The plasma treatment of contact lenses

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ABSTRACT

This thesis investigates the use of low temperature plasmas as a means of improving the surface properties of hard gas permeable contact lenses. It is important that the polymers used for this application should have good optical properties, should allow transport of oxygen to the cornea and be biocompatible, that is they should not stimulate an adverse response in the tissues which they contact. Whilst most patients have no problems with current materials there are a significant number who experience irritation of the eyes and abnormal build up of deposits on the lens surface. It has been found that mild oxygen plasma treatment of the contact lens can be helpful in alleviating these problems. In this volume the effects of such treatment are examined by x-ray photoelectron spectroscopy and alternative treatments proposed.

It is found that the oxygen plasma treatment increases the wettability of the lens surface by the incorporation of oxygen in the polymer. This effect decays with time but is not wholly lost on prolonged storage. The mechanism of this decay appears to be a migration of oxidized material from the surface and is dependent on the storage conditions.

During this decay an anomalous transient increase in hydrophilicity was encountered which can be associated with the temporary return of highly oxidized material to the surface. This effect is observed in other polymers and can be shown to be temperature dependent.

The use of plasma polymerization as an alternative treatment was investigated and a number of materials produced with similar surface properties to the oxygen treated lens material. It was hoped that a coating would be generally applicable to a variety of lens materials.

Adsorption studies showed that the oxygen treated material has the property of reversibly adsorbing glycoproteins which may account for its performance in the eye. Some of the plasma polymer coatings gave a similar response.

DECLARATION

The contents of this volume have not previously been submitted for any higher degree and are my own original work except where reference is made to the works of previous authors.

ACKNOWLEDGMENTS

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CHAPTER ONE

INTRODUCTION TO CONTACT LENSES AND THE TEAR FILM

1.1 Introduction

Contact lenses are in wide scale use throughout the world, the exact number is uncertain but has been estimated to be 50 million (1). These are not only for correcting defects in sight but also serve as "bandages" for patients who have undergone eye surgery and can deliver drugs in a controlled way to eye tissues (2). The wide variety of materials is constantly expanding as researchers attempt to overcome the difficulties associated with placing an object made of an artificial substance in intimate contact with the delicate tissues of the eye.

Contact lens wearers can suffer from a number of problems brought on by the presence of the lens in the eye. It has long been known that the lens blocks the normal method of oxygen supply to the cornea (3) though the introduction of modern materials, such as hydrogels, silicone rubber, and siloxane acrylates, has largely overcome this problem. In addition measurements have been made that indicate that the presence of a lens can affect the chemical composition of the tear fluid leading to symptoms very similar to dry eye syndrome (4,5).

This thesis is concerned with the performance of hard gas permeable lenses which are a development of polymethylmethacrylate lenses incorporating a siloxane acrylate co-monomer to improve oxygen permeability (6). These are some of the more recent developments in lens materials, a field in which an enormous variety of synthetic polymers have been evaluated (7). The development of new materials has been, until recently, an empirical process; new types often being derived from materials originally designed for use in other biomaterials applications (1).

1.2 Biomaterials

A wide range of materials have been used in a variety of devices designed to be implanted or placed in direct contact with living tissues. These include metals, glasses, ceramics and polymers. The compatibility of these materials with their environment is an important issue (8-10) with particular reference to blood contact applications, which have been studied using both in vitro (11) and in vivo (12) techniques. The reaction of blood to these materials is however just one factor to be taken into account when considering biocompatibility; changes in the material induced by the body, such as degradation of polymers and the subsequent effect of the products of this process, and adhesion, whether intentional or not, are also important (13).

Metal surfaces usually have a thin layer of oxide which can influence protein and cellular interactions. It has been suggested that oxides with a high dielectric constant inhibit cell deposition in an aqueous environment and reduce protein denaturation. The behaviour of titanium, which forms such an oxide and shows good bonding with bone, supports this hypothesis (14).

The polycrystalline surfaces of metals used in implants exhibit defects (15) which are reactive sites and also points at which trace elements in the metal can concentrate, possibly producing an unexpected response from surrounding tissues. Roughness can be beneficial, as in the case of implants into hard tissues such as bones and teeth where this enables the stress on the implant to be spread over a larger area, or detrimental; e.g. when exposed to blood flow roughness can induce turbulence (16).

Corrosion of metals in the body is caused by electrolytic body fluids and is accelerated in situations where the device is under some load. This not only changes the chemistry and roughness of the material's surface but also the corrosion products can produce an adverse reaction in the surrounding tissues (17).

Glasses are used as implant materials as well as for cell culture substrates (18) but in both uses the surface chemistry and structure are the primary factors influencing the interaction of the item with the tissues. Bioactive glasses (19) and ceramics (20) have now been developed which form a direct bond, over a period of time, to the tissues in which they are implanted. An alternative to this approach is to use materials which can gradually be absorbed or metabolised by the body. Examples of this type of material include polylactic-polyglycolic acid sutures, which are metabolised to CO_2 and water, and porous calcium phosphate ceramics which are used as absorbable hard tissue implants (19).

A wide variety of polymers have been incorporated into implants with varying degrees of success. Polytetrafluoroethene (PTFE) has been used in soft tissue replacements and vascular grafts. In the first of these applications it was concluded that no significant changes in the polymer occurred over a period of several years whereas the suitability of PTFE for vascular grafts is in doubt since poor blood compatibility has been observed in some cases (21,22). Silicone rubber has been used for a variety of purposes (23,24) including contact lenses (25). Another lens material, polymethylmethacrylate, has also been used as a bone cement (26) and as a material for chest wall reconstruction (27). Polyurethanes exhibit the useful properties of flexibility and durability under stress and appear to be well tolerated in implants. The range of physical properties they can be given has given rise to considerable work on these materials (28,29). The interaction of polyurethanes with biological systems may be influenced by the fact that the surface of the material may be different to the bulk of the polymer (30).

Another class of polymeric materials which has been used in a variety of applications are the hydrogels. One such, Poly(2-hydroxyethyl methacrylate), has been used as a wound dressing (31), for repairing cartilage defects (32), and as a component of an artificial tendon (33). Hydrogels contain large quantities of water which can either be bound to polymer chains or can be present as structured ice-like units. It has been suggested that this structuring is related to the biological behaviour of the polymers (34,35). The high water content also leads to a very open and mobile polymer structure able to reorganize to minimise its interfacial energy (36) and to exchange materials, such as low molecular weight organics and ions, between the environment and the bulk polymer (37).

Though only a few of the materials mentioned above have found uses as contact lenses, the literature on this subject does bring out certain points relevant throughout the biomaterials field. Firstly, the surface properties of a biomaterial are at least as important as its bulk properties, since it is the surface which interacts with the body, and secondly that the environment in which the material is placed must be considered in order to understand the body's response to this foreign material. Therefore before considering the various materials which have been used for contact lenses it is necessary to examine the environment in which they are used.

1.3 The Tear Film

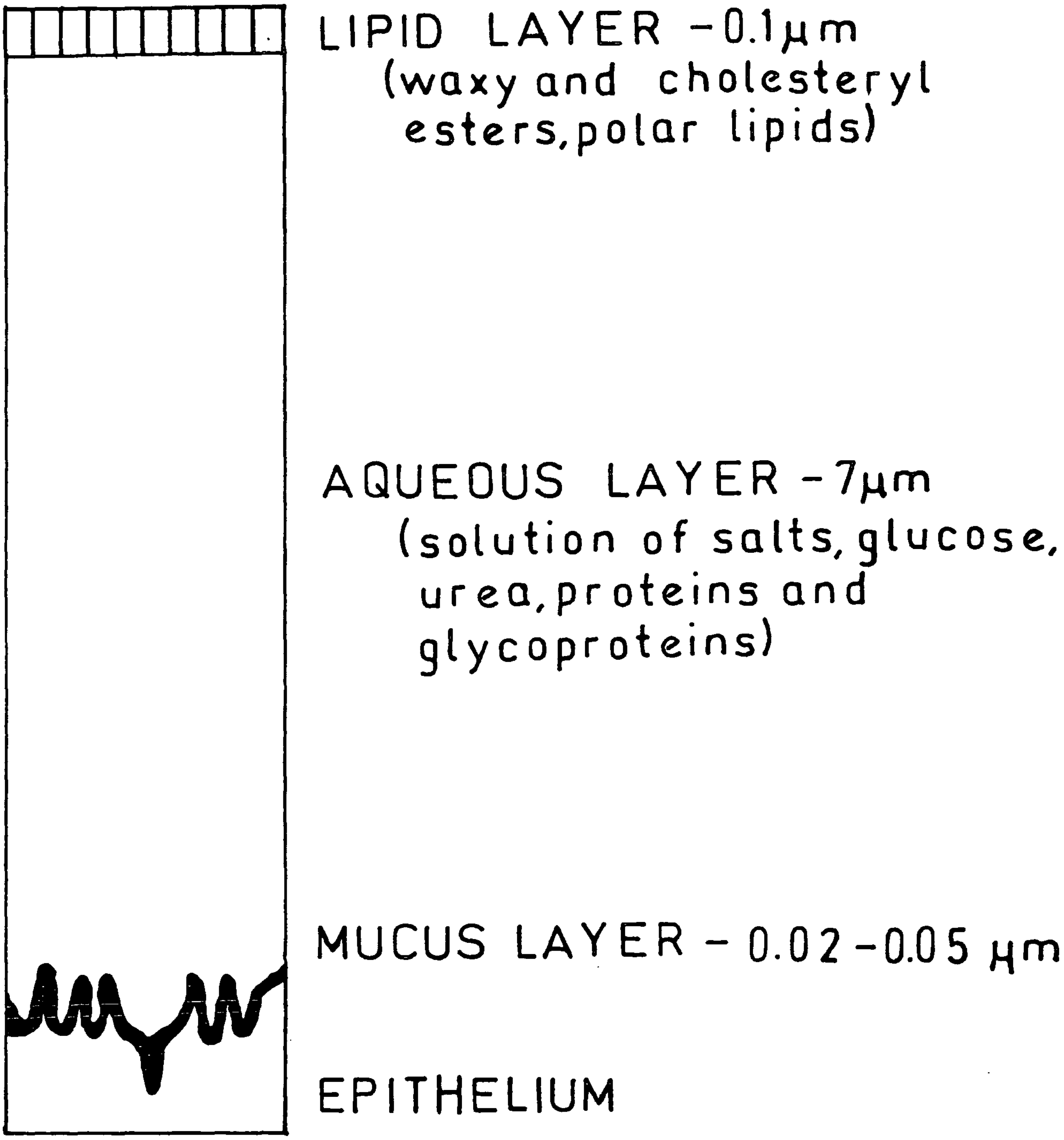
1.3.1 Composition and Structure

The tear film is composed of three distinct layers (38), figure 1.1. On the surface of the film is a layer of lipids with low polarity. These are derived from the Meibomian glands and are fluid at body temperature despite their high average molecular weight. Highly polar lipids are present in trace amounts (40-42).

The middle layer represents the bulk of the tear fluid. It is an aqueous solution of inorganic salts, glucose, urea, enzymes, proteins and glycoproteins (43) with some trace elements present in ionic form (44).

The lowest layer is a layer of mucin which coats the epithelium of the eye (45). Most of this mucin originates in the conjunctival goblet cells and is distributed over the cornea by eyelid motion during blinking. However the epithelial cells themselves produce small amounts of mucin which forms the foundation of the mucin layer. The mucin itself is a typical example of this type of glycoprotein consisting of a long polypeptide backbone with carbohydrate branches and ending with a sialic acid group (46).

Figure 1.1 Tear Film Structure.



1.3.2 Normal Functioning of the Tear Film.

When the eyelids close the lipid layer is compressed and the air-tear interface is destroyed. At the same time a layer of mucus is formed by the shear action between the eyelid and eyeball. As the eye opens an aqueous-air interface of high surface tension is created on which the lipids immediately spread. These are followed by a thin layer of mucin which also spreads across the surface originating at the eyelid edges (47). This combined layer has the effect of reducing the surface tension from 70 dyne/cm to about 40 dyne/cm. An additional function of the lipid layer is to retard the rate of evaporation of the aqueous layer. This it does very effectively, reducing loss of fluid to such a degree that only [illegible]% evaporates in one minute under normal conditions (48).

The mucin layer on the epithelium provides a hydrophilic base to support the aqueous layer (49). This is vital to the functioning of the tear film system since the corneal surface is hydrophobic (50) and is unable to sustain a continuous aqueous film without a coating of mucus. It has been shown that epithelial mucin can be adsorbed onto hydrophobic surfaces, such as PTFE, to render them hydrophilic (50,51). The mucin is spread in a very thin layer whose surface morphology therefore closely resembles that of the cornea. That is to say that it follows the contours of the numerous small projections, called microvilli and microplicae, which form the surface of the epithelium.

The mucin has a further role to play in the normal functioning of the eye. Proteins, lipids and other debris are deposited on the surface of the eye from the aqueous layer or from external sources. Through the shear action of the eyelid during a blink contaminated mucus is rolled up into threads which are gradually moved over a period of several blinks into the lower and upper fornix. From there the threads are washed by tear fluid through the puncta and into the nasal passages (52,53), figure 1.2.

1.3.3 Tear Film Breakup

In a normal eye the tear film is stable for between 15 and 50 seconds after which it breaks up and dry spots appear on the eyeball (55). The time taken for this to occur is referred to as the tear film breakup time (BUT). This break up has been explained by several processes.

In the first mechanism Holly and Lemp (51)(55), figure 1.3, propose that lipids from the uppermost layer of the tear film migrate to the epithelial surface, so contaminating the mucin layer and rendering it hydrophobic. Support for this hypothesis comes from the observation that the contact angle of the tear fluid at the boundary of a dry spot on the eye is greater than 30°, and that the contact angle of water on lipids

Figure 1.2 Tear Flow in the Eye.

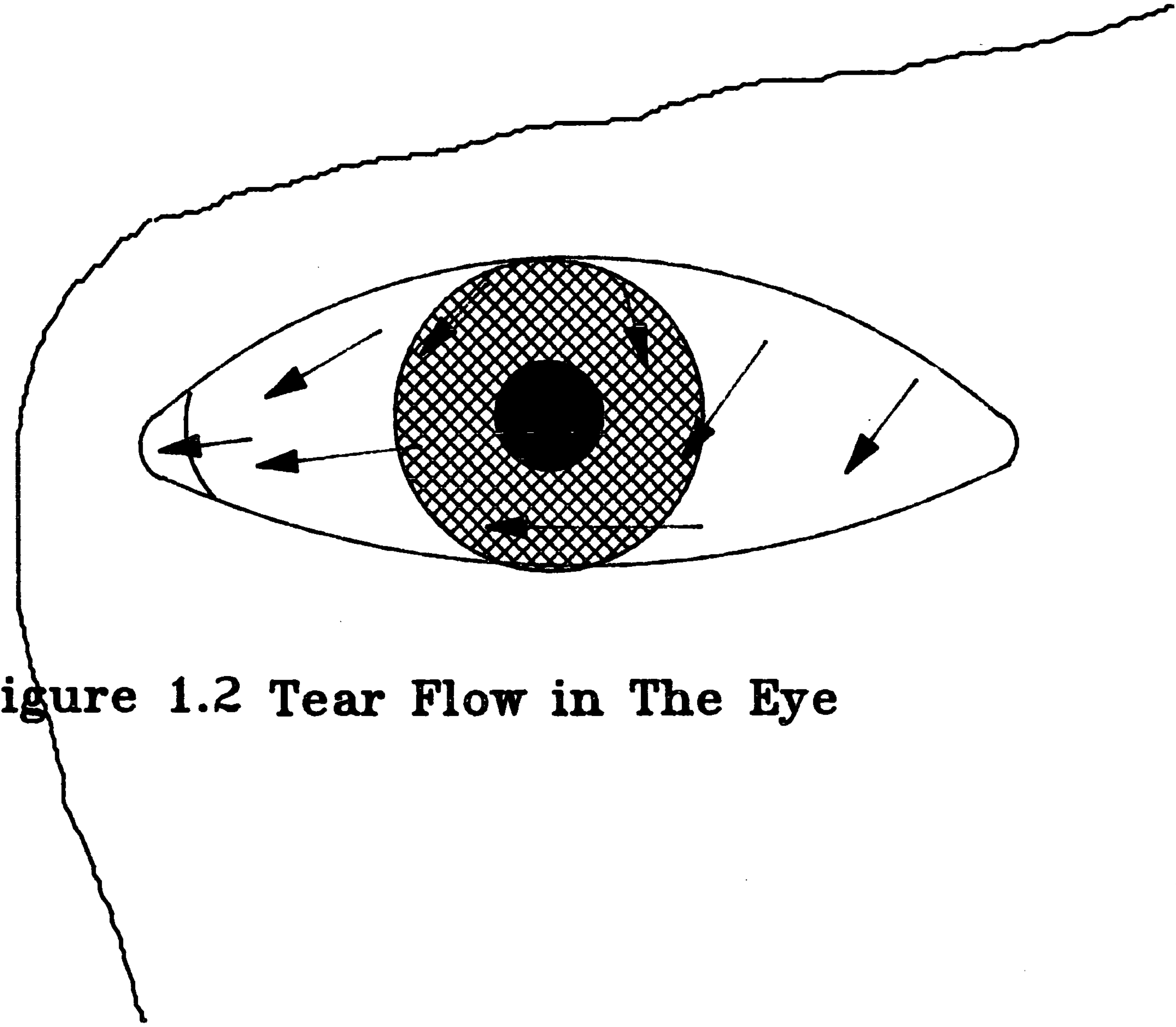


Figure 1.2 Tear Flow in The Eye

which have been adsorbed onto a surface is 50°. The process of lipid transfer to the surface would be accelerated by local thinning of the tear film due to surface tension gradients caused by uneven distribution of the lipids on the tear film surface. As the meniscus recedes across the eye it leaves lipids behind so heightening the effect. The contaminated mucin is then removed during the next blink preparing the eye surface for the new tear film. However Lin and Brenner point out that the surface tension gradients are in directions which would tend to oppose the proposed instability (56). Instead they believe that the rupture of the entire tear film is due to coherent London dispersion forces, with or without the assistance of gravity. This would occur at places where the local film thickness is in the order of ≈2μm. Thin areas will occur where there are gross irregularities in the epithelial surface or where there are deposits of lipids or foreign particles. They show that surface tension and viscosity are stabilizing factors. This theory does not however, take into account the layer structure of the tear film, treating it instead as a homogeneous fluid. This theory was tested by Sharma and Ruckenstein (57). They found that the dispersion forces were not strong enough to cause the rupture of tear films of thickness ≈1 to 10 μm in the normal (BUT) observed in patients.

Recently Sharma and Ruckenstein have devised their own mechanism for tear film break up (58). They discount Lin and

Brenner's dispersion model from their own observations. They also disagree with the idea of lipid contamination. This is because although lipids do migrate into the aqueous layer very quickly they are relatively insoluble. So the concentration in the aqueous layer is low and since the adsorption of lipids on the mucus layer is energetically unfavourable there is very little deposition of lipids. Lipid deposition can be shown to increase the interfacial tension, using the Gibbs adsorption equation (59), but not sufficiently to make the mucin layer non-wettable. Additionally, tear film rupture still occurs in the event of a complete destruction of the meibomian gland opening (60), which is the source of these lipids.

Therefore Sharma and Ruckenstein have looked at the mucin layer as a possibility for the cause of the break up. The mucin is deposited in a layer during the blink. This layer will be uneven due to the uneven shear distribution on the ridged surface of the cornea. Van der Waals dispersion forces act on the irregularities to amplify the inhomogeneities. This eventually exposes the hydrophilic epithelium resulting in the rapid breakup of the aqueous layer. In the absence of the mucin the migration of proteins and lipids to and their adsorption onto the eye is energetically favourable since this tends to lower the cornea- aqueous layer interfacial tension. Since this is insufficient to permit complete wetting of the hydrophobic areas caused by pin- point ruptures in the mucin these areas are amplified, so aiding in the breakup of the

Figure 1.3 Holly and Lemp Breakup Model

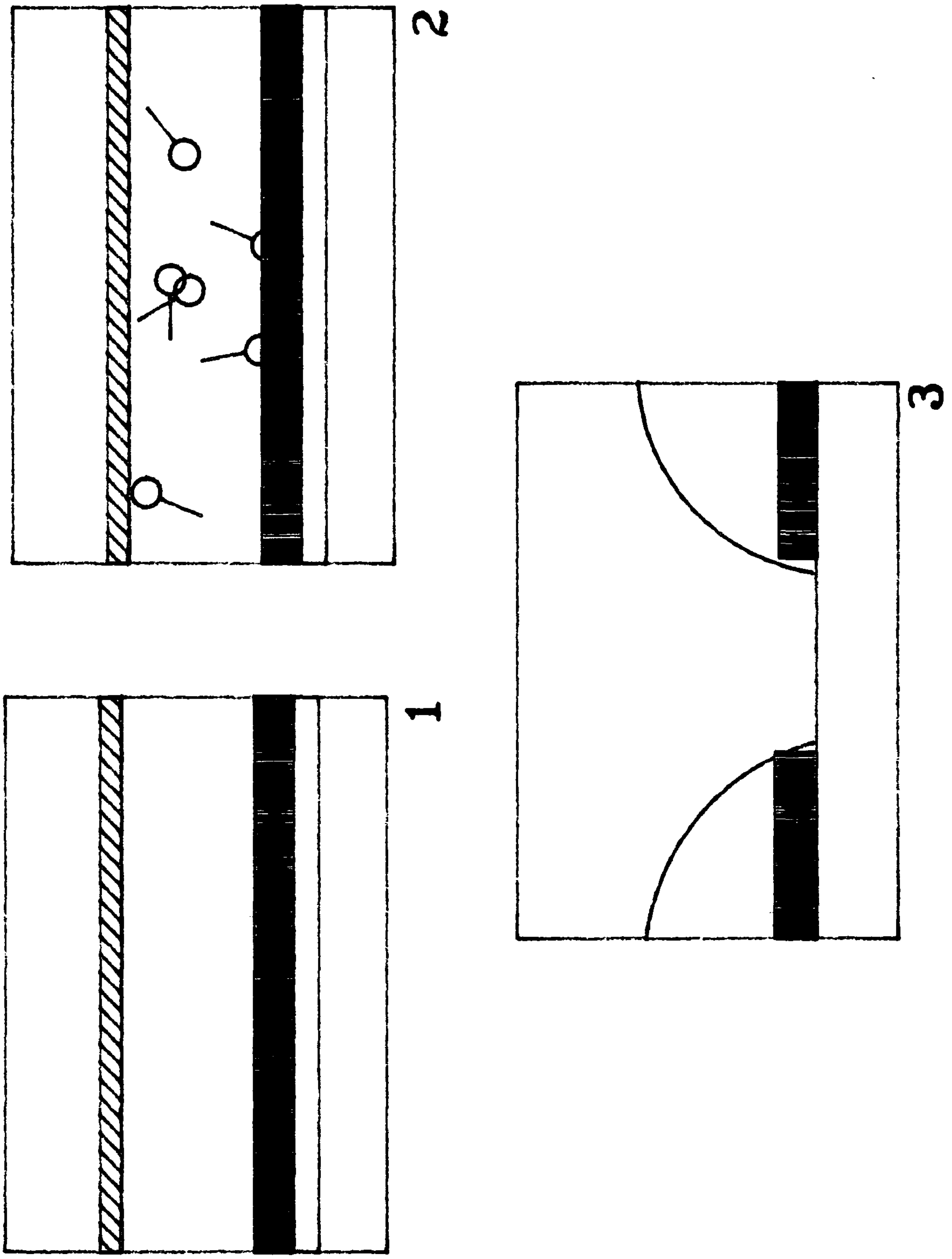


Figure 1.3 Holly & Lemp Breakup Model

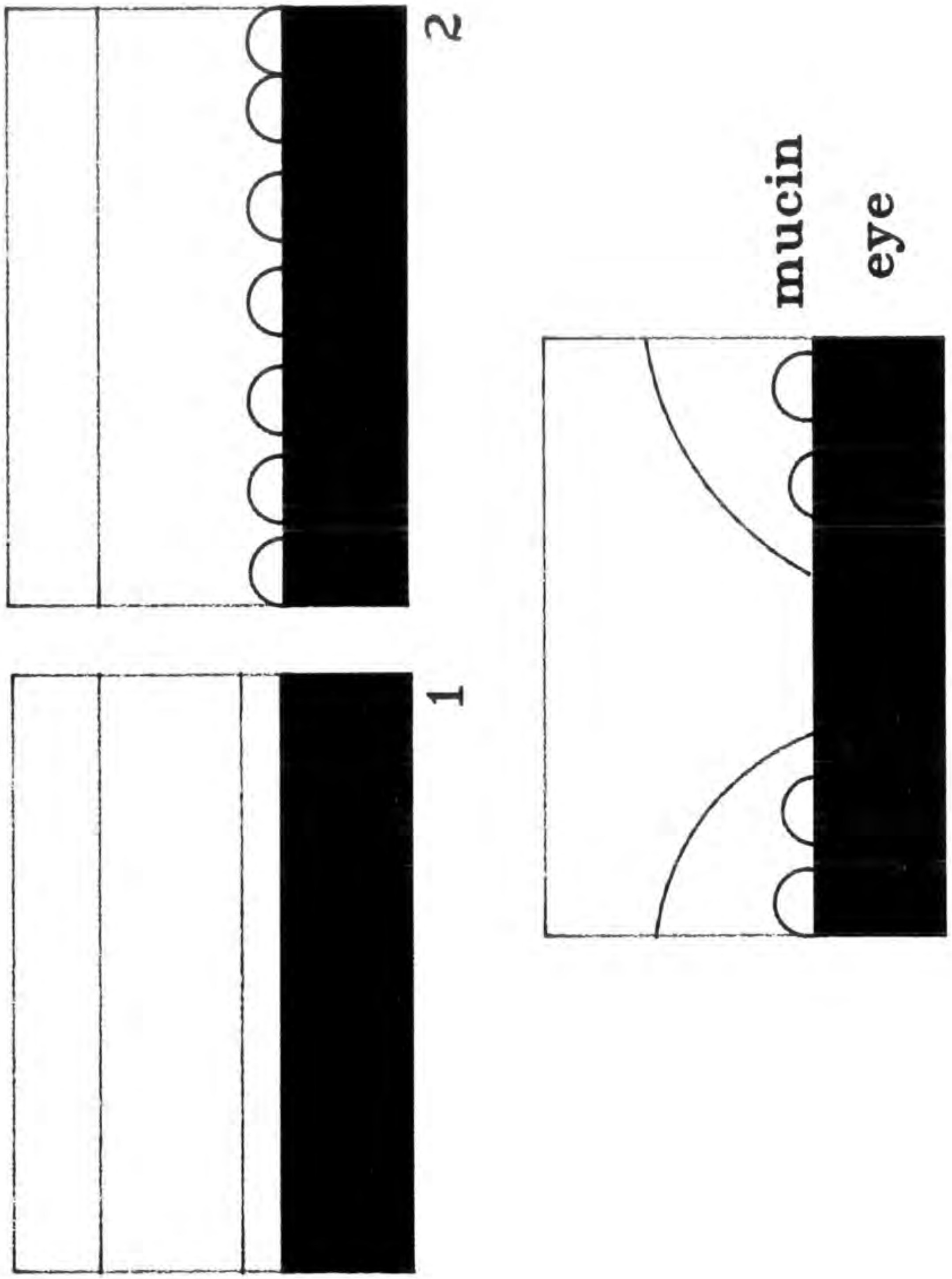
tear film. This also accounts for the observed contact angle at the tear's edge.

1.3.4 The Lens-Tear Film System

Hard gas permeable contact lenses are relatively hydrophobic (contact angle with water ≈80-100°) compared with clean epithelium (contact angle 50°) (50). However soon both surfaces become coated with a layer of mucus and can be wetted by the tear fluid. The initial period of adaptation can be eased by the use of an artificial tear solution containing a suitable wetting agent (51).

In a normal eye there is sufficient mucin to coat the lens in the same way that the epithelium is coated and in this case the BUT should be normal. However for patients with certain types of dry eye syndrome this may not be the case. This is particularly true if the eye suffers from a deficiency of mucin, which can be caused by a number of conditions (60) such as hypovitaminosis A, ocular pemphigoid, Stevens-Johnson syndrome, trachoma, chemical burns and certain forms of drug induced disease. These conditions are characterised by a decrease in BUT. Additionally the contact lens affects the lid-globe fit so that the distribution of mucin by the blink is uneven and reduced, which also results in a decrease in BUT.

Figure 1.4 Sharma and Ruckenstein Breakup Model.



1.4 Contact Lens Materials

The concept of a contact lens seems to have been first expounded by Descartes in his "Discources" of 1636 in which he suggested that a lens could be placed directly on the cornea. However probably the first use of a contact lens to correct a visual defect was by a Zurich opthalmologist called Fick in 1888.

This lens was made of glass and was of a scleral type, that is to say that the lens was large and rested on the sclera or white of the eye. The lens had no optical power of its own but relied on the liquid layer trapped between it and the cornea for its correcting ability (61). Unfortunately this type of lens is incapable of correcting the more severe errors of vision and so they were soon being ground to have their own optical power. These lenses were still of the scleral type and had poor comfort and tolerance properties. These problems arose because the cornea is one of the two areas of living tissue in the body which do not have a direct blood supply, the other being the cochlea of the ear. The corneal metabolism is maintained by diffusion from the limbal vessels around it and by diffusion of gases dissolved in the precorneal tear film. Restriction of the tear flow over the cornea reduces its oxygen uptake resulting in oedema, which produces swelling of the cornea and fogging of vision (62-64).

It was not until the late 1930s that polymeric lenses in the form of perspex were introduced. These lenses were still of a scleral type until the late 1940s when the first corneal lenses, which rest solely on the cornea, were produced. Perspex is light, easily shaped and has good optical properties. However it has poor oxygen permeability and so to compensate for this these lenses were, and still are, fitted so as to allow the tear fluid to flow under the lens.

In response to the need for materials with greater oxygen permeability a range of so called soft lenses has been developed. These are hydrogels made of slightly crosslinked hydrophilic polymers and copolymers that absorb substantial amounts of tear fluid. They include materials such as poly(2-hydroxyethylmethacrylate) (HEMA), and copolymers of this with methylmethacrylate, N-vinylpyrrolidinone (NVP), and glycerol monomethacrylate. Since hydrogel lenses conform very closely to the corneal surface the amount of oxygen transferred to the cells of the cornea by tear flow is very small and the oxygenation of the the cornea is largely through diffusion of gas across the lens (65).

Unfortunately hydrogels have several disadvantages in that they are more easily damaged than hard lenses, are more difficult to fit and require greater hygienic care, since bacteria can penetrate into the polymer and grow in the attractive environment it provides.

An alternative solution to the problem of oedema is the use of hard gas permeable materials such as cellulose acetate butyrate, and copolymers of methylmethacrylate and methacrylate derivatives containing siloxane moieties. These materials have oxygen permeabilities which, whilst lower than those of hydrogels, are sufficient for day to day wear, and in addition they are stronger and more durable than hydrogels (66). Their main disadvantage is that since the materials have generally poor wettability they can give rise to considerable patient discomfort, particularly in the early stages of a patients adaptation to the lenses. This is due to the rapid break up of the tear film leaving a dry lens surface, which in turn leads to a foreign body sensation in the eye. Poor wetting of the lens surface can also result in increased deposition of material from the tear fluid.

There is therefore a need for a technique which can improve the surface properties of this type of materials. Since the siloxane acrylate group of materials has been developed to possess a number of desirable properties it is preferable that any technique should only affect the surface and should leave the bulk of the lens unaffected.

1.5 Aims

The main aim of this thesis is to investigate the surface treatment of hard gas permeable contact lenses formed from siloxane acrylate materials. The goal of such treatments being to overcome the poor tear film stability found on such materials and to improve the resistance of these lenses to the formation of deposits of material from the tear fluid. To this end the following chapters present an examination of the methods of treatment and the analysis of the subsequent surfaces in terms of both their chemical composition and their surface properties.

In chapter two the techniques of surface modification are examined as are the various techniques available for the analysis of treated surfaces with a view to determining those most suitable for this application.

Chapters three and four examine the effects of plasma modification with oxygen on a typical siloxane acrylate. The changes induced in the chemistry of the surface are studied together with the wettability and frictional properties of the modified material. In addition the stability of the treatment is assessed and an attempt is made to elucidate the changes occurring as the surface ages.

In chapter five a number of plasma polymer surfaces are prepared and examined with respect to their suitability as coatings for hard contact lenses. Coatings derived from silicon containing monomers are considered in comparison to the plasma oxidized surfaces studied in chapter three. Polymers derived from N-vinyl pyrrolidinone are examined as a means of applying a hydrogel coating to a hard lens. The plasma polymer of allyl alcohol is used to produce a surface to which phosphoryl choline is attached. The intention here being to achieve biocompatibility by mimicking the tissues of the eye.

Finally in chapter six the adsorption characteristics of the surfaces produced are examined in an attempt to assess the resistance of these materials to deposition of organic material in the eye.

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CHAPTER TWO

SURFACE MODIFICATION

AND

ANALYSIS

2.1 Surface Modification

2.1.1 Introduction

The last forty years has seen the introduction on a large scale of many synthetic polymers. These have a variety of useful properties not found in natural materials, but they often have very poor surface properties with respect to their intended use, such as poor wettability with inks and adhesives. These problems often arise from a lack of polar groups in the polymer molecules. The problem could, therefore, be overcome by some form of surface treatment that would form polar groups either by addition to or modification of the surface. As a result of this demand surface modification techniques have become important to a range of material applications (1).

At first chlorine was tried, but due to economic and technical reasons the process was soon abandoned in favour of more efficient processes. Exposure to ozone and ultra-violet radiation has been used but the process is rather slow. Oxidation by chromic acid solutions (2) is very effective but suffers from the drawback of the hazardous nature of the chemicals, their possible inclusion in the bulk polymer, and the need for washing and drying the treated polymer. It is, therefore, not suitable for large scale use but it does have the advantage that the whole surface is treated at once and cavities and the interiors of objects can be treated effectively.

Treatment of hydrocarbons using chromium VI oxide in a mixture of acetic acid and acetic anhydride, has been used as a means of hydroxylating the substrate in solution (3) and the same reaction can be applied to a surface. In the case of polypropylene this results in a reduction in the contact angle with water of 10° after 10 hours (4). However this process has the drawback that there is a significant weight loss during the reaction. This is due to the break up of the polymer structure and the dissolution of modified polymer into solution.

Even chemically very inert materials can be treated using conventional chemical techniques. Polychlorotrifluoroethene (PCTFE) has been treated using a variety of lithium reagents to insert alcohol, aldehyde and carboxylic acid groups into the surface (5). As an alternative to direct reaction with the surface recent work (6) has utilised the reduction and crosslinking reaction of the benzoin dianion to produce a thin defluorinated layer on the PCTFE. This layer can then be reacted further to give specific functionalities such as halogen, hydroxyl, amino and carboxylic acid groups. One advantage of this technique is that the reaction time is only 15 minutes and the thickness of the modified layer can be controlled down to a minimum of 150 Å.

With all these solution state techniques there is the concern that solvents or reagents may be adsorbed into the polymer and later leached out into the eye. The use of such a method to surface treat contact lenses would therefore require careful post treatment purification of the lenses before use.

The aim of various heat treatments is to heat the surface of the polymer using hot air, infra-red radiation or by direct application of a flame, whilst keeping the interior of the polymer cold. This is extremely difficult in the case of small objects or thin films. Additionally the extent of treatment is not easily controlled and generally causes oxidation extending into the bulk of the sample (7-11).

Plasma techniques avoid the use of solvents and can be very surface specific. For the treatment of polymeric materials there are three main processes, corona and glow discharge modification and polymerization. Unless otherwise noted all plasma treatments used in this work are glow discharge processes.

Corona discharge is now commonly used for plastic film. The actual mechanics of this technique are very simple and make it ideal for continuous processing (62). A corona is produced by setting up an electric field between two electrodes under the appropriate power and pressure conditions. Often this means using a discharge in air at atmospheric pressure. The discharge can be induced by either a direct or alternating current and provided the gap between the electrodes is sufficiently small these will have the same effect. Whilst this technique is quick and solvent free, control of the chemistry of the modification is difficult and heating of the substrate may occur.

The glow discharge treatment of polymers has been the subject of considerable research (12). The major virtues of this technique are that it involves clean reactions and takes only seconds to achieve the result desired, whilst producing profound changes in the surface properties of the material. Additionally the overall bulk properties (optical and electrical characteristics, tensile strength, etc.) for which it was originally chosen remain unchanged. Though a vacuum system is required the operating pressures are moderate (0.1-0.01 torr) and therefore the necessary equipment is relatively inexpensive. The lack of solvents in the process means that reactants are unlikely to be absorbed into the polymer and later released. With careful control of the plasma conditions undue heating or ablation of the substrate can be avoided and the technique can be adapted to either batch or continuous processing (61), unlike corona this technique is not limited to thin film substrates. In the case of a glow discharge modification the thickness of the modified layer has been estimated to be in the range of 0-10μm (12) depending on the conditions of the plasma (pressure, power, gas, flow rate), though in the case of a plasma polymer coating a thick film may be brittle and discoloured (61). However the surface properties of a polymer sample are determined solely by the composition of the outermost few monolayers, which means that the surface chemistry of a treated sample is effectively governed by the modified material. These qualities make plasma modification and plasma polymerization ideal methods for treating contact lenses whose oxygen permeability and optical properties have already been carefully perfected and must be preserved. Therefore plasma treatment has been used in this work as the primary means of producing modified surfaces.

2.1.2 Plasmas

The term plasma refers to the partially ionized gaseous state consisting of molecules, atoms and ions in both ground and excited states (including metastable states) and electrons such that the concentration of positively and negatively charged species results in overall electrical neutrality.

Historically the use of gas discharges really began in the 19th century. Both the work of Crookes (1879) and Thomson (1897) on the properties of cathode rays emitted from discharge tubes were connected with the discovery of the induction coil by Ruhemkroff in 1851 (13). These initial experiments opened up the pathway for research into the nature of such discharges. The role of the electron in causing ionization and conduction and the nature of other charged species present were established by the early 1900s. In 1928 Langmiur coined the word plasma to denote the state of ionized gases formed in the electrical discharge (14).

Plasma are characterized by their electron density and the average electron energy; numerous forms of plasmas can be found, both in nature and in the laboratory dependant on these two parameters (15). Two types of plasma are of most interest to chemists, these are the "hot" and "cool" plasmas.

The "cool" plasma is a non-equilibrium plasma found in a glow discharge experiment characterized by electron densities in the range 10^{9}-10^{12} cm^{-3} with average electron energies of 1-10eV. The electron temperatures in these plasmas are some two orders of magnitude greater than the Boltzmann temperatures of the ions and molecules which are roughly ambient.

This is in contrast to the "hot" or equilibrium plasmas with similar electron densities. This class of plasma is characterized by a very high gas temperature which is approximately equal to the electron temperature. Due to the low thermal stability of organic molecules this type of plasma finds its use in the analysis of materials. The sample is fed into the high temperature plasma where it is broken down into atoms; atomic absorption is then followed by an associated emission, where analysis is achieved from the emission spectrum

(16). This technique is known as inductively coupled Plasma-Optical Emission Spectrophotometry (ICP-OES), and can be applied to the analysis of inorganic and metal systems as well as organic samples (17).

The "cool" plasma has found a use in several areas:

(i) Synthetic Organic/organometallic Chemistry

The work in this area has been dominated by Suhr and coworkers (18). Initial experiments were hampered by the very small yields obtainable through plasma synthesis; more success was achieved by the selection of experimental conditions which avoided high electron energies and elevated temperatures, which reduced the amount of damage to the organic molecule. All organic vapours, liquids or solids react in a glow discharge to some extent, so that an almost infinite number of organic plasma reactions are possible, although percentage yields may vary from a very small to an almost 100% conversion. The amount of energy available from the plasma, in comparison to conventional and photochemical techniques (≥10eV cf.. 4 and 6eV respectively (19)), means that super-excited states can be obtained which are beyond the reach of other synthetic methods and this makes plasma synthesis a very useful tool.

(ii) Surface Modification

A second major area of interest is the application of plasma techniques to the surface modification of polymers. This interest falls into three groups:

(a) Surface grafting (20) where the polymer surface is exposed to a plasma to create reactive sites. This activation of the surface initiates a conventional free radical polymerization process at the surface when the graft monomer is introduced into the reactor, there being no plasma present at this time. For example, attention has been placed on the modification of surfaces for improved wettability (21) and flame retardancy (22) purposes.

(b) A technologically important area of the use of "cool" plasmas for surface modification is in the micro-electronics industry, where a plasma, particularly of oxygen and/or halogenated gases, is used to selectively etch or remove organic polymeric resists (23) in the production of integrated circuit chips. This is a particularly active area of research given current trends towards a totally vacuum lithographic process.

(c) In the third group surface modification is achieved by the direct use of an inert or reactive, but non polymerizing, gas. The effects of active species and UV radiation produced in the plasma include production of unsaturated sites (24), oxidation of the polymer surface, often including oxidative degradation (25-28), production of a hydrophilic surface to enhance wettability (24,25), production of a gel-like surface layer (24) and improved printability and adhesion of polymer films (26,29,30).

(iii) Polymer Synthesis

The third area of application, one which perhaps equals the interest of plasma modification, is that of in situ polymer synthesis (31). The plasma polymerization of organic and organometallic compounds has been a particularly active area of research, especially since the process offers several advantages over conventional polymer synthesis, including the often superior nature of the deposited film in both physical and chemical properties. Starting compounds do not need to contain functional groups normally associated with conventional polymerization and this coupled with the one step synthesis in a "clean" environment makes plasma polymerization a particularly attractive method of polymer synthesis. It should be mentioned however that plasma polymers are not polymers in the normal sense. They contain no repeat unit and indeed the structure of the "polymer" need not resemble the monomer. It is perhaps better to consider these materials as highly crosslinked networks whose composition is related to, but is not necessarily the same as, the starting material.

2.1.2.1 Fundamental Aspects of Plasmas

Theoretically a plasma by definition must be electrically neutral, a condition which is satisfied when the dimensions of the discharged column are greater than the Debye length $(\mathrm{lambda})_D$ (15),

$$(\mathrm{lambda})_D = ((E_o\ kTe)/(ne^2))2\tfrac{1}{2} \tag{2.1}$$

which defines the distance over which a charge imbalance may exist, where E_o is the permitivity of free space

k is the Boltzmann constant

T_e is the electron temperature

n is the electron density

and e is the charge on the electron.

The ionization of molecules within the plasma zone is essential if the discharge is to be initiated and maintained. Electrons within the plasma are accelerated by the electric field and produce further ionization by collisions with other species. Collisions between an electron and a gas molecule result in one of two states; an elastic collision in which very little energy is lost or transferred by the electron (15), or an inelastic collision which results in the transfer of usable energy from the electron to the molecule. When the electron does not have enough energy to cause ionization of the molecule, the transfer of energy in an inelastic collision results in the production of a higher energy state of the molecule where the excess energy can be stored in rotational, vibrational and/or electronic excitation. It is from such inelastic collisions that electron energy is continuously lost. After collision the electron gains energy form the electric field, the amount of kinetic energy picked up before further collision is dependent on the mean free path of the electron in the gas (32) which is connected to the pressure of the system; at too high a pressure the mean free path is very small and the amount of energy gained is not very large. Too low a pressure results in a long mean free path such that gas collisions are not important. This results in a typical working pressure range of 0.05-10 torr. At charge densities of around 10^{10} cm^{-3} it has been calculated that the average lifetime of an electron against recombination is around a millisecond (33).

The average velocity, v, of an electron between collisions is given by:

$$v = ((Me^{2} E(\text{lambda}))/m^{3}) \qquad (34) \qquad 2.2$$

where M is the mass of the heavier particle

e is the charge on the electron

E is the electric field

lambda is the electron mean free path

and m is the mass of the electron .

Expressions describing the electron energy distribution in terms of energy input, discharge dimensions and gas pressure lead to a Maxwellian distribution of electron energies (33) .

Such numerical solutions are only possible for simple systems, but the form of the distribution has been analysed experimentally by probe measurements (35) and direct electron sampling (36). From figure 2.2 it can be seen that the average electron energy, in an inert gas or hydrogen, will be in the range 2-3eV (32), i.e. the energy distribution is such that that the electrons are more effective at producing excitation than ionization. In plasmas of organics average electron energies of around 7-8 eV are found. In fact neutral species dominate, the degree of ionization being low, 10^{-4}-10^{-7} cm^{-3} (18). Since only the electrons in the tail of the distribution will be effective in producing ionization, since ionization potentials are typically 10 eV or more, it may be expected that some of the major chemistry occurring in the plasma is connected, not with ionization but with excitation; since typical bond dissociation energies of organic compounds lie well below 10 eV.

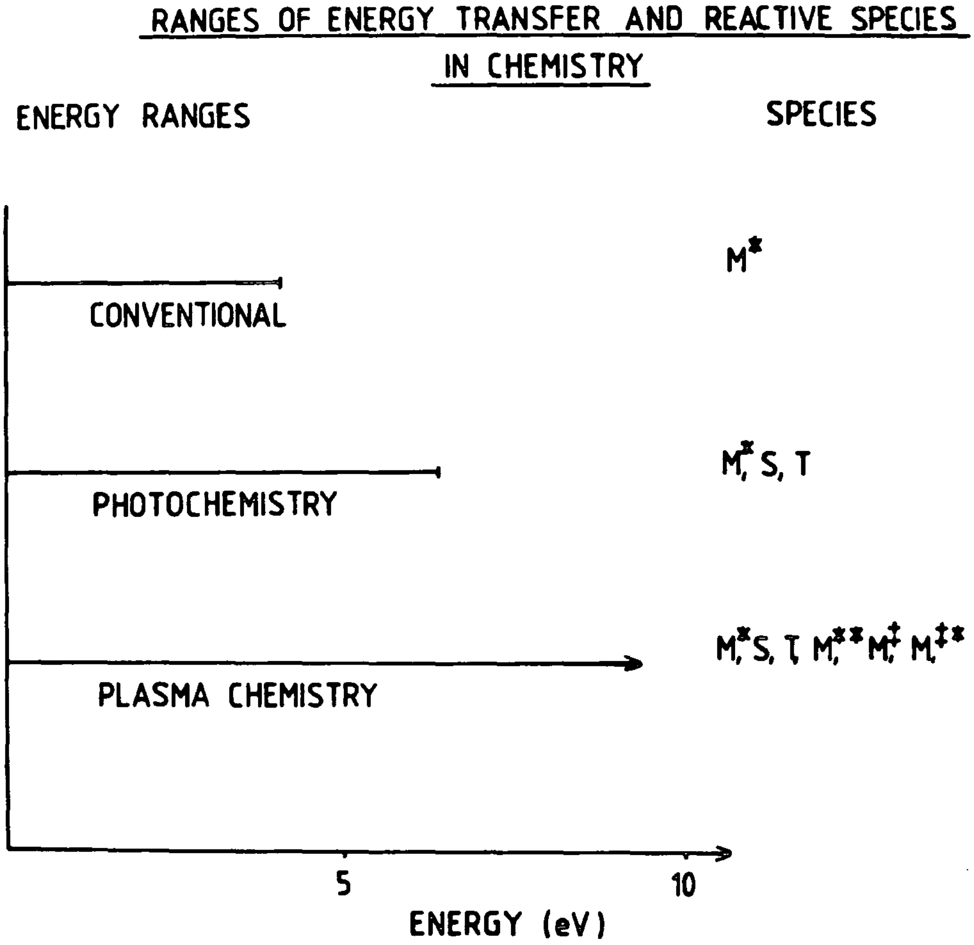
The collision process, shown in figure 2.1, results in the emission of electromagnetic radiation produced during the de-excitation of the various excited species that occur. Some of this output is in the visible region giving rise to the term "glow discharge" and the characteristic colours of different plasmas. However most of the radiation is in the UV/vacuum UV region, as has been shown for argon plasmas (37). This component has a role to play in the surface modification of polymers since it permits a transfer of energy to deeper regions in the surface than those which can be accessed by direct impact transfer. Both the IR and visible components are absorbed, but the IR radiation, which can be strongly absorbed, is dissipated through thermal reactions (38).

2.1.2.2 Plasma Techniques

In general there are three aspects which are of interest; the source of the electrical power used to sustain the plasma, the coupling mechanism and what can be described as the plasma environment. This is illustrated schematically in figure 2.2.

From Figure 2.2 it can be seen that there are two main types of coupling mechanisms, i.e. direct and indirect (39). In the direct method, resistive coupling, the glow discharge is initiated between electrodes, which consequently are part of the plasma environment and may therefore be deposited on if any polymer is formed. The indirect method, inductive and

Figure 2.1 Collision Processes in a Plasma



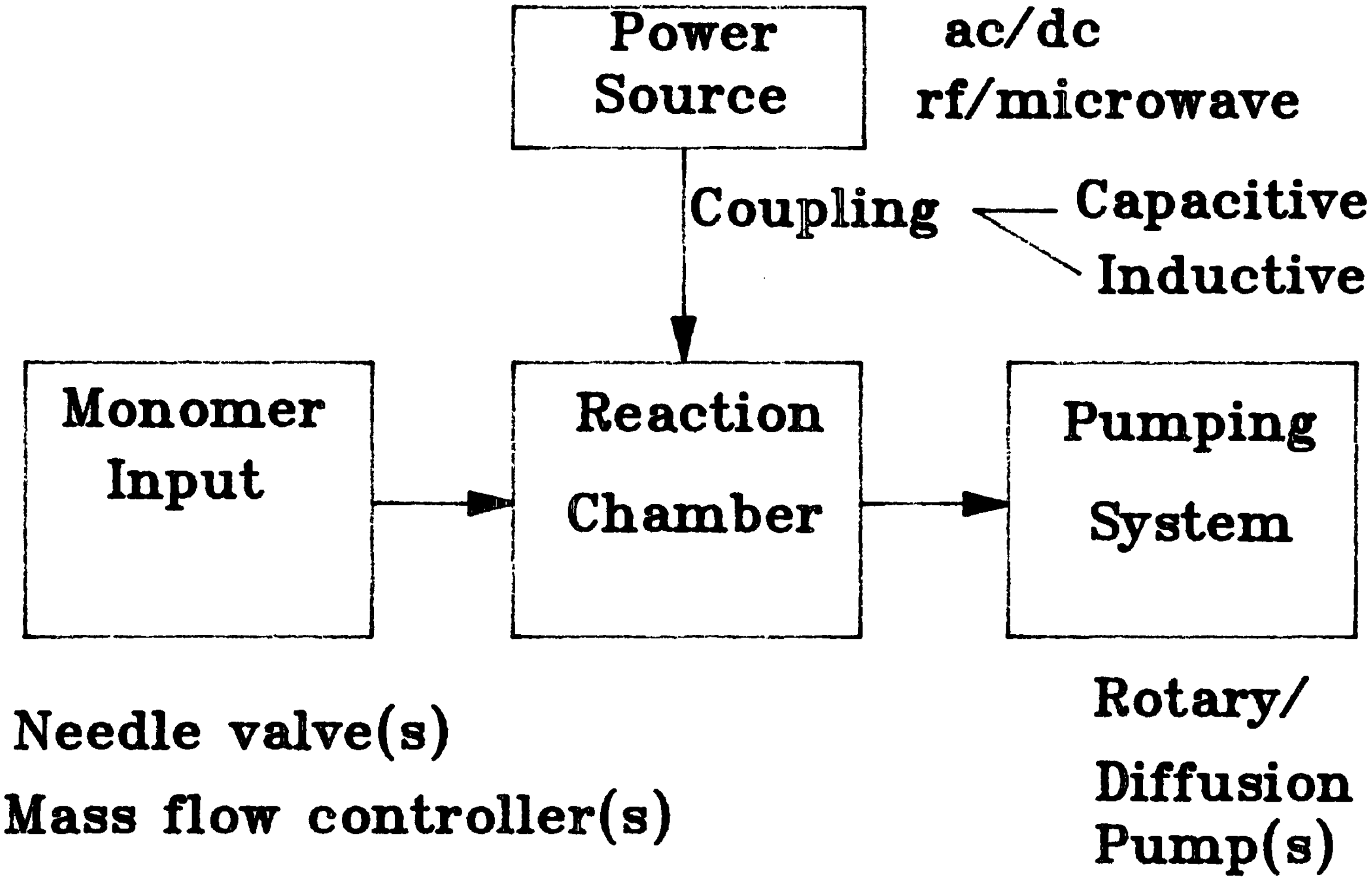


Figure 2.2 Elements in a Glow Discharge Experiment

capacitive coupling, allows the plasma to be formed by an apparatus which is isolated from it. This is achieved by means of a coil wound round the reactor or by use of external electrodes. Microwave discharges may also be excited inductively using a tuned cavity.

Indirect coupling mechanisms can only be used however with frequencies greater than 1MHz (18); below this frequency direct contact of the electrodes with the plasma is necessary for sufficient energy to be transferred to maintain the plasma. With internal electrodes, and low pressures, experiments have been performed over a wide range of frequencies from the acoustic to microwave region. Yasuda et al have employed frequencies of 60Hz, 10kHz and 13.56MHz (40), though there have been comparatively few studies of the effect of the exciting frequency on the nature of the product of the plasma (41).

The main operating parameters of a glow discharge experiment are those of power input and operating pressure. These typically vary form 0.1 watt to a few kilowatts and between 0.1 torr to one atmosphere respectively. Operating pressures using an RF discharge can range from 0.05 to 1 torr whilst power input is in the region 0.1W to 150W, using commercially available equipment. Low power levels (<1.0W) are generally difficult to sustain, but when using RF power a stable plasma can be accomplished by pulsing the power input.

Microwave discharges are less stable at low pressures. The use of an increased pressure leads to an increase in the gas temperature which can cause decomposition of organic species and is therefore not a preferred method for plasma polymerization. At higher power levels special cooling systems may be necessary, especially for the electrodes in a DC discharge. The use of DC does allow pressures of up to 1 atmosphere though this will again lead to an increased gas temperature. This factor together with the acceleration which ions in a DC plasma experience limits the utility of DC discharges in plasma chemistry.

Low frequency and DC discharges are generally characterized in terms of the voltage and current supplied to the electrodes. Typical operating voltages are in the range 10-100V and 1A at pressures of 1 torr. For RF and microwave plasmas the situation is less straightforward, the requisite instrumentation is needed to measure the power in the plasma, and to match the impedance of the generator with that of the coil volume in order to maximize the power transmitted to the plasma.

2.2 Techniques for Surface Characterization

Using plasmas the outermost surface of a material can be treated to give desirable properties. Additionally this can be achieved in such a way as to only affect these uppermost layers which leads to certain problems in studying the effects of such processes. Many forms of conventional analysis are of little or no use since the amount of modified material is too small to be distinguished from the bulk of the sample. In the case of a plasma polymer however a certain amount of information can be obtained if it is possible to produce a sufficient quantity of material.

2.2.1 Microanalysis

Micro analysis can be performed on such a plasma polymer which can be scraped from the walls of the reactor. It will however be hampered by the relatively insoluble nature, due to the high degree of crosslinking, of most of these materials. Also the results of such an elemental analysis should be regarded with some caution since the inclusion of some material from the substrate during collection of the sample is possible.

2.2.2 Infra-red Spectroscopy

Infra-red spectroscopy can be used to analyse plasma treated materials. In the case of a modified surface no difference will be seen between the untreated and treated samples using transmission infra-red unless the treatment is very extensive and has penetrated well into the bulk of the sample. However a film of plasma polymer may studied in this manner if supported on a suitable medium. The complex structure of plasma polymers makes a precise interpretation of the spectrum difficult, though useful information concerning the general nature of the material can be derived (42).

2.2.3 Nuclear Magnetic Resonanace Spectroscopy

Nuclear magnetic resonance (NMR) is another technique which is unable to study a plasma modified surface due to the small amount of treated material and its intimate attachment to the bulk of the sample. In addition, since plasma polymers are essentially insoluble in most organic solvents, solution state NMR cannot be directly applied to the analysis of the polymer. However solid state NMR is capable of providing some data (43) such as the presence of both saturated and unsaturated environments. For example, using plasma polymers derived from monomers labelled with ^{13}C, it has been possible to distinguish the relative degrees of unsaturation of films produced from a variety of hydrocarbons (44).

In general it is more useful to consider surface techniques when plasma modified materials to be investigated. Possibly the simplest of these is the contact angle.

2.2.4 Contact Angles

A drop of liquid resting on a surface will form a finite angle between the air liquid interface and the solid surface, this is known as the contact angle θ (45). It is one of the oldest techniques used in the characterization of surfaces but has the advantages of its simplicity, speed and low cost. It does have several disadvantages however. Contact angle measurements are artefact prone. Inaccuracies can be induced by contamination of the measurement liquid, by surface roughness and by penetration of the surface by the liquid or swelling induced by this. The liquid used may in fact alter the surface under study; a polar polymer with a high degree of chain mobility will undergo a configurational change to minimise the interfacial energy.

There are several methods for measuring contact angles (46) but one of the simplest is the sessile drop technique. In this process a drop of liquid is placed on top of the dry surface and its contact angle can then be determined either directly, using a goniometer, or indirectly by taking measurements of the width and height of the drop. The contact angle is related to these measurements via the formula

$$\tan(\theta/2)=2H/W \qquad 2.3$$

where H and W are the height and width of the drop respectively. This method has the advantage that the surface does not have to be exposed to the measuring liquid for a long time, in comparison to the sessile bubble technique where the surface may be soaked in the liquid for up to 48 hours before testing, and this minimizes any reorientation of the surface structure which may be induced by the test.

By measuring the contact angles of two liquids of known surface energies it is possible to calculate the polar and dispersion components of the surface energy of the solid using the formula below (47).

$$1 + \cos\theta = (2/Y_L)((Y^d_L\ Y^d_S)^{\frac{1}{2}} + (Y^p_L\ Y^p_S)^{\frac{1}{2}} \qquad 2.4$$

Y_L is the surface energy of the liquid
Y^d_L and Y^p_L are the dispersion and polar components of the surface energy of the liquid respectively
Y^d_S and Y^p_S are the dispersion and polar components of the surface energy of the solid respectively.

