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WETTABILITY AND HYDROPHILICITY OF RIGID AND SOFT CONTACT LENS SURFACES

by

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A Thesis submitted for the degree of
Doctor of Philosophy
(Ph.D)

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Dedicated to the Memories of My

Mother and Father

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KEY TO ABBREVIATIONS

B & L	Bausch and Lomb
B&L.W&S.S	Bausch and Lomb Wetting and Soaking Solution
CHG	Chlor-Hexidine Gluconate
CLMA	Contact Lens Manufacturers Association
DP	Degree of Polymerisation
HEMA	Hydroxyethylmethacrylate
H_R	Relative contact angle Hysteresis
MMA	Methyl-meth-acrylate
NVP	N-Vinyl-2-Pyrrolidone
PAM/NVP	Poly-alkylmethacrylate
pHEMA	Poly Hydroxyethylmethacrylate
PMMA	Poly-methyl-meth-acrylate
RSCA	Relative Sessile Contact Angle
SD	Standard Deviation
TBUT	Tear Break Up Time
UALLM	Un-separated Adherent Liquid/Laser Method
ALMFM	Adherent Liquid/Maximum Force Method

SYMBOLS

θ	Contact Angle / Wetting Angle
θe	Equilibrium Contact Angle
θ_A	Advancing Contact Angle
θ_R	Receding Contact Angle
γ	Surface Tension
γ_c	Critical Surface Tension
γ_L	Liquid Surface Tension
γ_S	Solid Surface Tension
γ_{SL}	Interfacial Tension of Solid/Liquid
μm	Micrometer = 10^{-6} m

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DECLARATION

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ABSTRACT

In the last two decades an abundance of contact lens materials with unknown surface properties have been introduced as well as new contact lens design. Recent studies have identified the importance of physical and chemical interactions between materials and liquids. The purpose of this experimental research work was to investigate the relationship between a contact lens surface and a liquid. The wettability and hydrophilicity of both soft and rigid contact lens surfaces were determined using two novel techniques and an established method. The two novel techniques were the un-separated adherent liquid/laser method and the adherent liquid/ maximum force method whereas the established technique involved monitoring the receding wetting angle and interface area diameter of a sessile drop.

Contact lens surface preparation and the method of removing a liquid from hydrated surfaces were found to be important variables when determining wettability or hydrophilicity. Experiments showed that the use of surface tension to remove liquid from hydrated surfaces significantly improved the reproducibility of subsequent measurements.

Variation of the sessile drop wetting angle and interface area diameter with evaporation time demonstrated different values for different contact lenses. The clinical consequence of monitoring the receding values would be; if a material to spread tear break up time occurs the dry patches will be advanced on PMMA, rather than Paraperm contact lens.

Surface hydrophilicity, if defined in terms of the maximum adherent force, describes the ability of a lens surface to attract a liquid, whereas wettability may be defined as the ability of a liquid to spread on a contact lens surface. The wettability and hydrophilicity, therefore, are two different issues. When a wetting angle is 0° or close to 0° the surface is described as wettable. Results demonstrated that Equalens had a greater surface wettability and hydrophilicity than the PMMA for pre-wear, but the post-wear hydrophilicity for PMMA was greater than Equalens. The use of each measurement method, therefore, resulted in a value that is intrinsically related to measurement method and definition. The clinical consequence of the values is to help practitioners prescribe a lens material either on wettability or hydrophilicity values.

In contact lens practice, a lens surface is required to maintain a stable tear film and produce a long tear film break up time. A combination of hydrophilicty and wetting angle values can help to determine the requirement of wettability and hydrophilicity in the contact lens industry and also in practice. It can be concluded that no single test can fully describe the surface properties of contact lens surface materials, but it is proposed that information and results from a series of tests provides the most useful clinical description.

Chapter 1. Introduction

1.1. Introduction

The surface properties of any material govern its interaction with external environments. In biological environments for example, the surface of a material interacts with water, ion molecules, protein and tissue (Figure 1.1). The chemical structure of the material surface, therefore, determines such properties including wettability and hydrophilicity. Wettability and hydrophilicity are specific properties of contact lens materials that form the basis of research in this thesis.

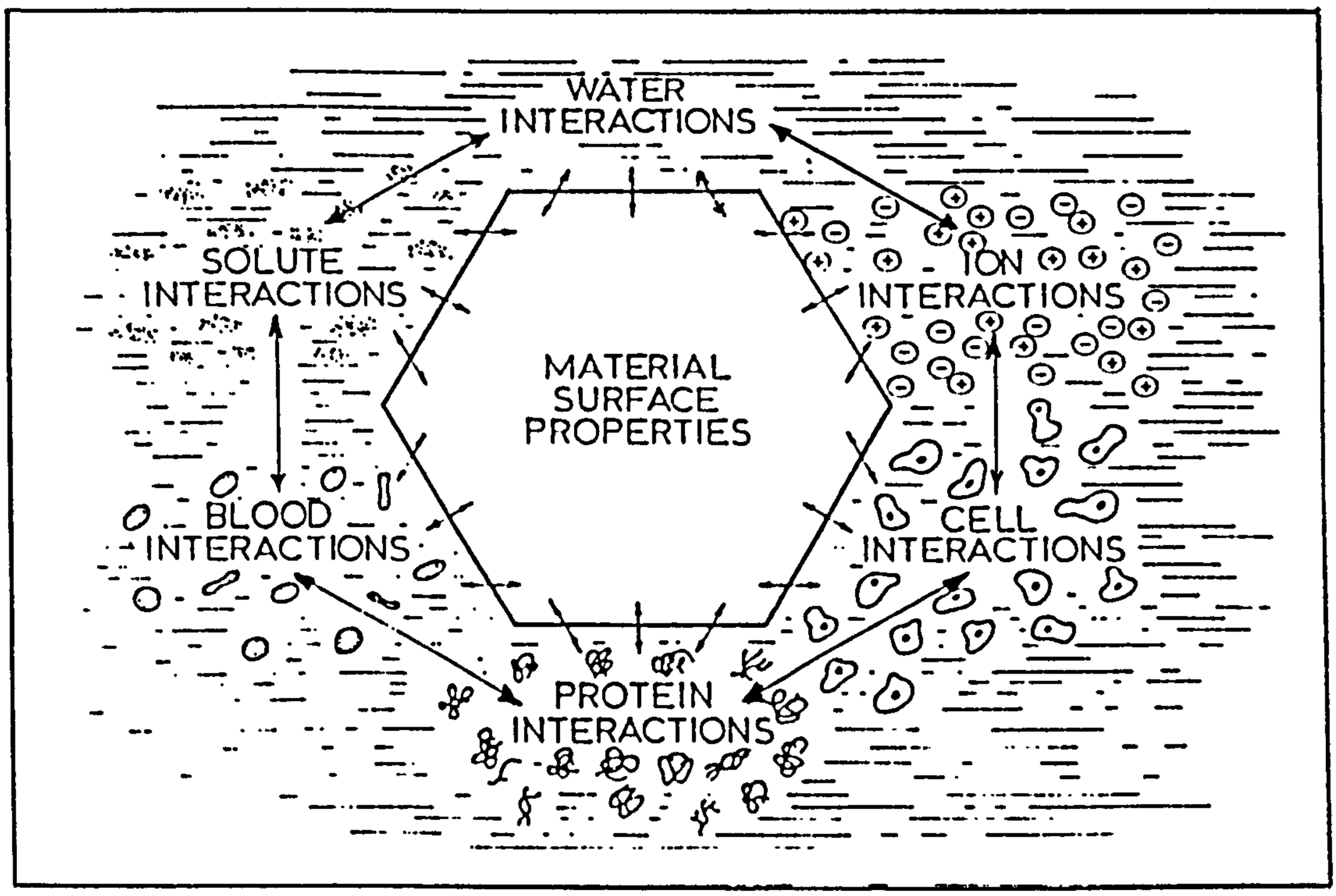


Figure 1.1. The figure shows that the surface of a material can interact with biological environments in a number of ways: interactions with water, ion macromolecules, protein and various tissues. These interactions are determined largely by the surface properties of the materials (Andrade, 1980; Treiber, 1988; Tighe 1990).

The importance of wettability has been recognised in many fields (Larke, et al 1973 and Hancock 1991). In the surface coatings industry, a paint must completely wet the surface to which it is applied, because there would be disastrous results if the

paint migrated into droplets after application. On the other hand with waterproof clothing it is essential to produce a surface on which water will not spread but will form droplets.

There are a number of ways in which the surface properties of a material can be evaluated in the laboratory. For example, surface tension (γ), interfacial tension of solid/liquid (γ_{SL}) or contact angle (θ) all provide a measure of the various intermolecular forces that determine the interaction of a material with its external environment. Before describing the specific properties of the material and how they arise various terms used in the subsequent discussion will be defined.

1.2. Covalent Bonds

There are several chemical bonds in nature and the most predominant stable one is the covalent bond. In a covalent bond, electrons are shared between the two atoms (strong bonds between neighbouring atoms). Sometimes, the shared electrons are equally attracted to each other. This results in a non-polar covalent bond. In other instances, the shared electrons are attracted to one atom more than the atom; this results in a polar covalent bond. From the studies of the positions of atoms in molecules, the energetic of molecules could be determined (Table 1.1; Billmeyer, 1971).

Bond	Bond Length, μm	Dissociation Energy, Kcal/mole
C-C	1.54	83
C=C	1.34	146
C-H	1.10	99
C-N	1.47	73
C≡N	1.15	213
C-O	1.46	86
C=O	1.21	179
C-F	1.32-1.39	103-123
C-Cl	1.77	81
N-H	1.01	93
O-H	0.96	111
O-O	1.32	35

Table 1.1. Typical primary bond lengths and energies.

1.2.1. Covalent Non-polar Bonds

In a non-polar bond, the electrons are shared equally by the nuclei of the two atoms, leading to electric charges being symmetrically distributed. The attractive force that an atom has for the shared electrons of the molecule is known as the electronegativity of the atoms. In non-polar bonds, the electronegativities of the atoms are equal. An example is hydrogen, which can form a strong covalent bond. The formation of a hydrogen molecule involves the overlapping and sharing of its electron orbits. In hydrogen molecules, each atom contributes one electron and the shared electrons are equally attracted to each nucleus (Figure 1.2).

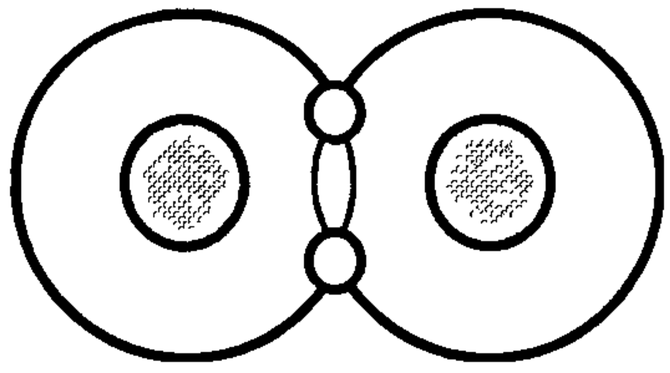


Figure 1.2. The non-polar covalent bond in a hydrogen molecule.

Another example of the non-polar bond is the carbon-hydrogen bond in a methyl group, which consists of a carbon atom and three hydrogen atoms. The electrons which are shared by the carbon and hydrogen atoms, are attracted equally to the two atoms. The carbon atom thus does not have a net electrical charge in relation to the hydrogen atom. The bond is, therefore, non-polar (Figure 1.3).

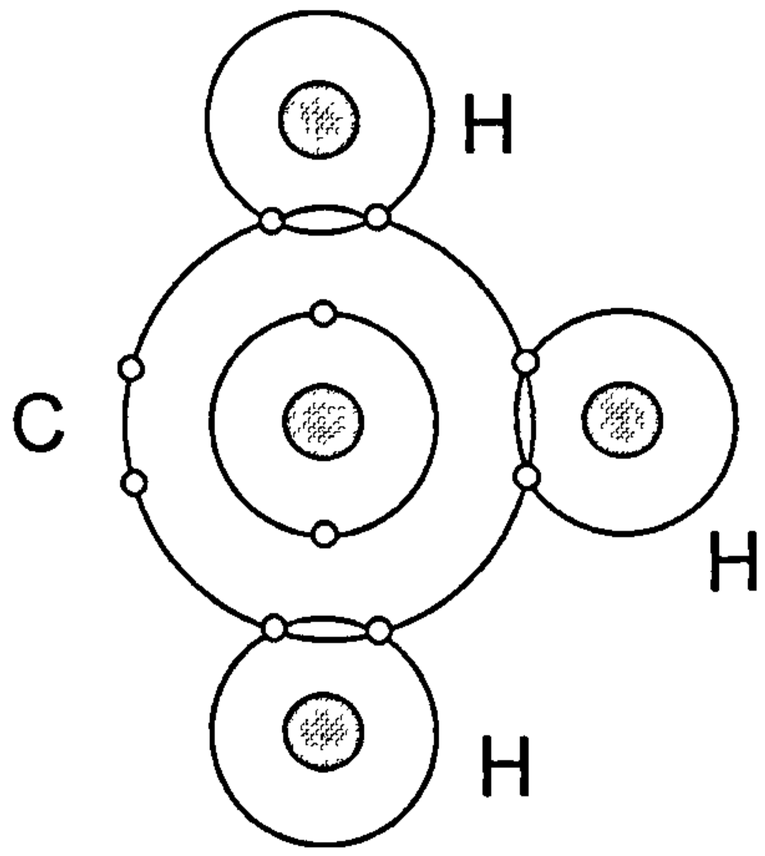


Figure 1.3. The non-polar covalent bond in a methyl group.

1.2.2. Covalent Polar Bonds

When a covalent bond is formed between two atoms of different electronegativities, the atom with the higher electronegativity attracts the shared electron pair more strongly. Consequently, the electron spends more time around the atom with the higher electronegativity, with this atom acquiring a partial negative charge and the other atom a partial positive charge (Figure 1.4).

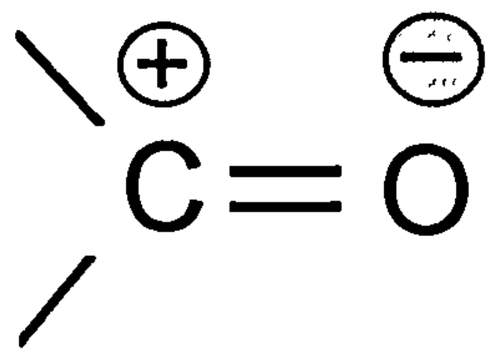


Figure 1.4. The polar covalent bond in a carboxyl group.

Since the sum of the charges is zero, however, the overall molecule is still neutral. The greater the electronegativity difference between the two atoms, the greater the polarity of the bond. An example of such a polar bond is the carboxyl group (C=O) in which the oxygen atom has a higher electronegativity and therefore takes on a small negative charge. The carbon atom subsequently has a small positive charge.

Another example of a polar compound is water. In this case, the oxygen atom has a greater attraction for the electrons, with the oxygen having a relatively negative charge and the hydrogen atom having a relatively positive charge. Since the hydrogen atom has a relatively positive charge, it will be attracted to the oxygen atom (relatively negative) of another molecule, forming a hydrogen bond. This bond is not very strong because it is only a partial charge, but it is very important in surface chemistry and wetting and is responsible for the existence of water in liquid form.

1.2.3. Hydrogen bond (Ionic bonds)

The hydrogen bond can be considered electrostatic or ionic in character. The hydrogen is usually attached to an acidic group typically a hydroxyl, carboxyl, amine or amide group. The other group could be basic usually oxygen such as carboxyls, ethers or hydroxyls or nitrogen such as amines and amides. The association of such polar liquid molecules as water, alcohols and hydrofluoric acid results in polar polymers such as nylon, cellulose and proteins because of hydrogen bonding (Ellison et al 1954a and b). Only fluorine, nitrogen, oxygen and occasionally chlorine have sufficient electronegativity to form hydrogen bonds (Weinschenk 1989; Figure 1.5).

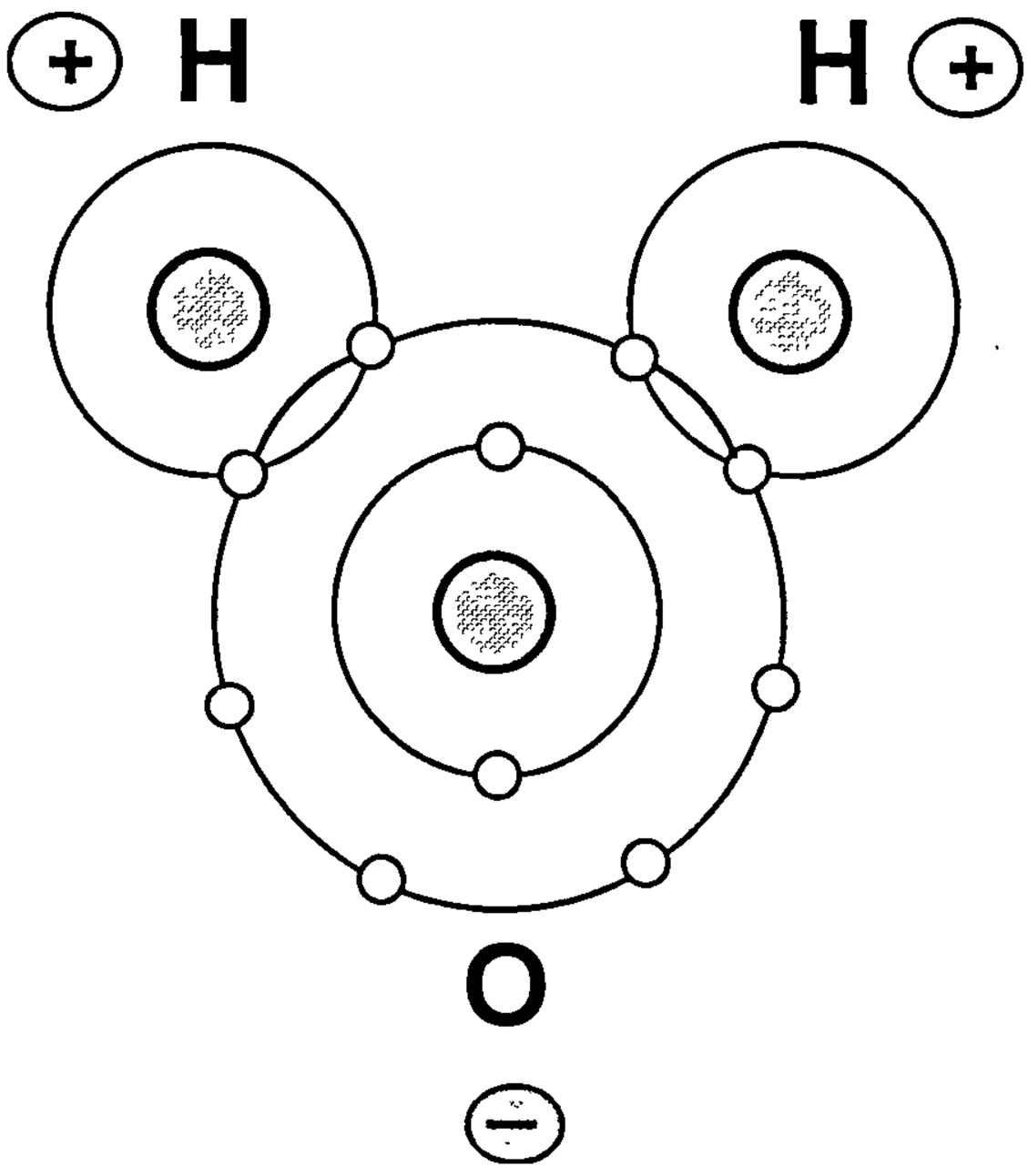


Figure 1.5. The polar-covalent bond of water. Hydrogen bonding is essentially electrostatic in character and relatively weak. When hydrogen is bound to an electronegative atom, such as oxygen, nitrogen or fluorine, the bonding electron is strongly displaced. This leaves a partial positive charge on hydrogen and a partial negative charge on the hetero-atom. Although such bonds are weak, they are important in ordering the arrangements of molecules in solutions.

1.3. Solid/Liquid Interactions

1.3.1. Intermolecular Forces

There is a difference between the intermolecular forces in the interior and at the surface of substances. They are known as the cohesion forces and the adhesion forces respectively (Dabezies et al 1984). The intermolecular forces however, consist of cohesion forces and adhesion forces that function between the molecules of substances. These attractive forces are the result of the interaction of fluctuating electric dipoles with the induced dipoles. They contribute to the cohesion in all substances with the magnitude of the intermolecular force depending on the type of material and its density. In the case of mercury, the inter-atomic force involves cohesion forces and the metallic bond, while in water, they comprise adhesion forces and dipole interactions (hydrogen bond).

1.3.1.1. Cohesion Force

Forces acting on the same types of molecules are called cohesive forces. If a drop of mercury is placed on a glass surface, for example, it retains its spherical shape. The molecules of mercury have a greater attraction for similar molecules of mercury and are less strongly attracted to the dissimilar molecules of glass (Figure 1.6a). The stronger the cohesive forces between molecules in a liquid, the higher is the surface tension (see 1.3.2).

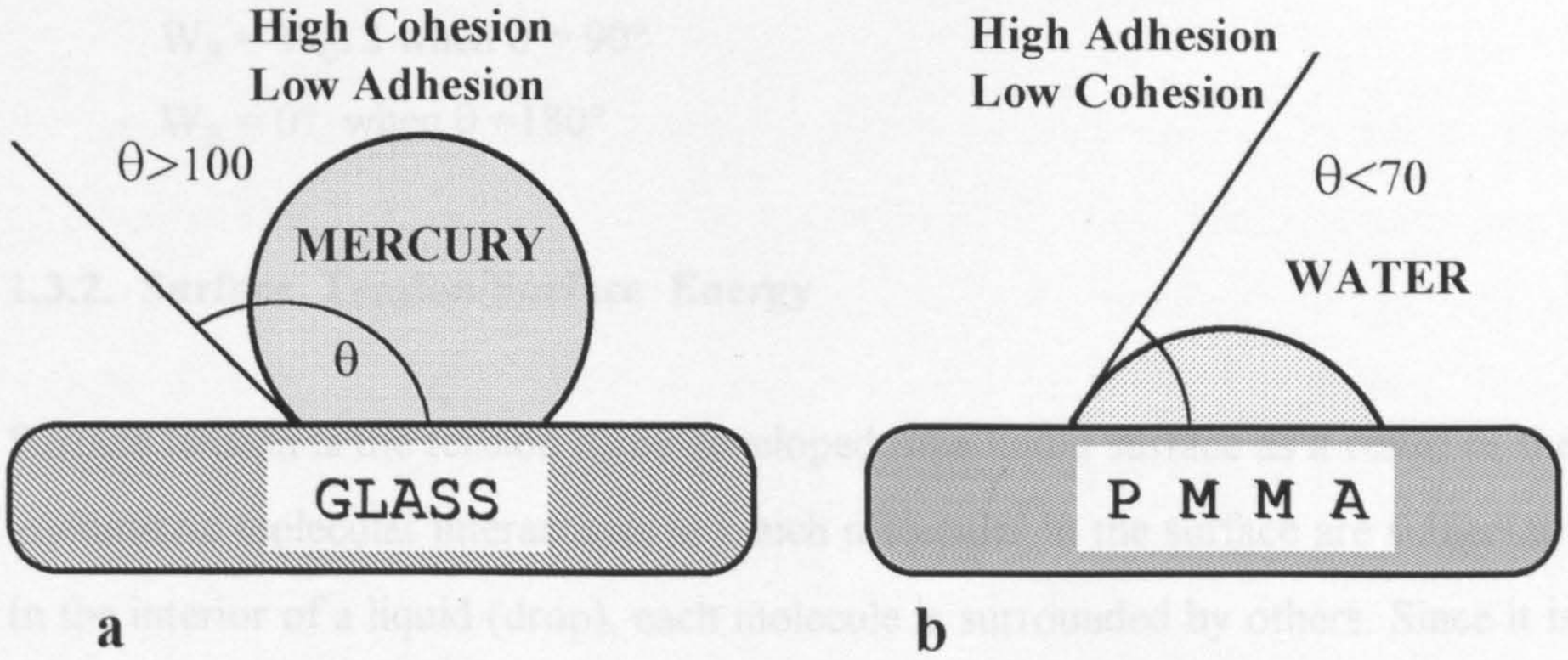


Figure 1.6. Cohesion and adhesion forces: **a** drop of mercury on glass and **b** a drop of water on PMMA material Dabezies et al 1984.

1.3.1.2. Adhesion Force

Forces acting on the molecules of two different substances are called adhesive forces. If a drop of water is placed on a polymethylmethacrylate (PMMA) for example, it spreads partially over the surface because water molecules, in addition to their attraction to other molecules of water, also have an attraction to molecules of PMMA (Figure 1.6b). The wetting of a solid by a liquid implies the adherence of the liquid to the solid despite the cohesive forces holding the liquid together (Gray, 1966). Blue (1966) and Fowkes (1968) calculated the adhesion forces through the wetting angle and stated that the adhesive forces increase as the contact angle decreases.

Rankin, et al (1970a) defined wetting in terms of the work of adhesion ($\mathbf{W_a}$) and the work of cohesion ($\mathbf{W_c}$). Work of adhesion contains three terms, the first is due to dispersion forces and can be expressed in terms of dispersion components of solid surface tension (γ_S) and liquid surface tensions (γ_L), the second term is due to forces arising from surface polarity and third is due to surface ions. The formulas below express the association between work of adhesion and work of cohesion:-

$$\mathbf{W_a} = \gamma_S = \gamma_L - \gamma_{SL} \qquad (1)$$

$$W_a = \gamma\,(1+\cos\theta)$$

$W_a = W_c$ when $\theta = 0°$

$W_a = W_c/2$ when $\theta = 90°$

$W_a = 0°$ when $\theta = 180°$

1.3.2. Surface Tension/Surface Energy

Surface tension is the tension force developed on a liquid surface as a result of the asymmetric molecular interactions to which molecules in the surface are subjected. In the interior of a liquid (drop), each molecule is surrounded by others. Since it is subject to attraction in all directions, the molecular forces cancel each other out. At the surface however, conditions are quite different (Figure 1.7).

The molecules at the surface are attracted to each other and to the molecules beneath, although there is no outward attraction to balance the inward pull. Hence, each surface molecule is subject to a strong unopposed inward pull. Due to this inward pull, the surface molecules continuously attempt to enter the interior bulk of the drop, lowering the surface area to contract until it reaches a minimum size for a given volume and no more molecules will fit into the interior of the drop. For a given liquid volume, the minimum surface area is achieved by assuming a spherical shape.

