.237 g cm$^{-3}$ for the DGEBA-DDS epoxy resin system$^{201}$).

### 6.1.4 Network Atomic Charge Assignment

The purpose of the thermoset network generation outlined previously is to use these models to characterise the physical interactions between the matrix and fibre phases in CFRP. The fibre models that have been developed incorporate a semi-empirical treatment for the calculation of atomic point charges used in molecular mechanics calculations. As noted in §5.2.2, to create a balanced energy expression the same charge and energy calculation should be applied to all components of a system being simulated.

The thermoset networks must be subdivided into discrete segments due to the incapacity of the semi-empirical calculation methods used in this work to incorporate periodic boundary conditions. Following structure optimisation using the DREIDING2.21 force-field for the DGEBA-DDS system and the newly-developed RDA-DR2.21_Inv force-field for the cyanate ester resin, portions of the two resin systems have been selected for use in the calculation of semi-empirical charges. In the cyanate ester resin a central sym-triazine ring with three $p$-tertiarybutyl phenoxy substituents has been used, and for the epoxy resin system a central DDS unit with four $p$-tertiarybutyl glycidyl phenyl ether molecules (each reacted to form the corresponding $\beta$-hydroxyamine). The structures, with added hydrogen atoms (required in the semi-empirical calculations), are shown in figure 6.8.

Single point energy calculations, using the PM3 Hamiltonian, have been performed to assign semi-empirically derived charges to the individual atoms but not alter the structural geometry. These models have then been reconstructed into the molecular mechanics periodic cell and the hydrogen atoms removed (only those bonded to carbon, not the hydroxyl hydrogen atoms) as standard with the united atom representation. The overall cell charge is then averaged to zero to account for the removal of the hydrogens and the structure optimised using these new charges.
6.1.5 Thermoset Matrix Mechanical Properties

The minimum representations of both epoxy and cyanate ester resin models assume 100% reaction of monomeric components to form the three-dimensional network, with no side-reactions or incomplete conversion. The mechanical properties of these representations have been calculated to analyse the computational accuracy of these theoretically fully-reacted resins; etherification of hydroxyl groups in the DGEBA-DDS system has not been included in this simple model as it would significantly complicate the three-dimensional network bonding aspects of the periodic boundary condition.

From the starting (minimum representation) models of the cyanate ester and epoxy resin, each containing semi-empirically derived atomic charges and having been energy minimised to convergence of less than 0.04 kJ mol$^{-1}$ using the RDA-DR2.21 Inv and DREIDING2.21 force-fields respectively, an algorithm has been used to sample conformational phase space and generate model structures. Random positional disorder (10 x 1Å) of all atoms has been introduced and the models re-minimised. This procedure has been employed to separately create 50 cyanate ester and 50 epoxy network models in a progressive fashion, i.e. perform the atom displacement and minimisation on the previous structure, not the original, each time. From analysis of the resulting energies, the five lowest energy models have
been selected for use in the calculation of the mechanical properties of the polymer networks.

The _SECOND DERIVATIVE_ method\(^{202}\) has been used to calculate the mechanical properties of the polymer network models. This routine uses a single point energy calculation to obtain the lattice energy with respect to the lattice parameters and the atomic coordinates as a function of applied strain. When the model is in a minimum energy state, the stiffness matrix is obtained from the second derivatives. Further details of the calculation are given in the Appendix. The results of these calculations compared with experimental data are given in tables 6.1 and 6.2.

**Table 6.1** Calculated mechanical properties for different cyanate ester resin models compared with experimental values\(^{200}\). The name 4+0 signifies that the model contained four _sym-triazine_ rings with no non-perfect flexible units, similarly for 8+4 and 12+8.

<table>
<thead>
<tr>
<th></th>
<th>4+0</th>
<th>8+4</th>
<th>12+8</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Modulus (GPa)</td>
<td>26.2</td>
<td>25.3</td>
<td>24.6</td>
<td>3.79</td>
</tr>
<tr>
<td>Young's Modulus (GPa)</td>
<td>29.7</td>
<td>29.4</td>
<td>29.8</td>
<td>3.39</td>
</tr>
<tr>
<td>Poisson's Ratio</td>
<td>0.340</td>
<td>0.325</td>
<td>0.349</td>
<td>0.35</td>
</tr>
<tr>
<td>Lamé Constant (\lambda) (GPa)</td>
<td>13.8</td>
<td>15.7</td>
<td>14.5</td>
<td>2.95</td>
</tr>
</tbody>
</table>

The simulated cyanate ester resin shows values of both bulk and Young's moduli roughly eight times greater than experimentally determined. The Poisson's ratio is, however, very similar to the experimental value. This indicates that although the moduli suggest the model has much greater stiffness than found experimentally, the compressive strains experienced (in the transverse direction) when a tensile stress is applied to the material are similar to experiment as shown by the Poisson's ratio, _i.e._ the distribution of the applied stress is represented well computationally.

To overcome the discrepancies between the mechanical properties of the models and the experimental values, an attempt has been made to lower the simulated moduli by inclusion of flexible, non-perfect units into the network structure. For the cyanate ester resin, the incorporation of a _sym-triazine_ ring segment where only two of the cyanate ester monomers have reacted through both functional groups has been used; the third monomer retains an unreacted -OCN end. This segment is thus only linear (as opposed to the other _sym-triazine_ rings with three independent chains propagating from them) and acts as a flexible insert between adjacent _sym-triazine_ rings. Semi-
empirical charges have been applied to this unit in a similar procedure to that carried out previously; the structure, with added hydrogen atoms, is shown in figure 6.9.

![Flexible linear 1,3,5-triazine unit](image1)

**Figure 6.9** Flexible linear 1,3,5-triazine unit (with unreacted cyanate group) used in the calculation of semi-empirical charges (white = H, grey = C, blue = N, red = O).

