Surface studies of carbon fibres

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SURFACE STUDIES OF CARBON FIBRES

By

Xiaoyan Ling

A thesis submitted in partial fulfilment of the requirements for the award of the degree of Master of Philosophy of the Loughborough University of Technology

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Department of Chemistry and Institute of Surface Science and Technology

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ABSTRACT

Effects of surface oxidation treatments on PAN-based Courtaulds high modulus (HM), low modulus (LM), and Akzo LM carbon fibres have been studied using XPS, chemical derivatisation, ATR-FTIR, contact angle measurement, and SEM. Surface oxygen concentration was found to increase with oxidation treatments. For Courtaulds fibres, the increase was more significant for LM fibre than for HM fibre, which was attributed to the less graphitic nature of LM fibre and more reactive edge sites present on LM fibre surface. High energy resolution XPS has shown that hydroxyl groups, ketones, and carboxylic acid groups were found to be present on carbon fibre surfaces, while quinone, enol, ester, and ether may also be present under some circumstances. Amine and amide may be observed on some fibre surfaces. Trifluoroacetic anhydride (TFAA) and trifluoroethanol (TFE) have been used to derivatise hydroxyl groups and carboxylic acid groups, respectively. Oxidation with nitric acid has been found to mainly increase acid groups and reduce hydroxyl groups, while anodic oxidation has little effects on them. SEM showed that fibre topographies were not obviously altered by anodic oxidations, however, changes for LM fibre surfaces were observed after nitric acid oxidation.

Surface oxidation treatments have been found to generally increase carbon fibre surface free energy. Oxidation with concentrated nitric acid has been found to be more effective in improving fibre surface wettability than commercial anodic oxidation treatments. The polar contribution to surface free energy, \( \gamma_s^p \), was found to generally increase with surface oxygen concentration, however, no clear relationship between \( \gamma_s^p \) and the concentration of -OH groups was observed. There seems to exist some relationship between \( \gamma_s^p \) and the concentration of surface -COOH groups.
To my parents

and

my husband, Enshan
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CHAPTER 1 INTRODUCTION

Carbon fibres are largely used as reinforcing agents for composites. The mechanical properties of the composites depend not only on the mechanical properties of the carbon fibre and the matrix, but also on their interfacial interaction. The interaction in turn depends considerably on the properties of the carbon fibre surface. It is, therefore, important to characterise carbon fibre surface, to have a knowledge of the nature and the amount of the surface atoms, surface functional groups, surface energetics, and the surface area as well as surface morphology.

This chapter gives an introduction to carbon fibres and some of the surface treatments for carbon fibres. Surface characterisation techniques which are used to study carbon fibre surfaces in this work are also reviewed in this chapter. They are X-ray photoelectron spectroscopy (XPS), chemical derivatisation, attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), contact angle measurement, scanning electron microscopy (SEM), and surface area measurement.

1.1 Carbon fibre

1.1.1 Manufacture

Carbon fibres are generally manufactured by the controlled pyrolysis of a precursor material (in fibre form), e.g., rayon, various pitches (petroleum and coal tar), and polyacrylonitrile (PAN). They normally contain 92–99+% carbon.

According to their tensile modulus and heat-treatment temperature, carbon fibres can be classified as in Table 1.1. High modulus carbon fibres (HM) are usually called Type I fibre, and low modulus (LM) or high strength fibres are called Type II fibre.
Among the most common precursors for carbon fibres, i.e. rayon, pitch, and PAN, PAN is presently the most important one. Steps involved in the PAN-based carbon fibre processing are: precursor preparation, stabilisation (preoxidation), and carbonisation.

The stabilisation is usually carried out for several hours at 200 – 300°C in air. The structure is changed from a linear polymer system to a highly condensed cyclised (ladder) structure of stacked, partially hydrogenated naphthyridine rings with conjugated >C=N bonds [1]. It can be written as follows,

\[
\begin{align*}
\text{PAN precursor} & \quad \xrightarrow{\text{Heat}} \quad \text{Stabilised PAN} \\
\left( \text{CH}_2 - \text{CH} \right)_n & \quad \xrightarrow{\text{Heat}} \quad \begin{array}{c}
\text{O} \\
\text{HO} \\
\text{NH}_2
\end{array}
\end{align*}
\]

In the presence of oxygen, chain scission, cross-linking, dehydrogenation, and cyclisation take place during this reaction. It has been suggested that the aromatic character of the structure can promote the thermal stability of the preoxidised PAN during the subsequent carbonisation process [2].
The stabilised PAN is then subjected to thermal pyrolysis (carbonisation) in an inert environment, usually in high purity nitrogen, at 1200–2000°C. In the 350–1300°C temperature region, a thermally stable pyridinoid structure is formed which subsequently collapses into a stacked-ring carbon structure. Continuing pyrolysis up to ~1500°C eliminates most of the residual non-carbon elements [3] as volatiles, such as H₂O, HCN, NH₃, CO, CO₂, and N₂ etc. to give carbon fibres with a yield of about 50%.

Additional heat treatment at high temperatures above 2500°C in argon or nitrogen (graphitisation) will further improve the preferred crystallite orientation and order, leading to ultra-high modulus products with no appreciable decrease in the weight of the fibre.

1.1.2 Structure

Techniques, such as X-ray diffraction, electron diffraction, optical and electron microscopy [2], and scanning tunneling microscopy [4-5] have been employed to investigate the structure of carbon fibres. Several structural models have been proposed and well documented [2].

Diefendorf and Tokarsky [6] examined PAN-based carbon fibres using X-ray diffraction, transmission electron microscopy, and scanning electron microscopy. A three dimensional model for PAN-based carbon fibres was constructed by combining the axial structure and radial structure (Fig. 1.1).

The structures are basically tree trunk and onion skin. The model suggests that the main elements of the fibre structure are the graphitic ribbons. The variation in these structural elements depends on the carbonisation temperature and processing of the particular fibre. The size of graphitic ribbons in the case of low modulus carbon fibres (1200–1400°C) is about 13 basal layers thick and 4nm wide whereas in the case of high modulus carbon fibres (1800–2500°C), the size of graphitic ribbons is about 20 basal layers thick.
and 7nm wide. These ribbons twist and undulate along the fibre axis. The ribbons on the surface have larger sizes and are generally better aligned parallel to the fibre axis compared to those in the interior of the fibre.

Fig. 1.1 A three dimensional structure for PAN-based carbon fibre after Diesendorf and Tokarsky [6]

Bennett and Johnson [7] proposed a similar structure for PAN carbon fibres. The heterogeneity of the proposed skin-core structure in PAN-based carbon fibre is a function of carbonisation temperature. For HM fibre a layer of approximately 150nm-250nm exists on the surface having larger crystallites and higher degree of orientation than the interior of the fibre. However, for LM fibre the skin-core structure is not so significant. The only evidence for a skin region is that the surface layer planes are less disordered than further inside the fibre. This skin-core structural heterogeneity was attributed to the initial preoxidation treatment, with the "skin" region formed from the fully stabilised outer region and the core from the partially stabilised inner region [2].
Therefore, there are more edge sites and less basal planes on LM fibre surfaces than those on HM fibre surfaces. This is a significant structural difference between the two types of fibres, resulting in the difference in their respective surface reactivities which will be discussed in Chapter 3.

1.1.3 Properties

Carbon fibre properties are highly anisotropic, the properties in the longitudinal (0° with respect to fibre axis) direction are distinctly different from the properties transverse (90° with respect to fibre axis). Table 1.2 gives the unidirectional (along the fibre axis) properties of PAN based carbon fibres [3].

Table 1.2 Properties of PAN-based carbon fibres

<table>
<thead>
<tr>
<th>Property</th>
<th>Low modulus</th>
<th>High modulus</th>
<th>Ultra-high modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>filament diameter, μm</td>
<td>5.5-8.0</td>
<td>5.4-7.0</td>
<td>8.4</td>
</tr>
<tr>
<td>density, g/cm³</td>
<td>1.75-1.80</td>
<td>1.78-1.81</td>
<td>1.96</td>
</tr>
<tr>
<td>carbon content, wt %</td>
<td>92-95</td>
<td>99-99+</td>
<td>99+</td>
</tr>
<tr>
<td>tensile strength, MPa</td>
<td>3105-4555</td>
<td>2415-2555</td>
<td>1865</td>
</tr>
<tr>
<td>tensile modulus, GPa</td>
<td>228-262</td>
<td>359-393</td>
<td>517</td>
</tr>
<tr>
<td>elongation at break, %</td>
<td>1.3-1.8</td>
<td>0.6-0.7</td>
<td>0.38</td>
</tr>
<tr>
<td>electrical resistance, μΩ m</td>
<td>15-18</td>
<td>9-10</td>
<td>6.5</td>
</tr>
<tr>
<td>thermal conductivity, W/(m K)</td>
<td>8.1-9.3</td>
<td>64-70</td>
<td>ca 120</td>
</tr>
</tbody>
</table>

Note: to convert GPa to psi, multiply by 145,000, to convert MPa to psi multiply by 145.

It can be seen that as tensile modulus increases (increasing degree of orientation along the fibre axis), carbon content, electrical conductivity, thermal conductivity, and density increase, while tensile strength and elongation decrease.

Carbon fibres are basically elastic, exhibiting linear stress-strain characteristic,
i.e. $\sigma/\varepsilon=E$, where $E$ is tensile modulus, $\sigma$ is the tensile stress, and $\varepsilon$ is the tensile strain. The effects of carbonisation temperature on tensile modulus and tensile strength were investigated by Moreton et al [8]. They found that the tensile modulus invariably increases with the temperature, whereas the tensile strength tends to go through a maximum in the range of 1300–1500°C.

1.1.4 Applications

Carbon fibres are seldom used alone, but often used to reinforce certain matrix materials under suitable conditions. There are three main types of carbon fibre composites, i.e. carbon-polymer composites (CFRP), carbon-metal composites, and carbon-carbon composites (CFRC). Epoxy resins are often chosen to form CFRP composites, which can not be used at very high temperatures. CFRC composites resulting from the carbonisation of CFRP are developed and often used for refractory and high temperature applications, such as aircraft breaks. Aluminum, nickel, and lead-tin alloy have been found most economic for fibre-metal composites. However, the composites have not been commercially exploited because of the complexity and difficulty in the manufacturing.

The low weight, high strength, and high stiffness characteristics of carbon fibre composites make them valuable materials for aerospace applications and sport articles. There are many other applications based on their outstanding heat resistance, high electrical and thermal conductivity, low thermal expansion coefficient, resistance to corrosion, etc. [2].

In the production of CFRP composites good adhesion between carbon fibres and matrices are necessary in order to produce composites with the required properties. However, for the production of CFRC composites strong interfacial bonding between the fibre and the matrix may hinder relaxation of the composites structure which is a necessary requirement after carbonisation shrinkage [2]. In both of the above cases, a good control of the
fibre-matrix interaction is needed. One method in achieving this control is to modify fibre surface chemistry and reactivity through surface treatments.

1.1.5 Effects of surface treatment

Surface treatment

The nature of a carbon fibre surface affects interfacial adhesion and a number of mechanical properties of its composites. Carbon fibre surfaces usually contain exposed active edge sites as well as basal planes. The carbons in these relatively high energy edge sites are reactive and are capable of forming chemical bonds \[9\], resulting in strong interfacial interaction between the carbon fibre and the matrix, while the lower energy basal planes may only interact with matrix by weaker intermolecular forces. Without any surface treatment, carbon fibres usually do not have enough high energy sites, and normally show insufficient adhesion to matrices. Several types of surface treatments have been developed to improve the interfacial bonding between the carbon fibre and the matrix.

These surface treatments include oxidation, coating and polymer grafting \[2\]. The oxidation treatments can be further divided into gas-phase oxidation and liquid-phase oxidation. Gas-phase oxidation treatments are typically carried out by heating the carbon fibre in oxygen or air at 400–500°C with the presence of a catalyst. Typical increase in shear strength by a factor of 2–3 has been found after this treatment \[10\]. Other oxidising gas environment with or without oxygen, e.g. CO\(_2\), Cl\(_2\), NO\(_2\)-NO, NH\(_3\), and plasma-ionised inert gases \[3\] etc. were also used at temperatures below 1800°C. Liquid-phase oxidation treatments include direct wet chemical oxidation and electrochemical (anodic) oxidation. The former includes aqueous solutions of nitric acid, chromic acid, sodium hypochlorite \[11-12\] etc. Aqueous electrolytic treatments employ electrolytes such as potassium dichromate, nitric acid, ammonium salt, and sodium hydroxide \[13-18\]. The gas-phase oxidations have been found
to be degradative, and can cause excessive burn-off of the carbon fibre surfaces, while the liquid-phase oxidations are mild and more practical [22].

**Effects of surface treatment on carbon fibre composites**

Surface treatment normally removes weakly bonded carbon layers, and increases surface oxygen content. Surface area is usually increased, and the surface morphology may also be changed by the treatment. All these changes lead to the increase in wettability and adhesion to the matrix, resulting in improved mechanical properties of the fibre composites.