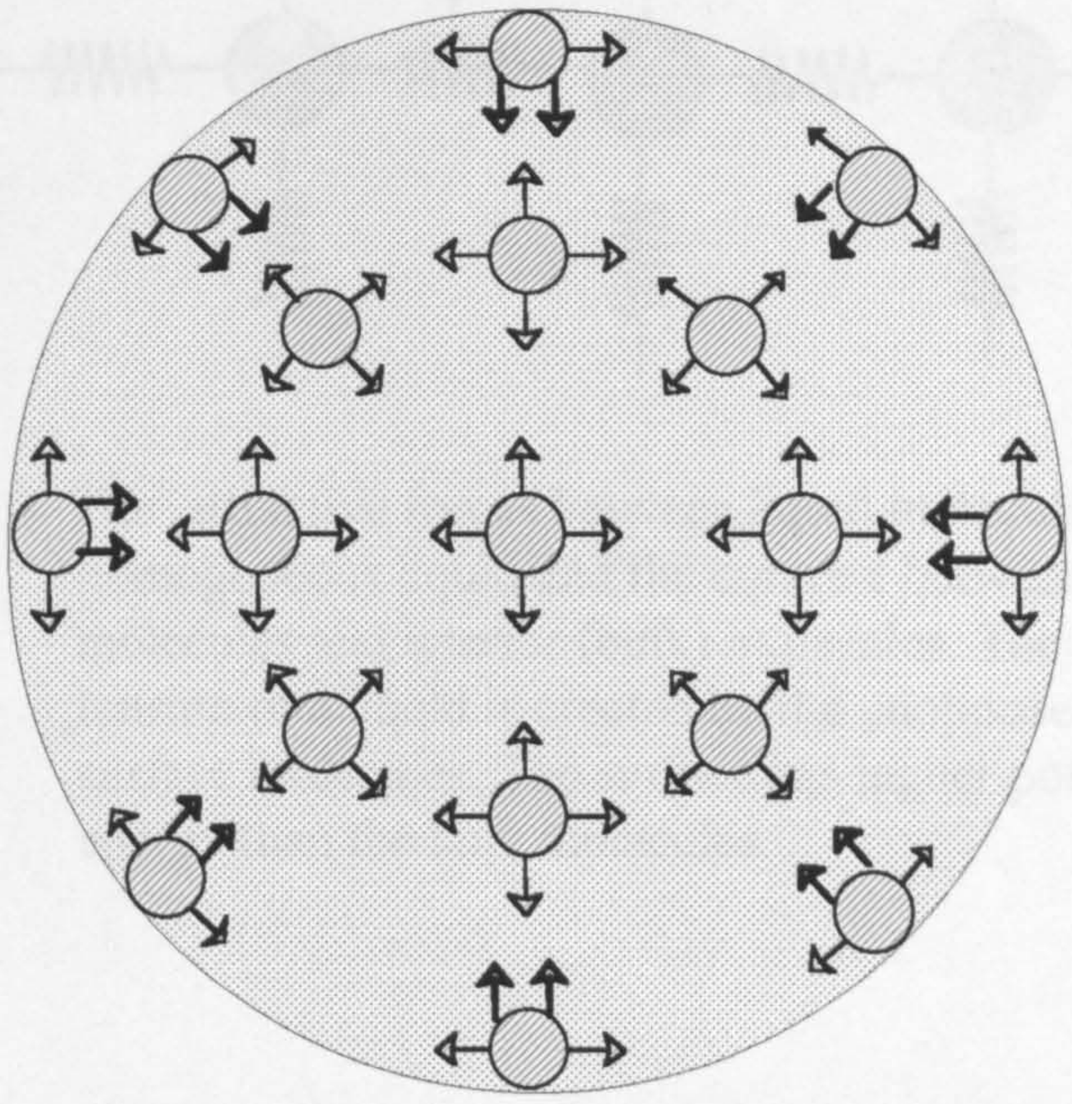


Figure 1.7. The surface tension of a liquid drop. Inward pull of surface tension results in a spherical shape.

Rocher (1975) suggested that the molecules on the surface have an excess amount of potential energy compared with the molecules in the bulk. The potential energy per unit area was called the surface tension or surface free energy. When a liquid volume changes, work being carried out to expand or deform the surface. Since work must be undertaken, energy is present (surface tension, Figure 1.8).

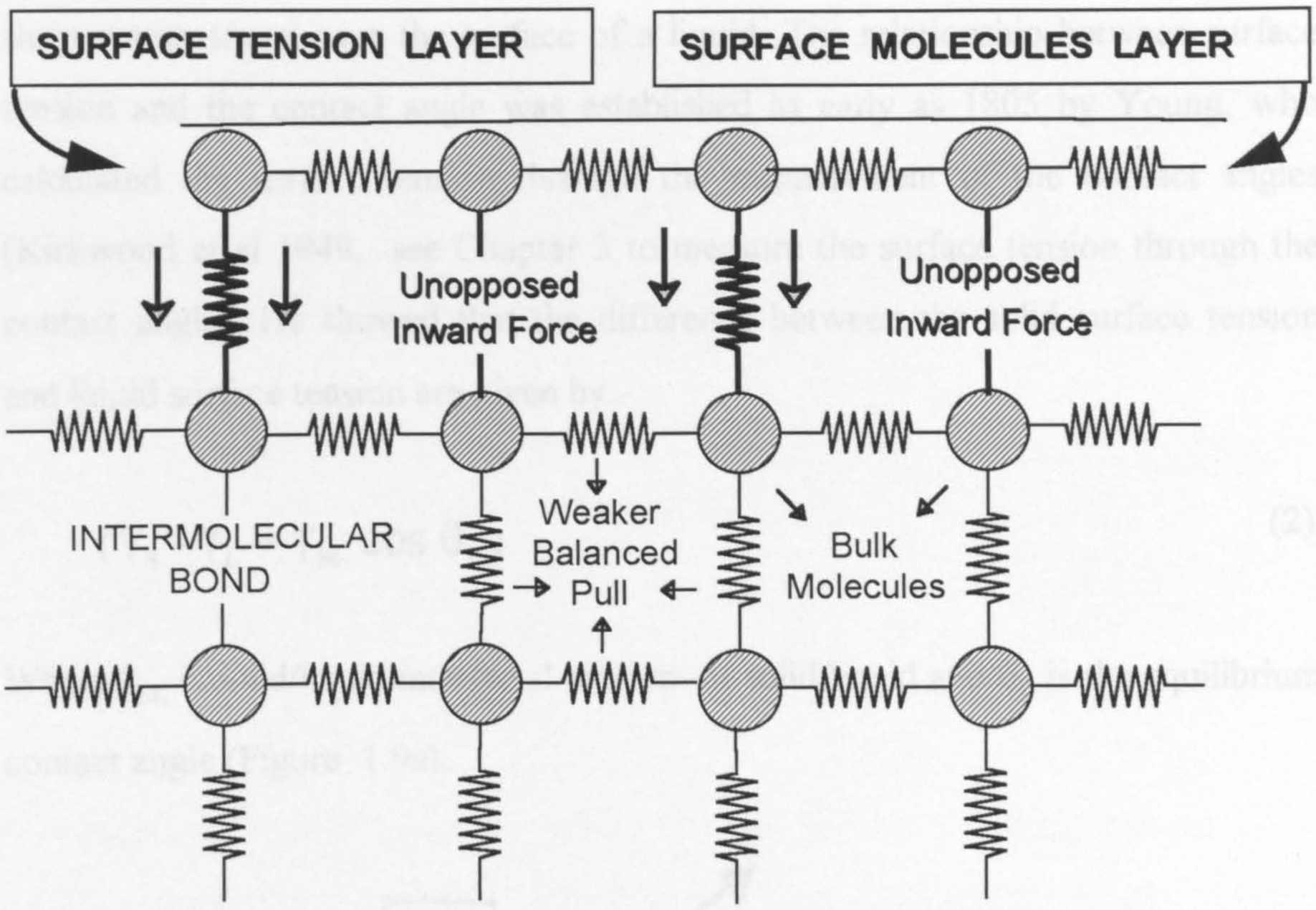


Figure 1.8. The attractive forces between liquid molecules of a homogeneous liquid and the contrast between surface molecules and interior (bulk) molecules. The surface tension of a liquid is created by the unopposed pull of surface molecules. The surface has higher potential energy than the bulk molecules.

Good (1977 and 1979) stated that work (energy) is required to bring molecules from the interior phase into the surface region to form the liquid. Hence, the surface molecules have free energy. For this reason, he preferred the term, surface free energy to surface tension. Rocher (1974) explained the surface tension as 'potential electronic charges between the molecules'. He pointed out that two molecules vigorously repulse each other if they are brought too near to each other, but attract each other if they are separated.

1.3.3. Surface Tension Measurement

Surface tension can be measured by several methods. Rayleigh (1890) measured the surface tension independent of contact angle using a ripple method in which

short waves travel over the surface of a liquid. The relationship between surface tension and the contact angle was established as early as 1805 by Young, who calculated the surface tension through the measurement of the contact angles (Kirkwood et al 1949, see Chapter 3 to measure the surface tension through the contact angle). He showed that the difference between the solid surface tension and liquid surface tension are given by:-

$$(\gamma_S - \gamma_L = \gamma_{SL} \cos \theta_e) \qquad (2)$$

Where γ_{SL} is solid/liquid interfacial tension of solid/liquid and θ_e is the equilibrium contact angle (Figure 1.9a).

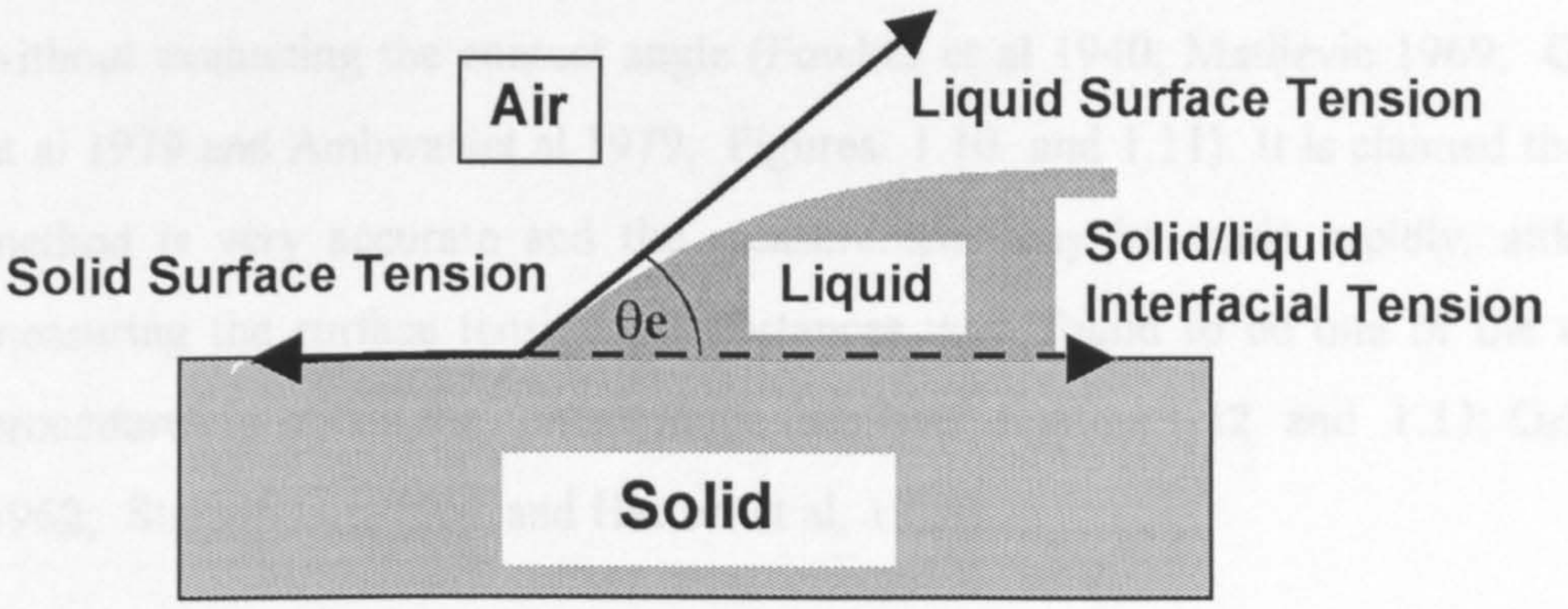


Figure 1.9a. The liquid/solid/air interface.

Sulman (1920) investigated the cause of discrepancies between recorded values of surface tension. He found that certain variations were because of conditions when measuring the contact angle (Advancing and Receding). MacDugall et al (1941) measured the surface tension of liquid using the equilibrium of a drop on a tilted plate. They suggested that the correct contact angle is the mean of the advancing and receding angles.(Figure. 1.9b). The surface tension was then calculated.

$$\gamma (\cos\theta_A - \cos\theta_R) = Apg \sin \alpha \qquad (3)$$

Where **p** is the density, **g** is the acceleration of gravity, γ is the surface tension of the liquid, α is the angle of tilted plate and **A** is area.

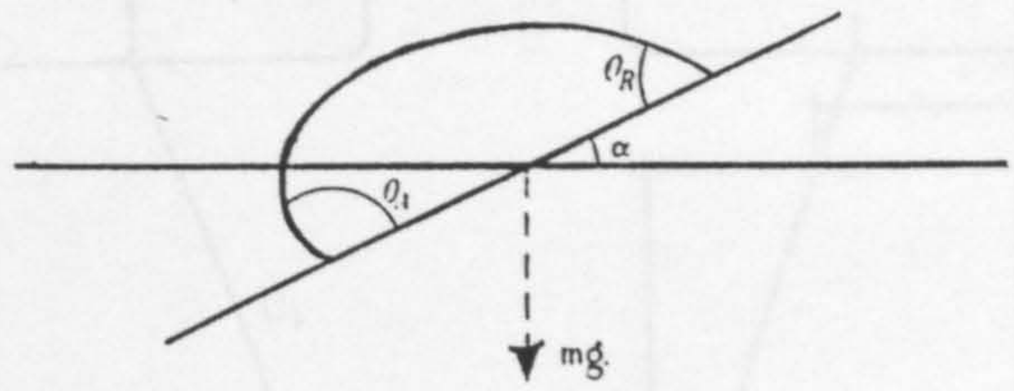


Figure. 1.9b. The equilibrium forces on a drop resting on an inclined plate (MacDugall et al 1941).

The surface tension of a pendant drop was calculated by measuring the dimensions without evaluating the contact angle (Fowkes et al 1940; Matijevic 1969; Goods et al 1979 and Ambwaniet al 1979; Figures 1.10 and 1.11). It is claimed that the method is very accurate and the measurement may be made rapidly, although measuring the surface tension of substances was found to be one of the useful procedures to obtain the contact angle (see later, Figures 1.12 and 1.13; Osipow, 1962; Staicopolus, 1962 and Hattori et al, 1978).

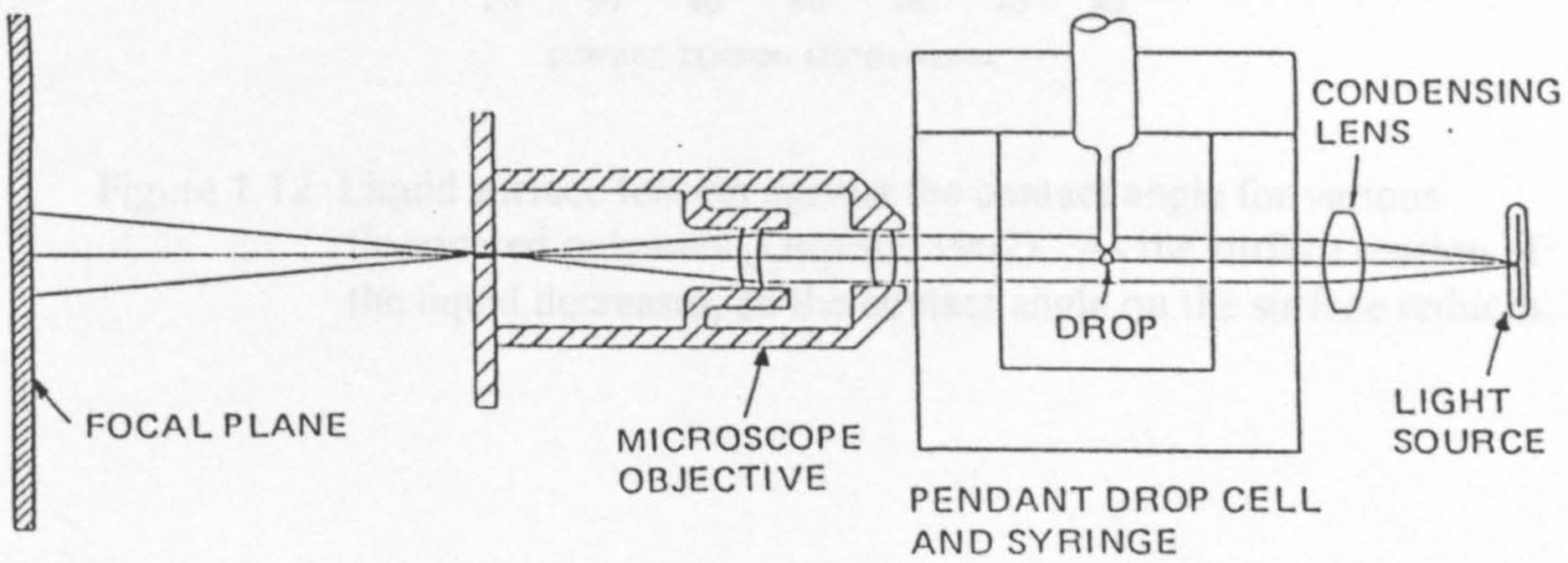


Figure 1.10. The pendant drop method device to measure the surface tension.

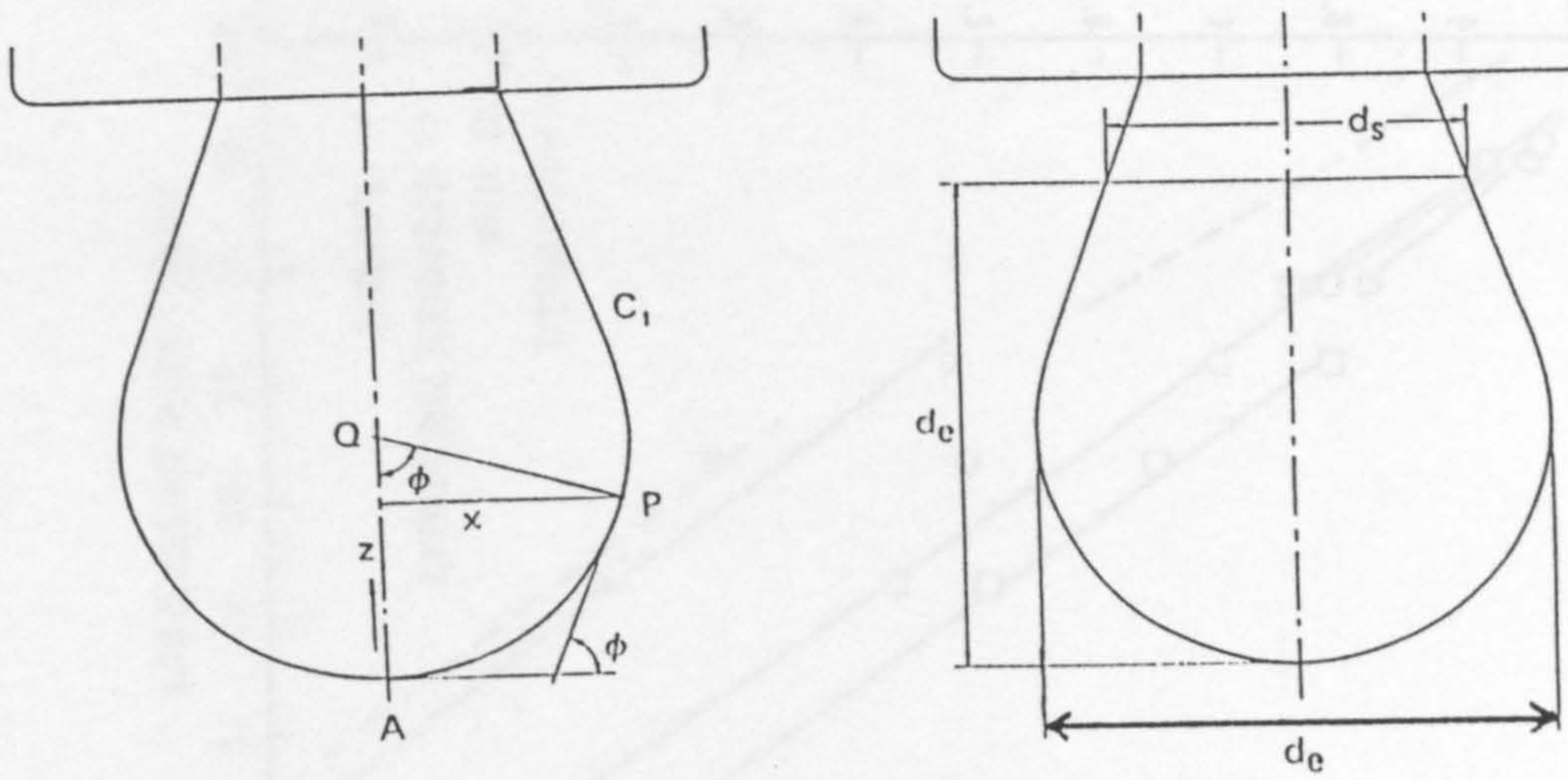


Figure 1.11. A schematic diagram of a pendant drop to measure dimensions to calculate the surface tension (Goods et al 1979).

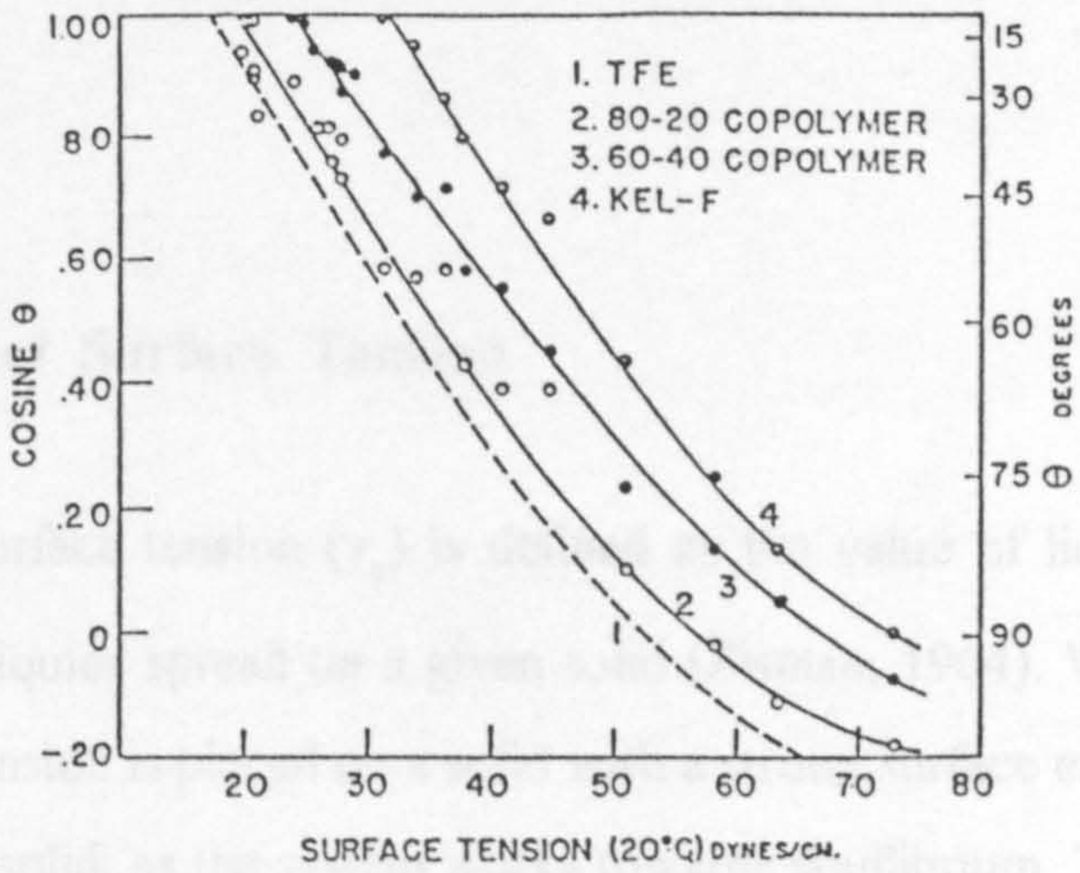


Figure 1.12. Liquid surface tension against the contact angle for various fluorinated polymers (Osipow, 1962). As the surface tension of the liquid decreases, so the contact angle on the surface reduces.

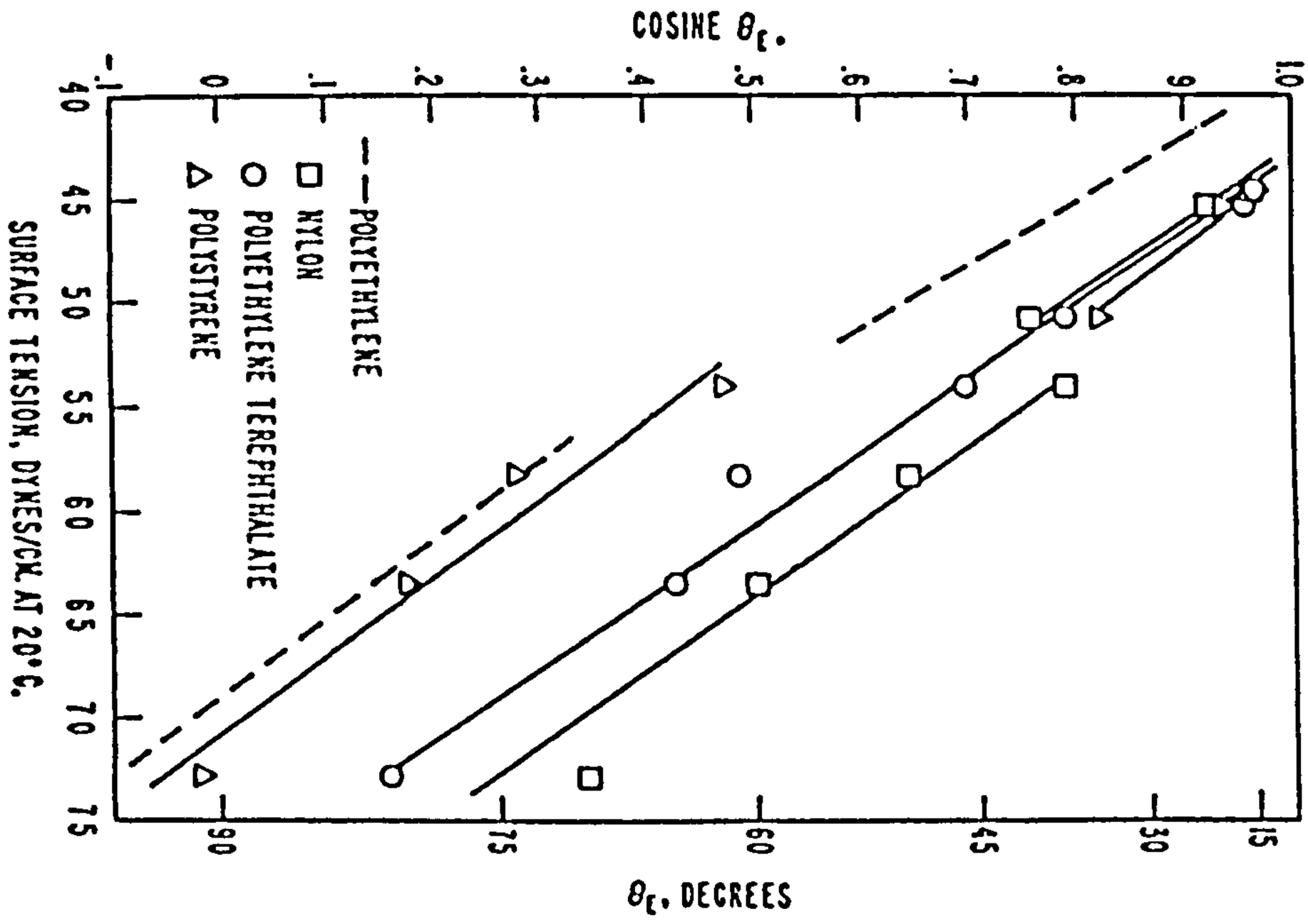


Figure 1.13. The liquid surface tension against the cosine contact angle for various materials (Osipow, 1962).

1.3.4. Critical Surface Tension

The critical surface tension (γ_c) is defined as the value of liquid surface tension below which liquids spread on a given solid (Zisman, 1964). When a liquid with a low surface tension is placed on a solid with a strong surface energy, the liquid will spread on the solid, as the system works towards equilibrium. The effective surface energy thus attracts and fixates the liquid. If the surface tension of the liquid is of the same order or higher than the critical surface tension of the solid (such as an organic solid), the liquid will not spread but will form drops, such surface will be non-wetting.

Jarvis et al (1964) reported that the ability of an aqueous solution to spread on a low-energy surface depends not only on the critical surface energy value of the surface but also on the concentration of different wetting agents that must be dissolved in water to depress the surface tension of water (Figures 1.14 and 1.15). The relationship between the critical surface tension and wettability was also

investigated by Shafrin et al (1967), Holly et al (1971a) Larke et al (1973) and Braudo et al (1974). The values of the critical surface tensions of several liquids, including fluorinated alcohol and water, have been determined by using contact angle methods (Zisman, 1964; Dann, 1970).