![Flexible linear DGEBA-DDS unit](image2)

**Figure 6.10** Flexible linear DGEBA-DDS unit used in the calculation of semi-empirical charges (white = H, grey = C, blue = N, red = O, yellow = S).

In the case of the DGEBA-DDS epoxy resin system, a linear unit has also been used to lower the moduli values of the simulated resin. The linear unit in this case consists of a DDS molecule which has reacted through only one of the hydrogens at each primary amine on either end of the monomer. A p-tertiarybutyl glycidyl phenyl ether group, to represent half of a DGEBA molecule, has reacted and covalently bonded to each of the amine nitrogen atoms to form the corresponding $\beta$-hydroxyamines (figure 6.10). Semi-empirical charges have been calculated for
this fragment as outlined previously. The unit is introduced into the original epoxy model as a flexible group between bonded epoxy and amine molecules.

Even with the inclusion of imperfect units into the network structure, the mechanical property values change very little (table 6.2). Unfortunately, there are no available literature values of the resin bulk modulus or Lamé constant $\lambda$, although the experimental $T_g$ is given as 198°C and the shear modulus as 1.30 GPa.

Table 6.2 Calculated mechanical properties for different DGEBA-DDS epoxy resin models compared with experimental values. The name 2-4-0 refers to the network model comprising two amine and four epoxide molecules with no linear flexible units, similarly for 6-8-4, 10-12-8 and 14-16-12.

<table>
<thead>
<tr>
<th></th>
<th>2-4-0</th>
<th>6-8-4</th>
<th>10-12-8</th>
<th>14-16-12</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>24.1</td>
<td>23.8</td>
<td>14.8</td>
<td>14.1</td>
<td>3.40</td>
</tr>
<tr>
<td>Poisson’s Ratio</td>
<td>0.329</td>
<td>0.358</td>
<td>0.311</td>
<td>0.326</td>
<td>0.312</td>
</tr>
</tbody>
</table>

For the cyanate ester resin (table 6.1), four flexible units have been inserted into the original model, and the structure generation, selection and mechanical property calculation then repeated. Furthermore, with twice as many flexible groups (now eight) added into the original model, the Young’s modulus is still 29.8 GPa and the bulk modulus 24.6 GPa. Similarly, the small decline in Young’s modulus with insertion of flexible groups into the DGEBA-DDS model indicates that very large systems will have to be considered if values approaching experimental measurements are to be simulated by this method.

At this point it should not be forgotten that the overall aim of this investigation is to study fibre-matrix interactions and not bulk resin structure. Furthermore, the computational restraints of constructing the interfaces mean that only a small (if any) degree of three-dimensional structure can be considered, due to the finite dimensions of the matrix layer in the model. To this end, the correlation of experimental resin mechanical properties with their computational representation, although a very interesting investigation, does not seem as significant as the consideration of the chemical functional groups in the structure. In future studies it may be possible to incorporate both aspects into the model networks. In the present work, however, because of the cell dimensions of the 5PLANE fibre models and the limited area in which to simulate the resin component of the composite, the foremost consideration is a comparison of the two different resin systems in terms of their functional groups.
6.2 Simulation of Interfacial Interaction Energy

6.2.1 Methodology

In §2.3.2 the work of adhesion has been defined as the "free energy change ... to separate unit areas of two different species from contact to infinity in a vacuum". Using an analogy with the Dupré equation (equation 2.11), simulations have been performed to calculate the effect of physical interfacial interactions on the energy of an alternating planar fibre-matrix composite model. The interfacial interaction energy ($E_{ii}$) is calculated as the energy of an optimised fibre-matrix composite model minus the energies of the individual fibre and matrix components, i.e. the energy arising from the presence of both components interacting with each other.

$$E_{ii} = E - E - E$$

Figure 6.11 Representation of the interfacial interaction energy ($E_{ii}$) as the energy of a composite model minus the energies of the individual components.

The non-bonded energy components of these calculations have been subdivided into dispersive, electrostatic, and hydrogen bonding terms, represented by Coulombic, Lennard-Jones 12,6, and Lennard-Jones 12,10 equations, respectively (equations 2.26, 2.25 and 2.27). The simulated interfaces consist of the epoxy and cyanate ester resin models developed in this chapter and the 5PLANE fibre models from §5.1.3. Calculations have been performed using the original 5PLANE model surface, i.e. comprising a single type of functional group, and the contribution of the scaling factors of §5.5.1 applied to relate these results to surface treated carbon fibres. The advantages of using these fibre models is that there are no correlation effects of different functional groups upon each other, as would be present if, say, a 0% surface treated carbon fibre model was constructed from the contribution data. Furthermore the particular interactions between the matrix resin and a single type of functional group can be observed. Thus, not only can it be seen how the energy components for a particular resin-carbon fibre composite change as a function of fibre surface
treatment, but the effect of specifically altering the concentration of certain functional groups may also be predicted.

Although attempts have been made to correlate simulated and experimental polymer matrix mechanical properties to network structure and defects, the limitation of the modelling software has only allowed a finite portion of each component to be considered. Thus, the fibre phase is represented by the 5PLANE models of three graphitic planes sandwiched between two oppositely facing functionalised surfaces. The matrix has also been represented as a network with covalent bonding across two of the periodic cell dimensions (the same as for the fibre planes) but only limited thickness in the third dimension. A typical interface model is shown in figure 6.12.

Figure 6.12 Composite model of an interface between a cyanate ester resin matrix (spheres) and carboxyl functionalised fibre (cylinders; white = H, grey = C, blue = N, red = O).
6.2.2 Calculation Procedure

The periodic cell used for the interfacial model has the dimensions $a = 29.4\,\text{Å}$,
$b = 22.14\,\text{Å}$, $c = 35\,\text{Å}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$. Following construction of the individual phases from the 5PLANE (fibre) and DGEBA-DDS or cyanate ester resin (matrix) models, the resin phase has been translated, as a single unit, in the $c$-axis so that it is equidistant from each surface of the 5PLANE fibre.