2.2.5 Friction

Friction is another property which is influenced strongly by the surface composition of a material. However elucidation of surface properties using friction measurements alone is virtually impossible in many cases since the frictional force between two surfaces can be broken up into a number of different components not all of which are dependant on the surface properties of the material. It is generally held that the frictional force can be resolved into two principle components (53,54); an adhesion component, F_A, and a displacement component, F_D. These in turn can be reduced to a number of terms relating to specific factors involved in the friction process. F_A arises from the combination of dispersion, polar, induction, hydrogen bonding and electrostatic forces (55) and F_D can be divided into an elastic and a plastic component and terms relating to shearing of the bulk material and of surface films. The relative importance of these components depends on the type of motion involved, the topography of the surface, and the properties of the materials involved. It has been stated by Bowden and Tabor that for most unlubricated polymer films the adhesion terms dominate (56). In extreme cases, such as some elastomers, the friction can result entirely from elastic displacement and the energy losses arising from elastic hysteresis.

In the case of a hard slider moving across the surface of an elastomer, energy is fed into the surface as the slider advances distorting the material. Some of this energy is restored to the slider by the elastic recovery of the surface behind the slider pushing it forwards, energy is lost to the surface in this process and this accounts for the force of work required to maintain sliding. If the slider forms a transient groove in the elastomer then the net energy loss is related to the input energy and the the loss properties of the material at the contact pressure, temperature and rate of deformation involved (57-59). In non elastomers a certain amount of permanent deformation may occur and the polymer can be considered to be a plastic solid with a well defined yield pressure. In most situations the loss properties of the polymer are most relevant in this sort of frictional phenomenon.

If a sharp slider is used, tearing and cutting of the surface may occur thus increasing the frictional force. It has been shown for rubbers that a sharp asperity will stretch the material around it until tensile failure occurs (60). It may be presumed that a similar situation exists for elastomers. A lip of material is left protruding for removal by interaction with successive irregularities in the hard surface. With polymers, a sharp point may act as a miniature cutting tool removing material (54), this process is usually termed abrasion.

It becomes clear therefore that it is difficult to arrive at precise chemical information from friction data, however a comparison of different materials interacting with a common substrate can be made. From measurements of the static and dynamic friction and a plot of the frictional force with time, it is possible to deduce something of the nature of the forces acting at the surface and the effect that a surface treatment has had.

2.2.6 Surface Spectroscopies

Over the last 20 years, stimulated partially by the need for well characterized surfaces in the electronics industry, a number of surface spectroscopic techniques have been developed which enable the chemistry of the surface to be probed directly. These techniques prove a variety of information from varying depths within the sample as illustrated in figure 2.3.

Currently it is necessary to employ a number of these techniques, possibly with older methods such as contact angles to build up the best possible picture of the surface. There are however two techniques which are complementary and which lend themselves particularly to the study of modified polymers, these are secondary ion mass spectroscopy (SIMS) and electron spectroscopy for chemical analysis (ESCA).

2.2.6.1 Secondary Ions Mass Spectroscopy

The application of SIMS to polymer surfaces (49) is still in its infancy and can only be applied with its full potential to systems which have been extensively studied, such as polyacrylates and methacrylates (50,51). The SIMS process uses an ion beam to sputter fragments of the sample from the surface. These are then analysed in a similar way to the fragments in a conventional mass spectrometer. One problem with the technique is that the high energy ion beam used to

Figure 2.3 Comparison of Some Surface Analytical Techniques with Respect to Depth of Analysis (48).

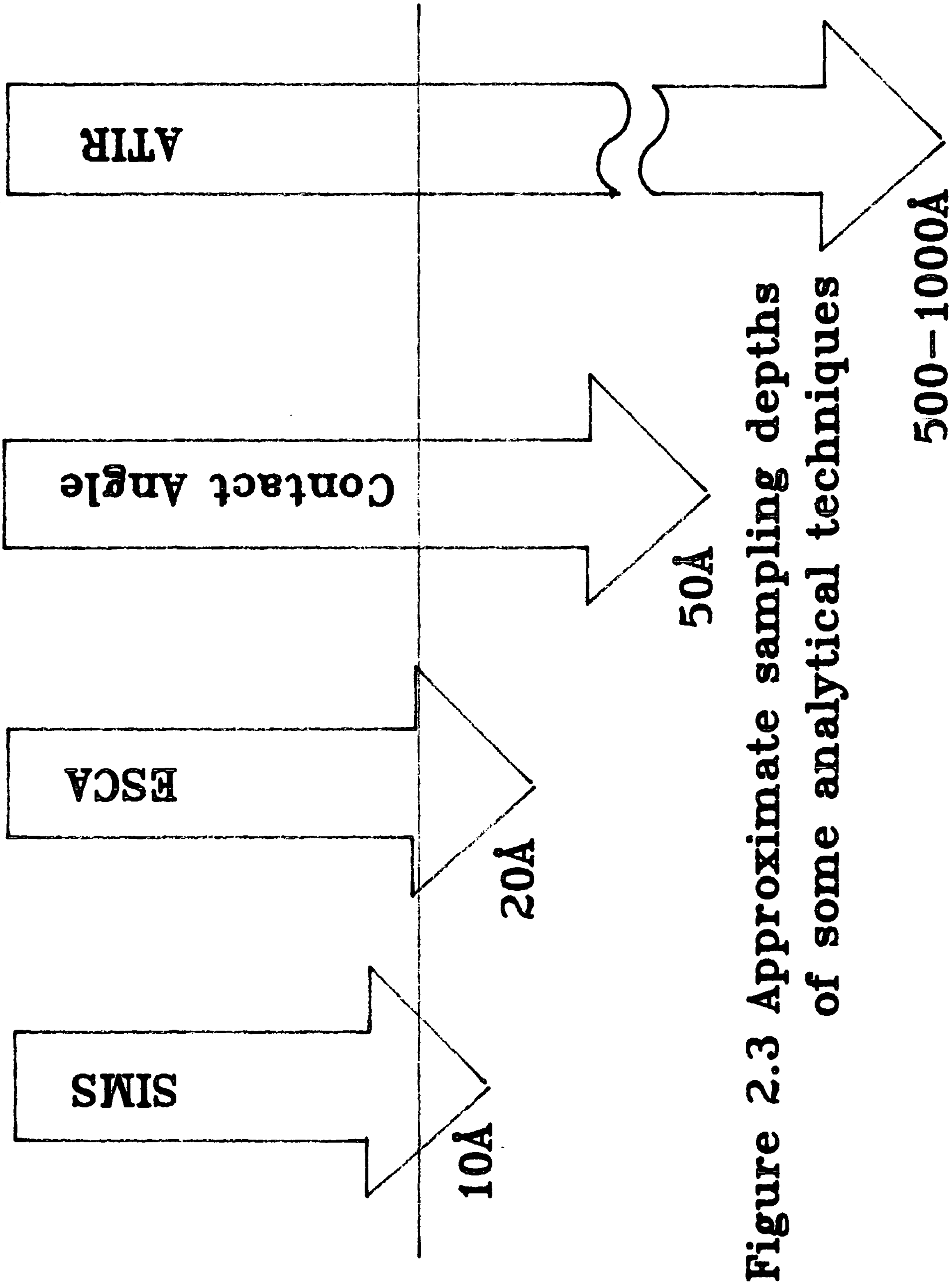


Figure 2.3 Approximate sampling depths of some analytical techniques

produce the ions from the surface can produce a plasma like state at the surface, this may alter those fragments before detection, though this is unlikely to have a large effect due to the low plasma density. Additionally the ion beam may induce changes in the substrate itself. These problems can however be minimized by adjusting the experimental conditions to optimize the spectrum of each sample. Its main advantage over ESCA is its superior surface sensitivity and molecular selectivity which enables a much greater level of structural information to be obtained, particularly in the case of a hydrocarbon sample. It can be a very sensitive technique providing detection of elements at concentrations of 0.1% and enabling different isotopes to be distinguished. Disadvantages include the very high cost of the technique and the level of operator training required to optimize the conditions of the experiment in order to obtain a spectrum of high quality. More importantly the quantification of SIMS data is a major problem and the charging of insulating samples may distort the spectrum.

2.2.6.2 Electron Spectroscopy for Chemical Analysis

The application of ESCA to the study of polymer surfaces has been excellently demonstrated by Clark et al. (52). In the ESCA experiment a beam of x-rays of known energy is used to produce photoemission of electrons from the sample. The x-ray energy is sufficient to eject core level electrons which are collected and analysed according to their kinetic energy. From this it is possible to calculate the binding energy of the electron since the sum of the photoelectrons binding and kinetic energies must be equal to the energy of the ionizing x-ray photon. It is an ideal technique for the investigation of modified surfaces since it is highly surface sensitive, due to the limited distance an electron of a given kinetic energy can travel before losing its energy, and essentially non destructive. ESCA can routinely provide the following information:

1. Elemental analysis of all elements except hydrogen and helium can be calculated from the relevant peak areas together with a knowledge of the appropriate sensitivity factors.

2. Functional group analysis; structural features can be determined from a knowledge of the binding energy chemical shifts produced in a particular core level spectrum, especially the C_{1s} core level, by the different functional groups within the sample. Where two groups produce similar shifts it is sometimes possible to distinguish between them by performing a surface reaction with one of them and then analysing for the presence of the new functionality introduced.

3. Information on the presence of unsaturated or aromatic features from shake-up (Π-Π^*) transitions.

4. Non destructive depth profiling; by increasing take off angle surface features can be enhanced. Additionally the sampling depth can be varied by use of x-ray sources of different energies.

The disadvantages of ESCA are that it is expensive and requires an ultra high vacuum system. Additionally it is not possible to study the hydrogen content of a material directly or to study the bulk of a sample without sectioning or etching it. ESCA also requires trained operators to achieve its full potential. Despite these disadvantages it is currently the best way to quickly assess the surface chemistry of a material and so it has been used throughout this work as a major investigative tool.

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CHAPTER THREE

OXYGEN PLASMA TREATMENT

3.1 Introduction

Siloxane acrylate lenses have been developed to possess a desirable degree of oxygen permeability by the inclusion of silicon containing units into an acrylic polymer with the required optical and mechanical properties. Unfortunately this results in an essentially hydrophobic material. Since the tear fluid does not wet the lens well the wearer experiences a foreign body sensation in the eye and deposits of organic debris can build upon the lens surface.

There have been a number of attempts to improve the wettability of this type of material. The inclusion of wetting agents, such as N-vinylcarbazole, N-vinylpyrrolidinone, hydroxynaphthyl methacrylate and many others (1), either by copolymerization with the acrylic and siloxane monomers, or as an additive present in the polymer matrix, is common. Unfortunately there is a trade off between wettability and the mechanical properties of the polymer which deteriorates with increased amounts of wetting agent.

A concept currently in use is to copolymerize with the siloxane acrylate a fluoro-acrylate component (1a). This of course decreases the hydrophilicity of the lens surface, in contrast to most other approaches, however idea here is to reduce the interaction between the surface and foreign material and therefore to reduce the irritation caused in this way. A typical HGP fluoro-acrylate material, Equalens, will be examined for comparison in this work.

An alternative that has been suggested is the use of dilute aqueous acid and alkali solutions (2). In this process the lens is first produced and machined normally and is then placed in a vessel containing water or a solution of acid or alkali. This is then typically refluxed for around 24 hours. Lenses treated in this way are reported as having a contact angle with water of 80°.

Treatment of the lens surface using a gas discharge has been used prior to the work reported in this volume. The lens manufacturers Menicon produced a lens which was subsequently treated using a DC discharge in oxygen (3). This had the effect of dramatically increasing the hydrophilicity of the lens but the resulting surface did not perform well in the eye, having serious problems with the deposition of proteins and other debris. Investigation of the treated surface showed that under high magnification it appeared to be composed of cone shaped structures packed closely together. Such surfaces are commonly observed in other applications where treatments involving accelerated ions interacting with the surface are used (4). It seems likely that this roughening of the surface produced a multitude of sites where contamination could lodge.

Despite the problems inherent in the Menicon treatment the glow discharge modification of a lens surface is a very attractive process since it is potentially simple, clean, quick and preserves the bulk properties of the polymer. Therefore it was decided to investigate the possibility of improving the compatibility of a contact lens using a plasma modification technique.

The initial simplistic concept was to consider the tear fluid to be an aqueous solution and to improve the wetting of the lens by use of an oxygen plasma. This would introduce hydrophilic groups into the surface which would be able to interact with the water in the tear solution. Since the lens would then be covered in a tear film it would be cushioned against the eyelid, rendering it more comfortable, and the continuous film would also inhibit the deposition of lipids and other detritus.

Initial experiments were performed on a variety of hard gas permeable (HGP) lenses, such as Boston II, Boston IV and Optacryl 60, which differed primarily in the relative amounts of siloxane units in the copolymer. Plasma treatment of these materials resulted in very large increases in hydrophilicity. This treatment was then applied to the lenses of patients with particularly acute compatibility problems, essentially as a last resort measure. It was found that these patients found the lenses much more comfortable than the untreated ones and it was also found that there was a significant decrease in the amount of protein and similar matter deposited on the lens (5). As a result of these successes an in depth study of the plasma treatment of these materials was undertaken.

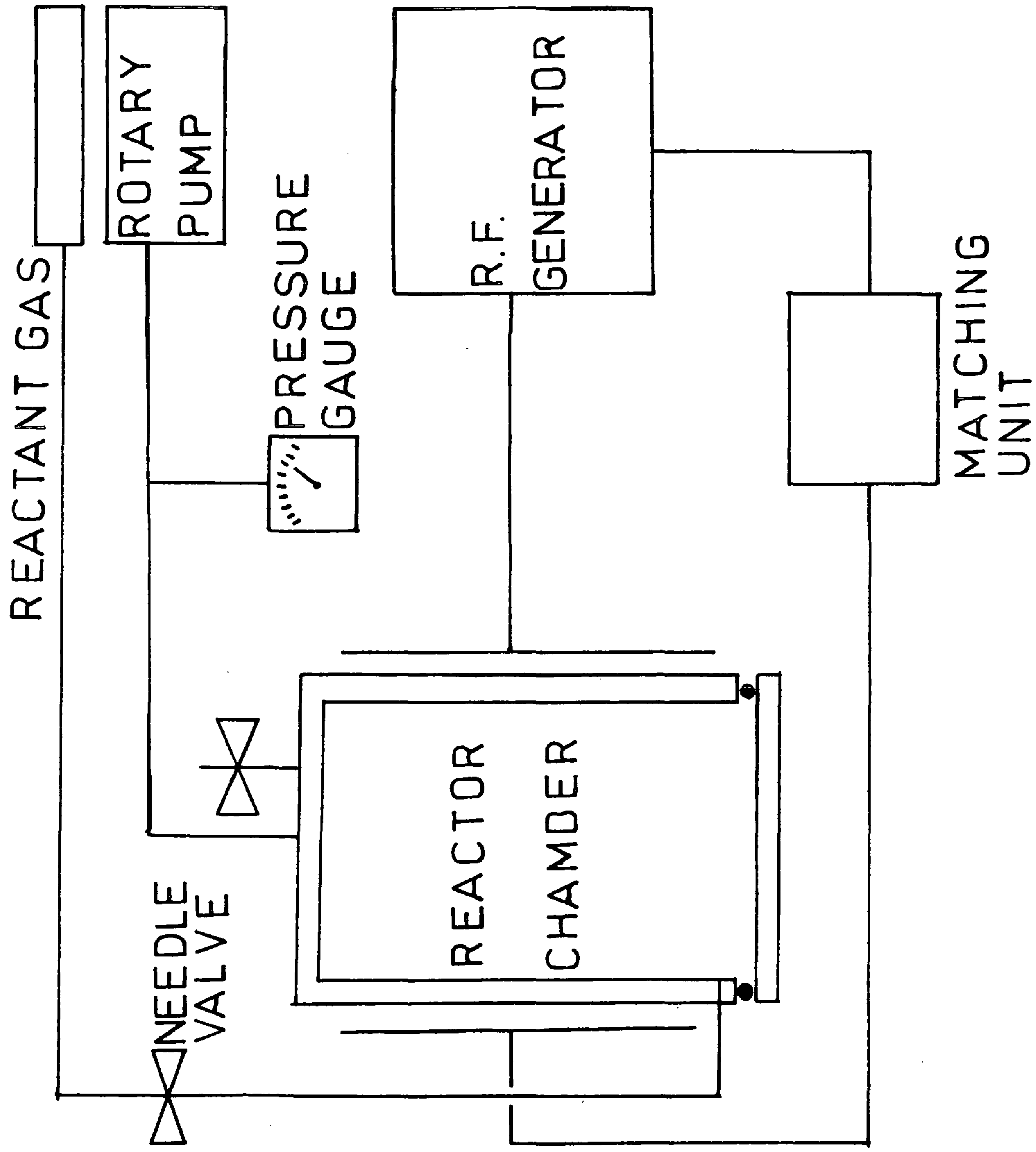
3.2 Experimental

3.2.1 Plasma Treatment

Plasma treatments were performed using a Polaron E2000 plasma asher/etcher unit, shown schematically in figure 3.1. The reactor vacuum piping was connected with a combination of Swagelok metal-metal pipe seals and metal flange joints with centring Viton O rings to give a grease free system. An Alcatel 2004A mechanical rotary pump, pumping speed $4.5m^3$/hour, was used to evacuate the chamber. This gave a typical base pressure of $3x10^{-2}$ mbar, as measured by the in built vacuum gauge.

Though this apparatus was only used with non polymerizable gases such as oxygen and argon it was still necessary to regularly clean the reactor, this was due to the probable deposition on the reactor walls of material removed from substrates during the plasma process. A cleaning regime of detergent and scouring powder followed by rinsing with iso-propanol was used. Additionally a high power, ≈100W, oxygen plasma was ignited for 15 minutes in the reactor after

Figure 3.1 Schematic of Polaron E2000 Plasma Asher/Etcher



rinsing with solvent to remove any remaining traces of contamination.

Before staring an experiment the leak rate of the reactor was tested by closing off the pumping and measuring the rate of increase of pressure. A high leak rate would have meant that atmospheric oxygen and nitrogen would be present in the plasma in significant amounts. If the leak rate was acceptably low the reactant gas was then admitted to the plasma chamber through an electrically operated needle valve and the valve adjusted to give the required pressure. At this stage the flow rate of the reactant gas could be measured by closing off the pumping and observing the rise in pressure in a similar manner to the determination of the leak rate. Reactant gas was then flushed through the chamber for 5 minutes after which the plasma was ignited and the required power level set. The RF power was supplied by the in built generator capable of producing up to 150W at 13.56MHz, capacitatively coupled to the chamber via four external electrodes. The system was then balanced to a position of minimum reflected power by matching the external load to the generator using a single variable capacitor connected to a constant inductance. The plasma was switched off and samples were then introduced on a glass slide, it having been previously determined that there was no significant positional variation of the treatment over the slide. The reactor was then pumped down and flushed for 5 minutes with reactant gas before the plasma was re-ignited and the samples treated for the appropriate length of time.

3.2.2 Contact Angle Measurement

Contact angles were measured using the sessile drop technique. Samples were placed on a glass slide supported on the microscope stage and these were then viewed from one side. A 3µl drop of liquid was then placed on the sample using a microlitre syringe; drops which appeared irregular could not be used to give reliable measurements and those samples were discarded. The drop size used was the minimum amount of liquid which could easily be transferred from the syringe to the surface. This was necessary since the equation used to calculate the contact angle only holds true for a for a drop which conforms to part of a sphere; a large drop is distorted by gravity into a non spherical shape. The microscope contained a graticule in the eyepiece and this was used to take measurements of the width and height of the drop. From these measurements it was possible to determine the contact angle using equation 2.3. It was estimated that the error involved in these measurements was less than ± 5°.

3.2.3 Friction Measurement

The coefficient of friction (COF) of samples was measured using two different types of apparatus. It was necessary to use two different methods because the first technique requires that a load of 200g be placed on the sample whilst the second technique permitted the samples to be tested under their own weight.

Since even the smoothest surface on a small scale is irregular the two surfaces will touch only at isolated regions (6), the real area of contact will always be less than, or equal to, the apparent area of contact. There will initially be only three points of contact but at even the smallest loading the pressure at these points will be sufficient to cause deformation leading to increased points of contact. Whilst the individual points of contact remain discrete the coefficient of friction is independent of load (7). At heavier loadings the increased size of the deforming asperities leads to interference between adjacent contact points, which results in a slowing down of the rate of increase of the real area of contact. Since the adhesion forces of friction require direct contact, the increase in frictional force is not proportional to the increase in weight and so the coefficient of friction falls. Thus the COF of a polymer measured under a heavy load can be lower than its value under a very light weight and this means that measurements of friction taken under a sample's own weight can provide additional information.

The first type of COF measurement was performed using an Instrumentors Inc. slip/peel tester model SP-101, figure 3.2. This was calibrated using a 200g weight to give a full scale deflection for a force of 2N. A piece of low density polyethene (LDPE) was affixed to the stage of the apparatus using double sided adhesive tape and cleaned using methanol to remove any grease. The sample was then attached to the under-side of a 200g sled also using double sided tape. This was placed on the LDPE film sample side down and connected to the strain gauge of the slip peel tester by a length of nylon monofilament (ASTM D-1894).

On activating the tester the stage was moved away from the strain gauge at a rate of 6 inches per minute so that the frictional force between the sample and the LDPE was equal to the force exerted on the strain gauge. The peak and average values of the COF could then be read off the meter of the device. During the run it was observed that some samples caused the sled to move to one side and these results were therefore discarded as this movement introduces additional forces which the tester does not take into account when displaying its results.

Since the slip/peel tester possesses an analogue output this was utilized in certain experiments, in conjunction with a Bryans 26000 A3 XY recorder, to produce a trace of COF with time.

The alternative method employs the apparatus shown in figure 3.3

Figure 3.2 SP-101 Slip/Peel Tester.

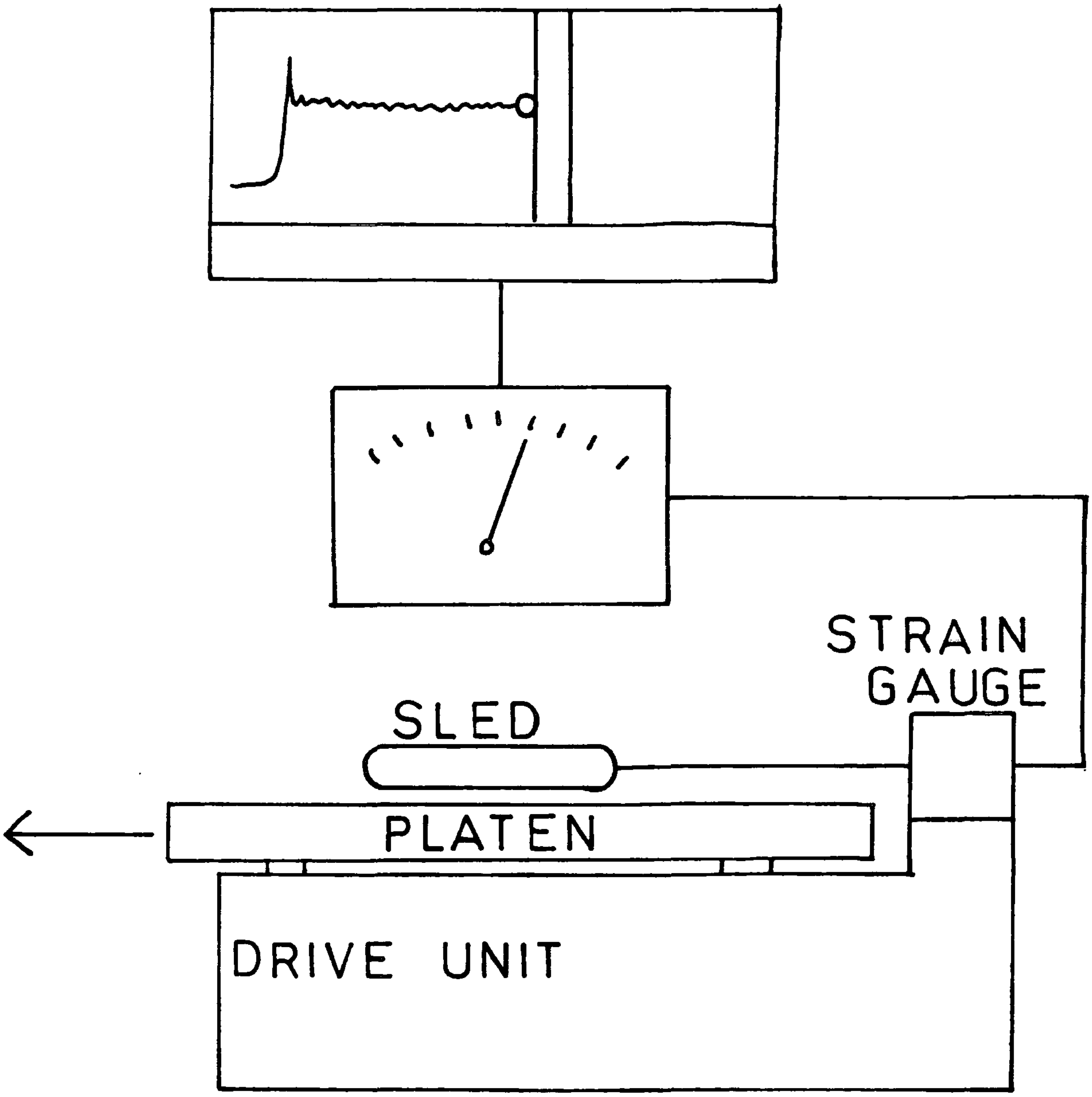
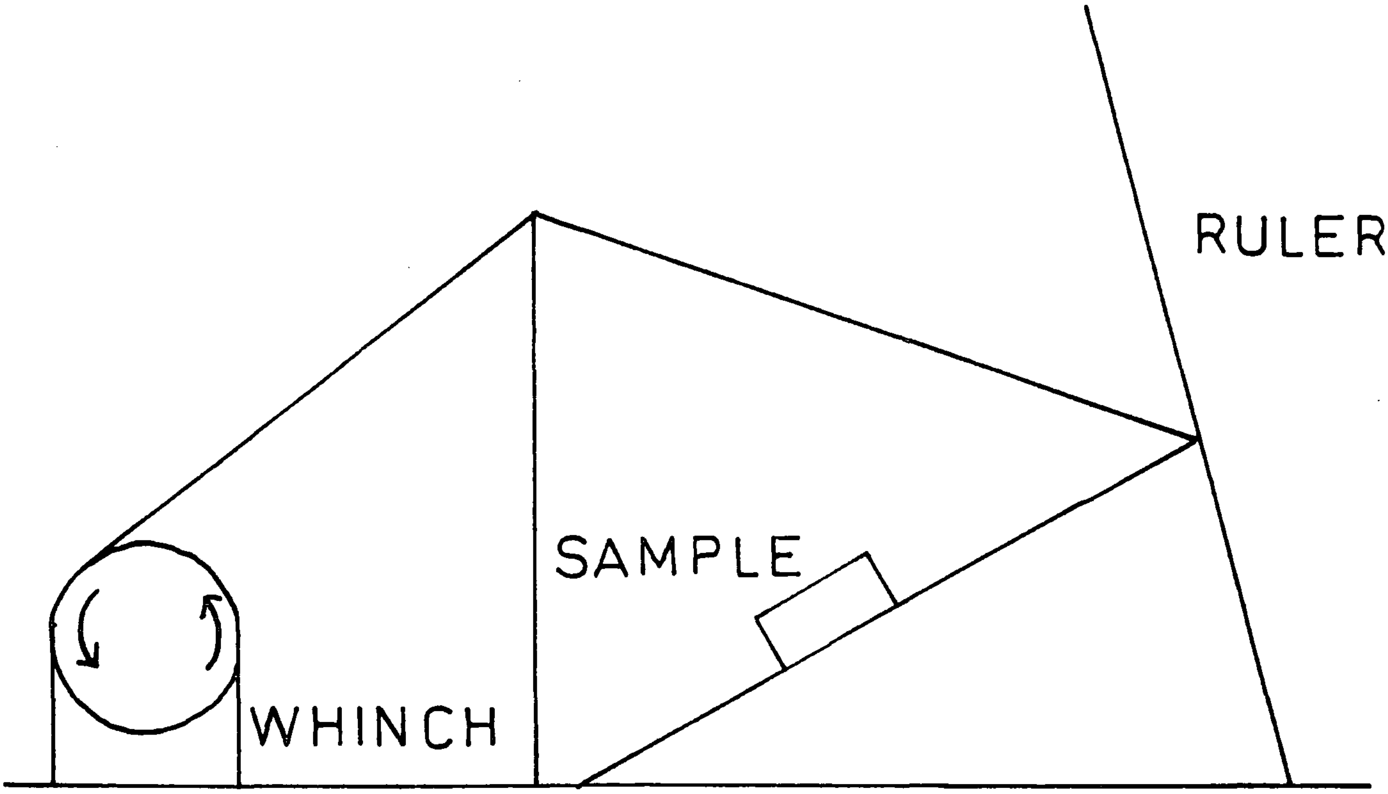


Figure 3.3 Inclined Plane Friction Tester.



The inclined plane friction tester works on the principle that an object placed on an inclined plane will slide down the slope when the force of gravity acting on the sample in a direction down the slope, just exceeds the frictional force between the sample and the slope. If the slope is at an angle of θ to the horizontal then it can be shown that,

$$\mu = \tan\theta$$

and so by measuring the length of the plane and recording the height of its far end at the point where the sample just slips the COF can be calculated.

The slope was first covered with LDPE as before and the sample placed at some point on it. The plane was then slowly raised by the electric motor until the sample began to slide, when it was immediately stopped. The height of the end of the plane could then be determined from the built in scale.

3.2.4 ESCA Analysis

Samples were mounted onto a three sided probe tip, measuring approximately 19mm by 6mm, using double sided adhesive tape. The tip was then attached to a probe rod and inserted into the spectrometer. Analyses were carried out on Kratos ES200 and ES300 spectrometers, all the samples from a particular experiment being run on the same instrument. When running spectra of contact lenses care was taken to ensure that the lens was directly in front of the x-ray window to minimize the contribution, if any, of the mounting tape to the spectrum. Samples were irradiated with $MgK\alpha_{1,2}$ x-rays, of 1253.6eV, using an electron take off angle of 30 degrees. Depth profiling was achieved by increasing the take off angle to 60°.

The ES300 spectrometer was controlled by the Kratos DS300 data system which is based on an LSI-11 minicomputer running under RT-11. Data was stored on floppy disk, and the continuous scanning of up to 10 regions was possible. The data analysis package permits the addition, comparison, subtraction, differentiation and integration of spectra, the subtraction of satellites and a peak fitting/synthesis routine.

The ES200 spectrometer was controlled by an Acorn BBC B+ microcomputer running Basic software developed at Durham University. This permitted scanning of a single region at a time which was then stored on floppy disk. The program also allowed peak fitting/synthesis in a manner essentially identical to that found on the DS300 system.

Peak component analyses were performed, following linear background subtraction, by using gaussian peaks of constant full width at half height. Correction for sample charging was performed using the hydrocarbon peak at 285eV as a standard.

Component peak positions were assigned by reference to the experimentally determined binding energies of the various functionalities in standard samples and are constant to within ±0.3eV. The one variable parameter is that of peak height. This was adjusted to give the best fit with the experimentally determined spectrum consistent with chemical possibilities.

3.3 Materials

Films of low and high density polyethene (LDPE,HDPE) polytetrafluoroethene (PTFE) and nylon 6 approximately 100 µm thick was supplied by I.C.I. plc. Polymethylmethacrylate (PMMA) powder, medium molecular weight, was acquired from the Aldritch Chemical Company Ltd. This was then made into films by dissolving sufficient powder in chloroform to give a 10% solution which was poured into a clean glass petri dish and allowed to set for at least two days to ensure that all the solvent was removed.

For contact angle measurements distilled water, surface tension 68±2 mNm^{-1} was available. Additionally for more accurate measurements, to determine polar and dispersion components of surface energy, water triply distilled from potassium permanganate solution was prepared. This had a surface tension of 71±2 mNm^{-1}, and for this experiment diiodomethane, 99%, was acquired from the Aldrich Chemical Company Ltd.

The lens material known as Boston IV was chosen as a typical example of a state of the art siloxane acrylate. This was provided, both as finished lenses of a standard curvature and as cylindrical "buttons" polished to commercial lens quality, by Cambridge Contact Lens Technology.

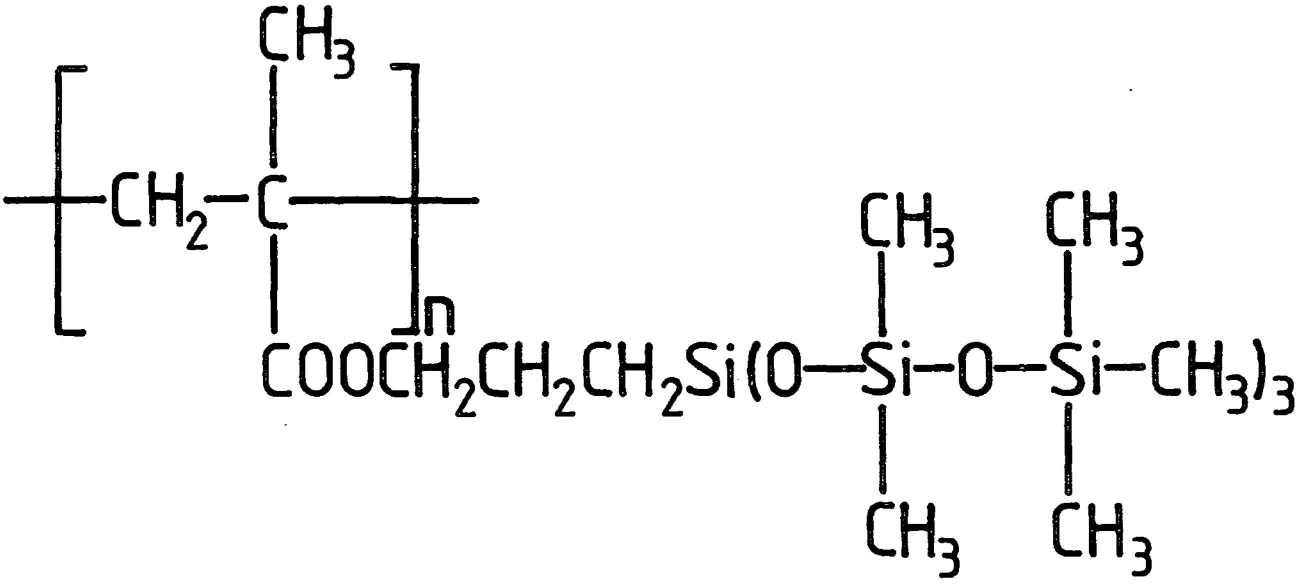
Boston IV is a copolymer of methyl methacrylate with a siloxanyl alkyl ester of methacrylic acid together with small amounts of colouring and wetting agents (1). It has been suggested, and upheld in the American courts (8), that Boston IV is essentially the same as a material known as Polycon whose silicon containing monomer is 3-[3,3,5,5-pentamethyl-1,1-bis[(pentamethyl disiloxanyl) oxy] trisiloxanyl]-propyl methacrylate (siloxane A), figure 3.4.

3.4 Results and Discussion

3.4.1 The Nature of Boston IV

Before investigating the effects of plasma treatment it is useful to consider the nature of the unmodified Boston IV in order to define its composition. A study of the transmission infra-red spectrum of a film of Boston IV, figure 3.5, shows the presence of a number of absorption bands which can be attributed to silicon containing functionalities. The peaks at 1380 and 1275 cm^{-1} can ascribed to $Si-CH_3$ and the band at 1065 cm^{-1} to Si-O-Si. Additionally the methacrylate ester is

Figure 3.4 Silicon Containing Monomer of Polycon



$$-\left[CH_2-\underset{COOCH_2CH_2CH_2Si(O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3)_3}{\overset{CH_3}{C}}\right]_n-$$

clearly shown by the bands at 1725, 1440 and 1240 cm^{-1}.

The ESCA spectra showing the C_{1s}, O_{1s} and Si_{2p} core levels are displayed in figure 3.6. The C_{1s} envelope is dominated by the large peak at 285eV which is due to species consisting of carbon directly bonded only to hydrogen or carbon. This arises not only from the innate hydrocarbon in the sample but also from a variety of sources of contamination. This can, in the case of a sample which has been prepared in a vacuum system be derived from pump oils. Additionally hydrocarbon contamination can be picked up during transferral of the sample between preparation and the spectrometer and also during the running of the spectrum itself (9,10). A major source of this form of contamination is material "boiling off" the x-ray window, this can be eliminated by cooling the x-ray cap and window with a liquid nitrogen or water jacket (11), however the contamination produced in this manner was not sufficient to require the use of such a device for these experiments.

The other peaks in the carbon spectrum can be attributed to a variety of types of oxidized carbon assigned as C-O 286.6eV, C=O 287.8eV and O-C=O 289.0 eV. The chemical shifts for carbon oxygen species have been determined experimentally from model compounds (12), but it is not possible to use these to distinguish between some functionalities e.g. C-OH and C-O-C.

Figure 3.5 Infra Red Spectrum of Boston IV

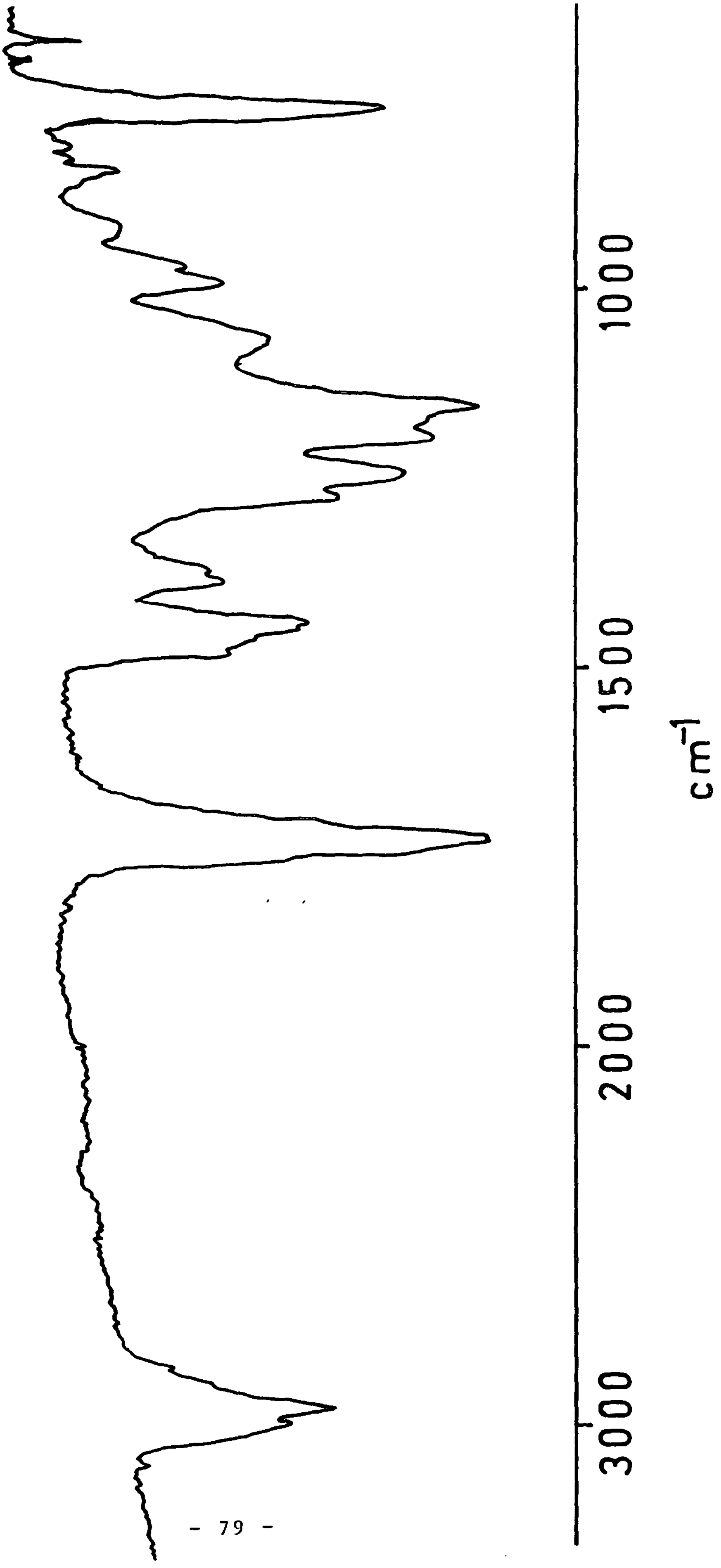
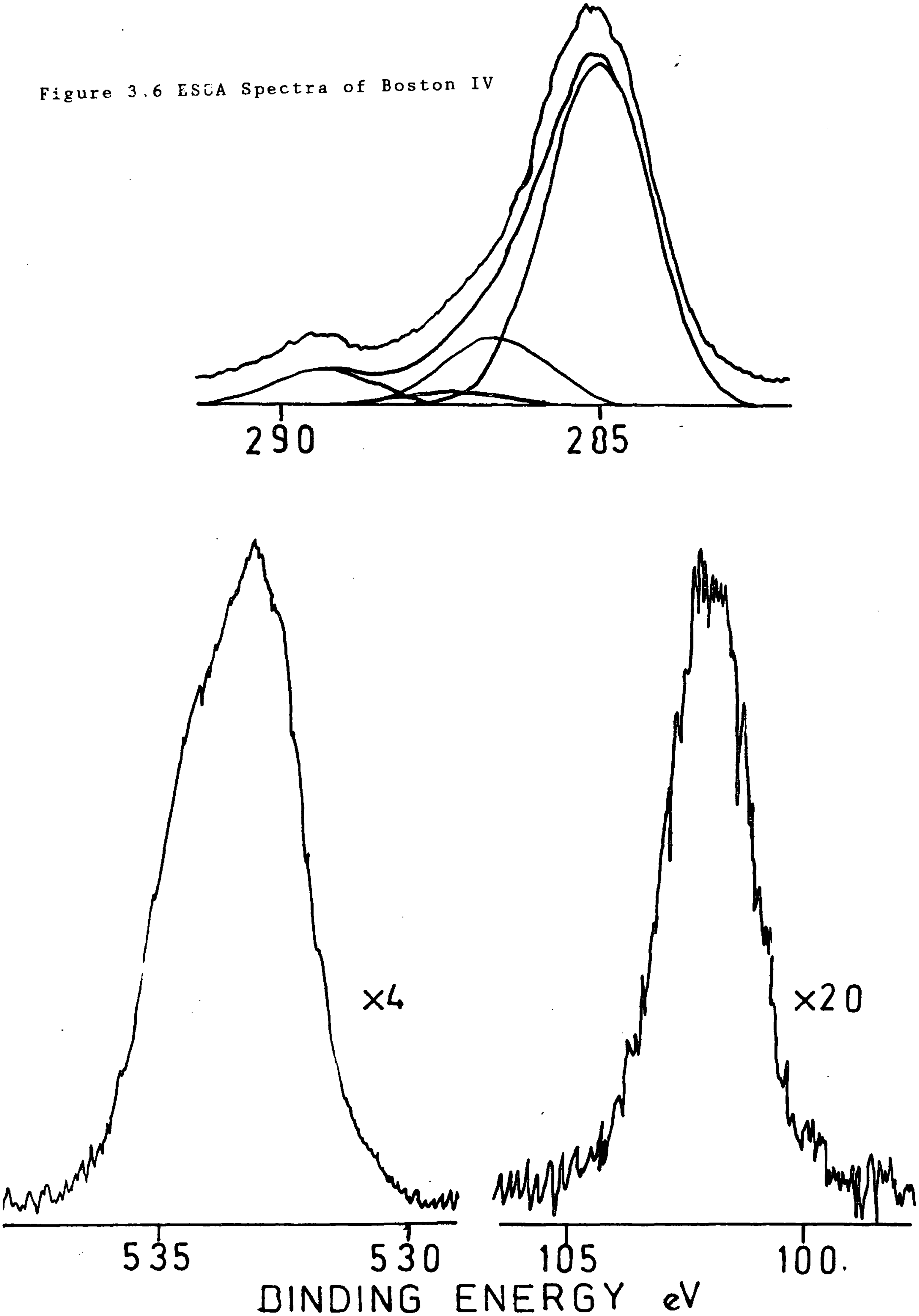


Figure 3.6 ESCA Spectra of Boston IV



It can be seen from the spectrum that in addition to the peaks corresponding to the ester group we expect in an acrylate there is a small amount of carbonyl present and that there is more C-O than can be accounted for by the amount of ester indicated by the acidic peak at 289 eV. This is most likely due to an additive such as a colouring or wetting agent, since the peak is always present even in a sample which has had the surface scraped off.

It will be seen that this peak fit makes no allowance for the silicon containing component of the copolymer, this is not intended to suggest that none of the carbon is directly bonded to silicon but is due to the fact that the C-Si chemical shift is only around 1eV (13) and cannot be clearly distinguished from the CH and C-O peaks. Since the overall silicon content of the material is only ≈3% the contribution of this to the carbon envelope will be very small and is unlikely to significantly affect the peak fit.

The O_{1s}d Core level is asymmetric and suggestive of two basic environments present in similar amounts with a slight excess of that at lower binding energy. The main environments will be O=C at 533.3 eV and O-C at 534.5 eV (12) corresponding mainly to the oxygen in the ester functionality. It is not however possible to obtain a reliable fit of the O_{1s} envelope in most cases because the separation between the peak positions of the different oxygen environments is too small. In the case of a pure polymer where the theoretical values for the relative amounts of each environment is known it is possible to attempt a fit, which can lead to an assessment of the purity of the polymer at the surface.

The excess intensity seen in the low binding energy area of the envelope can be explained in terms of a contribution from the carbonyl species observed in the C_{1s} envelope, whose oxygen would give a signal at ≈533.6 eV.

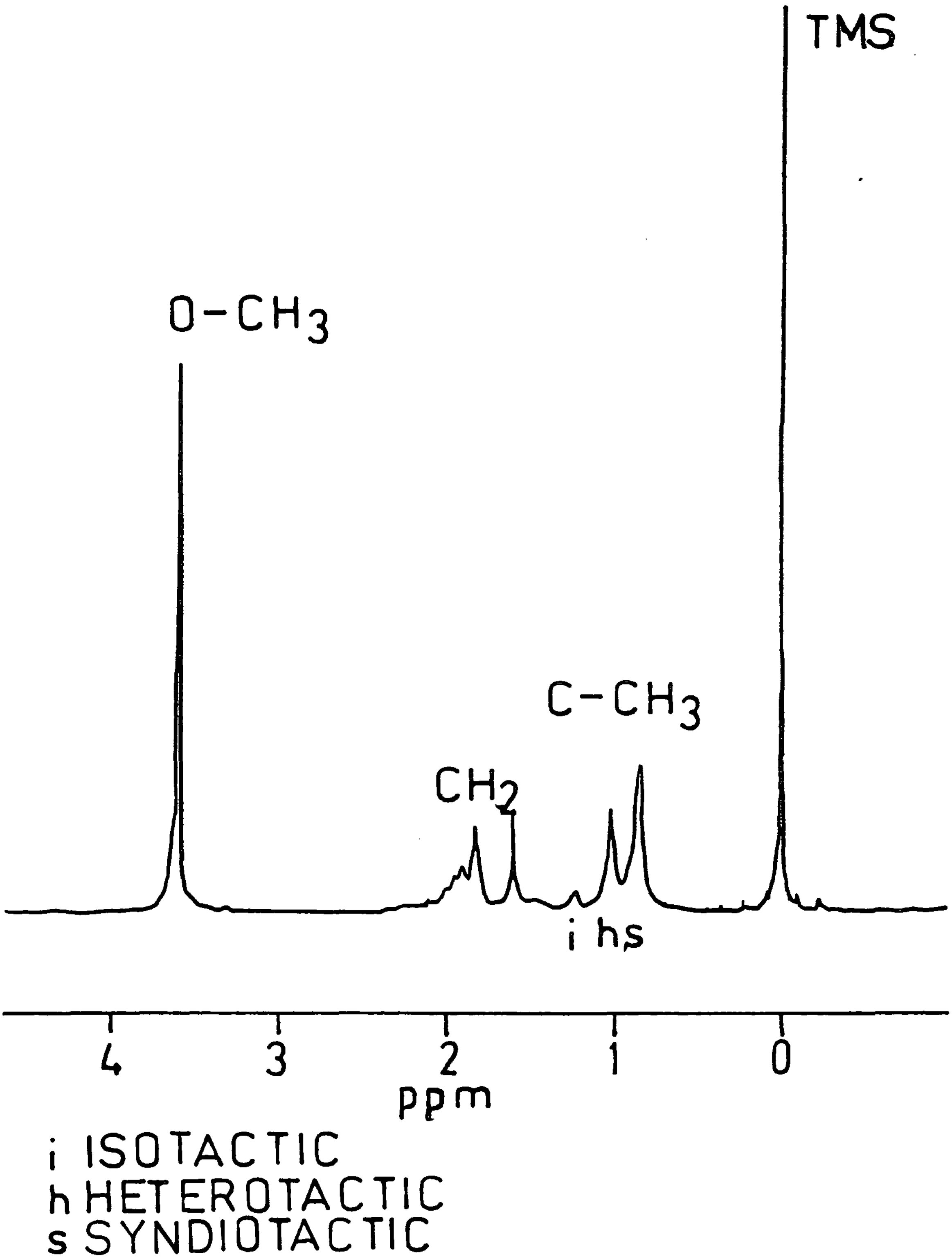
The silicon envelope is basically symmetrical, if rather broad, width at half maximum height (half width) 2.1 eV. This width is not surprising when it is considered that this spectrum is of the 2p orbitals. Spin orbit coupling (14) of the 2p- orbitals results in a doublet structure. The Si doublet has peaks separated by 1eV and in the ratio 1:2, the larger peak being at lower binding energy. The peak position, 102.1 eV, is consistent with a siloxane (13), and the symmetry of the peak suggests that there is more than one similar environment. If there was only one type of silicon present in the polymer then the spin-orbit coupling should render the peak asymmetric, whilst the presence of another species at slightly higher binding energy would tend to obscure the slight shoulder expected on the high binding energy side of the peak.

Comparison of the spectra yields O_{1s}/C_{1s} and Si_{2p}/C_{1s} area ratios of 0.42 and 0.04 respectively which can be converted, by use of the relevant sensitivity factors, to an elemental ratio. The sensitivity factors used throughout this work are 0.56 for the O_{1s} region and 0.83 for the Si_{2p} region. This gives an elemental composition of the surface of C:O:Si = 100:24:4. If the relative areas of the components of the C_{1s} envelope are now considered, it is found that a model which assumes that all of the peak at 289 eV is attributable to an ester gives an overall C:O ratio which is in good agreement with the area ratios. If this model also assumes that the excess area of the peak at 286.6 eV is due to C-O-C groups then the C:O ratio derived from this model is 100:21. Comparing this to the elemental composition calculated from the area ratios leaves 3 oxygens to be accounted for which may reasonably be assigned to the siloxane units in the polymer.

The ^1H NMR of a solution of Boston IV, figure 3.7, shows three distinct features, a large peak at 3.6 ppm due to CH_3-O-, a multiplet at around 1.9 ppm due to CH_2, three peaks around 1ppm due CH_3 and a large peak at 0 ppm from a combination of the tetramethylsilane (TMS) reference and other CH3-Si protons in the solution. The solvent was chloroform and its peak at 7.26 ppm is not shown on this diagram.

The three methyl group peaks show the relative proportions of iso-, hetero-, and syndiotactic polymer in the sample (15), and these are found to be in the ratio 1:3:6. Integrating the peaks gives the ratio of CH_3-O-:CH_2:CH_3-C to be 51:47:60. If

Figure 3.7 ^1H NMR Spectrum of Boston IV Dissolved in Chloroform.



we assume that Boston IV is indeed identical to Polycon then from the ratio of these groups it is possible to calculate the proportions of methyl methacrylate and siloxane A units present.

If there are x units of methyl methacrylate for y units of siloxane then since only the methacrylate contains $O-CH_3$,

$$3x=51$$

therefore $x=17$. Similarly $3x+3y=60$ and so $y=3$. If we now compare these numbers with the formula for CH_2 protons,

$$2x+4y=47$$

we see that it agrees to within one proton. However if we now use this composition to derive an elemental composition we get the ratio C:O:Si=100:38:14. This shows that Boston IV, at least at the surface, does not have the precise composition of Polycon. Of course it must be remembered that the surface of a polymer need not resemble its bulk that closely since surface energetics may drive certain materials to the surface and others away from it and there may also be surface contamination of some sort, often this is in the form of hydrocarbon. In addition the environment can react with the surface of a material, often photochemically, to produce a modified surface of some sort.

Microanalysis was carried out on samples of the material to ascertain the bulk elemental composition. This was found to give a ratio for C:H:O:Si of 100:160:40:1. Clearly this is not in agreement with the surface composition as determined by ESCA, the lower oxygen content can be explained as a combination of hydrocarbon contamination and some orientation effect. Since a surface with a lot of oxygen containing groups would have a very high surface energy, if the polymer structure is sufficiently mobile these groups can become turned or can migrate into the bulk polymer thus reducing the surface energy. A similar effect can be invoked to explain the higher silicon content of the surface, since siloxanes have relatively low surface energies migration of the siloxane component of the polymer to the surface will tend to lower the overall surface energy. The level of silicon determined by analysis of the ^{1}H NMR appears abnormally high, this suggests that the siloxane unit in Boston IV is either not identical to that in Polycon, but is a related siloxane containing less silicon, or the proportion of MMA to siloxane A in the copolymer is less than that suggested by NMR.

3.4.2 The Effect of Plasma Modification

Since the precise structure of Boston IV is unclear it was felt that understanding the effects of the plasma process would be simplified if a study of PMMA was made in conjunction with that of the lens material.

The samples were treated using a 20 watt oxygen plasma at a pressure of 0.4 mbar for 45 seconds. These conditions were chosen because they had been shown, in initial work by Dr. C. Till, to give the greatest improvement in wettability for Boston IV as can be seen from figure 3.8.

Unmodified PMMA had a contact angle with water of 92° (n=10, SD=3.3); after plasma treatment this was reduced to 47° (n=10, SD=3.6). Comparing the elemental ratios reveals that the C:O ratio has increased from 100:30 to 100:41. The ESCA spectra of the modified and unmodified PMMA are compared in figure 3.9.

The unmodified PMMA has three environments other than the hydrocarbon at 285 eV. These are due to the ester, which gives two peaks, at 288.9 eV and 286.7, and to the alpha carbon attached to the ester group, with a shift of 0.7 eV (14). It is possible to use a subpeak with such a low shift in this case because the peak position is well known and because this is a pure polymer containing only carbon, hydrogen and oxygen. The intensities of the various peaks within the C_{1s} envelope other than that due to hydrocarbon are all the same, which indicates that the PMMA is indeed pure. The slight excess of hydrocarbon observed may reasonably be explained as contamination, which helps to explain the unusually high contact angle. The O_{1s} envelope is symmetrical and flat topped suggesting two equal environments, presumably the two ester oxygens.