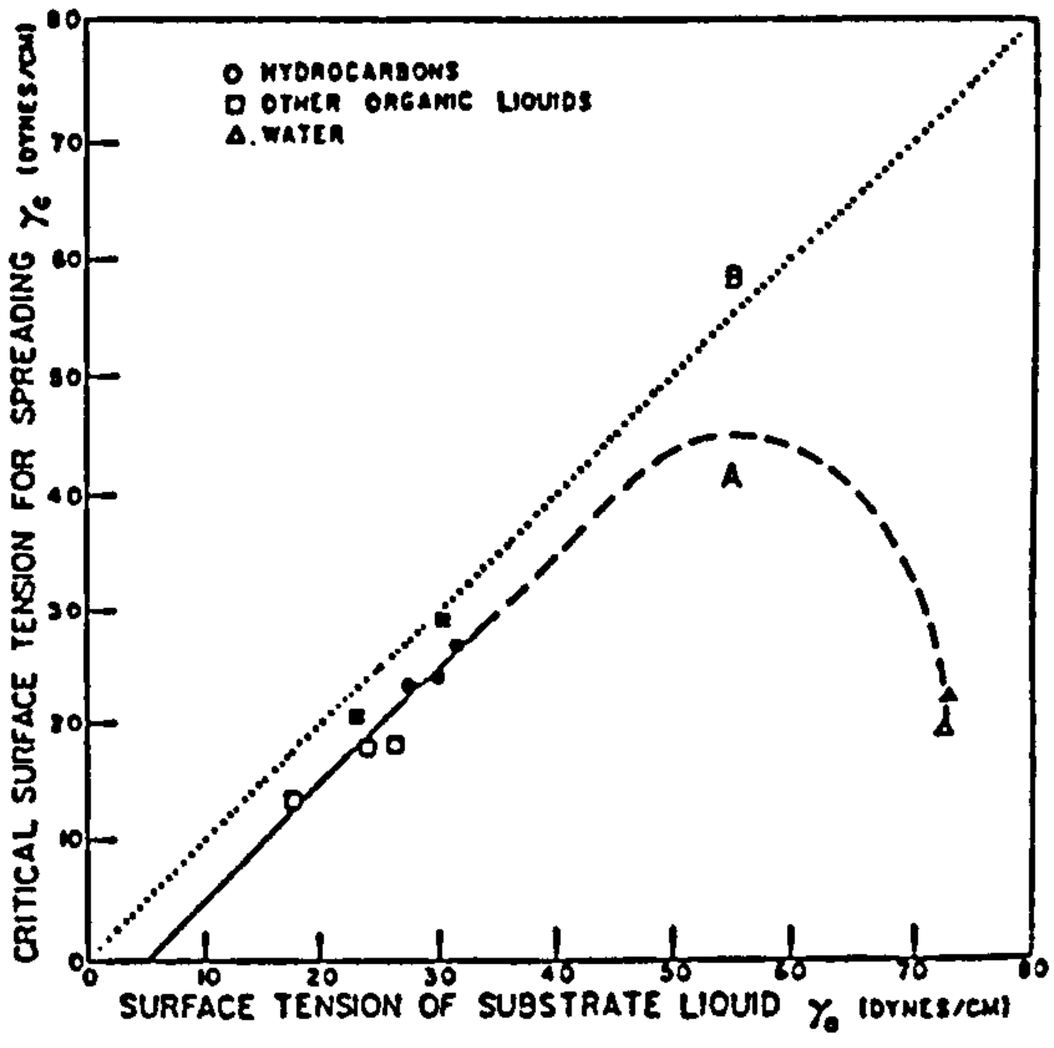


Figure 1.14. The relationship of the critical surface tension for spreading with the surface tension of some liquids (Zisman, 1964).

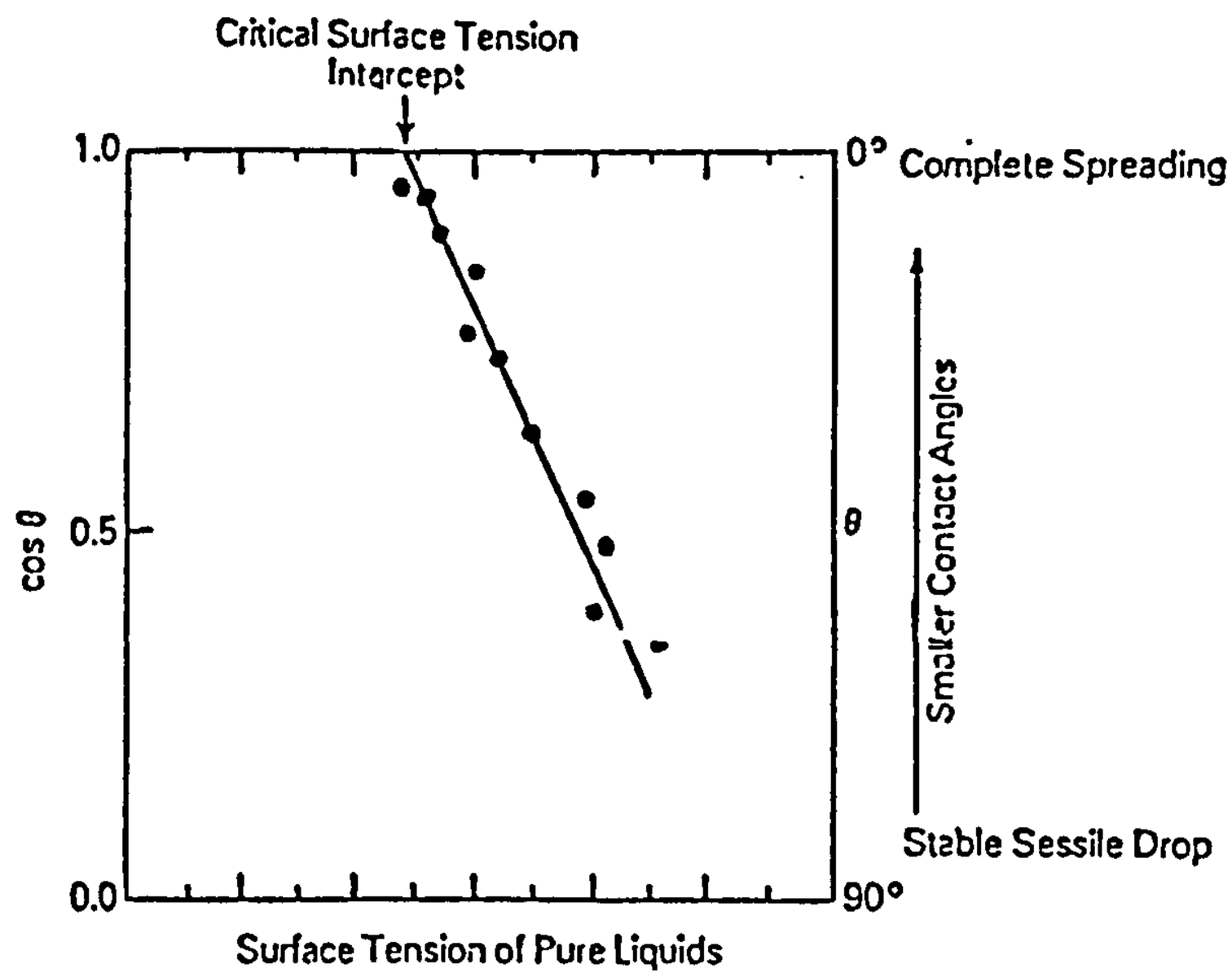


Figure 1.15. The contact angle related to the surface tension of inert liquids. Liquids with surface tensions below the critical surface tension will spontaneously spread over the surface, forming a contact angle of 0° (Jarvis and Zisman, 1964, Tighe 1976).

1.3.5. Interfacial Tension

When a liquid wets a solid, in addition to the unopposed inward attraction of the surface molecules of the liquid, the attraction forces of the other molecules must be considered (see 1.3.1.2). This changes the balance of the forces, with the surface molecules of the drop attracted inward by the molecules of the bulk, and also outward to the material surface. This lessens the excess energy of the liquid surface molecules. This new lower surface energy, or modified surface tension, is called interfacial tension (Figure 1.16).

There does not appear to be any method whereby γ_{SL} can be determined by direct experiment, so that the relation between γ_{SL} and the parameters (ϕ) γ_S and γ_L has received a lot of attention. If the surface molecules of the liquid are held tightly in place by cohesive forces, the liquid will have a high surface tension, hence, low interfacial forces, depends upon the second phase (Good 1977):

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\phi(\gamma_S \gamma_L)^{1/2} \quad (4)$$

In this case, the liquid tends not to spread over a solid surface. In other words, there is minimal interaction between the surface molecules of the liquid and those of the solid. As a result of the interfacial tension, the wetting will be poor. Thus, the key factor is the interaction between the surface molecules of the liquid and those of the solid.

Good (1979) evaluated the magnitude of the adhesion force contribution to surface energy in many liquids and solids by measuring interfacial tension and contact angles. Li et al (1992) reported that the adhesion and interfacial bonding are closely related to the involved energy. They strongly supported the existence of the localised chemical bonds at the interface as a result of the electron transfer at the interface. Shuttleworth et al (1948) stated that the equilibrium position of the liquid depends not only on the surface energies of the liquid, solid and solid-liquid interface, but also on such factors as, surface roughness (see chapter 3) and the way in which the liquid is placed on the solid. They also reported that there was no general agreement about the magnitude of the solid/liquid interfacial tensions. To

enhance wetting, therefore, either the cohesion forces within the liquid or the solid need to be lowered and or increased adhesion forces. This will result in a lower interfacial tension (Souheng, 1971 and Baker et al, 1977).

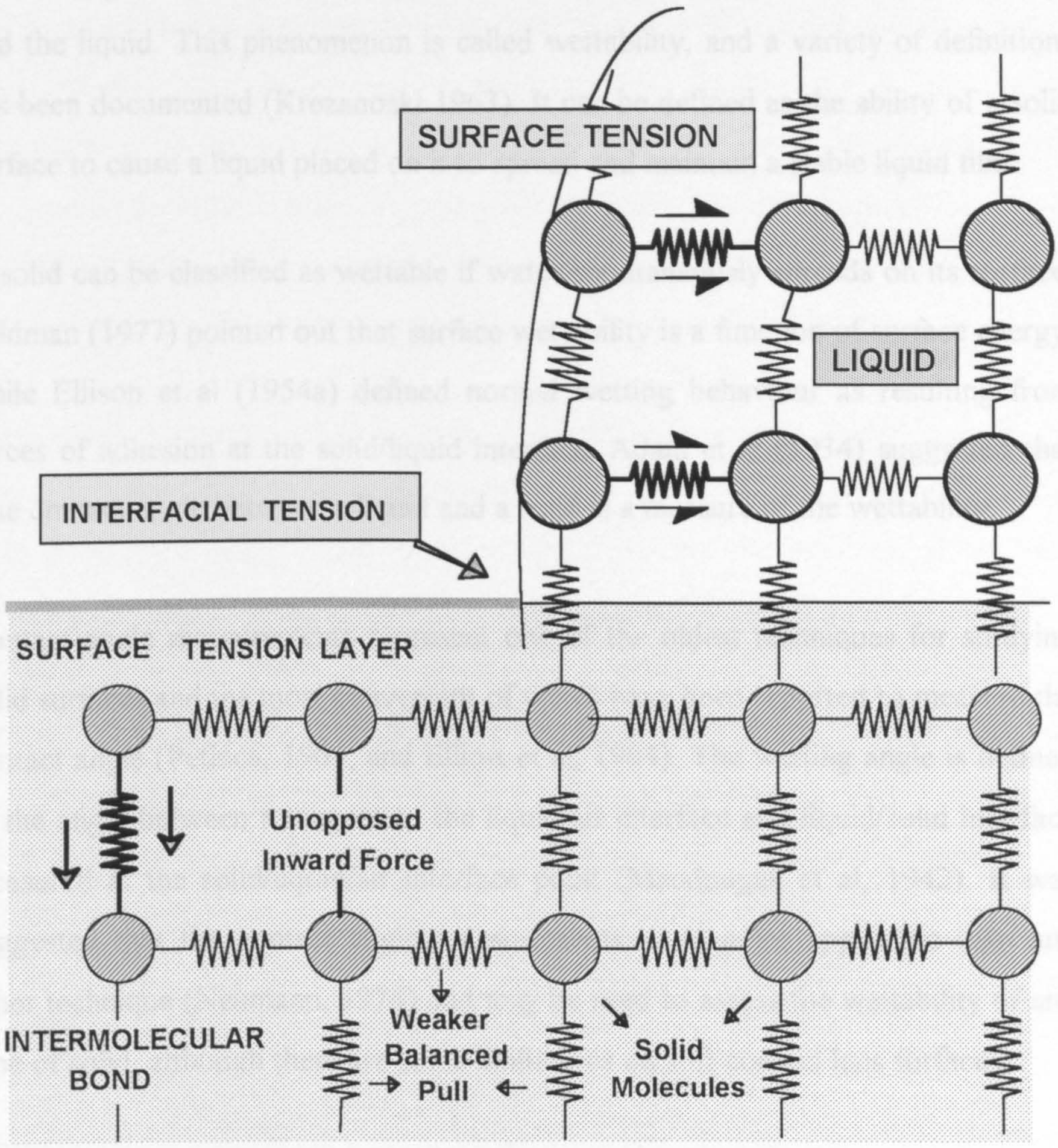


Figure 1.16. The interfacial tension and surface tension in a solid/liquid/air interface.

1.3.6. Surface Hydrophilicity

Surface hydrophilicity (surface attraction) can be defined as the ability of a material surface or a contact lens surface to attract a water. The values can be measured on both rigid and soft contact lenses directly. It could be influenced by several factors. See Chapter 6 for the novel measurement approaches, experiments and discussion. See 2.4.4 for material's hydrophilicity (Tighe 1989).

1.4. Wettability

When a liquid covers a solid surface, there is an adhesion force between the solid and the liquid. This phenomenon is called wettability, and a variety of definitions has been documented (Krezanoski 1963). It can be defined as the ability of a solid surface to cause a liquid placed on it to spread and maintain a stable liquid film.

A solid can be classified as wettable if water spontaneously spreads on its surface. Feldman (1977) pointed out that surface wettability is a function of surface energy, while Ellison et al (1954a) defined normal wetting behaviour as resulting from forces of adhesion at the solid/liquid interface. Adam et al (1934) suggested that "the contact angle between a liquid and a solid is a measure of the wettability.

Contact angle measurements represent one of the oldest techniques for studying solid surfaces and the most convenient of which have been reported to measure the contact angle (Pethica, 1961; and Elliott et al, 1964). The wetting angle is defined as the angle between a tangent to the liquid/air interface and liquid/solid interface measured at the solid/liquid/air interface point (Macdougall et al, 1942). It was suggested that the contact angle measurements were more applicable than any other technique (Neumann, 1974) and may be used to assess the wettability of any type of solid, although there are some limitations on soft contact lens surfaces.

The relationship between the contact angle and wettability is that the greater the contact angle, the less wettable is the test material, while the lower the contact angle, the more wettable is the test material. The contact angle and wettability are, therefore, relatedto one another. If a strong interaction exists between the liquid molecules bathing a material and the molecules of a test material, the liquid will spread over the surface, resulting in a low contact angle. If, however, there is only a weak interaction between the liquid and the surface, the liquid does not successfully cover the surface and remains beaded on its surface, which results in a high contact angle. In other words, wettability is a reflection of the relative

strength of the interaction between liquid molecules and the molecules of the test material.

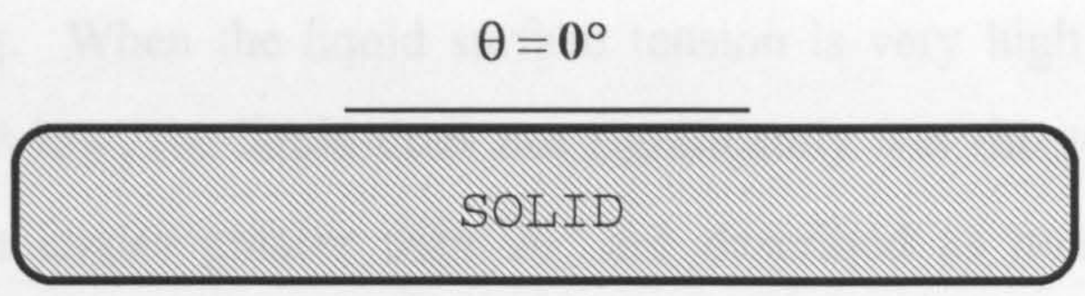
The wetting angle has been used as a quality control to detect material variation and accuracy during materials processing. Lippman (1989) stated that the contact angle between the liquid and a solid surface should give a quantitative measurement of the polarity of that surface. Measurement of the wettability to characterise solid/liquid interaction has a long and controversial history (Johnson et al, 1969). Young (1805) linked the wettability to surface energy. The measurement also demonstrated liquid penetration into a solid and liquid displacement.

Theoretically, wetting angles can be determined through a knowledge of the chemical bonds. Uncertain experimental values of the contact angle and conflict over theoretical interpretations were reported by Johnson et al (1969). Shuttleworth et al (1948) reported that the spreading of a liquid over the surface of a solid is a complex phenomenon because of influencing many factors (see later Zisman, 1964; and Andrade et al, 1979; Adamson, 1982), while Good (1979) and Gregonis et al (1982) believed that the contact angle is one of the techniques capable of assessing polymer-water interactions and it is extremely sensitive to surface energy, surface roughness contamination and heterogeneity.

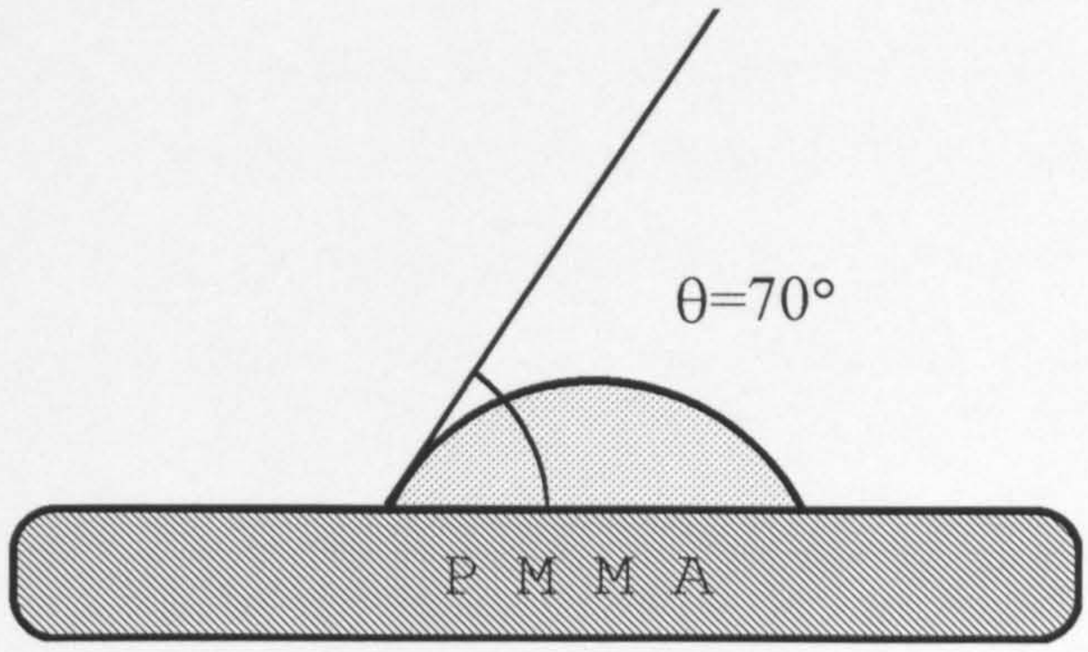
Tadros (1978) defined the spreading coefficient as $S=\gamma_{LV}(\cos\theta - 1)$. (5)

Where γ_{LV} is the surface tension of the solution and θ is the contact angle of the drop on the surface. He showed the variation of S with surfactant concentration. Wettability was connected with the adhesion and cohesion forces, as noted in section 1.3.1.2 (Ondarcuhu 1992), and as a result of these forces, it is possible to obtain complete wetting, partial wetting or non-wetting:-

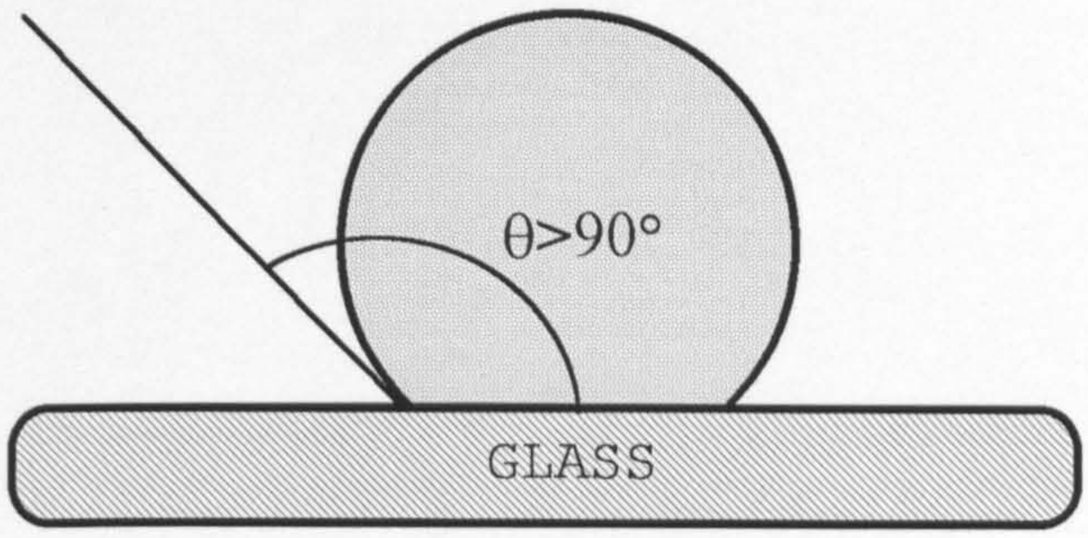
a. Complete Wetting. In complete wetting, the liquid surface tension and interfacial tension and also the solid surface tension are low; thus the contact angle is zero. An example of complete wetting is the spreading of oil over glass, as shown in Figure 1.17. a (Andrade, 1980).



a. Complete wetting. The contact angle is 0°.



b. Incomplete wetting or/partial wetting. The contact angle is between zero and 90°.



c. Non-wetting. The contact angle is greater than 90°.

Figure 1.17. Complete wetting, incomplete wetting and non-wetting.

b. Incomplete Wetting or/Partial Wetting. The liquid surface tension is too high or the solid surface tension is too low, so the liquid does not spread fully over the solid. An example of partial wetting is the spread of a sessile drop on PMMA material (Owens et al 1978 and Lamberts et al, 1984). Rankin et al (1970) Lemp et al (1970b) described incomplete wetting when the contact angle is between zero and 90° (Figure 1.17. b).

c. Non-wetting. When the liquid surface tension is very high and/or the solid surface tension is low, the liquid does not significantly wet the solid, for example Teflon. Contact angles greater than 90° are described as non-wetting (Figure 1.17c; Rankin et al, 1970; and Andrade, 1980).

1.5. Wettability of Contact Lens Materials

1.5.1. Contact Lens History and Materials Development

Leonardo da Vinci was, apparently, the first person to conceive of neutralising the cornea by replacing it with a new refracting surface, thus suggesting the concept of corneal correction and replacement with contact lenses. According to Mandell et al (1953), Da Vinci "sketched and described several forms of contact lens" in 1508. One was made by cutting little round ampoules of glass into two, one of the halves to be filled with water, to look through only one eye (Figure 1.18).

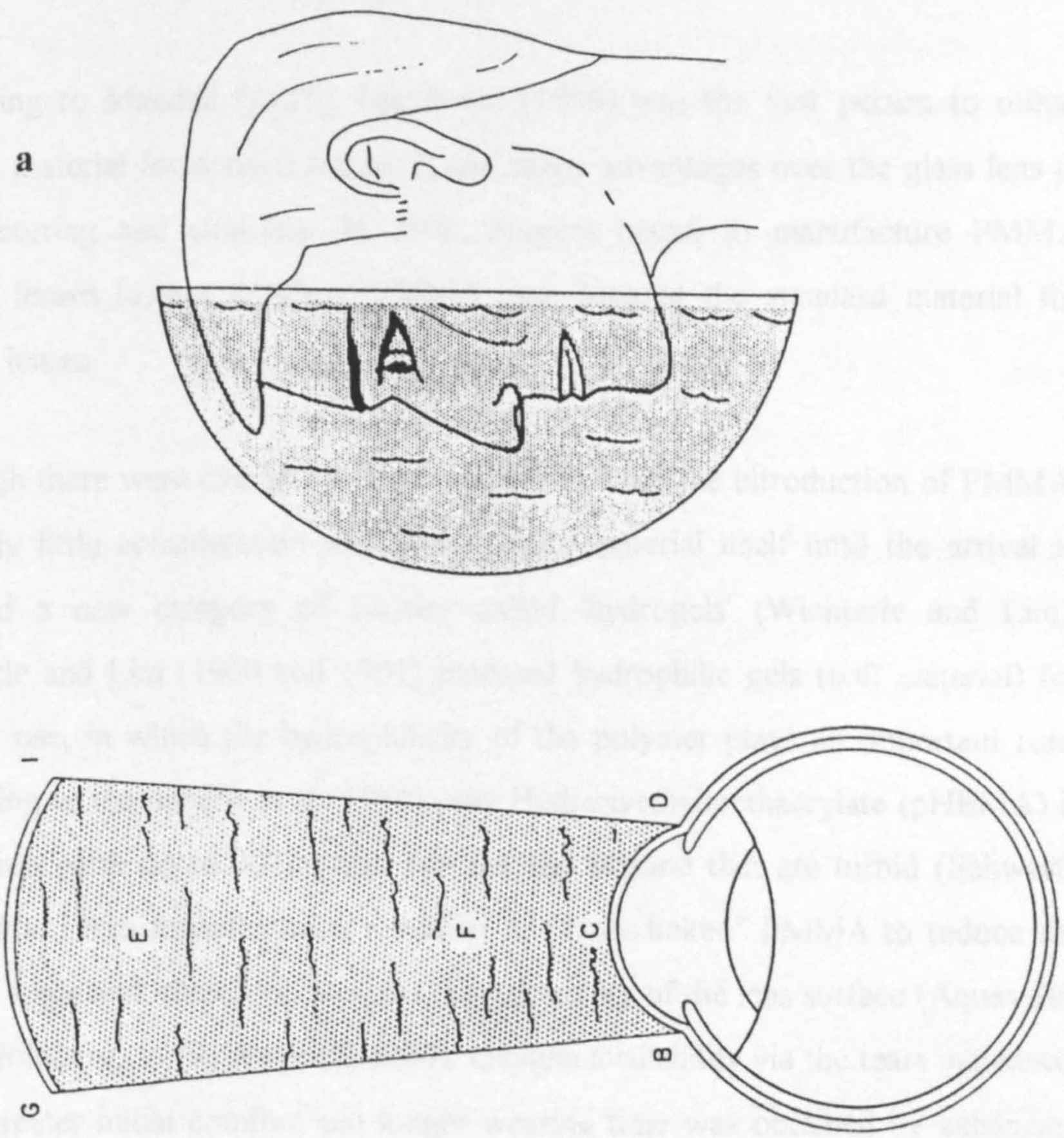


Figure 1.18. **a.** The concept of corneal neutralisation by a hollow glass semi-spheroid filled with water (Da Vinci); **b.** The first contact lens described by Descartes (1636).

Descartes (1636) described and illustrated a contact lens as one method to correct vision. He employed a tube full of water, like a cornea, against the eye, after which the refraction at the entry of this eye ceased (Figure 1.19.b). Young (1801) used a double convex lens with water in his eye and found changes in eye refraction 'to presbyopic'. Herschel (1823) suggested that the irregularity of the cornea would be adapted by a lens on the eye of nearly the same refractive power.

Fick (1887) described the first contact lenses with known refractive power. The lens was made of a thin glass which was 'the only suitable material at that time' to protect a cornea from desiccation due to lagophthalmos. Glass had many obvious limitations that would make it impractical for contact lenses, although it was used successfully for many years (Mann, 1938).