Bascom and Chen [19] studied the adhesion between plasma treated fibres and thermoplastic polymers using the single embeded filament adhesion test. The adhesion of carbon fibre to both polycarbonate and polysulfone were found to be significantly increased as the result of the increase in surface oxygen content after O2 plasma treatment. The effect on adhesion, however, was found dissipated after a week storage even though no decrease in surface oxygen content was found. The loss in the effectiveness of plasma treatment was suggested to be due to the reduction of overall surface free energy through the reorganisation of the surface high energy sites after exposure to air for extended periods of time. Moyer and Wightman [20] examined the effects of a series of plasma pretreatments on carbon composite bonding using wedge test method. The oxygen plasma pretreatment was found to be the best one for improving the bonding, this was attributed to the removal of the contaminants present on the carbon fibre surface and the increase in the oxygen containing functionality on the surface. A PAN-based LM carbon fibre was used by Brewis et al [11] to study the effects of various oxidation treatments, i.e. oxidation in air, chromic acid, sodium hypochloride and nitric acid. All the treatments caused large increase in the surface oxygen functionality. However, no significant effects on mechanical properties of carbon fibre composites were detected after these oxidation treatments. The adhesion was then suggested not to be dominated by the number of polar
groups on the fibre surfaces. When the surface oxygen concentration reaches about 4 atomic%, further oxidation of the carbon fibres could only result in moderate increases in adhesion.

Surface treatments in an electrochemical bath have been developed and employed in industry. The extent of oxidation was found to be variable with bath current, potential, treatment time, the nature and concentration of the electrolyte, pH value, and fibre type \(^{11,13,15,21-22}\). LM fibre has more edge sites, therefore it is more readily oxidised than HM fibre. The \(O : C\) ratio increases with bath current, potential, treatment time and the concentration of electrolyte. Acidic solution has been found to give rise to substantial surface oxidation, in contrast to alkaline solutions \(^{15}\). Harvey et al \(^{13}\) reported the increases in C=O and C-O- with the bath current or potential. The interlaminar shear strength (ILSS) of carbon fibre / epoxy resin composite was also found increased, but no relation between the rise in ILSS and the \(O : C\) ratio or the amount of carboxyl functionality present on the fibre surfaces was found. The mechanical keying of the resin into the fibre surface was then suggested to probably play a more important role in forming the fibre-resin bond. Jones \(^{23}\) pointed out that the chemical bonding between electrochemically oxidised fibres and epoxy resins was not crucial in determining the interfacial strength in carbon fibre composites. The removal of loosely bound crystallites from fibre surface was found to be able to promote bonding between carbon fibres and epoxy resins.

1.2 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), is a relatively new technique for surface analysis. It is capable of detecting all elements except hydrogen present in the outmost 50–100Å layer of a solid surface. Apart from quantitative elemental information, it is also possible to obtain the chemical nature of the surface by XPS. Over the last two decades, interest in XPS has grown rapidly in fields
involving surfaces or interfaces such as those in adhesion, adsorption, catalysis, and corrosion.

1.2.1 Basic principle

The sample to be analysed is placed in a vacuum chamber and irradiated with soft X-rays, usually Al Kα (1486.6 eV) or Mg Kα (1253.6 eV). Photoelectrons from the core levels of atoms present in the sample are generated (Fig. 1.2), collected and energy analysed. The measured kinetic energy (KE) of a photoelectron is given by

\[ KE = h\nu - BE - \phi \]  

1.1

where \( h\nu \) is the energy of the incident X-ray, \( BE \) is the binding energy with which the photoelectron is bound to the atom, and \( \phi \) is the spectrometer work function. The binding energy of a given core electron is characteristic of the element concerned, thus it is possible to identify elements present on the sample surface from the position of photoelectron peaks. Auger process may occur as a result of the de-excitation of the core hole.

![Diagram of the photoemission process](image)

Fig. 1.2 Diagram of the photoemission process
Two important factors associated with photoemission from solid surface are the total photoionisation cross-section ($\sigma$) and the inelastic mean free path ($\lambda$). The total photoionisation cross-section ($\sigma$) is a measure of the probability that an electron in a particular orbital will undergo photoemission $^{[24]}$. The greater the photoionisation cross-section of a particular orbital the more intense the photoelectron peak associated with it.

Electrons travelling through a solid have a relatively high probability of experiencing inelastic collisions with neighbouring bond electrons, thereby losing some of the kinetic energy, therefore they do not contribute to the characteristic photoelectron peak. If $I_0(x)$ is the photoelectron flux originating at a depth $x$ below the surface of a solid, the flux $I(x)$ emerging normal to the surface is given by

$$I(x) = I_0(x) \exp(-x/\lambda)$$  \hspace{1cm} 1.2

where $\lambda$ is the inelastic mean free path (IMFP) $^{[25]}$. $\lambda$ is material and kinetic energy dependent, and is normally in the range of 1~5nm. This means that only photoelectrons originating from atoms at or near the surface have a reasonable chance of emerging into vacuum with their original kinetic energy intact and therefore contributing to the photoelectron peaks, which makes the technique extremely surface sensitive.

1.2.2 Chemical shift and deconvolution

The binding energy of the core level electrons of a given element is strongly affected by the electronic environment of the individual atoms. Thus differences in the electronic environment of a given atom due to bond type or oxidation state in a molecule give rise to a small difference in binding energy. This difference in binding energy is termed as chemical shift. Published chemical shift data are often used in high energy resolution XPS to
characterise particular surface structures. For example, in polyethylene terephthalate (PET),

\[
\text{O-} \quad \text{C-CH}_2\text{-CH}_2\text{-O}\quad \text{O}
\]

three fundamentally different kinds of carbons in the compound produce CIs peaks at different positions in the spectrum. The peak at 284.6 eV is due to carbons in benzene ring. With respect to the 284.6 eV CIs peak, a shift of 1.5 eV towards high binding energy side corresponds to carbons in \(-\text{CH}_2\text{-O}\)-, and 4.0 eV to carbons in \(-\text{(C=O)}\text{O}-\) [26].

Adjacent photoelectron peaks may overlap due to broadening factors, such as, the line width of X-ray source, resolving power of the spectrometer. Removal of these broadening factors from XPS spectra, referred to as deconvolution [27-28], can improve XPS energy resolution and enable functional groups with small chemical shift differences to be distinguished.

1.2.3 Quantification

Quantitative surface analysis is obtained by measuring the relative intensities of the photoemission peaks from each of the elements present. For a homogeneous sample, the intensity of the photoelectron peak for element A \(I_A\) is given as follows [29],

\[
I_A = N_A \sigma_A L_A(\gamma) T(E_A) D(E_p) \lambda(E_A) = N_A S_A
\]

where \(N_A\) is the number of type A atom per unit volume; \(\sigma_A\) is the total photoionisation cross-section; \(L_A(\gamma)\) is the angular asymmetry parameter [30]; \(T(E_A)\) is the transmission of the energy analyser at kinetic energy \(E_A\) [31];
D(E₁) is the efficiency of the electron detector; λ(E₂) is the inelastic mean free path; Sₐ is the relative sensitivity factor. Sₐ can be calculated using semi-empirical equations, or determined using standard samples of known composition [29]. Therefore, quantitative analysis can be achieved by measuring the areas of XPS peaks.

1.2.4 Applications of XPS to carbon fibres

XPS may be used to characterise carbon fibre surfaces. It has been found that carbon fibres manufactured from different precursors have surface compositions consisting of various amounts of oxygen and nitrogen. Walterson [32] investigated Courtaulds fibres using XPS. Besides C, O, and N, other elements such as S, Cl, Na, Ca, and Si were found on carbon fibre surfaces which were thought to be impurity residues from PAN precursor or contamination. The surface composition was measured, and concentration gradient for oxygen within the fibre sub-surface was observed by varying the take-off angle. The oxygen content was found high at the surface, decreased down to a depth of about 40Å, and became constant thereafter. This oxygen gradient was also observed by other workers [33-34] using AES and XPS depth profiling. In Brewis' report [11], XPS showed that both oxygen and nitrogen contents were increased after surface oxidation treatments. The oxygen content was increased by a factor of 3−4 for all treatments used, from 4% for untreated fibre to 16−22% for the oxidised fibres. Meanwhile, the nitrogen content was doubled from 0.5% for untreated to about 1% for the oxidised one.

Investigations of functional groups present on carbon fibre surfaces have been carried out extensively [11], [34-37]. Sherwood and co-workers have made special contributions [14-18], [38-41]. Functional groups which have been proposed are aromatic or aliphatic alcohol (−OH), carboxyl (−COOH), lactone (−COO−), and carbonyl groups (>C=O). Quinone and enol [14], [22], and nitrogen containing groups such as amine and amide [16], [42] were also suggested to be
present on some fibre surfaces.

Drzal et al.\cite{43-44} carried out XPS analysis of thermally degassed PAN-based HM carbon fibres before and after oxidation in air. The oxygen content was reduced after degassing at 300°C. Mass spectrometry analysis indicated that the composition of desorption products was different in each case. The major constituents were water and CO for untreated fibres, CO\(_2\) and CO for oxidised ones. The evolution of CO\(_2\) was attributed to the decomposition of carboxylic groups, and that of CO to carbonyl and other oxygen containing groups. Ishitani\cite{34} and Takahagi et al.\cite{45} studied PAN-based LM carbon fibres. C1s spectra of oxidised carbon fibres indicated components with chemical shifts corresponding to C-O (+1.5 eV), >C=O (+2.5 eV), and -COOH / -COO- (+4.0 eV). Apart from these three C1s peaks, another peak with a chemical shift of just under +7.00 eV was observed by Proctor and Sherwood\cite{38}. This peak was assigned to a plasmon satellite, because such a big separation from primary peak would unlikely be due to a surface oxide species. A range of HM carbon fibres with different degrees of surface oxidation treatment were studied using barium labelling and XPS\cite{46}. The amounts of surface acid groups and other oxygen containing species were found increased with increasing levels of oxidation treatment, but the quantities reached maxima at medium levels of treatment. The existence of maximum quantities was attributed to that the evolution of CO\(_2\) during oxidation became dominant at higher levels of treatment. Chemisorptive sites were found to increase with the level of treatment. Either or both acid groups and chemisorptive sites were considered to play a major role in composite interface formation.

1.3 Chemical derivatisation

The demand to distinguish two functional groups with small chemical shift difference has led to the development of chemical derivatisation technique\cite{32, 45, 47}. An element which is not present in the original material and preferably has large cross-section for XPS detection is normally used to label a
specific functional group. Reagents containing fluorine or chlorine are often chosen for this purpose, as they have large photoionisation cross-section and therefore give rise to high XPS signal.

The application of derivatisation technique in conjunction with XPS (derivatisation XPS) allows the semi-quantitative analysis of certain functional groups to be performed. For a complex surface the use of derivatisation XPS requires the reagent to be highly selective towards the functional group of interest. Trifluoroacetic anhydride (TFAA) has been used to identify hydroxyl groups, and trifluorethanol (TFE) in the presence of dicyclohexylcarbodiimide (DCC) and pyridine for carboxylic groups, pentafluorobenzaldehyde (PFB) for primary amine groups, and hydrazine for carbonyl groups [48].

TFAA was found to react predominantly with hydroxyl groups on surfaces which also contain C=O and/or COOH [49-51]. Vapour-phase derivatisation of carboxyl groups on polymer surfaces with TFE in the presence of DCC has been criticised because the elevated temperature (60.0°C) used could result in substantial reorganisation of the polymer within the XPS sampling depth. Other artifacts could also be introduced due to the low volatility of DCC [52]. Di-tert-butylcarbodiimide (Di-tBuC) has been proved to be able to overcome these problems [53]. The selectivity of derivatisation with TFE in the presence of Di-tBuC was claimed to be excellent, and the yield of the reaction was reported to be 0.87± 0.15.

The selectivity of the reaction of hydrazine with carbonyl groups is quite poor, since some aromatic esters react with this reagent as well [53]. Unfortunately, no better reagent has been found so far.

XPS combined with vapour-phase derivatisation was used by Nakayama, et al [54] to estimate the quantity of functional groups introduced by oxidation treatment. -OH, -COOH and -NH2 were identified to be present on the
oxidised fibre surfaces, however, on the unoxidised fibre surfaces only the later two species were detected. The oxidation was found to mainly increase carboxylic acid groups.

1.4 ATR-FTIR

1.4.1 FTIR

Fourier transform infrared spectroscopy (FTIR) is based on the absorption of radiation in the infrared region owing to the bond vibration of the functional groups in the sample. The vibration frequency is sensitive to the environment of the bond. Certain bonds have distinguishing characteristics. Thus the vibration frequency of a specific bond appears within a characteristic range, which allows this specific bond to be identified through the peak's position. Therefore, FTIR can be used as a complementary technique to XPS to study surface functional groups.

1.4.2 ATR-FTIR

It has been found that at the interface between two media of different refractive indices, light extends on the order of one wavelength into the rarer medium beyond the reflecting surface. This phenomenon allows FTIR spectra to be obtained using attenuated total internal reflection (ATR-FTIR). The basic principle of ATR-FTIR is summarised as follows.

In ATR-FTIR, a prism with a high refractive index (e.g. Ge, KRS-5, ZnSe, and Si) is placed in contact with the surface to be studied (Fig. 1.3). The incident radiation undergoes total internal reflection within the prism, and interacts with the rarer medium (sample), resulting in the absorption of the reflected IR beam. The IR beam emerging from the prism is detected and Fourier transformed to yield the infrared spectrum of the sample surface.
In order to obtain total reflection, the angle of incidence ($\theta$) has to be greater than the critical angle $\theta_c$,

$$\theta_c = \sin^{-1} \left( \frac{n_2}{n_1} \right) \quad 1.4$$

where $n_2$ and $n_1$ are the refractive indices of the rarer medium (sample) and the prism, respectively.