Figure 3.8 ESCA Spectra of Modified and Unmodified PMMA

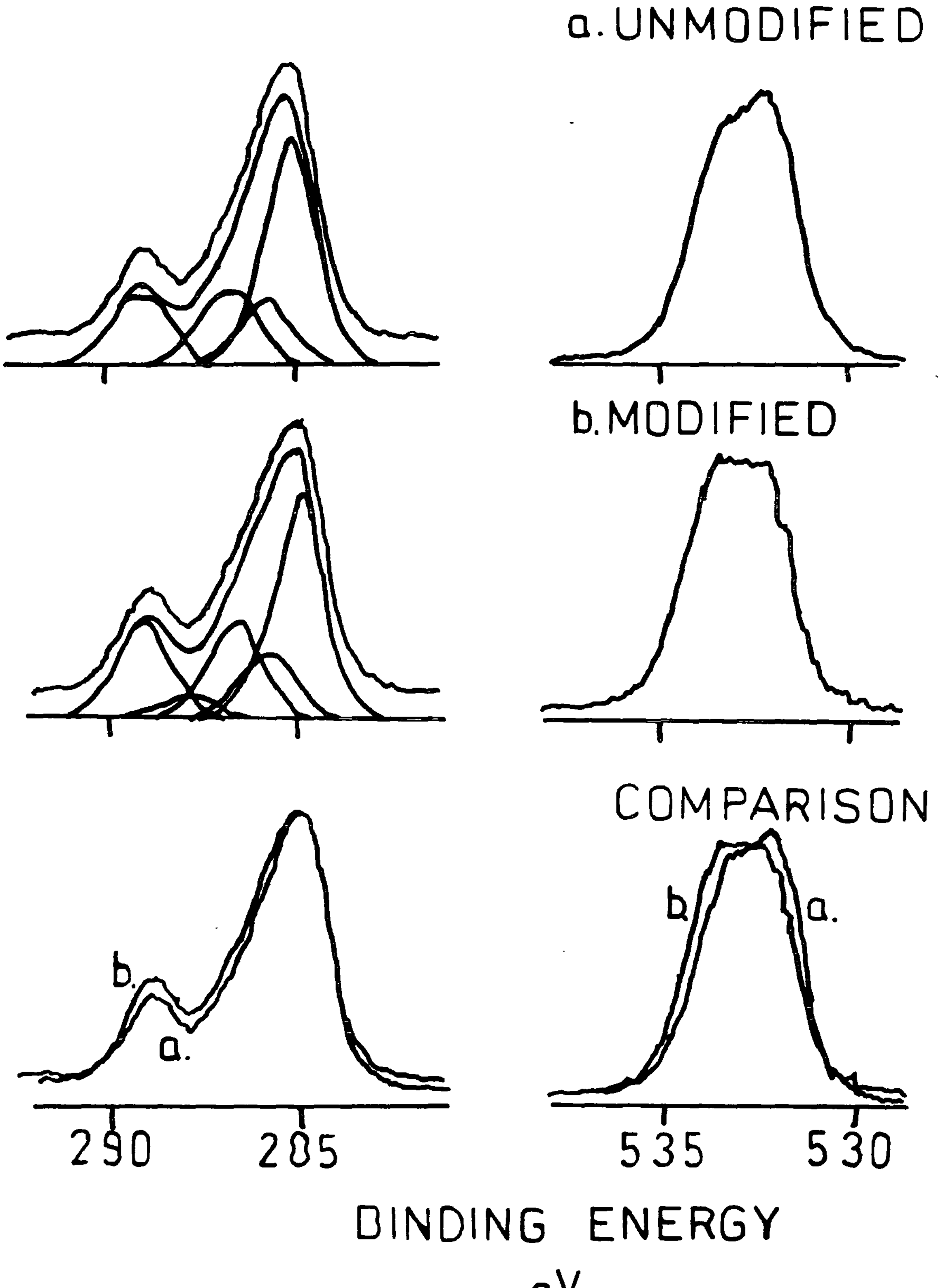
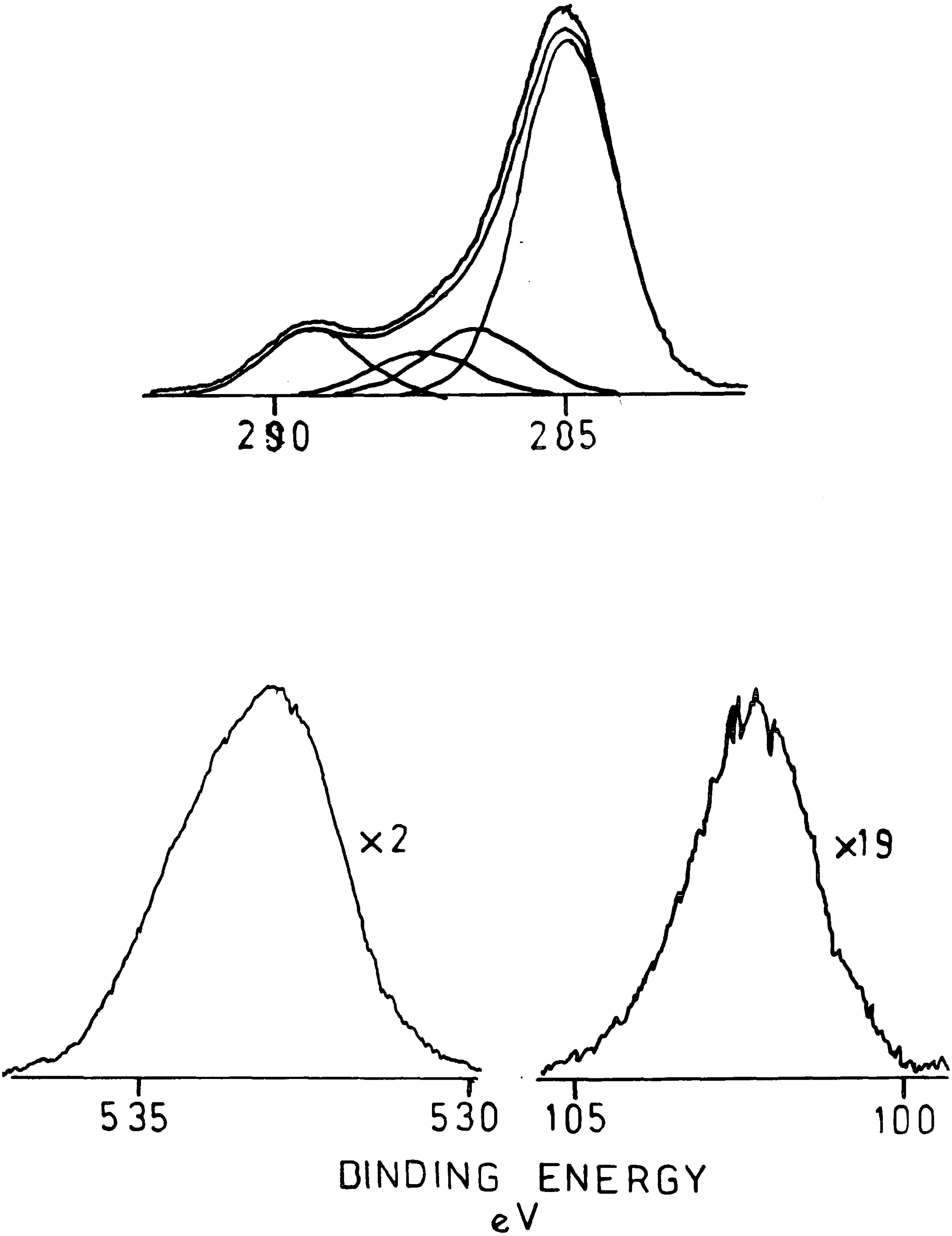


Table 3.1 <u>ESCA Data for modified and Unmodified PMMA (n=3, SD=2.1)</u>

Peak Position (eV)	Unmodified	Modified
285.0	46	35
285.7	17	17
286.7	20	20
287.8	--	5
288.9	17	23

The modified PMMA shows an increase in the intensity of the peak at 288.9 eV and the appearance of a peak at 287.8 eV. This second peak is due to the C=O environment which must be generated by the action of the plasma. Since the peak at 286.7 remains unchanged it is possible to deduce that the increase in the peak at 288.9 eV is due to the production of acid groups rather than the production of ester linkages, and modelling the expected carbon-oxygen ratio supports this prediction. Examination of the two hydrocarbon peaks shows that they have decreased in accordance to the increase in oxidized carbon. The O_{1s} spectrum is still symmetrical but more rounded, no longer exhibiting two distinct environments but suggestive of two main environments with a number of additional

Figure 3.9 ESCA Spectra of Modified Boston IV



ones.

Untreated contact lens material has a contact angle with water of 83° (n=10, SD=3.4) which was reduced on treatment to 45° (n=10, SD=3.7). The spectrum of the treated lens material, figure 3.9 shows an increase in the O_{1s}/C_{1s} area ratio from 0.42 to 0.63 representing an increase of 11 oxygens per 100 carbons. Modelling the contributions of the various carbon-oxygen environments indicates that the basic ester component is still present augmented by additional acid functionalities. Unfortunately it is not possible to tell from this whether the addition to the C-O peak is due to C-O-C linkages or to hydroxyl groups. The Si_{2p} envelope is similar to that of the unmodified sample, peak position 102.3 eV, and this means that the silicon in the sample has not been oxidized. This is perhaps surprising since previous work, by Fakes, on Boston II, a material very similar to Boston IV, did show that the silicon in the polymer was oxidized to silicate (15), binding energy 104 eV. It was also shown in this work that the amount of silicon in the surface was much larger in the treated sample, 20 silicons per 100 carbons as opposed to 6, calculations based on the treated Boston IV spectra show that the level of silicon in the surface remains 4 per 100 carbons after treatment.

The reason for this difference in behaviour was not clear and therefore a series of experiments was under taken to determine whether this behaviour was a general property of carbon-silicon polymers or of just Boston IV. Using the techniques described in chapter 5, a series of plasma polymers was prepared. These were produced by simultaneously introducing into the reactor flows of dimethylpropane (DMP) gas and tetramethylsilane (TMS) vapour. The pressures of these components were varied so that the desired ratio of flow rates was obtained; in this way a series of samples was produced, by plasma copolymerization, which contained a progressively lower proportion of silicon. All the samples were deposited onto clean aluminium foil using 20W plasmas over a period of 5 minutes. Portions of these were then plasma oxidized under the same conditions as the lens materials (20 W, 0.4 mbar of oxygen, 45 seconds). The results of the ESCA analysis are displayed in table 3.2.

Table 3.2 ESCA Data for a Series of Carbon-Silicon Plasma Copolymers (n=1)

TMS:DMP	Oxidized	Area ratios		Si_{2p} peak position
		$O_{1s}/C_{1s}d$	Si_{2p}/C_{1s}	eV
1:0	no	0.15	0.47	101
1:0	yes	3.79	1.13	103
1:1	no	0.18	0.13	101
1:1	yes	1.00	0.27	103
1:3	no	0.12	0.09	101
1:3	yes	0.60	0.18	103
1:9	no	0.11	0.04	101
1:9	yes	0.33	0.04	101

These samples clearly show two features in common; on oxidation the proportion of silicon in the surface increases by two to three times and the position of the $Si_{2p}d$ peak shifts to higher binding energy. It should be noted that the peak position is only quoted to ±0.5 eV. This is because there is always some higher binding energy component present even in the unoxidized samples which is formed during the polymerization process. Thus the peak position given is that of the most prominent environment. The shift in peak position is consistent with a change from an Si-C environment to a SiO_2 environment. The only sample which does not follow this trend is the 1:9 TMS:DMP ratio sample which neither changes in proportion of silicon or Si_{2p} peak position. There is an uptake of oxygen but this is proportionally much less than in the other samples. An examination of the C_{1s} envelopes of these samples show that all have been oxidized to about the same extent.

It seems reasonable to conclude from this that the last sample behaves differently because its initial silicon content is below some threshold value, which would appear to be around an Si_{2p}/C_{1s} area ratio of 0.06, considering the data from the contact lens materials (Boston II 0.07, Boston IV 0.05). When oxidation of the silicon occurs an increase in the relative amount of silicon is observed. This is probably due to loss of carbon, the carbon being oxidized and the polymer structure being broken up to some extent, yielding volatile fragments, by the action of the plasma. Since the silicon is being converted from Si-C to Si-O it is likely that much of the carbon that is lost was originally bonded to silicon, particularly when it is noted that there is no apparent loss of carbon when the silicon is unaffected, even though the carbon in that sample is still being oxidized.

3.4.3 The Effect of Plasma Oxidation on Friction.

Tests using the slip/peel tester were first performed on a number of pure polymer films in order to assess the sensitivity and reliability of the method. These measurements were made using a 200g sled and each polymer was tested against both itself and all the others. Following this similar measurements were performed on Boston IV lenses and PMMA films using LDPE as the base material. This was chosen as the base material because it gave a smooth, easily prepared hydrocarbon surface which is comparatively soft; it was thus felt to be a very crude approximation to a dry eyelid with respect to its physical behaviour. Static and dynamic COF was recorded by this technique, the static COF representing the initial resistance to movement and the dynamic COF representing the resistance to continued movement once the two surfaces were moving past each other. The results are displayed in table 3.3. The error in these measurements is ±0.03.

It is apparent from the measurements of standard polymers that this test can easily distinguish between the different materials. It is also possible to determine which material is on the sled and which on the base plate, since reversing the positions of the samples introduces slight differences in the COF. These differences are due to the fact that the sample on the sled is small and securely attached whereas the base film is a much longer section attached only at its ends, it is therefore more susceptible to stretching and wrinkling as the surfaces move past each other. This effect is most pronounced in the case of Nylon and LDPE, both of which are soft and fairly elastic materials. In comparison PTFE shows little variation, regardless of the material it is being tested against or whether it is on the sled or base plate, since it is a highly inert material which will have little interaction with the other surface, and since it is essentially inelastic. It is only in the case of PTFE on PTFE that any significant difference is observed. This lower value for the static COF can be ascribed to the lack of any significant interfacial interaction between the two surfaces.

The modified samples behave, in general, as might be expected, increasing in COF on oxidation. This will be due to the increased adhesive component provided by the polar groups introduced at the surface by the oxygen plasma.

Boston IV has a lower COF than PMMA and this can be attributed to the presence of the siloxane on the surface; the relatively good frictional properties of siloxanes in general have found applications in lubrication and release agents (16). It is somewhat more difficult to explain why its COF appears to decrease slightly when modified. As has already been seen from the ESCA spectra, extra polar groups are introduced into the surface and it would therefore seem reasonable to expect a significant rise in COF, comparable perhaps to that of PMMA

Table 3.3 Coefficients of Static and Dynamic Friction for a Series of Polymers (n=4, SD=0.03)

Base Material	Sled Material	Static COF	Dynamic COF
Nylon	LDPE	0.45	0.37
Nylon	PTFE	0.23	0.11
Nylon	Nylon	0.53	0.41
PTFE	LDPE	0.25	0.16
PTFE	PTFE	0.15	0.12
PTFE	Nylon	0.28	0.16
LDPE	LDPE	0.46	0.33
LDPE	PTFE	0.20	0.11
LDPE	Nylon	0.67	0.55
LDPE	Boston IV	0.35	0.32
LDPE	Treated Boston IV	0.31	0.29
LDPE	PMMA	0.39	0.30
LDPE	Treated PMMA	0.45	0.32
LDPE	Treated LDPE	0.61	0.48
LDPE	Treated Nylon	0.96	0.84

since Boston IV is based on PMMA. The drop in COF appears very small and it is possible that the effect of the siloxane, which does not seem to be affected by the plasma, predominates over the changes induced by plasma treatment.

Studying the plots of the variation of COF with time shows that the behaviour of the "simple" polymers is more complex than the average COF values might indicate. Triolo and Andrade have classified this kind of plot into five types describing different types of behaviour (17). Figures 3.10-3.14 show the traces obtained for modified and unmodified LDPE, Nylon, PMMA, and Boston IV.

An examination of the traces shows that they follow the general form of an initial peak followed by a lower plateau region. The high initial peak is indicative of the force required to cause the surfaces to begin to slide past each other which is greater than that required to keep them in motion. The plateau region of the trace for LDPE shows a large number of small amplitude, high frequency spikes. This is type C behaviour and is due to the sticking and slipping of the surfaces. When in contact a bond is formed between them by adhesive forces or mechanical interlocking. As the surfaces move they are stretched, increasing the force on the sled, until a point is reached where the interfacial forces fail or where the surface suffers mechanical failure and the sled jumps forward, suddenly reducing the force on the sled.

In comparison in the plateau region of the treated LDPE sample the amplitude of these spikes is much reduced. This

Figure 3.10 Variation of COF with Time for LDPE and Modified LDPE against LDPE.

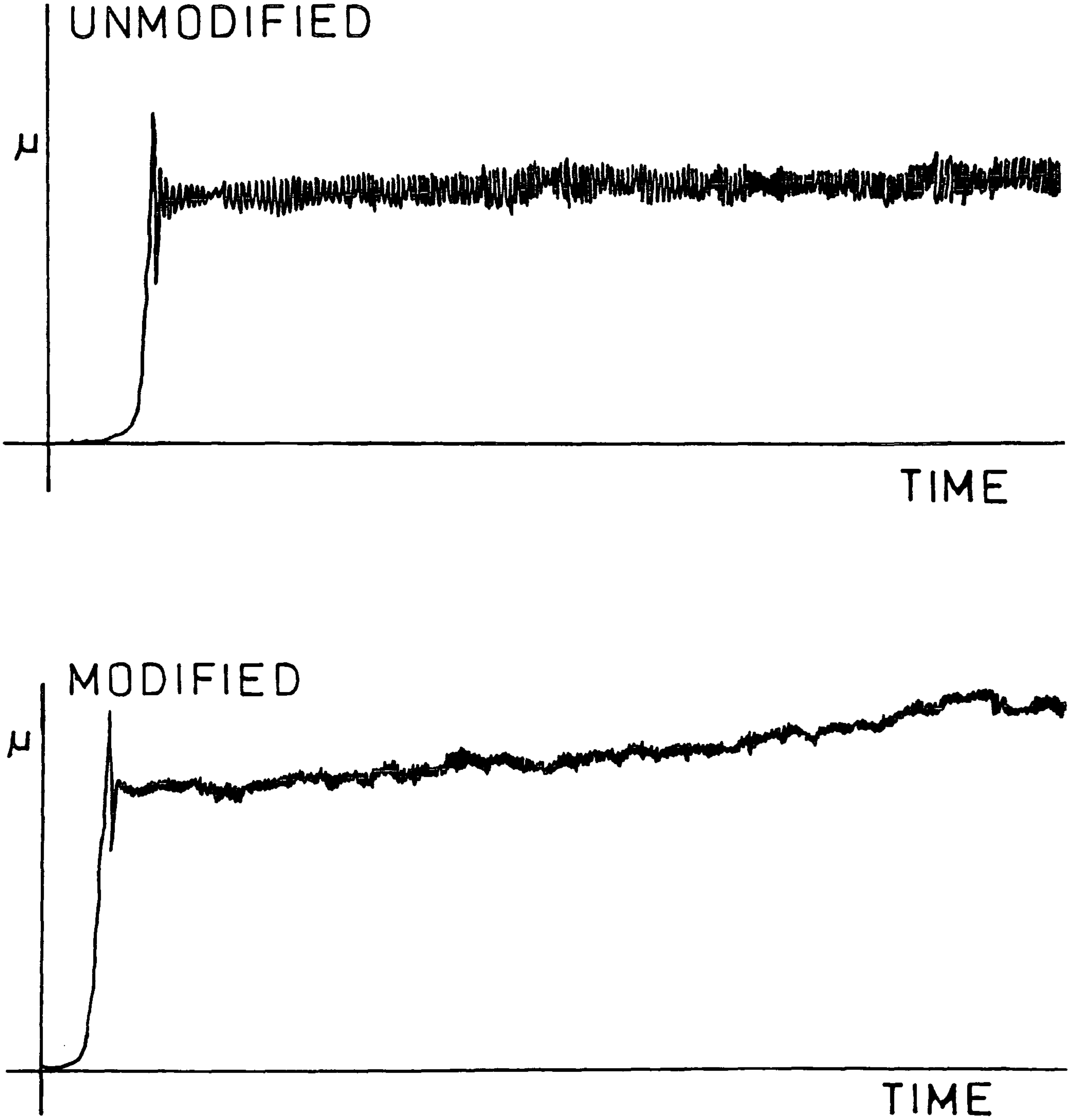


Figure 3.11 Variation of COF with Time for Nylon and Modified Nylon against Nylon.

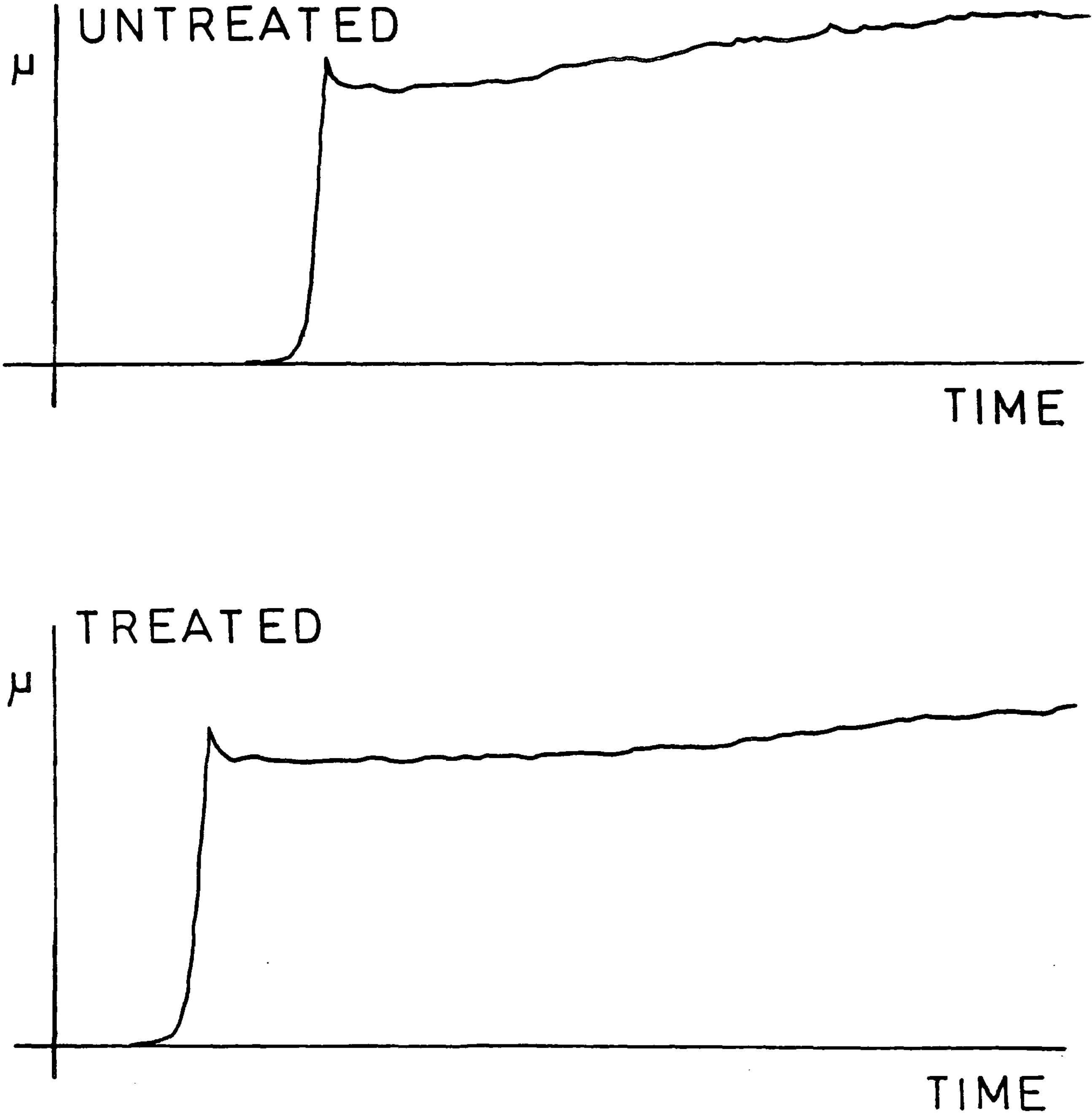


Figure 3.12 Variation of COF with Time for Nylon and Modified Nylon against LDPE.

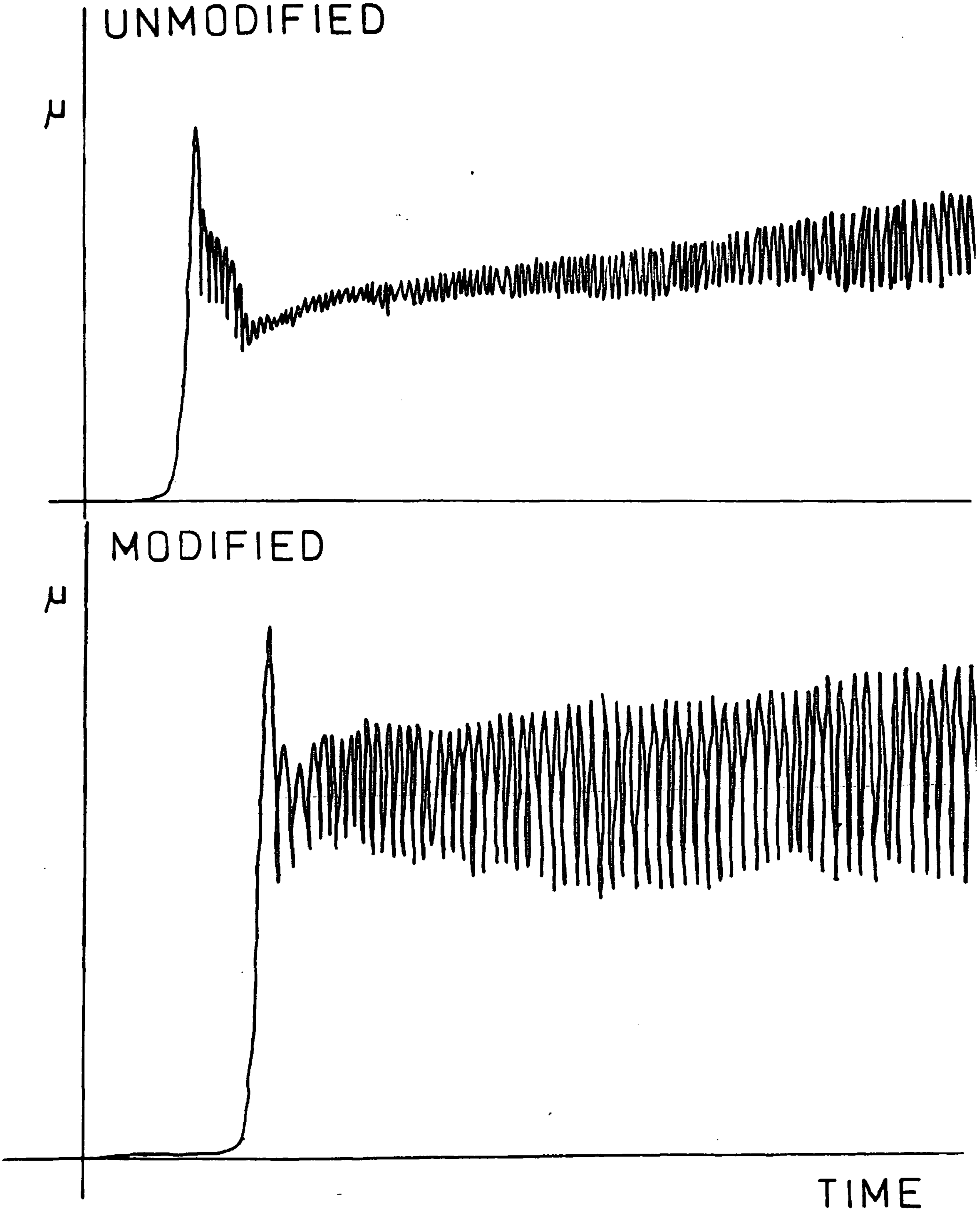


Figure 3.13 Variation of COF with Time for PMMA and Modified PMMA against LDPE.

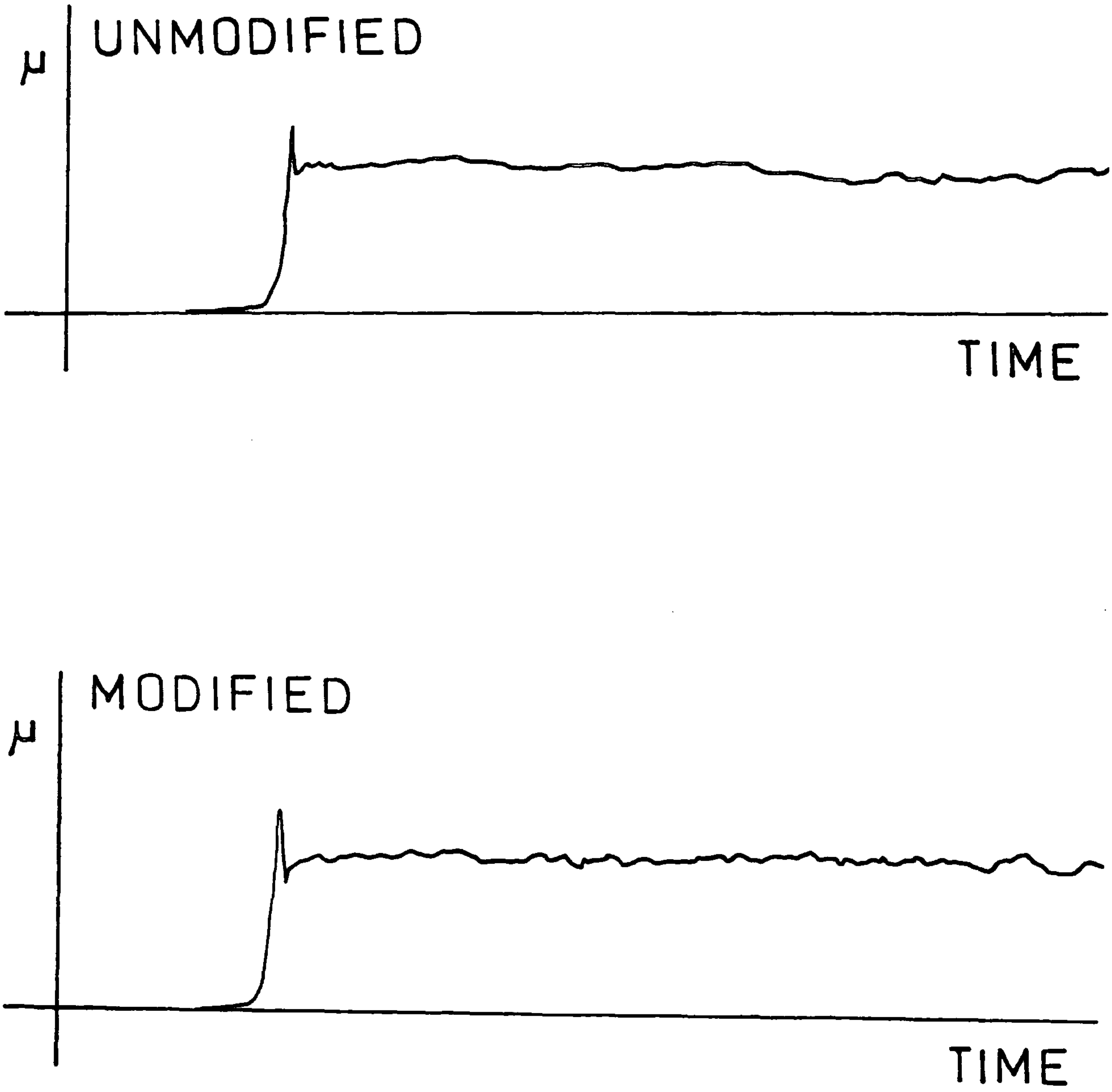
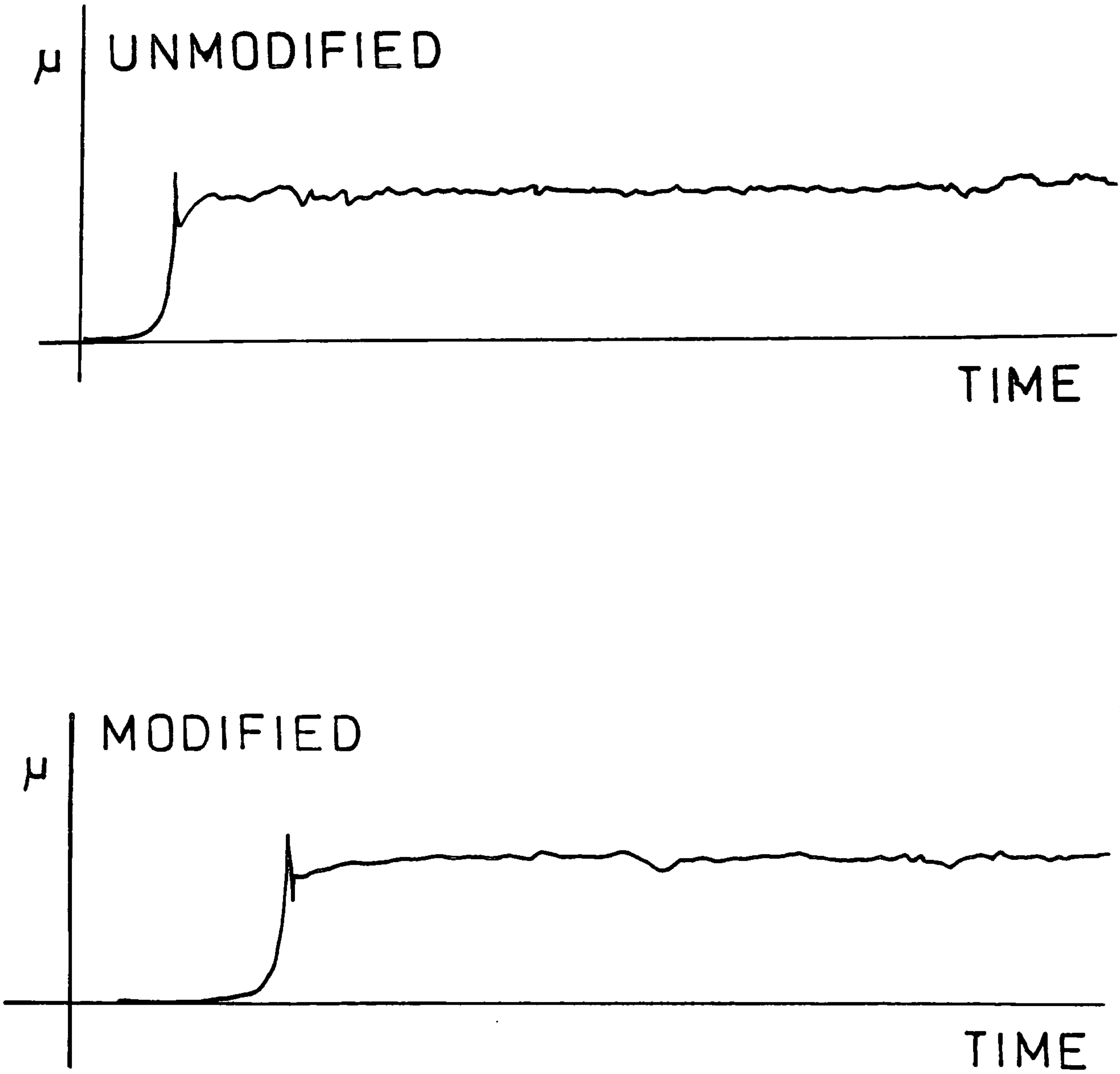


Figure 3.14 Variation of COF with Time for Boston IV and Modified Boston IV against LDPE.



could be due to one of three things; weaker interfacial forces, a more rigid structure rendering it less elastic, or a weak surface layer able to fail cohesively before the adhesive forces between the polymers fail. Since this material is treated we would expect the interfacial forces to be stronger due to an enhanced polar component, which is supported by the overall increase in the value of the COF. Plasma treatment with an inert gas, such as argon, could crosslink a surface (9), making it more rigid but an oxygen plasma tends to have the reverse effect, breaking up the structure of the surface. This is probably the reason for this change in behaviour.

The traces of nylon and modified nylon are both characteristic of type E behaviour, showing an initial spike followed by a smooth plateau which slowly rises. As above the spike is due to the force needed to overcome the initial forces between the surfaces. The rising plateau shows that there is some energy being stored in one of the surfaces but this is insufficient to cause a sudden failure of the interfacial forces leading to stick-slip behaviour as observed in the LDPE samples. This could be due it being stretched elastically such that the rate of recovery is less than the rate of stretching. Alternatively the forces between the surfaces could be increasing due to the generation of a static charge as the polymers rub against one another. Since it was observed that the nylon film readily became charged when rubbed this seems the most likely cause of the type E behaviour.

Nylon on LDPE exhibited type A behaviour in which, after an initial spike due to the initial movement as before, there are many large amplitude oscillations. The cause of these is the same as the cause of the oscillations seen in type C behaviour, described above, though in this case the forces involved are stronger and much more energy is stored before failure occurs allowing the sled to jump forward. On plasma treatment the amplitude of the oscillations increases and their frequency decreases, this clearly shows that the interfacial forces have increased. A greater force must be built up in order to break them, which increases the height of the spikes, and takes longer to reach the required level.

Both the PMMA and the Boston IV lens show very similar traces characteristic of type D behaviour. Once more there is the initial spike but here the plateau is level and without feature. Not much energy is stored in either of the surfaces and cohesive or interfacial bond failure occurs readily at a constant level.

Since a 200g sled was likely to cause significant deformation of the surface, measurements were performed using the inclined plane technique. The results are summarized in table 3.4.

Table 3.4 COF as Found by Inclined Plane Technique (n=12, SD=0.12)

Material	COF
PMMA	0.48
PMMA, treated	0.88
Boston IV, lens	1.25) (SD=0.24)
Boston IV, lens, treated	0.69)
Boston IV, button	0.81
Boston IV, button, treated	0.48
Equalens, button	0.38
Equalens, button, treated	0.42

These results show that the inclined plane technique distinguishes more clearly the difference between the treated and untreated lens material. The difference between the lens values and those for buttons is due to the fact that, since the lenses are curved they rock forward as the plane is raised. This not only makes the determination of the point of slippage difficult, but the angle to which the plane must be raised to cause the lens to slip is greater, since it will only slip after it has tilted as far as it is able. The error involved in measuring lens COF in this manner is ±0.24 whilst for buttons the error is reduced to ±0.12. This is still very large compared to the error involved with the slip-peel tester and is due to the fact that the determination of point of slippage must be done by eye, and the operator must then stop the device immediately to take a reading. Fortunately the difference between the treated and untreated Boston IV is quite clear, definitely showing that on plasma treatment its COF decreases. The PMMA sample increases in COF with treatment as shown previously, but again the difference between the two samples is accentuated. This increase in sensitivity over the slip-peel tester method is presumably due to the fact that the samples are being tested under their own weight thus minimizing the distortion of the surface due to compression.

The fluoro-siloxane acrylate Equalens was investigated using this technique and it can been seen from the above results that this material has the lowest COF. This is perhaps to be expected since the ESCA spectra of Equalens show a significant amount of fluorine in the surface, figure 3.15, and the concept behind Equalens is to reduce the interaction between it and foreign materials.

The spectra of Equalens show a very similar material to Boston IV differing mainly in the presence of fluorine, F_{1s}/C_{1s} area ratio 0.24 (n=1). Examination of the C_{1s} envelope shows the oxygen environment observed in Boston IV with an additional peak at 294.15 eV, such a large shift can only be due to carbon in a CF_3 group. This group normally appears at a shift of 8.3

from hydrocarbon and so the shift of 9.15 eV observed indicates that this is in fact a CF_3-O environment. Since Equalens is based on PMMA it is probable that the fluorine containing unit is a trifluoromethylester of some acrylate.

When Equalens is plasma oxidized under the same conditions as Boston IV (20W, 0.4 mbar, 45 seconds) roughly half the fluorine is lost from the surface, figure 3.16.

This is accompanied by a large uptake of oxygen with the corresponding increase in all the carbon-oxygen peaks in the C_{1s} envelope. In addition there is a new peak in the C_{1s} envelope at a shift of 4.85 eV; this may be caused by the carbonate ($O{=}CO_2$) environment or more likely a combination of carbonate and fluoroester peaks since carbonate is normally observed at a somewhat higher binding energy of 5.5 eV. The presence of this group indicates that the oxidation of this material proceeds further than the oxidation of Boston IV. It is interesting to note however that despite this the silicon in Equalens does not oxidize nor does it increase in the amount present in the surface, 4 silicons per 100 carbons. The peak position of the Si_{2p} envelope is 102 eV corresponding to a siloxane environment.

Contact angle studies using diiodomethane and triply distilled water were performed to investigate the surface energetics of these modified materials in greater depth. The

Figure 3.15 ESCA Spectra of Equalens

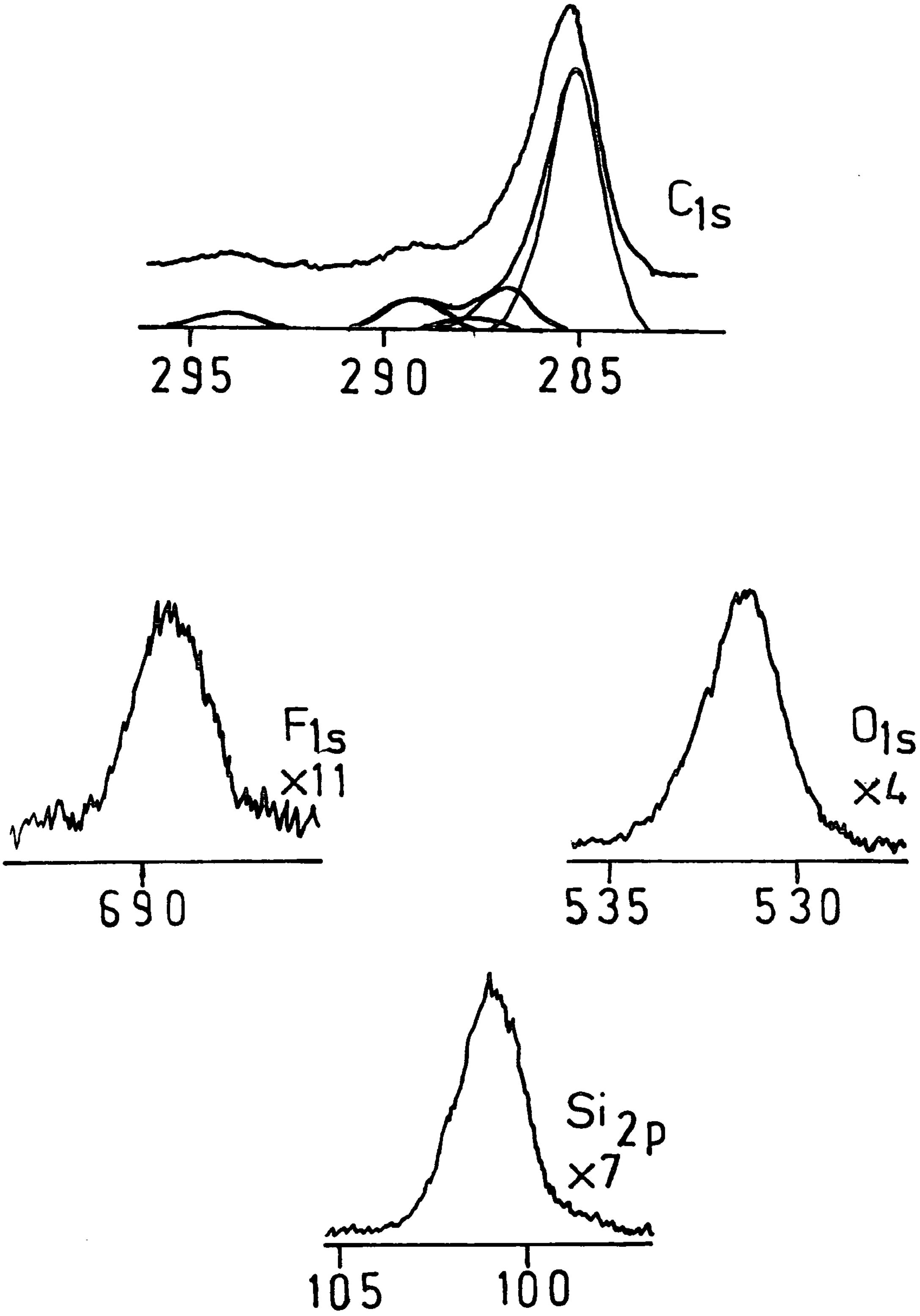
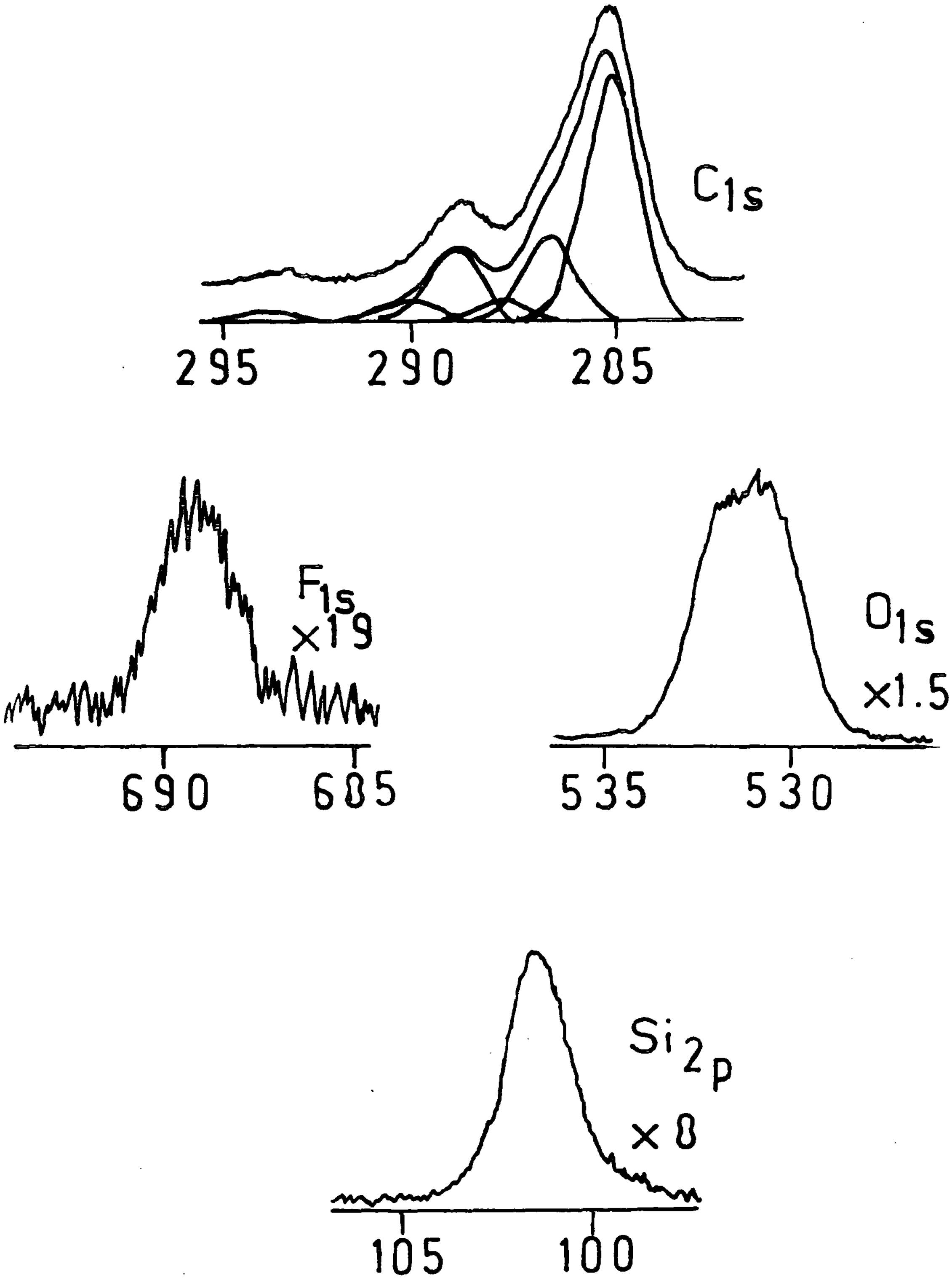


Figure 3.16 ESCA Spectra for Plasma Oxidized Equalens



results, as calculated according to equation 2.4, are shown in table 3.5.

Table 3.5 Polar and Dispersion Components of the Surface Energy of Some Lens Materials (n=5, SD=3.9)

Material	Contact Angle θ		γ_p	γ_d
	H_2O	CH_2I_2	dynes/cm	
Boston IV	85	45	3.1	34.8
Boston IV, treated	42	43	32.0	26.5
Equalens	103	56	0.1	32.1
Equalens, treated	35	59	45.2	17.0

These data show that all the polar components of the surface energy of all these materials increase dramatically when plasma treated. This agrees well with the ESCA spectra which in all cases show a large increase in the number of oxygen containing, and therefore polar, groups. Of greater interest from this experiment is the information on the variation of the dispersion component of the surface energy. In all cases this decreases, which is not surprising as it is expected that oxidation will convert some of the non polar regions of the polymer into polar ones and so some dispersion forces are bound to be lost. However it is significant that the loss of dispersion force is less in the Boston IV than in the others. Boston IV is the only material observed where the COF falls on oxidation. Though dispersion forces do contribute to the adhesive component of friction they are generally weaker than polar forces. Therefore since dispersion forces make up a greater proportion of the interfacial interaction than in similar materials such as PMMA, this, together with the presence of siloxane in the surface helps to explain its unusual frictional properties. The aforementioned conditions indicate that the increase in COF should be proportionately less than for other materials but it is necessary to invoke some other condition to fully explain why the COF should fall. One possibility is that the plasma treatment reduces surface roughness. Scanning electron micrographs of the surface of treated and untreated Boston IV show that surfaces both display a relatively smooth surface criss-crossed by a number of submicron grooves. These are believed to arise from the polishing of the lenses. There is no apparent topographical change on plasma treatment.

The remaining alternative is that the surface of the polymer is damaged by the plasma such that when tested for COF, cohesive failure of the material is facilitated. Unfortunately the above experiments are unable to determine whether or not this is the case.

3.5 Conclusion

The work in the proceeding pages can be summarized as follows:

a. Boston IV is a siloxane acrylate material containing both colouring and wetting agents. The siloxane co-monomer is present only in a very small percentage but appears to concentrate near the surface.

b. By using plasma oxidation the siloxane acrylate lens material can be made much more wettable to water by oxidizing the carbon in the polymer to give additional polar groups in the surface.

c. Despite the highly reactive species present in the plasma the siloxane component of the material is not oxidized. This appears to be because the amount of silicon in the surface is very low.

d. Friction tests showed that, unlike other polymers, the COF of Boston IV decreases when oxidized. This can be partially explained by the relatively low conversion of dispersion forces to polar forces when treated and to the continued presence of a siloxane in the surface after modification.

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CHAPTER 4

THE AGEING OF PLASMA TREATED POLYMERS

4.1 Introduction

In the preceding chapter it was shown that the plasma oxidation of PMMA and Boston IV substantially increases the oxygen content of the polymer surface greatly reducing its contact angle. As has also been mentioned a mobile polymer surface can rearrange its surface structure to minimize the surface energy; this was clearly seen in the case of Boston IV where there is significant migration of siloxane to the surface of the untreated material. It is reasonable, therefore, to expect that there might be some change in the surface after modification acting to reduce the high surface energy produced by the treatment.

This sort of reorganization has been observed before,in materials treated by glow discharge processes (1-3), those treated by conventional chemical techniques (4,5), and in polymers whose surfaces have been orientated during the manufacturing process (6). In this work it was observed that a high energy surface changed over a period of time into a lower energy surface. The initial high energy surface was due to the presence of polar groups oriented out of the surface. The decay of the surface properties of these materials could be associated with a loss of polar groups from the surface due reorientation or migration of the groups into the bulk of the polymer (7). This reduces the surface energy whilst placing the polar material in a polar environment where it can engage in some form of polar-polar interaction or hydrogen bonding. Where detailed experiments have been performed it was observed that the decay occurred rapidly in the initial stages before reaching a plateau which may be below the level expected for the unoriented material.

The way in which this decay occurs will be dependent on the nature of the preparation process, the solubility of polar material in the bulk polymer, the mobility of the polymer chains within the sample and environmental factors, such as temperature, which may affect this. It has been observed that in the case of corona discharge treated poly(ethylene terephthalate) (2) there is a loss of oxygen from the surface, as observed by ESCA; this suggests that modified material is able to migrate deep within the sample. In comparison corona treated LDPE loses its adhesive properties without losing the oxygen added by the discharge process (8). This suggests that in this case the polymer chains simply reorientate such that the polar groups are directed into the bulk. Heating LDPE which has decayed can increase the mobility of the polymer chains and bring treated material back to the surface (9), at least temporarily.

In the initial study of Boston IV the long term stability of the treated surface was considered. After 82 days the contact angle of the treated material had risen to 67°, though this is not such a simple case, as the lens was stored in water, to simulate conditions of use, and dried before performing the test.

The ageing characteristics of these treated materials is important because a lens treated in a laboratory will be stored whilst being transferred to the practitioner and eventually the patient. This delay could be up to one month. How the surface behaves during this period is not only important from the view of the durability of the treatment but also because it is this decayed surface which the patient initially experiences and which is found to perform in such a comfortable and compatible manner. Therefore a study of the changes which take place and of the surface which is finally produced is an invaluable aid in understanding the biocompatibility of this material in the eye.

4.2 Experimental

Boston IV contact lenses were placed on the central region of a glass slide which was then inserted into the Polaron plasma reactor. The lenses were then treated with an oxygen plasma (20W, 0.2 mbar, 45s) as described in detail in chapter 3. On removal from the reactor samples were placed in glass sample bottles to prevent accumulation of dust and grease during storage. Some of these samples were stored in air whilst others were stored respectively in distilled water or "Total" lens solution.

PMMA film deposited from a solution in chloroform was cut into sections and plasma treated under the same conditions as the lens material. Samples of PMMA were stored both in air and in distilled water. Polyetheretherketone (PEEK) film was cut into suitably sized pieces and oxygen plasma treated in the same manner as the Boston IV and PMMA but with slightly different plasma conditions,(5W, 20s, 0.4 mbar). It was found that at such a low power it was necessary to ignite the plasma using an electrostatic spark gun fired next to the reactor chamber. PEEK was stored in bottles in air and distilled water. In order to be able to reliably distinguish the treated and untreated sides of these films the samples were cut to a rectangular shape and the top right hand corner cut off; therefore only one orientation of the sample would present the cut in the correct position. The samples were stood upright in the containers with the minimum contact with the vessels walls.

For temperature dependent studies the samples were placed in either a freezer or hot water bath which was thermostatically regulated to the desired temperature. Otherwise samples were stored at room temperature in the dark.

Contact angles with distilled water were measured at suitable intervals using the sessile drop technique (chapter 3).

Samples which had been stored in water were allowed to dry in air for one hour before being measured. For comparison a sample was dried in vacuum for 15 minutes but no difference in the contact angle between this sample and one dried in air was observed. Samples stored in lens solution were rinsed in distilled water for approximately thirty seconds before being left to dry in air for one hour. Samples stored at different temperatures were tested immediately upon removal from their controlled environment.

ESCA spectra of these samples were recorded one at the same time as the contact angle was being measured. In the case of films the samples were cut into two segments and one half used for each measurement. With lenses a different lens was used for ESCA examination to that used for contact angle determination, though both were treated in the same batch.

An investigation of the vertical homogeneity of the samples was carried out in these experiments, using variable electron take of angle to vary the sampling depth. In this process the spectra were recorded at take off angles of both 30° and 60°. Considering a point in the sample a distance x below the surface, figure 4.01, at a take off angle of 30° a photoelectron emitted from this point must leave the surface travelling vertically to reach the analyser.

The electron must travel a distance d_1 through the sample before leaving the surface. At a take off angle of 60° a photoelectron from the same depth x must travel through a distance d_2 to leave the surface. Simple geometry shows that d_2 is greater than d_1 ($d_2 \approx 1.7 d_1$). A photoelectron of given kinetic energy can only travel through a certain distance before inelastic collisions with atoms in the sample prevent it from leaving the surface with its correct kinetic energy. Clearly the electron from depth x will not be able to escape from the surface if z is greater than the distance the electron is able to travel, though it may escape at a 30° take off angle. In effect at a higher take off angle the photoelectrons sampled will come from closer to the surface on average than at a lower take off angle.

The sampling depth for a particular photoelectron at a articular take off angle may be determined using the following expression (10),

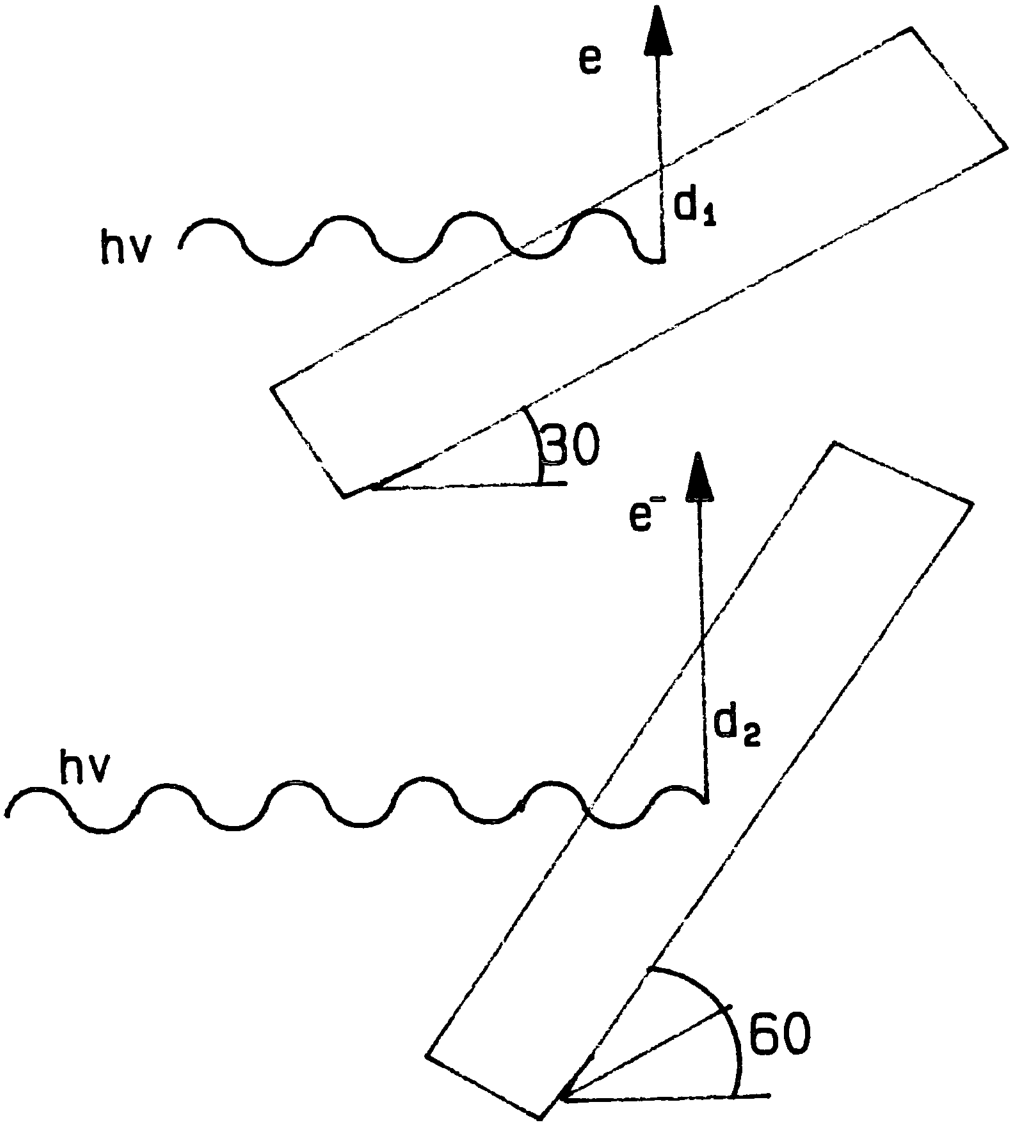
$$d = 3\mathrm{lambda}\cos\theta$$

where d is the sampling depth, θ is the take of angle and lambda is the electron mean free path. The electron mean free path can be calculated from the formula

$$\mathrm{lambda} = E/(a(\ln E+b))$$

where E is the kinetic energy of the electron and a and b are

Figure 4.01 Relation of Sampling Depth to Electron Take Off Angle



parameters which depend on the electron concentration and on the core levels of the element under study (11). From this the sampling depths of the core levels under study can be calculated and are displayed in table 4.1.

Table 4.1 Sampling Depths at Take Off Angles of 30° and 60°

Core Level of Photoelectron	Sampling Depth (Å)	
	30° TOA	60° TOA
C_{1s}	35	20
O_{1s}	20	12
Si_{2p}	37	21

Since it was found that there was a gradual decay of the surface treatment with time an attempt was made to arrest, or at least retard, this process by treating a series of samples of Boston IV with a plasma composed of a mixture of equal amounts of argon and oxygen; plasma conditions were 20W, 0.2 mbar oxygen, 0.2 mbar argon, 25 seconds. Argon plasmas have been reported before as a means of crosslinking a polymer surface (12), the intention being to inhibit the change in surface composition by reducing the chain mobility in the polymer.