Maintaining the atoms in the fibre portion rigid, the matrix atoms are individually, randomly translated a total of ten times by a distance of $0.5\,\text{Å}$. After application of the force-field parameters (DREIDING2.21 for the epoxy resin, RDA-DR2.21 Inv for the cyanate ester resin system), the matrix atoms are geometry optimised using the conjugate gradients method until an energy convergence of less than $0.04\,\text{kJ mol}^{-1}$ is achieved. The energy of the particular model fibre type-matrix resin system is then taken as the energy of the optimised composite model (figure 6.12). This optimised composite model is then saved.

The matrix phase is then deleted and solely the 5PLANE fibre model with these cell parameters optimised using the same routine as for the composite model. This is the energy of the individual fibre phase. From the original optimised composite model, the fibre phase is then deleted. The sole matrix phase is then optimised using the same routine as for the fibre and composite models. The three separate energies required for calculation of the interfacial interaction energy are thus obtained.

It is important to be thorough when checking the bonding (single, double, triple) of the models during their manipulation and construction of the composite model. It is found occasionally that the incorrect bonding characteristics, and thus atom types, are assigned by the software and these must be modified before simulation.

Very little modelling work has been previously published in the area of interfacial phenomena and adhesion. A micromechanical model based on "link points" and "connections" for a hypothetical fibre-matrix material has been presented by Kalinka and Leistner\textsuperscript{204}. The analysis does not, however, consider chemical atomic scale interactions in the model. Cherry and Porter\textsuperscript{205} have recently reported simulations to...
calculate the work of adhesion between inorganic substrates and silane adhesion promoters. The effect of moisture on the durability of the adhesive bonds is also discussed. They employ molecular dynamics to study diffusion behaviour of water and its effect on the silane-substrate interface.

Maguire et al.\textsuperscript{206} have used a molecular dynamics simulation to study the interphase region between an alumina surface and polymer adhesive, and Quesnel et al.\textsuperscript{207}, although not including any chemical information in their simulation, have applied molecular dynamics to look at the energy differences between two surfaces approaching each other and separating from each other. They suggest that the hysteresis behaviour exhibited between approach and separation can play a significant rôle in the adhesion of materials and related problems such as friction. Whilst molecular dynamics has been considered as a possible route to the interfacial interaction energy calculations presented here, limitations in terms of computing resources and time required for such bulk simulations have made this method prohibitive with respect to the conjugate gradients energy minimisation technique used in this work.

6.3 Analysis of Interfacial Interaction Energy Simulations

From the simulations using the various 5PLANE fibre surfaces with both matrix resin models, the components of the interfacial interaction energy have been calculated as described in §6.2.1. Applying the scaling factors of §5.5.1 to these data, the variation in total interfacial interaction energy, and its components, as a function of fibre surface treatment has also been calculated.

6.3.1 5PLANE-DGEBA-DDS Epoxy Resin Interfaces

The components of the interfacial interaction energy between the DGEBA-DDS epoxy resin matrix and the different 5PLANE model fibre surfaces are presented in table 6.3. All values are negative, \textit{i.e.} the energy of the composite system is less than
the energy of the individual fibre and matrix models, indicating energetically favourable fibre-resin interactions.

Table 6.3 Interfacial interaction energy components (kJ mol\(^{-1}\)) between 5PLANE models and DGEBA-DDS epoxy network.

<table>
<thead>
<tr>
<th></th>
<th>GR</th>
<th>N-N</th>
<th>COH</th>
<th>CO</th>
<th>COOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>van der Waals</td>
<td>-510.01</td>
<td>-505.62</td>
<td>-115.41</td>
<td>-120.53</td>
<td>-65.01</td>
</tr>
<tr>
<td>Electrostatic</td>
<td>-10.41</td>
<td>-62.27</td>
<td>-67.81</td>
<td>-93.60</td>
<td>-91.63</td>
</tr>
<tr>
<td>Hydrogen Bond</td>
<td>0</td>
<td>0</td>
<td>-1.03</td>
<td>-0.81</td>
<td>-2.81</td>
</tr>
<tr>
<td>Total</td>
<td>-520.41</td>
<td>-567.89</td>
<td>-184.25</td>
<td>-214.94</td>
<td>-157.49</td>
</tr>
</tbody>
</table>

The van der Waals interaction energy is most negative for the purely graphitic surface, followed by the nitrogen-containing surface then the carbonyl, hydroxyl and carboxyl-modified surfaces respectively. The values for the graphitic and nitrogen-containing surfaces are more than four times greater than those of the oxygen-containing surfaces. The van der Waals interaction energy is similar for the hydroxyl and carbonyl-functionalised surfaces, but they are roughly twice as large as the value for the carboxyl-functionalised surface.

The electrostatic interactions are quite different in nature to the van der Waals forces. They depend not only on the distance between the two atomic centres but on the partial atomic charges as well. The PM3 Hamiltonian has been used to apply charges to both the fibre and matrix phases; these charges were “fixed” (recalculation was not possible) during the course of the simulation. There is a relatively small electrostatic interaction between the DGEBA-DDS epoxy resin and the purely graphitic surface due to the small partial atomic charges assigned to the graphitic carbon atoms. The electrostatic interactions for the functionalised surfaces are much greater in magnitude than for the graphitic surface and increase in the order GR < N-N < COH < COOH < CO.