The angle of incidence, $\theta$, can be calculated using the following equation $^{[55]}$,

$$\theta = \theta_A - \sin^{-1} \left[ \sin \theta_A \theta_E \right] / n_1 \quad 1.5$$

where $\theta_A$ is the angle of incidence of the prism position, $\theta_E$ is the face angle of the ATR prism.

The penetration depth of radiation can be calculated as follows $^{[56]}$,

$$d_p = \frac{\lambda_1}{2\pi \left[ \sin^2 \theta - \left( \frac{n_2}{n_1} \right)^2 \right]^{1/2}} \quad 1.6$$
where \( d_p \) is the depth into the sample at which the amplitude of the radiation reduced to \( e^{-1} \) of its value at the interface, \( \lambda_1 = \lambda / n_1 \) is the wavelength of radiation in the prism, \( \lambda \) is the wavelength of the incident light. \( d_p \) can be altered by changing the angle of incidence and the prism material. Assuming \( n_1 = 2.4 \) (KRS-5), \( n_2 = 1.5 \), \( \theta = 50^\circ \), \( d_p \) is calculated to be 0.88\( \mu \text{m} \) at 1700 \( \text{cm}^{-1} \), indicating that ATR-FTIR is far less surface sensitive than XPS. ATR-FTIR has been used by Ishida et al \( ^{57} \) to study the effect of nitric acid oxidation on a pitch-based carbon fibre. Carboxylic acid (1705 \( \text{cm}^{-1} \)), lactone (1750 \( \text{cm}^{-1} \)), enol (1640 \( \text{cm}^{-1} \)), and quinone (1583–1570 \( \text{cm}^{-1} \)) were detected on fibre surface after the oxidation. The assignment was supported by the results of functionalisation reactions performed on the fibre.

1.5 Contact angle and surface free energy

Contact angle measurement has been widely used to determine the wettability of solid surface. This technique is highly surface sensitive because it only characterises the interaction between the liquid and the outmost atomic layer of the solid surface.

1.5.1 Contact angle

The relation between the contact angle at the three phase point (Fig. 1.4) (liquid-vapour-solid) and the surface free energies of liquid and solid was first described by Young \( ^{58} \). It can be represented as follows,

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

where \( \gamma_{lv} = \) surface tension of the liquid,

\( \gamma_{sl} = \) interfacial free energy at the interface of solid and the liquid,
\[ \gamma_{sv} = \text{surface free energy of the solid, and} \]

\[ \gamma_{sv} = \gamma_s^0 - \pi \quad 1.8 \]

where \( \pi \) is the spreading pressure of the adsorbed film of the liquid vapour, and is usually neglected for low surface free energy surfaces \([59-60]\). \( \gamma_s^0 \) is the surface free energy of a solid surface in vacuum.

Fig. 1.4 Sessile drop resting on a solid surface

1.5.2 Contact angle hysteresis

The contact angle measured by advancing the periphery of a drop over a surface is referred to as advancing angle (\( \theta_{\text{adv}} \)), and the receding angle (\( \theta_{\text{rec}} \)) is measured by pulling the drop back. The difference, \( \theta_{\text{adv}} - \theta_{\text{rec}} \), is called contact angle hysteresis. In general, contact angle hysteresis is caused by surface roughness, surface heterogeneity, or surface contamination \([61]\).

On a smooth but heterogeneous surface, there will exist patches whose surface free energies differ from each other. It has been suggested that the advancing contact angle is associated with low-energy portions, while receding angle with the high-energy portions \([61-62]\). On a rough surface, a
large number of metastable configurations exist. Contact angle hysteresis is
determined by a balance between the vibrational energy of the drop and the
heights of the energy barriers between metastable states. As the energy
barriers become smaller (or the vibrational energy becomes greater),
hysteresis becomes less. It has been suggested that roughness does not cause
significant contact angle hysteresis unless the rugosity is larger than
$\sim 0.5\mu m$ \cite{61}.

1.5.3 Treatments of contact angles

In Young's equation, $\gamma_{lv}$ and $\theta$ can be readily measured, but $\gamma_{sl}$ and $\gamma_{sv}$ can
not. In order to estimate $\gamma_{sv}$, a further equation is required.

**Fowkes' approach**

Fowkes \cite{59} first suggested to divide the surface free energy into several
independent components, such as London dispersion $\gamma^d$ and polar $\gamma^P$. Thus,

$$\gamma = \gamma^d + \gamma^P \quad 1.9$$

For systems with $\gamma^P = 0$ or $\gamma^P = 0$, the interfacial free energy can be given by

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2\left(\gamma^d \gamma^d\right)^{1/2} \quad 1.10$$

Combining the above equation with Young's equation (Eq. 1.7), Eq. 1.11 is
obtained,

$$(1 + \cos \theta) \gamma_{lv} = 2\left(\gamma^d \gamma^d\right)^{1/2} \quad 1.11$$
thus $\gamma_s^d$ can be calculated from contact angle measurement.

**Owens and Wendt's approach**

Owens and Wendt [63] extended Eq. 1.10 as

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2 \left( \gamma_s^d \gamma_l^d \right)^{1/2} - 2 \left( \gamma_s^p \gamma_l^p \right)^{1/2}$$  \hspace{1cm} (1.12)

By combining Eq. 1.7 and Eq. 1.12, the following equation can be obtained,

$$(1 + \cos \theta) \gamma_{lv} = 2 \left( \gamma_s^d \gamma_l^d \right)^{1/2} + 2 \left( \gamma_s^p \gamma_l^p \right)^{1/2}$$  \hspace{1cm} (1.13)

In cases where one of the phases is non-polar, Eq. 1.13 is the same as Eq. 1.11.

**Other approaches**

There are many other approaches in the treatment of contact angle data. Among them are Wu's approach [64], the equation of state approach [65], and acid-base interaction approach [66]. Wu suggested a harmonic mean method in dealing with the interfacial interaction instead of the geometric mean method in Eq. 1.12. Ward and Neumann proposed the equation of state,

$$\gamma_{sl} = f(\gamma_{sv}, \gamma_{lv})$$  \hspace{1cm} (1.14)

which means that the interfacial free energy is only the function of the total free energies of the two phases. The acid-base interaction theory was first proposed by Fowkes. According to this theory, nearly all intermolecular interactions at an interface can be reduced to two phenomena: London dispersion, and electron donor-acceptor (acid-base) interaction. Hydrogen bonds are considered to belong to acid-base interactions, and dipole-dipole
interaction is thought to be negligible.

1.5.4 Surface free energy of carbon fibre

Methods of measuring carbon fibre contact angle

Due to the difficulties in handling small filaments, only a few methods for measuring contact angle of a liquid drop in contact with a filament have been developed. Among them are the wicking rate method and the Wilhelmy technique. Bobka and Lowell [67] determined the wettability of carbon fibres by measuring the wicking rates either by the mass pick-up technique or by the surface velocity method. Contact angles were then calculated using the Washburn equation [68] derived for a system of uniform capillaries.

\[
dh/dt = (r \gamma \cos \theta / 4 \eta) - (r^2 \rho g / 8 \eta)
\]  

where \(dh/dt\) is the wicking rate in a capillary of radius \(r\). \(\rho, \gamma\) and \(\eta\) are the liquid density, surface tension, and viscosity, respectively. \(g\) is the acceleration due to gravity.

The Wilhelmy technique is widely used to determine the contact angle of a filament [44], [69-71]. Usually, a monofilament is brought into contact with a liquid, and advancing or receding contact angle is measured by raising or lowering the liquid container. The measured advancing and receding wetting forces (\(F\)) can be related to the contact angle (\(\theta\)) through the following equation,

\[
F = \pi D \gamma_v \cos \theta
\]  

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where $D$ is the diameter of the filament, and $\gamma_{lv}$ is the surface tension of the liquid used. Due to very small diameter of the filament, the buoyancy force can normally be neglected. $F$, $D$ and $\gamma_{lv}$ can be measured, and therefore contact angle $\theta$ can be calculated.

**Carbon fibre surface free energy**

The Wilhelmy technique has been used to examine the wetting properties of carbon fibre surfaces by a number of workers. Donnet et al (70), for example, measured the surface free energies of LM and HM carbon fibres before and after plasma treatment. For both fibres $\gamma_p$ was found to increase with increasing plasma treatment duration, until reaching a maximum of about 30 mJ m$^{-2}$. The increase in $\gamma_p$ was attributed to the increased amount of oxygen and the creation of edge sites by etch pits formation after plasma treatment.

The increase in $\gamma_p$ by surface treatment has also been reported by a number of other workers. Drzal et al (43-44) reported that $\gamma_p$ was 23.6±2.6 mJ m$^{-2}$ and 8.1±3.0 mJ m$^{-2}$ for untreated LM and HM PAN-based fibres, respectively. Values of $\gamma_d$ were 27.4±0.3 mJ m$^{-2}$ and 33.0±1.2 mJ m$^{-2}$. $\gamma_p$ was found increased with surface oxidation treatment, however, $\gamma_d$ remained unchanged. The increase in $\gamma_p$ was again attributed to the increased oxygen content induced by surface treatment. The reductions observed in $\gamma_p$ after vacuum heat treatment at 300°C were reflected by the correspondent decrease in oxygen concentration owing to the decomposition of surface oxygen functionalities.
Contact angle hysteresis was observed for PAN-based fibres [71] pyrolysed at 2500°C, while this hysteresis was absent with repyrolysation at 3000°C. SEM study indicated that surface heterogeneity rather than surface roughness could account for the contact angle hysteresis.

1.6 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is an important technique in materials science. The results are obtained rapidly and usually have sufficient information for deductions of structural significance. The principle of SEM is shown schematically in Fig. 1.5. A source of electrons is focused by the lens as a spot which is caused to move across the object (x→y→z). As the spot strikes each point on the object a response is produced, and these responses are collected sequentially and displayed to give an "image". Under ideal
conditions, the resolution of the instrument lies in the range of 0.5–20 nm [72]. One important feature of SEM is that it provides direct observation of the microstructure of the object of interest.

SEM is one of the most important techniques used to elucidate the structure and surface features of carbon fibres, as well as their fracture surface. SEM can also be applied to measure carbon fibre diameters [73]. Recent applications of SEM include studies of the fracture surface of carbon fibre composites [74], influence of surface treatments on surface morphology [19], [22], [71] etc.

1.7 Surface area

1.7.1 BET equation

When a clean solid is exposed to gas, it will attract gas molecules onto its surface. In a given volume container, it is possible to determine the number of molecules adsorbed under a certain pressure and temperature. With the number of adsorbed gas molecules known, it is possible to calculate surface area if the area occupied per molecule is known.

For multilayer adsorption on solid, the BET equation holds [75],

\[
\frac{p/p_o}{N(1-p/p_o)} = \frac{1}{CN_m} + \frac{C-1}{CN_m} \frac{p}{p_o}
\]

where \( p/p_o \) is relative pressure,

\( N \) is the moles of adsorbed gas (at S.T.P.),
\( N_m \) is the moles of gas required to form a monolayer (at S.T.P.),
\( C \) is a constant.

The plot of \( (p/p_o) / [N(1-p/p_o)] \) against \( p/p_o \) should be a straight line as
illustrated in Fig. 1.6,

![BET plot](image)

The slope is \( \frac{(C-1)}{(C \cdot Nm)} \), and intercept with Y axis is \( \frac{1}{(C \cdot Nm)} \). Thus,

\[
Nm = \frac{1}{(\text{slope} + \text{intercept with Y axis})}
\]

The specific surface area, \( Sm \), of the sample can be calculated according to the following equation

\[
Sm = \frac{(Nm \cdot Am \cdot NA)}{m}
\]

where \( NA \) is Avogadro's number, \( 6.02 \times 10^{23} \), \( m \) is the mass of sample, \( Am \) is the average area occupied by each adsorbed molecule. Nitrogen, argon and krypton are normally used. The average area occupied by an adsorbed molecule (\( Am \)) is 0.162, 0.138, and 0.195 \( \text{nm}^2 \) for nitrogen, argon, and krypton, respectively.

A plot of the amount of gas adsorbed against the relative pressure of...
adsorbate at a constant temperature gives the adsorption isotherm. Two common types of isotherms are shown in Fig. 1.7 [75].

Type I isotherms are referred to as Langmuir-type, and restricted to monolayer adsorption. Type II isotherms are the most common encountered type, referred to as BET isotherm, which represents multilayer physical adsorption. Point B approximates the formation of an adsorbed monolayer.

1.7.2 Carbon fibre surface area

The surface area of carbon fibres is generally obtained by the adsorption data of nitrogen or krypton using BET equation. Carbon fibre surface area was found to depend upon the nature of precursor material, the temperature of heat treatment, and the nature of surface treatment [21]. The surface area is low and ranges from 0.1 to 1.5 m²/g [10]. A study on HM graphite fibres [73], using low temperature N₂ and Ar adsorption by microgravimetry method indicated that the adsorption isotherms were of Type II shape.
Rand and Robinson [76] used N₂ adsorption and O₂ chemisorption measurement to study PAN-based HM carbon fibre surface properties. The micropore volume was found to increase with degassing temperature, which was attributed to the opening up of internal micropore structure during degassing process. Since heating in vacuo results in the decomposition of incompletely carbonised materials which had been trapped in the structure, the higher the temperature the greater extent the decomposition, giving rise to a corresponding larger measured micropore volume. The BET area was increased with the creation of micropores. The remarkably increased active surface area (38 times after 50 hours of nitric acid oxidation) measured by the chemisorption of oxygen was suggested to be due to the increased number of edge sites on the surface by prolonged oxidation.