In order to investigate the effect of orientation on these materials, films of PMMA and Boston IV were prepared by dissolving the solid in chloroform and casting this, over a period of at least two days. The films were then peeled away from the glass and both sides examined by ESCA and by contact angle measurements.

PEEK was supplied as a film, thickness approx. 100µm, by I.C.I. plc. Argon gas was supplied by B.O.C. Ltd.

4.3 Results and Discussion

As a first step in understanding the behaviour of these materials when their surface is perturbed from its equilibrium state, it is useful to consider the nature and decay of surfaces produced on a glass substrate. The samples are produced by peeling a film away from the substrate upon which it has been allowed to harden. It can immediately be seen that the contact angles of the surface produced in contact with the air and that produced in contact with the glass are radically different, table 4.2, and that after 1 week in air the higher energy surface has decayed to give a lower energy surface.

Table 4.2 Contact Angles of Films Cast Against Glass (n=10, SD=3.4)

Material	Contact Angle	
	Initial	After 1 week
PMMA, air contact side	80	83
PMMA, glass contact side	62	70
Boston IV, air contact side	103	104
Boston IV, glass contact side	90	107

If the ESCA spectra of the PMMA are studied in detail it can be seen that there are small differences between the side of the film that was exposed to air whilst hardening and the side in contact with the glass, table 4.3. The glass contact surface has a slightly higher oxygen content as evidenced by the O_{1s}/C_{1s} area ratio and examination of the component peaks of the C_{1s} envelope shows that there are slightly more oxygen containing groups in the surface of this sample. This is particularly clear in the spectrum taken at a take off angle of 60° where the signal originates from closer to the surface. It is possible therefore that the much smaller difference seen at a 30° take off angle is due to the difference observed in the outermost layers of the sample, since the spectrum at 30°

includes all the signal observed at 60°. It is also interesting to note that neither of the spectra conforms to the model spectrum expected from theoretical considerations, which would have the three environments in a ratio of 3:1:1, thus indicating that there may be some contamination present on both surfaces.

Table 4.3 ESCA Data for PMMA Film Peeled From Glass (n=1)

Sample	Take Off angle	O_{1s}/C_{1s} area ratio	Percentage of C_{1s} envelope		
			CH	C-O	O-C=O
Air side	30	0.67	66	17	17
Air side	60	0.64	67	16	17
Glass side	30	0.66	64	17	19
Glass side	60	0.69	63	16	21
Air side, 1 week	30	0.67	65	18	17
Air side, 1 week	60	0.62	68	17	15
Glass side, 1 week	30	0.67	62	18	20
Glass side, 1 week	60	0.63	66	16	18

The sample of the glass contact surface examined at a take off angle of 30° is very similar to that of the air contact surface and this implies that the contact angle is only affected by the outermost layers of the material, i.e. those observed at a 60° take off angle. This gives a sampling depth for contact angle measurements with water of less than 20Å.

After 1 week in air the contact angles of the two materials have converged to some extent and the ESCA data have also changed to more closely resemble each other. The oxygen content of the gas contact surface has dropped, particularly near the surface as shown by the comparatively large change in the O_{1s}/C_{1s} ratio at 60°. However this has also decreased slightly in the air contact surface which suggests an accumulation of some contamination, though this appears to be a considerably smaller effect. Both materials show changes in the composition of their C_{1s} envelopes, only the spectrum of the air contact sample at 30° remaining essentially unchanged. Near the surface both air and glass sides show a decrease in the O-C=O peak, though below the outermost layers in the case of the glass contact side there is an increase in this functionality, as shown by the 30° spectrum.

It has been shown that spin cast PMMA has a contact angle of around 62° and an ESCA spectrum which conforms to that expected from theory. When samples of the air and glass contact surfaces were examined using SIMS it was seen that the fresh glass contact surface most closely resembled PMMA and that the air contact surface appeared to be contaminated with hydrocarbon (13).

The conclusion that may be drawn from this data is that the PMMA is not visibly oriented by the glass. The difference between the samples is due to the migration to the air contact surface of a hydrocarbon impurity. This is in agreement with previous work (14,15) which has shown that the retention of material, other than the polymer, on film formation is dependent on the solvent and that the conditions in solution can produce time dependent variations of surface properties. It can be concluded from these and other studies (6) that chain configuration and mobility in solution strongly influence this behaviour.

The presence of a hydrocarbon impurity able to migrate to the surface, which results in a reduction of surface energy, helps to explain the changes occurring over time in the glass contact surface. At the outermost surface after 1 week a layer of hydrocarbon has begun to form, reducing the observed oxygen content. Since the area ratio assumes that the material is homogeneous the reduction of oxygen content in the outermost layers will be greater as the area ratio averages the composition over the top 35?.

The case of the contact lens material is somewhat simpler since it is already known that the siloxane component of the polymer is able to migrate to the surface to some extent.

Since in solution this mobility is greatly enhanced it is perhaps not at all surprising that there is a great difference in the composition of the two surfaces; what is unexpected is the complete absence of siloxane from one of the surfaces, table 4.4.

Table 4.4 ESCA Data for Films Deposited from a Solution of Boston IV (n=1)

Sample	O_{1s}/C_{1s}	Si_{2p}/C_{1s}	Percentage of C_{1s} envelope			
			CH	C-O	C=O	O-C=O
Air side	0.40	0.21	94	4	1	1
Glass side	0.77	0.00	49	30	5	16
Air side, Plasma treated	1.06	0.10	57	19	7	17
Untreated lens	0.42	0.04	75	15	3	7
Treated lens	0.63	0.05	64	20	6	10

All these data are derived from spectra taken at a take off angle of 30°. The differences between the two materials are dominated by the variation in silicon content, the siloxane component seems to be preferentially oriented at the air contact surface, drastically reducing the surface energy as shown by the very high contact angle of 107° as opposed to the glass side contact angle of 89°. The reason for the observed contact angle on the glass contact surface being higher than that of clean PMMA is not so clear since the composition of the C_{1s} envelope and the high overall oxygen content would suggest that the sample should have a comparatively high surface energy. It must therefore be assumed that there is some contaminant on the outermost surface of the material which is present in too thin a layer to be clearly distinguishable by ESCA.

Oxidation by plasma of the air contact surface provides an opportunity to produce supporting evidence for a theory propounded in chapter 3, to whit that the silicon in a surface will not be oxidized if its concentration is below a threshold value corresponding to an Si_{2p}/C_{1s} area ratio of about 0.06. Unfortunately the plasma polymers examined in studying this concentration effect contained Si-C species initially and were not that similar to the siloxane in Boston IV; therefore it is possible that the fact that the siloxane in Boston IV does not oxidize could potentially be attributed to the nature of the polymer, rather than the concentration of silicon in the surface. The air contact side of the contact lens film provides a surface with a high concentration of this particular siloxane. On oxidation there is a large uptake of oxygen, more than can be accounted for from the C_{1s} envelope, and the position of the Si_{2p} peak shifts from a binding energy of 101 eV to 103 eV. Modelling of the oxygen content from the area ratios and the components of the C_{1s} spectrum gives a Si:O ratio of 1:2, as opposed to a pretreatment ratio of 1:1. All this data indicates that the silicon in the surface has been oxidized to a silicate material. This shows that the nature of the siloxane in Boston IV does not prevent it from oxidizing and supports the idea that it is the normal concentration in the lens material surface which influences its behaviour.

4.3.1 The Ageing of PMMA in Air

The preceding results indicate that both PMMA and Boston IV can reorganize to present a surface with the minimum interfacial energy. In a plasma oxidation experiment the surface energy is raised by a large amount and there should therefore be some reorganization to reduce this interfacial tension. Additionally there will be a concentration of oxidized polymer at the surface and diffusion of this material may occur to relieve this concentration gradient. If a plot of the variation of contact angle with time after treatment for PMMA is examined, figure 4.02, it is seen that there is a rapid increase in contact angle over the first week after which there is a plateau region where there is comparatively little change, though over a long period there is a gradual increase.

The ESCA data for PMMA in air show two general features which are in agreement with the trend observed in the variation of the contact angle, the O_{1s}/C_{1s} area ratio falls, quickly at first and later more slowly, figure 4.03. It follows that the contact angle depends on the level of oxygen and hence polar groups in the surface, which is not unexpected. Additionally the amounts of the oxygen containing environments in the C_{1s} envelope decrease in a similar pattern, figure 4.4. As shown by these figures the trends are the same for spectra at both take off angles indicating that the changes are occurring reasonably uniformly throughout the top 35Å.

There is one anomaly in this data in that there is a noticeable increase in the amount of C=O functionalities after 15 days, from 3 to 6 percent of the carbon signal. This does not occur in the outermost layers of the sample as it is not seen at a take off angle of 60°. After this point the level of C=O drops to its original value.

4.3.2 The Ageing of Boston IV in Air

The variation of contact angle with time after treatment for Boston IV initially appears to follow the expected pattern, as for PMMA figure 4.02, that of a sharp initial rise followed by a plateau region where the contact angle rises only very slowly. However at the 22 day point there is a sudden increase in wettability, shown by a drop in contact angle of almost 10°. By the 27 day point the contact angle has risen again and continues to rise over the next few days.

ESCA spectra of Boston IV during this four week long period show a number of unusual features. Initially the overall oxygen content falls, as shown by the O_{1s}/C_{1s} area ratio, figure 4.06, and during the same period the Si_{2p}/C_{1s} area ratio remains constant. Then at 22 days there is an increase in the overall oxygen content of the surface concurrent with the drop in contact angle observed at this time. This increase in oxygen content can be linked to increases in the oxygen containing components of the C_{1s} spectrum, figure 4.07, particularly of the C-O group. The effect is most noticeable near the surface, take off angle of 60°. The doubling of the amount of C=O at this time and depth is reminiscent of the anomalous increase of carbonyl groups observed during the ageing of the plasma treated PMMA and it is therefore possible that a common process is involved, the presence of silicon in the Boston IV material introducing a further effect.

At the 24 day point there is another more severe change in the surface composition- there is a simultaneous fall in the overall oxygen content and dramatic rise in the silicon content of the surface. Examining the data for the composition of the C_{1s} envelope at this time reveals that most of the oxygen containing functionalities have been lost, particularly the carbonyl and acid/ester groups. These changes occur throughout the surface since the ESCA spectra at 60° and 30° are very similar.

Figure 4.02 Variation of Contact Angle with Time after Treatment for PMMA Stored in Air.

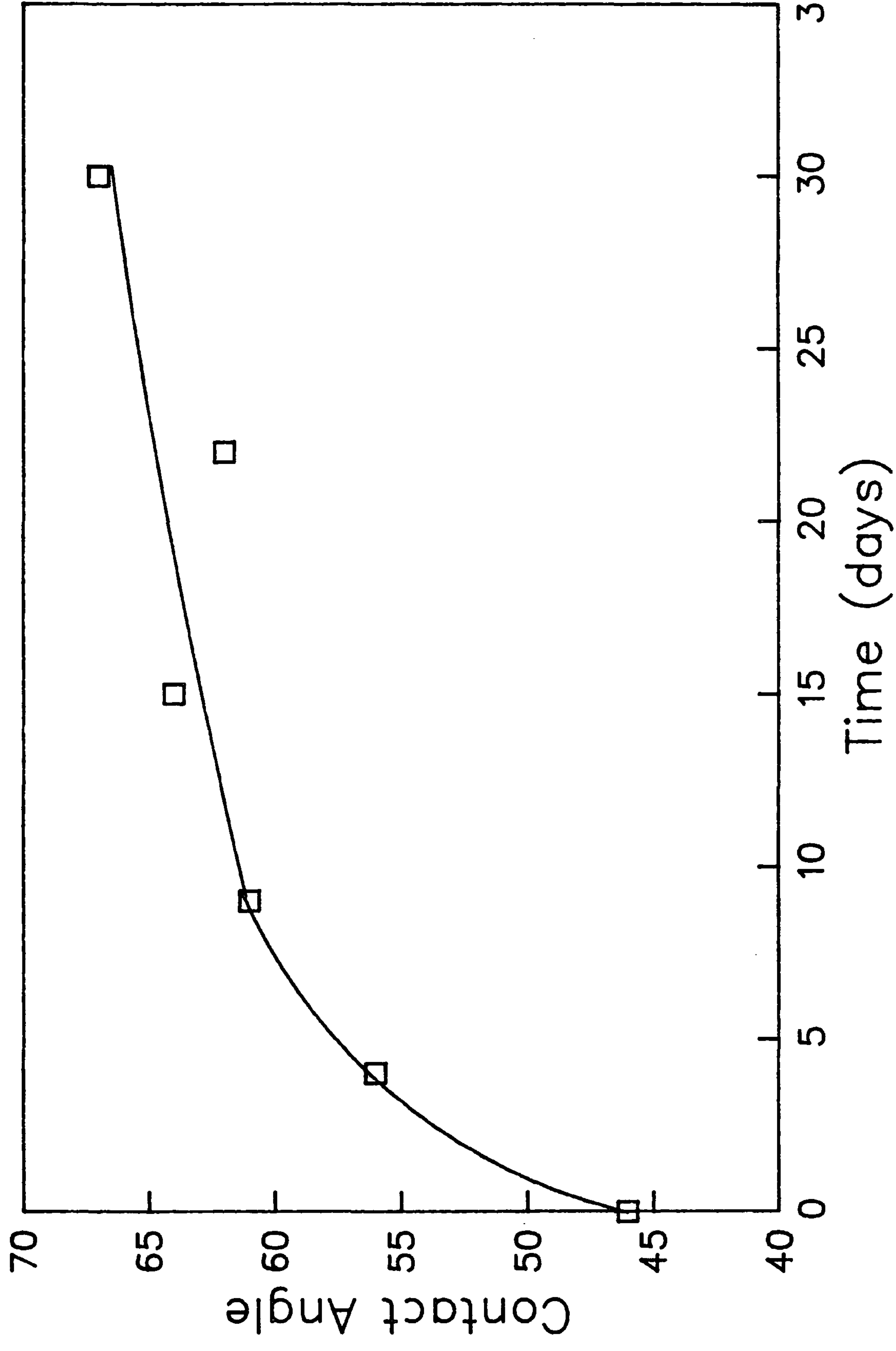


Figure 4.03 Variation of O_{1s}/C_{1s} Area Ratio with Time after Treatment for PMMA Stored in Air.

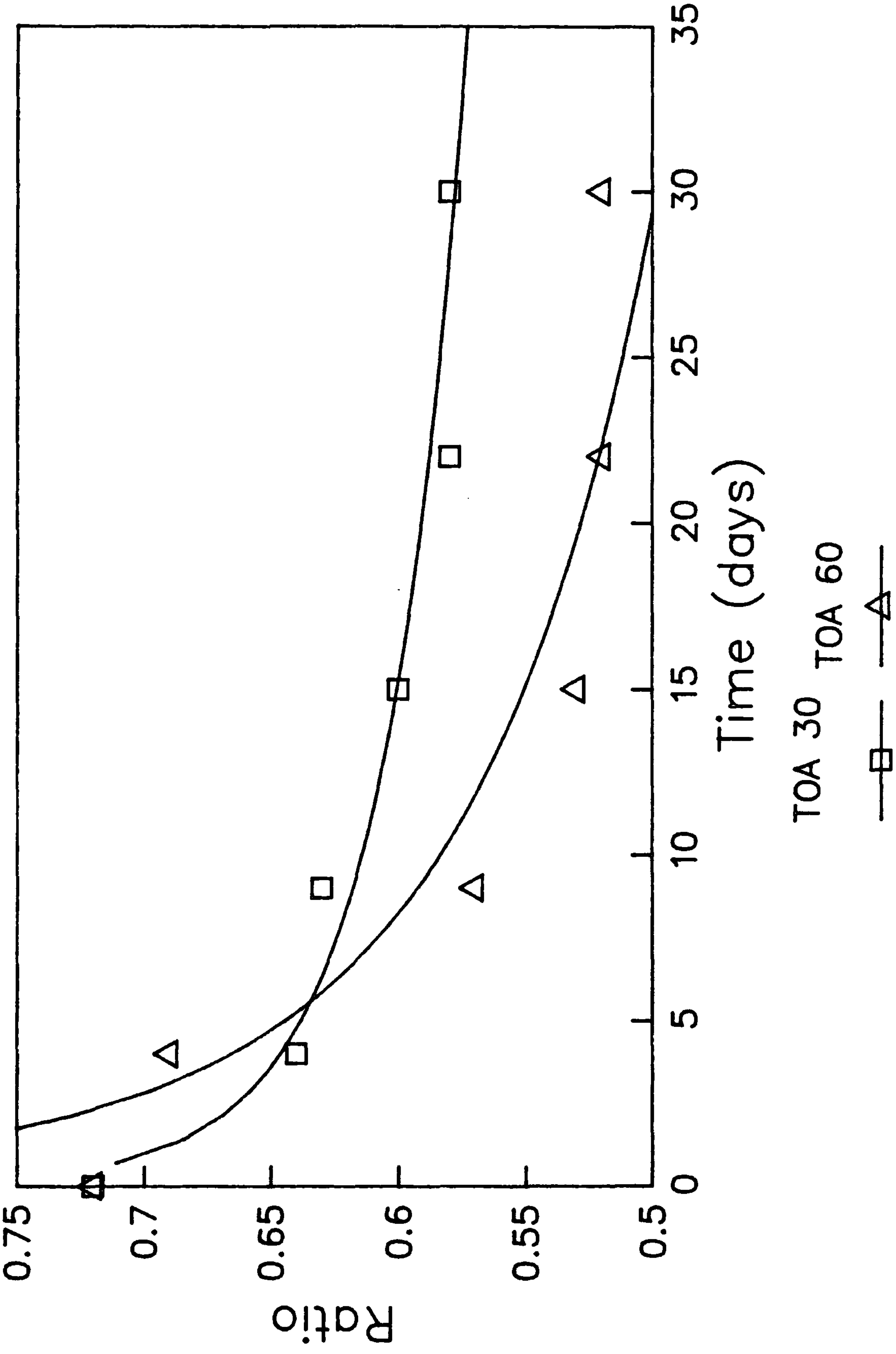


Figure 4.04 Variation of Oxygen Containing Components of the C_{1s} Envelope with Time after Treatment for PMMA Stored in Air.

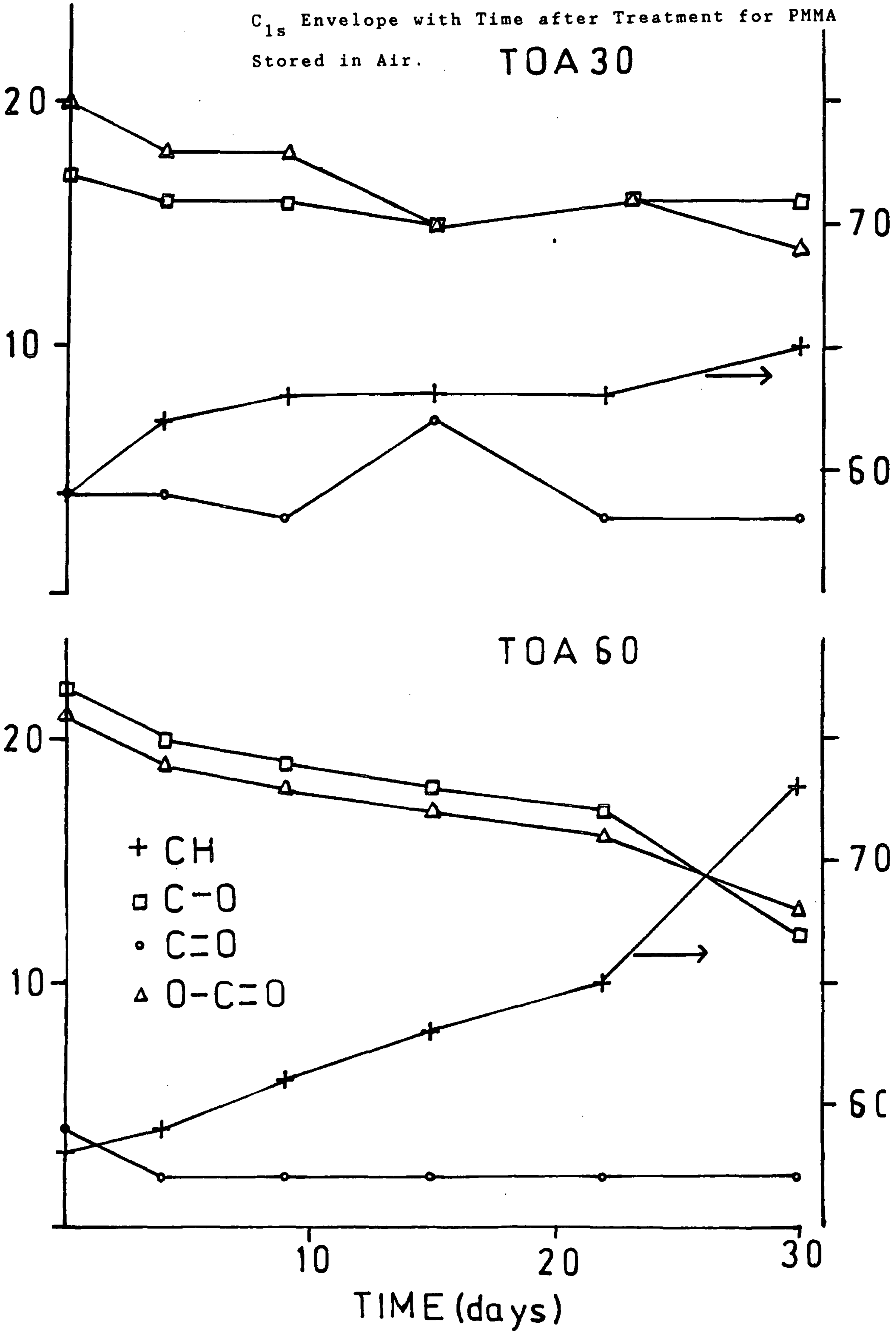


Figure 4.05 Variation of Contact Angle with Time after Treatment for Boston IV Stored in Air.

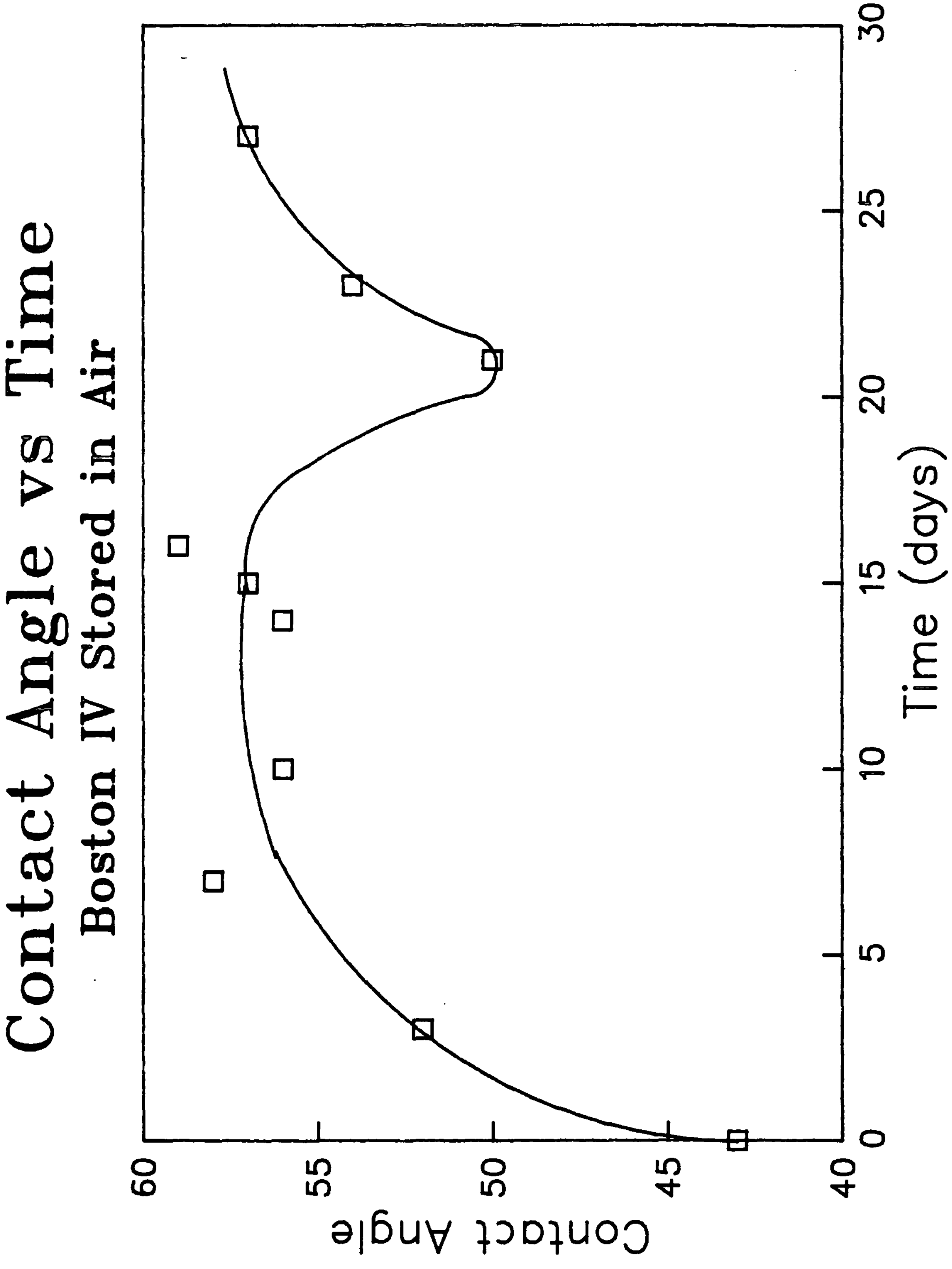
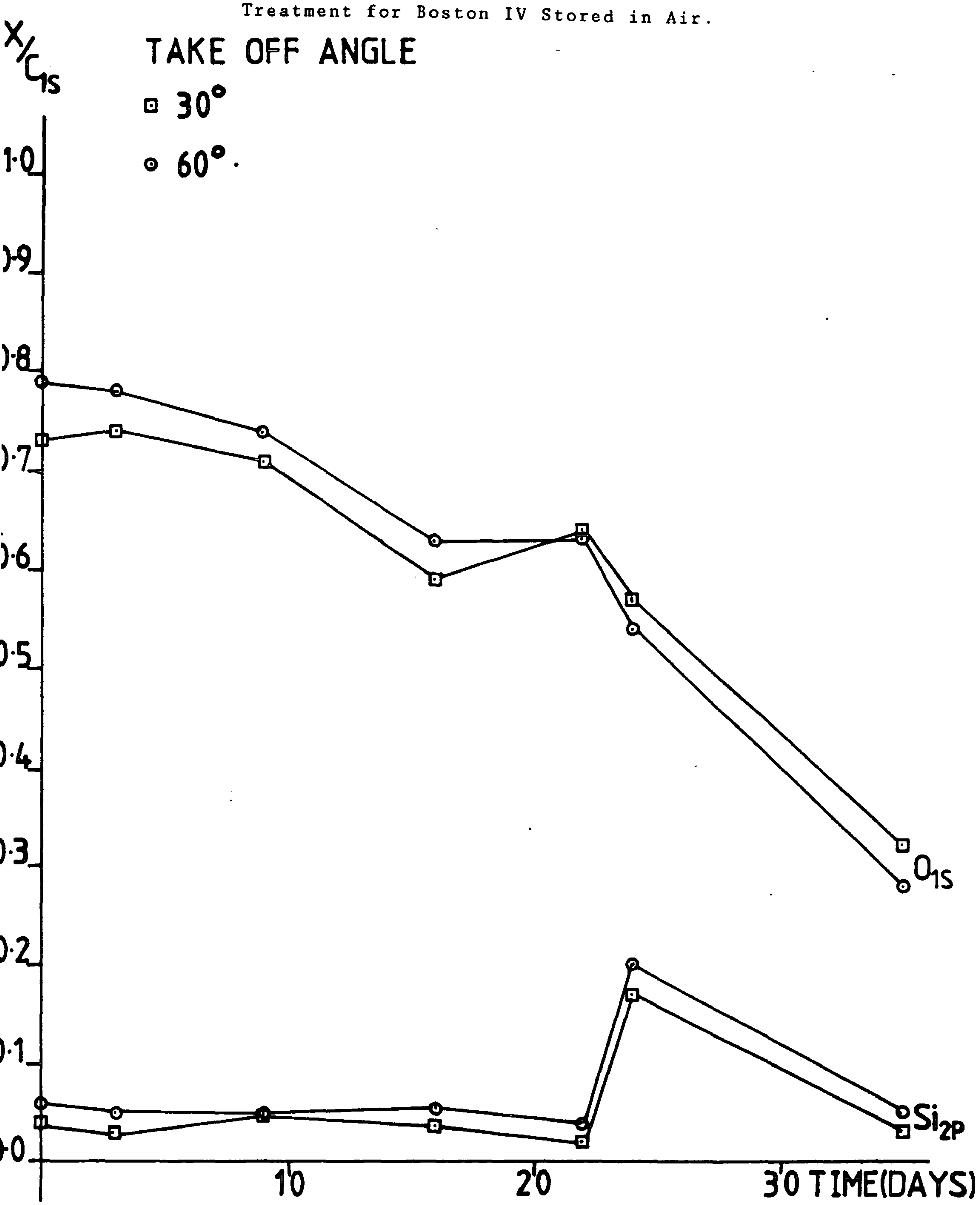


Figure 4.06 Variation of O_{1s}/C_{1s} and Si_{2p}/C_{1s} Area Ratio after Treatment for Boston IV Stored in Air.



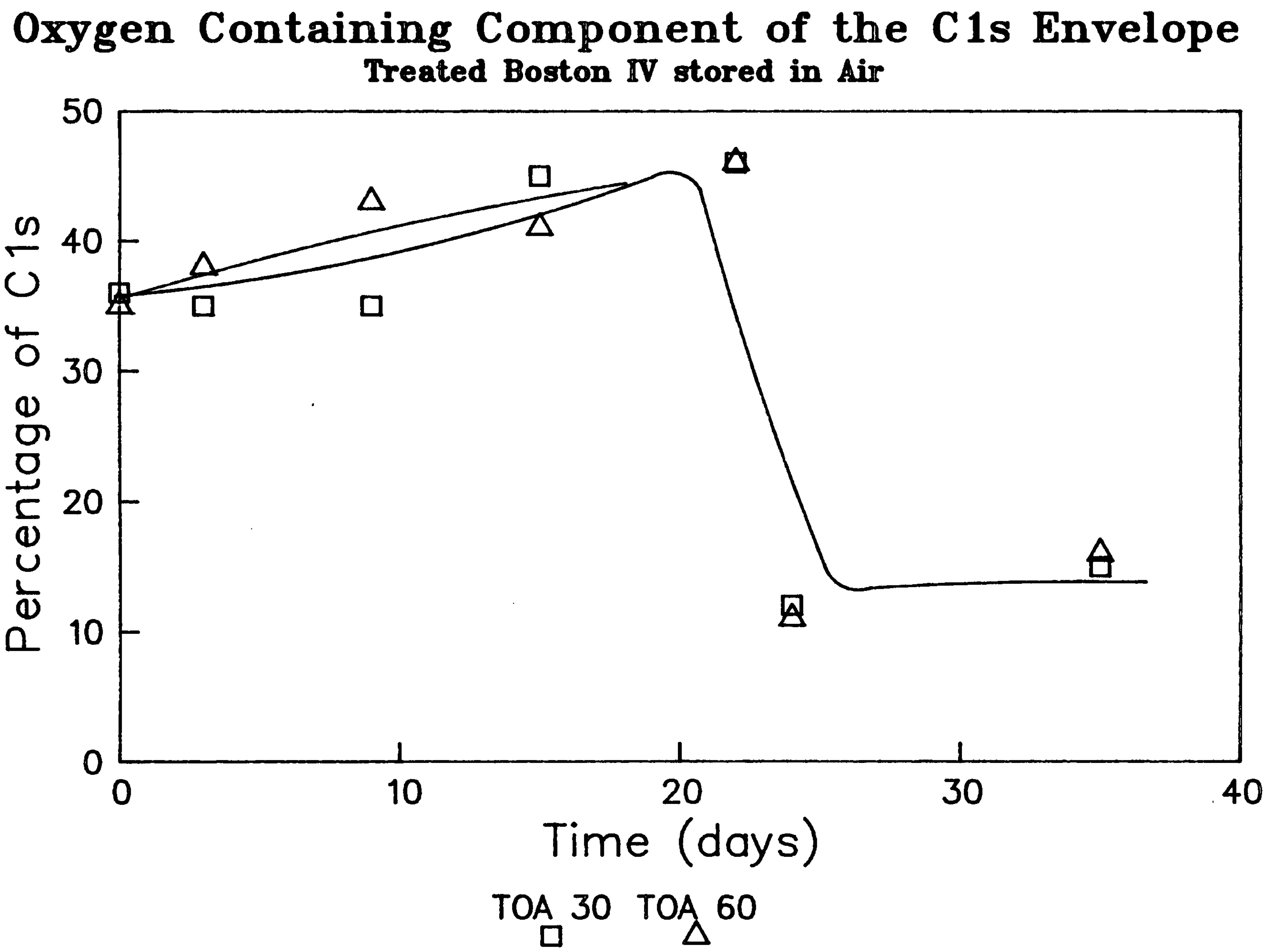


Figure 4.07 Variation of the Oxygen Containing Components of the C_{1s} Envelope for Boston IV Stored in Air.

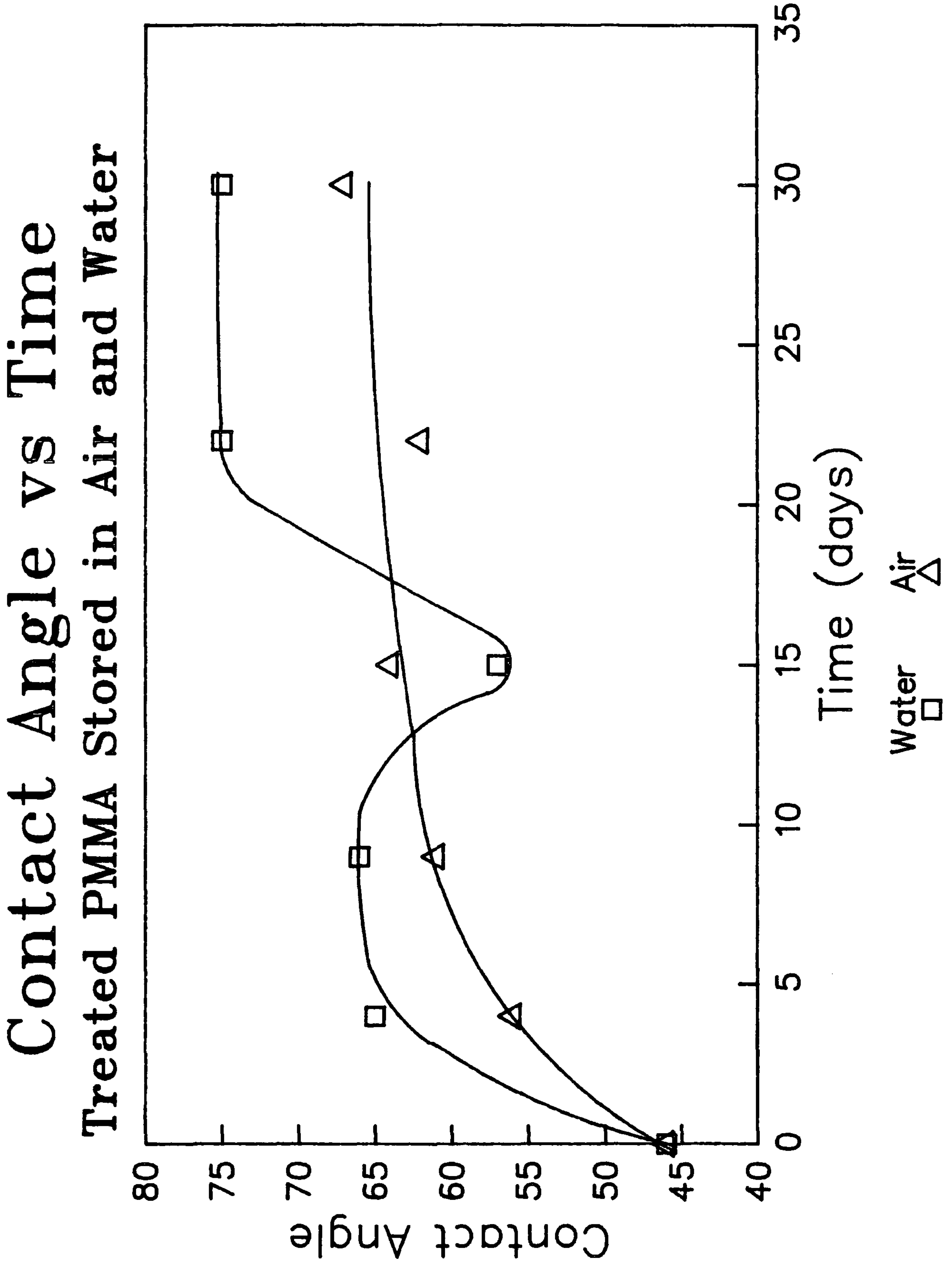
The high concentration of silicon at the surface is short lived and by 30 days the level of silicon has returned to its original value. In contrast the oxygen content, and corresponding oxygen functionalities, do not recover at all, and it appears that the overall effect of these changes has been to remove the modified material from the surface completely and at the same time rearrange the polymer structure to present less of the original carbon- oxygen species at the surface.

4.3.3 The Ageing of PMMA in Water

When a sample is stored in water it may be expected that its behaviour will be different as the liquid may penetrate into the surface, and the polar nature of the water might help to retain the polar material produced in the plasma at the surface, since the interfacial energy can be lowered by interactions with the liquid such as hydrogen bonding. However the contact angle of PMMA stored in water after treatment increases more rapidly than for the sample stored in air and levels off at a higher plateau level, figure 4.08.

The ESCA spectra of these samples show a rapid initial drop in O_{1s}/C_{1s} area ratio, figure 4.09, followed by a levelling out after three days to a value which falls slowly thereafter. This initial drop in oxygen content is greater than in the air stored sample which accounts for the relative rates of change

Figure 4.08 Comparison of the Change in Contact Angle with Time After Treatment for PMMA Stored in Air and Water.



in contact angle.

After 15 days storage there is a sudden increase in the hydrophilicity of the surface, as evidenced by the abrupt decrease in contact angle. This is not however associated with changes in the overall elemental composition of the material, as in the case of the perturbation seen in the lens material above, since there is no significant change in the elemental ratios at either of the two take off angles. There is however a change in the surface chemistry. Examination of the components of the C_{1s} spectrum, figure 4.10, shows that at this point there is a substantial increase in the peak assigned as carbonyl and also a smaller increase in the acid/ester peak. This effect is only observed at a take off angle of 60°; though a smaller increase in the C=O environment is seen at 30° this is most likely the effect of the change near the surface, which is more clearly seen at 60°. It must be remembered that the signal collected from a take off angle of 30° includes all the signal observed at a take off angle of 60°, in addition to data from material deeper in the surface. Thus a strong effect near the surface only appears as a small change when combined with the signal from the whole surface layer.

By twenty two days the contact angle has returned to a level comparable to that observed before the change and continues to rise slowly after this point. These changes are mirrored in the ESCA data from the C_{1s} spectrum, with the various oxygen

Figure 4.09 Variation of the O_{1s}/C_{1s} Area Ratio for Plasma Treated PMMA Stored in Water.

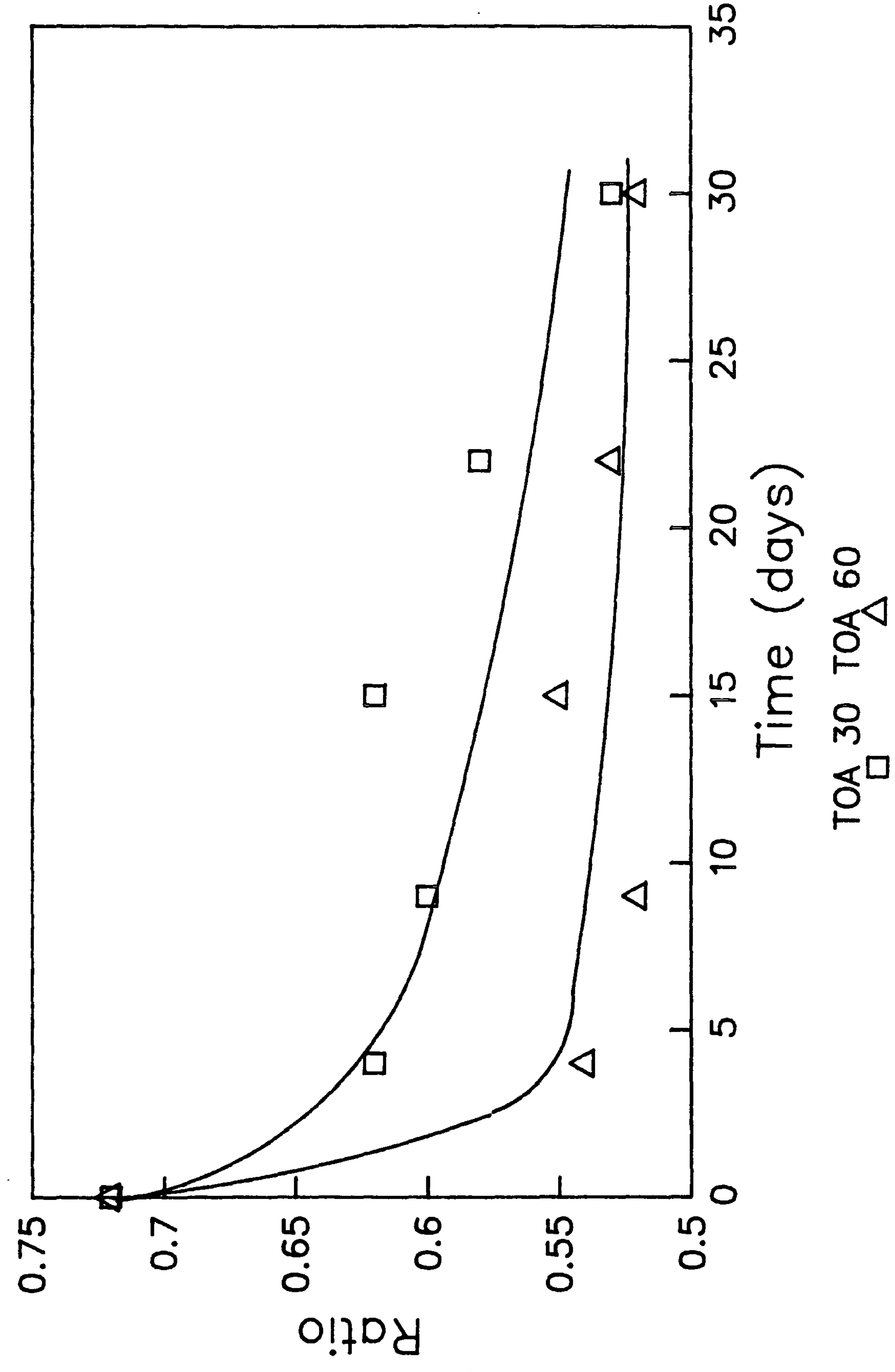
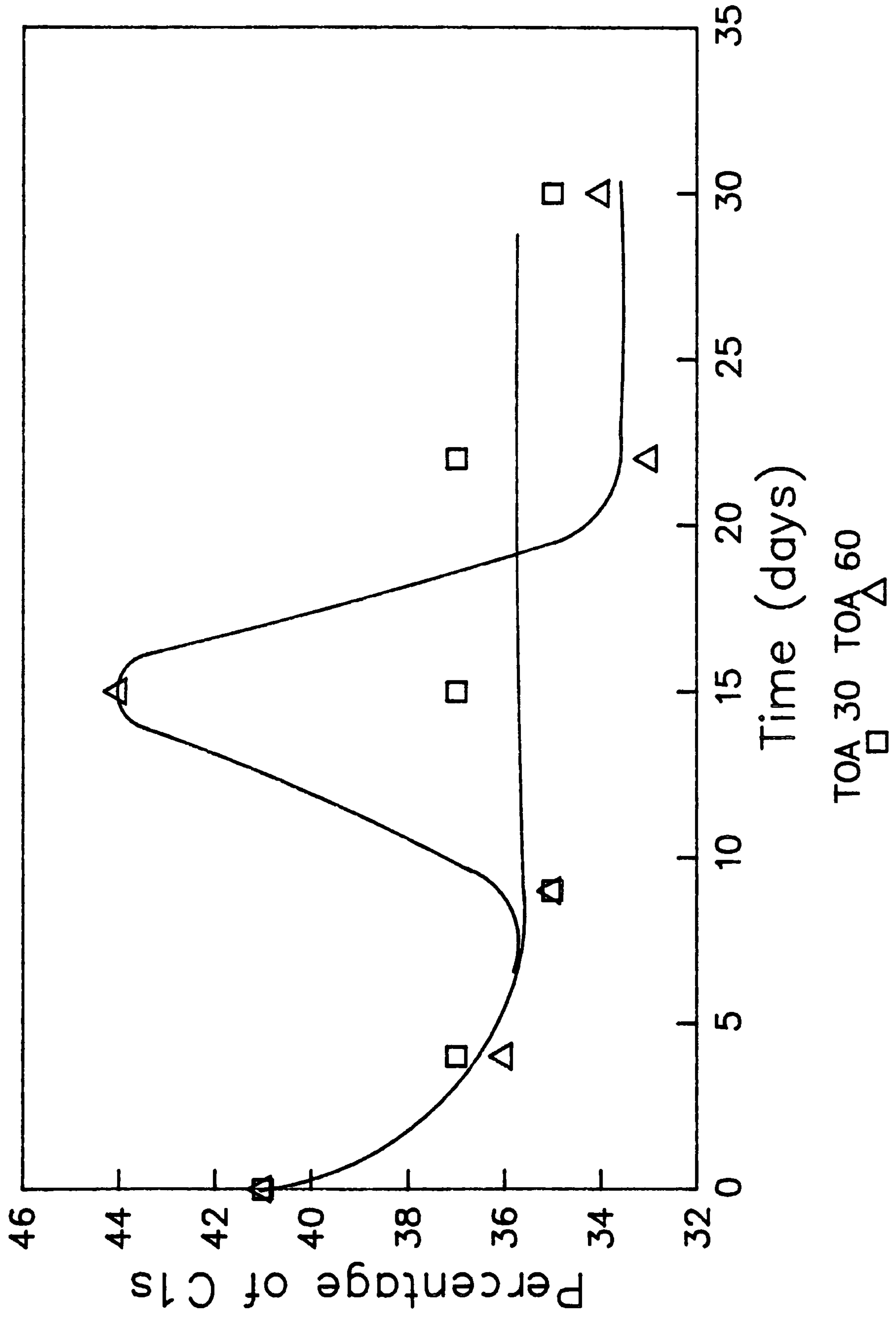


Figure 4.10 Variation of the Oxygen Containing Components of the C_{1s} Spectrum for Plasma Treated PMMA Stored in Water.



containing environments returning to levels similar to those seen in earlier spectra. There is no indication of a change i the contact angle or the ESCA spectra at the 22 day point, as was observed in the lens material stored in air.

4.3.4 The Ageing of Boston IV Stored in Water

When stored in water the lens material has very similar behaviour to the PMMA in water, with the same changes observed at 15 days but none at 22 days as seen in the Boston IV stored in air, figures 4.11-4.13. After 15 days there is a sudden drop in contact angle which persists for only a short time before rising to the plateau level again, figure 4.11. Throughout this time the Si_{2p}/C_{1s} area ratio remains constant.

The changes in the C_{1s} core level spectra obtained at a take off angle of 30° are very similar to the above but are less pronounced.

4.3.5 The Ageing of Untreated Boston IV

As a comparison to this experiment a study of the behaviour of the untreated lens material stored in water was undertaken. This showed that the contact angle gradually decreased with time, figure 4.14. The ESCA spectra showed a small initial uptake of oxygen but otherwise the overall elemental composition of the samples remained essentially unchanged over

Figure 4.11 Variation of Contact Angle with Time for Plasma Treated Boston IV Stored in Water.

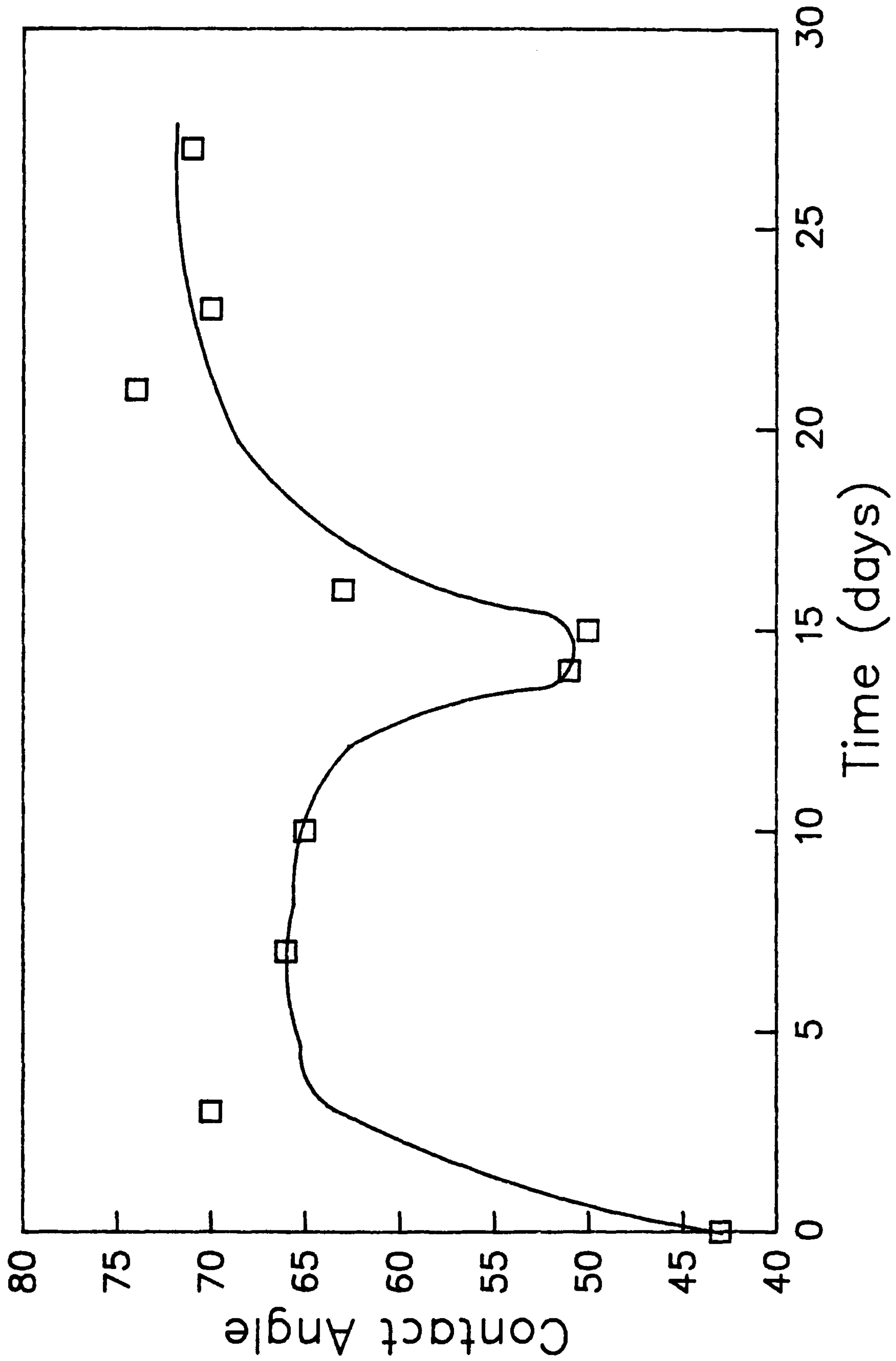


Figure 4.12 Variation of the O_{1s}/C_{1s} and Si_{2p}/C_{1s} Area Ratios for Modified Boston IV Stored in Water.

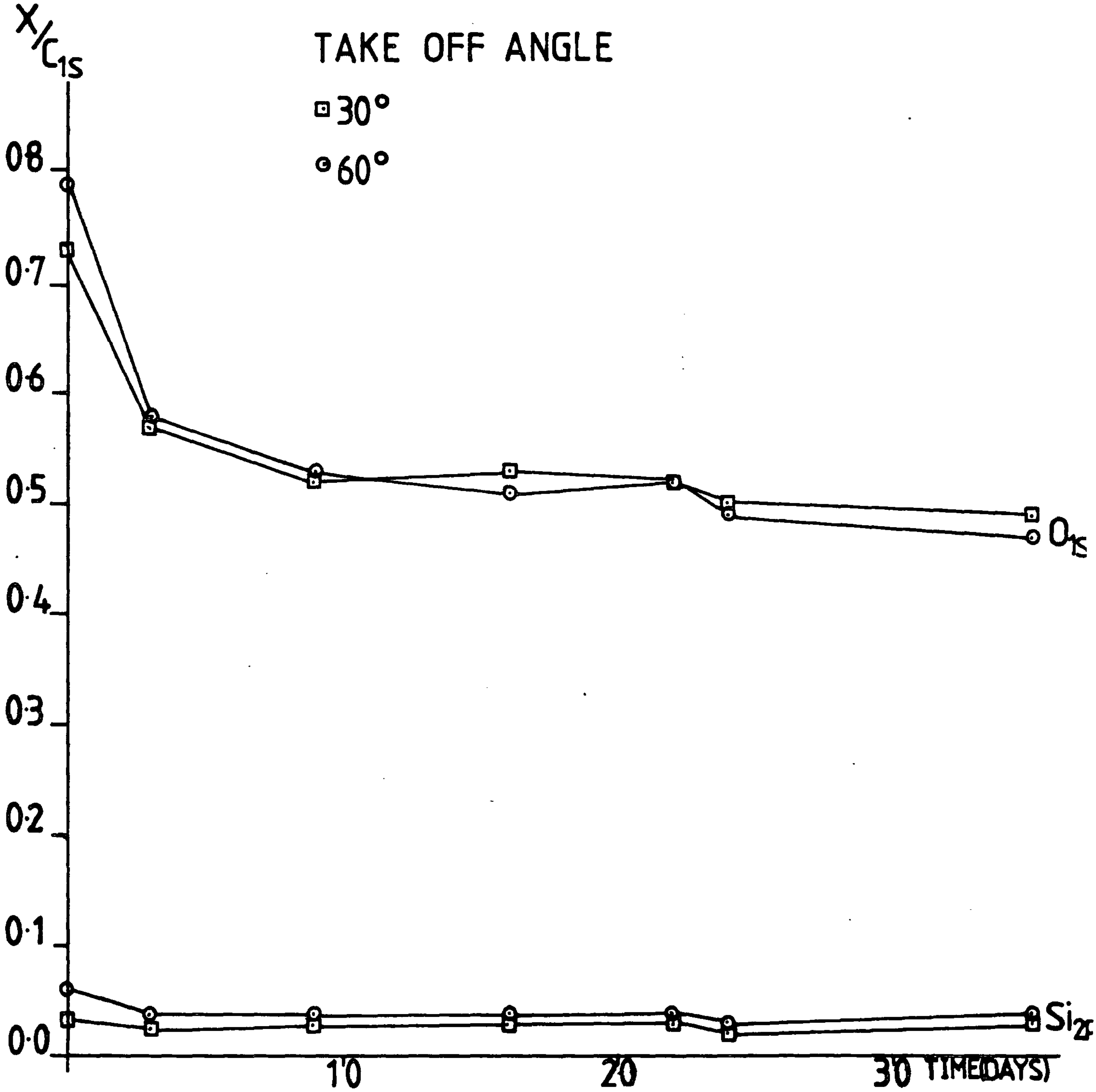
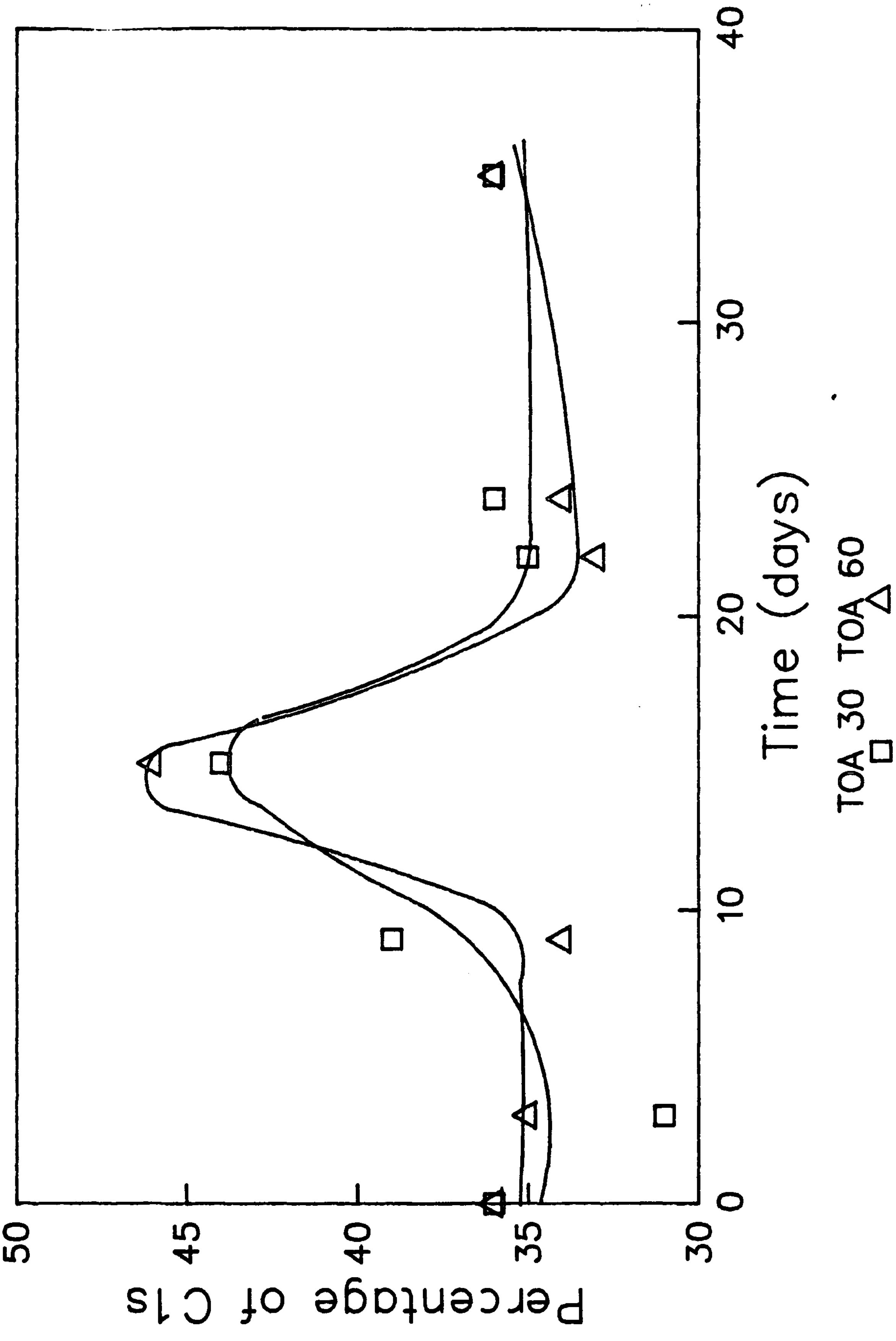


Figure 4.13 Variation of the Oxygen Containing Components of the C_{1s} Envelope for Boston IV Stored in Water.



a 36 day period, figure 4.15. The initial increase in oxygen content was mirrored by the initial rise in the level of oxygen containing functionalities shown in the C_{1s} envelope, figure 4.16. It is possible that this rise in the level of oxygen in the surface is due more to removal of oxygen deficient contamination from the surface and orientation of the hydrophilic groups in the polymer than to any chemical reaction with the water. The continual slow decrease in contact angle can be attributed to absorbed water. In the ultra high vacuum (10^{-8} torr) of the ESCA spectrometer this water would be lost and no increase in overall oxygen content of the surface would be observed. The dissimilarity between this and the behaviour of the treated lens material indicates that its performance on storage after treatment is dependent more on the nature of the treated surface than on an interaction of the water with the polymer.