The introduction of functionalities into the graphitic surface results in a six-fold increase in the electrostatic interfacial interaction energy component initially, \textit{i.e.} in progressing from the graphitic to the nitrogen-containing surface. The magnitude of the electrostatic energy is greater for the carbonyl and carboxyl surfaces, which have similar values, than for the hydroxyl surface. This implies that oxidation of the
hydroxyl group, e.g. by oxidative surface treatment, results in a stronger electrostatic interaction between the fibre and an epoxy resin matrix.

In the case of the graphitic surface, the electrostatic energy component is only roughly one-fiftieth of the van der Waals energy component. The nitrogen-functionalised surface, although being largely of dispersive character and containing the nitrogen within the graphitic framework, has an electrostatic energy component just less than one-eighth of the van der Waals energy. The oxygen-containing functionalised surfaces show van der Waals and electrostatic interfacial interaction energies of much closer magnitude.

In the hydroxyl-functionalised surface the electrostatic energy component is just under two-thirds of the van der Waals energy. For the carbonyl-containing surface this relationship has changed so that the electrostatic energy value is more than three-quarters of the van der Waals value, and for the highly oxidised carboxyl-functionalised surface the electrostatic energy component is actually nearly 1.5 times greater than the van der Waals energy component. This effect indicates that as the oxidation state of the functional group on the model fibre surface increases, the nature of the interfacial interaction energy with an epoxy resin changes from being dominated by van der Waals interactions to comprising mainly electrostatic forces.

Hydrogen bonding forces are present in both the hydroxyl-containing functionalised fibre models (COH and COOH) as well as in the carbonyl-functionalised model due to interactions with the hydroxyl groups of the epoxy resin. The hydrogen bonding of amines and epoxies to oxygen-containing functional groups on the carbon fibre surface has been investigated by Horie et al. They report that this hydrogen bonding increases with the extent of fibre oxidation.

The hydrogen bonding interfacial interaction energy is of greatest magnitude for the carboxyl-functionalised surface, followed by the hydroxyl and carbonyl-functionalised surfaces respectively. Interestingly, the value of the hydrogen bonding energy component for the carboxyl-functionalised surface is greater than the sum of both the hydroxyl and carbonyl model values. This indicates that the
presence of a hydroxyl group and double bonded oxygen atom bonded to the same carbon centre exhibits a synergistic effect. A possible explanation of this would be a hydrogen bonding interaction between a hydroxyl group of the epoxy resin with the carbonyl-type oxygen atom of the fibre carboxyl group, coupled with a hydrogen bonding interaction between the hydroxyl section of the fibre functional group and either the ether oxygen atom of the epoxy resin or one of the sulphone oxygen atoms.

Although it has not been studied in this work, covalent bonding between epoxide or amine monomers and carbon fibre surfaces, specifically hydroxyl and carboxyl functionalities, has been reported\textsuperscript{209,210,211}. The preferential migration of either component to create an amine- or epoxy-rich interphase region could be a significant factor in the ultimate fibre-matrix adhesion properties. The limited work in this area so far has, however, provided conflicting reports and arguments for both cases\textsuperscript{212,213}.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
 & 0 & 25 & 50 & 100 & 200 \\
\hline
van der Waals & -283.29 & -218.21 & -157.22 & -206.04 & -165.06 \\
Electrostatic & -69.95 & -71.40 & -79.86 & -77.32 & -80.38 \\
Hydrogen Bond & -0.81 & -1.10 & -1.47 & -1.14 & -1.41 \\
Total & -353.72 & -290.25 & -237.83 & -284.01 & -246.16 \\
\hline
\end{tabular}
\caption{Interfacial interaction energy components (kJ mol\textsuperscript{-1}) of 5PLANE-DGEBA-DDS epoxy network interface as a function of fibre surface treatment.}
\end{table}

\textbf{Figure 6.13} Non-bonded interaction energy components of the simulated carbon fibre-epoxy resin interface as a function of fibre surface treatment (\(\triangle\) = electrostatic, \(\diamondsuit\) = van der Waals, \(\Delta\) = total).
The interfacial interaction energy components for the various fibre surface-epoxy resin model simulations have been combined with the coefficients of proportionality from §5.5.1 to produce the data in table 6.4. The variation of calculated energy components as a function of fibre surface treatment is displayed graphically in figure 6.13. The hydrogen bonding energy component has not been included on the graph due to the very low contribution to the total interfacial interaction energy throughout the model interfaces.

The van der Waals interfacial interaction energy component decreases in magnitude from untreated to 50% surface treated before increasing again at the standard 100% treatment. Upon 'over-treatment' (i.e. 200%) the van der Waals energy component decreases in magnitude to roughly that of the 50% treated value. During the initial reduction in magnitude of the van der Waals interfacial interaction energy to 50% treatment, some 45% of the van der Waals energy of the untreated surface has been lost. The large van der Waals interfacial interaction energy of the untreated surface is not surpassed by any of the treated model surfaces. An undulating shape is seen for the trend in the van der Waals interfacial interaction energy as a function of fibre treatment. This is in accord with the concept of the surface treatment removing the outermost graphitic fibre layer in a desheathing process.

The electrostatic interfacial interaction energy component increases in magnitude initially from the untreated carbon fibre value then appears to level off after 50% surface treatment. The changes in the electrostatic energy are not as great as seen in the van der Waals energy component, the lowest value being just ca. 13% less than the highest value. Significantly, however, although for the untreated carbon fibre surface the electrostatic energy is only roughly one quarter of the van der Waals energy, at 25% surface treatment it has increased to one third of the van der Waals energy value and is of the order of one half of the van der Waals energy component for both the 50% and 200% values.