1.8  Aims of the study

Aims of the project were to study the surface effects of commercial surface treatments and laboratory nitric acid oxidation on carbon fibres. PAN-based Courtaulds low modulus (LM) and high modulus (HM), and Akzo LM fibres were used. The comparison of these surface treatments was carried out by comparing fibre surface elemental compositions, surface functionalities, and surface wettabilities.

XPS was the major tool used in the study to investigate the surfaces of carbon fibres. For both untreated and treated fibres, broad scan spectra were collected and surface elemental compositions calculated. Deconvolution of high energy resolved C1s, O1s, and N1s XPS spectra were also carried out to study fibre surface chemistry. Vapour-phase derivatisation in conjunction with XPS was used to estimate the amount of surface hydroxyl (-OH) groups and carboxylic acid (-COOH) groups. ATR-FTIR spectra were also collected, and tentative assignments of some peaks were made.

Carbon fibre wetting forces in water and diiodomethane were measured.
Contact angles of water and diiodomethane, and thus surface free energies were calculated. Unoxidised and oxidised Akzo LM fibres were also incorporated into epoxy resin to form fibre composites. The interlaminar shear strength (ILSS) was tested using three point bend method. SEM and surface area measurement were performed to study carbon fibre surface morphology and their surface porosity, respectively.
CHAPTER 2 EXPERIMENTAL

2.1 Materials and chemicals

Courtaulds untreated and anodically oxidised PAN-based HM and LM carbon fibres were used. The commercial anodic oxidation was carried out in ammonium bicarbonate solution.

Akzo PAN-based untreated and anodically oxidised LM carbon fibres were provided by Ciba-Geigy. The same fibres sized with bisphenol-A were also supplied by Ciba-Geigy.

Trifluoroacetic anhydride (TFAA) was used to derivatise -OH groups present on carbon fibre surfaces. Chemicals for the derivatisation of carboxylic acid groups were trifluoroethanol (TFE), di-tert-butylcarbodiimide (Di-tBuC), and pyridine. Pyridine was used here as a catalyst. Liquids for contact angle measurement were diiodomethane and lab made triple distilled water. Diiodomethane was stored in a brown bottle to lessen photolytic decomposition. All the chemicals used were of high purity (+99%) and purchased from Aldrich. Concentrated nitric acid (69.7%) used for carbon fibre surface oxidation treatment was purchased from Fisons.

2.2 Vacuum frame

A vacuum frame used to perform vapour-phase derivatisation is shown schematically in Fig. 2.1. It is composed of a rotary pump, a diffusion pump, two liquid nitrogen traps, a main frame, three sub-frames, and a vacuum gauge. The pressure in the main frame can reach as low as 10^-5 torr by the use of diffusion pump, rotary pimp, and liquid nitrogen traps.

Three sub-frames were used for chemical reactions. To eliminate cross
Fig. 2.1 Schematic of vacuum frame
contaminations, different reactions were carried out at different times with a time interval of at least 24 hours.

2.3 Surface oxidation and vapour-phase derivatisation

2.3.1 Surface oxidation of carbon fibres with concentrated nitric acid

The oxidation treatment was carried out by refluxing carbon fibres in concentrated HNO₃ (69.7%) for 3 hours. The sample was then copiously washed at least three times with triple distilled water, and soaked in triple distilled water for 48 hours, followed by drying in a vacuum frame for 24 hours at room temperature (~25°C).

2.3.2 Vapour-phase derivatisation

Vapour-phase derivatisation in vacuum frame was carried out by putting the derivatising reagent in a flask on one side of a sub-frame. Air in the flask was pumped out through the main frame by opening the valve above the flask after the flask had been immersed in a jar of liquid nitrogen for 5 minutes. After 10 minutes, the valve was then closed and the reagent allowed to melt by removing the liquid nitrogen. This pumping process was repeated several times in order to expel impurities in the flask. A tow of carbon fibre was put in a tube on the other side of the sub-frame, which was pumped down to a vacuum of $10^{-4}$ torr by opening the valve above the tube. The reaction was started by closing the valve above the sub-frame and opening the valves between the flask and the tube. The flask was kept at ~18°C (room temperature was ~25°C) using a water bath during the reaction to avoid the condensation of the reagent on the fibre surface. After the reaction, a jar containing liquid nitrogen was used to freeze the reagent, followed by pumping the sub-frame for 10 minutes. The reagent was then sealed, and the derivatised fibre was pumped for 24 hours to remove any physically adsorbed molecules of the derivatising reagents or products of the reaction.
Vapour-phase derivatisation of hydroxyl groups with trifluoroacetic anhydride (TFAA) was carried out with different durations on Courtaulds fibres in order to find out the optimum reaction time. It was found that 7 hours of reaction time is adequate. This reaction time was used for later derivatisation reactions of other carbon fibres with TFAA.

The procedure reported by Chilkoti et al [53] for the vapour-phase derivatisation of carboxyl groups with TFE was used with minor modification. The reaction was carried out in the vacuum frame, and all three chemicals, TFE (0.9 ml), Di-tBuC (0.3 ml) and pyridine (0.4 ml) were mixed in a flask at the same time. Work carried out in the same lab has shown that the same reaction on model polymer (polyacrylic acid, PAA) surface is complete in 10 hours [77]. The reaction on carbon fibre surface was, therefore, allowed to proceed slightly longer (15 hours) to ensure a complete reaction.

2.4 XPS

Samples for XPS analysis were prepared by cutting carbon fibre into about 15 mm in length, kept roughly parallel to each other and fixed onto a metal stub with a copper frame. All samples were carefully handled to minimise possible contamination.

XPS measurements were carried out using a VG ESCALAB MKI spectrometer at a power of 200W and in a vacuum of 10^{-7} torr. Al Kα radiation (1486.6 eV) was used as X-ray source. All spectra were collected and stored in a computer. Broad scan spectra were collected with a pass energy of 85 eV and an aperture of B1 (4 mm x 10 mm, rectangle). All peaks were calibrated with reference to the graphite C1s peak at 284.6 eV. Surface compositions were calculated by measuring the areas under the respective photoelectron peaks after subtraction of a Shirley type background.
Correction was made for the angular asymmetry of photoemission [30], transmission of the energy analyser [31], photoionisation cross section [24], and inelastic mean free path of the photoelectron [25].

Conditions for recording narrow scan spectra of Cls, O1s, and N1s were different, considering their different sensitivity factors and different concentrations on the fibre surfaces. For Cls spectrum, a pass energy of 17 eV and an aperture of A4 (a circle with a diameter of 4 mm) were used. As for O1s spectrum, an aperture of A4 and a pass energy of 19 eV were selected. An aperture of B1 and a pass energy of 20 eV were selected for N1s spectrum. Each spectrum was the sum of 50 scans, the scanning range was just broad enough for the analysis of the peak interested. X-ray exposure was not found to cause any obvious surface damage under the conditions used. To improve the energy resolution, deconvolution of high energy resolution XPS spectrum was performed by removing the broadening effect of Al Kα line shape using a modified Van Cittert deconvolution algorithm [28].

2.5 ATR-FTIR

Single-pass multiple reflection ATR prism KRS-5 (50 mm x 10 mm x 3 mm) with a face angle of 45° was used. Two bunches of carbon fibres were made by cutting fibres into ~7 cm in length and held together at both ends using adhesive tape. Each bunch of the fibre was used to bind up a rubber pad (about the KRS-5 prism size) with the fibre ends folded at the back of the rubber pad. The two rubber pads were then squeezed against both sides of the prism to ensure a firm contact of the carbon fibre surface and the prism. The angle of the prism position used was 50°. The layer of the fibre used to cover the rubber pad was thick enough to prevent any incident infrared beam from reaching the rubber.

The ATR attachment was then put in a Nicolet 20 DXC FTIR spectrometer
equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector to record infrared spectra. The spectrum was collected after the sample compartment had been purged with dry air for 5 minutes. All spectra were collected at a resolution of 4 cm⁻¹, and for each sample 300 scans were collected and signal averaged to improve the signal-to-noise ratio.

2.6 Contact angle measurement

Carbon fibre wetting force was measured using Wilhelmy technique at room temperature. An electronic balance used for the wetting force measurement was kept in a closed box (Fig. 2.2). A single fibre filament of about 2–3 cm in length was attached to a glass hook with small amount of adhesive. The adhesive was placed firstly on the hook and the fibre was brought into contact with it.

![Fig. 2.2 Schematic diagram of the microbalance](image)
The glass hook with the carbon fibre was then suspended on the arm of the electronic balance. The balance was zeroed before each measurement. A beaker containing liquid for the contact angle measurement was raised slowly and gently with the help of a lab jack until the fibre tip came in contact with the liquid indicated by a force response displayed on the balance recorder. For each filament, six readings were taken by raising the liquid about 1mm each time. The forces recorded in this way were referred to as advancing forces. The receding forces were obtained similarly by lowering the beaker. The balance recorder was capable of measuring the equilibrium force within an accuracy of ± 0.01 mg.

Two sets of parallel measurements under the same conditions were carried out, and were found to agree well with each other. Their average forces (F) were used in the calculations of contact angles (θ) and surface free energies (γ) by using equations 1.16, and 1.13.

\[ F = \pi D \gamma_{lv} \cos \theta \]  \hspace{1cm} 1.16

where D is the diameter of the fibre which can be measured by SEM. \( \gamma_{lv} \) is surface tension of the liquid used, and it can be found in literature. Water and diiodomethane were used for contact angle measurement and their surface tensions including their dispersion and polar components are listed in Table 2.1 [78]. Since F can be measured and \( \gamma_{lv} \) is known, contact angle (θ) can be calculated using Eq. 1.16, therefore by using

\[ (1 + \cos \theta) \gamma_{lv} = 2 (\gamma_{s}^d \gamma_{p}^d)^{1/2} + 2 (\gamma_{s}^p \gamma_{p}^p)^{1/2} \]  \hspace{1cm} 1.13

\( \gamma_{s}^d \) and \( \gamma_{p}^p \) can be easily calculated from contact angle measurement of water and diiodomethane. A BASIC computer program (Appendix V) was written.
to calculate $\gamma_i^d$ and $\gamma_i^P$. Surface tensions of water and diiodomethane used were measured using a Kruss K10T tensiometer with Du Nouy ring at room temperature. The results obtained agreed well with literature values in Table 2.1.

Table 2.1 Surface tensions of water and diiodomethane (mJ m$^{-2}$)

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$\gamma_i^d$</th>
<th>$\gamma_i^P$</th>
<th>$\gamma_{iv}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>21.8</td>
<td>51.0</td>
<td>72.8</td>
</tr>
<tr>
<td>diiodomethane</td>
<td>50.8</td>
<td>0.0</td>
<td>50.8</td>
</tr>
</tbody>
</table>

Calibration of the electronic balance

The balance was calibrated in order to obtain more precise wetting forces. Five fine copper wires with different lengths were used. The electronic balance was calibrated using the copper wires whose masses ($M$) were measured precisely with a Precisa 40 SM - 200A balance. The relationship between the true mass ($M$) and the measured value ($M_m$) was obtained as,

$$M = 1.06 M_m + 4.18 \times 10^{-3} \text{ (mg)}$$

All wetting forces recorded were calibrated using the above equation.
CHAPTER 3 RESULTS AND DISCUSSION

Carbon fibres used in the study are listed in Table 3.1. Untreated fibres were oxidised in the laboratory using concentrated nitric acid, and the results obtained were compared with those from commercially oxidised fibres.

Table 3.1 Carbon fibres and their surface treatments

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Designation</th>
<th>Surface treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Courtaulds</td>
<td>HMU</td>
<td>untreated</td>
</tr>
<tr>
<td></td>
<td>HM(a)</td>
<td>anodically oxidised in ammonium bicarbonate</td>
</tr>
<tr>
<td></td>
<td>HM(n)</td>
<td>oxidised in concentrated nitric acid for 3 hr</td>
</tr>
<tr>
<td></td>
<td>LMU</td>
<td>untreated</td>
</tr>
<tr>
<td></td>
<td>LM(a)</td>
<td>anodically oxidised in ammonium bicarbonate</td>
</tr>
<tr>
<td></td>
<td>LM(n)</td>
<td>oxidised in concentrated nitric acid for 3 hr</td>
</tr>
<tr>
<td>Akzo</td>
<td>LMU</td>
<td>unoxidised, unsized</td>
</tr>
<tr>
<td></td>
<td>LM(a) *</td>
<td>anodically oxidised</td>
</tr>
<tr>
<td></td>
<td>LM(n)</td>
<td>oxidised in concentrated nitric acid for 3 hr</td>
</tr>
<tr>
<td></td>
<td>LMU/sized</td>
<td>unoxidised, and sized</td>
</tr>
<tr>
<td></td>
<td>LM(a)*/sized</td>
<td>anodically oxidised, and sized</td>
</tr>
</tbody>
</table>

*Note: the electrolyte used for the anodic oxidation of Akzo fibre was not disclosed by the company due to confidentiality.