According to Mandell (1953), Feinbloom (1936) was the first person to utilise PMMA material for contact lenses. It had many advantages over the glass lens in manufacturing and clinically. In 1948, Nugent began to manufacture PMMA corneal lenses instead of glass. PMMA then became the standard material for contact lenses.

Although there were changes in lens design following the introduction of PMMA, relatively little consideration was given to the material itself until the arrival in 1960 of a new category of plastics called 'hydrogels' (Wichterle and Lim). Wichterle and Lim (1960 and 1961) patented hydrophilic gels (soft material) for medical use, in which the hydrophilicity of the polymer plays an important role. According to Rosenberg et al (1960) poly Hydroxyethylmethacrylate (pHEMA) is transparent with up to 40% water content and beyond that are turbid (Schwartz 1987). Hard lens manufacturers modified or "cross-linked" PMMA to reduce the wetting angle and, therefore, increase the wettability of the lens surface (Aquavella, 1976; Goldberg, 1979; Wyckoff, 1980). Oxygen availability via the tears increased, and a greater initial comfort and longer wearing time was obtained by enhancing wettability.

The first gas-permeable rigid lens was made of cellulose acetate butyrate (CAB). It was fabricated from naturally occurring materials: cellulose from wood and cotton,

acetic acid from vinegar and butyric acid from natural gas. There are now many variations of CAB for use in industry. The wetting angle of CAB lenses has been reported to be lower and higher than PMMA lens (Gasson, 1981). But problems reported with CAB lenses include instability (Sarver et al, 1978), corneal oedema (Hill, 1977a); deposits (Seidner, 1987 and Maskell, 1981), scratches (Clark et al 1993), flexure and patient discomfort (Cappelli, 1982 and Fowler et al, 1990). In 1982, Barnes-Hind introduced a lathe-cut surface treated of CAB II to overcome the problems.

Silicone acrylate lenses were introduced to practitioners in 1978, consisting of copolymers of siloxanyl-alkyl-methacrylate (siloxane acrylate, commonly called silicon/acrylate), silicone resin, styrene acrylate, fluorocarbon polymer and styrene acrylate siloxane. Silicone has excellent oxygen permeability characteristics but by itself is limited by its wettability (Espy 1978, Yang et al 1983, Lindridge 1989, McLaughlin 1989). There are several problems with silicone acrylate. One, which is related to wettability, is 'subjective dryness' Sarver et al (1978) reported that dryness and redness are possible because of its poor wettability, while Pole et al (1987) stated that there is a tendency for the lens surface both to attract protein and lipid deposits as a result of the surface low wettability (Wilsher, 1982).

The further development of high oxygen materials with Dk values significantly higher than those of soft contact lens materials has resulted in contact lens wear with minimal corneal oedema (Barr et al, 1989). These have a wide range of gas permeability and surface wetting properties.

Boston II silicon/acrylate lens is composed of a methylmethacrylate-dimethylitaconate siloxanyl material that was claimed to be inherently wettable and as dimensionally stable as PMMA (Barr et al, 1984). Silificone A is made from a 100% silicone resin material and is lathe cut and then surface treated to render the surface wettable. The manufacturing process can result in a lens that has wettability problems, the patient and practitioner need to handle the lens with care to avoid scratching, which will cause the scratched surface area to become non-wettable. The lens is bottled in liquid to assure optimum wettability. Dehydration usually reduces the lens wettability, although the treated lens, after drying, is still more

wettable than the Polycon II lens (Bailey 1960, Benjamin et al, 1983). The main disadvantage of the lens is the polishing after manufacturing, which may result in a non-wettable lens surface. It has been documented that some patients with dry eyes may be able to wear silicone treated or silicone rubber contact lenses because of their highly wettable surface (Barr et al, 1981 and 1984; Woodward, 1984; Kossmehl et al, 1988).

The Menicon contact lens was made of silicon/acrylate that was surface treated (Maskell 1981, Port 1985 and Benjamin, 1992a). It has been claimed that the cleaning effect on the lens surface aligns the molecular structure of the surface, resulting in effective wettability (Mackeen et al 1992), although 3 and 9 o'clock staining have been reported in 25 out of 80 fittings (Philipp et al, 1984; Barr, 1988). Fluorinated contact lens materials recently dominated the industry regarding the higher Dk and the enhancement of wettability (Lippman 1990). These characteristics were changeable according to the amount of fluorine and the manufacturing process (Jacob 1989, Lembach 1990). Comprehensive research by scientists, has produced a wide range of contact lens materials with various properties that are available to practitioners.

1.5.2. Contact Lens Wettability In vivo

Assessment of contact lens wettability in vivo was recommended by several investigators, but a majority of workers still believe that wettability measurement in vivo, evaluate the tear film of the individual patient, and not the assessment of contact lens materials' wettability. Isaacson et al (1989) and Davis (1994) evaluated and assessed the contact lens wettability in vivo using various methods, including tear film analysis, pre-lens tear film analysis, non-invasive tear break-up time (TBUT), tear drying time, tear thickness and lipid presence (Loveridge, 1993; Lemp, 1973 and Douthwaite et al, 1992) and corneal oedema (Fink et al, 1993). A significant individual variation was observed because of the difference in quality of tear production. Recent documents showed that different contact lens wettability can be observed clinically in the same PMMA wearer (Hill, 1995). Tear wettability for a particular eye is not a single value for the same patient, but also depends on the environment, age, diet, medications and the health of the eye. Even changes of

blink frequency and eye orientation may affect the tear wettability (Lemp 1973; Hill et at,1975; Hill et at,1976; Terry et al, 1978; Benjamin et al 1986; Caffery 1989 and Tomlinson et al 1991 and 1992).

Several investigators studied in vivo wettability using an interferometric method (Lydon et al, 1984; Guillon, 1987; Guillon et al, 1990). The latter demonstrated that a thin lipid layer is usually present on the front surface of the soft lens tear film. In the case of PMMA corneal lenses, a lipid layer in the pre-lens tear film was rarely detected, with similar results recorded by Hill (1977b). Carroll et al (1994) and Pole et al (1987) used TBUT on the front surface of different rigid gas-permeable (RGP) lenses and stated that the surface chemistry of RGP lens materials might cause lens surface drying, the accumulation of debris on the surface, peripheral corneal staining, lens discomfort and visual problems.

Bagnall et al (1980) used the contact angle method in vivo and reported that measurement is not sufficient to estimate and speculate on protein absorption. Bourassa and Benjamin (1987) utilised the in vivo 'relative sessile contact angle' (RSCA see Chapter 3) and found a significant variation in wettability. Yeager et al (1987) used the sessile drop method on several different rigid contact lens care regimens and reported a reduction of in vivo contact angles to nearly zero. Finnemore et al 1980 and Finnemore (1984) analysed the contact lenses in vivo by lens surface drying and patients' comfort, stating that the lower the wetting angle, the more comfortable it was. Benjamin et al (1983) and Rankin et al (1970) however, stated that post-wearing wettability is most accurately predicted by the wetting angle measurement carried out immediately after wear.

Fonn et al (1988), Bennett et al (1988) and Morgan et al (1992) utilised the indirect measuring of contact lens wettability as another method of evaluating the wettability. They compared the comfort and vision quality of RGP Boston IV with Bausch and Lomb (B & L) hydrogel contact lenses. Non-wetting contact lenses are uncomfortable and wearers experience reduced visual acuity because of the disrupted tear film on the surface. The later stated that controlling polish and tool

pressure during contact lens manufacturing did not affect contact lens wettability in vivo. But Herskowitz (1989) used photoelectron scanning chemical analysis technique and stated that over polishing or dry polishing fluorinated contact lens materials results in frictional heating of the lens surface with associated chemical changes of decarboxylation and defluorination which manifests as an affinity poor wettability. Surface wettability was also evaluated with the biomicroscope by measuring tear coverage over the lens at each time interval blink (Feldman, 1977; Bourassa, et al 1989; Vaghmaria, 1993 and Hatfield, et al 1993). They stated that the surface wettability of all contact lens materials is particularly important for both patient comfort and vision, with a 5 to 1 scaled evaluation being:

5= Tear film regular and smooth for all the lens surface, no break-up of tear film between normal blinks.

4= Tear film regular and smooth, and there may be areas of thin or irregular tear film with less than 25% of the total lens surface being non-wetting.

3= Tear film thin and irregular, with 25-50 % of the total lens surface being non-wetting.

2= Tear film thin and irregular, with 50-75% of the total lens surface being non-wetting.

1= Tear film does not wet the lens surface.

1.5.3. Contact Lens Wettability In vitro

Fatt (1990) stated that there are clearly dozens, if not a multitude of combinations of the factors controlling the tear film in the living eye. The in vitro contact lens wettability measurement helps in identifying the interactions by allowing variations of one component at a time. The in vitro results are therefore, more accurate. It is one useful method in detecting several defects (see 1.5.6, Holly 1983a and b).

Holly (1978) related the receding wetting angle in vitro to in vivo wettability. The lower the receding wetting angle (see Chapter 3), the stronger a material will try to keep an aqueous layer associated with it. In general, the more wettable the material, the thinner a film can be on a surface before it spontaneously ruptures,

with the result that a material with a low receding angle may be more suitable for patients in hot and dry environments.

Holly (1983b) stated that the advancing contact angle is a poor indicator of surface wettability. The values on PMMA reported between 73°-90° and there is no agreement on the current methods, although Ong (1976) suggested that the sessile drop method is preferable to the captive bubble method, which only gives receding angles.

In most contact lens materials, there is a varying ratio of polar to non-polar groups in the molecules. As the relative ratio of polar groups increases, the surface molecules of the polymer will have a greater tendency to interact with the surface molecules of a liquid. Because of this interaction, more adhesion occurs between the liquid and the materials, which in turn, reduces the interfacial tension and so enhances wetting. The wetting angle measurements evaluate both chemical and physical effects, processing and environmental factors. The development of these sophisticated polymers is stimulated by three major objectives (Feldman 1981 and Feldman et al, 1987):

1. To increase oxygen permeability.

2. To increase wettability and resistance to deposition mucous adhesion to the point at which lens spoilage no longer occurs (Knop et al 1992).

3. To increase the comfort level to that of a soft lens while maintaining the physical and dimensional stability of a rigid lens.

Wettability of polymers can be enhanced (see Chapter 2) by changes in the formulation or surface treating of the final product. Both methods try to place wettable groups on the surface to counteract the unwettable nature of the bulk formulation (Refojo 1984). These monomers fall into three types: acidic, basic or neutral compounds. Familiar neutral monomers include 2-Hydroxyethyl-methacrylate (HEMA) and N-vinyl-2-pyrrolidone (NVP). Acidic monomers

include simple unsaturated acids, such as acrylic and methacrylic acid, while basic monomers include simple unsaturated amines, such as aminomethacrylates.

Andrade et al, (1982) suggested that polyacrylate silicone appear to be unwettable in air and wettable in water and is able to absorb water reversibly into their surfaces, which can be explained by surface mobility. Initial contact angle measurements (Captive bubble method) of Polyacrylate silicone are typically 60°-70° (Andrade et al, 1982). When placed in water, the surface slowly becomes wettable, and after a week, contact angle measurements were at 20°-30°, indicating improved surface wettability (Poster, 1978a and Benjamin, et al 1983) and permanent loss of wettability will occur after several hours of dehydration (Madigan et al, 1986). These results suggest that the measurements need to be carried out in a hydrated condition.

Such properties as elasticity, optical clarity, hardness, wettability and gas permeability are maximised by a judicious choice of monomers and methods of polymerisation. As materials that contain a high percentage of unwettability silicone containing monomers are non-wettable, they require surface treatment, coating, grafting and free radical initiated polymers. Because these techniques result in surface modification it is possible that even slight changes in the surface, such as scratches or rigorous cleaning, will adversely affect its wettability. These have not been successfully prepared as inherently wettable materials because of the type of polymerisation process (step growth and condensation; Flory 1953; Mark et al 1979, Olson, 1982 a and b).

An 'ideal' solid surface would be homogeneous and at the molecular level. Most surfaces are heterogeneous, although surfaces that have not been carefully prepared and preserved are usually heterogeneous or become contaminated non-uniformly (Good, 1979). The heterogeneous nature of common surfaces may arise from at least three causes:-

a. The material has a different chemical composition.

b. Essential components of the material may be impure.

c. A difference in the density of atom packing in separate planes, which leads to different energies of cohesion and, hence to varying values of solid surface tension.

d. Different kinds of molecular groups exposed in separate planes (Good, 1979).

Fowkes et al (1940) reported that of all the known methods for determining the contact angle, the tilting plate was chosen as the most effective for cases in which it can be employed. The main requirements for an accurate measurement of contact angles by the tilting plate method are three-fold (it is not applicable for contact lenses, see Chapter 3):

i. The surface of the liquid must be kept clean while measuring the contact angle.

ii. The observed edge of the solid-liquid intersection must lie on the axis of rotation of the solid surface.

iii. There should be a mechanism to move the slide up and down in the liquid and parallel to the length of the slide.

1.5.4. Contact Lens Wettability: Clinical Implications

The wettability of all contact lens materials is important for patient comfort, corneal integrity and excellent visual acuity (Holly et al 1971b). Wetting alteration could change the oxygen-permeability of lenses as a result of hydration, dehydration and the lens surface desiccation (Benjamin et a, 1983). Bier et al (1980) reported that, if the surface of the contact lens does not wet properly, the lens will be uncomfortable and will reduce visual acuity from a disrupted tear film on the lens surface. Wetting changes can affect the quality and quantity of the surface deposition, and the alteration of the contact lens wettability can influence the movement of the contact lens in vivo, and the duration of contact lens wearing.

The wettability of a contact lens is important to the clinician in selecting the appropriate lens material for patients. Ideally, clinicians should be able to analyse the possible changes in wettability as a result of an alteration in environmental factors which could be the key behind successful contact lens wearing (McMonnies 1991). Lakkis et al (1993) surveyed 11 properties of RGP materials: wettability, Dk, strength, machinability, deposit resistance, durability, vision, range of tints, availability, cost and rigidity/stability. Manufacturers viewed rigidity, stability and wettability as the most important, with vision, Dk and deposit resistance also rating highly. Practitioners emphasised the significance of rigidity, stability, Dk and wettability respectively.

Madigan et al (1986) stated that measurement of the in vitro wetting angle of even a soaked or hydrated lens provides, at best, an index of the wettability of the material itself. It is suggested that a better estimate of the wetting performance of a lens would be obtained by measuring the lens wetting angle after it has been worn (Madigan et al, 1983), but some contact lens fitting sets, which are available in the practitioner's offices, are based on the lens design (and not the materials), that limits measurement only to available fitting set materials. This limitation of the material of fitting sets directly or indirectly leads the practitioner to fit the contact

lenses on the basis of in vitro values. The only method, therefore, of predicting the lens wettability is through in vitro measurement (Taylor 1979).

Some relatively high wetting angle materials, such as PMMA, perform adequately if a wetting solution is employed for insertion, as the tear film then forms over the wetting film. But with some other materials, such as silicone, this will not happen unless a special coating is used. With low wetting materials, no auxiliary solutions or special coatings are necessary (Fitzgerald, 1983b). It is generally assumed that a low wetting angle is preferred to a high wetting angle (Woodward, 1984). Jho (1983) stated that wettability is a manifestation of interfacial energy involving the surface that not only gives a validity to wettability phenomena but also helps to find chemical bond energy between solid and material molecules. Naturally, laboratory measurements are not only necessary for research and development, but are also important for predicting clinical on-eye performance.

Hoffman (1983a) discussed the nature of surface properties stating that one of the major problems identified was the need to develop reliable methods to characterise surfaces of bio-materials. Other documents, however, show that there is a significant variability in wetting angle types with each method of measurement (see Table 1.2. and Chapter 3, Hales 1982), and it is not clear which method most effectively describes the wettability of the various lens types (Sarver et al, 1984). Although there is some agreement among different workers, the extreme values vary widely, which is a result of the different procedures and conditions that are used by the investigators. Several factors have been identified causing contact angle variation.

I. **Wetting solution.** Some materials, such as PMMA, have adequate wettability if a wetting solution is employed, after which the tear film forms over the wetting solution (Kokoski et al 1963; Zekman et al 1972; Gelner et al 1989).

II. **Treated contact lenses.** Some contact lens materials, such as silicone, require a special coating to turn the unwettable surface into a wettable one (O'Brien et al 1965, Gesser 1967, Yasuda 1981, Feldman 1981, Yasuda et al 1982,

Fowler et al 1987, Ho et al 1988 and Laferla 1991). The coating lens surface quality, coating procedure and coating material need to be precise (the poly vinyl pyrrolidone and fluorine contents).Increased PVP at the surface result in higher wettability (Blue, 1967).

No	VARIATIONS	θ°	S.D.	Reference
1	24 hours in distilled water	90.0	-	Fatt (1990)
2	" "	59.0	2.0	Gregonis et al (1982)
3	Air in water, Receding	49.0	2.0	Jho (1983)
4	7 days in distilled water	45.5	0.5	Keates (1984)
5	PMMA # C, In saline	45.3	3.6	Poster (1984)
6	" # Blue In saline	41.6	2.9	Poster (1984)
7	" # 4, Lab E	28.0	0.5	Poster et al (1978)
8	" # 4, Lab B	25.3	1.2	Poster et al (1978)
10	" # 4	24.3	3.8	Anan (1979)
11	" # 4, Lab A	19.0	0.7	Poster et al (1978)
12	" Clear	18.3	0.5	Anan (1979)

Table 1.2. Wetting angle values of hydrated PMMA materials using bubble techniques by various authors.

III. **Soft contact lens manufacturing.** No auxiliary solutions, treating solution or special coatings are necessary with hydrated hydrogels materials, although the variation in hydrogel lens manufacturing produces different lens surface wettability (see 2.3).

IV. **Polymer manufacturing.** More wettable contact lens materials (Rankin et al 1970, Gaylord 1974 and Ewbank 1992). The main factor determining wettability appears to be the chemical structure of the polymeric network at the interface (Braudo et al, 1974).

V. **Contact lens manufacturing,** Such as polishing (Meszaros 1986, Herskowitz 1989) and Lens surface treatments (Gesser et al, 1965 and 1967).

Several phenomena have been suggested as affecting the polymer structure or contact lens surface wettability. The measurement of wettability can, however help to determine the effects of :-

1. Polymerisation quality and polymer impurity (Hattori et al, 1978; Keller, 1980 and Jones 1994).
2. Differences between manufacturing methods, such as moulding and lathing-polishing.
3. Polishing quality.
4. Surface treatment, such as coating.
5. Contact lens care products.
6. Contact lens spoilation.
7. Contact lens ageing.

1.6. Purpose

The purpose of this research is to:

a. Introduce a method to prepare hydrated contact lens surfaces, to measure both rigid and soft contact lens wettability.

b. Develop novel, straightforward techniques in vitro which are relevant to in vivo performance, to measure contact lens wettability.

c. Measure and observe the wettability of both rigid and soft contact lens surfaces before and after wearing.

d. Develop a new technique to measure the surface hydrophilicity of both soft and hard contact lenses.

e. Measure and observe the hydrophilicity of both rigid and soft contact lens surfaces before and after wearing.

f. Study the effect of the length of time wearing contact lenses on the wettability and hydrophilicity of the contact lens surface. Variations in the values are the subject of part of this research.

g. Establish the effect of the wetting solution on the contact lens surface's wettability and hydrophilicity.

h. Investigate the effect of the manufacturing contact lens processes of lathe cut, cast moulded and spin cast on wettability and surface hydrophilicity values, for both rigid and soft contact lenses.

i. Investigate standardising the current methods of sessile drop and dynamic contact angle (DCA) for both soft and rigid contact lenses.

Chapter 2. Contact Lens Polymers

2.1. Polymers

2.1.1. Introduction

Polymer properties have been recognised as being important in the use of materials for contact lenses. Among these properties, the surface wettability and surface hydrophilicity have been found as important properties in material design and contact lens production as might be oxygen permeability (Table 2.1). Contact lens properties have been influenced by many factors, including the polymer material structures, type of polymerisation (configuration), kinds of contact lens manufacturing and contamination.

Material Characteristics	Eye-Contact Lens Function
Oxygen Permeability	Corneal Respiration
Surface Property	Corneal Respiration Tear Film Integrity Deposit Formation
Mechanical stability	Visual Stability and Comfort

Table 2.1. The contact lens properties in relation to eye/contact lens function.

2.1.2. Polymers Structure

Contact lens materials are synthetic polymers, often called macromolecules, while the small molecules that become linked together by covalent bonds are known as monomers. Under appropriate conditions, the molecules (the monomers) combine with each other, creating long chains of repeating units, with the final result being a large molecule (macromolecule), that is referred to as a polymer, which can exist as liquids, hydrogels or solids (rubbery and glassy solids).

The average number of monomers in the long chain is termed the degree of polymerisation (DP) and may be 100 to 10,000 for most materials, while the molecular weight of most polymers is between 10,000 and 1,000,000. Some polymers occur in nature, such as cellulose whereas other polymers are produced synthetically in the laboratory, example being PMMA that is linear polymer. Polymers can be classified in several different ways, according to their monomer arrangements there are five types of polymers (Figure 2.1):

a. **Linear Homo-polymer.** The polymer can be a homo-polymer, in which only one type of monomer is used, and hence each repeating unit is the same.

b. **Linear Random Copolymer.** When more than one monomer is present in a copolymer (a polymer formed by the simultaneous polymerisation of two or more monomers), which has two or more repeating units (GP 1989). These can be in random order, with relative frequencies depending on the concentration of the monomers and their relative reactivates. Repeating units can also be linked in a more orderly or non-random way.

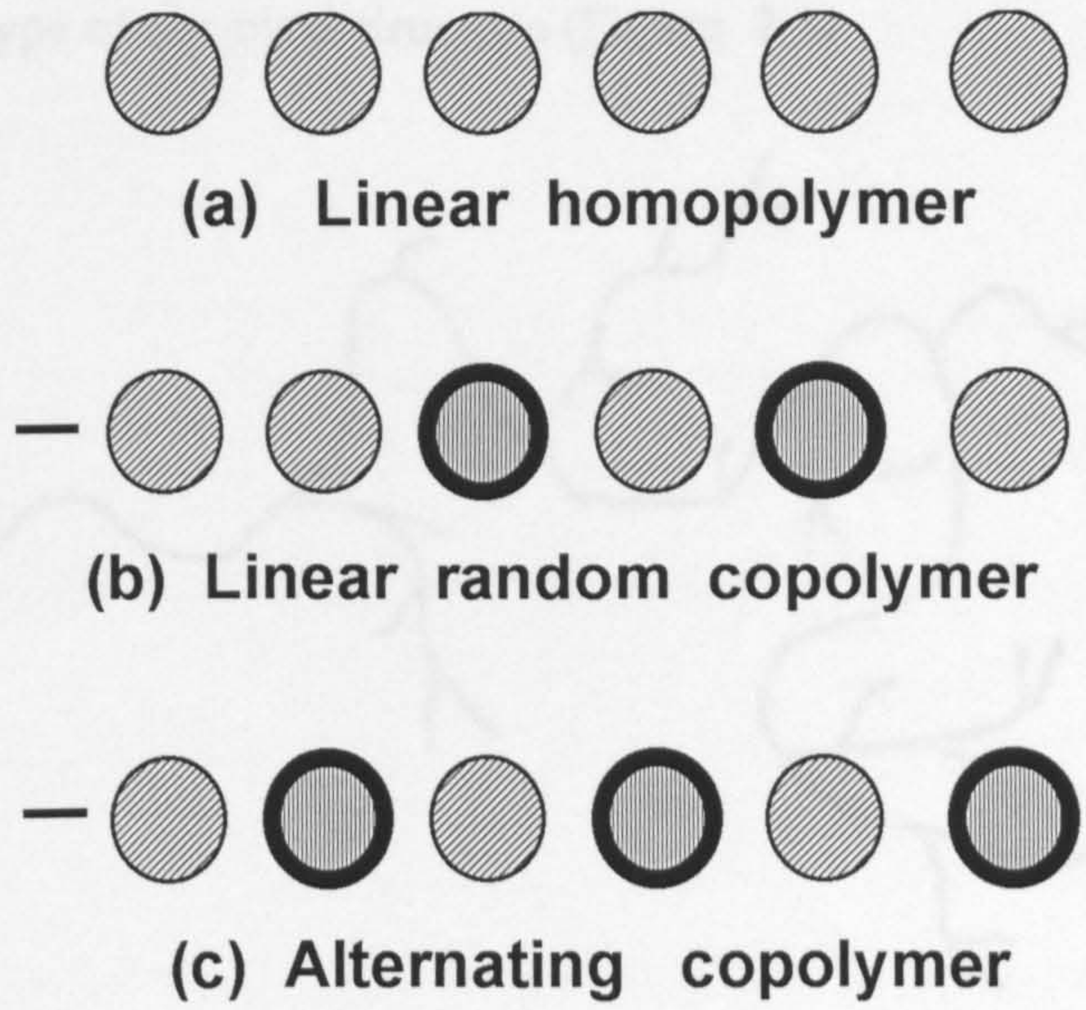
c. **Alternating Copolymer.** Where there are two different monomers with such chemical structures that one will react only with the other, an alternating copolymer is created. In other words, the monomers alternate in a fixed order.

d. **Block Copolymer.** A copolymer can also be formed that has repeating sequences of monomers, in which one polymer chain of one type of monomer is joined to another polymer chain of a different type of monomer.

e. **Graft Copolymer,** A copolymer is called a graft copolymer, in which one monomer is attached to a polymer of another monomer.

The physical and chemical properties of a copolymer are different, depending on whether it is a random, alternating block or graft copolymer and the relative percentage of each monomer used. The addition of a small amount of a second monomer can differentiate the properties of a polymer from those that a homo-

polymer would normally possess. The structure of the polymer affects the physical and chemical property of the material, so that the polymer can thus also be classified by the shape and the structure of the copolymer. They are (Bier et al 1980):



(a) Linear homopolymer

(b) Linear random copolymer

(c) Alternating copolymer

(d) Block copolymer

(e) Graft copolymer

Figure 2.1. Five types of monomer arrangements to form different polymers.

i. **Branch Polymer;** As it can be seen on Figure 2.2, there is not only a long chain but also connected branching of the same repeating structure.

ii. **Cross-Linked Polymer;** Where adjacent long polymer chains are connected to each other by side chains or molecules. Many (hydrogel) lens materials have this type of chemical structure (Figure 2.3).