The small changes in the absolute values of the electrostatic interfacial interaction energy mean that the total interfacial interaction energy shows a similar relationship to that of the van der Waals energy component, i.e. the undulating, desheathing
Chapter 6: Predictive Modelling of Fibre-Matrix Adhesion in CFRP

phenomenon. Although not shown on the graph due to the very low absolute values, the hydrogen-bonding interfacial interaction energy component increases in magnitude initially to 50% surface treatment then drops at 100% surface treatment before increasing again upon overtreatment. This is the same relationship as exhibited by the 5PLANE carboxyl functionalised surface shown in figure 5.9, indicating the importance of this particular group in hydrogen-bonding interactions.

It is unfortunate that the non-bonded energy terms used in the molecular mechanics energy expression cannot be compared directly with the experimental dispersive and polar surface energy components as determined by IGC and other techniques such as contact angle analysis. Aside from this being a potential further comparison between the model developed here and available experimental data, it has been shown that there is a linear relationship between IFSS and fibre dispersive surface energy\(^{214,215}\). The effect of fibre surface treatment and the enrichment of oxygen species at the surface have also been shown to increase IFSS\(^{216}\) or ILSS\(^{217}\) initially before reaching a plateau at higher values. This implies that there is a limit to the extent to which adhesion can be improved by fibre surface treatment.

6.3.2 5PLANE-Cyanate Ester Resin Interfaces

The interfacial interaction energy components for the simulations using the 5PLANE model surfaces and the bisphenol-A based cyanate ester resin model are given in table 6.5. With the exception of the hydrogen bonding component of the carboxyl-functionalised model fibre interface, all of the values are negative indicating a reduction in the energy of the composite compared with the individual fibre and matrix phases. Thus, the composite is favoured in all but the carboxyl-functionalised model interface hydrogen bonding interaction.

<table>
<thead>
<tr>
<th>Table 6.5 Interfacial interaction energy components (kJ mol(^{-1})) between 5PLANE models and poly(cyanurate) network.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>van der Waals</td>
</tr>
<tr>
<td>Hydrogen Bond</td>
</tr>
<tr>
<td>Total</td>
</tr>
</tbody>
</table>
Chapter 6: Predictive Modelling of Fibre-Matrix Adhesion in CFRP

The magnitude of the van der Waals interaction energy is greatest for the purely graphitic surface and decreases in the order GR > N-N > CO > COH > COOH. The nitrogen-containing surface has a van der Waals interfacial interaction energy component only slightly lower in magnitude than for the graphitic surface, yet the oxygen-containing surfaces have van der Waals energy components of only between one-third and two-thirds that of the nitrogen-functionalised surface.

The magnitude of the electrostatic interfacial interaction energy component decreases in exactly the opposite order to that of the van der Waals energy component, i.e. for the model fibre interface energies COOH > COH > CO > N-N > GR. All of the functionalised (oxygen- or nitrogen-containing) model fibre surfaces have electrostatic energy components more than four times greater than that for the purely graphitic surface. The basic nitrogen- and carbonyl-functionalised models have similar values for the electrostatic interaction whilst a more energetically favourable interaction occurs with the acidic fibre surface containing carboxyl groups.

For the purely graphitic surface the electrostatic energy component is less than one percent of that of the van der Waals interaction. The electrostatic energy increases in importance for heteroatomic surfaces. The electrostatic interfacial interaction energy is between two and three percent of that of the van der Waals component for the nitrogen-functionalised surface. Both of these surfaces have very high van der Waals energy components compared to the models with oxygen-containing functional groups. For the carbonyl, hydroxyl and carboxyl-functionalised surfaces the percentage of the electrostatic energy component with respect to the van der Waals energy component increases from ca. 5% to 7% to 18% respectively.

Owing to the lack of hydroxyl functional groups in the poly(cyanurate) the only hydrogen bonding interactions occur with the hydroxyl and carboxyl-functionalised fibre surfaces. A relatively strong hydrogen bonding interaction energy is calculated for the hydroxyl-functionalised surface, greater than for any involving the DGEBA-DDS epoxy resin matrix composite model. As this model of the cyanate ester resin cannot act as a proton donor, it implies that the fibre (proton donor) – resin
(proton acceptor) hydrogen bonding interaction is stronger than the resin (proton donor) – fibre (proton acceptor) interaction.

This phenomenon is also observed by Snow and Armistead\(^{218}\) in their study of hydrogen bonding between AS4 (high strength) carbon fibre and epoxy or cyanate ester matrices. They report a positive linear correlation between fibre-matrix IFSS (measured by a single fibre fragmentation technique) and the hydrogen bonding basicity of the resin (determined by spectroscopic measurements of the formation constant of samples with pyridine N-oxide hydrogen bond acceptor). The IFSS was greater for the cyanate than the aromatic amine-cured epoxy matrix microcomposite sample. This is reinforced in this computational work by the lowest (weakest) occurring hydrogen bonding interaction of the epoxy matrix composite being between the resin hydroxyl groups (proton donor) and the fibre carbonyl group (proton acceptor). The calculated hydrogen bonding interfacial interaction energy components are, however, low in comparison with the van der Waals and electrostatic interfacial interaction energy components.

Surprisingly, despite the relatively strong hydrogen bonding interaction between the poly(cyanurate) and the hydroxy-functionalised fibre surface, there is a repulsive hydrogen bonding interaction between the poly(cyanurate) and the carboxyl-functionalised surface. The explanation of this could be due to the physical size of the carboxyl group being prohibitive to interactions with the ether oxygen atoms attached to the triazine ring structure. The size of the fibre hydroxyl groups is much smaller, hence this steric effect should not occur for their hydrogen bonding interactions. The magnitude of the repulsion is however very small (less than 0.1% of the total interfacial interaction energy for the carboxyl-functionalised fibre-cyanate ester resin composite) and does not affect the overall fibre-matrix interaction characteristics greatly.