3.1 SEM

Fig. 3.1 and Fig. 3.2 show SEM micrographs of Courtaulds LM and HM carbon fibres, respectively.
a) Courtaulds LMU

b) Courtaulds LM(a)
c) Courtaulds LM(n)

Fig. 3.1 SEM micrographs of Courtaulds LM fibres

a) Courtaulds HMU
b) Courtaulds HM(a)

c) Courtaulds HM(n)

Fig. 3.2 SEM micrographs of Courtaulds HM fibres
The untreated LM fibre surface has the longitudinal, spinning process related grooves (Fig. 3.1.a). Anodic oxidation did not seem to have significant effect on the surface topography, although some deposits were observed after oxidation (Fig. 3.1.b). However, on the HNO₃ oxidised fibre, the etching effect was more noticeable. The longitudinal spinning process related grooves were almost completely removed, and a micropore surface might have been produced (Fig. 3.1.c).

For HM carbon fibres (Fig. 3.2), neither anodic oxidation nor concentrated nitric acid oxidation had any notable etching effects on the fibre surface. The surfaces are smooth, possibly with some debris on the untreated fibre surface.

Different topographies observed for HNO₃ oxidised LM and HM fibres may suggest that LM carbon fibre is more readily etched by oxidation treatments, which is consistent with carbon fibre structure as discussed in Chapter 1. LM fibres are less graphitic and have more edge sites, therefore they are more readily oxidised by HNO₃.

Fig. 3.3 shows the micrographs of Akzo LM carbon fibres. The untreated fibre surface (Fig. 3.3.a) is similar to that of Courtaulds LMU fibre (Fig. 3.1.a). Anodic oxidation did not seem to have any surface topographical effect on the fibre (Fig. 3.3.b). However, the longitudinal, spinning process related grooves disappeared on the HNO₃ oxidised fibre surface (Fig. 3.3.c) as for Courtaulds LM fibre (Fig. 3.1.c).

Carbon fibre diameters were directly measured from SEM micrographs. The value listed in Table 3.2 for each fibre was the average of two SEM measurements. Carbon fibre diameters were later used in the calculation of surface free energies (Section 3.5).
c) Akzo LM(n)

Fig. 3.3 SEM micrographs of unsized Akzo LM fibres

Table 3.2 Carbon fibre diameters as measured from SEM

<table>
<thead>
<tr>
<th>carbon fibre</th>
<th>diameter (± 0.1 μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Courtaulds</td>
<td></td>
</tr>
<tr>
<td>HMU</td>
<td>6.1</td>
</tr>
<tr>
<td>HM(a)</td>
<td>6.2</td>
</tr>
<tr>
<td>HM(n)</td>
<td>6.2</td>
</tr>
<tr>
<td>LMU</td>
<td>6.4</td>
</tr>
<tr>
<td>LM(a)</td>
<td>6.1</td>
</tr>
<tr>
<td>LM(n)</td>
<td>6.6</td>
</tr>
<tr>
<td>Akzo</td>
<td></td>
</tr>
<tr>
<td>LMU</td>
<td>6.5</td>
</tr>
<tr>
<td>LM(a)</td>
<td>6.4</td>
</tr>
<tr>
<td>LM(n)</td>
<td>5.9</td>
</tr>
</tbody>
</table>
3.2 XPS

3.2.1 Surface elemental compositions

Two broad scan XPS spectra were collected for each carbon fibre, and elemental composition results were averaged. Apart from carbon, oxygen was detected on all carbon fibre surfaces. Nitrogen was present on most of the fibre surfaces. Surface elemental compositions of carbon fibres are listed in Table 3.3, and are discussed in detail below.

Table 3.3 Carbon fibre surface elemental compositions measured from XPS

<table>
<thead>
<tr>
<th>carbon fibre</th>
<th>atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Courtaulds</td>
<td></td>
</tr>
<tr>
<td>HMU</td>
<td>96.5</td>
</tr>
<tr>
<td>HM(a)</td>
<td>93.6</td>
</tr>
<tr>
<td>HM(n)</td>
<td>97.2</td>
</tr>
<tr>
<td>LMU</td>
<td>92.0</td>
</tr>
<tr>
<td>LM(a)</td>
<td>83.0</td>
</tr>
<tr>
<td>LM(n)</td>
<td>76.6</td>
</tr>
<tr>
<td>Akzo</td>
<td></td>
</tr>
<tr>
<td>LMU</td>
<td>93.0</td>
</tr>
<tr>
<td>LM(a)</td>
<td>89.1</td>
</tr>
<tr>
<td>LM(n)</td>
<td>75.2</td>
</tr>
</tbody>
</table>

*Note: 0.2% is the detection limit for N and Na by XPS under the conditions used.

Courtaulds carbon fibres

As shown in Table 3.3, nitrogen was detected on untreated HM and LM fibre surfaces. On HMU fibre only small amount of nitrogen (0.3%) was detected, whereas for LMU fibre relatively larger amount of nitrogen (3.3%) was present on the surface. Nitrogen is usually found on PAN-based carbon fibre surfaces that have been carbonised at relatively low temperature. The
nitrogen could be residual material from incomplete decomposition of PAN precursor, and/or residual impurities left in the fibre from the spinning operation \[^{44}\]. The lower amount of nitrogen present on HMU fibre surface is probably a result of the much higher carbonisation temperature (\(-2500^0\) C) used. The oxygen level in LMU fibre surface (4.7%) was found higher than that in HMU fibre surface (3.2%), and this may be explained as follows. Owing to different carbonisation temperatures used, the surface of LM fibre (carbonised at \(-1400^0\)C) is less graphitic than that of HM fibre, resulting in more edge sites for LM fibre. These edge sites can be highly reactive. Therefore, the more edge sites, the more oxygen can be expected as a result of reaction with the atmosphere. The lower carbonisation temperature for the production of LM fibre may also leave more oxygen on the surface which was previously incorporated during preoxidation treatment in the fibre.

Additional oxygen may be introduced onto fibre surfaces through oxidation treatments. More oxygen would be expected to be introduced onto LM rather than HM fibre surface, since LM fibre surface is less graphitic and has more reactive edge sites.

Effects of oxidation treatment based on carbon fibre structure considerations are in good agreement with experimental XPS results listed in Table 3.3. Oxygen level is about doubled for LM fibre after anodic oxidation, while only an increase of 30% was obtained for anodically oxidised HM fibre. Surface nitrogen content was consequently increased on both LM and HM carbon fibre surfaces after anodic oxidation in ammonium bicarbonate (NH\(_4\)HCO\(_3\)). Kozlowski and Sherwood \[^{16}\] attributed this increase in nitrogen to the reaction of surface oxygen complexes with ammonium ions in solution.

As for oxidation using nitric acid, oxygen content on LM fibre surface was increased by a factor of nearly 4, nitrogen concentration was slightly decreased. This could imply that nitrogen is not introduced onto fibre surface through HNO\(_3\) oxidation. Oxidation with HNO\(_3\) is much more effective than
anodic oxidation in NH₄HCO₃ to oxidise LM fibre. Surprisingly, HNO₃ oxidation of HM fibre was found to slightly reduce the oxygen level. The reason for decreased oxygen concentration on HNO₃ oxidised HM surface is not fully understood. One possible explanation may be that HNO₃ could have removed some of the surface oxidised layer from HM fibre, while having little oxidation effect on the surface since there are fewer edge sites present for HM fibre.

**Akzo carbon fibre**

Anodic oxidation of Akzo LM fibre showed somewhat different behaviour to that of Courtaulds LM fibre. The surface oxygen content of Akzo LM fibre (Table 3.3) was doubled from 4.2% to 8.3% after anodic oxidation, but the oxidation did not result in any rise in surface nitrogen concentration. This might imply that the oxidation was conducted in a different electrolyte rather than ammonium salt as in the case of anodic oxidation of Courtaulds LM fibre. Little amount of sodium was detected on both surfaces. Drzal [44] believed the source of sodium to be sodium sulphur salts used in the PAN spinning process. As in the case of Courtaulds LM fibre, HNO₃ oxidation of Akzo LM fibre also noticeably increased surface oxygen concentration by a factor of about 4.

### 3.2.2 Surface chemistry

To investigate functional groups present on fibre surfaces, high energy resolution C1s, O1s, and N1s XPS spectra were recorded. These high energy resolved spectra were then deconvolved to remove the broadening effects of Al Kα line shape. Binding energies of C1s, O1s, and N1s peaks in different chemical environments are listed in Appendices I, II, and III, respectively. According to these, tentative assignments were made.
C1s spectrum

All high energy resolved C1s spectra collected exhibit asymmetric tails towards the higher binding energy side, suggesting that the graphitic nature of fibre surfaces remains largely intact even after surface treatments as severe as nitric acid oxidation. C1s spectra of HM fibres (untreated and oxidised) are narrower than those of LM fibres. This is not surprising as the very high graphitisation temperature (~2500°C) used in the production of HM fibre results in more graphitic surfaces.

The broad and asymmetric C1s spectra have indicated the existence of more than one type of carbon present on the surfaces. Deconvolved C1s spectra of Courtaulds HM and LM, and Akzo LM fibres are shown in Fig. 3.4, Fig. 3.5, and Fig. 3.6, respectively.
a) High energy resolution Cls peak envelopes from the surfaces of Courtaulds fibres. (1) HMU, (2) HM(a), and (3) HM(n)
b) Enlarged (x2) chemically shifted peaks in Fig. 3.4.a
   (1) HMU, (2) HM(a), and (3) HM(n)

Fig. 3.4 Deconvolved C1s XPS spectra of Courtaulds HM fibres
a) High energy resolution Cls envelopes from the surfaces of Courtaulds fibres. (1) LMU, (2) LM(a), and (3) LM(n)
b) Enlarged (x2) chemically shifted peaks in Fig. 3.5.a
(1) LMU, (2) LM(a), and (3) LM(n)

Fig. 3.5 Deconvolved C1s XPS spectra of Courtaulds LM fibres
a) High energy resolution C1s peak envelopes from the surfaces of Akzo fibres. (1) LMU, (2) LM(a), and (3) LM(n)
b) Enlarged (x2) chemically shifted peaks in Fig. 3.6.a
(1) LMU, (2) LM(a), and (3) LM(n)

Fig. 3.6 Deconvolved Cls XPS spectra of Akzo fibres
Fig. 3.4 shows deconvolved C1s spectra of Courtaulds HM fibres. It can be seen that anodic oxidation or nitric acid oxidation has little effect on HM fibre surface chemistry. This is again consistent with the proposed structure for HM fibre, i.e. HM fibre is highly graphitic and does not have many reactive edge sites on the surface, therefore not much oxidation can be introduced. One peak at \( \sim 1.5\) eV is clearly resolved. This peak can be attributed to C-OH/C-OR. There is some weak structure at about 2.2–2.6 eV and 3.1–3.5 eV. Exact assignment is difficult. Possible assignments are aromatic C=O for the 2.2–2.6 eV peak, and aromatic COOH/COOR for the 3.1–3.5 eV one. Since HM fibre is highly graphitic, it is likely that aromatic C=O and COOH/COOR rather than aliphatic C=O and COOH/COOR are dominant on the surface. These aromatic C=O and COOH/COOR have lower chemical shifts (\( \sim 2.4\) eV and \( \sim 3.6\) eV respectively) than the aliphatic ones (\( \sim 3.0\) eV for R-C=O, and \( \sim 4.0\) eV for R-COO\(^{-}\))\(^{79}\) (see Appendix I).

For LM fibres (Fig. 3.5), peaks with chemical shifts of \( \sim 1.5\) eV, \( \sim 3.0\) eV, and \( \sim 3.9\) eV were observed for all fibres. They may be assigned to C-OH/C-OR, aliphatic C=O, and COOH/COOR, respectively. An extra peak with a chemical shift of \( \sim 2.0\) eV was found on untreated LM fibre surface. Sherwood et al attributed this peak to quinone/enol\(^{14, 16, 22}\). This peak may also be accounted for by the following phenol type structure. High energy resolution C1s spectra of the sizing agent (bisphenol-A) has demonstrated that the same type carbon has about the same chemical shift (Section 3.6).

![Schematic structure I](image-url)
Marked differences were observed on LM fibre surface after oxidation treatments. The most significant change induced by anodic oxidation was the emergence of the peak with a chemical shift of $\sim -0.9$ eV. Considering the significant amount of nitrogen (7.8%) present on LM(a) surface, this peak is most likely due to C-N carbons. The peak at a chemical shift of $\sim -2.0$ eV as seen for LMU fibre may also be present. Fig. 3.5 also shows that the most striking effect of nitric acid oxidation of LM fibre is the significant increase in the amount of surface COOH/COOR groups. It can be seen that the peak due to C-OH/C-OR became much weaker after nitric acid oxidation. This may be because that some C-OH/C-OR groups have been converted into higher oxidation state functional groups, such as COOH/COOR, by this severe oxidation treatment.

**Akzo fibres**

Peaks which may be assigned to C-OH/C-OR, C=O, and COOH/COOR were also observed for Akzo fibres (Fig. 3.6). The peak with a chemical shift of $\sim -2.0$ eV observed for LMU and LM(a) could also be assigned to quinone/enol according to Sherwood at al [14, 16, 22], or to the phenol type structure (Schematic structure I). As in the case of Courtaulds LM(a) fibre, C-N type carbons with a chemical shift of $\sim -0.9$ eV was also seen here for Akzo LM(a) fibre, and the same peak might also be present with a weaker intensity on the C1s spectrum of LMU fibre. Again HNO3 oxidation of Akzo fibre significantly increased the intensity of COOH/COOR peak (chemical shift: $\sim -3.9$ eV). Some fractions of other functional groups may have been converted into COOH/COOR by HNO3 oxidation, since their intensities appear to have been reduced after the oxidation (Fig. 3.6).