Both the materials studied so far are acrylates and have similar behaviour, the main differences being attributable to the presence of a siloxane component in the Boston IV. In an attempt to shed further light on the reorganization of the of polymer surfaces a study of a dissimilar material, PEEK, was undertaken.

4.3.6 The Ageing of PEEK

The oxygen plasma treatment of PEEK was carried out under

Figure 4.14 Variation of the Contact Angle with Time of Untreated Boston IV Stored in Water.

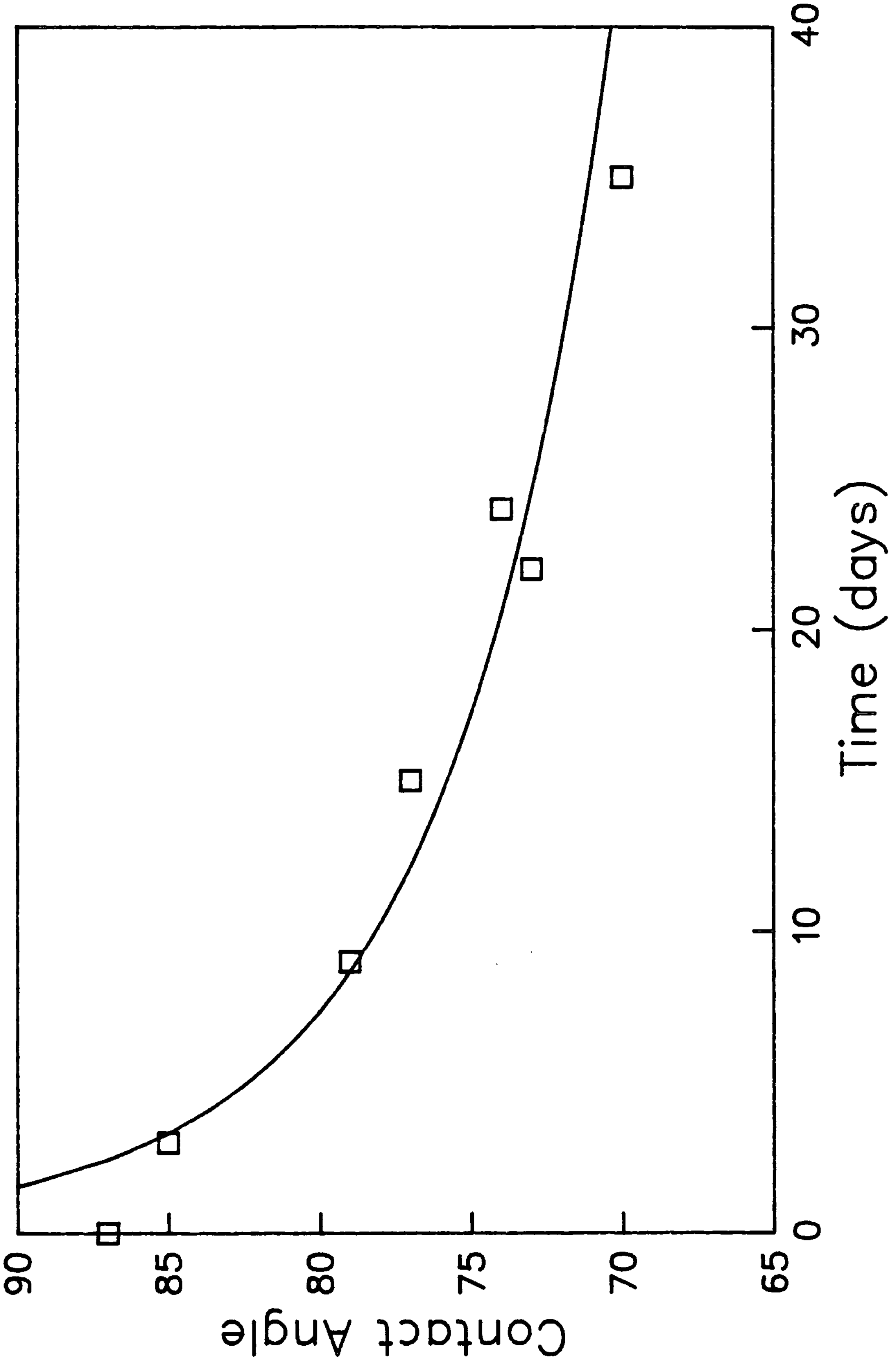


Figure 4.15 Variation of the O_{1s}/C_{1s} and Si_{2p}/C_{1s} Area Ratios with Time for Untreated Boston IV Stored in Water.

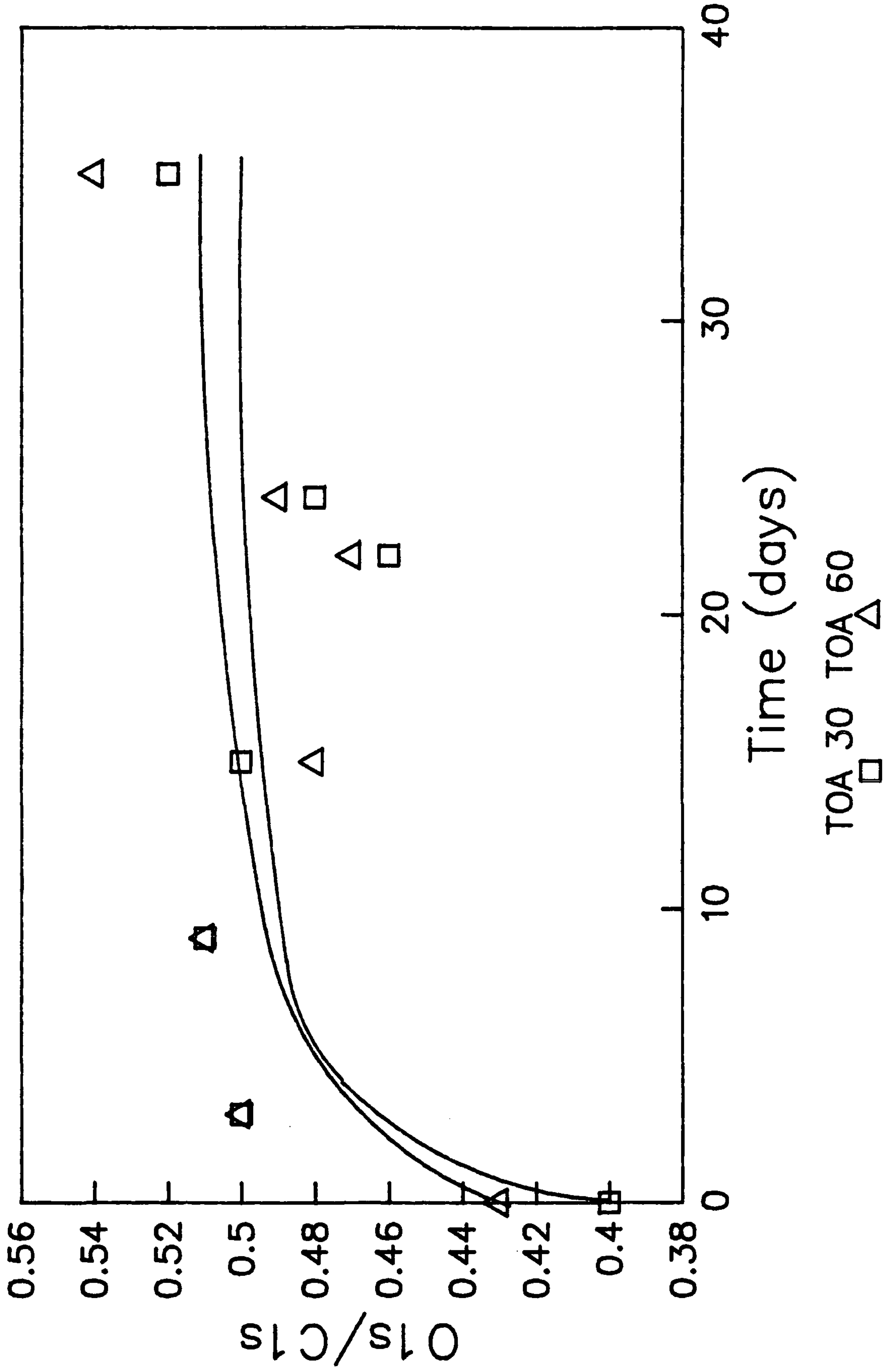
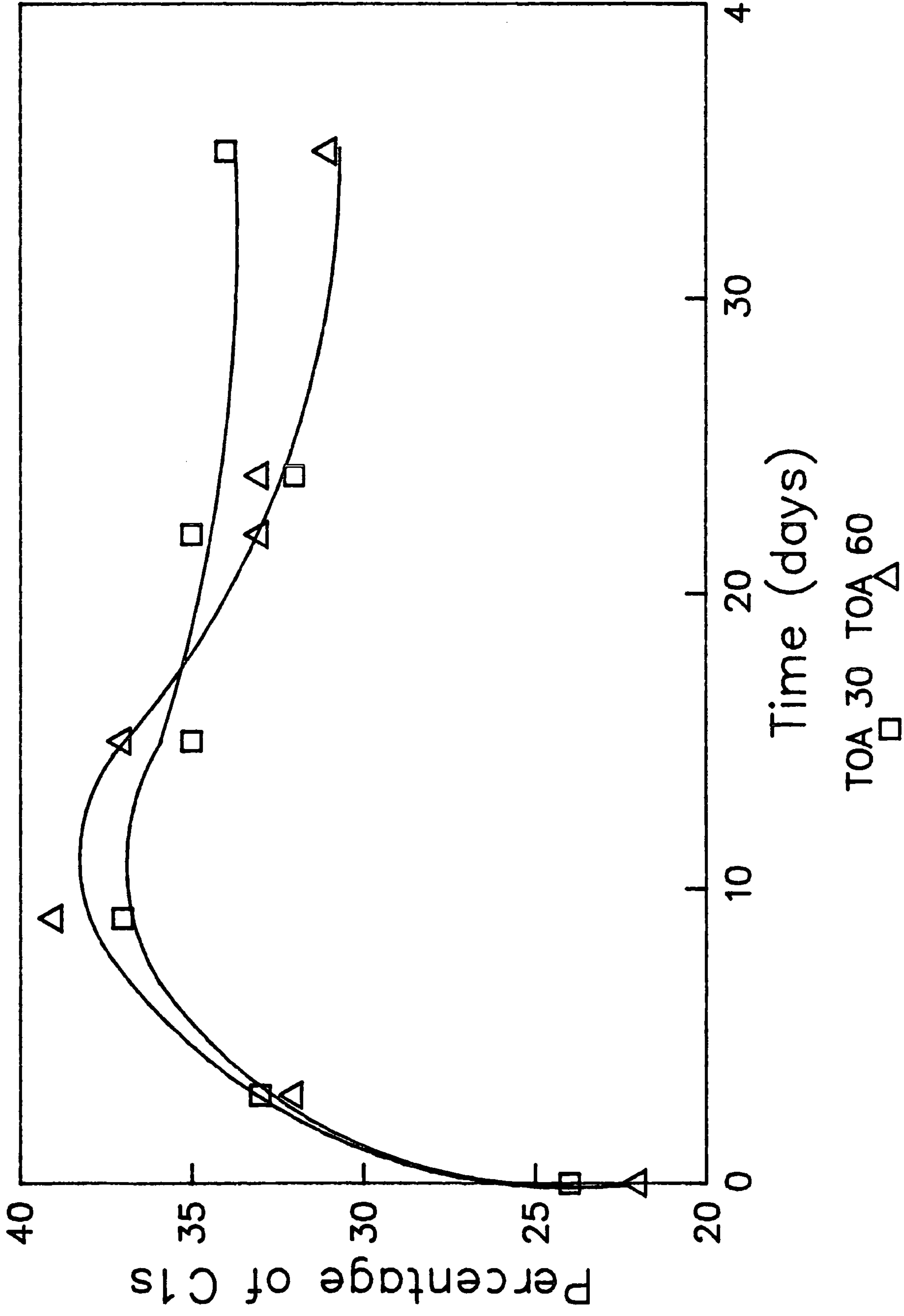


Figure 4.16 Variation of the Oxygen Containing Components of the C_{1s} Envelope with Time for Boston IV Stored in Water.



slightly different conditions to the treatments of Boston IV and PMMA, since the initial criteria of maximum hydrophilicity could only be obtained by using dissimilar settings. It can be seen from the ESCA spectra of modified and unmodified PEEK that substantial changes in the chemistry of the surface have been made by the oxygen plasma, figure 4.17. The spectra of the untreated material are as expected, showing that there is no carboxylate peak in the C_{1s} envelope and that there is a new peak at 291.6 eV which can be attributed to a $\Pi-\Pi^{*}$ shake up transition. The plasma oxidized specimen shows a considerable uptake of oxygen with the appearance of carboxylate and carbonate (289,290 eV) (16,17,18) functionalities together with increases in the C=O and C-O environments. As a result of this treatment the contact angle with water of this material drops from 87° (n=10, SD=3.5) to ≈4°.

The initial behaviour of modified PEEK is very similar to that of the lens materials, there being a rapid rise in contact angle at first which can be correlated with the fall in oxygen content, shown by the O_{1s}/C_{1s} area ratios, figures 4.18, 4.19. It is after this initial period, lasting about 5 days, that differences appear. The PEEK stored in air shows a brief decrease in contact angle at 15 days, and the C_{1s} envelopes of spectra recorded at 60° show changes similar to those observed at a take off angle of 60° in the case of lens material stored in water, figures 4.20 and 4.13. However in this case the increase in the carbonyl functionality is observed throughout

Figure 4.17 ESCA Spectra of Untreated and Oxygen Plasma Treated PEEK.

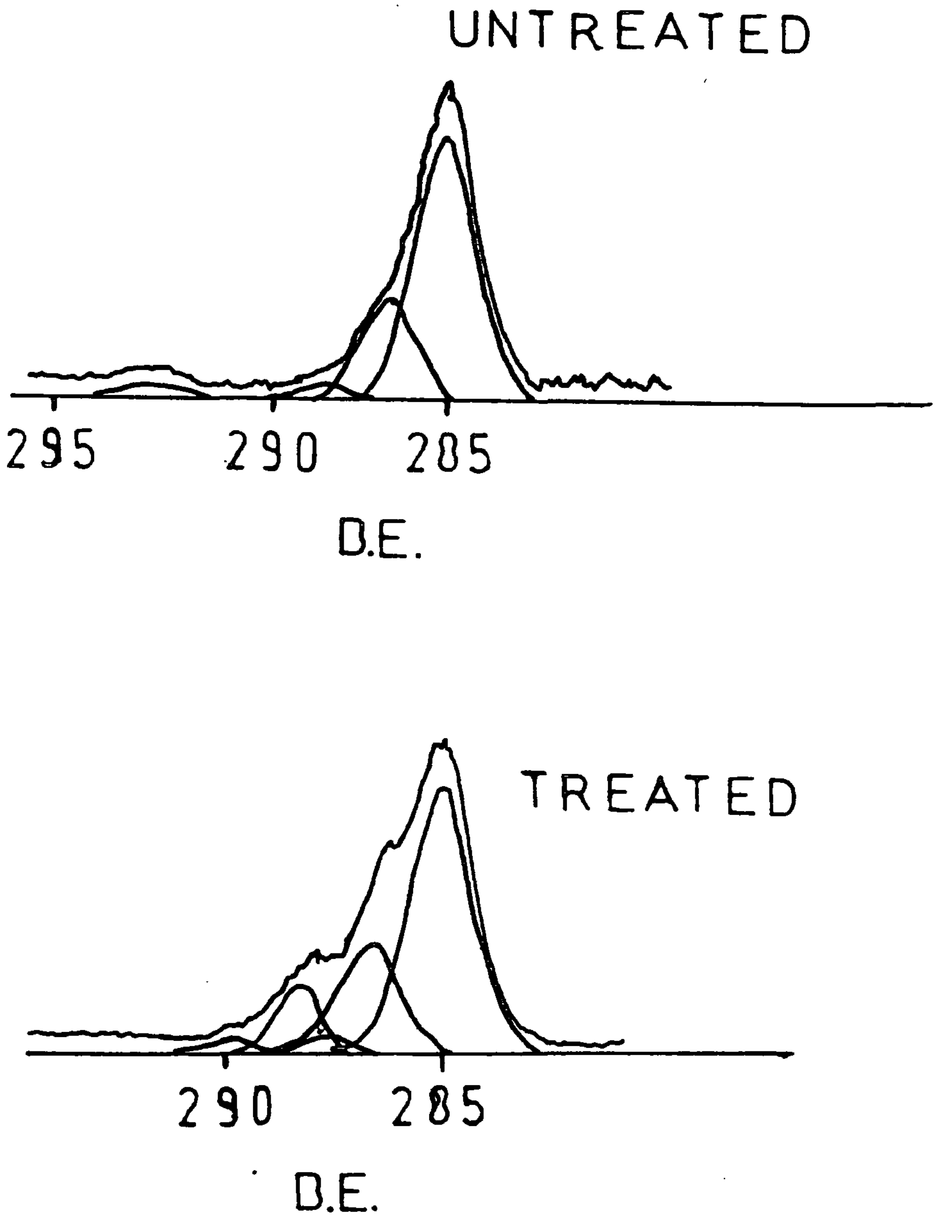


Figure 4.18 Variation of Contact Angle with Time for Plasma Treated PEEK.

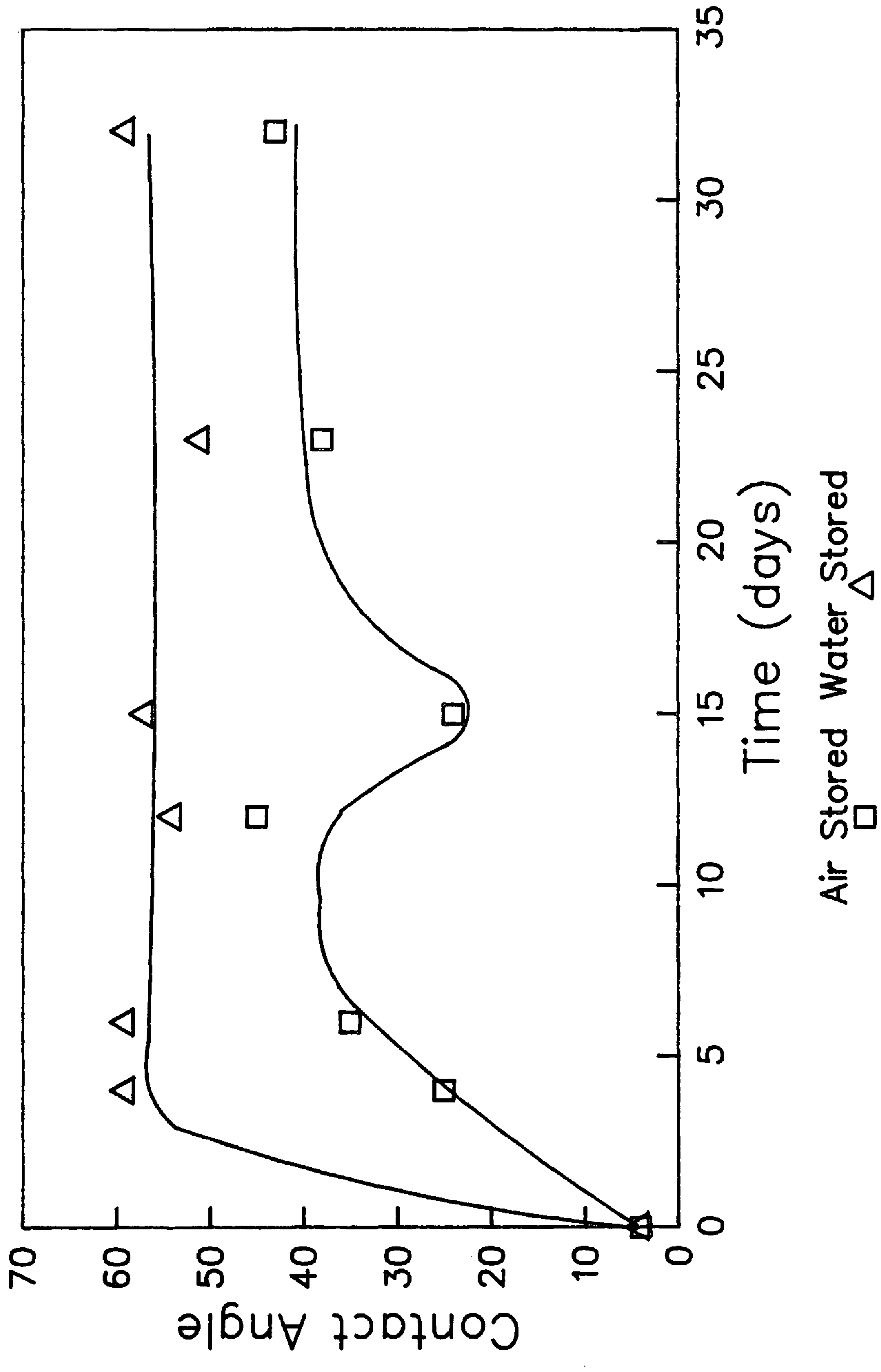


Figure 4.19 Variation of the O_{1s}/C_{1s} Area Ratio for Modified PEEK Stored in Air and Water.

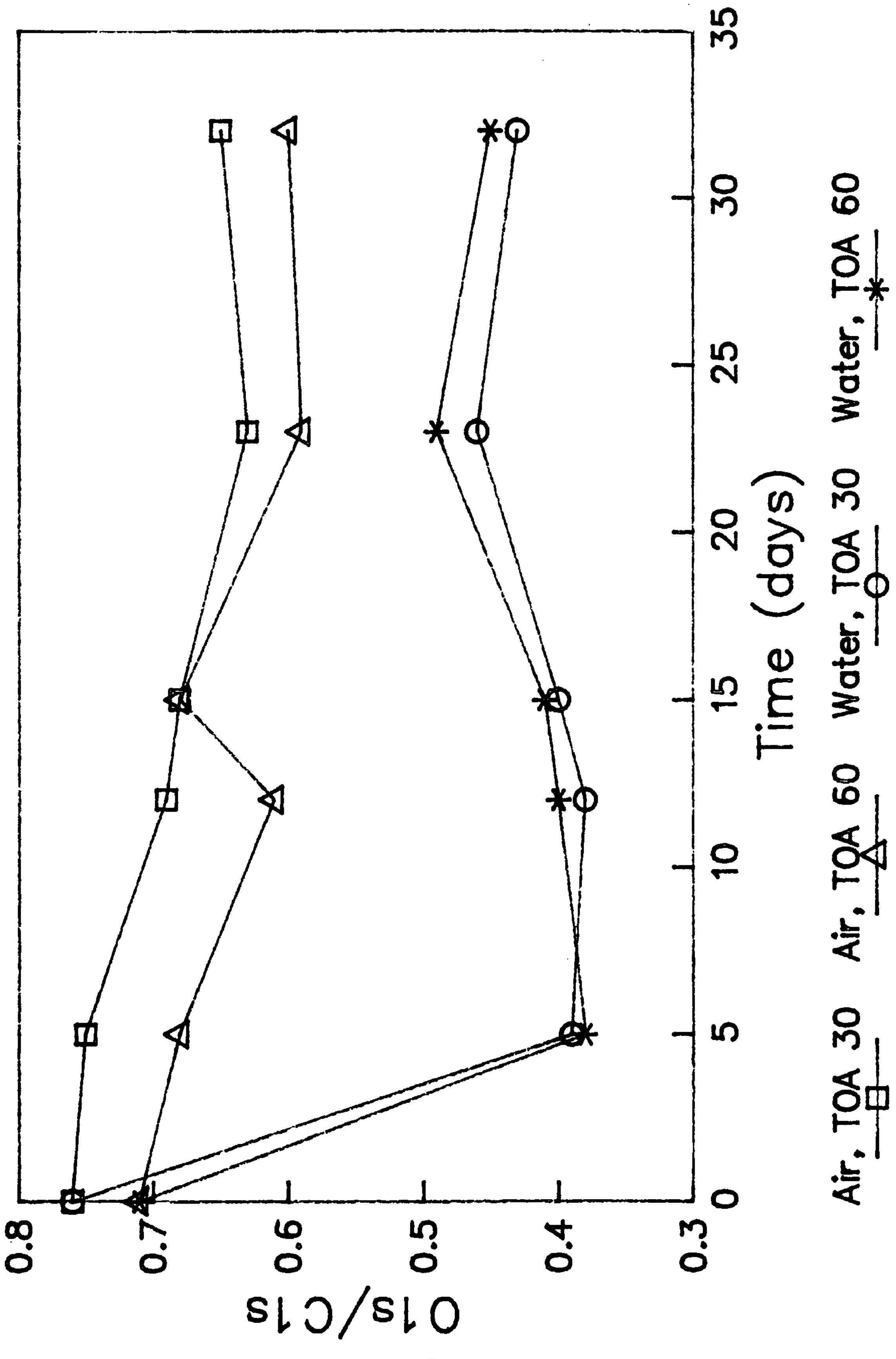
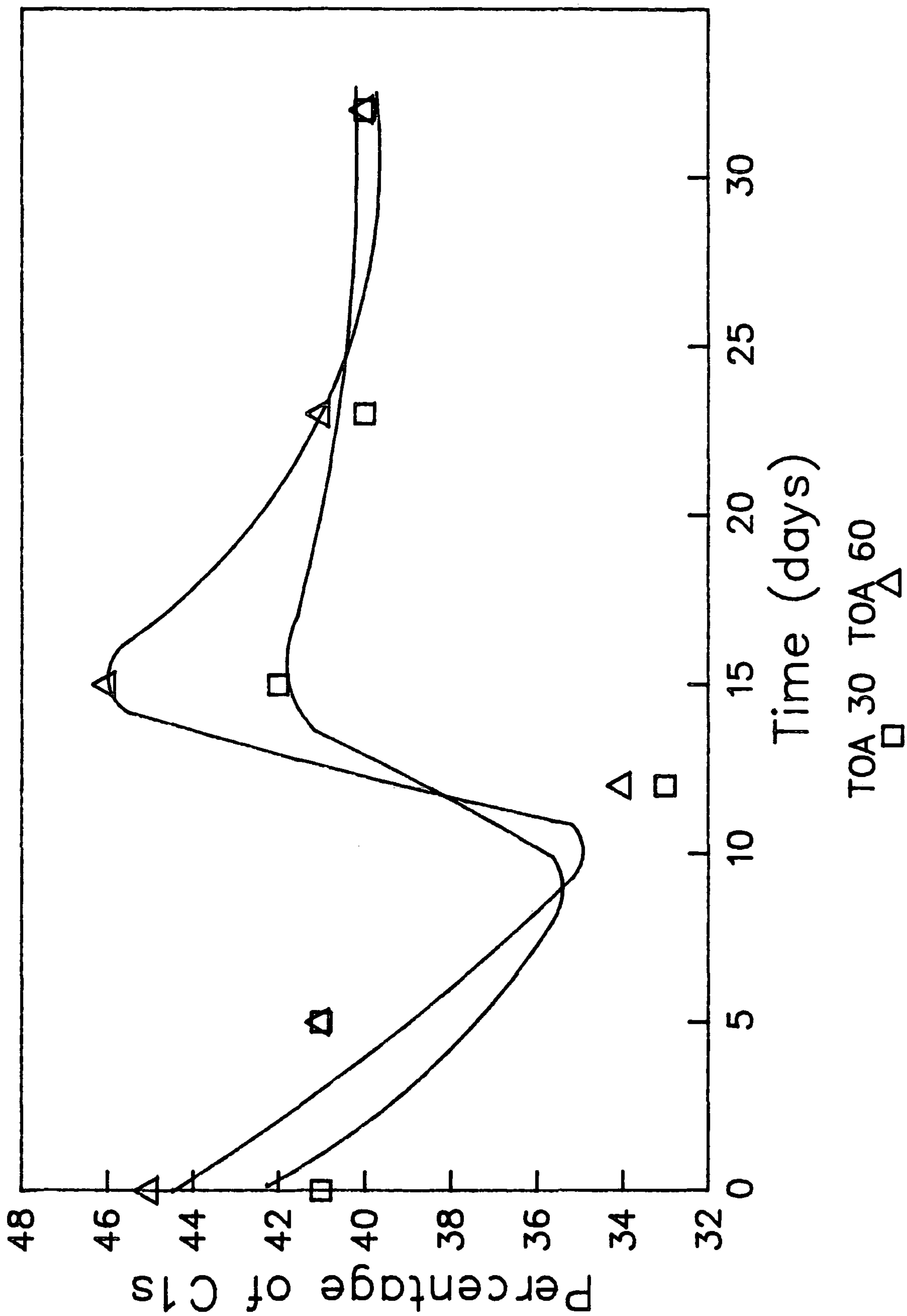


Figure 4.20 Variation of the Oxygen Containing Components of the C_{1s} Envelope for Plasma Treated PEEK Stored in Water.



the surface, and there is a noticeable increase in the O_{1s}/C_{1s} area ratio at this point. There is no perturbation in either the contact angle or the surface chemistry as shown by ESCA at the 22 day point.

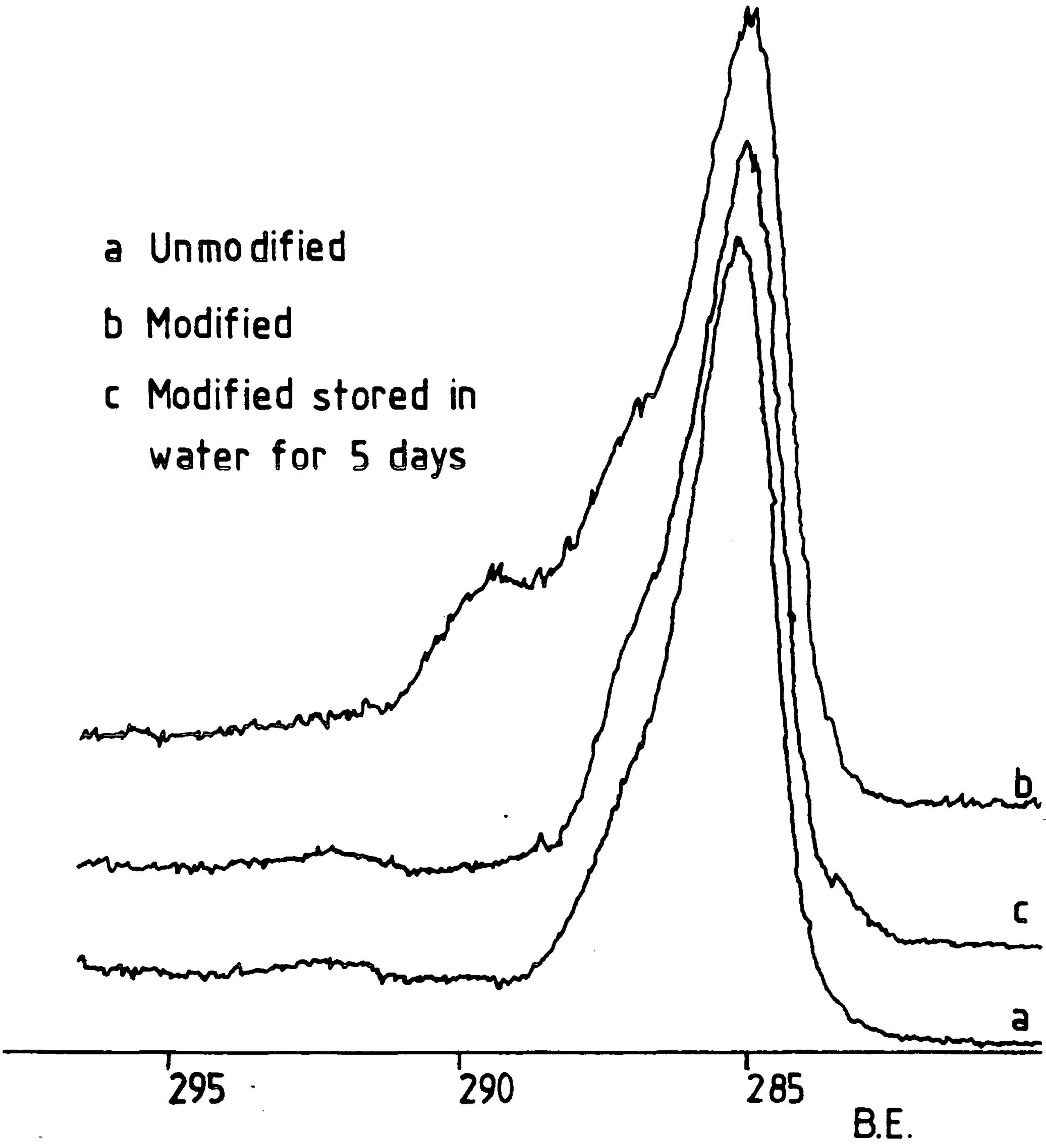
Water stored PEEK shows no apparent changes after the initial loss of hydrophilicity, there being only slight changes in its surface chemistry; this is characterized by the almost total loss of the more highly oxidized species after the first few days. A comparison of the C_{1s} envelopes of PEEK, untreated, freshly treated, and treated then stored for 5 days in water is shown in figure 4.21. It is immediately apparent that the spectrum of the sample stored in water is virtually identical to that of the untreated material. This suggests that the modified surface layer of PEEK has been completely removed by storage in water and so few changes in contact angle, resulting from the plasma treatment are to be expected on further storage.

In considering an explanation for the behaviour of these materials on storage several points must be addressed: the initial rapid increase in contact angle, the plateau regions where there is little change in surface chemistry, the two points at which there is an unexpected increase in hydrophilicity, and the relation of the chemical changes occurring at various depths to these phenomena.

The first of these points, the behaviour over the first 5-7 days, is relatively easy to explain. As mentioned earlier the plasma treatment produces a highly polar surface with a high surface energy. Therefore there is a significant energetic advantage to be gained, in a non polar medium such as air, by the loss of highly polar, oxygen containing material from the surface. This loss may occur in a variety of ways; if the polymer structure is sufficiently mobile any low molecular weight species may be able to migrate away from the surface, or if they are unable to migrate they may reorientate to turn their polar groups into the surface. The upper layers of the polymer will be more compatible with these polar groups than the air since the plasma treatment will have penetrated some distance into the material increasing the polar nature of the outer layers of the sample. During plasma treatment the highly reactive gas, in addition to modifying the chemistry of the surface can also break up the polymer chains into relatively low molecular weight fragments. These can also migrate away from the surface and indeed it has been shown that functionalized polymeric material can travel more than 1 μm into the interior of the polymer (19).

This material will migrate until the polymer structure ceases to be sufficiently compatible to permit these fragments to move further into it. In a polar medium such as water these small fragments may well be lost into solution, as is clearly shown in the case of water stored PEEK where most of the modified

Figure 4.21 ESCA Spectra of PEEK, Untreated, Treated, and After 5 Days Storage in Water.



material disappears from the surface within a few days.

When the polarity of the surface has decreased to the stage where the surface energy is low enough to be compatible with the environment, or when the energetic advantage to be gained by reorganization of the polymer structure is too small to overcome the constraints on the polymer chains, an equilibrium will be attained. At this point the surface energy ,and therefore the contact angle, will be constant and there should be no further change in the surface chemistry, since there is no energetic driving force to induce such a change. This period corresponds to the plateau region observed for all samples in the 7-14 day period.

The sudden fall in contact angle after 15 days storage is therefore unexpected since it acts against the thermodynamic driving force which caused the initial loss of oxygen from the surface. Considering first the case of PEEK, which is the simplest since here the rearrangement occurs in air, the evidence from the ESCA spectra suggest that there is a migration of oxygen containing material towards the surface, since at this time the overall oxygen content of the surface, as shown by the O_{1s}/C_{1s} area ratio, rises. The speed with which this change happens suggests that the fragments involved are highly mobile and therefore small. Comparison of the freshly treated material and the surface during this change shows that not all of the modified material which was lost has returned to the surface. Thus it can be concluded that after passing beyond the sampling depth of ESCA there is some interaction between the polar migrating material and the bulk polymer which has the result of driving the smaller more mobile fragments back to the surface. Following this reorganization the original driving force of reduction of surface energy comes into play once more, and the fragments migrate back into the bulk, as shown by the return of the ESCA spectra to the levels seen before this perturbation. Since there is no recurrence of this phenomena, within the timescale studied, there must be no further resistance to the diffusion of these fragments into the bulk.

In the case of PMMA the reduction in contact angle is only observed in the sample stored in water. When the spectra of the water stored samples are studied there is no apparent increase in the oxygen content of the surface as shown by the O_{1s}/C_{1s} area ratio. This indicates that no new oxygen containing material has entered the oxygen sampling depth, so any migration must be occurring below this level but within the carbon sampling depth, since in the C_{1s} spectrum there are changes during the period of renewed hydrophilicity comparable to those occurring in the air stored PEEK during the same time interval. The similarity of these changes suggests that there may be a similar cause for the reorganization process. In the air stored PMMA the same changes in the C_{1s} envelope are observed at a greater depth. This depth difference could be due to the fact that there will be a greater resistance to the resurfacing of this polar material in air than in water, since as a polar medium water should encourage polar material to remain at the surface, but in view of the evident solubility of the outermost surface of modified PEEK it is likely that some material is lost into solution from the water stored sample. The effect of this would be to uncover the region of the material in which the reorganization occurs.

A similar mechanism can be invoked to account for the difference in behaviour of air and water stored Boston IV up to the 22 day stage. The rearrangement that occurs after this time is quite distinct from any observed in the pure polymers since it occurs throughout the surface and involves the silicon containing component of the polymer. This process begins with an increase in the oxygen content of the surface, shown by the changes in O_{1s}/C_{1s} area ratios, which could be a continuation of the migration of fragments towards the surface which reached the upper layers of the material stored in water on day 15. Movement of such material below 25 Å was observed at 15 days and it may be that it takes the intervening time to reach the upper levels of the surface. However the changes seen at 15 days in the C_{1s} envelope show this migrating material to be rich in highly oxidized carbon species, such as C=O and O-C=O, whereas at 22 days it is the C-O environment which increases. It therefore seems more likely that this represents movement of material other than that observed at 15 days, though it may be influenced by the changes occurring at greater depth. Whatever the cause, the result is a major restructuring of the samples surface; at 24 days the surface becomes coated in silicon containing material which persists briefly before subsiding to its previous level. The curious fact is that though migration of siloxane to the the surface might be energetically favourable, the extent to which this occurs, in comparison to the amount present in the bulk material (1%), is extremely high. The implication is that this siloxane either was not copolymerized with the acrylate originally or that the plasma treatment in breaking up the polymer structure has enabled the siloxane rich products of the reaction to separate out from the fragments mainly derived from acrylate. Since the patent for Boston IV (20) clearly states that the siloxane is copolymerized with the acrylate the separation of the acrylic and siloxane components must be attributable to the effects of the plasma treatment. This separation of the material's components in this region of the surface is short lived and decays into a surface with an elemental composition very similar to the untreated Boston IV. The implication is that the rearrangement involving the separation of the fragments rich in siloxane enables much of the remainder of the plasma treated material to be lost from the surface, presumably by migration into the bulk polymer. The resulting surface is deficient in carbonyl and carboxylate functionalities though richer in carbon species singly bonded to oxygen.

4.3.7 Temperature Dependance of Ageing

Both these reorganization processes should be dependant on the mobility of the polymer species involved and should therefore be dependant on the temperature at which the samples are stored. Accordingly a study was made of the effect of temperature on the storage characteristics of plasma oxidized PEEK. PEEK was chosen as the material for this study since it was possible to observe the 15 day change for samples stored in air thus avoiding any complications due to the presence of water.

A comparison of the variation of contact angle with time for samples stored at -20, 20, 40, and 60 °C is shown in figure 4.22. This clearly shows that the onset of the change is temperature dependant, the time interval needed decreasing with increasing temperature. It also shows that the initial rise in contact angle over the first few days is also related to temperature in the same way, and that the extent to which the modified surface is lost is dependant upon this parameter. However the rate of change of contact angle during the temporary increase in hydrophilicity at 15 days does not appear to be dependant on the storage temperature.

An activation energy for the initial migration can be calculated form an Arhenius plot, fig 4.22b, which gives a good straight line, plotting ln (rate of decay of contact angle) straight line, plotting ln (rate of decay of contact angle) versus reciprocal temperature. The activation energy is the slope of this line multiplied by R, and is found to be 19.1 kJmol^{-}(n=1) This must be regarded as only an approximate value for a number of reasons. Firstly there is the inherent error in the contact angle measurement and also the fact that the rates were determined from the initial gradients of the contact angle plots, which are not in fact straight lines. Secondly this value represents an average species migrating into the bulk whereas in fact the plasma treatment will produce a variety of species of differing compositions and molecular weights.

The results of this experiment show that as the temperature rises the polymer fragments are more able to migrate through the sample in both an inwards and outwards directions. Since the plateau region is not only reached quicker, but is less hydrophilic at higher temperature this suggests that the increase in molecular motion permits more and larger fragments to permeate into the bulk of the material, since more of the modified surface is lost.

4.3.8 Argon-Oxygen Plasma Treatment of Boston IV

Plasma treatment of the Boston IV lens material using a mixture of argon and oxygen was performed in an attempt to arrest or reduce the effects of ageing. It was hoped that the

Figure 4.22 The Dependance of the Contact Angle of Plasma Treated PEEK with Storage Time and Temperature.

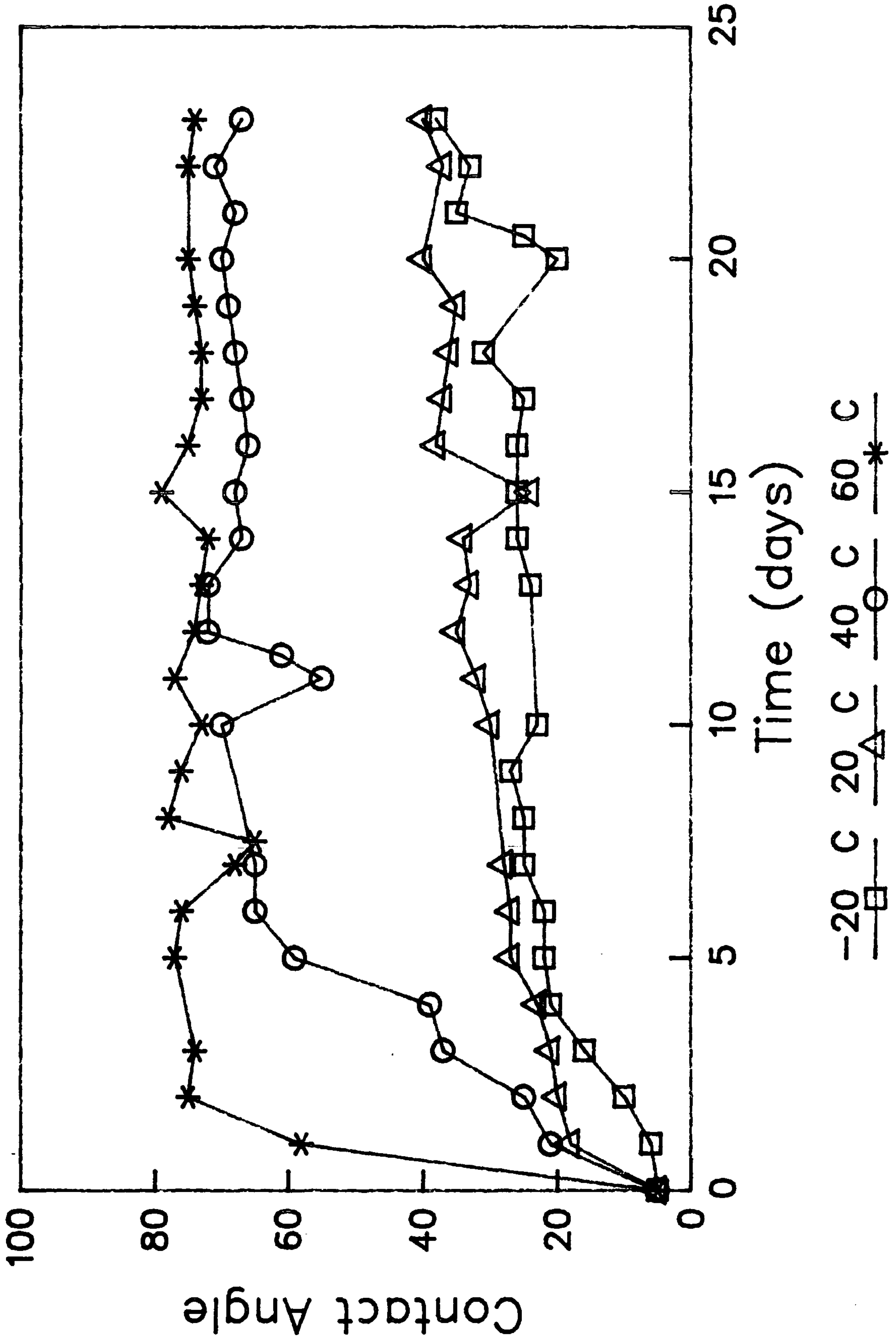
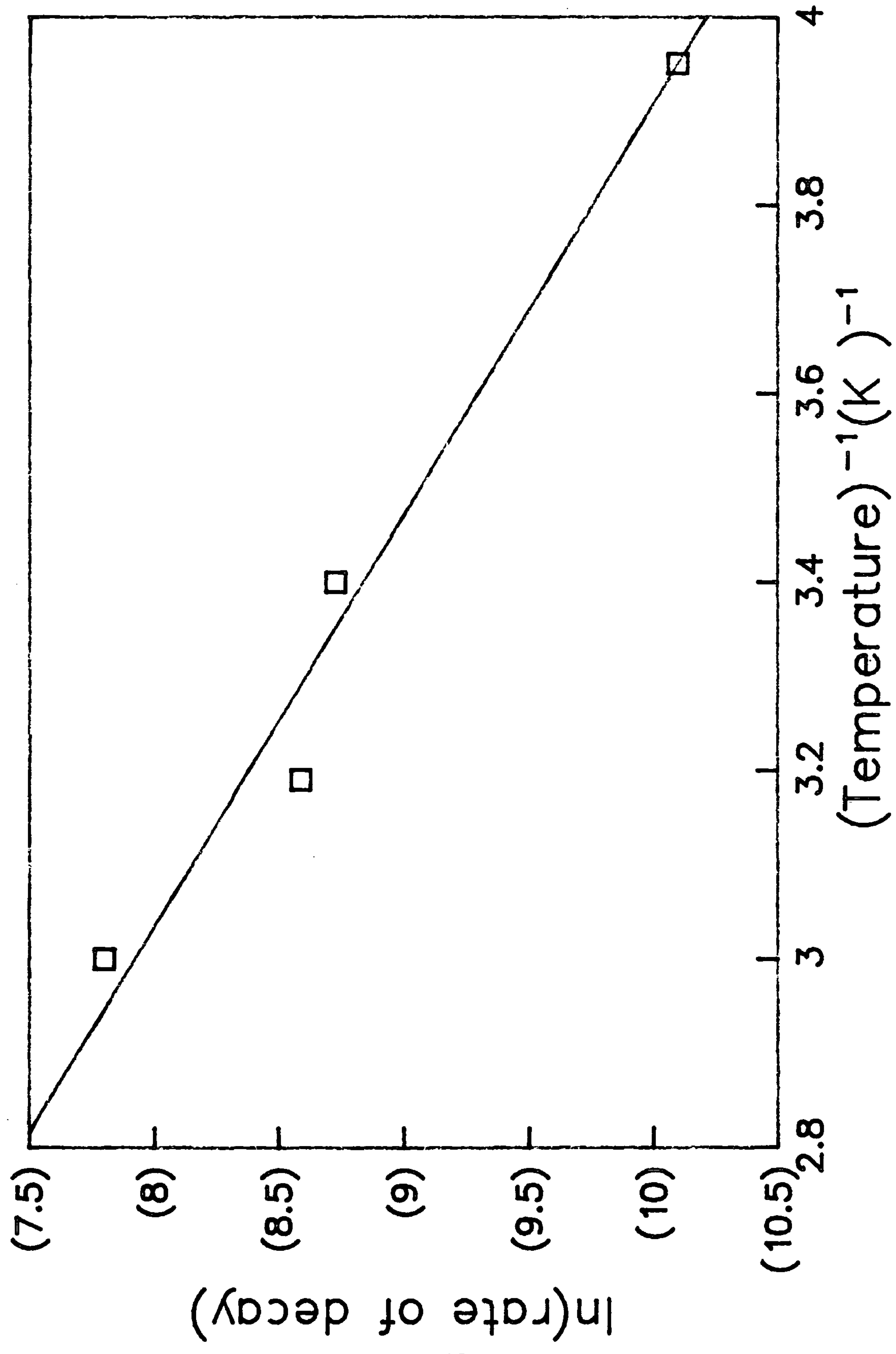


Figure 4.22b Initial Ageing of Treated PEEK, Arhenius Plot

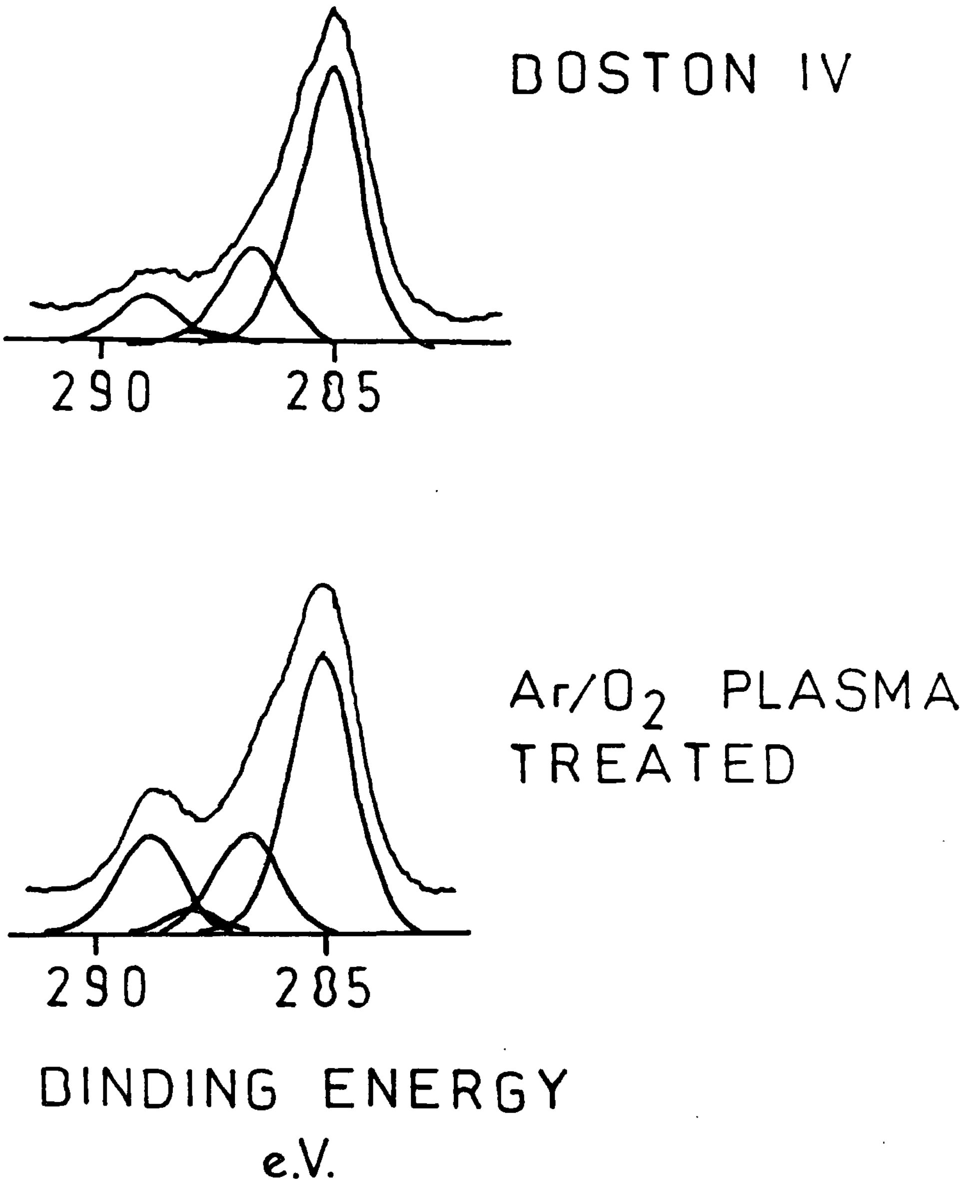


argon would induce crosslinking of the polymer at the surface and thus reduce the chain mobility inhibiting migration and reorientation of the modified material. The immediate effect of treatment with the mixed gas plasma was to reduce the contact angle with water from 83° to 36°. A comparison of untreated and argon- oxygen plasma treated samples shows very similar changes to those introduced by the normal oxygen plasma treatment, though there are some slight differences, notably in the amounts of the different oxygen containing functionalities introduced into the C_{1s} envelope, figure 4.23.

On storage in air and water the contact angle changes in a manner more reminiscent of PEEK than oxygen treated Boston IV, figure 4.24. There is still the fast initial decay characteristic of these materials, which levels off into a plateau. However there is a decrease of contact angle after 15 days storage in air and no change at 22 days. The water stored sample shows no significant changes after the plateau region is reached.

Consideration of the ESCA spectra of the samples during this time shows a similar pattern of changes to those seen in PEEK. In the air stored case there is an increase in the C-O environment throughout the surface coincident with the drop in contact angle the 15 day point, figure 4.25, though in this case there is no significant change in the overall oxygen content of the surface, figure 4.26.

Figure 4.23 ESCA Spectra of Untreated and Argon-Oxygen Plasma Treated Boston IV.



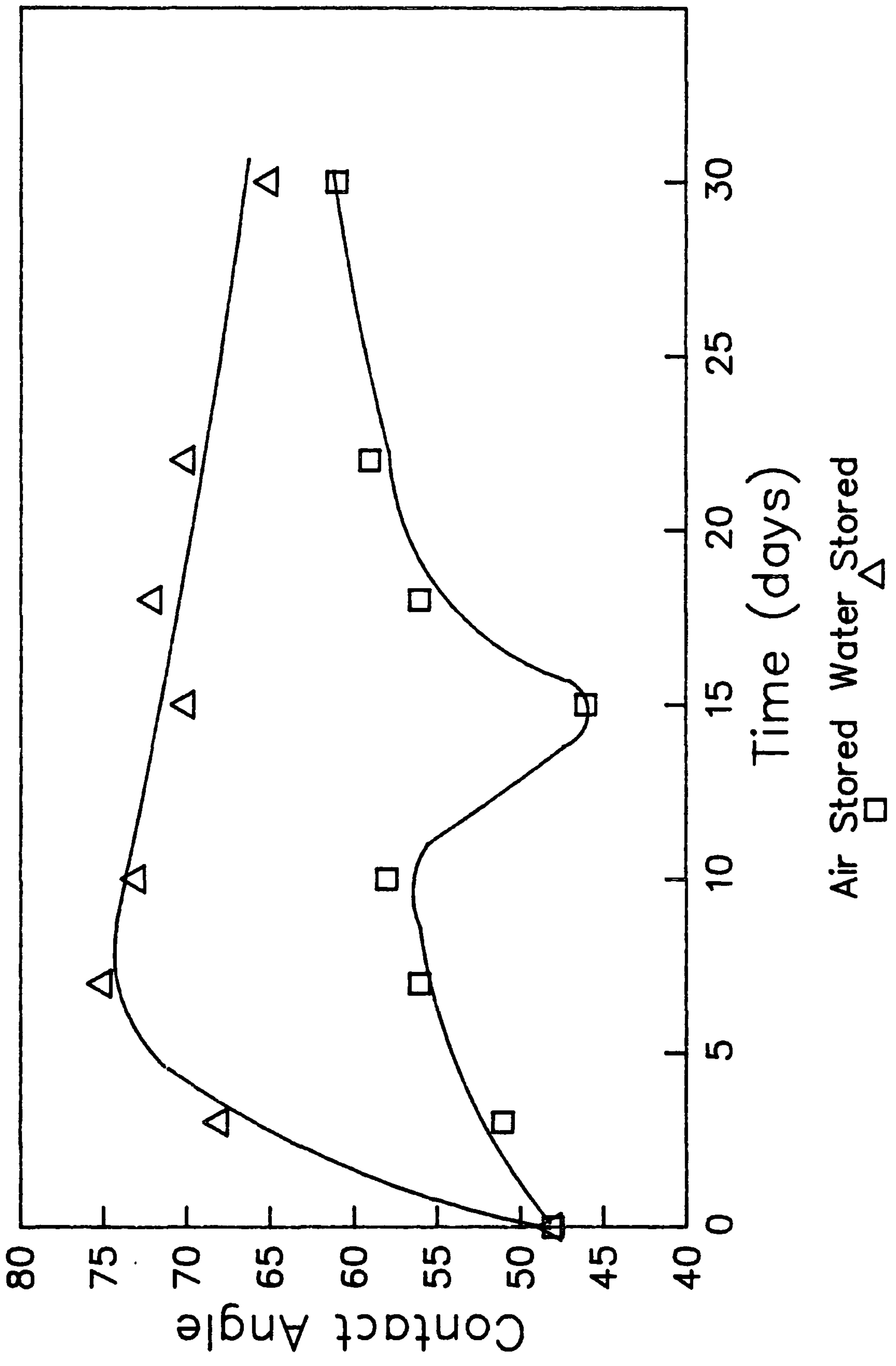


Figure 4.24 Variation of Contact Angle with Storage Time for Argon-Oxygen Treated Boston IV Stored in Air and Water

In the case of samples stored in water most of the modification appears to be lost within 1 week, figures 4.27 and 4.28, suggesting that, as in PEEK, the modified surface layer has been lost into solution. The conclusion to be drawn from this is that the addition of argon to the plasma results not in crosslinking but in increased fragmentation of the surface. Clearly a modified surface which can be completely removed by water is of no use for contact lens treatment and therefore no further study of this process has been made.