Using the coefficients of proportionality from §5.5.1 the data in table 6.5 have been scaled to show the variation in interfacial interaction energy components as a function of fibre surface treatment (table 6.6). The new data are displayed graphically in figure 6.14. As for the epoxy matrix composite calculations, the hydrogen bonding
interfacial interaction energy component has not been plotted due to the very low contribution to the total energy throughout the model fibres.

Table 6.6 Interfacial interaction energy components (kJ mol⁻¹) of 5PLANE-poly(cyanurate) network interface as a function of fibre surface treatment.

<table>
<thead>
<tr>
<th></th>
<th>0</th>
<th>25</th>
<th>50</th>
<th>100</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>van der Waals</td>
<td>-491.94</td>
<td>-437.65</td>
<td>-378.02</td>
<td>-428.55</td>
<td>-386.79</td>
</tr>
<tr>
<td>Electrostatic</td>
<td>-22.61</td>
<td>-25.00</td>
<td>-27.93</td>
<td>-25.79</td>
<td>-27.64</td>
</tr>
<tr>
<td>Hydrogen Bond</td>
<td>-0.48</td>
<td>-1.17</td>
<td>-0.77</td>
<td>-0.80</td>
<td>-0.72</td>
</tr>
<tr>
<td>Total</td>
<td>-515.16</td>
<td>-464.05</td>
<td>-406.96</td>
<td>-455.33</td>
<td>-415.37</td>
</tr>
</tbody>
</table>

The van der Waals interfacial interaction energy show a reduction in magnitude of roughly one-quarter of the original value initially to 50% surface treatment, followed by an increase to the standard treatment (100%). This value is however not as great as either the untreated or 25% treated values. There is a decrease in van der Waals energy upon overtreatment (to 200%) although this value is still greater than that of the 50% model surface. As for the DGEBA-DDS epoxy matrix composite model an undulating trend in the van der Waals energy component is observed, consistent with the hypothesis of the surface treatment desheathing the outermost fibre plane.

The electrostatic interfacial interaction energy is relatively small in comparison to the van der Waals energy and does not contribute more than 7% to the total energy throughout the model fibre surfaces. The trend in electrostatic energy also exhibits
an undulating form although of the opposite manner to that observed for the van der Waals energy, i.e. it increases in magnitude from untreated to 50% treatment, dips slightly for the 100% model surface before increasing again upon overtreatment.

Although very small with respect to the total energy, the hydrogen bonding component increases in magnitude sharply upon initial surface treatment before decreasing and leveling off beyond 50% treatment. This effect follows the same relationship as the contribution of the hydroxyl functionalised surface to the total model shown in figure 5.9. The hydrogen bonding repulsions of the carboxyl group are small in comparison to the attractive hydrogen bonding interactions of the hydroxyl group towards the poly(cyanurate).

Owing to the small differences in the absolute values of the electrostatic energy component and the negligible contribution from the hydrogen bonding energy component, the variation in the total interfacial interaction energy follows the same trend as displayed in the van der Waals energy, again demonstrating the desheathing effect.

6.4 Application of Methodology to Composite Materials Science and Engineering

6.4.1 Choice of Matrix Phase

Two different crosslinked polymer network models have been considered in this study; an amine cured epoxide thermoset (DGEBA-DDS) and a bisphenol-A based poly(cyanurate). The simulations highlight differences in non-bonded physical interactions of the two polymers with a range of functionalised carbon fibre models.

It is evident from tables 6.3 and 6.5 that the total energy for the poly(cyanurate) interfaces with the functionalised fibre models is more negative in all cases than for the corresponding epoxy interface. This implies that the poly(cyanurate) interfaces are more stable, i.e. a stronger fibre-matrix interface would result when compared to a
DGEBA-DDS epoxy matrix. The magnitude of the total energy increases in the order carbonyl < hydroxyl < carboxyl < graphitic < nitrogen-functionalised fibre interface for both matrices. Although the purely graphitic and nitrogen-functionalised fibre interfacial interaction energies for a particular resin are of a similar magnitude, the oxygen-containing fibre interfacial interaction energies are markedly smaller in magnitude.

The van der Waals interfacial interaction energy components are greater in magnitude for the poly(cyanurate)-fibre interfaces than the epoxy-fibre interfaces for all functionalised fibre types. Conversely the electrostatic interfacial interaction energy components are greater in magnitude for all the epoxy-fibre interfaces over the corresponding poly(cyanurate)-fibre interfaces. This may well be due to the specific functional groups present in the epoxy resin network, e.g. sulphone, hydroxyl and tertiary amine. Furthermore, the cyanurate moiety is the principal heteroatomic functionality in the poly(cyanurate) network. The analyses of x-ray crystallography data in §3.3 have shown this unit to exhibit three-fold symmetry, hence large dipoles and electrostatic forces would not be expected.

6.4.2 Fibre Surface Chemistry

Comparing the different interfacial interaction energies for the two thermoset matrices with the same functionalised fibre, the poly(cyanurate) shows a 30% more negative energy with the purely graphitic carbon fibre surface than the epoxy. For this fibre surface the epoxy matrix exhibits a greater contribution of electrostatic interactions to the total energy than the poly(cyanurate), although both values are relatively low. This further indicates the stronger polar character of the epoxy matrix over the poly(cyanurate).

In the case of the nitrogen-containing model fibre surface, the interfacial interaction energy with the poly(cyanurate) is only 20% greater than that of the epoxy. This is mainly due to the large increase in electrostatic interactions for the epoxy resin interface. Whereas the electrostatic interfacial interaction energy component only contributes ca. 3% of the total energy for the poly(cyanurate)-nitrogen-functionalised
fibre composite interface, it makes up 11% of the total energy of the corresponding interface with the epoxy matrix.