**O1s spectrum**

It is not easy to resolve peaks with different chemical shifts for O1s peak due to its relatively broad full width at half maximum, as compared to that of
Fig. 3.7 Deconvolved O1s spectra of Courtaulds HM fibres
(1) HMU, (2) HM(a), and (3) HM(n)
Fig. 3.8 Deconvolved O1s spectra of Courtaulds LM fibres
(1)LMU, (2) LM(a), and (3) LM(n)
Fig. 3.9 Deconvolved O1s spectra of Akzo fibres
(1) LMU, (2) LM(a), and (3) LM(n)
C1s [38]. Figs. 3.7-3.9 are the deconvolved O1s spectra for Courtaulds and Akzo carbon fibres. In the figures all peaks have been charge referenced to primary C1s peak at 284.6 eV.

It can be seen that two peaks with binding energies of \(-531.5\) eV and \(-533\) eV are present for all carbon fibres. The one with a binding energy of \(-531.5\) eV may be assigned to double bonded oxygen in \(\text{C}(=\text{O})\)-O (carboxylic acid or ester), and C=O, while that of \(-533\) eV may be due to single bonded oxygen in \(\text{C}(=\text{O})\)-O* (carboxylic acid or ester), C-OH, and C-O-C. No additional peaks were found after oxidation treatments. However for each type of carbon fibre, the relative intensity of \(-533\) eV peak was increased after oxidation treatments, especially after HNO3 oxidation, indicating the introduction of carboxylic acid groups by oxidation treatments.

N1s peaks

Due to the low sensitivity factor of N1s and its low concentration in the fibre surfaces, the N1s signal was very weak. N1s spectra were obtained from some fibres using a larger aperture (B1) and a slightly higher pass energy (20 eV). Deconvolved N1s spectra are illustrated in Figs. 3.10-3.12 for Courtaulds and Akzo fibres. N1s binding energies in different chemical environments related to the primary C1s peak at 284.6 eV can be found in Appendix III.

For Courtaulds fibres, the collection of N1s spectra was only managed for HM(a), LMU, and LM(a). Two peaks were observed for Courtaulds HM and LM fibres (Fig. 3.10 and Fig. 3.11). They may be due to \(-\text{NH}_2\) with a binding energy of \(-399.4\) eV and \(\text{CONH}_2\) with a binding energy of \(-400.7\) eV. For LM fibre, anodic oxidation increased the amount of \(\text{CONH}_2\) groups.

Two peaks with binding energies of \(-397.9\) eV and \(-400.7\) eV were observed for Akzo LMU and LM(a) fibres (Fig. 3.12), they may be \(-\text{C}={\text{N}}\) and \(\text{CONH}_2\), respectively. Anodic oxidation did not alter the types of nitrogen containing
groups. However, the relative intensity of \(-\text{C}=\text{N}\) peak was found decreased after the oxidation. An extra peak with a binding energy of \(-399.4\) eV was observed for Akzo LM(n). It may be due to \(-\text{NH}_2\) from the bulk as it may be possible to expose some bulk \(-\text{NH}_2\) after HNO\(_3\) etching.

![Deconvolved N1s spectrum of Courtaulds HM(a) fibre](image)

**Fig. 3.10** Deconvolved N1s spectrum of Courtaulds HM(a) fibre
Fig. 3.11 Deconvolved N1s spectra of Courtaulds fibres
(1) LMU, and (2) LM(a)
Fig. 3.12 Deconvolved N1s spectra of Akzo fibres
(1) LMU, (2) LM(a), and (3) LM(n)
3.3 Vapour-phase derivatisation

3.3.1 Hydroxyl groups

Trifluoroacetic anhydride (TFAA) was used to derivatise -OH groups present on carbon fibre surfaces. The reaction was carried out with different durations for Courtaulds carbon fibres to evaluate the kinetic effects on the reaction. Fig. 3.13 is a plot of fluorine concentration as detected by XPS against reaction time.

![Graph](image)

**Fig. 3.13** A plot of fluorine concentration against reaction time with TFAA for Courtaulds fibres

It has been shown in Fig. 3.13 that the fluorine concentration detected by XPS on each fibre surface reaches a limiting value after a finite period of time (about 7 hours), and does not change thereafter. Based on this, TFAA derivatisation of -OH groups on other fibres was conducted for a duration of 7 hours. Derivatised carbon fibres were analysed with XPS as soon as possible.
to minimise any aging effects.

According to the esterification reaction between -OH and TFAA, 3 fluorine atoms are introduced onto the surface for each -OH group (see Appendix VI).

\[
\begin{align*}
\text{C-OH} + \text{CF}_3\text{C-O-CF}_3 \rightarrow \text{O-} \text{C-CF}_3 \\
+ \text{CF}_3\text{-C-OH}
\end{align*}
\]

It is, therefore, possible to calculate the concentration of -OH groups tagged by TFAA from measured fluorine concentration.

Table 3.4 Carbon fibre surface -OH atomic% from TFAA derivatisation

<table>
<thead>
<tr>
<th>Carbon fibre</th>
<th>-OH% from derivatisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Courtaulds</td>
<td></td>
</tr>
<tr>
<td>HMU</td>
<td>0.47</td>
</tr>
<tr>
<td>HM(a)</td>
<td>0.43</td>
</tr>
<tr>
<td>HM(n)</td>
<td>0.20</td>
</tr>
<tr>
<td>LMU</td>
<td>1.17</td>
</tr>
<tr>
<td>LM(a)</td>
<td>1.40</td>
</tr>
<tr>
<td>LM(n)</td>
<td>0.17</td>
</tr>
<tr>
<td>Akzo</td>
<td></td>
</tr>
<tr>
<td>LMU</td>
<td>0.90</td>
</tr>
<tr>
<td>LM(a)</td>
<td>1.50</td>
</tr>
<tr>
<td>LM(n)</td>
<td>0.90</td>
</tr>
</tbody>
</table>

TFAA derivatisation of -OH groups has been checked with a model polymer (polyvinylalcohol, PVA), and the reaction was found complete in 2 hours under the same conditions [80]. Table 3.4 shows the -OH concentrations present on the surface for all carbon fibres as determined by vapour-phase TFAA derivatisation. -OH% has been found approximately proportional to
the relative intensity of the peak with a chemical shift of -1.5 eV on C1s XPS spectra (Figs. 3.4–3.6).

For Courtaulds fibres, Table 3.4 indicated that untreated or anodically oxidised LM has more -OH groups on its surface than HM. There is virtually no difference in -OH concentration between HMU and HM(a), or between LMU and LM(a) fibres. This indicates that surface anodic oxidation in ammonium bicarbonate does not significantly alter the concentration of -OH groups on fibre surfaces. However for both HM and LM fibres, surface -OH concentration was found much lower (~0.2%) after HNO3 oxidation. This suggests that as a more severe surface treatment HNO3 oxidation may have converted -OH groups into a higher oxidation state, such as COOH/COOR.

For Akzo fibres, the amount of -OH groups was found higher on the anodically oxidised fibre surface than on the untreated fibre surface.

3.3.2 Carboxylic acid groups

Vapour-phase derivatisation with trifluoroethanol (TFE) has been used to estimate the surface carboxylic acid concentration of carbon fibres. According to the following reaction between carboxylic acid groups and TFE in the presence of a coupling agent (Di-tBuC) and a catalyst (pyridine),

\[
\text{O} \quad \text{C-OH} + \text{CF₃CH₂OH} + (\text{CH₃})₃\text{CN}=\text{C}=\text{N} \cdot \text{C}(\text{CH₃})₃ \quad \xrightarrow{\text{CsFBN}} \quad \text{O} \quad \text{C-O-CH₂CF₃} + (\text{CH₃})₃\text{CNH-C-NHC(CH₃)}
\]

the concentration of surface carboxylic acid groups can be calculated from the measured concentration of fluorine after derivatisation (Table 3.5).
It has been shown in Table 3.5 that surface -COOH concentrations estimated from TFE derivatisation appear to be considerably lower than those expected from high energy resolution C1s XPS spectra (Figs. 3.4-3.6), especially for HNO3 oxidised LM fibres. While ester (-COOR) groups may be present on the fibre surfaces, it is unlikely that the increase in total oxygen concentration by HNO3 oxidation (about a factor of 4 for LM fibres) was mainly caused by the introduction of -COOR groups rather than -COOH groups. High energy resolution C1s XPS spectra (Figs. 3.5-3.6) have shown an intense peak at a chemical shift of $-3.9 \text{ eV}$ after HNO3 oxidation of LM fibres. Considering the nature of the surface treatment these groups must be mainly due to -COOH. One possible explanation for the difference between derivatisation and high energy resolution results could be that not all -COOH groups detected by XPS are available for TFE derivatisation. Some -COOH groups may be at places where TFE molecules can not reach.

### 3.4 ATR-FTIR

ATR-FTIR has been used to investigate carbon fibre surface functionalities.
KRS-5 prism (refractive index n=2.4) was used as the internal refractive element. It has been suggested $^{[57]}$ that the refractive index of carbon fibre surface containing functional groups is close to that of a normal polymer material ($n=1.35\sim1.7$). The angle of incidence ($\theta$) must be, therefore, greater than $\theta_c = 34.2\sim45.1^\circ$ to get total reflection at the interface between KRS-5 and carbon fibre. The angle of incidence of the prism position used in this study was $\theta_A = 50^\circ$, which corresponds to an effective angle of incidence of $\theta = 48^\circ$ according to Eq. 1.5.

Figs. 3.14-3.16 are the ATR-FTIR spectra of Courtaulds and Akzo carbon fibres. Atmospheric water spectrum has been subtracted from these spectra. Absorption peak assignments found in literature of some chemical groups are collected in Appendix IV.

For Courtaulds HM fibres, Fig. 3.14 has shown that there might be some weak absorption at around 1070 cm$^{-1}$, which may be attributed to C-O stretching. No other peaks were clearly observed from the spectra. However, for Courtaulds LM fibres (Fig. 3.15) there are some evidence for the presence of some surface functional groups. A peak was detected at $\sim$1070 cm$^{-1}$, which is much stronger than the one observed for HM fibres, and may again be attributed to C-O stretching. There may also be some weak absorptions at $\sim$1400 cm$^{-1}$, 1650 cm$^{-1}$, 1700-1750 cm$^{-1}$. The absorption at $\sim$1400 cm$^{-1}$ may be assigned to OH in-plane bending, and the absorption at 1650 cm$^{-1}$ to C=O stretching in quinone / enol groups. The peak at 1700-1750 cm$^{-1}$ can be attributed to ketone, carboxylic acid or ester groups.
Fig. 3.14 ATR-FTIR spectra of Courtaulds HM fibres (1) HMU, (2) HM(a), and (3) HM(n)
Fig. 3.15 ATR-FTIR spectra of Courtaulds LM fibres
(1) LMU, (2) LM(a), and (3) LM(n)
Fig. 3.16 ATR-FTIR spectra of Akzo LM fibres
(1) LMU, and (2) LM(a)
Both figures for Courtaulds HM and LM fibres do not show much change with surface oxidation treatments. However, XPS has shown significant surface effects by oxidation treatments (Section 3.2). This discrepancy may be explained in terms of the different sampling depth for these two techniques.

The sampling depth of ATR-FTIR is about 1μm calculated for carbon fibres used in the study (see Section 1.4), therefore it can detect the "bulk" chemistry of the fibres. As for XPS, the sampling depth (≈3λ, where λ is the inelastic mean free pass) is calculated to be about 60Å according to the following empirical equation for λ [81],

\[
\lambda = \frac{49}{E^2} + 0.11E^{1/2}) \times 10/\rho \text{ (Å)}
\]

where ρ is the density of carbon fibre (~1.8 g / cm³), E is the kinetic energy of the photoelectron in electron volts. Thus XPS is much more surface sensitive than ATR-FTIR.

The ATR-FTIR spectra of Akzo fibre surfaces (Fig. 3.16) are similar to those of Courtaulds LM ones. A clear peak is observed at ~1070 cm⁻¹, and again can be assigned to C-O stretching. The peak due to ketone and/or acid may be present at ~1700 cm⁻¹, and the one due to O-H in-plane bending may also be present at ~1400 cm⁻¹. A peak at ~1540 cm⁻¹ probably due to quinone was clearly seen for LM(a).

ATR-FTIR study of the three different types of carbon fibres may suggest that LM fibres have more functionalities in the ATR-FTIR sampling depth region than HM fibres. This agrees well with the difference in the proposed structure (Chapter 1) between HM and LM fibres. ATR-FTIR is therefore useful in probing surface with a greater depth than XPS can.
3.5 Carbon fibre surface free energy

3.5.1 Surface free energy

Wetting forces of Courtaulds and Akzo fibres in water and diiodomethane were measured using the Wilhelmy method. Carbon fibre contact angles of water and diiodomethane were then calculated from wetting forces using Eq. 1.16. Table 3.6 and Table 3.7 show the wetting forces and contact angles of water and diiodomethane. Their surface free energies calculated using Eq. 1.13 are illustrated in Table 3.8. Carbon fibre surface elemental compositions are also included in Table 3.8 for comparison.

Contact angles of diiodomethane and/or water are zero for some of the fibres investigated, therefore their surface free energies can not be calculated.