4.3.9 Ageing of Boston IV Stored in Lens Solution

The most complex system studied by these experiments was the lens stored in "Total" lens fluid. "Total" is a brand of lens fluid intended for both storage and cleaning of hard contact lenses. The manufacturers state that the fluid is a buffered solution of polyvinyl alcohol (PVA), disodium edetate and benzalkonium chloride (BAK), and as such is similar to many other brands currently on the market (21). The recommended method for using this formulation is to soak the lens overnight in the solution; it is not necessary to wash off the solution before inserting the lens in the eye since the solution has the added function of providing initial wetting of the lens, so reducing the discomfort of inserting a dry lens into the eye.

The initial contact angle performance was completely different for the lenses stored in the lens fluid. There

Figure 4.25 Variation of the Oxygen Containing Components of the C_{1s} Envelope for Argon-Oxygen Treated Boston IV

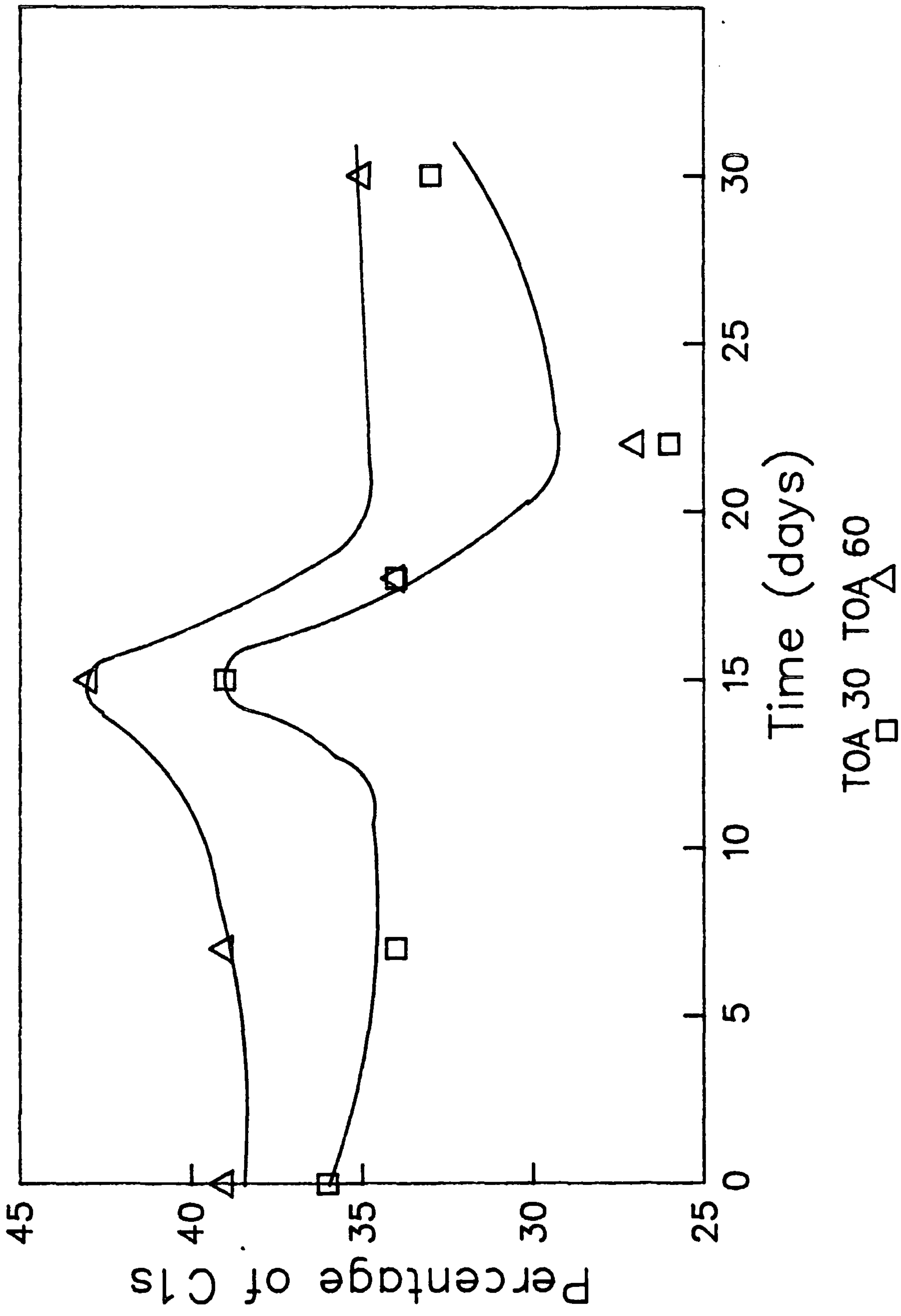


Figure 4.26 Variation of the O_{1s}/C_{1s} Area Ratio for Argon-Oxygen Treated Boston IV Stored in Air.

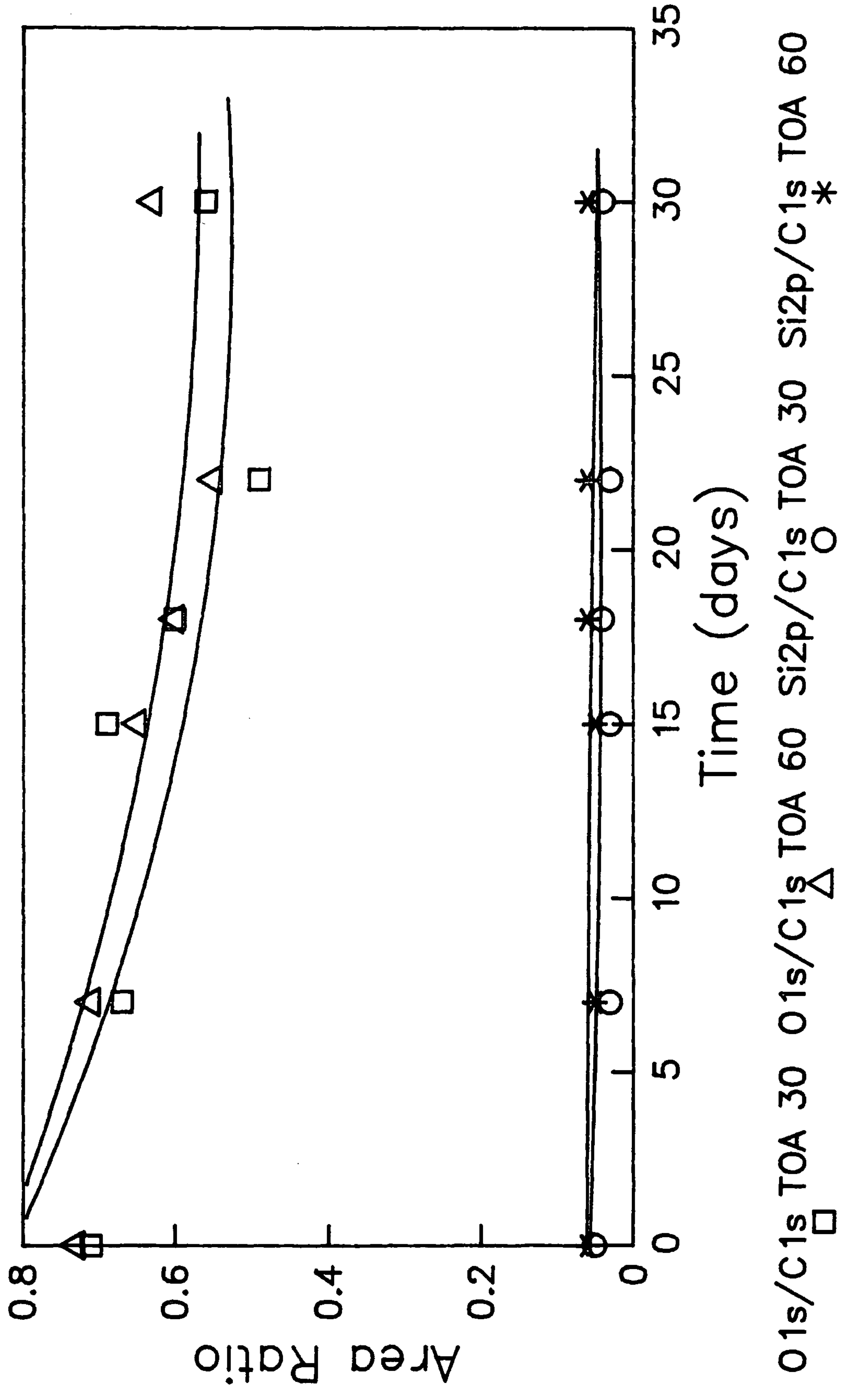


Figure 4.27 Variation of the O_{1s}/C_{1s} Area Ratio for Argon-Oxygen Treated Boston IV Stored in Water.

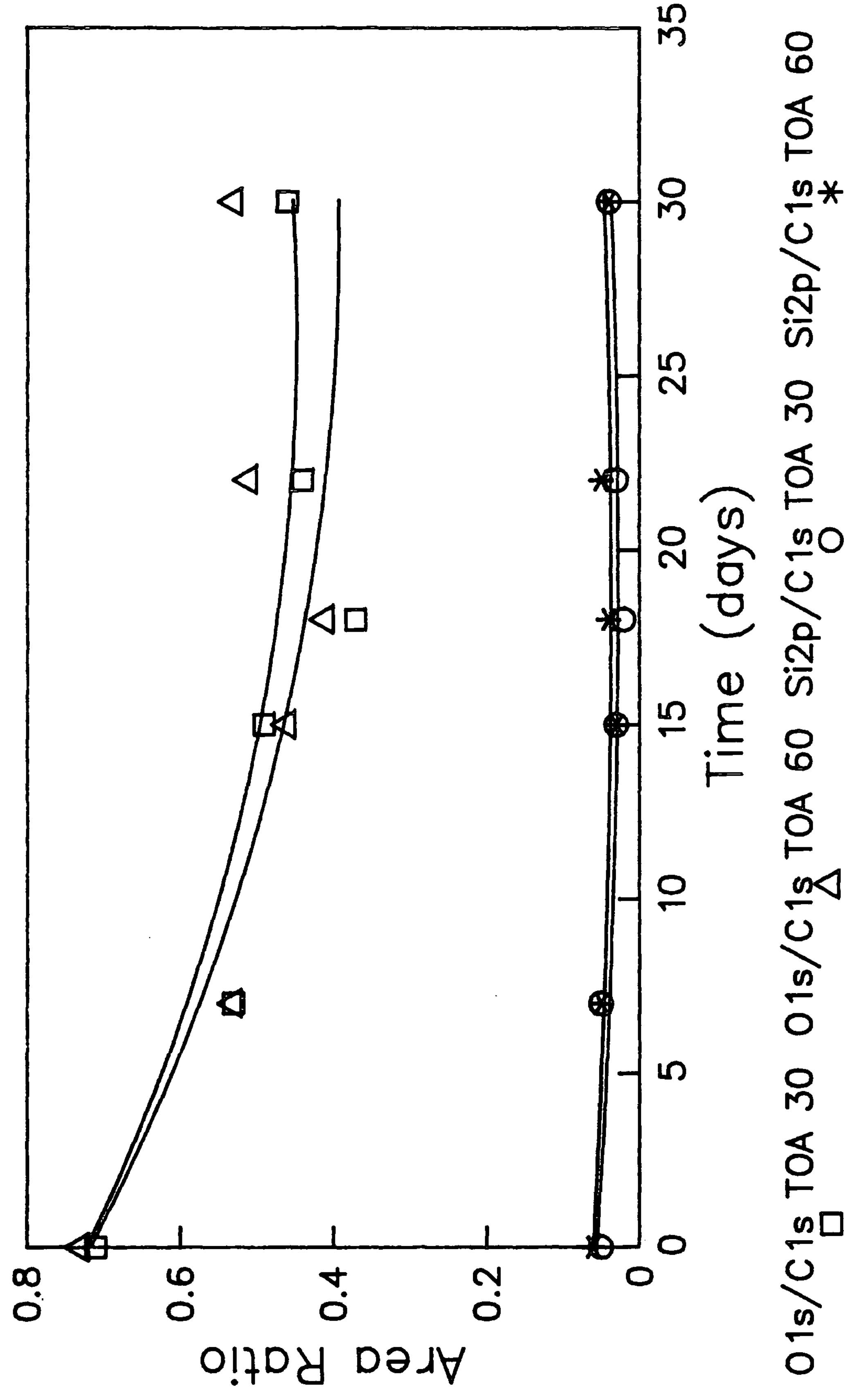
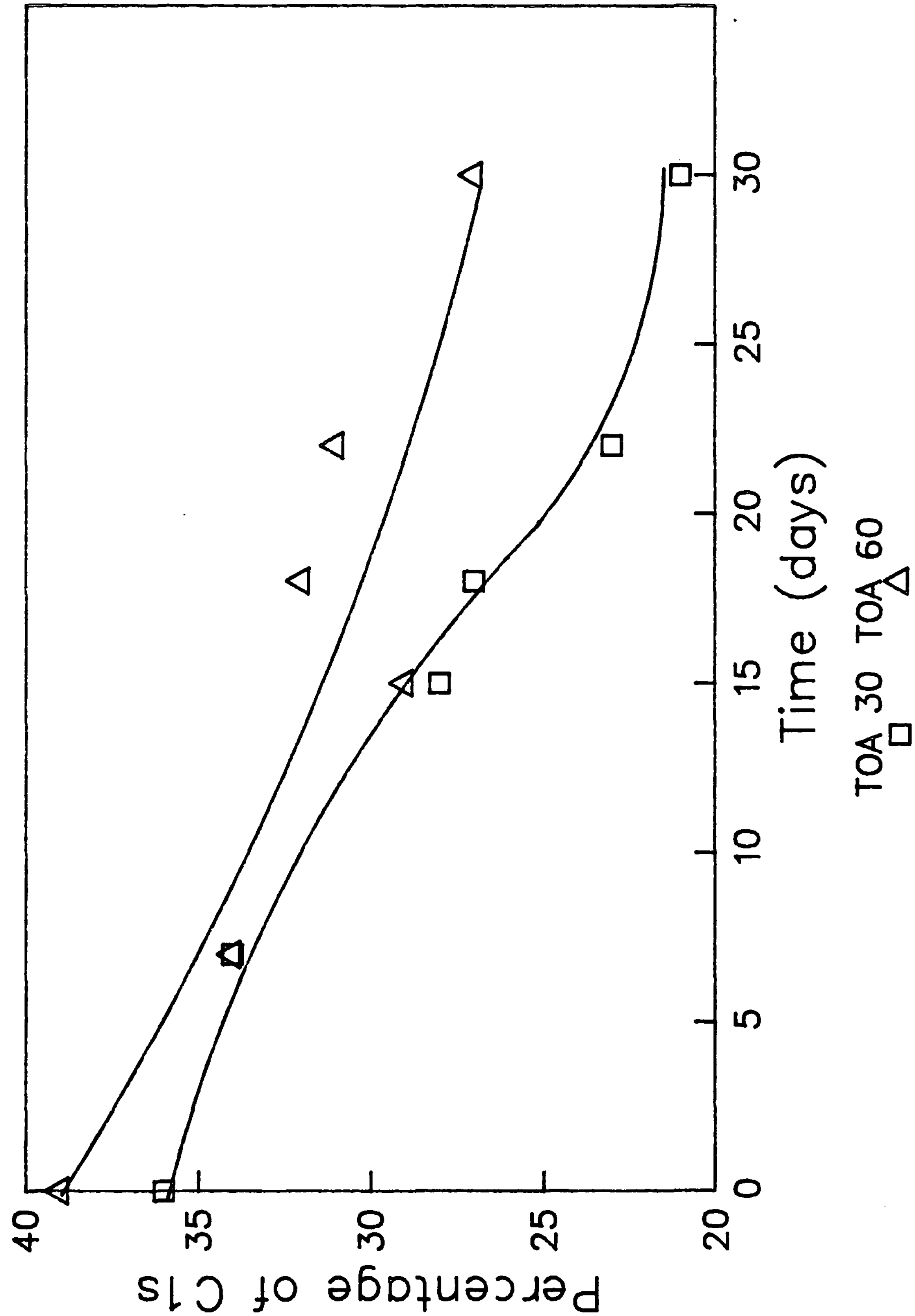


Figure 4.28 Variation of the Oxygen Containing Components of the C_{1s} Envelope for Argon-Oxygen Treated Boston IV Stored in Water.



appeared to be no decay of the contact angle with time, figure 4.29. On examining the ESCA data it was seen that the overall oxygen content of the surface had dropped after a week's storage, as had the silicon content, as shown by the area ratios for these elements, figure 4.30. Further examination of the C_{1s} spectra revealed a large and immediate drop in the proportion of C=O and O-C=O functionalities with a comparatively small loss in the C-O peak, figure 4.31. These levels then remained largely unchanged throughout the storage period.

The changes in the ESCA data, particularly the decrease in the silicon content of the surface and the composition of the C_{1s} spectrum, suggest that there is some foreign material being adsorbed onto the surface, presumably from the lens solution. Likely candidates for this are PVA and BAK. PVA, in small quantities, would account for the changes in the Cls spectrum, since it only contains the C-OH functionality. There has been some concern over the adsorption of BAK onto siloxane acrylate lenses (22), since BAK has been observed to cause tissue damage at very low concentrations, 0.001% (23), and can disrupt the lipid layer of the tear film (24). Consequently the Cl_{2p} core level was studied for a sample stored in "Total" for 2 weeks and rinsed in distilled water to remove excess solution, this showed that no chlorine was present. The conclusion therefore is that a small amount of PVA is adsorbed from solution.

Figure 4.29 Variation of Contact Angle with Time for Plasma Treated Boston IV stored in "Total".

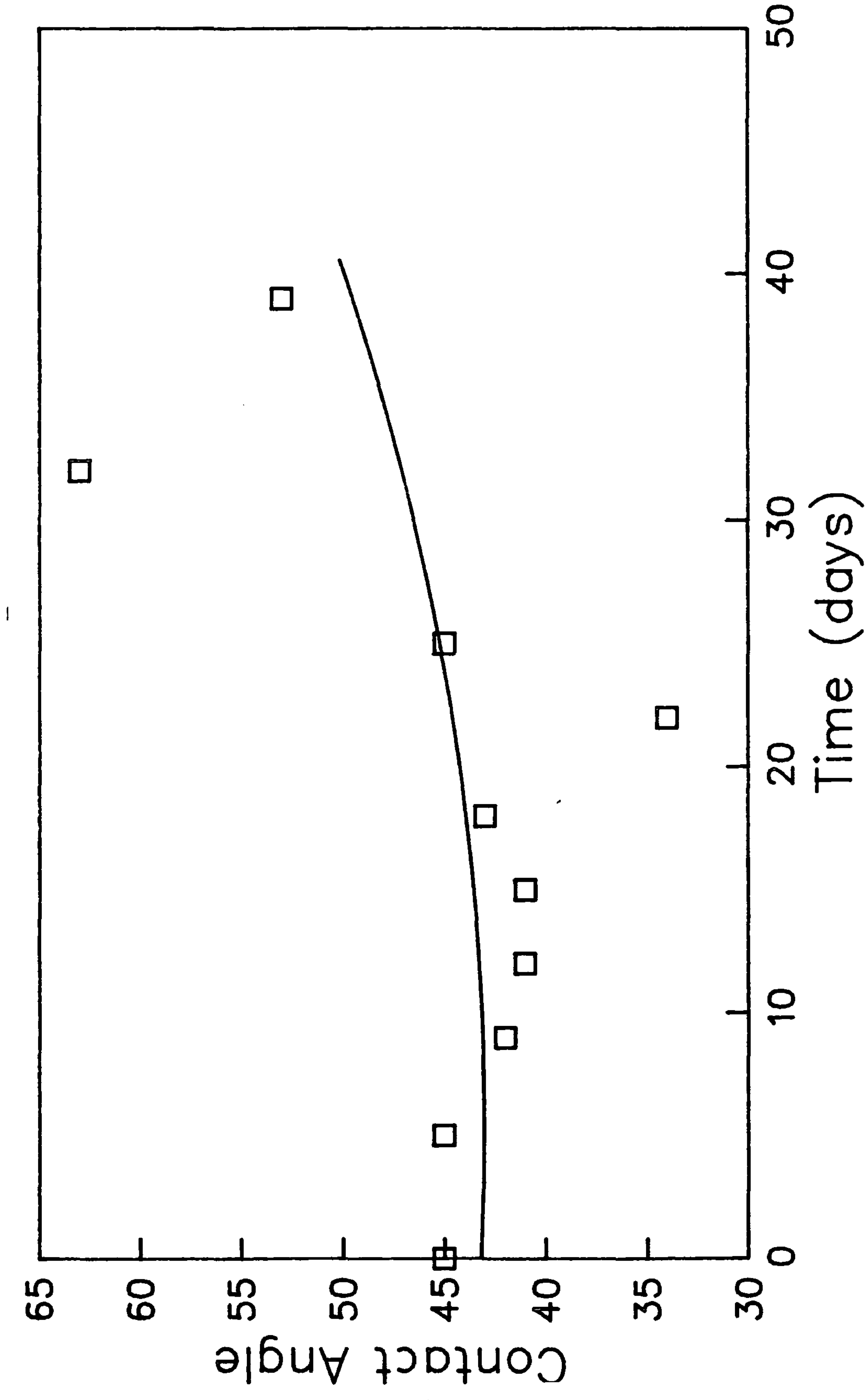


Figure 4.30 Variation of the O_{1s}/C_{1s} and Si_{2p}/C_{1s} Area Ratios During Storage of Plasma Treated Boston IV in "Total" Lens Solution.

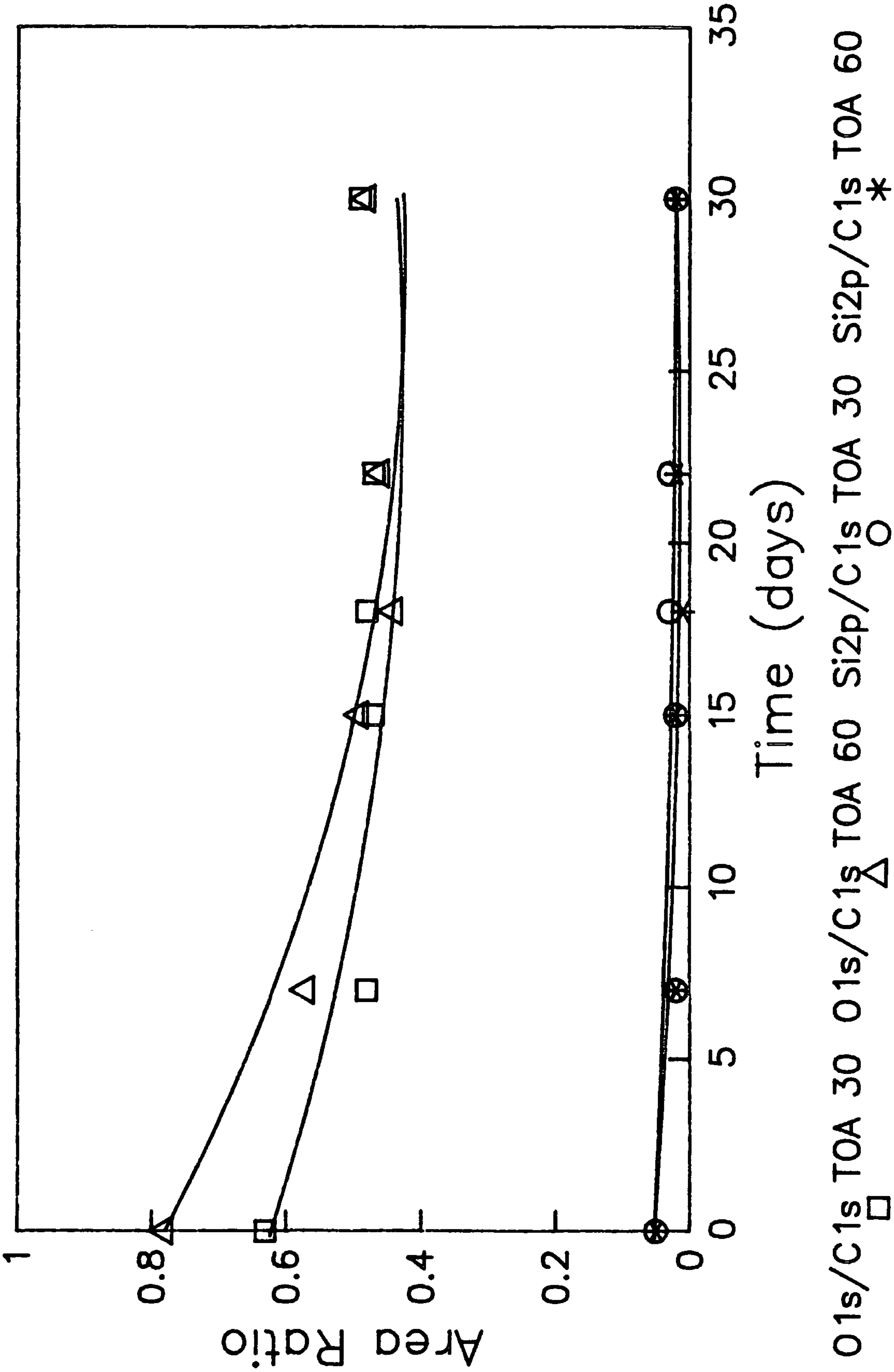
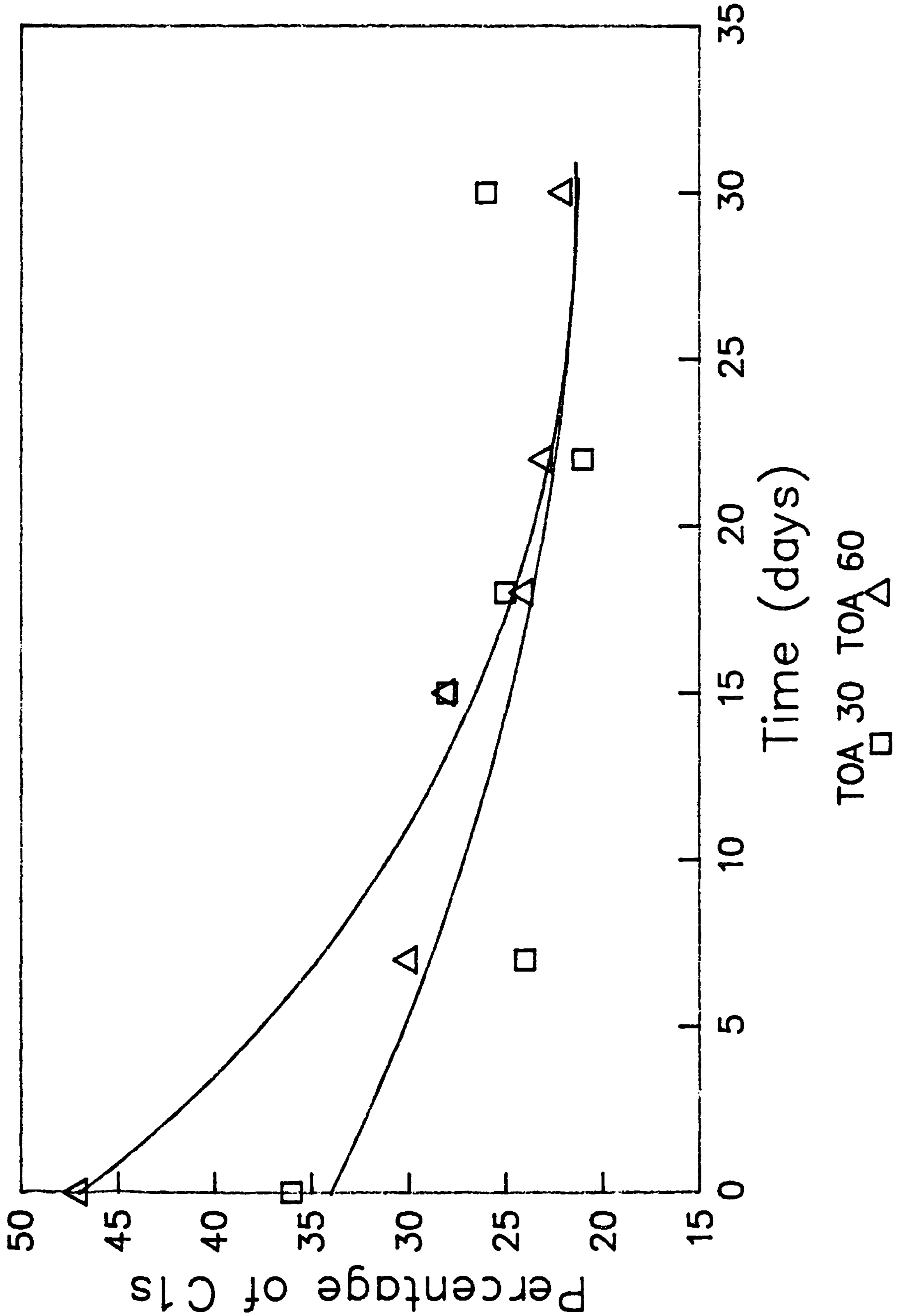


Figure 4.31 Variation of the Oxygen Containing Components of the C_{1s} Envelope During the Storage of Plasma Treated Boston IV in "Total" Lens Solution.



As a result of this conclusion the experiment was repeated using identical conditions but increasing the rinsing time to 5 minutes, in order to remove the adsorbed material and observe the ageing of the lens surface. When this was done the contact angle vs. time profile shown in figure 4.32 was obtained. This appears to be very similar to that of the treated lens material stored in water, though the actual values are on the whole lower the trends are the same. There is the sharp initial rise and plateau followed by a drop at 15 days followed by a further plateau. The ESCA spectra show similar trends to modified Boston IV stored in water, in the overall elemental composition of the surface from the area ratios, figure 4.33, but the changes in the chemistry of the carbon are slightly different. The C_{1s} envelope shows that the proportions of the different oxygen containing environments change in a similar but not identical fashion, figure 4.34. There is more C-O in these samples and more of the carboxylate functionality is lost, particularly from the outer layers of the surface, as shown by the data from a take off angle of 60°. The contact angle anomaly at the 15 day point again appears to be associated to the temporary reappearance of carbonyl and carboxylate in the surface. Since the decay process is so similar it is reasonable to ascribe a similar mechanism for the decay of these samples as was postulated for the water stored samples.

The overall slightly lower contact angles observed in these specimens may well be due to some residual adsorbate, but if

Figure 4.32 Variation of Contact Angle with Time During Storage of Boston IV in "Total", Samples Rinsed Thoroughly.

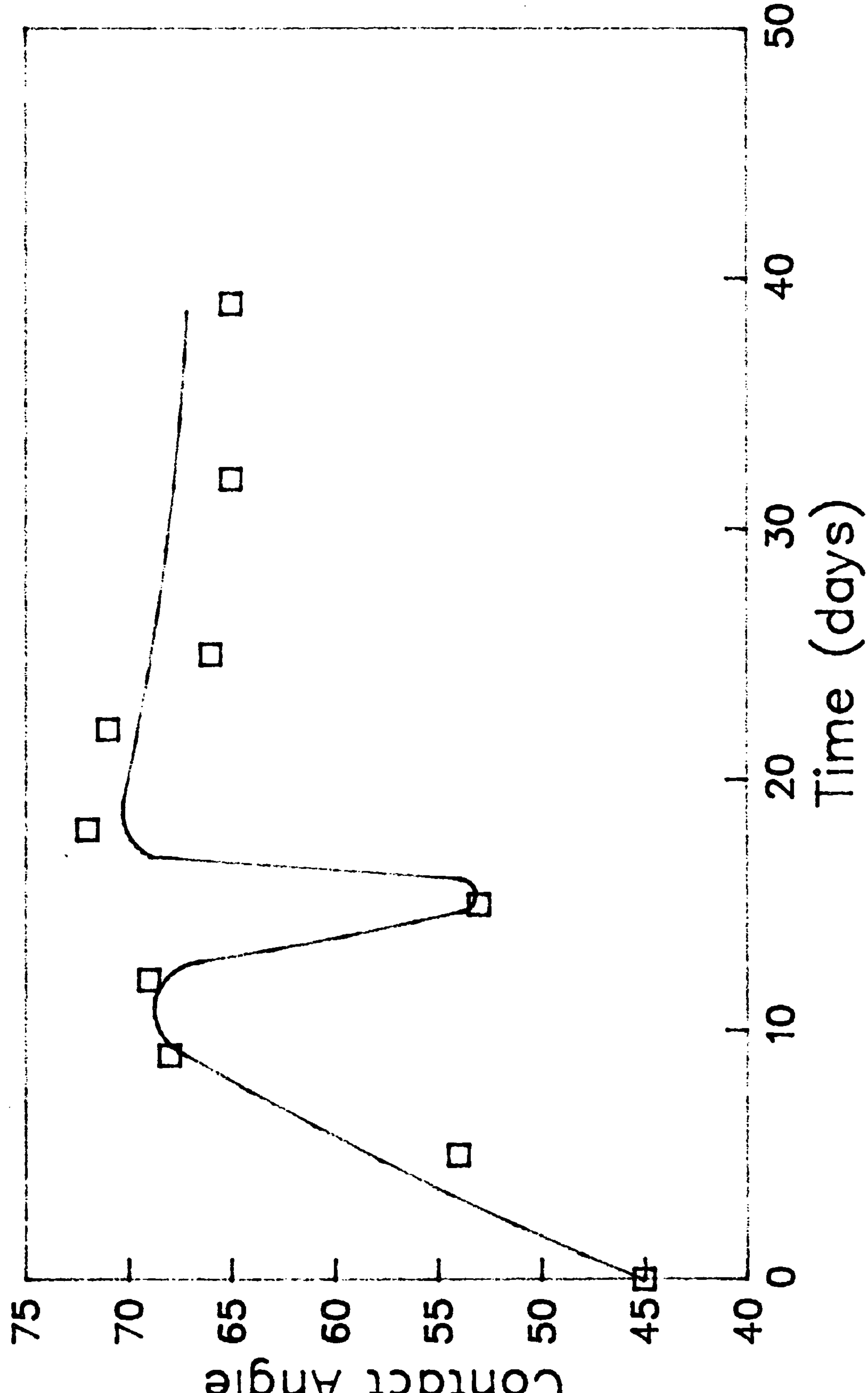


Figure 4.33 Variation of the Elemental Ratios with Time During Storage of Boston IV in "Total", Samples Rinsed Thoroughly.

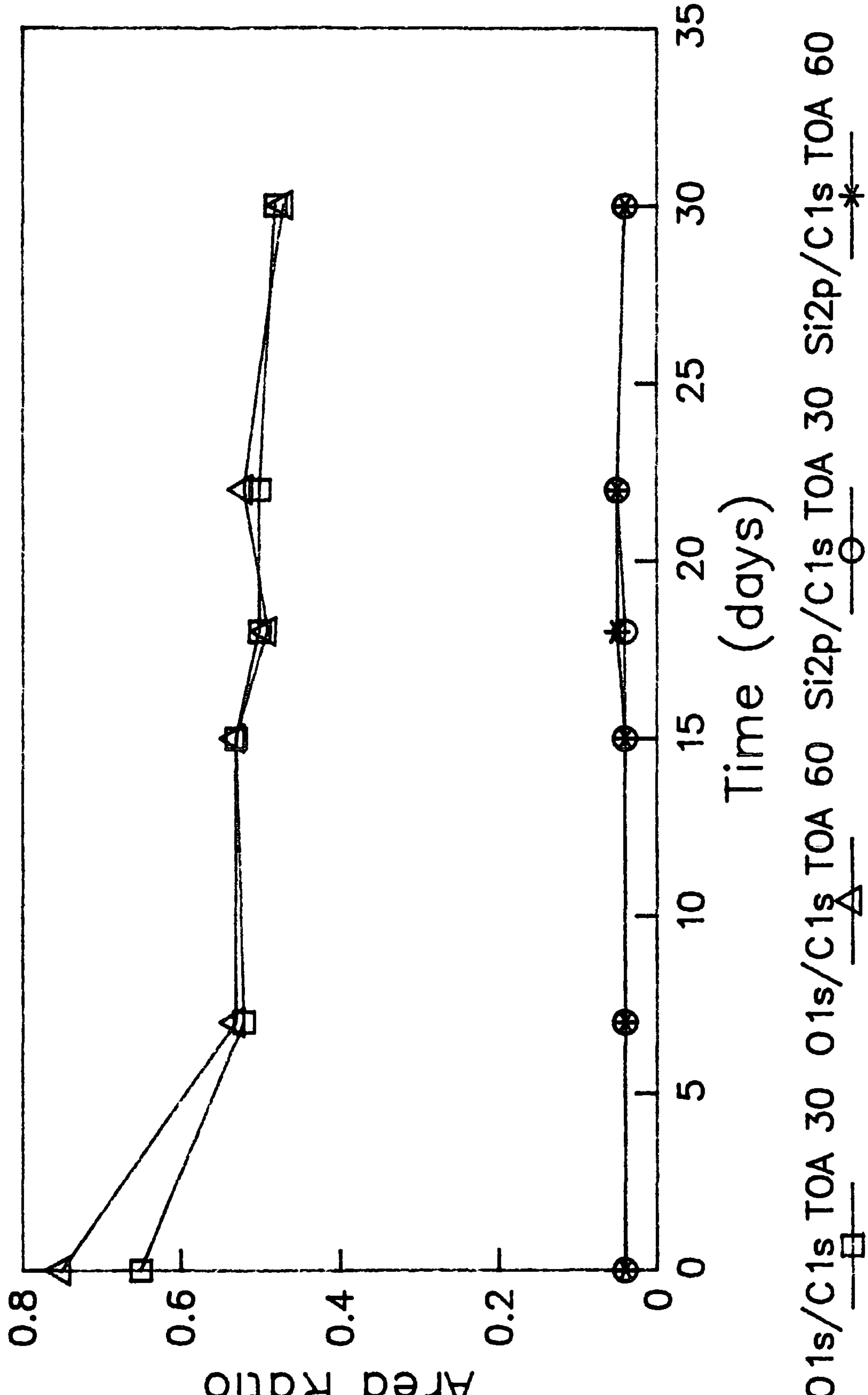
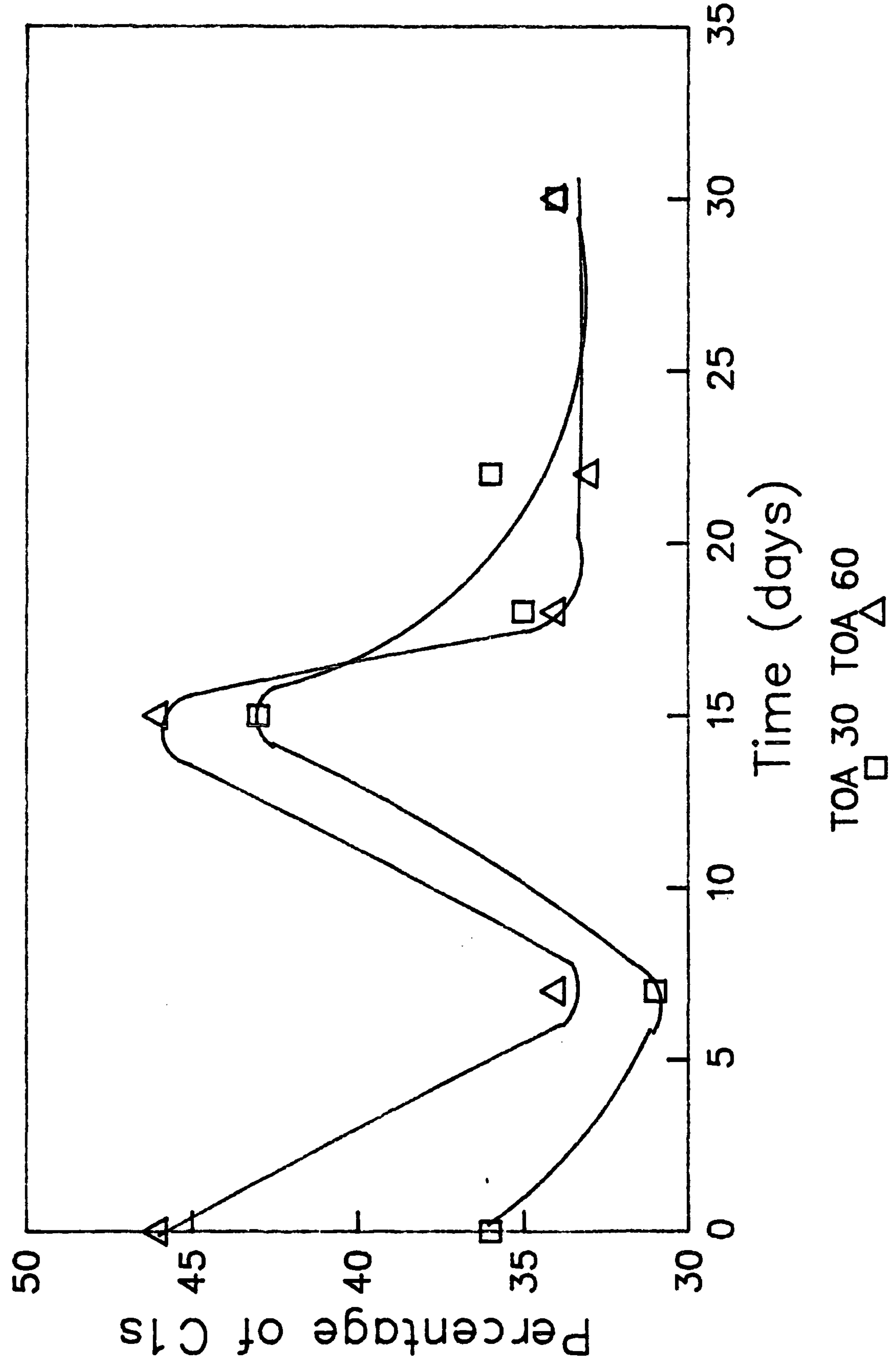


Figure 4.34 Variation of the Oxygen Containing Components of the C_{1s} Envelopes with Time During Storage of Boston IV in "Total", Samples Rinsed Thoroughly.



this is the case it can only be present in a very small amount since it is insufficient to observably obscure the Si_{2p} signal. An alternative explanation is that the different distribution of the oxygen amongst the types of polar groups leads to a higher surface energy than in the case of water stored Boston IV.

4.4 Conclusion

As predicted the surface treatment applied to the lens material was seen to decay over a period of time, reaching an equilibrium state after about a month. Though the general pattern of the decay followed the expected form there were periods of anomalous hydrophilicity. From studies of Boston IV, PMMA and PEEK in various environments it was found that the behaviour of all these materials followed a similar pattern, and the ESCA data revealed that the processes contributing to the decay in hydrophilicity were also very similar. The overall process of the decay was elaborated by a consideration of the chemical changes observed in these samples during the storage period and can be summarized as follows.

The plasma modification produces a surface which has a high surface energy due to the large numbers of polar, oxygen containing groups present. The polymer at the surface is also broken up into fragments, the extent of this damage being dependent on the material and the plasma involved. When stored those fragments with sufficient mobility migrate into the bulk of the material thus lowering the surface energy. When stored in a solvent, such as water, some or all of the modified material may be lost into solution. In those cases where material does migrate into the bulk some of this material is driven back to the surface after a period of 15 days. The precise driving force for this rearrangement is unknown, but may be due to an incompatibility between the highly polar surface material and the less polar bulk polymer. This resurgence of material is observed at different depths in different samples depending on their storage conditions. Immediately after reappearing near the surface this material is again driven inwards reducing the surface energy. In air stored Boston IV there follows another reorganization of the surface structure which may be induced by the first. In this phenomenon the surface briefly becomes more hydrophilic and then loses most of the oxygen from the surface whilst the amount of silicon at the surface increases dramatically. This appears to be due to the separation of silicon rich and oxygen rich fragments of polymer at the outermost surface of the sample.

Crosslinking of the polymer structure using argon was attempted, with the intention of inhibiting the decay, but this resulted in increased damage to the polymer structure, resulting in a greater loss of the modified surface. Additionally, controlled temperature studies showed that the migration processes are temperature dependent and that the rate and extent of migration can be controlled by storage at an appropriate temperature. This also suggests that the mobility of the polymer chains and hence the orientation and crystallinity of the polymer may also influence this behaviour.

Finally studies of the treated lens material stored in a typical lens solution showed that there was a small but significant amount of PVA adsorbed onto lenses stored this way. The amount was sufficient to influence the contact angle of the lens but could easily be removed by rinsing in distilled water, revealing a surface which decayed in the same way as treated lenses stored in water. This observation demonstrates that the treated lens, even when aged, has an affinity for materials containing large numbers of hydroxyl groups, and also that these materials once adsorbed, can easily be removed.

4.5. References - Chapter 4

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CHAPTER FIVE

PLASMA POLYMERIZED COATINGS FOR CONTACT LENSES

5.1 Introduction

Plasma polymer is the term used to describe the thin films formed by a great variety of materials when reacted in a glow discharge experiment. These films are generally highly crosslinked, insoluble, pin-hole free and adhere well to the substrates on which they are deposited (1). As was mentioned in chapter two these films usually bear little resemblance to conventional polymers. This fact can be demonstrated by the observation that the "polymer" is often chemically dissimilar to the monomer. For example the plasma polymer of perfluorobenzene contains CF_3 and CF_2 groups (2). A second important point is that it is possible using this technique to produce films from monomers, such as saturated hydrocarbons and perfluorocarbons (2,3), that do not form conventional polymers. Monomer in this case simply means any material which can give a sufficient vapour pressure in the apparatus, and which will deposit a film under glow discharge conditions.

Mechanism

The mechanism of plasma polymerization is not fully understood, however certain features of the process have been identified.

The most important factor in creating and maintaining the plasma is electron impact ionization, but this is not necessarily the most important step in plasma polymerization. It has been shown that materials very similar to plasma polymers can be produced by surface photopolymerization using UV radiation incapable of causing ionization (4). This suggests that these materials must be derived from reactions initially involving electronically excited states. In a plasma these states would be produced by electron impact, rather than by light generated within the plasma (5).

Since typical bond dissociation energies for organic molecules are below their ionization energies, bond cleavage occurs frequently in the plasma. This results in much larger concentrations of radicals than ions (6). Though this does not indicate the relative reactivities of these species it has been observed that in some cases the amount of polymer formed is too great to be solely due to reactions of ions (7).

The presence of large quantities of radicals trapped in the polymer films is indicative of their contribution to film formation. Though it has been shown that a non polymerizing gas plasma can produce radicals in glass samples (8) it has also been shown, by comparison of coated and uncoated glass substrates, that the radicals in the polymer film arise as a result of the polymerization process. The presence of these radicals means that after formation the films can often readily oxidize on exposure to air (9).

The growth of plasma polymers cannot readily be explained by classical growth mechanisms and consequently Yasuda (8) has proposed a rapid step growth mechanism to rationalize polymer formation, following the production of the initial reactive species.

A final consideration is that formation of a film is the result of competitive processes of deposition and ablation. Plasmas are commonly used to ablate material from surfaces whether by sputtering using a non reactive gas (10), or by etching using a reactive gas such as CF_4 (11). This means that the loss of deposited material may be a significant factor in determining the chemistry of the polymer produced.

5.2 Plasma Polymers as Biomaterials

Plasma deposited polymers can have many advantages in biomedical applications. As has been mentioned they can be used to modify surface properties without affecting bulk properties, and the wide range of starting materials means that it is possible to tailor the surface properties by varying the parameters of the deposition process and the mixture of monomer gases used. For example if fluorinated monomers are used a low energy surface is produced, whilst addition of oxygen to the gas mixture increases the surface energy in proportion to the number of of oxygen groups incorporated into the surface (12). The degree of crosslinking of the plasma polymer can be used to retard the leaching of low molecular weight compounds from the material (13). Varying this can modify the lifetime of drug release devices (14). Additionally the barrier properties of plasma polymers has been utilized to prevent the permeation of body fluids into devices such as oxygen sensors (15) and neurological electrodes (16).

The use of plasma polymerization to modify polymers for improved blood compatibility has been investigated with a variety of monomers. Surfaces coated with plasma polymers of tetrafluoroethene have been shown to have a good response to blood in a variety of tests (17,18) when applied to some polymers.

Silicone polymers are some of the most biocompatible polymers known (19) but it has been observed that they have far greater blood compatibility when they do not contain any silica filler (20,21). Therefore it has been proposed that plasma polymers of siloxane materials, such as hexamethyldisiloxane (HMDS) or hexamethylcyclotrisiloxane (HMCTS), could be applied to filled silicones to improve their blood compatibility (22) and to other materials to improve their response in the body (23).

The use of plasma polymers to improve the surface properties of contact lenses has been investigated by Yasuda and coworkers (24). Using a plasma polymer formed from a mixture of ethyne, nitrogen and water significantly improved the wettability of a

PMMA lens whilst reducing the amount of debris which accumulated on the lens surface during wear.

In this study the following plasma polymers have been considered: copolymers of tetramethylsilane (TMS) and dimethylpropane (DMP) treated with oxygen in an attempt to duplicate the elemental composition observed in plasma oxidized Boston IV; polymers formed from HMDS and HMCTS, since as has been mentioned silicones are regarded as very biocompatible materials; NVP polymers, which can form a hydrogel coating, thus mimicking the surface properties of soft contact lenses, and allyl alcohol plasma polymers. The latter were not expected to convey a particular degree of biocompatibility, though it might be anticipated that they would posses improved hydrophilicity. It has been observed that in blood compatible tissues the simplest common feature is the presence of large quantities of phosphorylcholine containing phospholipids (25). Previously, coatings formed from this material have been deposited using the Langmuir Blodgett technique to produce multiple layers of phosopholipid (26). However even when a suitably functionalized lipid, which can be polymerized after deposition (27), is used the forces of attraction between the layers are still weak and therefore the films are unstable. An alternative approach involving the reaction of suitably functionalized phosphoryl choline derivatives with surface hydroxyl groups has been reported as being more successful (28). Therefore it was hoped that a surface containing large quantities of hydroxyl groups could be deposited using allyl alcohol and that this would enable the phosphoryl choline group to be bound to the surface. Thus a surface resembling the outer surface of cell membranes would be produced which would have a similar response to the tissues of the cornea, i.e. it would be a biomimetic surface.

5.3 Experimental

5.3.1 Plasma Polymerization

Plasma polymerizations were performed in tubular glass reactors of two designs, shown in figure 5.01. Samples were placed on a glass slide which was inserted into the reactor. The reactor was an integral part of a grease free vacuum line, joints being sealed with Viton O rings or Cajon ultra torr couplings on ground glass. PTFE Youngs taps were used throughout the system which is displayed schematically in figure 5.02.

The system was pumped by an Edwards ED2M2 $2ls^{-1}$ rotary pump in conjunction with a liquid nitrogen cooled cold trap, to prevent backstreaming of pump oils and to trap out reactive products before reaching the pump. The system was capable of maintaining a base pressure of $2x10^{-2}$ torr. Pressure was monitored using a Pirani thermocouple gauge.

Figure 5.01 Reactor Designs.

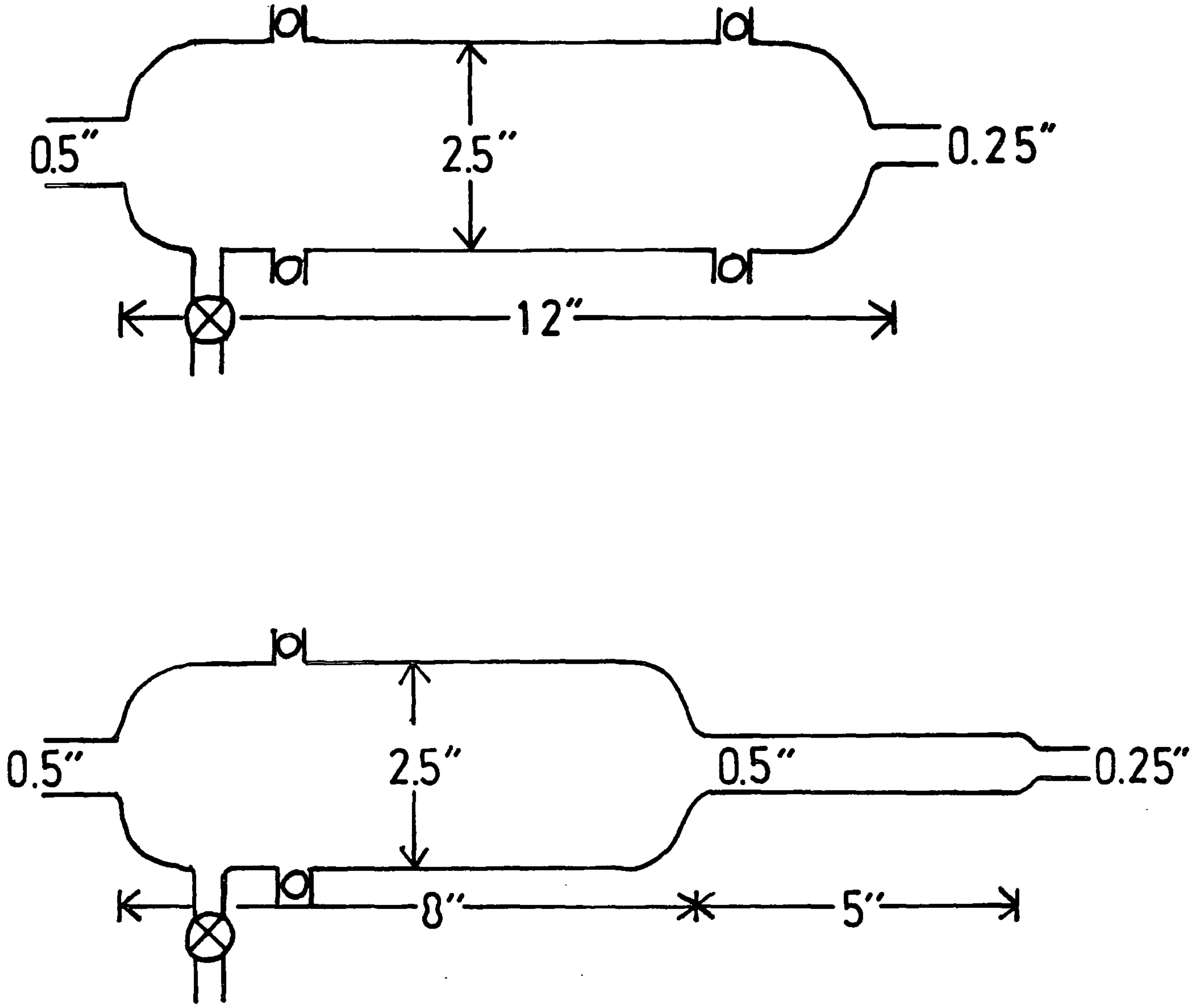
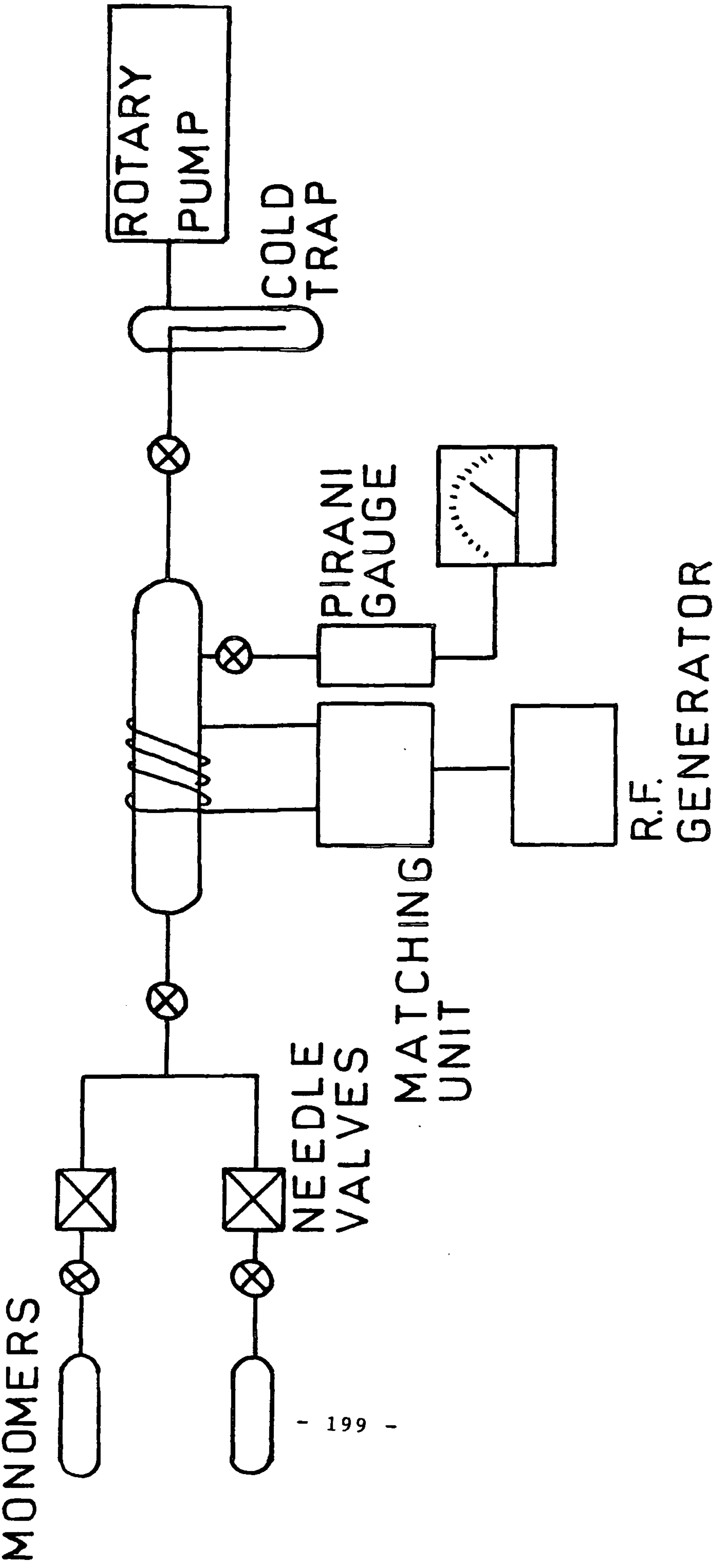


Figure 5.02 Experimental Configuration for Plasma Polymerization.