For the interfaces with the hydroxyl-modified fibre models, the interfacial interaction energy with the poly(cyanurate) is more than twice that with the epoxy matrix due to the large van der Waals energy component. The poly(cyanurate) interface has a contribution of ca. 6% electrostatic and 1% hydrogen bonding to the total energy, whereas the epoxy has a much greater 37% contribution of electrostatic energy to the total and, despite having hydroxyl groups present in both fibre and matrix phases, only just over 0.5% contribution from the hydrogen bonding energy.

The carbonyl-functionalised model fibre interface, whilst exhibiting over twice the interfacial interaction energy with the poly(cyanurate) in comparison to the epoxy composite, further highlights the van der Waals and electrostatic energy component differences between the two matrices. The electrostatic energy only makes up ca. 5% of the total for the poly(cyanurate) matrix composite but ca. 45% of the total for the epoxy. Even in absolute values, given that the total interfacial interaction energy of the epoxy composite is half that of the poly(cyanurate), the electrostatic energy value for the epoxy matrix composite is more than four times that of the poly(cyanurate).

Although the differences in absolute values are not as pronounced as for the carbonyl-functionalised fibre interfaces, for the highly oxidised fibres containing carboxyl groups the electrostatic energy contribution to the total interfacial interaction energy has increased to ca. 15% for the poly(cyanurate) and is actually larger than the van der Waals energy component for the epoxy, being 55% of the total. There is a small contribution (1.5%) of hydrogen bonding interactions between the epoxy matrix and the carboxyl groups; however, in the case of the poly(cyanurate) the interaction is actually repulsive although the value is very small.

The models developed in this chapter have been used in a way that separates the interfacial interaction energy components into those between the matrix resins and fibre models comprising a single type of functional group. Therefore, the effect of
the individual functional groups in the interfacial energy can be determined. This has important consequences in the design of composite materials for specific applications, as the variation of functional groups in the models can be used to simulate the interfacial energy of novel fibre-matrix interfaces. In particular, the use of plasma treatments to modify fibre surface chemistry is becoming increasingly popular, with the potential of very specific incorporation of functional groups at the surface. This is an ideal case where a modelling approach such as this could be applied to predict the properties of a range of tailored composite interfaces, with a view to ultimately being a tool for initially directing research towards the optimum surface chemistries, treatments, polymeric matrices, etc., before laboratory scale experiments.

6.4.3 Summary

The calculations of interfacial interaction energies for the model composite interfaces show that the poly(cyanurate) matrix is favoured energetically over the DGEBA-DDS epoxy matrix. This implies stronger physical interfacial interactions for the poly(cyanurate) matrix carbon fibre composites. This is mainly a result of van der Waals dispersion interactions which are appreciably greater between the functionalised fibre surfaces and the poly(cyanurate) than the epoxy.

In their work on high strength carbon fibre-reinforced epoxy and cyanate ester composites, Armistead and Snow report a smaller critical fibre length \((l_c)\), as determined by fragmentation testing, and thus larger load transfer of ca. 30% for the cyanate ester over the epoxy matrix resin. This value is similar to the difference in interfacial interaction energy calculated in this work.

The epoxy resin shows a much greater electrostatic energy component than the poly(cyanurate) and in order to increase the magnitude of these interactions surfaces with higher concentrations of heteroatomic functional groups (both oxygen- and nitrogen-containing) would be required. It is also interesting to note that the most negative total interfacial interaction energy does not occur at what is considered the standard 100% fibre surface treatment as simulated in this work. It may be concluded from this that other factors, such as chemical bonding and surface
roughness effects, also influence interfacial adhesion in carbon fibre-reinforced composites.
Chapter 7: Conclusions and Future Work

The various studies reported in this thesis have been used in a complementary manner to construct models to describe aspects of fibre-matrix adhesion in fibre-reinforced thermoset matrix composites. Initially, sym-triazine and cyanurate moieties have been analysed in terms of their conformational phenomena, using experimental X-ray crystallographic data, for use in the modelling of cyanate ester resin systems. In addition to this, calculations have been performed using ab initio quantum mechanics, semi-empirical quantum mechanics and molecular mechanics methods for comparison with the experimental data, and to explain the observed conformations in terms of the electron distributions of the molecules. A combination of these techniques has been used to define new parameters to describe the sym-triazine functional group, for use in force-field calculations of cyanate ester resins.

It has been shown that the sym-triazine ring exhibits a non-planar conformation, with alternating internal ring angles at nitrogen and carbon atoms of ca. 112° and 128° respectively. The force constants of the ring bending and stretching motions are much greater than those of the monoatomic analogue benzene, thus the sym-triazine units would be more rigid as part of a cured aromatic cyanate ester resin network than the aromatic backbone. The electron density of the sym-triazine ring system decreases upon addition of any substituents (other than hydrogen) to the ring, evidenced by the increased C–N bond length in the crystallographic data of these molecules over that of sym-triazine itself.

The technique of inverse gas chromatography (IGC) has been performed at infinite dilution to measure the surface energetics of a range of surface treated carbon fibres, and thus elucidate some effects of fibre surface treatment. It is seen that the dispersive component of the fibre surface energy decreases rapidly with initial surface treatment and then levels off with higher treatments. The acid-base interactions become more favourable as treatment is applied, and the surface changes from being basic initially, to acidic, and becomes amphoteric at higher treatment levels. The
surface area, as measured by BET nitrogen adsorption, has been shown to vary little throughout the range of fibre treatments studied.

Comparing the experimental IGC data with computational simulations, performed to study the interactions between model fibre surfaces and probe molecules, a model of the changes in chemical functional groups on the fibre surface as a function of surface treatment has been produced. The concentration of nitrogen at the surface decreases sharply at first, before recovering and decreasing again upon over-treatment. The concentration of carboxyl groups shows exactly the opposite trend; it increases initially, before dipping and rising again upon over-treatment. The model predictions compare reasonably well with analysis of the atomic percentages of carbon, nitrogen and oxygen at the surface, as measured by XPS.