<table>
<thead>
<tr>
<th>Table 3.6 Advancing and receding wetting forces of carbon fibres studied</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon fibre</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Courtaulds HMU</td>
</tr>
<tr>
<td>HM(a)</td>
</tr>
<tr>
<td>HM(n)</td>
</tr>
<tr>
<td>LMU</td>
</tr>
<tr>
<td>LM(a)</td>
</tr>
<tr>
<td>LM(n)</td>
</tr>
<tr>
<td>Akzo LMU</td>
</tr>
<tr>
<td>LM(a)</td>
</tr>
<tr>
<td>LM(n)</td>
</tr>
</tbody>
</table>
Table 3.7 Advancing and receding contact angles of carbon fibres studied

<table>
<thead>
<tr>
<th>carbon fibre</th>
<th>advancing</th>
<th>receding</th>
<th>hysteresis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>θ H2O (degree)</td>
<td>θ dim (degree)</td>
<td>θ H2O (degree)</td>
</tr>
<tr>
<td>Courtaulds</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HMU</td>
<td>72.6</td>
<td>32.7</td>
<td>69.1</td>
</tr>
<tr>
<td>HM(a)</td>
<td>46.0</td>
<td>16.4</td>
<td>36.8</td>
</tr>
<tr>
<td>HM(n)</td>
<td>45.8</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>LMU</td>
<td>63.1</td>
<td>29.2</td>
<td>57.2</td>
</tr>
<tr>
<td>LM(a)</td>
<td>15.8</td>
<td>32.8</td>
<td>12.5</td>
</tr>
<tr>
<td>LM(n)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Akzo</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LMU</td>
<td>46.4</td>
<td>6.2</td>
<td>29.4</td>
</tr>
<tr>
<td>LM(a)</td>
<td>52.7</td>
<td>14.0</td>
<td>41.8</td>
</tr>
<tr>
<td>LM(n)</td>
<td>0.0</td>
<td>8.8</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 3.8 Carbon fibre surface free energies and surface elemental compositions

<table>
<thead>
<tr>
<th>carbon fibre</th>
<th>atomic percentage</th>
<th>γ_{advancing} (mJ m^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>O</td>
</tr>
<tr>
<td>Courtaulds</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HMU</td>
<td>96.5</td>
<td>3.2</td>
</tr>
<tr>
<td>HM(a)</td>
<td>93.6</td>
<td>4.1</td>
</tr>
<tr>
<td>HM(n)</td>
<td>97.2</td>
<td>2.8</td>
</tr>
<tr>
<td>LMU</td>
<td>92.0</td>
<td>4.7</td>
</tr>
<tr>
<td>LM(a)</td>
<td>83.0</td>
<td>9.2</td>
</tr>
<tr>
<td>LM(n)</td>
<td>76.6</td>
<td>20.7</td>
</tr>
<tr>
<td>Akzo</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LMU</td>
<td>93.0</td>
<td>4.2</td>
</tr>
<tr>
<td>LM(a)</td>
<td>89.1</td>
<td>8.3</td>
</tr>
<tr>
<td>LM(n)</td>
<td>75.2</td>
<td>21.5</td>
</tr>
</tbody>
</table>
It can be seen from Table 3.6 and Table 3.7 that surface oxidation treatments generally increase carbon fibre wetting forces in water, however the diiodomethane wetting forces were generally not affected significantly. Experimental errors were within $10 \times 10^{-5} \text{mN}$ and $10^\circ$ for wetting force and contact angle, respectively. An error of $10^\circ$ in contact angle has been found to give rise to an error of $3-4 \text{mJ m}^{-2}$ in surface free energy calculated.

Contact angle hysteresis especially diiodomethane contact angle hysteresis was observed for some fibres, for example, diiodomethane contact angle hysteresis on Courtaulds HMU fibre surface was as large as $32.7^\circ$. Generally the hysteresis is more significant for HM than for LM fibre. SEM micrographs (Figs. 3.1–3.3) have not shown any significant surface roughness along the fibre axis for any of the fibres. Therefore, contact angle hysteresis is unlikely to be due to surface roughness. It could be attributed to the surface heterogeneity. According to the proposed structure for carbon fibres [6–7], there are graphitic basal planes as well as edge areas present on fibre surfaces. Because of the higher graphitic nature of these basal planes, more conduction electrons with high mobilities can be expected. This may lead to higher polarisability and therefore higher $\gamma_s^d$ for the graphitic basal planes (associated with $\theta_{rec}$) than for edge areas (associated with $\theta_{adv}$). Since HM fibre is highly graphitic, higher $\gamma_s^d$ for those high energy graphitic basal planes can be expected for HM rather than LM fibre, while $\gamma_s^d$ for those relatively low energy edge areas may be similar for the two fibres. Therefore, HM fibre surface may be less energetically homogeneous than LM. This has been reflected by the experimental diiodomethane contact angle hysteresis data (Table 3.7). For example, diiodomethane contact angle hysteresis for Courtaulds HMU is $32.7^\circ$, which is much higher than that of LMU ($7.7^\circ$). Anodic and nitric acid oxidation may have removed some or all of the less graphitic edges from the HMU fibre surface, thus reduced $\theta_{adv}$ of diiodomethane, resulting in the less contact angle hysteresis ($16.4^\circ$ and $0^\circ$,
The high water contact angle hysteresis observed for HM(n) (45.8°) is thought to be due to the chemical heterogeneity of the surface.

Surface free energies of Courtaulds carbon fibres

Comparing total surface free energies of unoxidised with those of anodically oxidised fibres, surface oxidation treatment significantly increased the surface free energy of both HM and LM fibres (Table 3.8). Further inspection of the polar ($\gamma_s^p$) and dispersion ($\gamma_s^d$) components of surface free energy has shown that $\gamma_s^d$ remained virtually unchanged, while $\gamma_s^p$ was significantly increased by a factor of about 2-3 after the anodic oxidation for both HM and LM fibres. The increase in $\gamma_s^p$ is in agreement with XPS results. Anodic oxidation increases carbon fibre surface oxygen and nitrogen concentrations, and is therefore expected to increase the surface polarity. Thus the increase in $\gamma_s^p$ by anodic oxidation can be explained in terms of the increased surface polarity induced by the introduction of more oxygen and nitrogen on the surfaces.

Real surface free energies of nitric acid oxidised HM and LM fibres can not be obtained due to the zero contact angle(s) measured (Table 3.7). Table 3.6 shows that HNO₃ oxidation of HM fibre markedly increased its water wetting force, although its surface oxygen content as measured by XPS was slightly reduced. It is probable that HNO₃ oxidation may only change the chemistry of the outmost fibre surface layer. It may also be that nitric acid oxidation has exposed more graphitic substrate by removing the outmost oxidised layer, hence increased $\gamma_s^d$ as reflected by the rise in diiodomethane wetting force. Contact angle characterises the interaction between the liquid and the outmost layer on the surface (sampling depth <10Å), and is therefore more
surface sensitive to the effects of nitric acid oxidation. XPS has a sampling depth of ~60Å and may not reflect these very near surface changes. As for LM fibre, the oxygen level was found nearly 4 times higher after HNO₃ oxidation as detected by XPS, and this may account for the increased interaction with water. Table 3.6 has also indicated the rise in the interaction between LM(n) and diiodomethane, i.e wetting force was increased, which may also be due to the exposure of graphitic substrate by the removal of outmost oxidised layer.

Values of γₛ d as low as ~30 mJ m⁻² were reported for HMU and LMU by Drzal et al [43, 44]. These values are much lower than anticipated and are close to those of polypropylene (PP) or polyethylene (PE). Carbon fibres have much higher density (~1.8 g/cm³) than that of PP or PE (~0.9 g/cm³), and moreover carbon fibres are graphitic and contain polarisable conduction electrons. Therefore, higher γₛ d would be expected for carbon fibres than for PP or PE.

**Surface free energies of Akzo fibres**

Akzo LM fibre surface shows different wettability to that of Courtaulds LM fibre (Table 3.8) although they were both made from PAN precursor. γₛ d was found similar for both Akzo LM and Courtaulds LM fibres. However, γₛ P of Akzo untreated LM fibre (15.7 mJ m⁻²) has been found to be about twice of that of Courtaulds untreated LM fibre (8.2 mJ m⁻²), even though their surface oxygen and nitrogen levels are similar. This may be caused by the difference in surface chemistry between these different types of fibres.

The polar component of anodically oxidised fibre surface was almost unchanged, in contrast to XPS observation that the oxygen concentration is about doubled. This could be explained in terms of sub-surface oxidation. Anodic oxidation increased the oxygen concentration below the outer
surface, but did not significantly affect the oxygen concentration or the chemistry at the outer surface. Therefore, the increase in oxygen concentration would not affect the surface free energy. Oxidation treatment with HNO₃ again significantly increased the water wetting force, and may be attributed to the significant increase in surface oxygen concentration (about a factor of 4).

3.5.2 Correlation between $\gamma_S$ and surface functional groups

$\gamma_S$ is plotted against total surface oxygen concentrations in Fig. 3.17, and it shows no simple correlation between them.

![Graph showing $\gamma_S$ against O%]

Fig. 3.17 A plot of $\gamma_S$ against O%

$\gamma_S$ is tabulated with -OH% and -COOH% as estimated from derivatisation in Table 3.9.
Table 3.9 Values of $\gamma_s P$, -OH%, and -COOH%

<table>
<thead>
<tr>
<th>carbon fibre</th>
<th>$\gamma_s^P$ (adv.) (mJ m^-2)</th>
<th>-OH% from derivatisation</th>
<th>-COOH% from derivatisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Courtaulds</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HMU</td>
<td>5.4</td>
<td>0.47</td>
<td>0.10</td>
</tr>
<tr>
<td>HM(a)</td>
<td>15.2</td>
<td>0.43</td>
<td>0.27</td>
</tr>
<tr>
<td>HM(n)</td>
<td>/</td>
<td>0.20</td>
<td>0.10</td>
</tr>
<tr>
<td>LMU</td>
<td>8.2</td>
<td>1.17</td>
<td>0.20</td>
</tr>
<tr>
<td>LM(a)</td>
<td>32.5</td>
<td>1.40</td>
<td>0.40</td>
</tr>
<tr>
<td>LM(n)</td>
<td>/</td>
<td>0.17</td>
<td>1.33</td>
</tr>
<tr>
<td>Akzo</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LMU</td>
<td>15.7</td>
<td>0.90</td>
<td>0.32</td>
</tr>
<tr>
<td>LM(a)</td>
<td>12.9</td>
<td>1.50</td>
<td>0.30</td>
</tr>
<tr>
<td>LM(n)</td>
<td>/</td>
<td>0.90</td>
<td>1.43</td>
</tr>
</tbody>
</table>

It indicates no correspondence at all between $\gamma_s P$ and -OH% on the surfaces. This suggests that -OH groups do not play a dominant role in determining $\gamma_s P$. However, there seems to be some correlation between $\gamma_s P$ and -COOH%. $\gamma_s P$ generally increases with -COOH%.

High energy resolution C1s XPS (Section 3.2.2) has indicated that possible surface functional groups are -OH, C=O, -COOH, and NH$_2$, etc. Therefore, the measured $\gamma_s P$ may be the combined contributions of these groups, i.e.

$$\gamma_s P = \sum_{i=1}^{4} K_i [\text{OH}] + \sum_{i=1}^{4} K_i [\text{C=O}] + \sum_{i=1}^{4} K_i [\text{COOH}] + \sum_{i=1}^{4} K_i [\text{NH}_2] + \cdots$$

where $K_i$ (i=1, 2, 3, 4, ... ) are constants. While there is some experimental evidence, it is too early to conclude that carboxylic acid groups play a dominant role in determining $\gamma_s P$ since other functional groups are
uncertain. Further derivatisation of other functional groups will be necessary in the studies of functional group effects on surface free energy.

3.6 Fibre sizing

Akzo LMU and LM(a) fibres were also sized by Ciba-Geigy.

Fig. 3.18 shows SEM micrographs of sized Akzo LMU and LM(a) fibres. The surfaces were found smoother than those of their respective unsized fibres (Fig. 3.3).

XPS analysis of these two sized fibres has revealed that they contain only carbon and oxygen. No nitrogen or sodium was detected. The concentration of oxygen was almost the same for both surfaces, ~17%. High energy resolution C1s XPS spectra of the sized fibres (Fig. 3.19) have not shown signals due to C=O at -3.0 eV and COOH/COOR at -3.9 eV as observed for the unsized fibres (Fig. 3.6). This may indicate that the fibre surfaces have been fully covered by the sizing agent, and the thickness of the film formed on fibre surfaces is greater than XPS sampling depth.

Two identical high energy resolution C1s XPS spectra have been observed (Fig. 3.19) for both sized fibres. A chemically shifted peak (~2.0 eV) was observed. The sizing agent is known to be bisphenol-A epoxy resin, and the structure of bisphenol-A is shown below. The chemically shifted peak at ~2.0 eV can be attributed to C-O in the sizing agent.

\[
\text{Bisphenol-A} \\
\begin{align*}
&\text{HO-} \quad \text{C-} \quad \text{OH} \\
&\text{CH}_3 \quad \text{CH}_3 \\
\end{align*}
\]
Fig. 3.18 SEM micrographs of sized Akzo fibres

a) sized Akzo LMU

b) sized Akzo LM(a)
Fig. 3.19 Deconvolved C1s XPS spectra of sized Akzo fibres
(1) LMU/sized and (2) LM(a)/sized
Fig. 3.20 ATR-FTIR spectra of sized Akzo fibres
(1) LMU/sized and (2) LM(a)/sized

ATR-FTIR spectra of the two sized surfaces are shown in Fig. 3.20 and they are virtually the same. All the bands may be attributed to the sizing agent. The band at 770 cm\(^{-1}\) can be assigned to out-of-plane C-H bending of benzene ring, 1030 cm\(^{-1}\) to C-O stretching of phenolic OH, 1170 and 1220 cm\(^{-1}\) to
-C(CH₃)₂- skeletal vibration. All the bands at 1450 cm⁻¹, 1500 cm⁻¹, and 1540 cm⁻¹ can be attributed to the aromatic ring.