Radio frequency power was supplied by a Tegal RFG/100P generator at 13.56 MHz capable of delivering up to 100 watts. This was inductively coupled to the reactor via an external copper coil. The circuit was completed with an L-C network, used to match the generator to the external inductive load, and a meter to monitor input and reflected power.

Before commencing each deposition the leak rate of the system was measured. When this was acceptable the monomer was leaked into the reactor through a needle valve. The flow rate of monomer was determined by isolating the pumping system and observing the rate of pressure rise due to the flow of monomer into the reactor. The flow rate could then be calculated using the following equation (29).

$$F = (\delta P/t)(V/RT) \text{ mols}^{-1} \qquad 5.1$$

Where δP is the pressure rise, in torr,

t the time taken, in seconds,

V the volume of the system, in cm^3,

R is the gas constant, $Jmol^{-1}K^{-1}$,

and T the temperature, in kelvin.

This flow rate is converted to the usual units by the relation

$$\text{Flow rate} = F \times 60 \times 22414 \quad cm^3min^{-1}.$$

The flow rate was used to enable the same material to be prepared in repeated experiments and to set the proportions of monomers in copolymerization experiments.

The procedure for igniting and balancing the plasma was identical to that used for the plasma modification of surfaces described in chapter 3. Since the polymer was deposited throughout the reactor this was thoroughly cleaned between each experiment to avoid any contribution to the new polymer from material ablated from the reactor walls.

5.3.2 Labelling of Allyl Alcohol Plasma Polymer Surfaces

One disadvantage of ESCA as a technique for examining polymer surfaces is that it is incapable of distinguishing between certain functionalities, such as hydroxyl and ether groups (30). As a result attempts have been made to derivatise surface groups in order to distinguish them from one another. Numerous solution state reactions have been used (31) but there are several problems inherent in the use of solution state reactions. The solvent may permeate into the bulk of the polymer and can induce reorganization of the surface (32). Additionally low molecular weight material can be leached out under such conditions (31). In this study the vapour phase reaction of trifluoroacetic anhydride (TFAA) was used to label hydroxyl groups in the surface of allyl alcohol plasma polymers. Though TFAA also reacts with acid groups in solution this reaction does not occur in the vapour phase (33). TFAA does react with amines under these conditions but in this case this was not a problem.

The samples were left in the reactor after plasma polymerization and the pumping system was closed off. TFAA vapour was then introduced at its vapour pressure. After 30 minutes exposure, the vapour was condensed into a tube by cooling with liquid nitrogen and the system was pumped down to remove any remaining TFAA.

Reaction with choline acetate dichlorophosphate (CADP) was achieved by simply immersing the sample in the CADP for five minutes. The sample was then rinsed in dilute sodium hydrogencarbonate solution and distilled water to hydrolyse the remaining reactive chlorine and to remove excess reagent.

5.3.3 Materials

TMS 99.9+%, NVP 99+%, allyl alcohol 99.9+% and TFAA 99+% were obtained from the Aldritch Chemical Company. DMP gas was obtained from BDH Ltd. CADP was kindly supplied by Dr. A. Durrani of the Royal Free Hospital, London.

5.4 Results and Discussion

5.4.1 TMS/DMP Copolymers

The copolymers of TMS and DMP were deposited onto aluminium substrates over a period of 5 minutes at a total pressure of 0.2 torr with 20 watt input power. These conditions ensured that sufficient polymer was deposited for there to be no visible signal from the aluminium substrate. A typical spectrum of a TMS plasma polymer is shown in figure 5.03. The C_{1s} core level displays a broad peak which will contain contributions from CH, C-C and C-Si groups, however it is not possible to distinguish between these. There is also likely to be a small contribution from carbon-oxygen functionalities since plasma polymers invariably pick up a little oxygen, either by the reaction of radicals with the atmosphere (29) or by reaction with oxygen containing species present in the plasma.

The O_{1s} spectrum shows a small peak, corresponding to 9 oxygens per 100 carbons. This is a level which is greater than might be anticipated from the C_{1s} envelope. It can be seen from the Si_{2p} spectrum that there are two silicon environments present. The major contribution is from C-Si at a binding energy of about 101 eV but there is a noticeable shoulder to higher binding energy indicating the presence of some Si-O functionalities. This would be sufficient to account for the amount of oxygen seen in the polymer.

It was observed that the composition of the plasma polymer was not constant throughout the reactor, table 5.1. It is noticeable that there is a correlation between the the amount of silicon and the amount of oxygen in the plasma.

Table 5.1 The variation of composition with position for plasma polymers of TMS (n=1)

Distance from end of reactor (cm)	O_{1s}/C_{1s}	Si_{2p}/C_{1s}
3	0.17	0.56
6	0.08	0.23
9	0.15	0.42
12	0.15	0.47

The position 6 cm from the end of the reactor corresponds to the position of the induction coil around the reactor. It is clear from these figures that only in this coil region does the composition of the plasma polymer approach that of the monomer. he copolymers are very similar in appearance, differing mainly in the amount of silicon present. A typical example, 50/50 TMS/DMP, shown in figure 5.04.

Figure 5.03 ESCA Spectra of TMS Plasma Polymer.

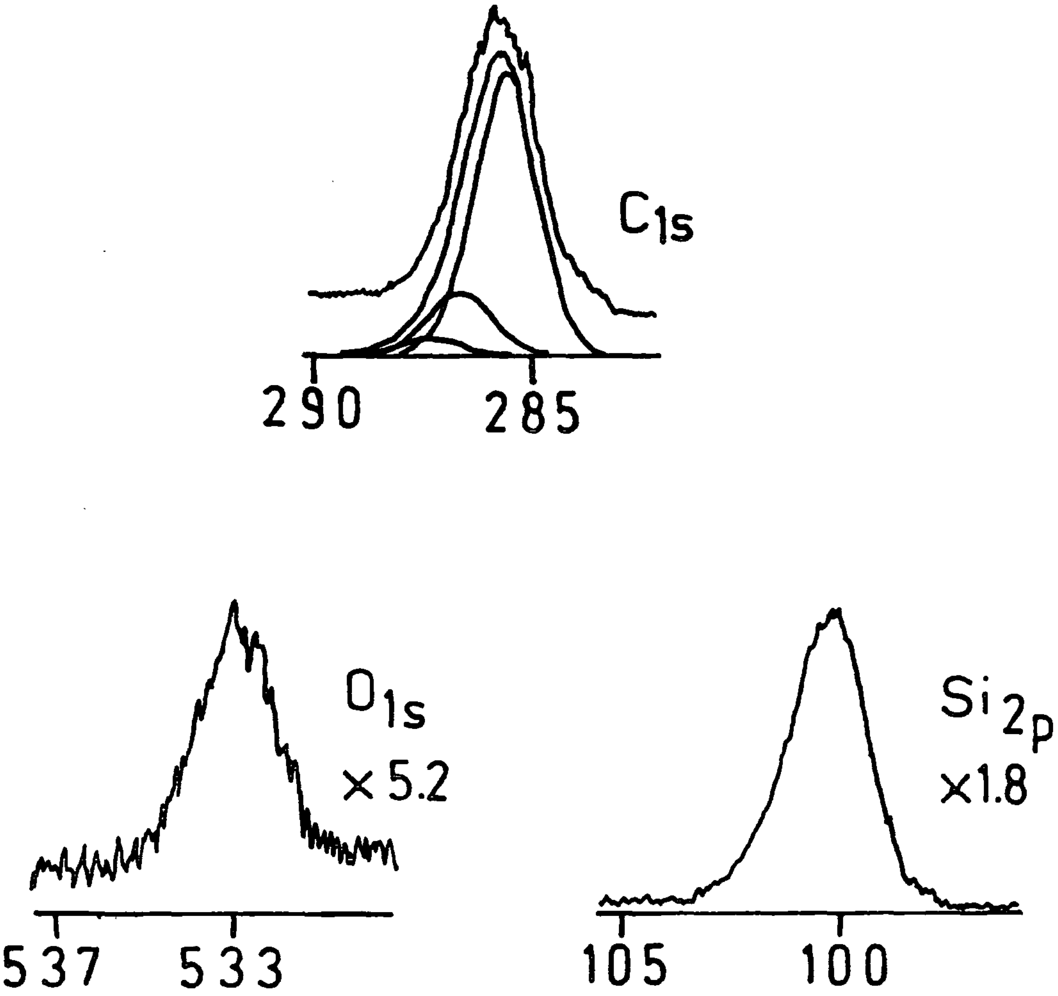


Figure 5.04 ESCA Spectrum of Plasma Polymer of a 50/50 Mixture of TMS/DMP.

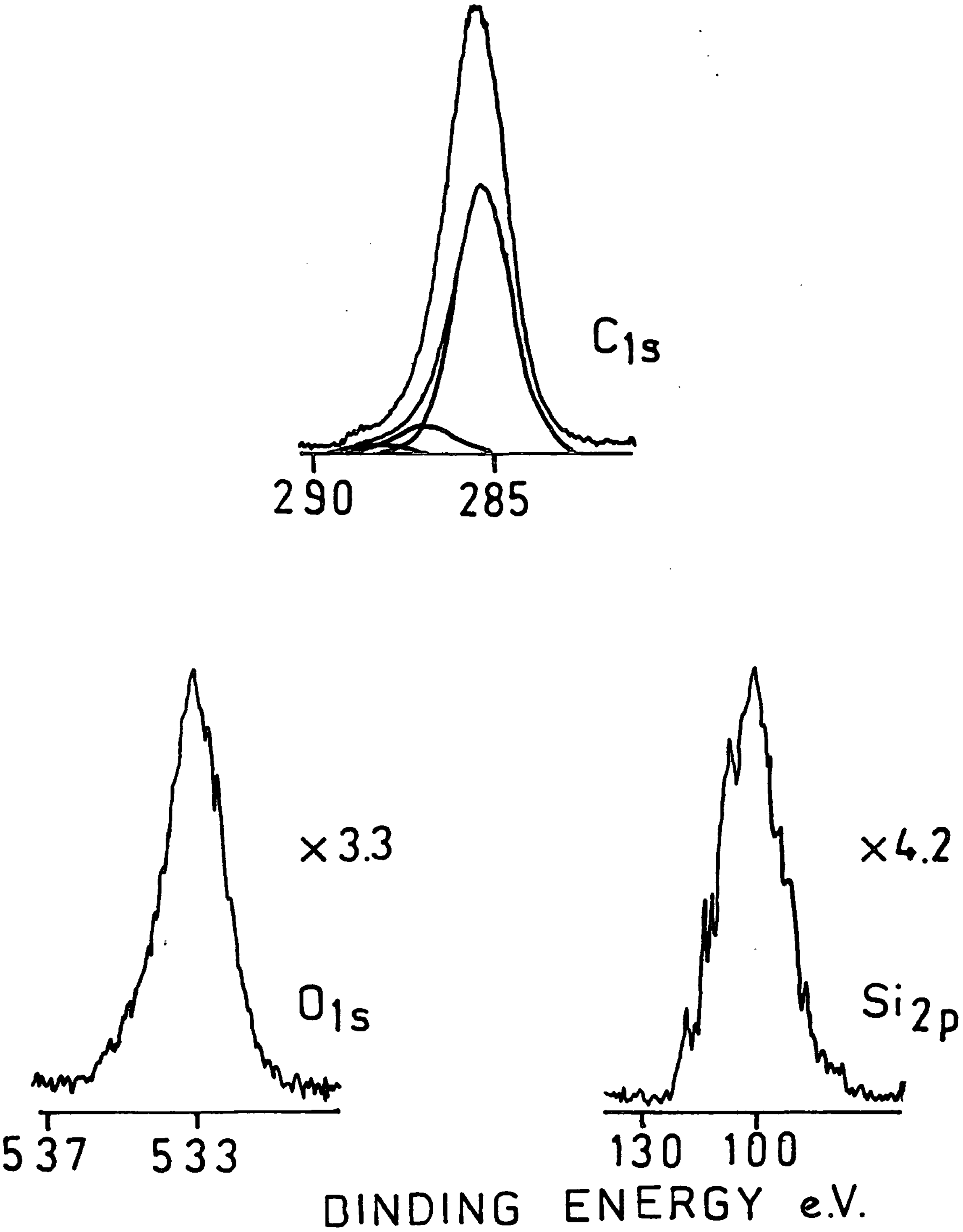
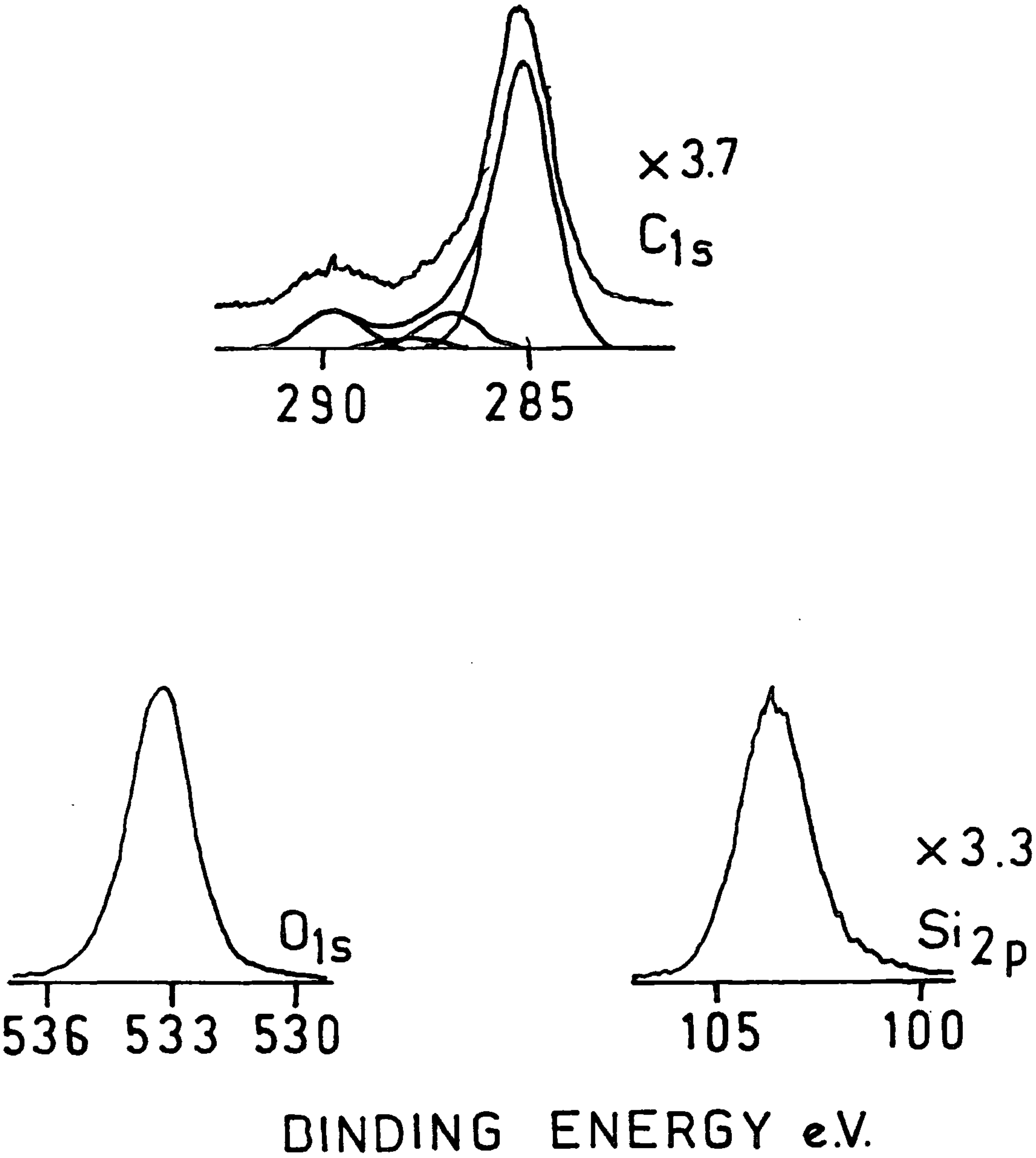


Figure 5.05 ESCA Spectrum of Oxygen Plasma Treated TMS Plasma Polymer.



When treated with an oxygen plasma these polymers undergo extensive changes as shown by the spectrum of oxygen plasma treated TMS plasma polymer, figure 5.05.

The plasma polymers were treated under the same conditions as the contact lens material, 20 watts, 0.4 mbar of oxygen, for 45 seconds. The area ratios for these experiments were reported in chapter 3. The important change noted there was the conversion of the Si-C moieties to SiO_2 with a simultaneous increase in the overall amount of silicon present. This is clearly shown here by the shift in peak position from 101 eV to 103.35 eV and the doubling in size of the peak.

From being a single broad peak the C_{1s} spectrum can now be resolved into four distinct peaks at 285.0, 286.7, 287.8 and 289.5 corresponding to CH/C-Si, C-O, C=O, and O-C=O respectively. These component peaks have a full width at half height, or half width, of 1.8 eV. This is rather broad since the C_{1s} half width in a regular polymer would be of the order of 1.3 eV (29). This increased width is indicative of a number of closely related environments resulting from the complex and non uniform nature of the plasma polymer.

The O_{1s} spectrum has increased in intensity and it can be shown that this represents more oxygen than can be accounted for by the C_{1s} envelope, confirming the uptake of oxygen by the silicon in the surface.

A comparison of the elemental compositions of the copolymers is given in table 3.1. Comparing the C_{1s} spectra of these copolymers reveals changes in the way the carbon is oxidized as the amount of silicon decreases. The pure TMS polymer shows slight oxidation as noted above; in comparison the copolymers are much more highly oxidized, figure 5.06. The 50/50 copolymer shows the greatest degree of oxidation having a peak at 289.95 eV corresponding to the CO_3 functionality. The 20/80 mix does not show this peak, though it still appears more highly oxidized than the 100% TMS polymer.

A possible explanation for this behaviour is that those polymers containing most silicon oxidize the most and generate small highly oxidized carbon species which are either ablated in the plasma reactor or are sufficiently volatile to be lost in the ultra high vacuum of the ESCA spectrometer. This is suggested by the comparative lack of oxidized carbon in the TMS polymer and the fact that the carbon in the 50/50 mix can be oxidized to a greater extent than that in the 20/80 copolymer. The 50/50 copolymer then represents a halfway stage between the two extremes in that the carbon is highly oxidized but the structure of the polymer surface has not been broken up sufficiently to cause this modified material to be lost.

The contact angles of these materials and their coefficients of friction, both before and oxygen plasma treatment, are summarized in table 5.2.

Figure 5.06 Comparison of the C_{1s} Spectra of a Series of TMS/DMP Copolymers.

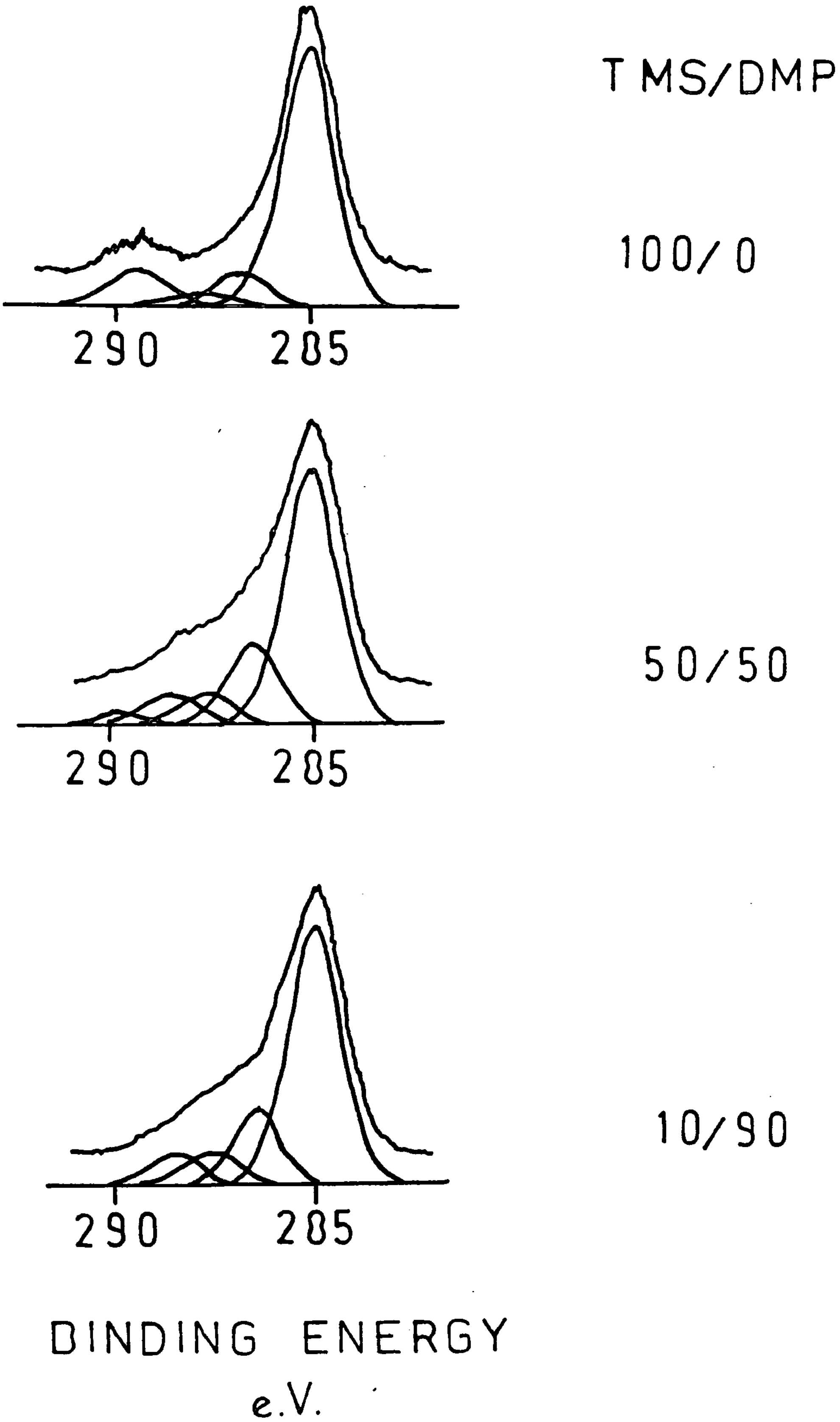


Table 5.2 Surface Properties of a Series of TMS/DMP Plasma Copolymers.

Polymer	Contact angle (n=10, SD=4.0)	COF (average) (n=10, SD=0.03)
TMS	104	0.34
TMS, oxygen treated	104	0.26
50/50 TMS/DMP	95	0.35
50/50 TMS/DMP, oxygen treated	40	0.43
25/75 TMS/DMP	91	0.33
25/75 TMS/DMP, oxygen treated	38	0.47
10/90 TMS/DMP	90	0.34
10/90 TMS/DMP, oxygen treated	30	0.46

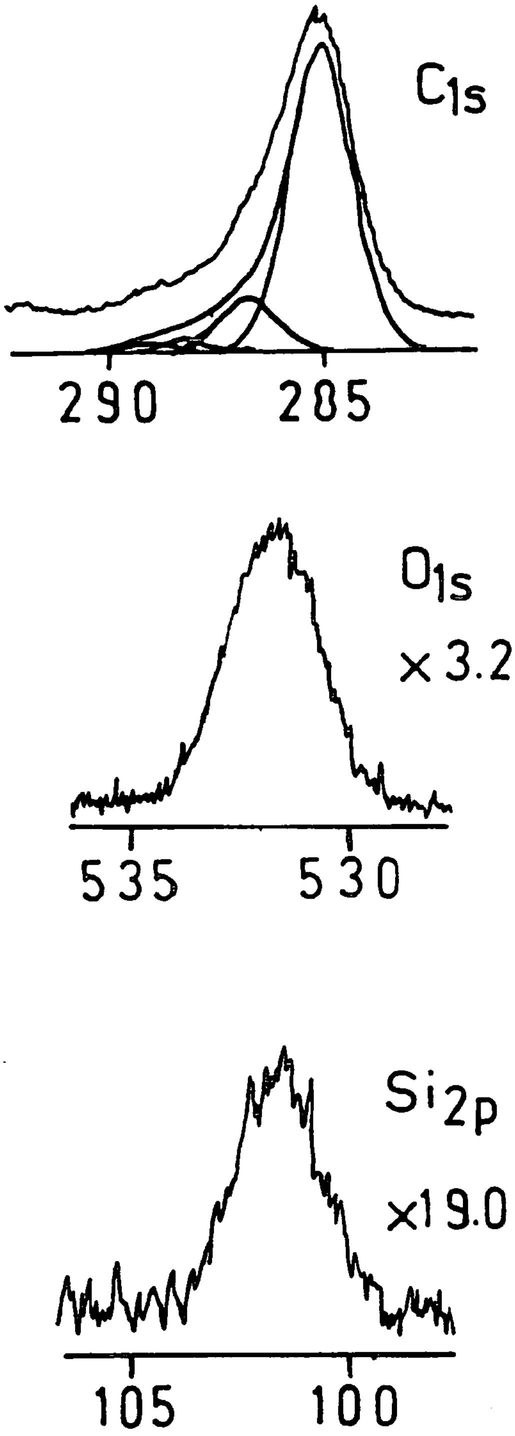
From these results it can be seen that these materials have high initial contact angles and that their improvement in hydrophilicity when oxygen plasma treated is comparable to that of Boston IV. Initial COF values are comparable to that of Boston IV, however the COF rises on plasma treatment by a significant degree. The only exception is the 100% TMS polymer. The lack of any change in contact angle is surprising since there is some uptake of oxygen, though the majority of this appears to be bound to silicon. The fall in COF suggests that, since there seems to be no change in the interfacial forces as shown by the contact angle, the treated surface may fail under stress and thus there is a reduction in the components of the COF due to the shearing of surface films or of the bulk polymer (~~29~~34). This supports the theory that in copolymers with a high silicon content the carbon in the surface can be sufficiently oxidized to break up the structure of the polymer.

It has been shown by the above results that it is not possible to reproduce the surface of plasma treated Boston IV by combining monomers containing the requisite elements in a simple process. This indicates that the presence of silicon in the polymer is not sufficient to produce the desired effects, it may be necessary for the silicon to be in the form of a siloxane. Whilst some of the polymers produced have certain of the required properties, it has not proved possible to achieve both a good degree of hydrophilicity and a low COF. Additionally the surface chemistry of these materials is dissimilar to that of Boston IV.

5.4.2 Polymers of HMDS and HMCTS

Plasma polymers of these materials were deposited onto aluminium substrates from a 20 W plasma over 5 minutes at a pressure of 0.1 torr. These conditions ensured that no signal from the substrate was visible.

Figure 5.07 ESCA Spectra of Hexamethyldisiloxane Plasma Polymer.



A typical spectrum of HMDS plasma polymer is shown in figure 5.07. The C_{1s} envelope shows the presence of CH/C-Si and C-O, 285 and 286.6 eV, as the major components with much smaller contributions from C=O and O-C=O functionalities, 287.8, 289.0 eV.

The Si_{2p} core level appears at 101.6 eV, it is interesting to note that this is approximately 1 eV above the binding energy observed in the starting material showing that a change in the chemistry of the material has occurred (35).

This ESCA data is in agreement with the work of Akovali and Bölük who have studied thin films of plasma polymerized HMDS using infra-red spectroscopy (36). Their results show the presence of Si-O-Me, $Si-CH_3$, Si-O-Si, and $Si-Me_2$ functionalities and that the relative amounts of these groups depended on the plasma conditions.

The elemental composition of the polymer as determined from the area ratios is C:O:Si=100:25:9. This is considerably different to the monomer, C:O:Si=100:17:33, indicating a significant loss of silicon during deposition.

The contact angle with water for this material is 59° (n=10, SD=3.8) showing surprisingly good hydrophilicity for a siloxane (36). The average COF, as determined by the slip peel tester, was 0.35 (n=10, SD=0.04) which compares favourably with the

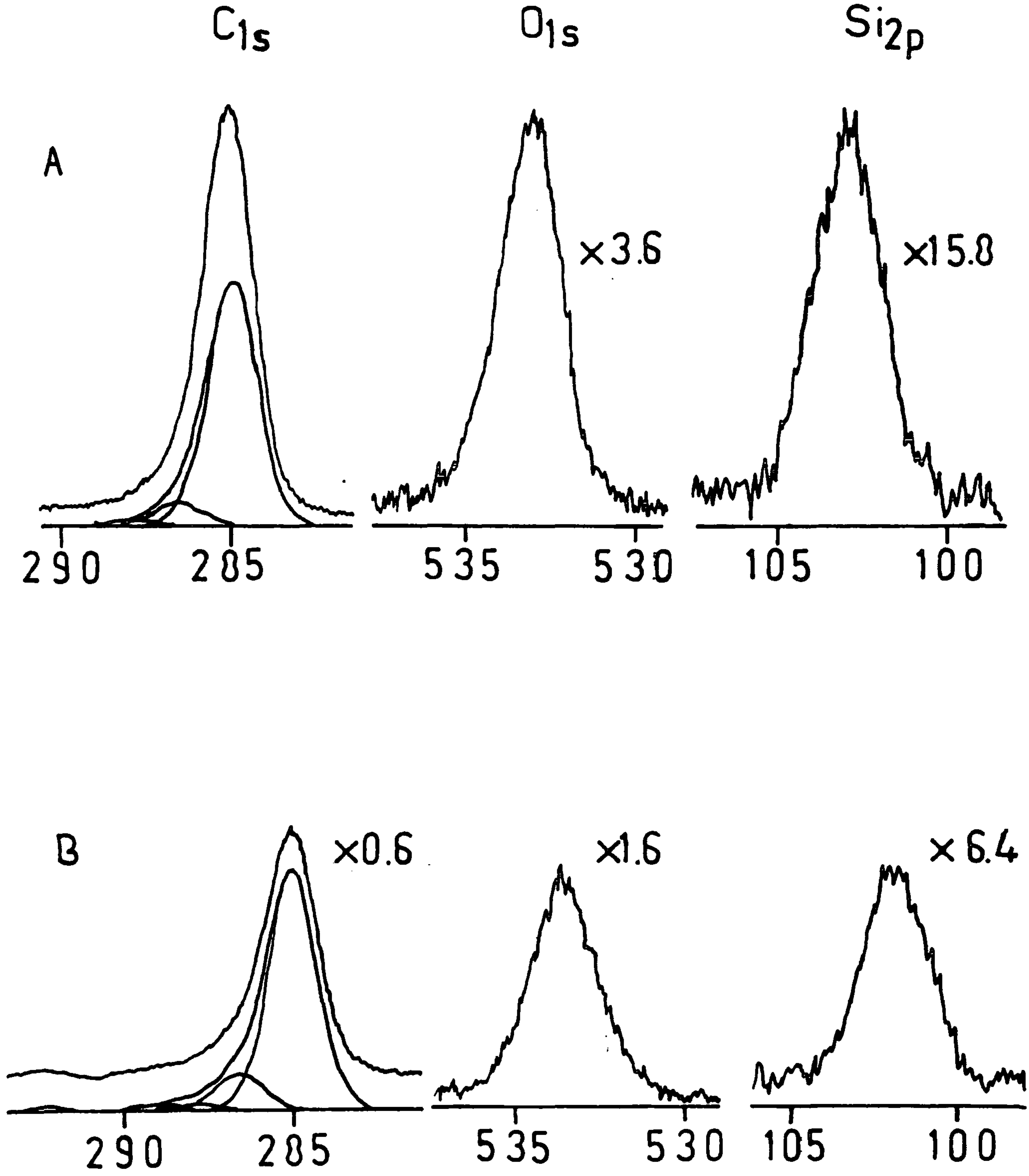
Boston IV lens material. Overall the properties of this plasma polymer are very promising; it has good wettability, an acceptable COF, chemical similarities between it and the treated and aged Boston IV lens material, the presence of siloxane rather than silicate, which, as has been mentioned, can be detrimental to biocompatibility (20,21), and C-O being the most significant functional group aside from CH/C-Si. The main differences are the virtual lack of more highly oxidized carbon species and the overall lower oxygen content.

Examples of the plasma polymers of HMCTS are shown in figure 5.08. Spectrum A is of a sample collected from the coil region of the longer reactor, which lies approximately half way along it, whilst spectrum B was collected in the coil region of the shorter reactor i.e. directly after the inlet. The most obvious difference is the position of the Si_{2p} peak which is at 103.0 eV in spectrum A and at 101.8 eV in spectrum B. This shows that in the first sample the siloxane has been converted to silicate whilst the siloxane functionality is retained in the second sample. Additionally, comparison of the overall oxygen content, determined from area ratios, and the oxygen content of the C_{1s} envelopes shows that in the case of spectrum A the Si:O ratio is 1:2 whereas in the case of spectrum B it is 1:1.

Analysis of the two C_{1s} spectra reveal two differences: in sample B there are more carbon oxygen species (including C-O, C=O, and O-C=O; with C-O being the most prominent), and spectrum B also contains a small shake up peak at 292.3 eV. This is characteristic of the presence of unsaturation in the polymer (29) and occurs when photoionization is accompanied by the simultaneous transition of a valence level electron into a higher unoccupied state. Short range unsaturation, such as is found in butadiene or naphthalene, gives rise to a distinct peak, which is typically more intense for aromatic structures, whereas long range unsaturation, in a conductor for example, produces asymmetric tailing of the main peak as the number of potential transitions increases and the individual satellites merge into one another.

Since both these polymers were deposited under identical plasma conditions it follows that the differences in chemistry are due to the position of the samples in the reactors and to the design of the reactors. Reactor design has been recognized by others as a crucial factor in determining the result of a plasma polymerization reaction and some attempt made to quantify it (38,39). Since, as has been previously noted, silicate has been found to be detrimental in a biomaterial (20,21) the material represented by sample A was discarded at this stage and further experiments performed using samples coated in material B. It should perhaps be noted that the presence of silicate on the surface of a contact lens may not be intrinsically detrimental, since a small number of lenses of Boston II have been plasma treated and have performed

Figure 5.08 ESCA Spectra of Two HMCTS Plasma Polymers



reasonably well.

The contact angle of this plasma polymer was found to be 78° (n=10, SD=4.0) which is comparable to untreated Boston IV lens material, however the average COF of the polymer was 0.65. This is a much higher value than that for lens material. Additionally this figure is the average over 5 runs during which the measured COF declined rapidly from a value of 1.36 to 0.39. After five runs there was significant observable damage to the LDPE base layer and therefore it would appear that the plasma polymer attached to the sled had picked up material from the base polymer. Thus after five runs the COF was approaching that of LDPE on LDPE, 0.33, since the plasma polymer was coated with LDPE accumulated from the base polymer. Therefore it must be concluded that a true value for the COF of this material is 1.36 or possibly even higher, and consequently this material was not considered suitable for use as a lens coating.

5.4.3 NVP Plasma Polymers

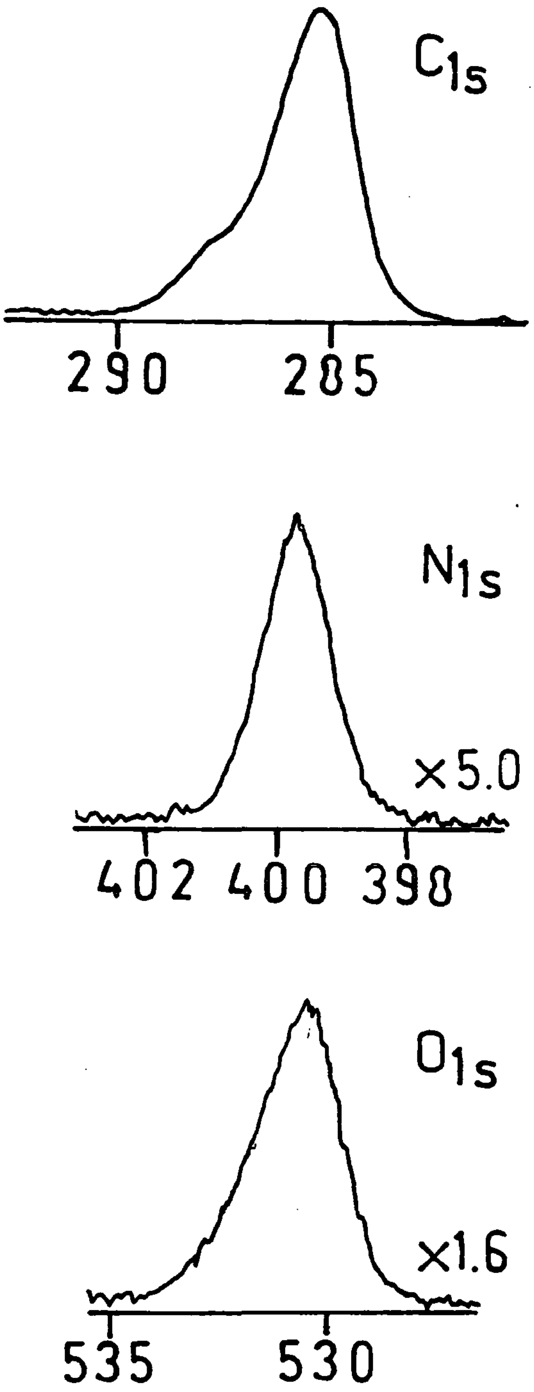
It has been previously observed that NVP produces two distinct types of plasma polymer (40) which can be produced by varying the flow rate used in the experiment. At low flow rates the polymer produced has a contact angle of ≈ 55° whereas the polymer produced under high flow rate conditions has a contact angle of less than 5°. This difference is due to the fact that in the high flow rate case the product appears to have been formed involving primarily reaction through the vinyl group since it resembles conventionally polymerized NVP under ESCA analysis. The low flow rate NVP polymer gives a different ESCA spectrum and appears to be formed by a more complex mechanism (41).

Using a flow rate of 0.74 cm^3min^{-1} and power of 5 watts at a pressure of 0.2 mbar the plasma polymer was deposited over a period of 5 minutes. To achieve these conditions it was necessary to remove the needle valve from the inlet and connect the monomer tube directly to the reactor. The ESCA spectrum of the polymer produced is shown in figure 5.09.

The C_{1s} spectrum shows the presence of peaks corresponding to C-N and N-C=O at 286 and 287.4 eV with a small contribution from O-C=O at 288.7 eV. The O_{1s} peak is sharp indicating a single main environment.

The contact angle, with water, of this material was so low as to be unmeasurable, regardless of the position in the reactor from which the sample was taken. It was also observed that this film once wet could be removed from the aluminium substrate on being rubbed firmly. Since the initial adhesion to the substrate was good this suggests that the water was able to penetrate through the film to the interface between it and the aluminium (42) thus inducing adhesive failure. The COF of the dry polymer was high, average value 0.71 (n=5, SD=0.06),

Figure 5.09 ESCA Spectra of the High Flow Rate Plasma Polymer of NVP.



and it was not possible to measure the COF in the hydrated state due to the adhesion problem noted above. The purpose of producing the NVP plasma polymer was to attempt to provide a hydrogel coating on a hard lens. Since this appeared to have been achieved the high COF in the dry state was not felt to be a problem, once in the eye the excellent hydrophilicity of the coating should result in complete wetting by the tear film thus lubricating the lens.

5.4.4 Allyl alcohol plasma polymers

Plasma polymers of allyl alcohol were deposited under two sets of conditions. Initially standard conditions of 20 watts and 0.1 mbar were used. A sample of this plasma polymer was exposed to TFAA vapour to label any OH groups present in the surface. The spectra of the labelled and unlabelled polymer are shown in figure 5.10.

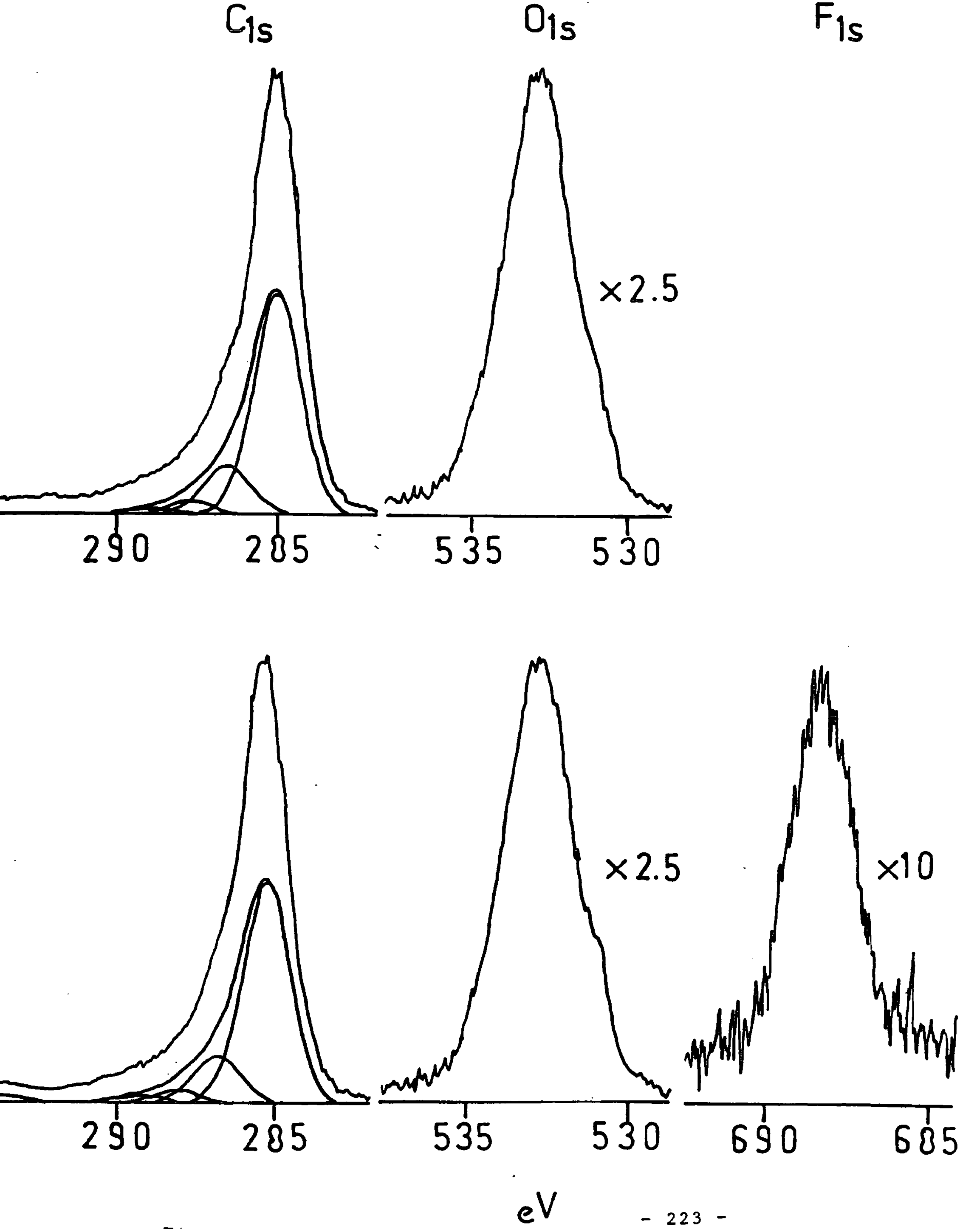
It can be seen from the C_{1s} spectrum of the unlabelled polymer that there are two main environments, binding energies 285 and 286.6 eV, corresponding to CH and C-O respectively. In the polymer these functionalities are present in the ratio 3:1 as opposed to the 2:1 ratio in the monomer. There is also a small contribution from C=O, binding energy 287.8 eV. The O_{1s} spectrum is sharp and symmetrical suggesting a single species.

In the spectrum of the polymer treated with TFAA two additional peaks are manifest in the C_{1s} envelope, at 289.0 and 293.5 eV, corresponding to O-C=O and CF_3 respectively. These peaks form a very small contribution to the C_{1s} envelope and it may therefore be concluded that very little of the C-O peak represents C-O-H.

The spectrum of the polymer produced at 5W and 0.2 mbar, figure 5.11, is virtually identical to that produced at higher power. However comparison of the TFAA treated polymers shows that much more fluorine has been added to the low power polymer. Analysing the C_{1s} envelope of this spectrum, figure 5.11, shows that 61% (n=1) of the C-O peak is due to C-O-H functionalities.

It would appear therefore that to produce a hydroxyl containing surface from allyl alcohol a low power must be used. However it is also worth noting that to produce the low power polymer it was necessary to employ the highest pressure and flow rate obtainable which permitted the ignition of the plasma. Therefore it is perhaps more correct to say that the composite parameter W/FM, described by Yasuda (8), should be minimized. Under these conditions it appears that allyl alcohol displays a tendency to react preferentially via its double bond.

Figure 5.10 ESCA Spectra of Allyl Alcohol Produced Under Conditions of 20W, 0.1 mbar Before and After Labelling with TFAA.



5.4.5 Reaction with CADP

The ESCA spectra for the allyl alcohol plasma polymer after treatment with CADP are shown in figure 5.12. From the area ratios the elemental composition of the surface is 100 C: 33 O: 4 N: 8 P (n=1). It is immediately apparent from this that the CADP appears to have decomposed at some point. Examination of the N_{1s} and P_{2p} spectra show that the phosphorous appears to be present as a single environment whilst there is a distinct shoulder on the N_{1s}peak to low binding energy. The binding energy of the main nitrogen peak, 402 eV, suggests that it exists as N^+ whilst the remainder is due to a neutral nitrogen species. There are two possible causes for this decomposition: either the reagent can breakup during the reaction with the surface, or the reacted layer is damaged by the x-ray irradiation used in an ESCA experiment. It has been observed before in reactions with hydroxylated polymer surfaces that a multifunctional monomer can react to give a variety of products even though one may be a more favourable reaction (43). This is because although the reagent may be present in large amounts there is still often an excess of OH groups at the surface. X-ray degradation of nitrogen containing compounds is well known (44,45) and can give rise to a low binding energy nitrogen containing product (46). In this case x-ray degradation seems the most likely explanation since ESCA spectra of CADP, figure 5.13, show a similar discrepancy in the N:P ratio and the sample is noticeably discoloured after

Figure 5.11 ESCA Spectra of Allyl Alcohol Plasma Polymer Produced at Low Power, Before and After Treatment with TFAA.

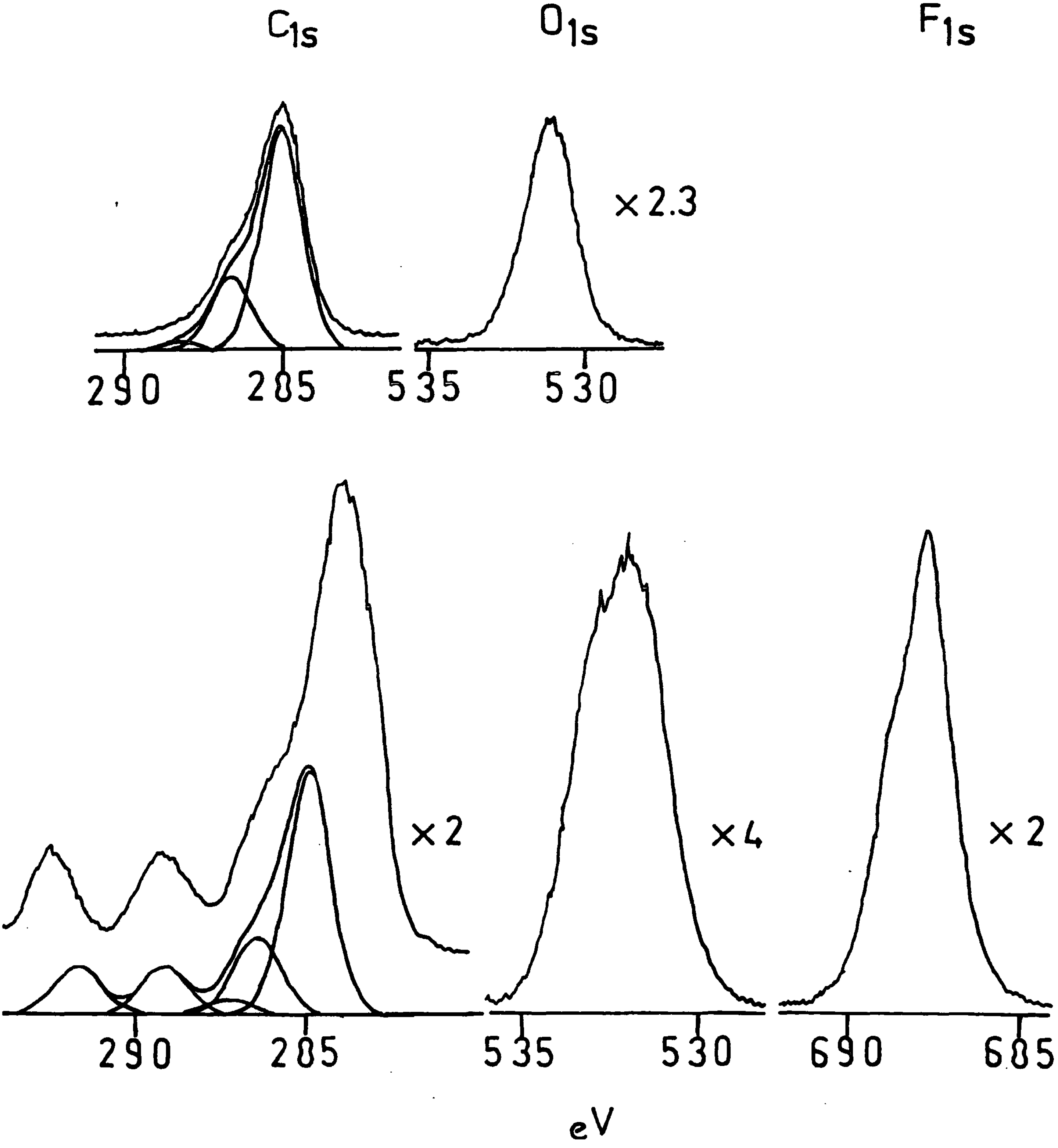
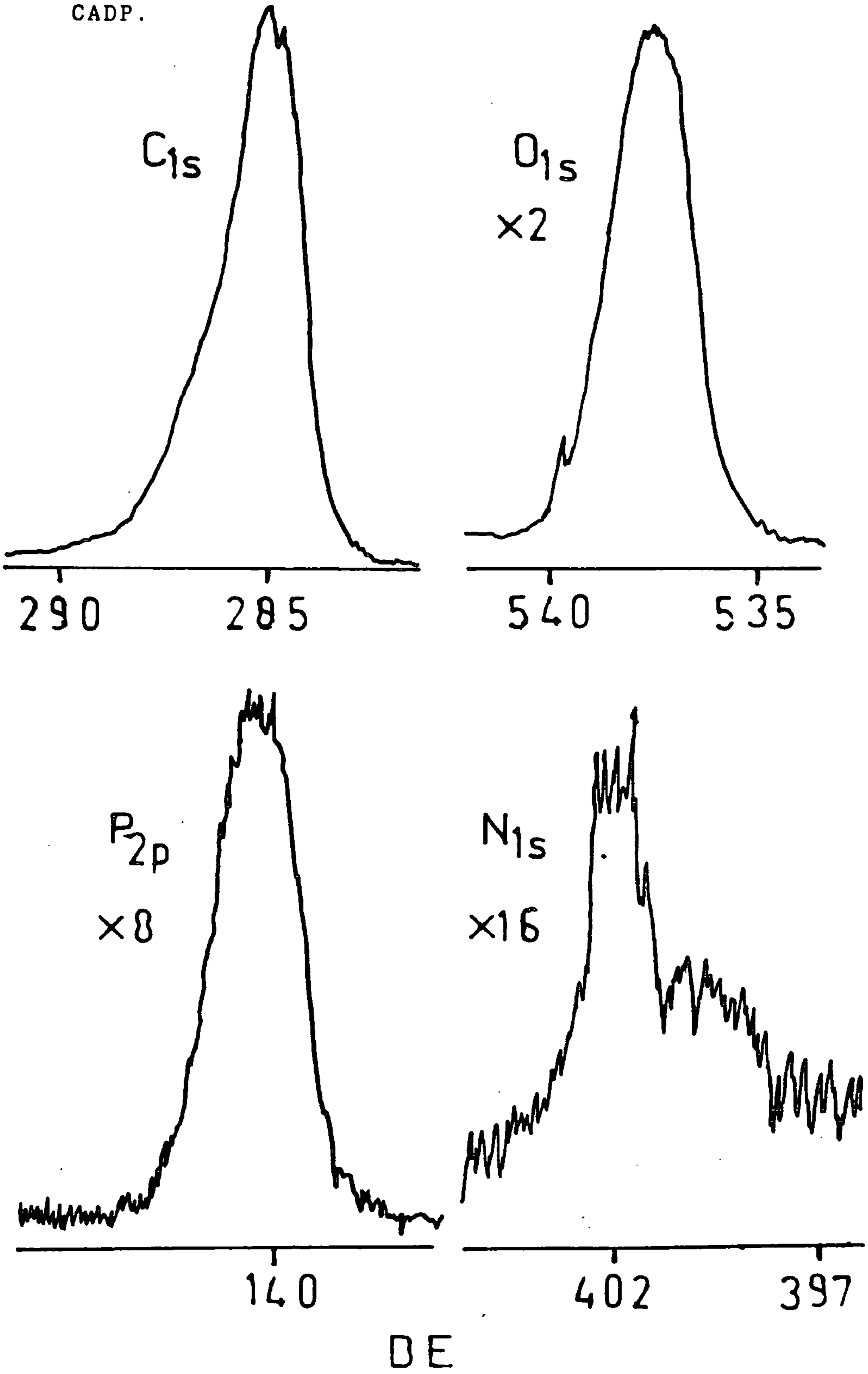


Figure 5.12 Allyl Alcohol Plasma Polymer After Treatment with CADP.



running the spectrum. The N_{1s} spectrum of the reagent does not show a low binding energy shoulder, which suggests that the uncharged nitrogen containing material may be volatile. In the case of the allyl alcohol plasma polymer it seems likely that some of this material reacts with or is adsorbed onto the surface.