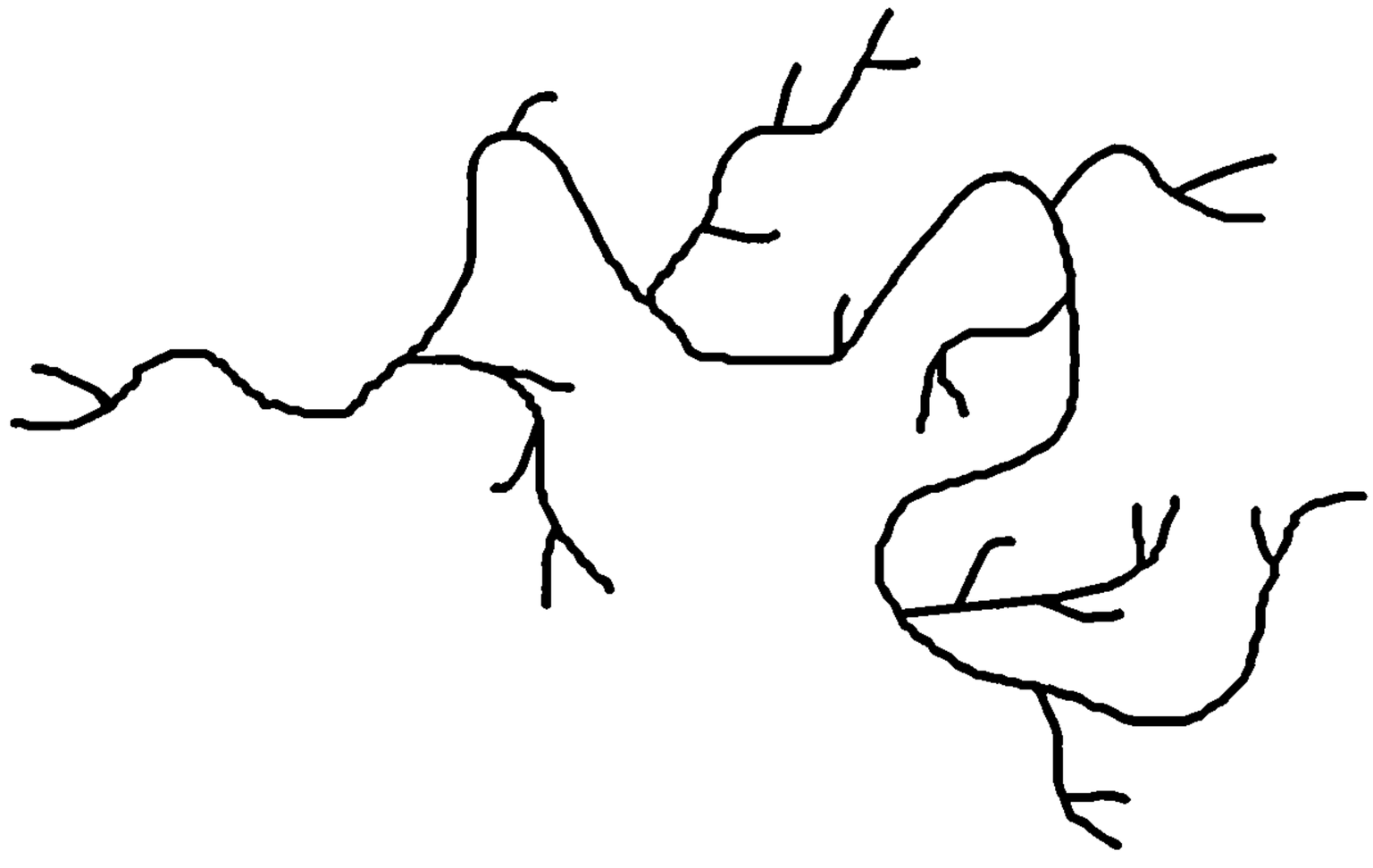


Figure 2.2. Branch polymer.

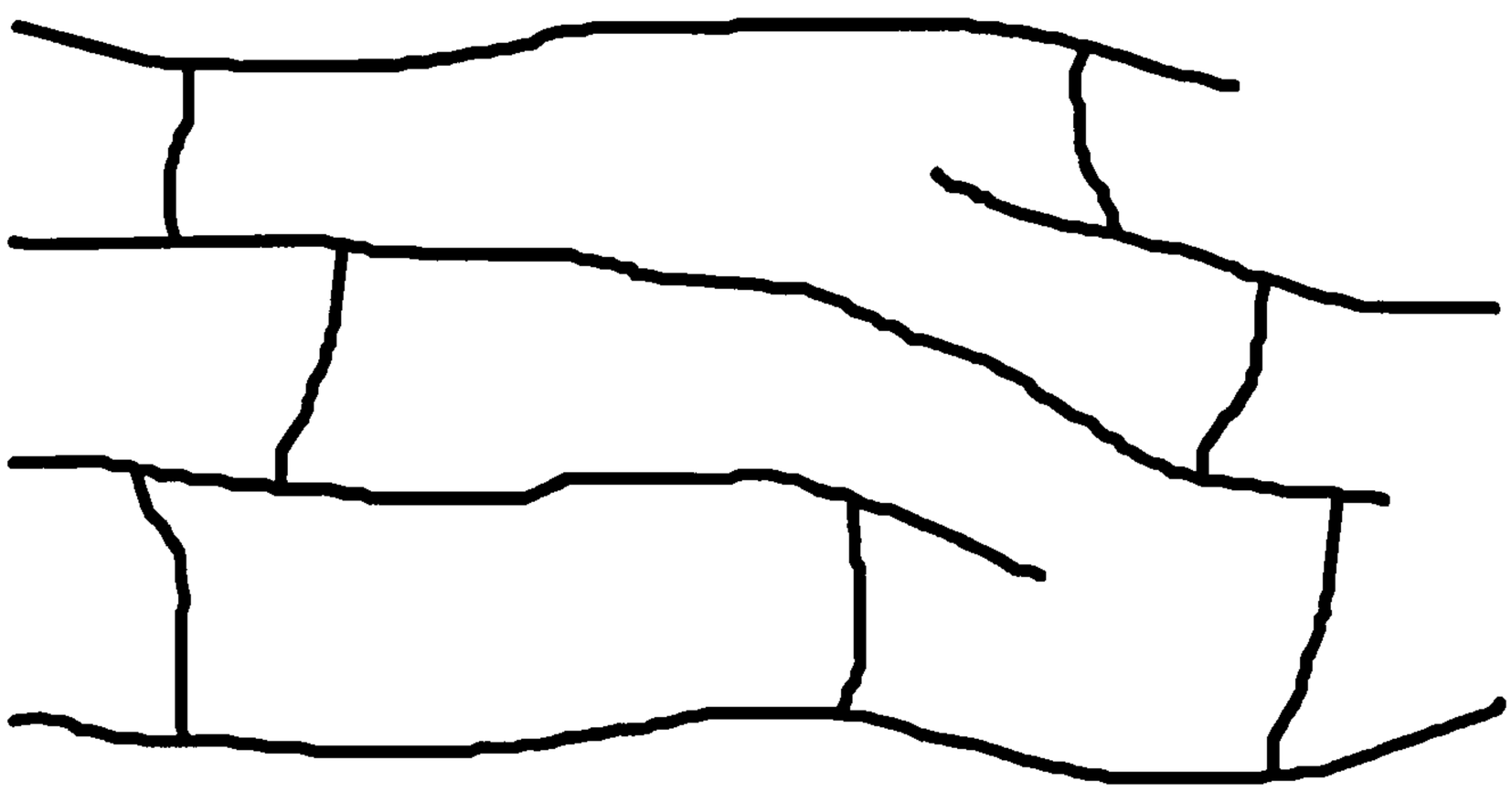


Figure 2.3. Cross-linked polymer.

The geometrical arrangement of atoms in a polymer is important because it affects the properties of a polymer. Certain arrangements, often referred to as configurations, can not be altered unless chemical bonds are adjusted and, therefore, they are classified as (Refojo 1978, Figure 2.4):

- **Isotactic**. When a large proportion of the substituent side groups lies only on one side of a chain.

- **Syndiotactic**. When the substituent groups of polymer can alternately lie above and below the plane.

- **Atactic.** When the substituent groups of polymer can be in a random sequence.

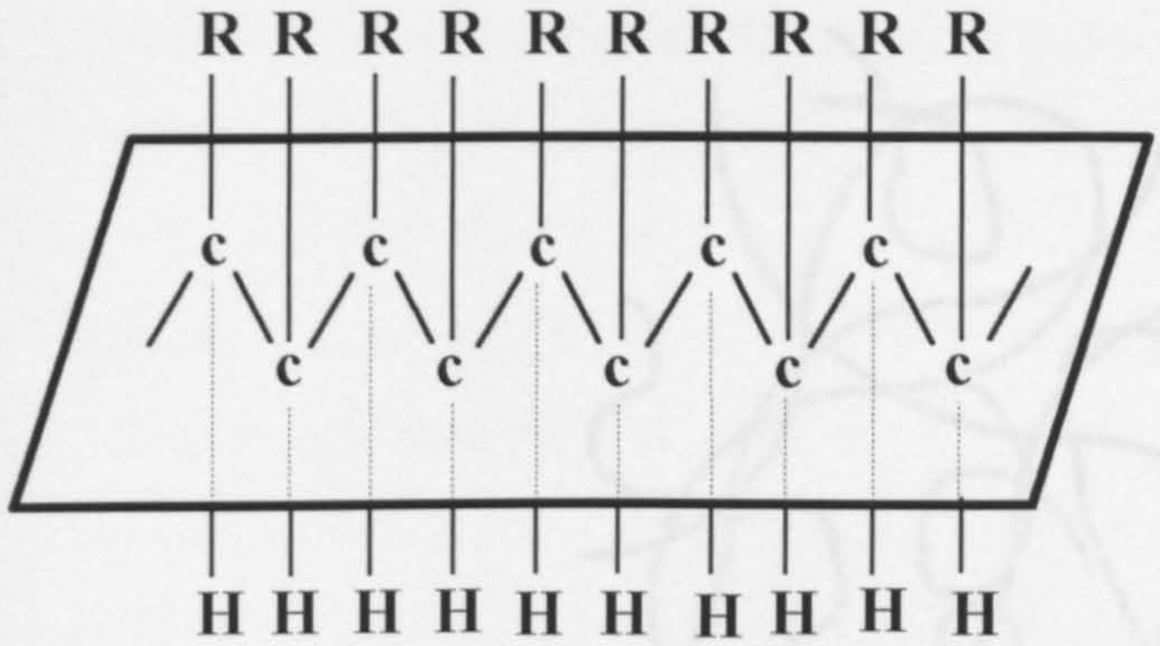
- **Cis isomers.** In this configuration, involved carbon double bonds prevent rotation around a bond and hold constituent side groups in fixed positions. When similar side groups are on the same side of the bond, it is called cis (Smith et al 1982a).

- **Trans isomers.** When similar side groups of cis are on opposite sides, it is called 'trans'.

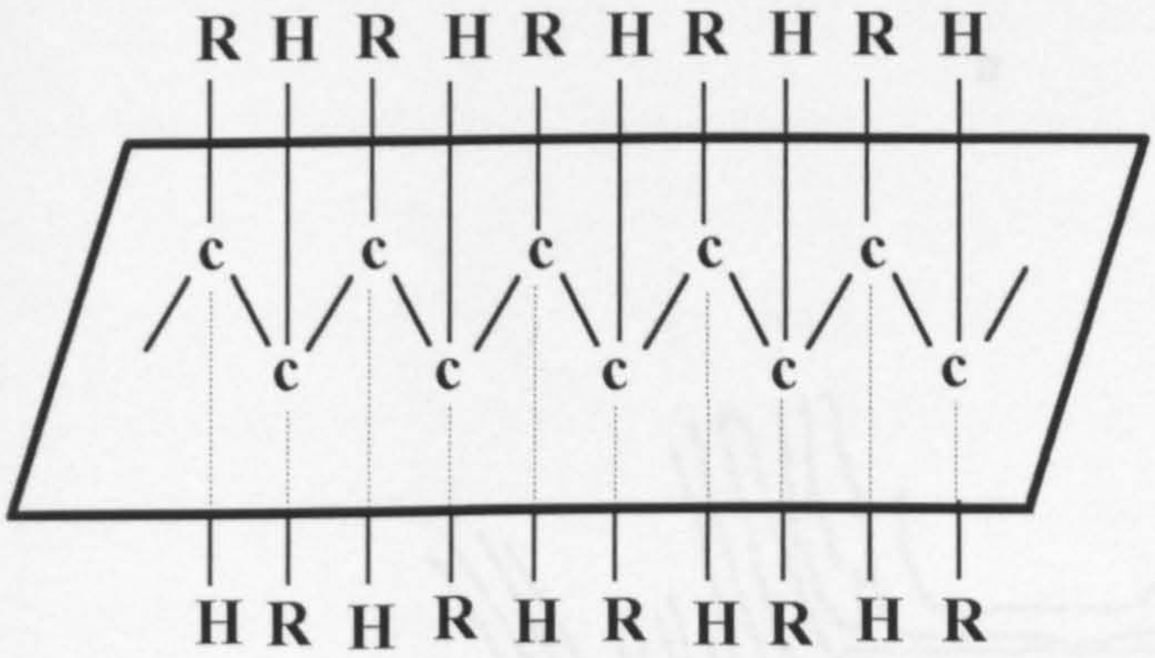
Polymers are often classified as either crystalline or amorphous (Figure 2.5. a and b):

I. **Crystalline polymers.** They have a geometrically regular structure, are stiff are extremely resistant to chemicals and are tough, but have limited uses as contact lens materials because of poor optical qualities, such as Nylon.

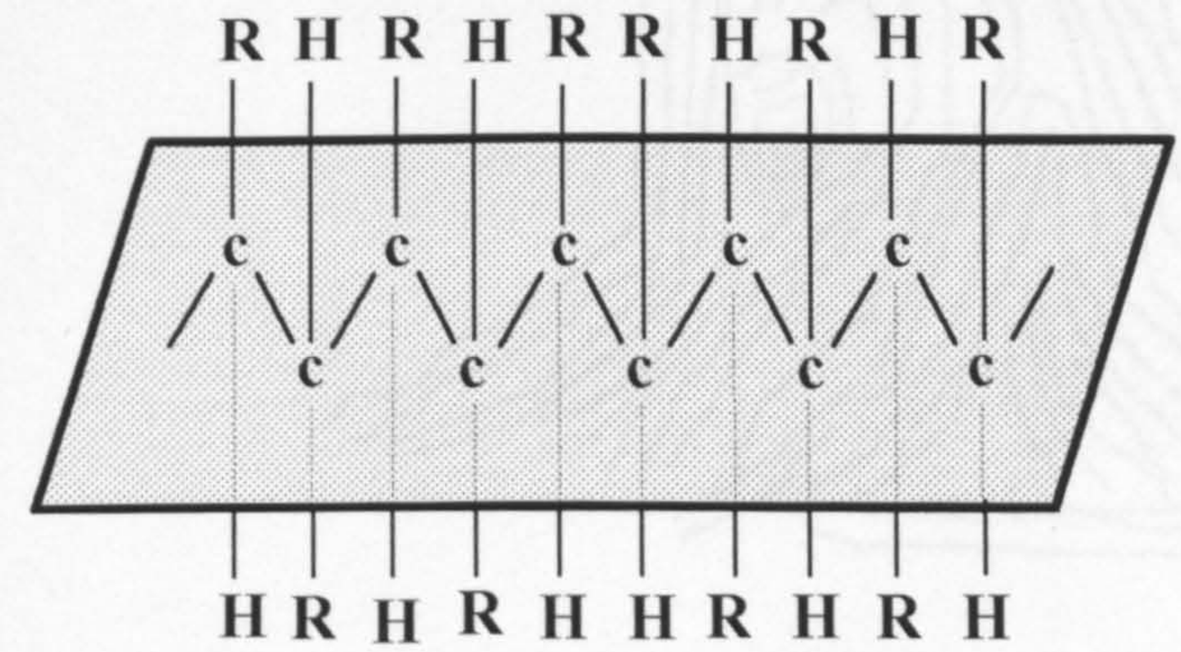
II. **Amorphous polymers.** Amorphous polymers do not have a regular structure and the polymer chains intermingle and are in random positions. Most contact lens materials are of this form.



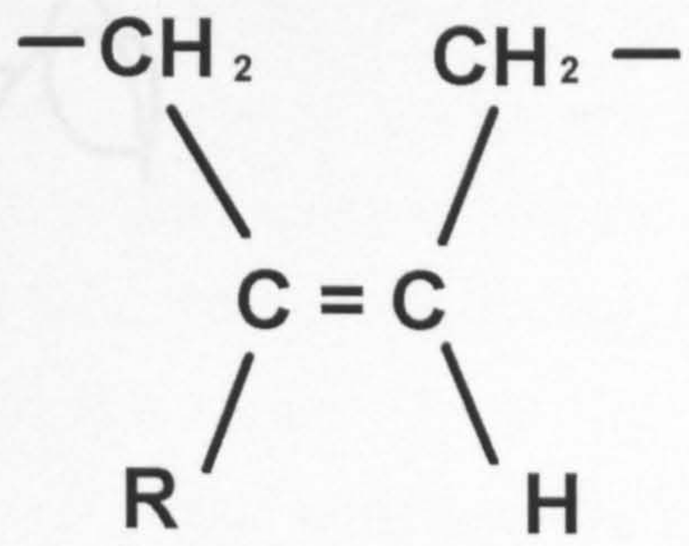
Isotactic



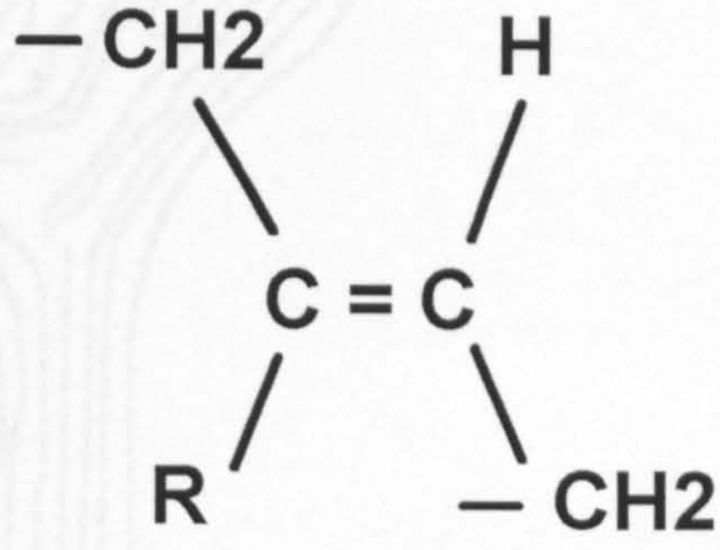
Syndiotactic



Atactic

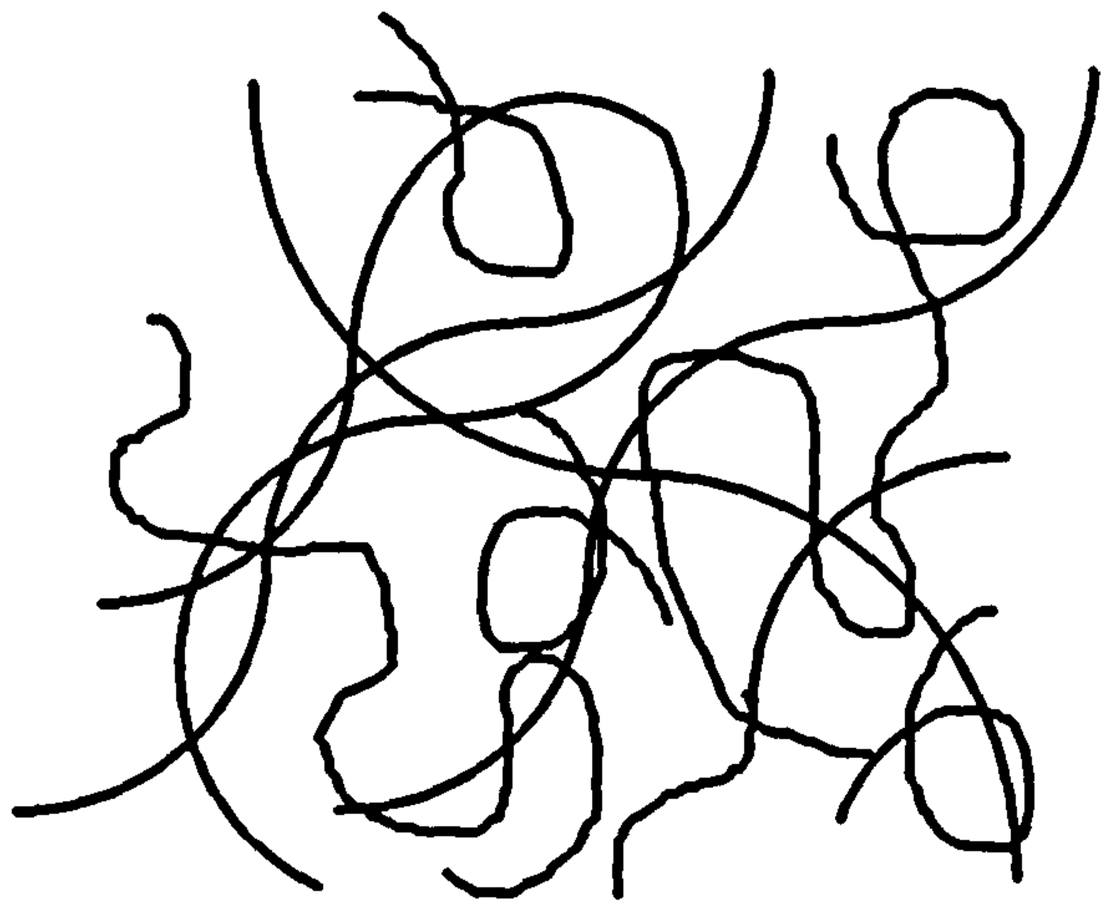


Cis

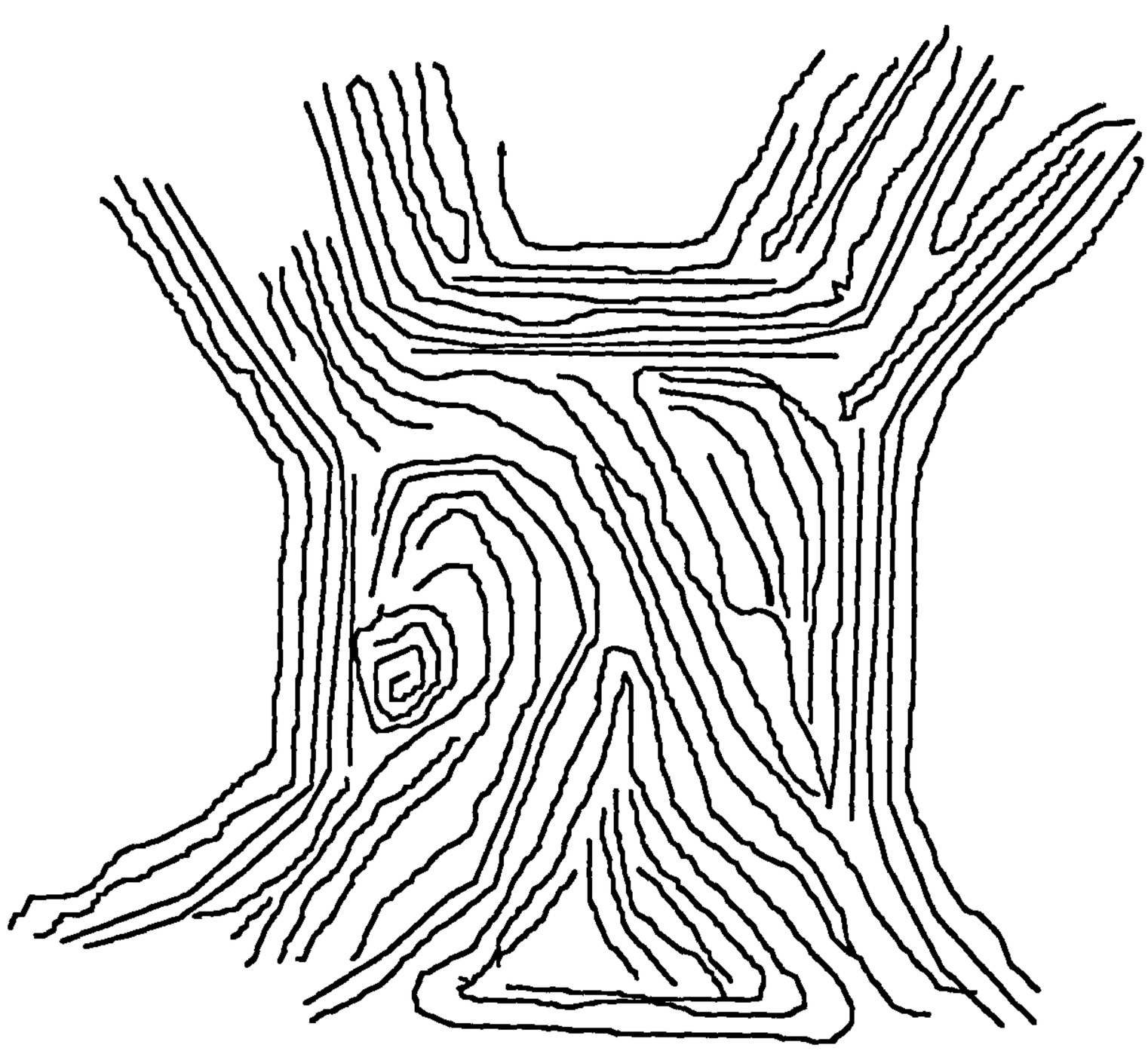


Trans

Figure 2.4. Isotactic, syndiotactic, atactic, cis and trans polymer configurations (Bier et al 1980).



a



b

Figure 2.5. **(a)** amorphous and **(b)** crystalline form of polymers.

2.1.3. Polymerisation Methods

2.1.3.1. Addition Polymerisation

Addition polymers are formed through the reaction of the monomer units with each other. In the resulting chain therefore, the repeating unit has the same composition as the monomer from which it is derived. The monomer is usually a compound, with one or more carbon-carbon double bonds and it is subjected to an initiator (which is activated by heat or another form of energy), the double bond between the two carbon atoms is broken, resulting in a new compound with an unpaired electron on the end carbon atoms. This transient compound is the free radical of the monomer which combines with another monomer, resulting in another new compound. Again, an un-shared electron is present at the end carbon of the new compound, which combines with another monomer unit, forming yet another, longer compound with an un-shared electron on the end carbon through this addition of monomers, the polymer chain is propagated almost instantaneously. The growth of the polymer chain is terminated when the free radical is lost. Depending on the polymerisation technique, the growing chain may be terminated by recombination, disproportionation or chain transfer. Typical examples of addition polymerisation are the synthesis of PMMA, which could be polymerised by one of the following techniques:

a. Initiator Materials. Several substances may be used to initiate (activate) the monomer to polymerise, for example, benzoyl peroxide. In the first step, a molecule of benzoyl peroxide, under the influence of heat, fragments to form two benzoate free radicals, in each of which the oxygen atom has an unpaired electron. The oxygen atom now seeks another electron to complete its outer orbital with eight electrons (Figure 2.6), while the benzoate free radical reacts with the MMA monomer, resulting in a free radical of MMA in the following way. The MMA monomer has a carbon-to-carbon double bond, in which the carbon atoms share four electrons (Figure 2.7), one of which becomes paired with the unpaired electron of the benzoate free radical, leaving three electrons. Two of these three electrons form a stable covalent bond between the carbon atoms, leaving one unpaired electron on the end carbon of the polymer.

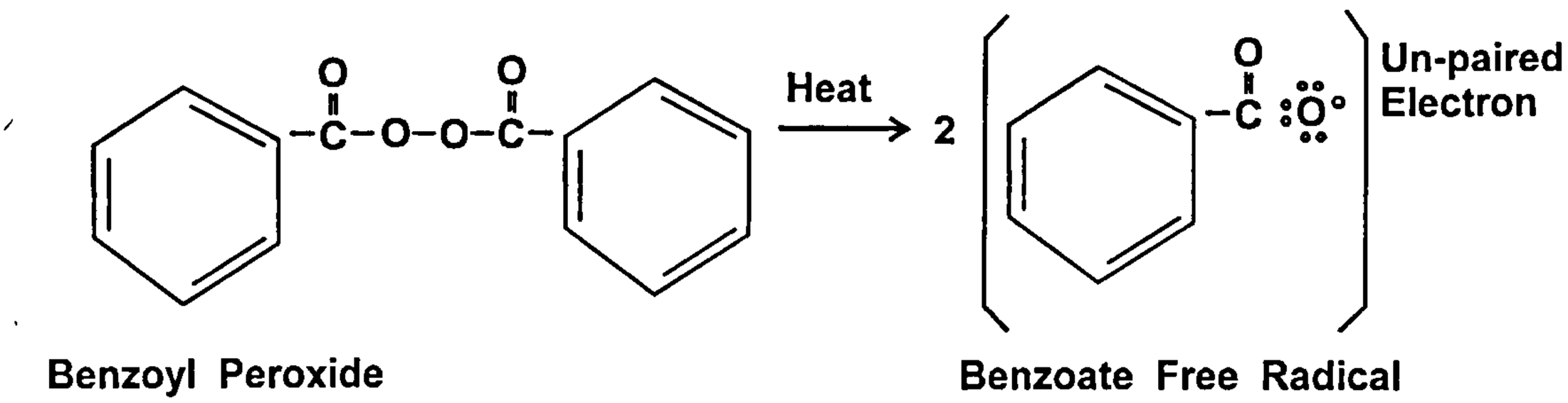
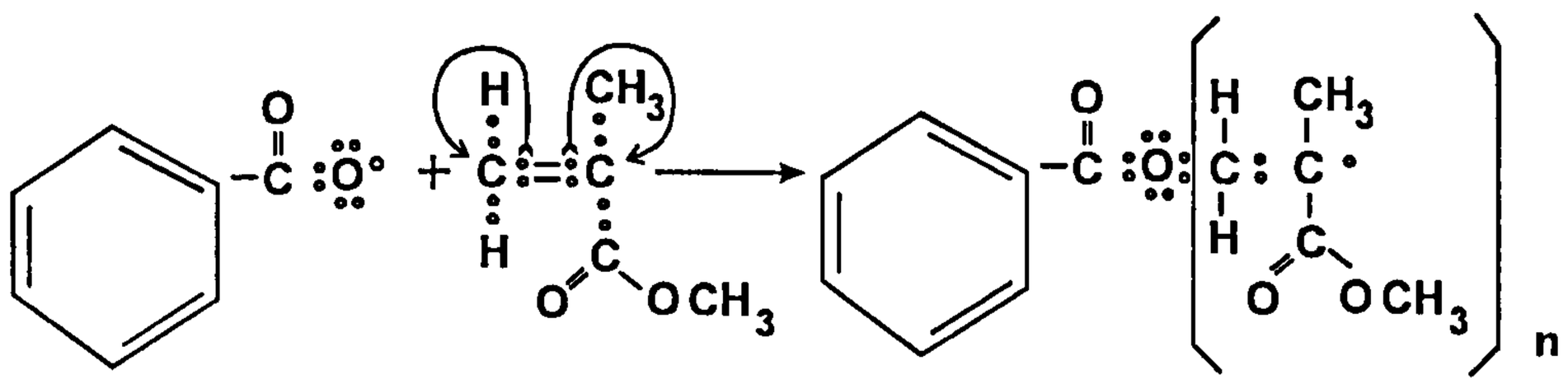


Figure 2.6. Activation of the initiator (Benzoyl peroxide). Outer orbital of the oxygen atom has an unpaired electron. Benzoyl peroxide initiates the reaction in which a monomer of MMA becomes a free radical, and the Benzoyl peroxide molecule reacts with and is attached to the monomer of MMA.