3.7 Mechanical properties of fibre composites

Epoxy resin composites were made by Ciba-Geigy using Akzo LMU/sized and LM(a)/sized fibres. The interlaminar shear strength (ILSS) was measured by Ciba-Geigy using three point bend method [82]. For each composite twelve samples were used, and low standard deviation was found. Table 3.10 shows the average ILSS values measured.

Table 3.10 ILSS values of Akzo fibre composites

<table>
<thead>
<tr>
<th>Composite</th>
<th>ILSS (MPa)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>LMU/epoxy resin</td>
<td>78.3 ± 1.1</td>
<td></td>
</tr>
<tr>
<td>LM(a)/epoxy resin</td>
<td>102.2 ± 5.4</td>
<td></td>
</tr>
</tbody>
</table>

It has been shown by Table 3.10 that surface oxidation treatment has significantly increased ILSS. Contact angle measurement has already revealed that anodic oxidation did not improve the fibre surface wettability. SEM micrographs have also shown that there is not any notable difference in fibre topography between the oxidised and unoxidised fibre surfaces. Therefore the increased ILSS of the fibre composite could neither be explained according to fibre surface wettability, nor to topographical effects. Since the surface areas of carbon fibres were not obtainable in the study (Section 3.8), it is not clear that if the increase in ILSS is a result of increase in surface area by oxidation treatment. On the other hand, it is possible that anodic oxidation may have removed a weak boundary layer from the unoxidised fibre surface, and this may be a reason for the improved ILSS [23].
3.8 Surface area

Carbon fibre surface area measurement was carried out using low temperature N2 adsorption by volumetric method. For each fibre two parallel measurements under the same conditions were performed, and the BET surface area was calculated using BET equation (Eq. 1.17). Unfortunately, carbon fibre surface area can not be obtained due to the poor reproducibility between the two measurements. The poor reproducibility in BET surface area is thought to be due to the high system error in measuring small volume change of N2 resulting from the low surface area of the fibres studied.
CHAPTER 4 CONCLUSIONS.

Surfaces of PAN-based Courtaulds high modulus (HM) and low modulus (LM), as well as Akzo LM carbon fibres have been studied using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), chemical derivatisation, attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), contact angle measurement, and surface area measurement. According to the results discussed in Chapter 3, the following major conclusions can be drawn.

(1) XPS has shown less oxygen and nitrogen on the surface of untreated HM fibre than on that of untreated LM fibre. The HM fibre has been found to be oxidised less readily than LM fibre, which can be explained in terms of the difference in the surface structure. LM fibre surfaces are less graphitic and have more edge sites than HM fibres, and therefore are more easily oxidised anodically or by concentrated nitric acid.

(2) Oxidation with concentrated nitric acid is much more effective than anodic oxidation in altering the fibre surface topography and increasing surface oxygen concentration. Anodic oxidation in ammonium bicarbonate has been found to increase the nitrogen concentration on carbon fibre surfaces.

(3) Functional groups such as C-OH/C-OR, C=O, COOH/COOR, quinone/enol, NH2, and CONH2 may have been identified to be present on carbon fibre surfaces from high energy resolution XPS results.

(4) Since trifluoroacetic anhydride (TFAA) and trifluoroethanol (TFE) have been proved to be successful in selectively derivatising -OH and -COOH groups respectively, they have been used in conjunction with XPS in this study to estimate surface concentrations of -OH and -COOH.
Effects of oxidation treatments on the surface concentrations of these two functional groups were studied. Both high energy resolution C1s XPS and derivatisation XPS have shown that surface -COOH concentration was significantly increased, while -OH concentration was decreased by nitric acid oxidation. This may be due to the conversion of C-OH into -COOH by this oxidation. However, anodic oxidation has been found to have little effects on the concentrations of surface -OH and -COOH groups. Therefore, different oxidation treatments may have different surface effects on carbon fibres. Further studies of various oxidation treatments may help to provide choices of surface treatments of carbon fibres for different applications.

(5) The polar component of surface free energy ($\gamma_p$) broadly increases with increasing surface oxygen and nitrogen concentrations. No clear relationship has been observed between $\gamma_p$ and -OH%, however, there seems to exist some correlation between $\gamma_p$ and -COOH%.

(6) Differences in the functionalities within ATR-FTIR sampling depth between HM and LM fibres may have been revealed by ATR-FTIR. Because of the difference in the sampling depth between XPS (~60Å), ATR-FTIR (~1μm), and contact angle measurement (<10Å), care should be paid in the interpretation in terms of surface oxidation treatment.
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APPENDICES

Appendix I  C1s chemical shifts related to the primary C1s peak at 284.6 eV

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<th>functional group</th>
<th>C1s chemical shift (eV)</th>
<th>references</th>
</tr>
</thead>
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<tr>
<td>C-N</td>
<td>0.94</td>
<td>[79]</td>
</tr>
<tr>
<td>C-OH/C-OR</td>
<td>1.6±0.1</td>
<td>[14-15], [17], [34], [41-42]</td>
</tr>
<tr>
<td>ph-C=O</td>
<td>2.4</td>
<td>[79]</td>
</tr>
<tr>
<td>quinone/enol</td>
<td>2.1±0.1</td>
<td>[14-16], [22]</td>
</tr>
<tr>
<td>C=O</td>
<td>3.0±0.1</td>
<td>[17], [34], [41-42], [79], [83]</td>
</tr>
<tr>
<td>ph-C=O</td>
<td>3.6±0.1</td>
<td>[79]</td>
</tr>
<tr>
<td>C=O</td>
<td>4.2±0.2</td>
<td>[14-17], [22], [34], [41-42], [79], [83]</td>
</tr>
<tr>
<td>-C-O-C-</td>
<td>4.4</td>
<td>[79]</td>
</tr>
<tr>
<td>-O-C-O-</td>
<td>5.4</td>
<td>[79]</td>
</tr>
</tbody>
</table>
## Appendix II  O1s binding energies in different chemical environments

(related to C1s peak at 284.6 eV)

<table>
<thead>
<tr>
<th>functional group</th>
<th>O1s binding energy (eV)</th>
<th>references</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-O-C</td>
<td>532.6−533.3</td>
<td>[79]</td>
</tr>
<tr>
<td>C-OH</td>
<td>532.9−533.6</td>
<td>[15], [17], [22], [41-42], [79]</td>
</tr>
<tr>
<td>C=O</td>
<td>531.3−532.3</td>
<td>[15-17], [34], [41-42], [79]</td>
</tr>
<tr>
<td>C-C-O²</td>
<td>1 531.7−532.6</td>
<td>[79], [83]</td>
</tr>
<tr>
<td></td>
<td>2 533.1−534.0</td>
<td></td>
</tr>
<tr>
<td>C-O²C</td>
<td>1 532.6</td>
<td>[79]</td>
</tr>
<tr>
<td></td>
<td>2 533.9</td>
<td></td>
</tr>
<tr>
<td>C-O²-C-O²</td>
<td>1 532.3</td>
<td>[79]</td>
</tr>
<tr>
<td></td>
<td>2 533.9</td>
<td></td>
</tr>
</tbody>
</table>
Appendix III  N1s binding energies in different chemical environments (related to C1s peak at 284.6 eV)

<table>
<thead>
<tr>
<th>functional group</th>
<th>N1s binding energy (eV)</th>
<th>references</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CN</td>
<td>398.7−399.6</td>
<td>[41],[79]</td>
</tr>
<tr>
<td>-NH2</td>
<td>400.5±0.3</td>
<td>[16]</td>
</tr>
<tr>
<td>O</td>
<td>400.0−401.0</td>
<td>[16],[79]</td>
</tr>
<tr>
<td>C-NH2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO2</td>
<td>405.5</td>
<td>[79]</td>
</tr>
<tr>
<td>-ONO2</td>
<td>408.2</td>
<td>[79]</td>
</tr>
</tbody>
</table>
## Appendix IV Absorption frequencies of some chemical groups in IR

<table>
<thead>
<tr>
<th>Group</th>
<th>Band (cm⁻¹)</th>
<th>Vibration</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>-NH₂</td>
<td>3500–3300</td>
<td>N-H stretching</td>
<td>[84, 85]</td>
</tr>
<tr>
<td></td>
<td>1640–1560</td>
<td>N-H bending</td>
<td></td>
</tr>
<tr>
<td></td>
<td>900–650</td>
<td>out-of-plane bending</td>
<td></td>
</tr>
<tr>
<td>R-NH₂</td>
<td>1230–1030</td>
<td>C-N stretching</td>
<td>[85]</td>
</tr>
<tr>
<td>Primary amide</td>
<td>1650</td>
<td>amide I, C=O stretching</td>
<td>[84, 85]</td>
</tr>
<tr>
<td>CONH₂</td>
<td>1640</td>
<td>amide II, mostly N-H bending</td>
<td></td>
</tr>
<tr>
<td>Aromatic rings</td>
<td>-1600, -1580, -1500, -1450</td>
<td>phenyl nucleus</td>
<td>[84, 85]</td>
</tr>
<tr>
<td></td>
<td>860–800</td>
<td>out-of-plane C-H bending of para-substituted aromatic ring</td>
<td>[84, 85]</td>
</tr>
<tr>
<td></td>
<td>810–800</td>
<td>C-H bending of three adjacent hydrogen</td>
<td></td>
</tr>
<tr>
<td>Ether and alcoholic C-O</td>
<td>1150–1040</td>
<td>C-O stretching</td>
<td>[84, 85]</td>
</tr>
<tr>
<td>Ester</td>
<td>1300–1050</td>
<td>C-O-C stretching</td>
<td>[85]</td>
</tr>
<tr>
<td>O-H</td>
<td>1500–1300</td>
<td>in-plane bending of O-H, frequently two</td>
<td>[85]</td>
</tr>
<tr>
<td>Ester and lactone</td>
<td>1750–1730</td>
<td>C=O stretching</td>
<td>[14] [57] [84, 85]</td>
</tr>
<tr>
<td>Acid</td>
<td>1690–1720</td>
<td>C=O stretching</td>
<td>[57] [83, 85]</td>
</tr>
<tr>
<td>Ketone</td>
<td>1690–1725</td>
<td>C=O stretching</td>
<td>[14] [57] [84, 85]</td>
</tr>
<tr>
<td>Quinone</td>
<td>1550–1675</td>
<td>C=O stretching</td>
<td>[57] [84, 87]</td>
</tr>
<tr>
<td>Enol</td>
<td>1640</td>
<td>C=O stretching</td>
<td>[57] [84]</td>
</tr>
</tbody>
</table>
Appendix V  Computer program (BASIC) for the calculation of surface free energy according to Fowkes

10 REM METHOD ACCORDING TO FOWKES
20 D1 = 21.8
30 P1 = 51
40 D2 = 50.8
50 P2 = 0
60 PRINT "INPUT CONTACT ANGLES, Z1, Z2 (IN DEGREE), FOR WATER AND DIODOMETHANE"
70 INPUT Z1, Z2
80 LET Z1 = Z1 * 3.14159/180
90 LET Z2 = Z2 * 3.14159/180
100 LET X1 = (P1/D1)^.5
110 LET Y1 = ((D1 + P1) * (1 + COS(Z1))) / (2 * D1^.5)
120 LET X2 = (P2 / D2)^.5
130 LET Y2 = ((D2 + P2) * (1 + COS(Z2))) / (2 * D2^.5)
140 LET P = ((Y1 - Y2) / (X1 - X2))^2
150 LET D = (Y1 - (P^.5) * X1)^2
160 PRINT
170 PRINT "SURFACE FREE ENERGY ACCORDING TO FOWKES: "
180 PRINT "DISPERSION COMPONENT IS: "; D
190 PRINT "POLAR COMPONENT IS: "; P
200 PRINT "TOTAL SURFACE FREE ENERGY IS: "; D + P
210 PRINT
220 END
Appendix VI Calculation of surface -OH atomic% from TFAA derivatisation

The reaction between hydroxyl groups and trifluoroacetic anhydride (TFAA) can be written as follows,

\[
\text{OH} + \text{CF}_3\text{O-C-C-VP} = \text{O-C-CF}_3 + \text{CF}_3\text{-C-OH}
\]

(TFAA)

Assuming that all elements are homogeneously distributed in the surface layer within XPS sampling depth both before and after the derivatisation, the relationship between the -OH concentration \([\text{OH}]\) (in percentage) and the surface fluorine concentration can be derived as follows. Suppose there are 100 atoms (excluding hydrogen atoms) before derivatisation. After the derivatisation, each hydroxyl group introduces 6 extra atoms (2 C, 3 F, and 1 O). Therefore, after derivatisation surface fluorine concentration \([F]\) (in percentage) is,

\[
[F] = \frac{3[\text{OH}]}{100 + 6[\text{OH}]} \times 100
\]

Thus,

\[
[\text{OH}] = \frac{100[F]}{300 - 6[F]}
\]