The extent to which the reaction proceeds is important in considering the nature of the outermost surface of the polymer and to assess this it is necessary to calculate the thickness of the phosphorylcholine layer. This can be determined by comparing the signal intensity of an element after a reaction with either the intensity before the reaction or the intensity of that element in the reagent. Which of these procedures is used depends upon the nature of the materials involved as it is preferable to study an element present in only one of the substrate and reagent. Using equation 5.1 or 5.2 as appropriate the overlayer thickness may then be calculated.

$$d = -l\cos\theta\ln(I_A/I^0{}_A) \qquad 5.1$$

$$d = -l\cos\theta\ln((I^\infty{}_A-I_A)/I^\infty{}_A) \qquad 5.2$$

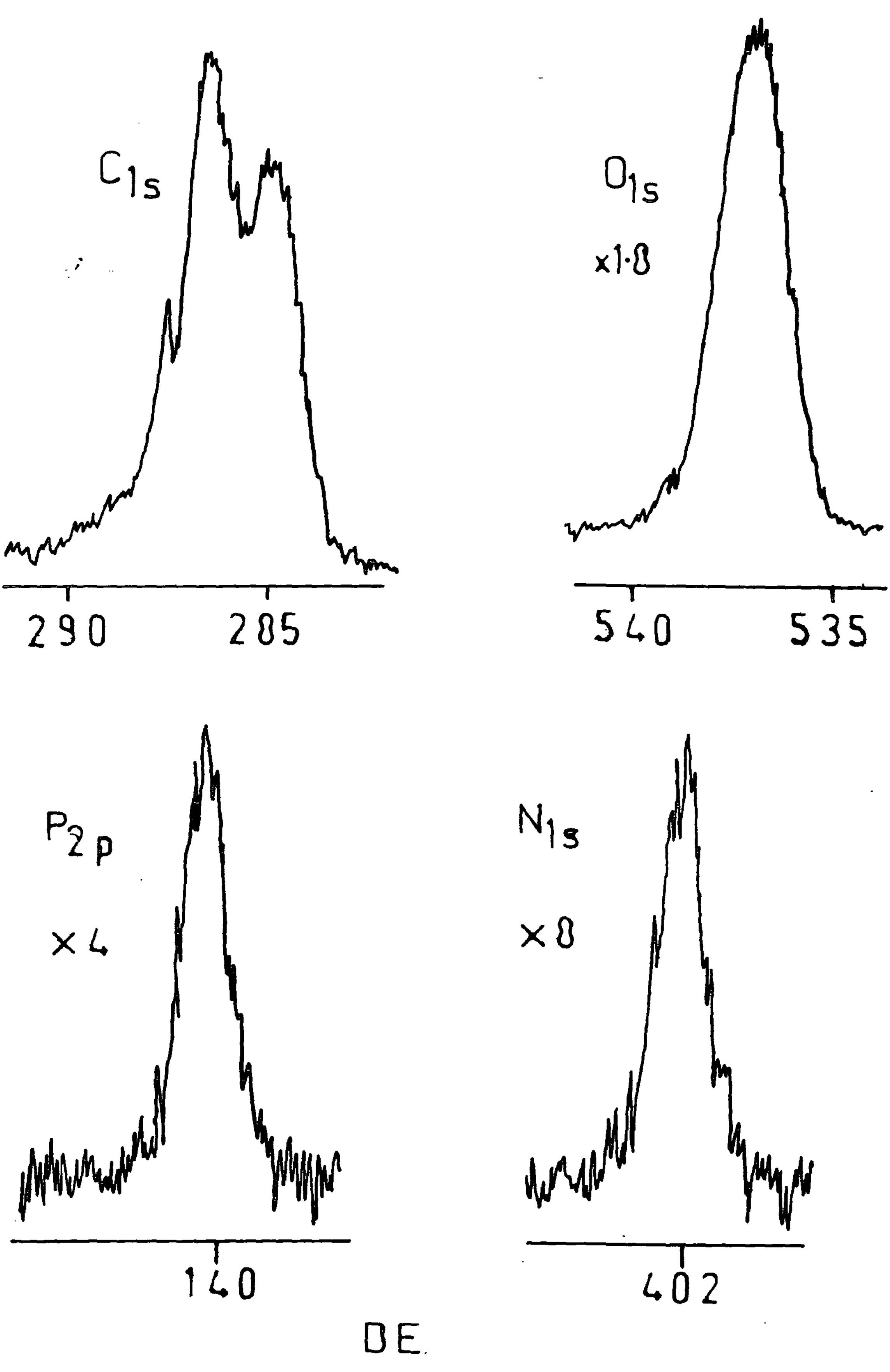
Where d is the overlayer thickness in angstroms,

l is the electron mean free path,

θ is the electron take off angle,

I_A is the intensity of the signal from element A,

Figure 5.13 ESCA Spectra of CADP.



I^0_A is the intensity of the signal from A in a clean substrate,

and I^∞_A the intensity of the signal from A in pure reagent.

Since it is clear from the N_{1s} spectrum that the nitrogen containing part of the phosphorylcholine group was damaged by the x-rays the P_{2p} spectrum in the sample and reagent was used in conjunction with equation 5.2 to calculate the overlayer thickness. This was found to be 3Å which represents less than a monolayer of material. To judge the extent of coverage it is therefore necessary to estimate the signal intensity expected from a monolayer coverage and compare this to the observed signal. Assigning a value of 9Å to the thickness of a monolayer yields figures which indicate a 45% coverage of the surface. The TFAA labelling experiment showed that 61% of the C-O peak was attributable to C-O-H which corresponds to 15% of the surface. These data indicate that a large proportion, if not all, of the available hydroxyl groups have reacted. This assumes that the damage observed is due to the x-ray irradiation and that bound phosphorous is not lost as a result of this degradation.

The above analysis assumes that the CADP is incorporated only at the very surface of the polymer. It is more likely that reaction would occur throughout the sampling depth of the ESCA spectrometer. In this case the percentage of OH groups which have reacted can be estimated by calculating the elemental ratios which would be observed for 100% reaction throughout the ESCA sampling depth and comparing this with the observed data. This method yields a figure of 84% for the proportion of hydroxyl groups which have reacted. Again it is assumed that phosphorous is not lost in the spectrometer from x-ray degradation.

5.5 Conclusion

From the results detailed above it can be seen that it was not possible to reproduce the surface properties and chemistry of the treated Boston IV lens by means of simple plasma polymerization. In the majority of cases examined the silicon was not present in the form of siloxane initially and when oxidized was converted into silicate species which are not considered to be biocompatible. In the remaining example the silicon was unaffected by the oxygen plasma.

Plasma polymers produced from siloxanes did incorporate this functionality into the surface. In the case of the plasma polymers of HMDS it was possible to produce a surface with properties very similar to those of the Boston IV lens material. Using HMCTS produced a polymer with an acceptable degree of wettability but with a very high COF and consequently this material was not felt to be suitable as a contact lens coating.

By choice of suitable plasma parameters it was possible to synthesise a highly hydrophilic, hydrogel like coating from NVP. Though it appeared to adsorb water readily it did not adhere very strongly to the aluminium substrate and so its utility as a lens is uncertain.

After some study an allyl alcohol plasma polymer rich in hydroxyl groups was produced. This was reacted with CADP and ESCA analysis indicated that a large proportion of the available hydroxyl groups had been functionalized. It was seen during this study that the phosphoryl choline moiety is readily damaged by x-rays. It is to be hoped that the resulting surface proves to act in a biomimetic fashion. This and all the above surfaces which possess desirable properties will be tested in the following chapter with respect to adsorption characteristics.

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CHAPTER SIX

ADSORPTION ON CONTACT LENS MATERIALS

6.1 Introduction

Protein molecules have an important part to play in the interaction of any surface with a biological system. In the biocompatibility of synthetic materials, cell adhesion, blood coagulation, immune reactions and certain other processes the first step is the adsorption onto the surface of a layer of protein (1). The precise reaction of the body to the surface depends not only on the nature of the protein but also on to the surface on which it is adsorbed. For example the adsorption of fibrinogen onto glass prevents red blood cells adhering (2), whilst adsorption of the same material to silicone rubber enhances the adhesion of fibroblasts (3). These differences are probably due to the presence of receptor sites on the cell surface sensitive to specific proteins, or segments of protein, when presented to the cell in a specific orientation.

A protein consists of a sequence of amino acid residues in the form of a polypeptide chain whose secondary structure is determined by hydrogen bonding between the peptide units. The conformation or tertiary structure is defined by bonds between remote parts of the molecule which may be hydrogen, ionic or hydrophobic bonds or disulphide bridges. This conformation is subject to change due to breaking of these intramolecular bonds as a result of physical or chemical treatment, as part of the natural functioning of the protein or as a result of its interaction with the surface (1). An additional important factor is the hydration shell of the protein. The properties of a surface which are relevant to the adsorption of a protein, including the hydration (4), must be complementary to the surface properties of the protein.

Proteins are intrinsically able to interact with a variety of surfaces due to their amphoteric nature (5). The multiplicity of functional groups present on the surface of the protein together with its large size means that multiple contact points with the surface can be established. Since non polar residues tend to be internalised in the protein in solution (6) and proteins may adsorb via non polar interactions the adsorption onto a surface may require conformational changes in order to maximize the number of surface protein interactions (7). If the protein's structure is changed due to adsorption then it is said to be denatured. The surface also may be "denatured" if its structure is sufficiently mobile to permit surface reorientation (8).

Protein structure and denaturation studies have shown that the normal state is only marginally stable. The free energy change involved is only of the order of 5 to 14 kcal/mol (9-11). Since the free energy of adsorption is around 5 to 20 kcal/mol it is quite probable that adsorption will induce denaturation (12). This in turn can lead to an alteration in its interaction with the environment as its surface properties change with the change in structure.

The reversibility of protein adsorption would seem to be related to the conformational changes that can occur at the surface. Using transmission infra-red spectroscopy to study the adsorption of protein onto silica particles has shown that at high concentrations the protein forms fewer bonds to the surface than at low concentrations (13). Additional studies on silica plates using ellipsometry showed that the protein film was thinner when adsorbed from low concentrations in solution than when formed from a higher concentration, even though each film represented one monolayer. The conclusion drawn from this was that at high solution concentration the rate of collision of protein molecules with the surface is so high that the adsorbed protein does not have the time or room to optimize its interaction with the surface. This results in a densely packed layer with each molecule making just enough bonds to the surface to prevent desorption. At low concentrations the molecules are able to spread out and form a large number of hydrogen bonds to the surface, resulting in conformational changes in the adsorbed protein. This observation also hold true at the air-water interface where similar phenomena have been observed (14).

A certain amount of time is needed for this conformation change to occur and as time progresses more of the adsorbed protein may take on a more strongly bound form. This can occur over periods of up to ten days (15). From their studies Soderquist and Walton (16) have proposed that during the initial period of contact, approximately one minute, adsorption is rapid and reversible. The protein is adsorbed in a random arrangement resulting in up to 50% coverage of the surface. When a greater percentage of the surface is covered ordering may develop which leads to an increased amount being adsorbed. With time adsorbed protein molecules may undergo conformational changes leading to increased interaction with the surface which may result in the desorption of less well bound molecules to create vacant sites for the spread of the denatured protein. This effect has been observed in the adsorption of human plasma albumin (17). The desorption rate decreases with time and the desorbed protein may be permanently denatured (18).

Desorption is related to the hydrophobicity of the protein and of the surface. It has been established (19) that the interaction between a protein and a surface increases with increasing hydrophilicity and that desorption from hydrophobic surfaces generally does not occur whilst proteins can be removed from hydrophilic surfaces by changes in pH, ionic strength, or by extensive rinsing. It has been seen that, though after a time the denatured protein may be irreversibly adsorbed on a surface, it can still exchange with proteins in solution. This apparent anomaly has been explained by Jennissen in the following manner (20-22). For a protein attached to a surface at multiple binding sites then it is statistically likely that periodically some of these bonds to the surface will break and others will form. For desorption to occur all these bonds must be broken at the same time, which is highly improbable. However when there are other proteins colliding with the surface in the local environment they can form bonds to sites which are made vacant as the original protein makes and breaks its points of contact with the surface. Eventually the original protein may have all its binding sites taken over by the new protein and will be lost from the surface. This is most likely to occur if the new protein can form more or stronger bonds with the surface. It has been shown that in a competitive adsorption process there is an exchange hierarchy and for a mixture of proteins those able to most strongly bind to the surface come to dominate (23).

The study of proteins adsorbed on surfaces is a complex process due to the wide variety of information that may potentially be obtained such as the amount of protein present, the rate of adsorption, the degree of reversibility of the adsorption, configurations of the adsorbed proteins and the thickness and uniformity of the protein layer. In view of this complexity it is useful to consider the interaction of small, related molecules, such as amines and amino acids, to model the behaviour of proteins. This allows for the characterization of the local interactions between specific groups and the surface.

Salaneck and coworkers have studied the behaviour of glycine adsorbed on a variety of surfaces. Infra-red reflection adsorption spectroscopy (IRAS)(24) showed that the conformation changes associated with the adsorption of fibrinogen on metal surfaces were related to an interaction between the metal and the amide groups present in the protein. In the case of glycine adsorbed onto gold the it was seen that the molecule in zwitterionic form is oriented with its NH_3^+ group towards the gold (25). In other studies (26,27) it was found that glycine forms a stable double layer, even under UHV conditions, on hydrophilic gold and graphite surfaces. As before the glycine was observed to bind to the surface via the amine group, with the molecule in its zwitterionic form. In the adsorption of glycine onto a variety of silica surfaces it was seen that a similar, stable double layer was formed on hydrophilic SiO_2 but not on other silicates (28). On non hydrophilic silica the glycine C-C bond breaks.

The behaviour of glycine on a range of materials has led to the classification of its adsorption into three categories. In class 1 behaviour the glycine forms a stable, zwitterionic double layer, in class 2 the glycine also form a zwitterionic double layer but this evaporates under UHV. On surfaces exhibiting class 3 behaviour the glycine is present in a non zwitterionic form and may be degraded (29). In this study the behaviour of glycine on these materials has been linked to their known degree of biocompatibility. Of the materials studied, living tissue is known to react favourably to titanium (30) and oriented graphite (31) which both exhibited class 1 behaviour. Copper, which is rejected by living tissue (32), and hydrophobic gold, which is known to denature proteins and which is less compatible with collagen than titanium (30), showed class 3 behaviour. PTFE, which is found to be blood compatible over short periods of time (33), exhibited class 2 behaviour. From these observations it is concluded that there may be a relation between the behaviour of glycine on the surface and the behaviour of proteins and hence the biocompatibility of the surface.

The most important protein in the tear film system is the mucin which coats the epithelium of the eye, supporting the aqueous portion of the tear film. There are many mucosal surfaces in the body and the function of the layer of mucus is to lubricate epithelial cells and to protect them from micro-organisms and the toxins they produce (34-36). Glycoproteins possess a protein backbone with pendant saccharide and oligosaccharide units. Mucins (37) are a sub class of glycoprotein distinguished by the large number of sugar side chains they contain. In an aqueous environment the molecule adopts a conformation such that the saccharide units are presented outwards to provide a hydrophilic surface.

As was mentioned earlier it should prove possible to remove a hydrophilic protein from a hydrophilic surface by rinsing (19). In the eye the mucin must be deposited on the epithelium to render it sufficiently wettable to support the aqueous layer of the tear film. This mucin becomes contaminated with proteins, lipids and other debris, but the action of blinking removes this from the eye, replacing it with fresh mucin. It is desirable in a contact lens for this procedure to occur thus keeping the lens surface clean and for rinsing in lens solution to remove any remaining contaminants. The mucin is a hydrophilic protein and a number of lens surfaces with improved hydrophilicity have been produced. In the following pages the adsorption properties of the surfaces of these lens materials are investigated with a view to establishing which are likely to perform well in the eye.

6.2 Experimental

The gas phase adsorption of diamines was performed in a vacuum line essentially the same as that used for plasma polymerization (chapter 5). The sample was placed in the reactor chamber and pumped down to a base vacuum of 0.02 mbar. The pumping system was then closed off and the vessel opened to a reservoir of diamine. For 15 minutes the sample was exposed to the diamine at its vapour pressure and then excess diamine was pumped away. Pumping continued until the base pressure was reached to ensure that any condensed reagent was removed.

Solution phase adsorptions were performed by making up a solution of the required concentration using distilled water in clean volumetric glassware. The sample surface was then placed in this solution and left for fifteen minutes. After this time the sample was removed and briefly rinsed in distilled water to remove excess solution. When required this rinsing was continued for fifteen minutes Experiments involving protein adsorption were also performed in buffered solutions, pH 7.2, and in this case the samples were rinsed in buffer solution instead of water. All samples were then allowed to dry in air before being examined with ESCA.

6.2.1 Materials

1,2-diaminoethane, 99%, and 1,10-diaminodecane, 98%, were bought from Lancaster Synthesis Ltd. 1,4-diamnobutane, >99%, 1,6-diaminohexane, 97%, and 1,8-diaminooctane, >98%, were acquired from Fluka AG. These were degassed before use in gas phase experiments by a series of freeze thaw cycles. Since diaminobutane is air sensitive it was transferred to a monomer tube under dry nitrogen and immediately placed under vacuum.

Glycine, 99%, was obtained from Lancaster Synthesis Ltd. Mucin, gastric, purified, was acquired from BDH Biochemical Reagents and was stored in a freezer at -15°C. Buffer tablets, pH 7.2, BDH Chemicals Ltd., were used to make up buffered solutions.

6.3 Results and Discussion

6.3.1 Diamine adsorption

The adsorption properties of amines are of interest for several reasons; firstly the amine group is present in proteins and will therefore influence their interaction with the surface, secondly simple molecules are easier to study using ESCA since the effect of a single type of group can be studied and thirdly the amino acid glycine, which binds to the surface via its amine group, may
indicate the relative biocompatibility of the surface. Diamines are ideally suited to a study of this nature since they contain two amine groups an thus will give larger ESCA signals even at low levels of adsorption, and also because as the size of the diamine grows its hydrophilicity decreases.

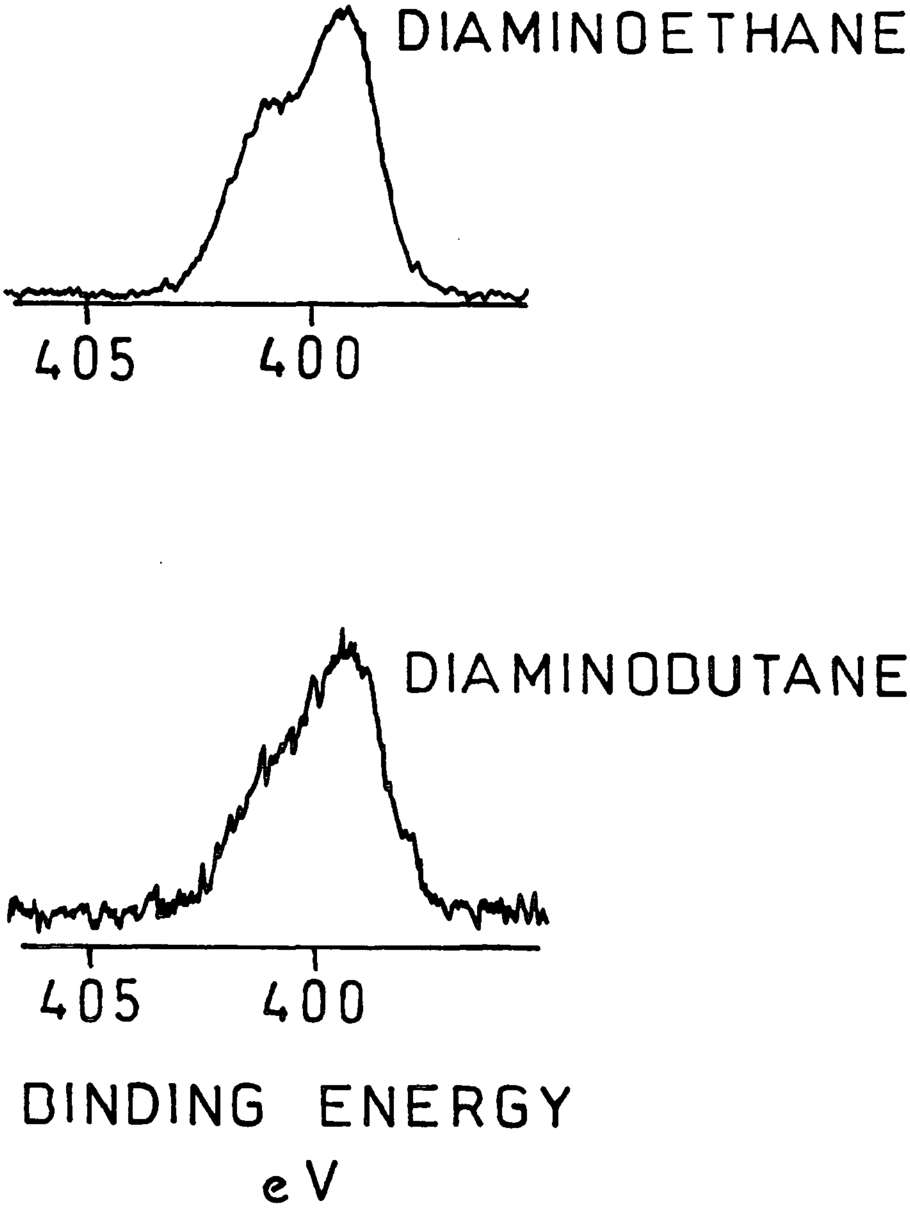
First the vapour phase adsorption of the diamines was considered to investigate the mode of binding of the diamine in the absence of any influence from a solvent. Both untreated and freshly plasma oxidized lens material were used in these experiments. The results of this work are shown in table 6.1.

Table 6.1 The Vapour Phase Adsorption of a Series of Diamines onto Untreated and Plasma Oxidized Boston IV (n=3, SD=0.02)

Diamine	N_{1s}/C_{1s} Area Ratio	
	Untreated	Treated
Diaminoethane	0.01	0.06
Diaminobutane	0.02	0.07
Diaminohexane	0.01	0.10
Diaminooctane	0.00	0.06
Diaminodecane	0.03	0.10

It is immediately apparent from this data that the treated lens material adsorbs more diamine than the untreated material. This is undoubtedly due to the increase in oxygen containing functionalities produced by the plasma, which can act as binding sites for the diamine. Study of the N_{1s} envelopes of these samples reveals that in the case of diaminoethane and diaminobutane there are clearly two distinct nitrogen environments present in approximately equal amounts, figure 6.1. There is a peak at 399 eV corresponding to the neutral amine and another at 401 eV which is indicative of an N^+

Figure 6.1 N_{1s} Spectra for Diaminoethane and Diaminobutane Adsorbed on Plasma Oxidized Boston IV.



species.

In the spectra of the other diamines the N_{1s} envelope consists of essentially one environment which corresponds to the N^+ species observed in the smaller amines, figure 6.2.

This difference can be explained by a consideration of the chain length of these molecules. In the case of the shortest two diamines once one end of the molecule is bound to the surface either there are no more eligible surface sites within range of the remaining amine, or the geometry of the molecule prevents the second amine from being brought into sufficient proximity to the surface. The increased length and flexibility of the larger diamines means that both sites can be brought into play in binding to the surface and thus both appear at the same binding energy in the ESCA spectrum.

The solution phase adsorption of diamines was carried out using 0.1M solutions. The ESCA data is not as clear for these experiments since the level of adsorption was lower in most cases than for the gas phase adsorption. The results of this series are displayed in table 6.2. It was not possible to perform comparable experiments using diaminobutane due to its unstable nature and diaminodecane proved to be insufficiently soluble in water to produce a suitable solution.

Figure 6.2 N_{1s} Spectra for Diaminohexane, Diaminooctane and Diaminodecane Adsorbed on Plasma Oxidized Boston IV.

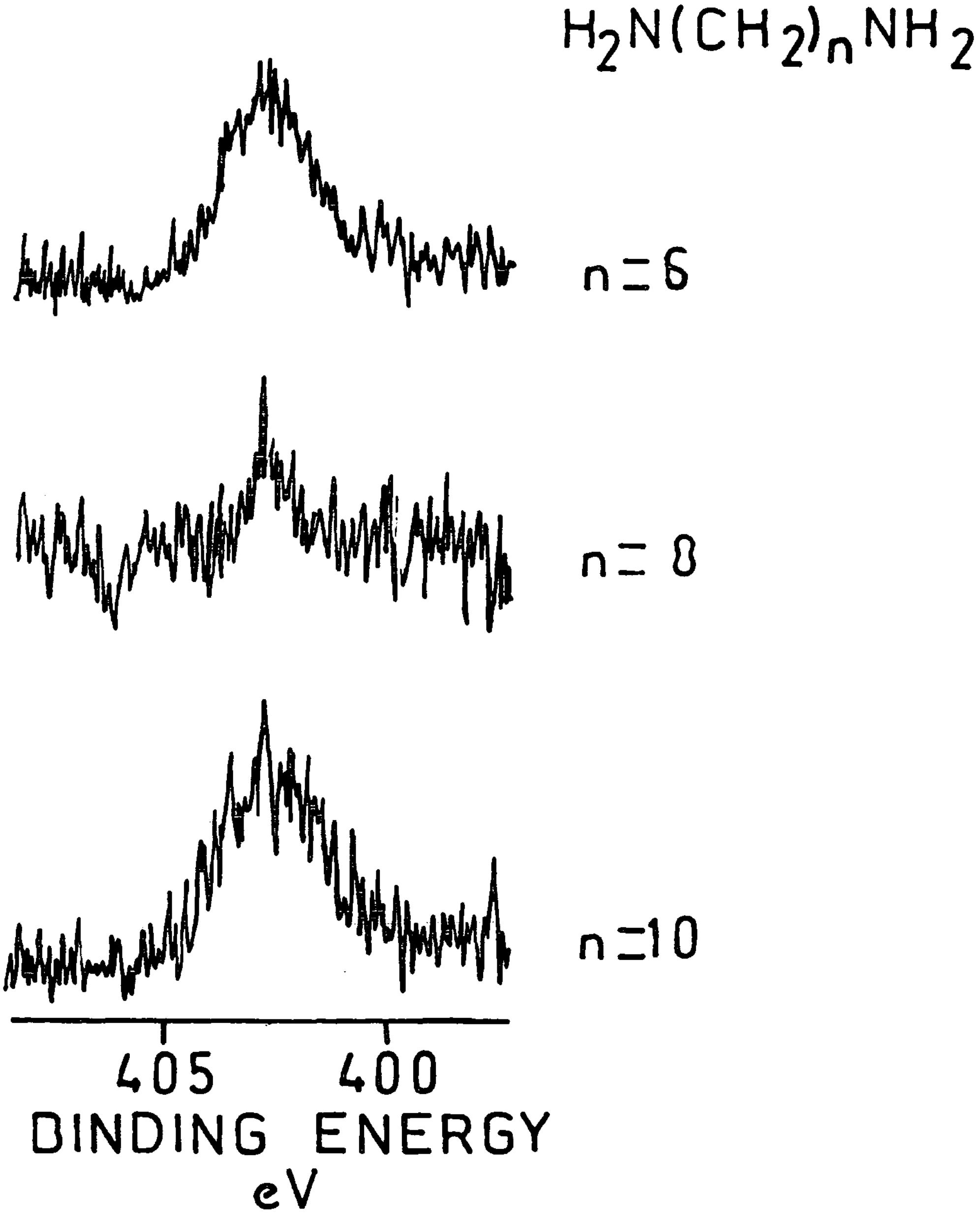


Table 6.2 Solution Phase Adsorption of Diamines onto Untreated and Plasma Oxidized Boston IV.

Diamine	N_{1s}/C_{1s} Area Ratio	
	untreated	treated
Diaminoethane	0.03	0.01
Diaminohexane	0.03	0.04
Diaminooctane	0.01	0.03

It can be seen here that there is little difference between the treated and untreated samples. This may be due to the binding of water to the surface in solution, which may occupy surface sites that would otherwise be used to bind amines. Alternatively the hydrogen bonding of water to the diamine may inhibit its adsorption. If the latter were the case it would be expected that both types of sample should exhibit less adsorption. In fact only the plasma oxidized samples show a reduction in bound amine and so the first possibility seems more likely. Presumably the highly oxidized plasma treated surface is able to bind water, by hydrogen bonding, strongly enough to prevent diamine adsorption.

All these samples appear to show only one nitrogen peak, centred around 401 eV. This may be due to the low intensity of the peaks but if genuine this indicates that both ends of the molecule are bound to something. Since the gas phase experiments showed that diaminoethane is incapable of making two bonds to the surface it is possible that the end of the molecule not bound to the surface is bound to water, though the water molecule or molecules would have to be strongly bound in order to remain at the surface in the UHV of the ESCA spectrometer. An alternative explanation requires either a change in the organization of the surface (38) to permit the diaminoethane to bond to it with both amines, or the breakdown of the molecule along its central C-C bond, in a surface process similar to that observed for glycine (28).

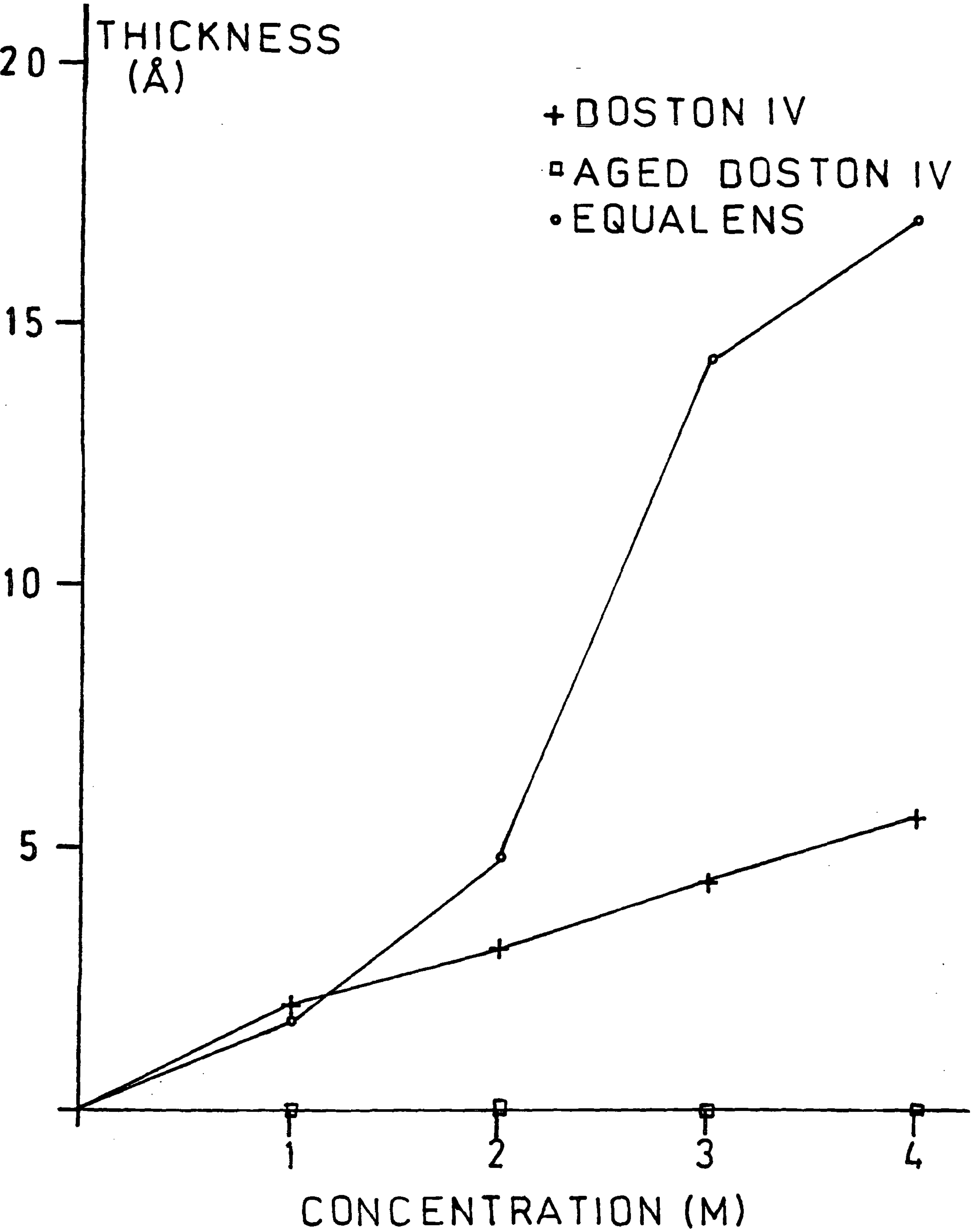
The treated surface studied above was used immediately after treatment whereas, as has already been shown in chapter four, the lens surface decays and is considerably different by the time it is received by the patient. Therefore a similar experiment was attempted using the treated and aged material with diaminoethane for comparison. No adsorption was observed on this surface.

In order to investigate the effect of concentration on the adsorption process a series of experiments using increasingly concentrated solutions of diaminoethane were undertaken. Samples of untreated Boston IV, plasma oxidized and aged Boston

IV and the fluoro-siloxane acrylate material, Equalens, were used to compare the effect of plasma treatment to the incorporation of fluorine as a means of inhibiting adsorption. From the ESCA spectra obtained the thicknesses of the adsorbed layers could be calculated by use of equation 5.1 and the relative signal intensities of the Si_{2p} peaks, figure 6.3.

It can be seen from this data that whilst both the Equalens and untreated Boston IV adsorb diamine irreversibly, there is no permanent adsorption on the treated and aged lens. The untreated Boston IV shows a gradual increase in the amount of adsorbed diamine with increasing concentration of the solution. This increases to approximately one monolayer coverage at a solution concentration of 4M. In comparison, the Equalens samples initially adsorb at a similar rate to the Boston IV up until the two molar point, when monolayer coverage is attained. This is followed by the rapid adsorption of material to a level equivalent to a thickness of three monolayers. This sudden increase is most likely to be a property of the diamine rather than of the surface but it was not possible to confirm this by comparison with the Boston IV. This is due to the fact that at a concentration of 5M the adsorbed layers are sufficiently thick in both cases to obscure the substrate silicon signal. This in itself is indicative of a sudden rise in adsorption since the silicon signal should have been visible if the proportional increase observed on Boston IV had continued. However this does not show that the increase in adsorption was

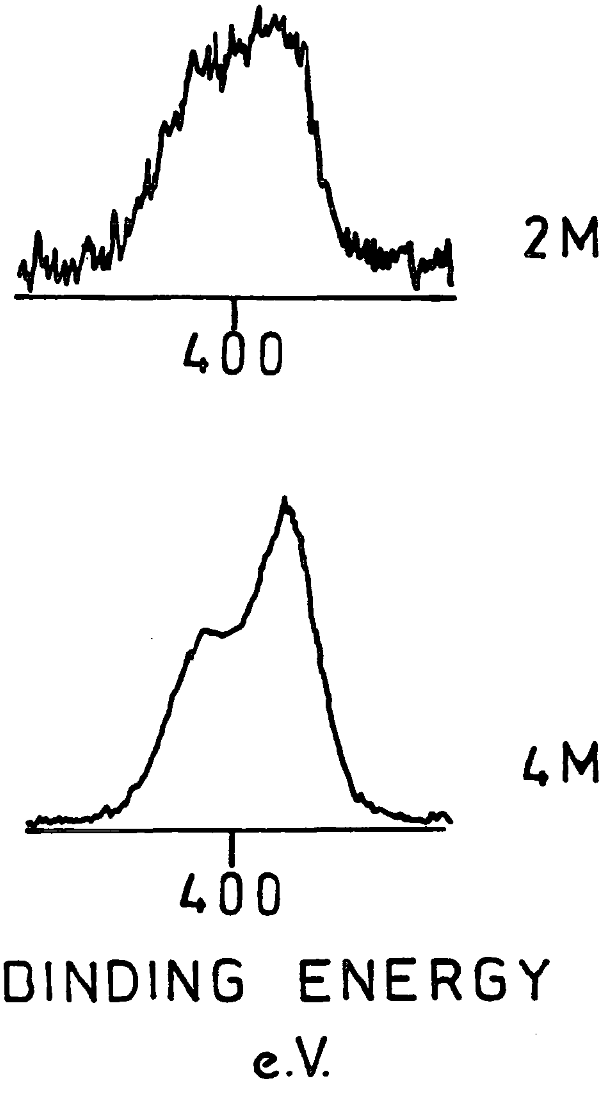
Figure 6.3 Variation of the Thickness of Adsorbed Layers of Diaminoethane on Various Lens Materials with Concentration.



similar to that seen at lower concentration on the Equalens, since Boston IV has a lower initial silicon content at the surface and could therefore be obscured by a lesser thickness of diamine. The signal from the silicon can penetrate the same thickness of material but the intensity of that signal may be too low to be distinguishable from the background in the case of Boston IV.

The lack of adsorption in the case of the treated and aged Boston IV is perhaps indicative of behaviour equivalent to the type 2 behaviour of glycine observed by Salaneck and Co. on other materials (29). This should not be too surprising since it appears from the ESCA spectra that the interaction between the diamine and the surface is similar to that of glycine. In the cases where adsorption was observed two nitrogen environments were seen. At low concentrations these were present in equal amounts but at higher concentrations, those equivalent to thicknesses of more than one monolayer, there was an excess of the lower binding energy component. This is most clearly shown by a comparison of the 2M and 4M adsorptions on Equalens, figure 6.4. Excess of the low binding energy component at high concentration can be attributed to the outermost layer or layers in a multilayer system where the interaction between molecules is weaker than at the surface and does not result in the formation of fully charged nitrogen species. Thus the signal from these molecules is not shifted to higher binding energy.

Figure 6.4 Comparison of the N_{1s} Spectra for Diaminoethane Adsorbed on Equalens from 2 and 4M Solutions.



6.3.2 Adsorption of Glycine.

For the adsorption of glycine a 1 molar solution in distilled water was used. Samples of Boston IV, plasma oxidized and aged Boston IV, Equalens, and HMDS plasma polymer were investigated. The results of these experiments are shown in table 6.3.

Table 6.3 Adsorption of Glycine onto a Series of Materials (n=1)

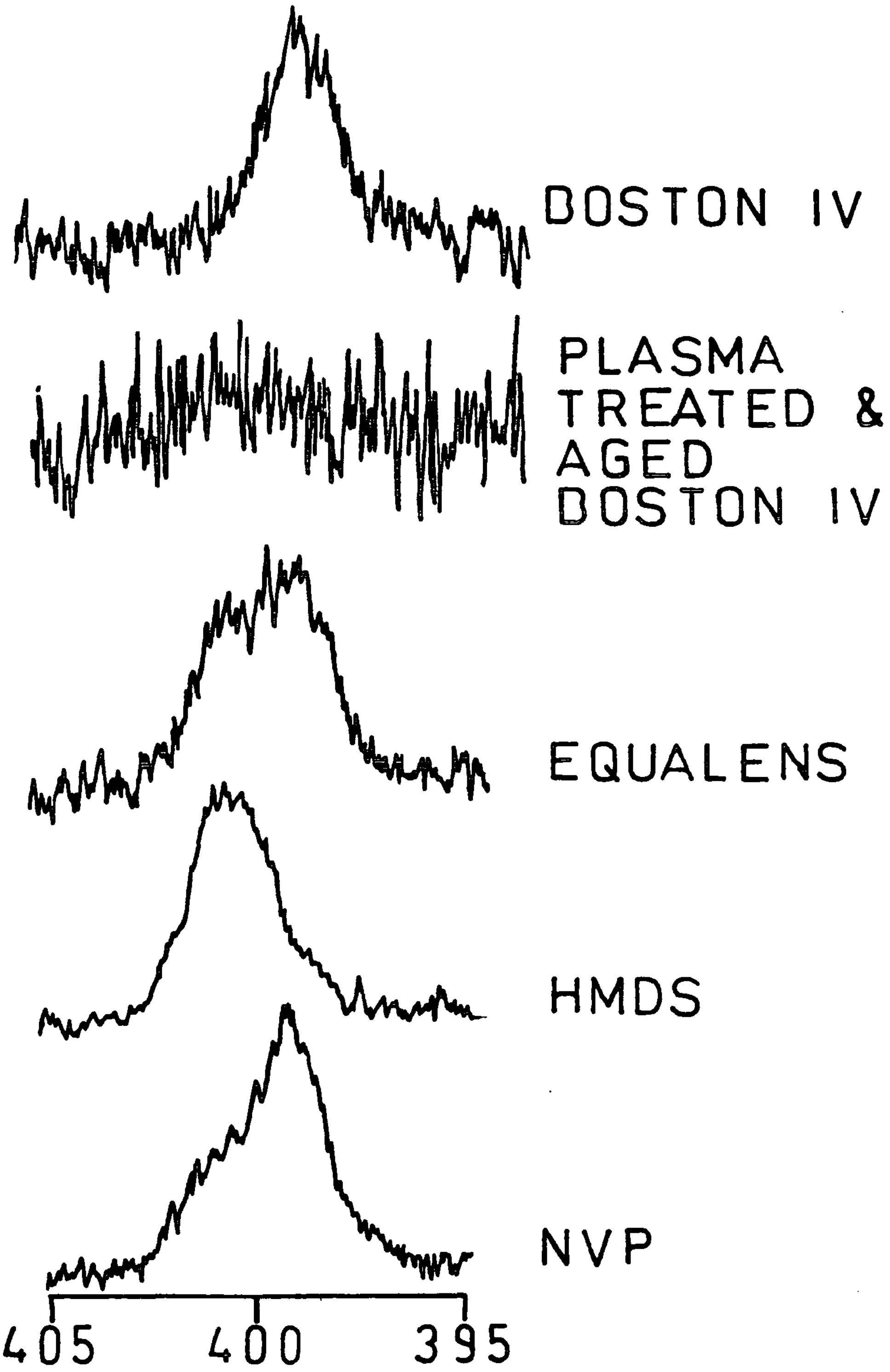
Sample	Thickness of adsorbed layer (Å)
Boston IV	3
Plasma oxidized, aged Boston IV	0
Equalens	6
HMDS plasma polymer	13

In addition to the thickness of the adsorbed layer the nature of the adsorbed material is of particular interest. The N_{1s} spectra of the adsorbed glycine is different in each case, figure 6.5. On Boston IV the spectrum shows one environment at about 399 eV corresponding to uncharged nitrogen which suggests that the glycine has been degraded. The thickness of the adsorbed layer also precludes the possibility of the formation of a stable double layer, which has been estimated as being 8 Å thick (28). By the system proposed by Salaneck et al. (29) this is type 3 behaviour and would therefore be expected to interact unfavourably with proteins. This agrees with the observation that even in healthy eyes there is a build up of deposits on the lens surface.

The treated and aged Boston IV shows no apparent adsorption corresponding to class two behaviour, or to the fact that all the adsorbed glycine has been removed on rinsing. This surface would therefore be expected to show good short term interactions with proteins. As has been mentioned the plasma treated lens has in tests shown improved resistance to the formation of deposits in day to day wear (40).

Equalens and the HMDS plasma polymer both show two nitrogen environments, at ≈ 401 and 399 eV, corresponding to positively charged and neutral species respectively. In the case of Equalens these are of approximately equal intensity indicating that half the adsorbed material is degraded whereas in the case of the HMDS plasma polymer only around 25% of the nitrogen is in the lower binding energy form. The Equalens shows a film thickness slightly below that expected for a double layer, whilst the HMDS has an adsorbed layer thickness suggesting the presence of three monolayers of glycine. Both these materials would therefore be classed as showing type three behaviour

Figure 6.5 N_{1s} Spectra of Glycine Adsorbed on a Variety of Materials.



since some of the glycine is degraded. Since only a portion of the adsorbed material is affected it might be anticipated that these materials would perform better than untreated Boston IV. However this method of classification is only qualitative at best and, whilst the system seems to work well in terms of broad groupings, to produce fine distinctions within a class is not reasonable.

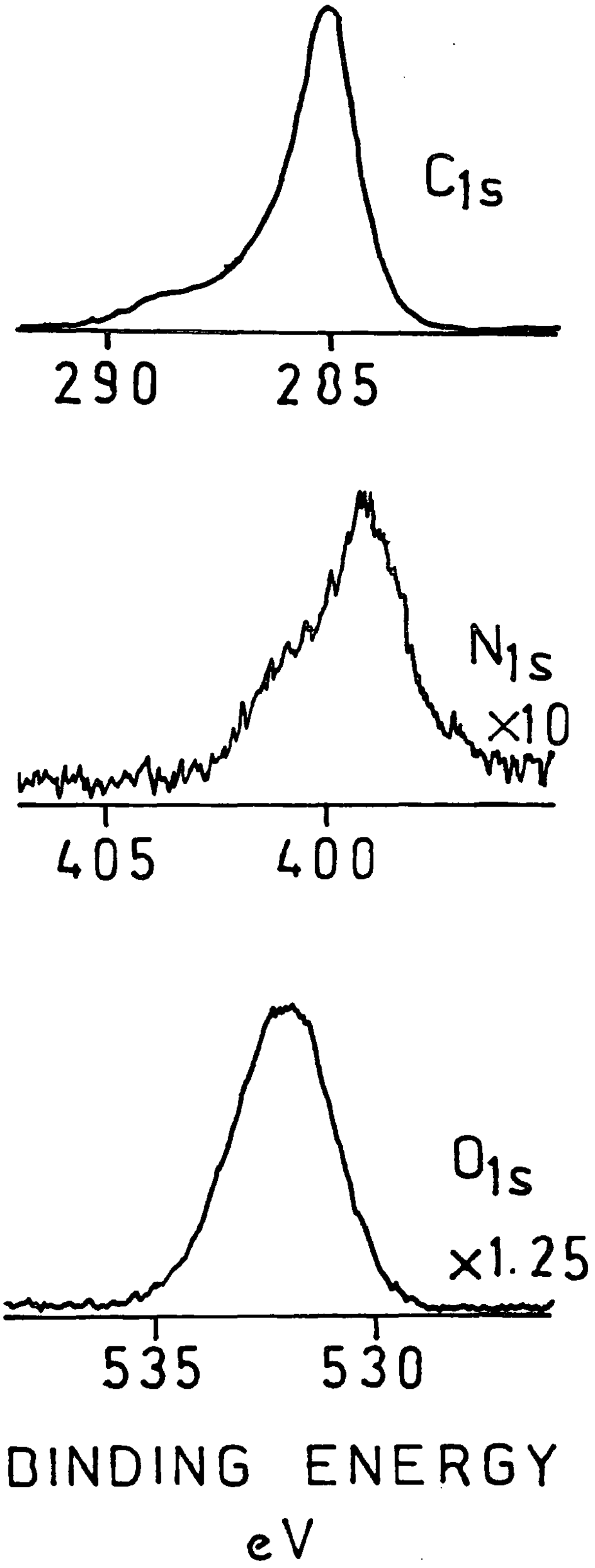
The adsorption of glycine onto the NVP plasma polymer is much harder to interpret. This is due to three factors; firstly NVP already contains nitrogen and therefore it is not possible to assess the thickness of the adsorbed layer, secondly all the samples studied showed an increase in the amount of hydrocarbon in the sample after the adsorption experiment and thirdly the hydrogel like nature of this plasma polymer means that some absorbed water seems to be present, as shown by from the anomalously high oxygen content of the sample after the experiment. There does not seem to be sufficient increase in the high binding energy components of the carbon envelope to account for this as the product of trapped radicals in the polymer reacting with air or water. However examination of the spectra of the plasma polymer after the experiment, figure 6.6, clearly shows the presence of adsorbed glycine. The shoulder on the high binding energy side of the C_{1s} peak is greatly extended compared to the fresh polymer, showing the presence of the O-C=O functionality in significant amounts. There is also a shoulder to the high binding energy side of the N_{1s} peak which is at the correct binding energy position for zwitterionic glycine and which comprises 30% of the nitrogen signal. The N_{1s} envelope can be resolved into two peaks, the larger of which is due to the nitrogen containing component of the polymer with a possible contribution from degraded glycine. Unfortunately it is not possible to determine from this data the extent of degradation, if any, of the glycine.

There is the possibility that the observed degradation in all these experiments may be due to the x-rays used in the ESCA experiment and this must be considered as a possible explanation. Accordingly glycine powder was examined using ESCA under the same conditions as the samples with adsorbed glycine. The glycine spectrum showed a distinct single peak for the N_{1s} envelope, binding energy 401 eV, and the area ratios gave the expected elemental composition. It seems therefore that under the x-ray conditions used (magnesium anode, 8 mA, 12kV, analysis time ≈ 36 minutes) there was no x-ray degradation. As an additional safeguard in all cases the nitrogen region was acquired first, to minimize any possible effect of the x-ray irradiation.

6.3.3 Adsorption of Mucin

In these experiments a 1% solution of the mucin made up with distilled water or buffer solution (pH 7.2) was used. Since the precise composition of the mucin was not known mucin powder

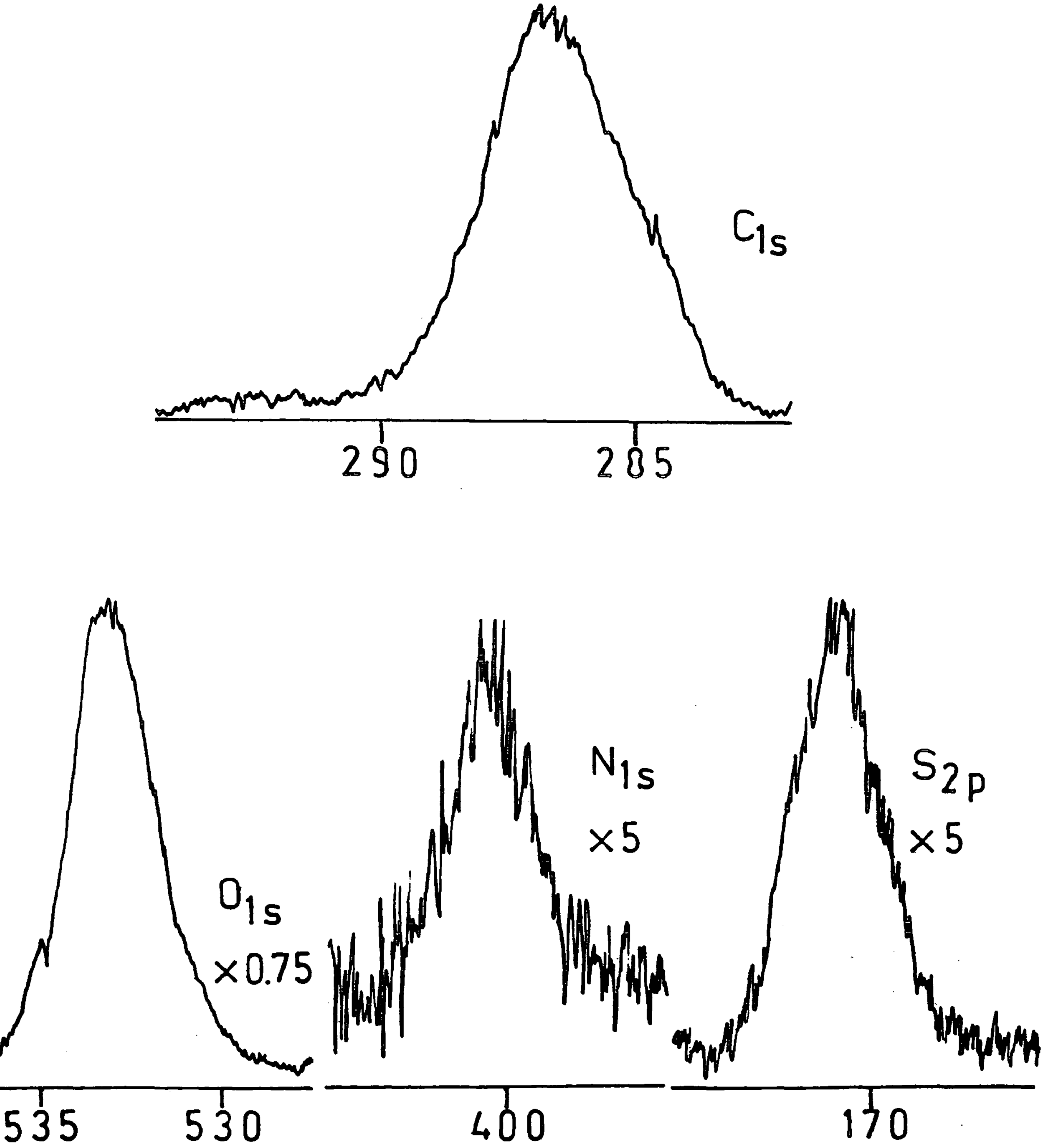
Figure 6.6 ESCA Spectra of NVP Plasma Polymer After Adsorption of Glycine.



was first examined using ESCA, figure 6.7. The peak area ratios show the presence of a large amount of oxygen and significant quantities of nitrogen and sulphur. Consideration of the C_{1s} envelope shows that the dominant feature is not hydrocarbon but C-O, binding energy 286.7 eV. This is not unexpected and is due to the presence of the numerous saccharide side chains of the glycoprotein. One other feature of interest is the prominent shake up peak, at 292.5 eV, indicating a substantial degree of delocalization in the protein. This can probably be attributed to amino acid residues containing delocalized systems, such as tyrosine which has been found as a component of epithelial mucins (35). The N_{1s} peak is at 400 eV and is consists of a single environment, its position is comparable to that observed for uncharged nitrogen in proteins (41) and may be ascribed to the peptide nitrogen. The sulphur peak occurs at 170 eV and must therefore be assigned as sulphate, though this does not necessarily imply the existence of sulphate in the protein as it has been found that organic sulphur can be converted to sulphate by x-rays in the presence of residual water (42). The probable source of the sulphur is from cysteine (35). In order to prevent x-ray damage to the nitrogen this region was acquired first and therefore the sample had been irradiated for some time before the sulphur region was accumulated.

The results for the adsorption of mucin from aqueous solution are displayed in table 6.4. The thicknesses of the adsorbed

Figure 6.7 ESCA Spectra of Mucin.



layers were calculated from the intensities of the N_{1s} signals as previously described, except in the case of the NVP plasma polymer where the S_{2p} level was used since the substrate in this case contained nitrogen.

Table 6.4 <u>Thickness of Mucin Layer Deposited from Aqueous Solution (n=1)</u>

Sample	Thickness (Å)
PMMA	16
PMMA, rinsed	16
Boston IV	∞
Boston IV, rinsed	∞
Plasma oxidized, aged Boston IV	16
Plasma oxidized, aged Boston IV, rinsed	3
HMDS plasma polymer	∞
HMDS plasma polymer, rinsed	∞
NVP plasma polymer	1
NVP plasma polymer, rinsed	0

As has been discussed it is desirable to be able to remove proteins from the surface of a biomaterial for use in the eye. In the case of mucin it is also desirable that the mucin should adsorb well to render the surface of the lens wettable to the aqueous layer of the tear film and to enable the eye's natural cleaning mechanism to operate correctly. From the above data it can be seen that all these materials initially adsorb mucin, with the exception of the NVP plasma polymer. Only in the case of the plasma treated and aged Boston IV lens material is the mucin readily removed by simple rinsing. Examination of the ESCA spectra of an adsorbed layer, for example that on PMMA, figure 6.8, shows no observable change in the binding energies of the species present. The presence of the mucin can clearly be seen from the N_{1s} signal and the C_{1s} envelope has been altered by the presence of the C-O component due to the saccharide side chains of the mucus. Since the nitrogen peak is not shifted as in glycine, it would appear that the bonding to the surface is not via nitrogen containing groups. Considering the structure of glycoproteins it is most likely that hydrogen bonding via the pendant sugar chains is the main contribution to the binding of the mucin to the surface. This would not influence the ESCA spectra of the elements greatly. ESCA spectra for the protein adsorbed on the other surfaces are essentially the same and it is therefore reasonable to suppose that the interactions between the surfaces and the mucin are also similar. The differences in the levels of adsorption must therefore be attributed to differences in the number of binding sites per unit area of surface and the strength of these interactions.

The use of a buffered solution enables the charges on a protein to be regulated and hence promotes the stability of the protein conformation in solution. Experiments performed in buffered solution, rinsing in clean buffer, where carried out on all surfaces prepared as possible contact lens materials. The results obtained are displayed in table 6.5. The thicknesses were calculated as before from the N_{1s} signal intensities, and in the case of NVP the sulphur peak was used.

Table 6.5 Thickness of Mucin Layer Deposited from Buffered Solution.

Sample	Thickness (Å)
PMMA	∞
PMMA, rinsed	11
Boston IV, plasma oxidized, aged	16
Boston IV, plasma oxidized, aged, rinsed	5
HMDS	∞
HMDS, rinsed	11
NVP	1
NVP, rinsed	0
CADP	16
CADP, rinsed	6

The trends in these results are very similar to those observed in the unbuffered case, the main difference is in the degree to which the mucus is removed on rinsing from the PMMA and HMDS plasma polymer. This indicates that the protein is less degraded than in the unbuffered case. Since the surfaces involved are identical this must be due to the presence of the buffer stabilizing the protein conformation.

In both these experiments it is clear that the thicknesses of the protein layers are less than would be expected for molecules the size of proteins. This indicates that there is not total surface coverage, but it is not possible to estimate the extent of coverage, since the original size of the molecule is not known and neither is the thickness of the denatured protein irreversibly bonded to the surface.

6.4. Conclusion

From these results it can be seen that all these surfaces adsorb mucin readily, with the exception of the NVP plasma polymer, and therefore ought to be capable of supporting the aqueous portion of the tear film. There is however a definite order of performance in considering the ease with which the mucin can be removed. The untreated Boston IV is clearly the worst case as there was no observable desorption on rinsing. The HMDS plasma polymer has a comparable performance to that of PMMA, which is slightly better than that of the siloxane acrylate. This indicates that a HMDS lens should perform better in the eye, and indeed it has been found that PMMA lenses suffer less from deposition problems than siloxane acrylate lenses (43). The plasma treated and aged Boston IV shows very little irreversible adsorption and should therefore perform much better than the untreated lens material. In practice this treatment has been successful in cases of patients with very bad lens contamination (40). The allyl alcohol plasma polymer treated with CADP has very similar adsorption characteristics to the plasma treated lens material and may therefore have similar performance in the eye. However these results do not give any indication of the stability of this surface in use and further testing would be required before an in vivo experiment could be attempted.

The NVP plasma polymer shows very little adsorption of mucin, though its hydrogel nature means that it should be capable of supporting the tear film. The fact that there is no irreversible adsorption is a good indication that this material would not experience severe problems in the eye. The only questionable factor in the use of this plasma polymer is in its adhesion to the substrate. It was found that this polymer when wet could easily be removed from the sample. It should be possible by careful choice of the plasma conditions to improve this adhesion. The adhesion of plasma polymers to substrates can be enhanced by depositing an initial layer of polymer at high power (44), and then reducing the power to produce a hydrophilic outer layer.

6.5 Summary

As can be seen from chapter 1, the normal functioning of the tear film is dependent on the integrity of the mucin layer. This makes the surface of the eye sufficiently hydrophilic to support the aqueous component, and provides the mechanism by which the eye's surface is kept clean.

It was seen in chapter 3 that the hydrophilicity of a contact lens surface can be greatly increased by the use of an oxygen plasma. Whilst such a surface is very wettable, adsorption experiments indicate that its interaction with proteins will be poor. Also though mucin will readily coat the surface it is difficult to remove. This initial treated surface rapidly decays, chapter 4. A change in the surface chemistry occurs giving rise to a surface which is still more wettable than the untreated sample but which has a higher proportion of carbon singly bonded to oxygen species. Testing of this material shows that it appears to be compatible with proteins and readily adsorbs a layer of mucin. However this mucin layer can be readily removed. This reversibility indicates a weaker interaction between the polymer and the mucin,which may be attributable to the reduction in the number of more highly oxidized functionalities at the surface. The reversibility of the adsorption of mucin to the plasma treated and aged lens material is likely to be the major factor in the improved patient response to these lenses over untreated lens materials.

Alternatives to oxygen plasma treatment have concentrated on the use of plasma polymers in an attempt to provide a universal treatment for all lens materials. In vitro tests suggest that the plasma polymers of HMDS and NVP offer some advantages over untreated siloxane acrylate materials.

As a more complex solution samples of lenses coated with phosphorylcholine were produced to mimic the surface of the eye and this showed a similar performance in adsorption tests to the aged plasma oxidized lenses. It would therefore be anticipated that this material might perform successfully in the eye.

6.6 References - Chapter 6

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