Benzoate Free Radical

Breakage of the carbon-to-carbon double bond (MMA)

Addition of a free radical to the monomer. propagation the monomer to polymer (PMMA)

Figure 2.7. Breakage of the carbon-to-carbon double bond. Electron dot representation. PMMA consists of a hydrocarbon backbone, to which one methyl group and one methoxycarboxyl group are attached.

B. Addition of the Free Radical. The MMA free radical joins another monomer of MMA, resulting in a new intermediate compound that has an un-shared electron on the carbon the polymer chain is then propagated by the addition of new monomers of MMA, with the resultant chain possibly consisting of thousands of monomer units (Figure 2.7).

2.1.3.2. Condensation Polymerisation

Condensation polymers are produced by the reaction of monomeric units with each other, eliminating a small molecule, such as water. Within the polymer, the repeating unit is different from the monomer from which it was derived which is because a molecule, such as water, was eliminated during the polymerisation process. For the reaction to occur, one monomer must have a functional group that can react with the functional group of a second monomer, such the hydroxyl group (-OH). Examples of condensation polymerisation include the formation of silicone and cellulose, with silicone being synthesised in the laboratory, while cellulose occurs naturally.

Silicone (poly siloxane) results from the condensation polymerisation of monomer units of silanol. Initially, two molecules of silanol combine to form siloxane, and, in a further condensation reaction, siloxane combines with another molecule of silanol. The final polymer, poly (siloxane), is frequently used as a construction material for contact lenses ('Silsoft' and 'Silicon' manufactured by Bausch and Lomb). The polymerisation of the poly (siloxane) begins with a halosilane that is hydrolysed to form silanol, which is a very reactive monomer. (A halosilane is a compound composed of halogen atoms, a silicone atom, and alkyl groups.) The condensation polymerisation of two molecules of silanol yields siloxane and water (Figure. 2.8a), and the siloxane molecule then combines with another molecule of silanol (Figure 2.8.b), which begins the formation of a long chain (polymer).

2.1.4. Polymerisation Termination.

Polymerisation can be terminated by a number methods:

a. Recombination Method. This occurs when two free radicals meet, share their un-paired electrons, and so form a covalent bond between the atoms. As there is no longer an unpaired electron on the end carbon of the chain, polymerisation of the chain is completed (Figure 2.9).

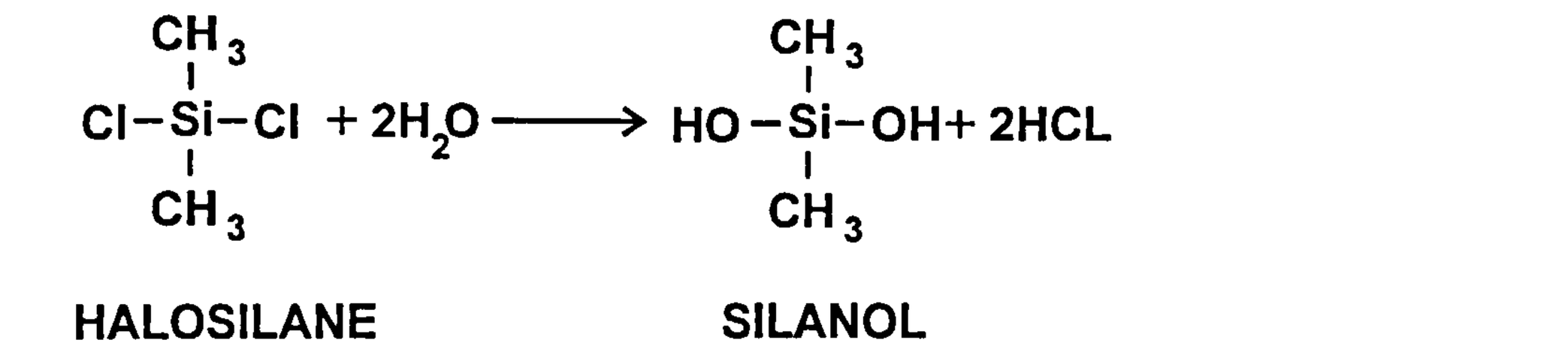


Figure 2.8. The condensation polymerisation: **a.** the formation of silanol and **b.** the formation of siloxane, which is termed silicone polymer.

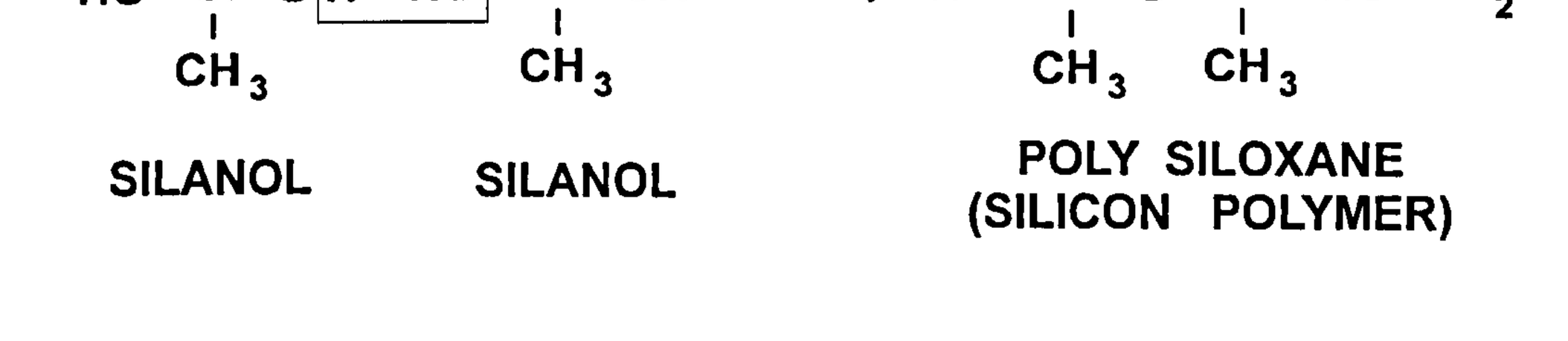


Figure 2.9. Termination of polymerisation by the recombination method, in which two unpaired electrons of two free radicals one shared.

c. Disproportionation Method. The hydrogen atom and one of its shared electrons are extracted from the carbon-hydrogen bond of the next-to-last carbon atom. This leaves an un-shared electron, which then combines with the un-shared

electron on the end carbon, resulting in a double covalent bond. This terminates the polymerisation of the chain, and the hydrogen atom that was extracted with its single electron then combines with the free radical of another growing chain and, thus, terminates the polymerisation of the chain (Figure 2.10).

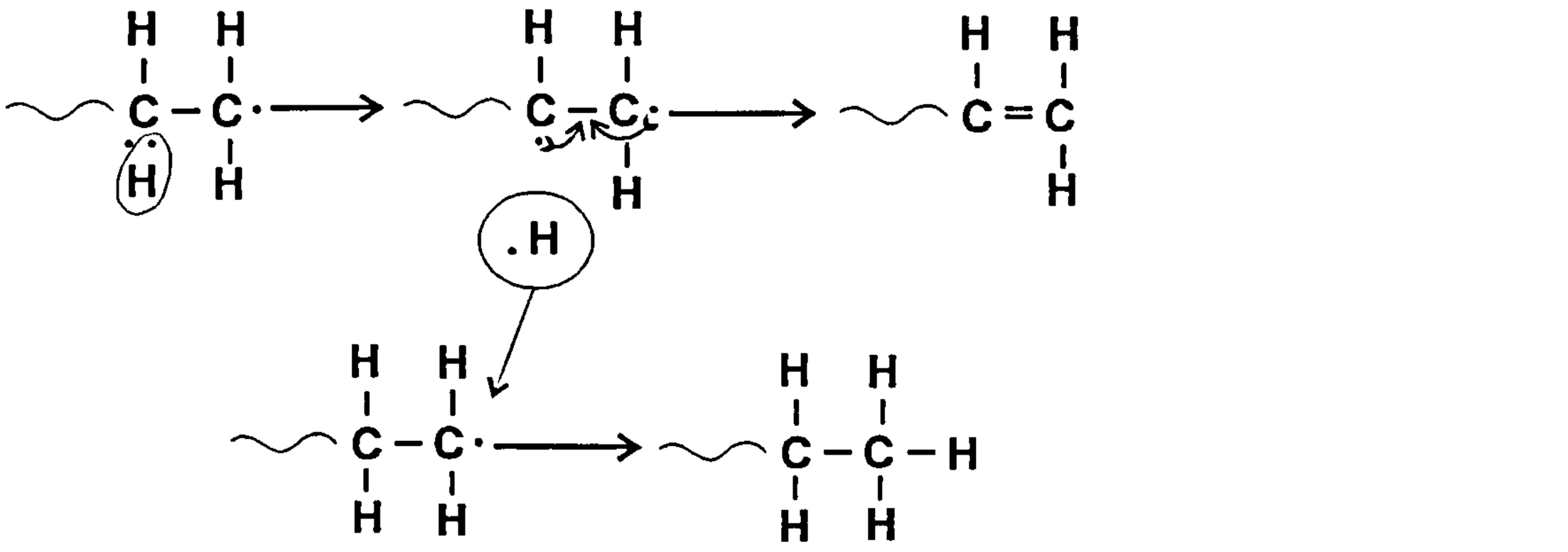


Figure 2.10. Termination of polymerisation by the disproportionation method.

b. Chain Transfer. The growing polymer chain, which has a free radical on the end carbon, pulls a hydrogen atom from another polymer chain (in which polymerisation has been completed). The polymerisation of the previous growing polymer chain is now complete, although chain in which polymerisation has been completed now has a free radical and grows again. As the hydrogen atom was transferred from one chain to another, the process is identified as chain transfer (Figure 2.11).

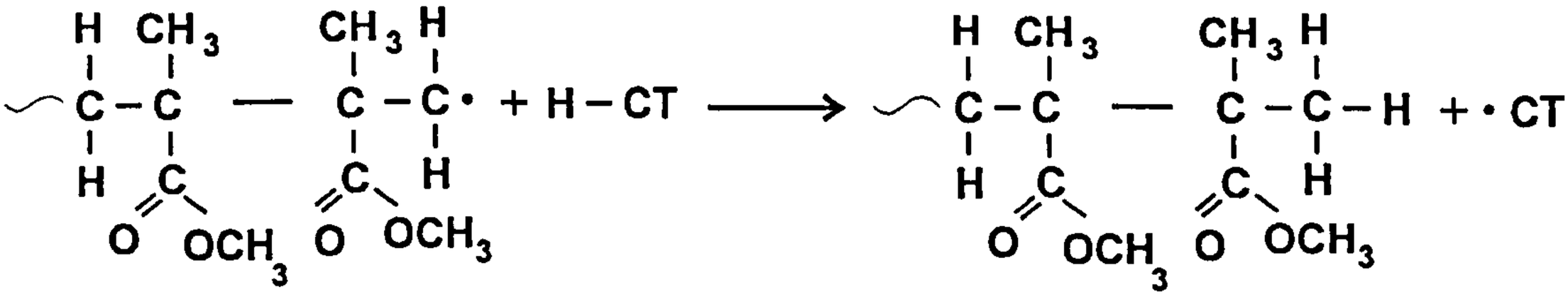


Figure 2.11. Termination of polymerisation by chain transfer.

2.2. Rigid and Soft Contact Lens Materials

2.2.1. Rigid Contact Lens Polymers

PMMA is an amorphous thermoplastic, composed of linear-linked polymers (70-75 per cent syndiotactic) of MMA. As can be seen in Figure 2.12, both methyl groups (–CH3) and carboxyl groups (–CH2–, =CO) are exposed at the surface of the surrounding liquid and that there are no free OH-groups. Oxygen of the carboxyl (=C=O) group has a relatively negative charge, and because water is a polar compound existing in a dipole state the hydrogen atom of water will be attracted to the oxygen atom of the carboxyl group, while is hydrogen bonding. In the carboxyl group, however, this hydrogen bonding is relatively weak, so only a limited amount of wetting occurs. Furthermore, as the methyl groups are non-polar, the water is not able to bind to these groups (Wyckoff 1980). The methyl groups act as neutral wettability surface (Figure 2.13b), which means they neither attract, nor repel the water molecules. PMMA wettability values are used as a standard to compare the wettability of the other contact lens materials (Stahl et al, 1974; Table 2.2) and the contact angle for conventional PMMA is 60°-75°.

Advantages of Standard PMMA	**Disadvantages of Standard PMMA**
• Good optical qualities • Greater mechanical stability • Little tendency to accumulate deposits	• Practically no oxygen permeability • Moderate wettability • Unsuitability for permanent wear lenses
Bp Flex is a composition of cross-linked PMMA and is claimed to have: • a good wettability (Wyckoff 1980) • a degree of gas-permeability (Hill 1977a)	

Table 2.2. Some advantages and disadvantages of the standard and Bp flex PMMA contact lenses.

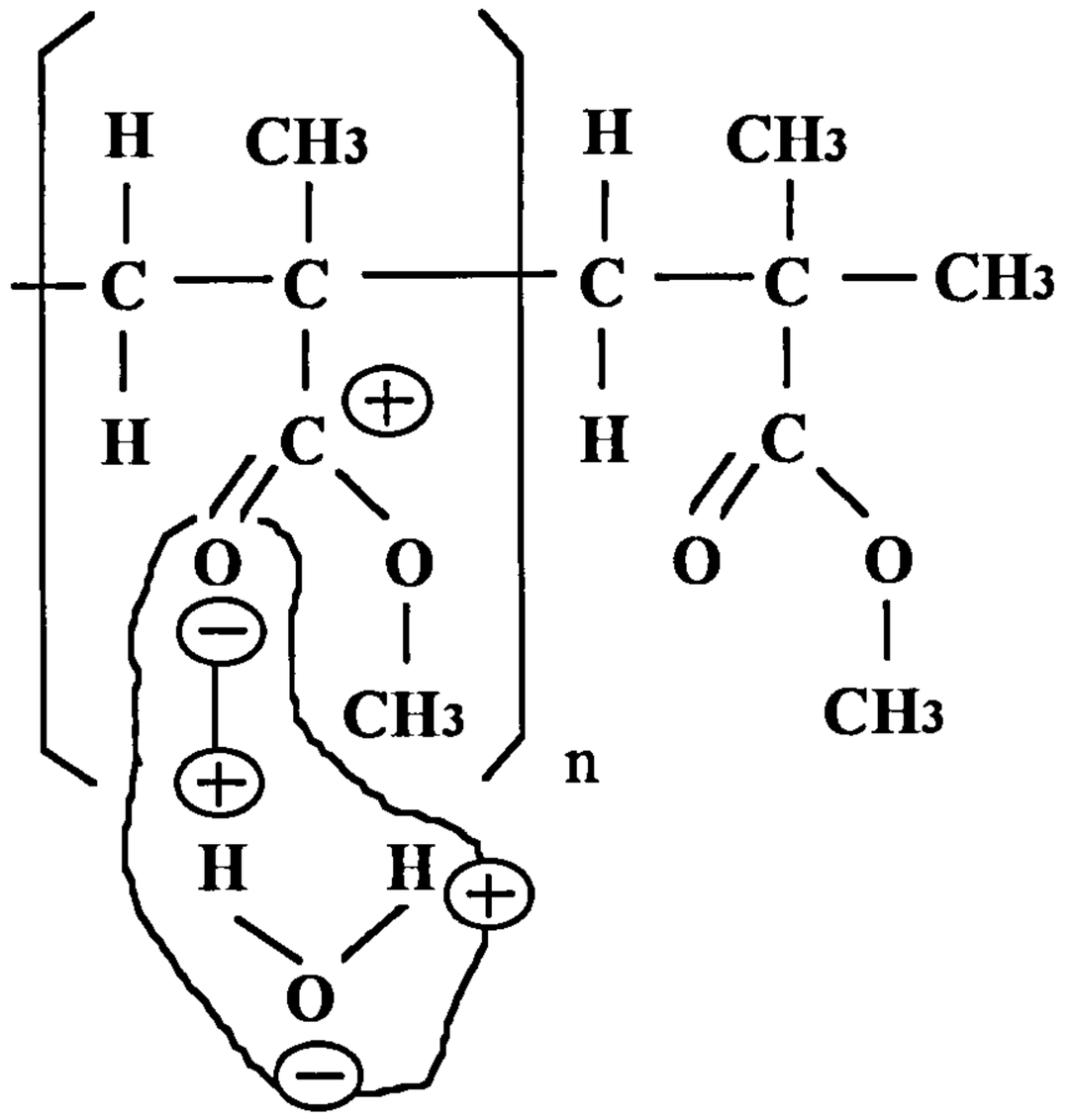


Figure 2.12. The wettability of PMMA. It consists of a hydrocarbon, backbone to which one methyl group and one methoxycarboxyl group are attached. The hydrogen bond of water a has relatively positive charge, while the oxygen atom has a relatively negative charge. The carbon-hydrogen bonds of the methyl group are non-polar, and carbon does not have a net electrical charge in relation to hydrogen. as these bonds are not polar, the methyl groups are not wettable. By contrast, the oxygen of the carboxyl group, because of its tendency to attract electrons, has a slightly negative charge, which produces wettability.

2.2.2. Soft Contact Lens Materials

Soft contact lenses have been developed from a large group of acrylic polymers that contain water attractive groups, such as hydroxyethyl or glyceryl side chains, so the resulting polymer will spontaneously attract water. The water content of these polymers can be changed by increasing or reducing the amount of cross-linking of the polymer, with some degree of polymer cross-linking necessary to prevent the hydrogel from going into solution (Gumpelmayer, 1972; Stone et al, 1989). One would assume that these hydrogels have a wettable surface, although, this is only partially true (see Chapters 5 and 6). The reports reveal that when these gels are exposed to saturated water vapour or to non-polar liquids, they have only moderate wettability. In fact, the wettability of the surface varies inversely (usually) with the water content.

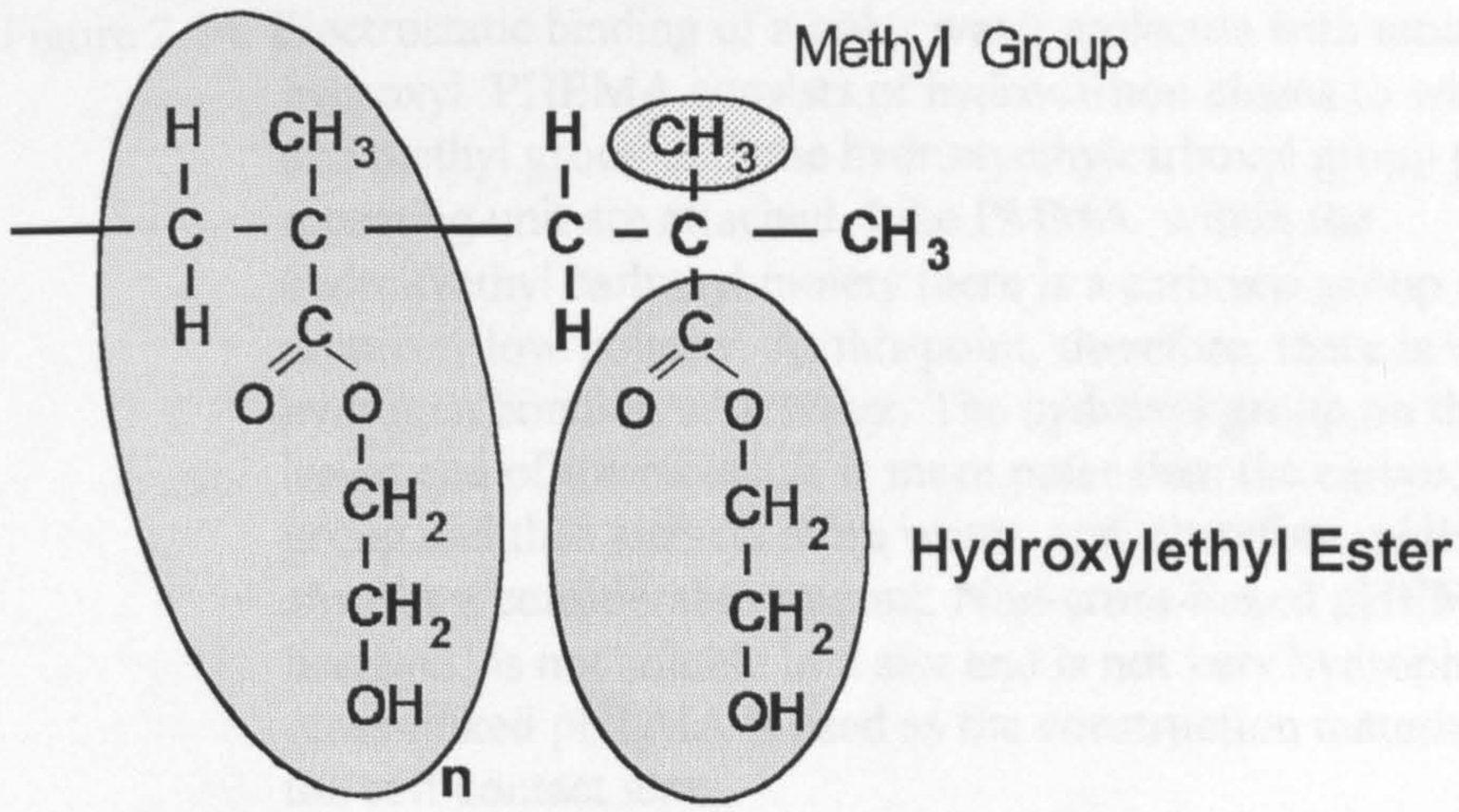


Figure 2.13. The pHEMA soft contact lens material structure.

PHEMA is the most extensively used hydrogel (Figure 2.13), is amorphous and cross-linking It is hydrophilic because of the hydroxyl groups (-OH) on the side chains of the polymer. These groups have a slightly negative charge and, since water molecules are polar, there are electrostatic forces created that allow the water to be taken up by the polymer (Figure 2.14). For the same reason, any small, polar molecule will be absorbed by the polymer and will cause it to swell.

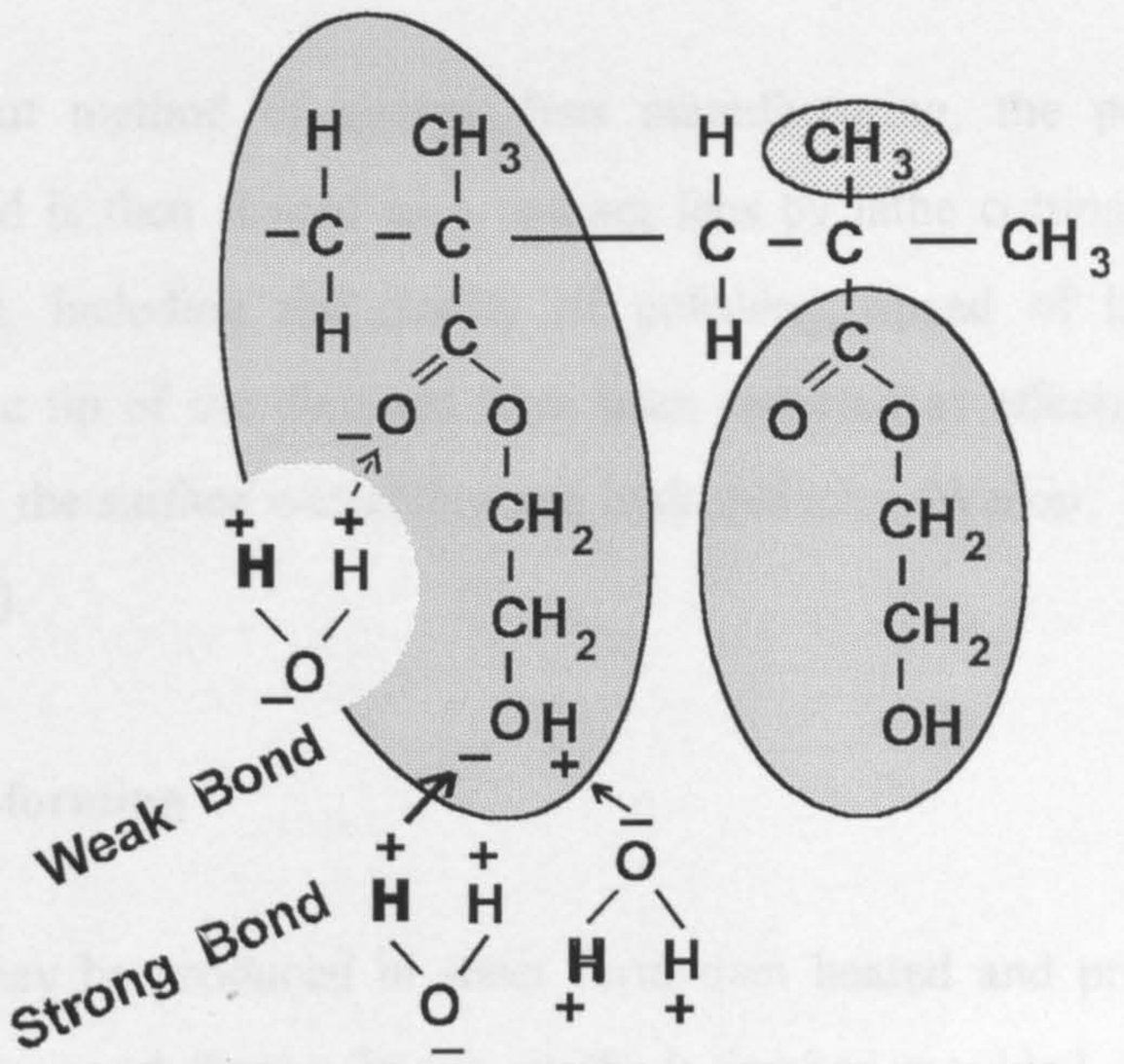


Figure 2.14. Electrostatic binding of a polar water molecule with molar hydroxyl. PHEMA consists of hydrocarbon chains to which one methyl group and one hydroxyethylcarboxyl group per repeating unit are attached. Like PMMA, within the hydroxyethyl carboxyl moiety there is a carboxyl group of relatively low polarity. At this point, therefore, there is weak hydrogen bonding with water. The hydroxyl group on the lower end of the molecule is more polar than the carboxyl group and thus attracts more water, and, therefore, pHEMA absorbs a considerable amount. Non-cross-linked pHEMA, however, is not soluble in water and is not very hydrophilic. cross-linked pHEMA is used as the construction material of the soft contact lens.