The model developed in Chapter 5 has been used to study the interaction energetics between the fibre surfaces and two polymeric matrices: a cyanate ester resin and an amine-cured epoxy resin. Through a series of molecular simulations, it has been shown that the cyanate ester resin is favoured energetically over the epoxy resin. This is mainly a result of stronger van der Waals interaction forces. The predicted adhesion differences are in agreement with literature data. The use of this approach has allowed the simulated interactions of specific surface functional groups with the different matrices to be determined.

Although the work reported in this thesis has combined a variety of methods, ultimately to study carbon fibre surfaces and their interfaces in carbon fibre-reinforced composites, there remains some room for further study in the techniques employed. In the IGC work there is scope for applying very accurate quantum mechanics calculations to the calculation of probe molecule properties. In particular, the cross-sectional surface area values presented here have been taken from literature data, which provided no details of the calculation employed. A study into the correlation of sub-atomic structure and properties would provide a more theoretical basis for the parameters used.
To progress this modelling approach further, it would be interesting to examine the formation of the interphase region in terms of monomer concentrations at the fibre surface. This is particularly applicable to composites with amine-cured epoxy resin matrices, where a build-up of either amine or epoxy monomers at the fibre surface could influence final composite properties. This remains an attractive application for modelling, with the potential for studying other systems, e.g. glass and aramid fibres, and a variety of polymeric matrices.
Appendix

Simulation of Mechanical Properties

The mechanical properties of a polymeric material can be calculated after an initial energy minimisation, followed by a second derivative energy minimisation calculation under a small fixed strain. The expression used to calculate the potential energy of the system under a small strain is as follows:

\[ U = U_0 + \sum_i \frac{\partial U}{\partial \varepsilon_i} \varepsilon_i + \frac{1}{2} \sum_{ij} \frac{\partial^2 U}{\partial \varepsilon_i \partial \varepsilon_j} \varepsilon_i \varepsilon_j + \ldots + \frac{1}{n} \sum_{ij} \frac{\partial^n U}{\partial \varepsilon_i \partial \varepsilon_j} \varepsilon_i \varepsilon_j \]

where \( U \) is the energy, \( U_0 \) is the equilibrium energy, and \( \varepsilon \) is the strain. The second derivative of the energy is used to calculate the components \( C_{ij} \) of the stiffness matrix, where the stiffness matrix is related to the energy by,

\[ C_{ij} = \frac{\partial^2 U}{\partial \varepsilon_i \partial \varepsilon_j} \]

where \( C_{ij} \) is the stiffness matrix, \( U \) is the total energy, \( V \) is the volume and \( \varepsilon_i \) and \( \varepsilon_j \) are the strains applied to the system. The stiffness matrix computed by this method is always symmetric (i.e. \( C_{ij} = C_{ji} \)) and is defined as follows:

\[
C_{ij} = \begin{pmatrix}
C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\
C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\
C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\
C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\
C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\
C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66}
\end{pmatrix}
\]
The stiffness matrix for an isotropic material can be written in terms of the two Lamé constants ($\mu$ and $\lambda$),

$$
C_{ij} = \begin{pmatrix}
2\mu + \lambda & \lambda & \lambda & 0 & 0 & 0 \\
\lambda & 2\mu + \lambda & \lambda & 0 & 0 & 0 \\
\lambda & \lambda & 2\mu + \lambda & 0 & 0 & 0 \\
0 & 0 & 0 & \mu & 0 & 0 \\
0 & 0 & 0 & 0 & \mu & 0 \\
0 & 0 & 0 & 0 & 0 & \mu
\end{pmatrix}
$$

where $\mu$ is related to the shear modulus ($G$),

$$
\mu = G = \frac{E}{2(1+\nu)}
$$

where $E$ is the Young’s modulus and $\nu$ is the Poisson’s ratio. $\lambda$ has no physical meaning and applies only to isotropic materials. It is given by the equation,

$$
\lambda = \frac{\nu E}{(1+\nu)(1-2\nu)}
$$

The compliance matrix ($S$) is calculated as the inverse of the stiffness matrix, i.e. $S = C^{-1}$. The mechanical properties Young’s modulus ($E$), bulk modulus ($B$), shear modulus ($G$), Poisson’s ratio ($\nu$), and Lamé constants ($\lambda$ and $\mu$) of a polymer can be calculated from the compliance and stiffness matrices.

The Young’s modulus can be found from the compliance matrix for the three directions under consideration, i.e. $x$, $y$ and $z$, but for an isotropic system all three values are expected to be the same.

$$
E_x = \frac{1}{S_{11}}, E_y = \frac{1}{S_{22}}, E_z = \frac{1}{S_{33}}
$$
The compliance matrix gives the bulk modulus as:

\[ B = \frac{1}{S_{11} + S_{22} + S_{33} + 2(S_{21} + S_{31} + S_{32})} \]

The compliance and stiffness matrices give the shear modulus as:

\[ G = \frac{1}{2}(S_{11} - S_{12}) = \frac{1}{3}(C_{44} + C_{55} + C_{66}) \]

The compliance matrix gives Poisson’s ratio in its different directions in space as:

\[ \nu_{xy} = -\frac{S_{21}}{S_{11}}, \nu_{yx} = -\frac{S_{21}}{S_{22}}, \nu_{xz} = -\frac{S_{31}}{S_{33}} \]

\[ \nu_{zx} = -\frac{S_{31}}{S_{11}}, \nu_{yz} = -\frac{S_{32}}{S_{22}}, \nu_{yz} = -\frac{S_{32}}{S_{33}} \]

The elastic constants are interrelated by the equation,

\[ E = 2G(1+\nu) = 3B(1-2\nu) \]

such that it is sufficient to determine two elastic constants as the other can be obtained from this equation.
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