2.3. Contact Lens Manufacturing Techniques

2.3.1. Lathe Cut

In the lathe cut method of contact lens manufacturing, the polymer is bulk polymerised and is then shaped as a contact lens by lathe cutting and polishing. Several factors, including the quality of polishing, speed of lathing and the sharpness of the tip of the diamond have been reported as effecting lens surface quality, such as the surface wettability and hydrophilicity (Walker, 1982 and 1988, Meszaros 1986).

2.3.2. Thermoforming

The polymer may be produced in sheet form then heated and pressurised to be moulded into designed shapes. In this method, finished moulded or semi-finished moulded lenses can be made, and the semi-finished lens is then edged to the final product. The essential factor for the mouldable material is to have a linear un-cross-linked structure. It can subsequently be cross-linked in the mould for the necessary physical stability. A moulded material of sufficient rigidity can easily be made in the lathe-cut forms, while the cast moulded method may be used to manufacture rigid contact lenses of PMMA and Fluorofocon.

2.3.3. Cast Moulded

In this contact lens production method a material may be polymerised in a shaped contact lens mould (Acuvue, Medalist 66, Hydron Z4 and SeeQuence). The advantages of moulded contact lens productions would be the cheaper cost and a better surface quality.

2.3.4. Spin Casting

In the spin casting method of manufacturing soft contact lenses, a liquid monomer mixture in a lens mould is spun about its central axis to complete polymerisation, and the centrifugal force results in the direct formation of a lens form. The finished

de-hydrated lens is then stored in a sterile saline condition and autoclaved to produce a soft contact lens (Wichterle et al 1960 and 1961). According to Coombs (1982), several equations have been documented for this kind of lens production, for example a cylindrical co-ordinate system:

$$z(r) = \frac{w^2(r)^2}{2g} + \frac{\sigma}{pg}\left[\frac{1}{R_s} + \frac{1}{R_t}\right] \qquad (6)$$

Where,

z(r)	is surface height
w	is rotational speed in radians per second
g	is gravitational acceleration
σ	is surface tension
p	is liquid density
Rs	is liquid sagitta radius of curvature
Rt	is surface tangential radius of curvature

Because of high precision techniques involved in the manufacture of such small articles and the nature of polymerisation (ie random co-polymerisation), reproducibility of this kind of contact lens manufacturing was unsatisfactory. But in recent years, the use of high technology has resulted in a massive production of inexpensive disposable soft contact lenses and there are some differences between the spin cast and lathe cut lenses in terms of strength and extensibility (Tighe et al 1990, see Chapter 5 and 6). It also reported (Dubow 1992) that rigid contact lenses of Fluorofocon A (Fluorocarbon) material can be manufactured by spin-cast for both daily or extended wear, because of good wettability and high oxygen permeability.

2.4. Methods to Enhance Contact Lens Wettability

The wetting of a polymer surface has always been of concern. Untreated high wetting angle contact lenses have a very dull appearance, indicating the absence of wetting by tears, while subjects also noted physical discomfort that increased with time in the eye with the non-wetted lens, in addition to blurred vision in the non-wetted lens (Lin et al, 1973). Several procedures have been advocated, however, with varying degrees of success, to increase effective contact lens surface wettability, which traditionally are called 'surface treatment'. The wettability can be enhanced by hydration and changes in the formulation or surface treatment of the final product (Gesser et al, 1965, Pearson 1977 and 1979). Several approaches have been used to treat and increase the wettability of contact lenses, which include coating on hard lenses, special lens surface treatments (Blue, 1967; and Gesser et al, 1967), more wettable hard lens and soft lens materials (Rankin et al 1970), special soaking and wetting solutions (Kokoski et al 1963, Berman et al 1963, Pearson 1989) and use of tear substitutes (Harris et al, 1973).

2.4.1. Surface Coating

In the coating treatment method, a thin layer of a wettable material, such as Silica (SiO_2) or titanium dioxide (TiO_2), will be coated on a low-wettable contact lens surface, i e silicone polymer (Ong et al, 1976b; Cordrey, 1983; Harris et al, 1973; Morrison, 1963; Wade et al 1991). In the treatment cases, it is possible for reactions to occur on the surface, resulting in a permanent, and materials bound to the surface in this fashion become part of the surface and can only be removed by chemical reaction or physically machining or re-polishing the surface.

The silicone polymer has alternating silicone and oxygen atoms in the backbone structure. Two organic side groups, usually methyl ($-CH_3$), are attached to each silicone, which are highly unwettable, with a wetting angle of over 90° (±8), and this has been one of the major disadvantages of using silicone for contact lenses. As tears will not wet such an unwettable surface, the lens must be made more wettable by treating the surface with an alkyl titanate, such as tetraisopropyl titanate or titanium tetra-alkoxide.

Glow discharge has also been used (the plasma glow was generated with almost any gas but typically oxygen or nitrogen) for coating treatment to increase the wettability of the samples. Collision with gas molecules caused the ionisation of the gas, which produced positive ions and additional electrons. Both caused further ionisation the contact lenses, even after drying, that were glow discharged for 2, 5, 7, 5, 10 and 20 minutes, showing a decrease in the wetting angle values. The exchange of the protons with Na^{+} and Ca^{++} improves the wettability character of the surfaces in the order Na<Ca. Due to the disadvantages of treating lenses with this method, and as coatings tend to scratch or wear off, these procedures have not been widely employed. This method, however, has been successfully used by the Menicon for many years (Blue, 1967; Phillips, 1969; Rankin et al, 1970; Baszkin et al, 1971; Lippman, 1981; Benjamin et al, 1983; Anderson, 1982; Fakes, 1986; Hough, et at 1986; Sharma et al, 1987; Ho et al, 1988; Walker, 1989; Sunny et al, 1991, Yasuda et al 1975, Yasuda 1976, McBriar 1991 and Watt 1993).

2.4.2. Acidic Treatment

Sulphonating and acidic agents, such as formic acid, chlorsulphonic acid, phosphoric acid and oxides of chromium or ammonia (Sunny et al 1991), may be used to treat the contact lens surface and activate the contact lens surface, producing wettable groups on the contact lens surface, such as Aquasil contact lenses. The most common explanation of surface changes of the type described here is the production of more wettable carboxyl, carboxyl and hydroxyl groups through the oxidation of the hydrocarbon surface. Aquasil is a silicone acrylate co-polymer that, when immersed in a weak acidic solution, produces a thin wettable layer. It is claimed that the material provides a high level of comfort due to 'well wettability'. The use of nitric acid, led to a reduction in the wetting angle on treated materials (Ong et al 1976b). Moreover, the C=O body of the ester group is said to lie perpendicular to the surface of the plastic, and, if the direction of this bond is away from the surface, it would explain the failure of hydrogen-bonding liquids to cause increased wetting, which needs to be treated.

2.4.3. Wetting and Soaking Solutions

A surfactant may be defined as a substance that lowers the surface tension of a solution; some mobile components in polymers may display this property after migrating from the bulk to the polymer surface GP (1989). Hind et al (1959, 1963) and Rankin et al (1970) characterised wetting as 'the selective adsorption of a solute by the surface with the qualification that the hydrophobic ends of the adsorbed molecule orient towards the hydrophobic materials and the hydrophilic ends orient towards the aqueous phase'. Wetting agents (Kokoski et al, 1963), such as methacrylic acids, increase the surface wettability of soft and RGP contact lenses. Such chemicals carry a significant negative surface charge and produce a situation in which the overall net charge of the lens is highly negative. Olson (1982a and b) and Benjamin et al (1984) pointed out that the addition of benzalkonium chloride to the contact lens wetting and the storage solution has been thought to detract from the wettability of silicone-acrylate surfaces. They concluded that some solutions promise to be more efficient in providing initial comfort to the rigid lens wearer and imparting a better 'first impression' for the first few post-insertions of prospective hard lens wearers, although later success with contact lens care regimes may be dependent on other attributes of these solutions, such as their pH, toxicity buffering, and preservatives, because the tear fluid of each patient must then assume the principal role of wetting the contact lens surface.

A number of studies (Fowler et al, 1984; Sack et al, 1987; Lin et al, 1991 and Yorav et al, 1992) have shown that such a charge causes the lens to attract a far greater number of deposits than those that are relatively inert. Jones (1992) believed this was because of the positive charge on the surface of the protein. Indeed, this is also believed to be of much greater aetiological significance for deposit formation than water content (Kokoski et al, 1963). In solutions, solvated ions can associate with charges on a surface in contact with the solution, which can exchange freely, depending on the surface environments. Random thermal motion at room temperature is sufficient to exchange solvated ions at most charge surface sites.

The solution or solvent incompatibility can adversely affect rigid gas-permeable lens surface quality (Lippman 1989), thereby resulting in increased deposition of substances on the lens (Olson 1982 b). A number of effective care systems have now evolved that combine with the reactive sites on the surface of the silicone acrylate material by one or more of the following mechanisms:-

1. Electrostatic interaction (Andrasko et al 1988).
2. Hydrogen bonding (Brennan et al 1986).
3. Hydrophilic interaction (Caroline 1988).

The interaction of the conditioning solution with the reactive sites on the lens surface reduces, at least for a time, the affinity of the lipid-protein-mucus deposits to the surface of the contact lens material.

PHEMA is hydrophilic because of the hydroxyl groups (-OH) on the side chain of the polymer (Bier et al (1980). These groups have a slightly negative charge and electrostatic forces that allow the water to be taken up by the polymer for the same reason that any small, polar molecule will be absorbed by polymer.

2.4.4. Hydration

A hydrophilic contact lens material generally means one with a bulk water content. Polymer hydrophilicity, in particular, indicates the ability of a material to absorb water into the polymer and swell, which is dependent on the ratio of hydrophilic to hydrophobic functional groups in the polymer (Tighe 1989). Most contact lens materials absorb some water when immersed in water, and the amount taken up can be expressed, most commonly, as a percentage of the weight change or as a volume change. The percentage of water can be calculated by subtracting the dry weight (d) of a specimen from the wet weight (w), and then dividing this value by the wet weight and multiplying by 100 to obtain a percentage (Andrasko et al 1980, Brennan 1983, Figure 2.15). The absorption of water by polymer changes the contact lens surface wettability to a greater value, which is believed to produce a great acceptability by contact lens wearers.

The quantity of water that the polymer will imbibe is controlled by the amount of the cross-linking agent, the extent of water or water-ethylene glycol to dilute the monomer and the quantity of the initiator (such as ammonium per sulphate and sodium metabisulphite). The electrostatic forces will pull water into the material until the forces of the cross-linkages match those of the electrostatic between polymer and water molecules. For HEMA cross-linked with ethylene glycol, the gel is homogeneous and thus transparent with a water content of up to 40 per cent, while above this the material is a heterogeneous gel and becomes translucent or opaque. The material loses its transparency above 40 per cent water content because water is a poor solvent for the monomer, and with greater dilution there is phase separation between water and monomer, resulting in a disrupted polymeric material (Refojo et al 1965a). When the concentration of the solvent in the monomer during polymerisation is such that there is no change in the volume of the gel when placed in water after formation, the gel is said to be isovolumic.

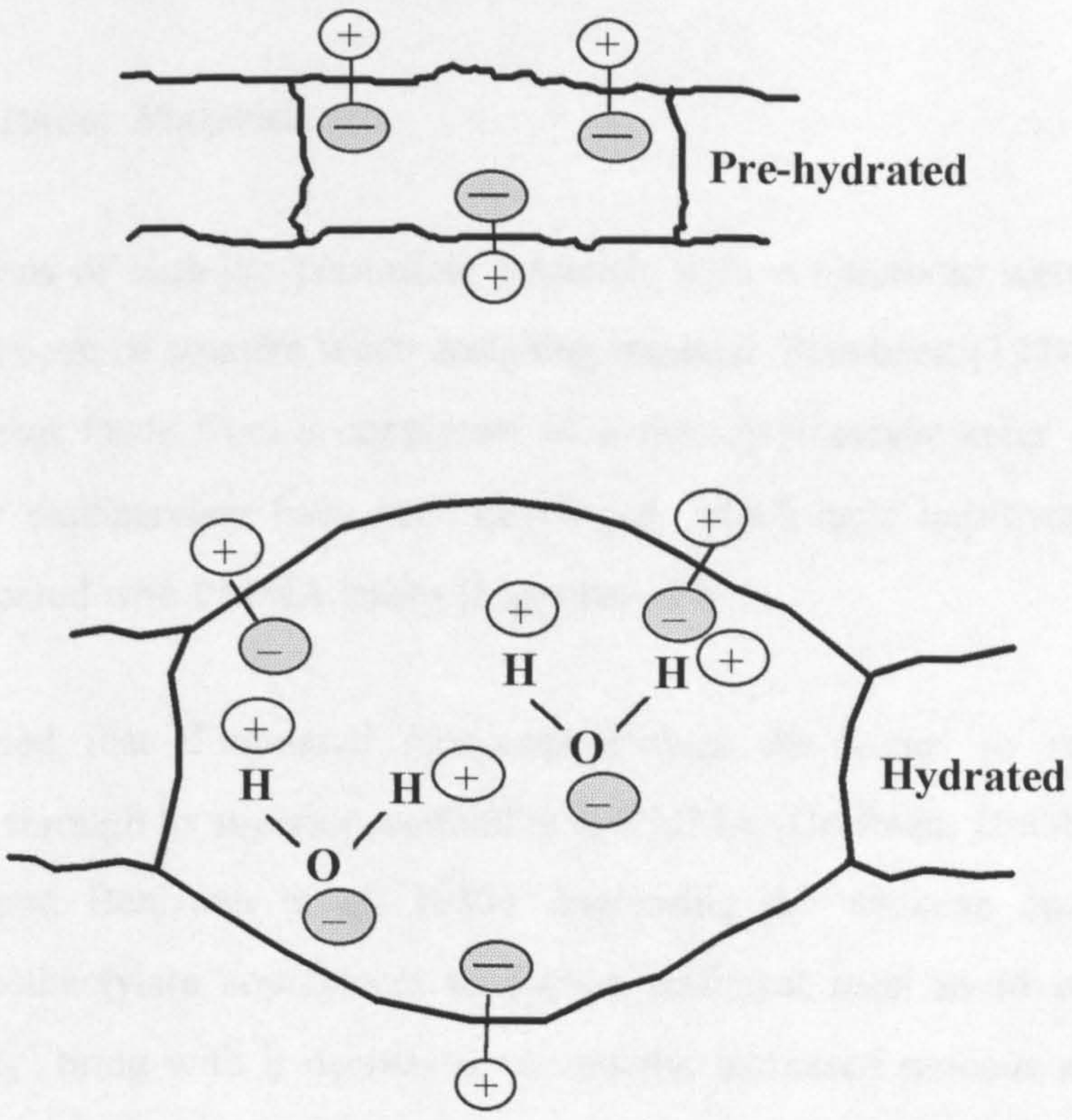


Figure 2.15. Hydration (swelling) of a cross-linked polymer.

The HEMA-ethylene glycol crossed-linked material has a softening point of about 120 °C and can thus withstand heat sterilisation when hydrated. Water content for

contact lens material is usually 38-39 per cent, and with this composition the refractive index is 1.43, while in the dehydrated state, it is 1.52 and the index is dependent on the water content. In its dehydrated state, the material is transparent, but quite hard and brittle, but hydrated, it is flexible, soft and can be torn. A lens size specimen will almost completely hydrate when immersed for two hours and take about five hours to dehydrate. The material can be elongated 10-30 per cent and still recover fully (Yasuda et al 1966).

After the hydrogel is formed, the percentage of water it contains varies with the temperature, pH of the bathing solution and any polar or ionic materials in it. If the medium in which the material is immersed is hypertonic and contains a high concentration of molecules, water will be drawn out of the lens until the concentration is the same as in the medium, but if the solution is hypotonic the opposite is true. On the eye, once the lens has equilibrated with lacrimal fluids, these factors are held reasonably constant.

2.4.5. Wettable Materials

The synthesis of high-gas-permeable materials with a non-ionic wettable surface has always been of concern when designing material. Plambeck (1978) stated that contact lenses made from a copolymer of a fluoralkyl acrylic ester and an alkyl acrylate or methacrylate have been developed, which have improved wettability when compared with PMMA lenses (Lippman 1990).

It is claimed that fluorinated monomer enables the lenses to resist surface deposition through its superior wettability to PMMA (Hoffman, 1983b; Baszkin et at, 1979 and Benjamin et al, 1983). Increasing the siloxane content in the Siloxanylmethacrylate copolymers to such a sufficient level as to obtain 'super permeability' bring with it decreased wettability, increased mucous and adhesion and tenacious protein deposits (Feldman et al, 1987 and Brown, 1992). But Pearson (1986) demonstrated that the wettability of siloxane methacrylate is not significantly different from that of PMMA.

Chapter 3. Wettability Measurement Methods

3.1. Introduction

The reasons for measuring the wetting angle were explained in Chapter one. Theoretically, the wetting angle can be calculated from the polymer chemical structure, particularly by the quantity of wettable groups in a monomer and a polymer. The chemical nature of a surface can be evaluated by total internal reflectance, infrared spectroscopy, and electron spectroscopy for chemical application (ESCA, Keller 1980 and Hough 1989). ESCA can analyse the topmost 100 μm of the surface and is particularly useful in detecting impurities, oxidation, and hydrophobic and hydrophilic groups bound to carbon, but the method is destructive to the contact lens. As polymer manufacturing is influenced by such factors as contamination and the percentage of polymerisation, theoretical calculation appears to be unrealistic. Practically, wettability could be measured by creating a liquid/solid/air interface, such as a sessile drop or a liquid/solid interface, a dynamic contact angle (DCA) for example. Wettability has been measured using a solid/liquid/air interface by various measurement techniques (Table 3.1).

Wetting angle methods described in the literature			
	Solid/liquid Interface Methods		
Measurement techniques	**Sessile drop**	**Captive bubble**	**Meniscus**
Dimensions	✓	✓	-
Goniometer	✓	✓	✓
Photographic	✓	✓	✓
Projection	✓	-	✓
Laser assisted	✓	-	✓
Reflecting	✓	-	✓

Table 3.1. Solid/liquid/air interface methods and wetting angle techniques to measure the wettability of materials and contact lenses (Mandell 1984, Kneen et al 1937, Good et al 1963, Padday 1963, Bennett et at 1983, Hansen et al 1971, Scheer et al 1978, Dussan 1979).

3.2. Sessile Drop

3.2.1. Drop Delivery

There are three different ways of producing a sessile drop on a solid.

a. Dripping Drop. To obtain an equilibrium drop, the droplet freely falls from the tip of a syringe needle on to a solid surface (Figure 3.1) and for the best repeatability the distance between the droplet and the surface was recommended to be less than 1 mm (Huff et al, 1988 and Knick et al, 1991). The volume of the drop delivery can be controlled by modifying the tip of the syringe, for example roughness, smoothness and sharpness (Figure 3.1.d).

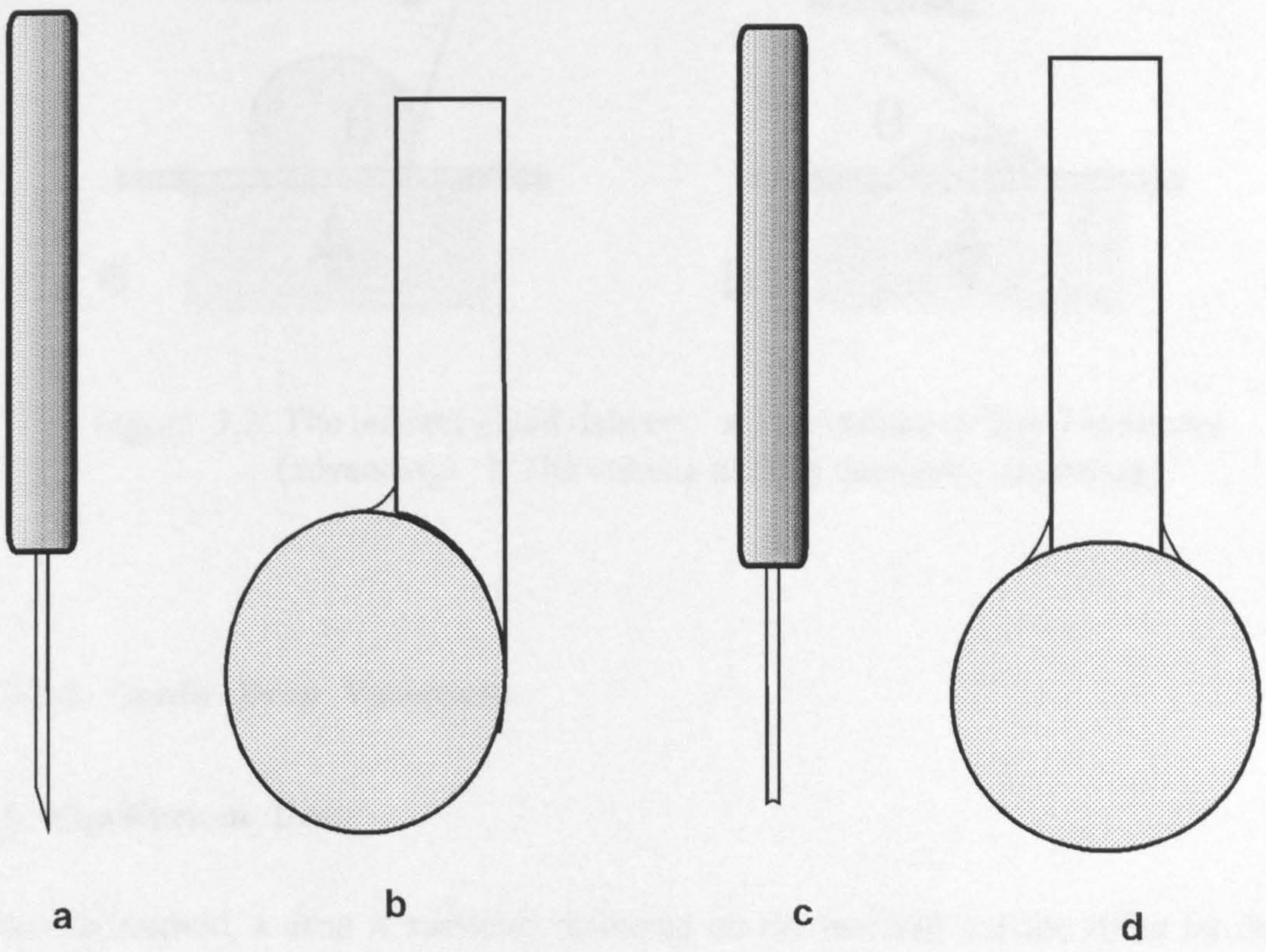


Figure 3.1. Drop delivery methods. **(a & b)** The tip of the syringe needle was cut obliquely. **(c &d)** The tip of the syringe needle was cut horizontally and flat. The adhesion area of the oblique cut was greater than the flat cut, and where the tip of the needle was well polished and sharpened the droplet did not make an adhesion meniscus to the needle material. Hence, the droplet can be dropped freely on a surface, which may enable one to produce a specific volume of liquid at the tip of the needle on the surface.

b. Contact Drop (Pendant Drop). The contact lens is moved slowly to a prepared droplet on the tip of a syringe needle until it touches the droplet. Tomlinson et al (1963), for example, utilised the tip of a platinum wire to place a drop.

c. Indirect Drop (Expanding-Contracting Drop). By making a hole in the surface of a material, a sessile drop can be created through the hole and the volume of the drop can be either increased (advancing, Figure 3.2a) or decreased (receding, Figure 3.2b) at any desired rate (Geer et al 1961, Gaudin et al 1963, Phillips 1965).

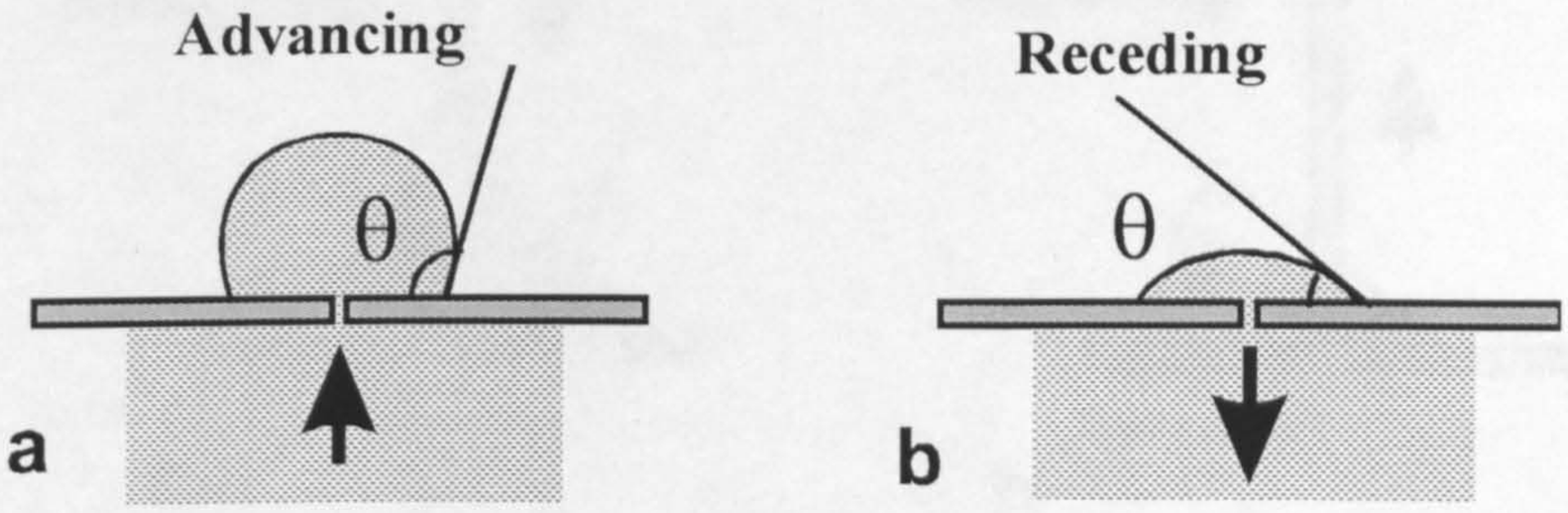


Figure 3.2. The indirect liquid delivery. **a** The volume of liquid increases (advancing). **b** The volume of drop decreases (receding).

3.2.2. Sessile Drop Variations

I. Equilibrium Drop

In this method, a drop is suddenly delivered on the material surface either by the 'dripping drop' or by the 'contact drop' method (Gaudin et al 1963).

II. Advancing Drop

The advancing wetting angle is a measure of a material's un-wettability (hydrophobicity), which is defined as the resistance of a dry material to the advance of an aqueous film across its surface (Fitzgerald 1983a). In this method, after the drop delivery, the volume of liquid is increased either through a syringe needle

(Petke et al 1969 and Figure 3.3) or through a hole (Figure 3.2, O'Brien 1965, Davidson et al 1971, Lemp et al 1972, Fakes et al 1987 and Li et al 1992). Dabezies (1989) stated that, when the droplet is advanced on a fresh, dry and clean surface, the advancing wetting angle can be measured. The solid can be classified as wettable if water spontaneously spreads on its surface, which implies that the spreading coefficient of water is positive and, thus, the advancing contact angle of water is zero. By this criterion, only a few solid surfaces can be classified as wettable (Holly 1983b).

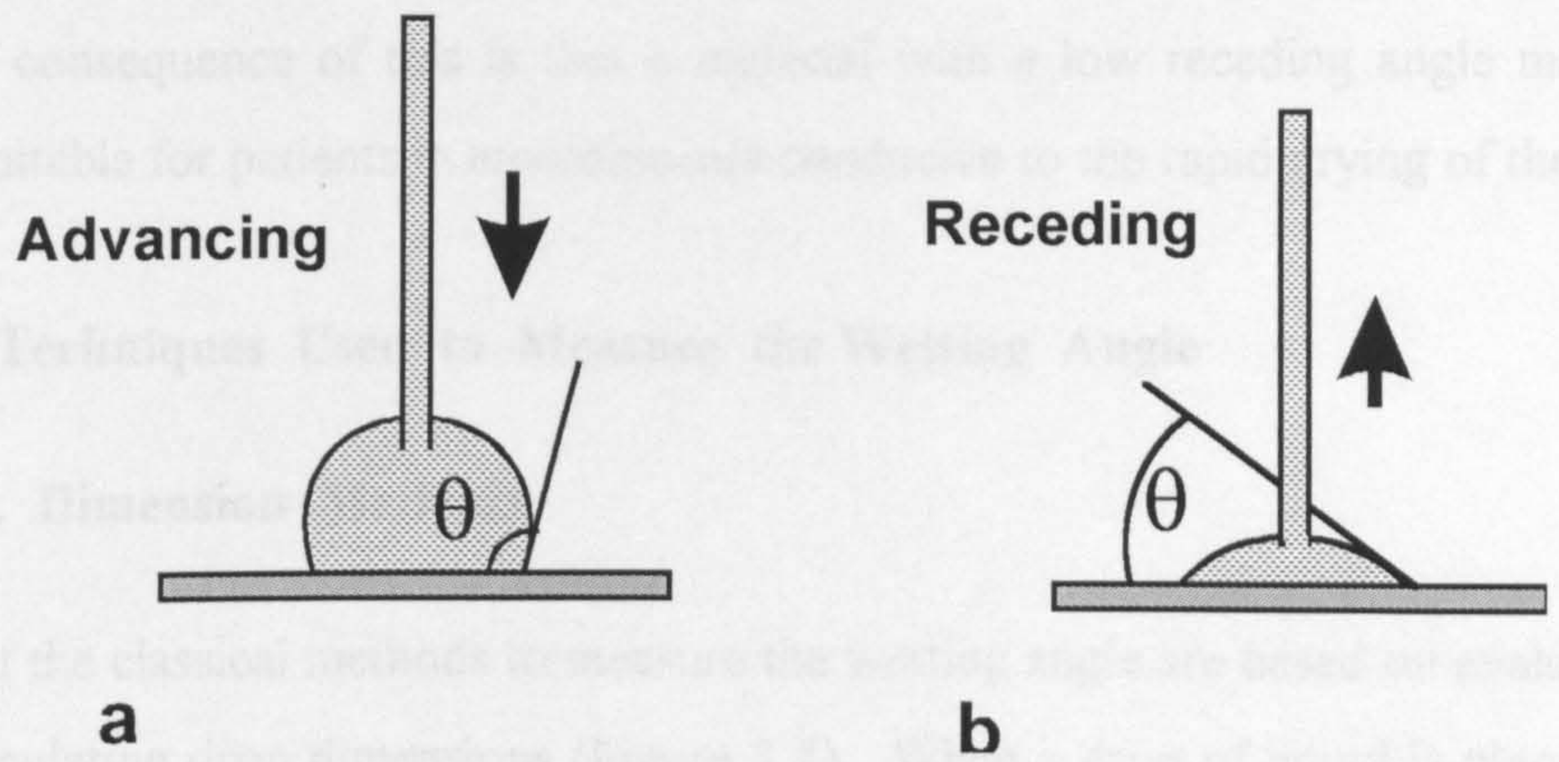


Figure 3.3. Advancing and receding sessile drop wetting angle.

III. Receding Sessile Drop

The receding wetting angle is defined as a measure of the degree of attraction that a wetted material surface has for the wetting layer. In this method, the volume of a droplet after placement is slowly removed by a syringe or evaporation and the meniscus that is formed at the point where the edge of the droplet intersects the surface of the material will be observed to stick in place, until a significant volume of water has been removed from the droplet. At this point, the meniscus will break free and move across the surface of the material and the receding wetting angle can be measured (Figures 3.2 and 3.3; Baszkin et al, 1979) with literature showing that the receding angle is more unstable than the advancing angle (Cassie 1948), although Shirafkan et al (1994) found the receding wetting angle of PMMA to vary

between 50°- 0° and concluded that the current methods of measuring the sessile drop receding wetting angles are unreliable.

Fitzgerald (1983b) compared the wettability of eight rigid contact lens materials with a surface treated polyacrylate silicone copolymer material and reported that accurate measurements below 10° were impossible. He argued that the receding wetting angle is a better measure of a material's wettability and concluded that because the surfaces of contact lenses in the eye are hydrated the receding angle is probably the best indicator of a material's clinical performance on the eye. The clinical consequence of this is that a material with a low receding angle may be more suitable for patients in environments conducive to the rapid drying of the eye.

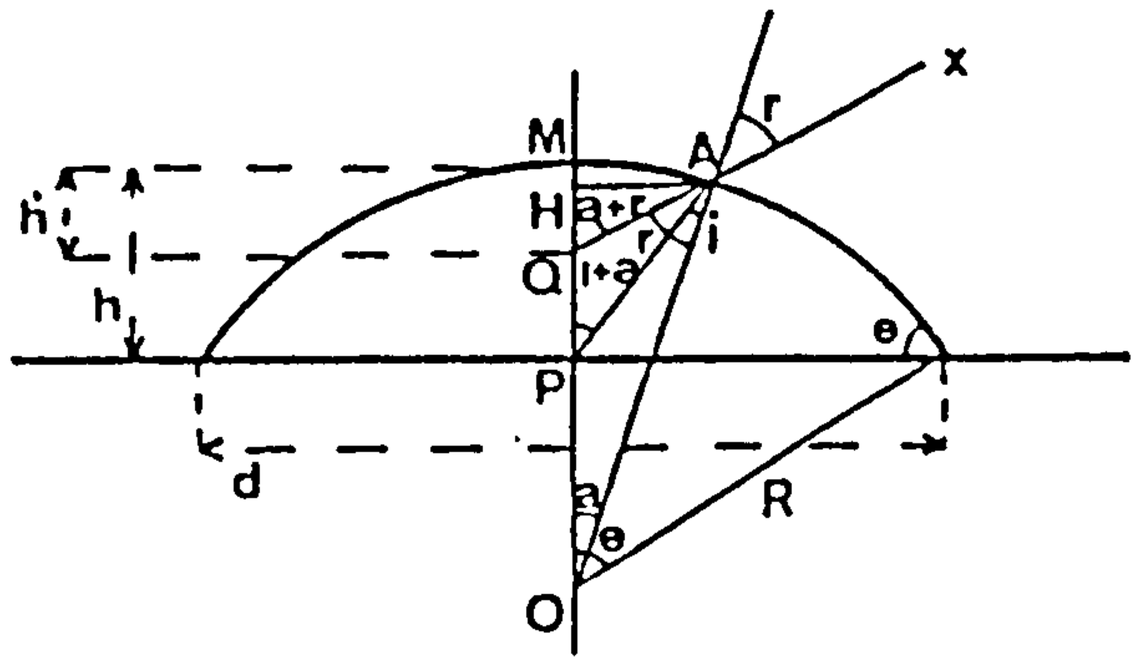
3.2.3. Techniques Used to Measure the Wetting Angle

3.2.3.1. Dimension Methods

Most of the classical methods to measure the wetting angle are based on evaluating and calculating drop dimensions (Figure 3.4). When a drop of liquid is placed on the surface of a solid, it may spread to cover the solid surface or remain as a stable drop on the solid. In the absence of a gravitational field, a drop that does not spread will lie on the solid surface as a segment of a sphere in a gravitational field, but, if the drop is very small, surface forces will predominate over the force of gravity and the shape of the droplet will not differ greatly from a true segment of a sphere. If the drop is quite large, the gravitational force will be the more important and the sessile drop will be distorted so that it is horizontal at the top. A drop of liquid of intermediate size would be partially flattened.

Osipow (1962) stated that another important method for measuring the contact angle of a liquid on a solid surface is the height of a sessile drop. If a small quantity of a liquid is placed on a level solid surface, provided that the liquid does not spread spontaneously, a sessile drop will be formed, and, if liquid is added to the drop, the height increases until it reaches a maximum value. Further additions of liquid increase the diameter of the drop, but not its height above the solid surface.

a



b

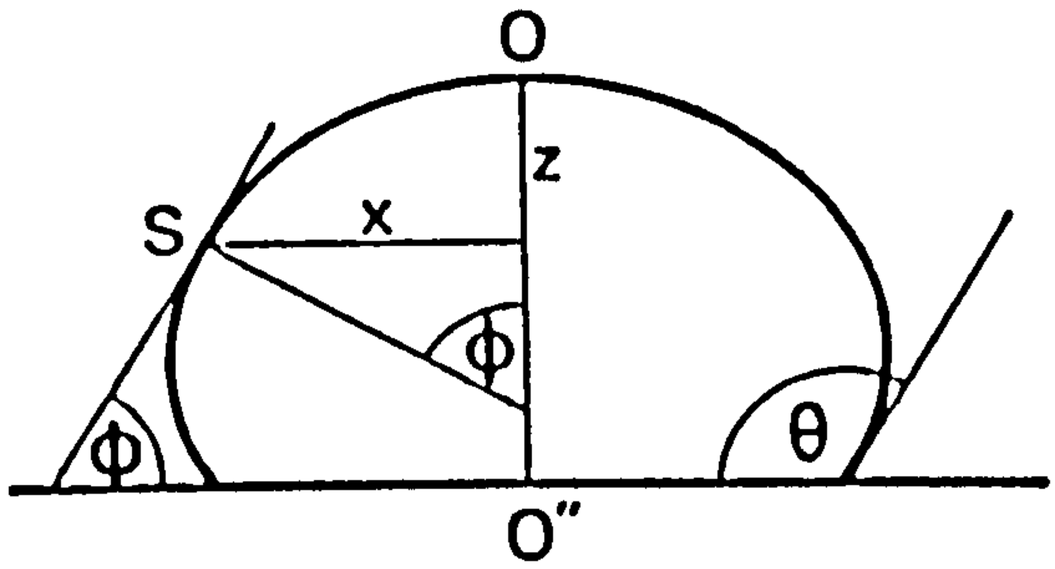


Figure 3.4. Geometrical parameter of a sessile drop by (a) Farnariore (1984) and (b) Neumann and Good (1979).

The relationship between the height **h** of the sessile drop and the contact angle θ is:

$$1 - \cos\ \theta = \frac{p\, g\, h^{2}}{2\, \gamma_{L}} \qquad (7)$$

where **p** is the density of the liquid, **g** is the acceleration of gravity and γ_L is the surface tension of the liquid. Lin et al (1973) calculated the wetting angle by projecting a sessile drop on to a screen and measuring its height and diameter for a spherical drop with base diameter **d** and drop height **h** (Figure 3.4).

$$\frac{2h}{d} = \frac{\tan\theta}{2} \qquad (8)$$

Farnariere et al (1984) described a variation of the drop dimension method and claimed ease of use, although the technique required a conventional microscope to

measure the dimensions. Due to gravity effects, the droplet is not rigorously spherical, but the deviation from sphericity is negligible when:

$$h\,\frac{d}{2} = \frac{g\,\Delta p}{\gamma} \qquad (9)$$

The wetting angle can also be derived from an equation relating the base diameter and the drop volume (**V**):

$$\frac{d^3}{V} = \frac{24\sin^3\theta}{2\text{-}3\cos\theta + \cos^3\theta} \qquad (10)$$

It was difficult accurately to measure **V** , **d** and **h** of the drop, while the drop size effect and the inaccessibility of the receding and advancing angles of these methods have restricted their popularity and use (Mack and Lee 1936). But several formulae have also been recommended by investigators to determine the wetting angle of large and non-spherical drops (Staicopolus 1962 and Maze et al 1969).

3.2.3.2. Goniometer Method

The first commercial contact angle goniometer instrument was developed by Zisman (1964) to measure the contact angle of a sessile drop or a captive bubble, which consisted of a telescope incorporating two cross-hairs. The horizontal cross-hair is rotated until it corresponds to an imaginary tangent to the profile of the droplet. Examiners then shift their gaze to a reticule assembly that is mounted within the telescope, and the value of the wetting angle is read on the scale of the reticule, which is graded in 1° increments. The sample chamber is mounted on an optical bench so that both horizontal and vertical movements are possible, which requires the eye-piece cross-hair being brought into alignment at the three-phase interface. The optical-quality glass windows enable drop viewing from one direction and illumination using a fibre optic cold-light source to prevent heating effects from the other. The wetting angle was measured directly at x 20 magnification using a goniometer protractor eyepiece attached to a telemicroscope (Figure 3.5).

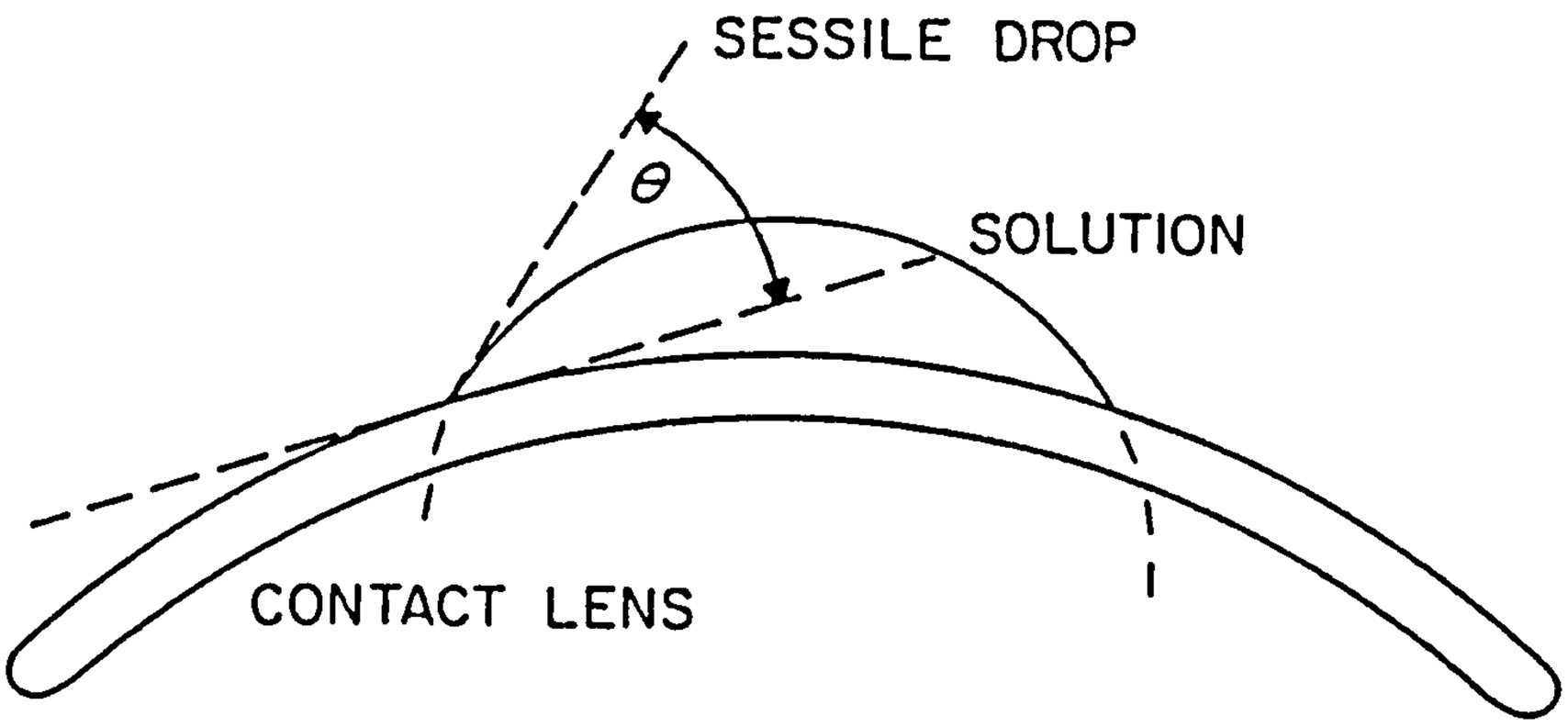


Figure 3.5. Sessile Drop method to measure the wetting angle using the Rame-Hart goniometer.

The measurement was performed by aligning the cross-hair so that the horizontal bisects the view of the drop and its reflected image and the intercept coincides with the three-phase point or interface. The protractor (zero) reading is then recorded, the eyepiece is rotated until the cross hair forms a tangent to the surface at the three-phase interfaces and the wetting angle, through the liquid phase, is read from the protractor. This procedure is carried out for both sides of the drop and the wetting angle recorded is the average of the two. Advancing and receding conditions of contact angles are established by prompting the meniscus to advance or recede over the surface.

This method has been widely used by investigators [Bruun et al (1965), Davidson et al (1971), Lemp et al (1972), Adamson (1976), Neumann et al (1979), Andrade (1980), Fitzgerald (1983), Benjamin et al (1983), Fatt (1984), Sarver et al (1984), Fakes (1986), Sunny et al (1991)]. However, Huff et al (1988) and Bush et al (1988) believed that the contact lens goniometer method presented a number of variables that were often difficult to control, such as temperature and humidity. Ong (1976) concluded that the drop method was in many ways preferable, to the bubble method, which only gave the receding angle. Fox and Zisman (1964) compared the wettability of different liquids on a clean cornea and a PMMA

material and O'Brien (1965) reported that the advancing wetting angles are 50 to 70 percent higher than the receding wetting angles.

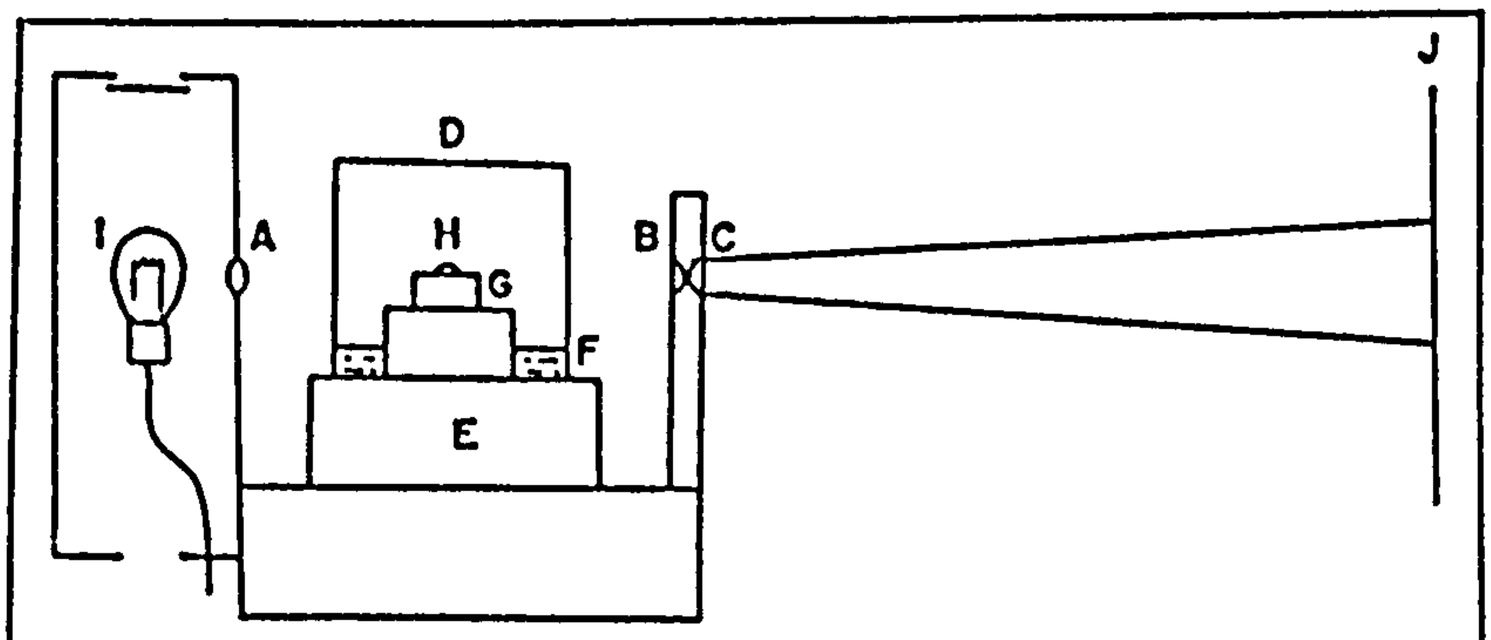
3.2.3.3. Photographic Method

In this technique, the wetting angle is photographed and the contact angle is determined by a graphical method. Photographing the drop in contact with a solid and using a projection or enlargement of the image enabled the contact angles to be measured through a protractor. Harris et al (1973) reported a significant variation 10° to 24° in different PMMA materials and concluded that the difference must be due to variations in preparing of the solid surface, the measurement procedure or analysis of the photographs. O'Kane (1930), Staicopolus (1962), Neumann et al (1979), Adamson (1982), and Li et al (1992) used the sessile drop method with photographic measuring techniques in the advancing phase. The latter strongly supported the existence of the localised chemical bonds at the interface as a result of the electron transfer at the interface.

3.2.3.4. Projection Method

The wetting angle can be measured directly by projecting an image of a drop on a screen (Kneen et al 1937, Osipow 1962, Bikerman 1970 and Lin et al 1973). The apparatus consisted of an arc lamp, condensing lens system, adjustable stage and a small picture frame, which is shown schematically in Figure 3.6a and b. A thin sheet of paper was fastened to the picture frame by thumb tacks so that it lay flat against the glass. The measurements were carried out in a darkened, closed room, with the light from the arc lamp passing through the condensing lens and across the plane surface to be measured. The plane surface is placed in the path of the beam, and the image of the drop is projected through the glass and paper, where it may be outlined in pencil by hand. The paper may then be removed and the contact angle measured by a protractor. Ong et al (1976b) measured the wetting angle by using the projection technique and by the advancing method on treated lenses.

a



G = polymer button A, B, C = lenses
H = water droplet D = glass cell
I = light source E = stand
J = screen grid F = water layer

b

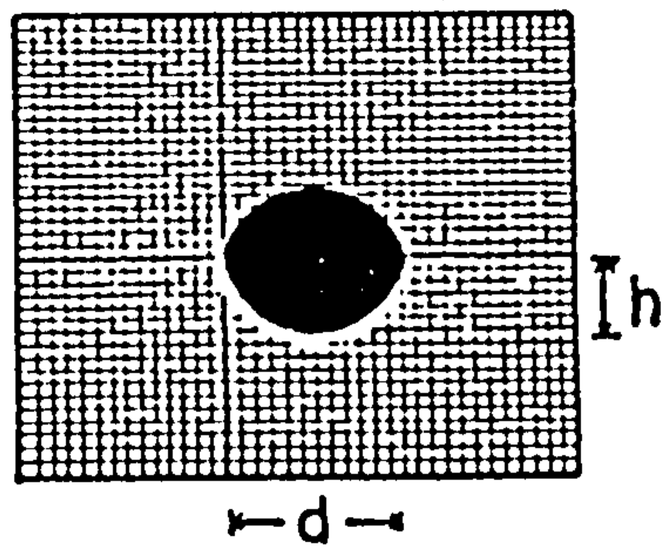


Figure 3.6. a Apparatus for measuring contact angle θ, b screen grid (front view, h=height, d=diameter).

3.2.3.5. Laser Assisted Method

This method is based on reflection of a laser beam at the solid-liquid-air interface (Figure 3.7). The technique is reported to be less subjective, and is superior to Goniometry [Bush et al (1988) and Knick et al (1991)]. They utilised this technique to measure the wetting angle of a sessile drop on rigid contact lenses and Shirafkan et al (1994 and 1995) used the laser to measure the wetting angle of unseparated adherent liquid on both soft and rigid contact lenses (see Chapter 5).

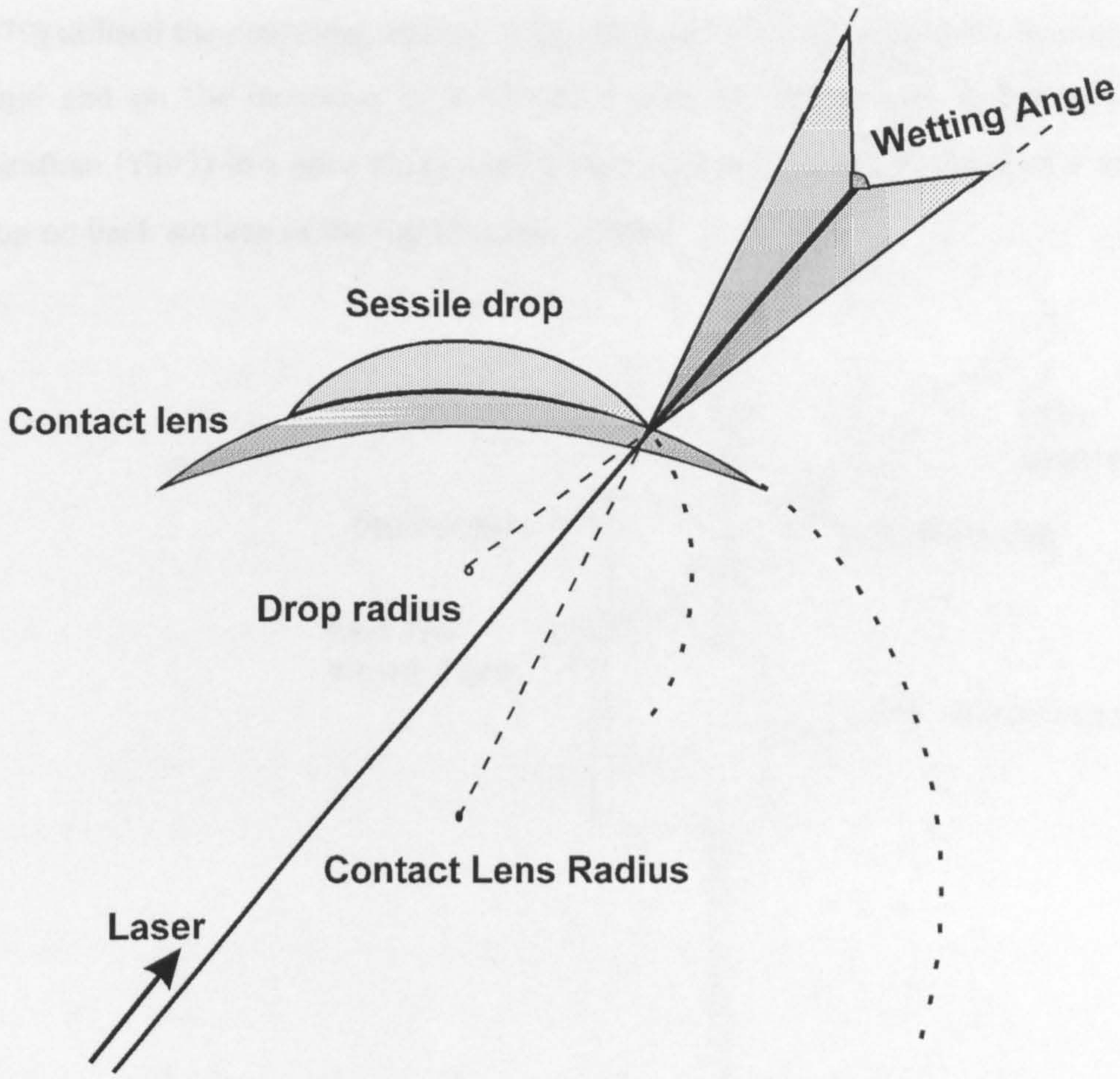


Figure 3.7. The reflection of the laser from the contact lens surface and from the liquid surface at the solid/liquid/air interface, which makes the wetting angle visible on a protractor.

3.2.3.6. Reflecting Method

The method employs a light source mounted on a beam, which is pivoted on an axis containing the liquid/solid/air interface at which the contact angle is to be measured. This may be at the edge of a drop or a meniscus at a flat plate or rod, or on the inside of a tube. The observer sights along the beam to observe the specular reflection from the liquid surface, with the measurement consisting of pivoting the beam on its axis and determining the orientation at which the specular reflection disappears (Figure 3.8). For the angles of incidence lower than θ, there is no reflection. Langmuir-Schaefer (1937) and Fort et al (1963) used this method to measure the wetting angle of a sessile drop on a flat material, Good et al (1963,

1979) utilised the reflecting wetting angle method on a Teflon plate by dipping it in liquid and on the meniscus of a tube that was half submerged in benzene and Shirafkan (1993) in a pilot study used a laser source to measure the θ of a sessile drop on back surface of the rigid contact lenses.

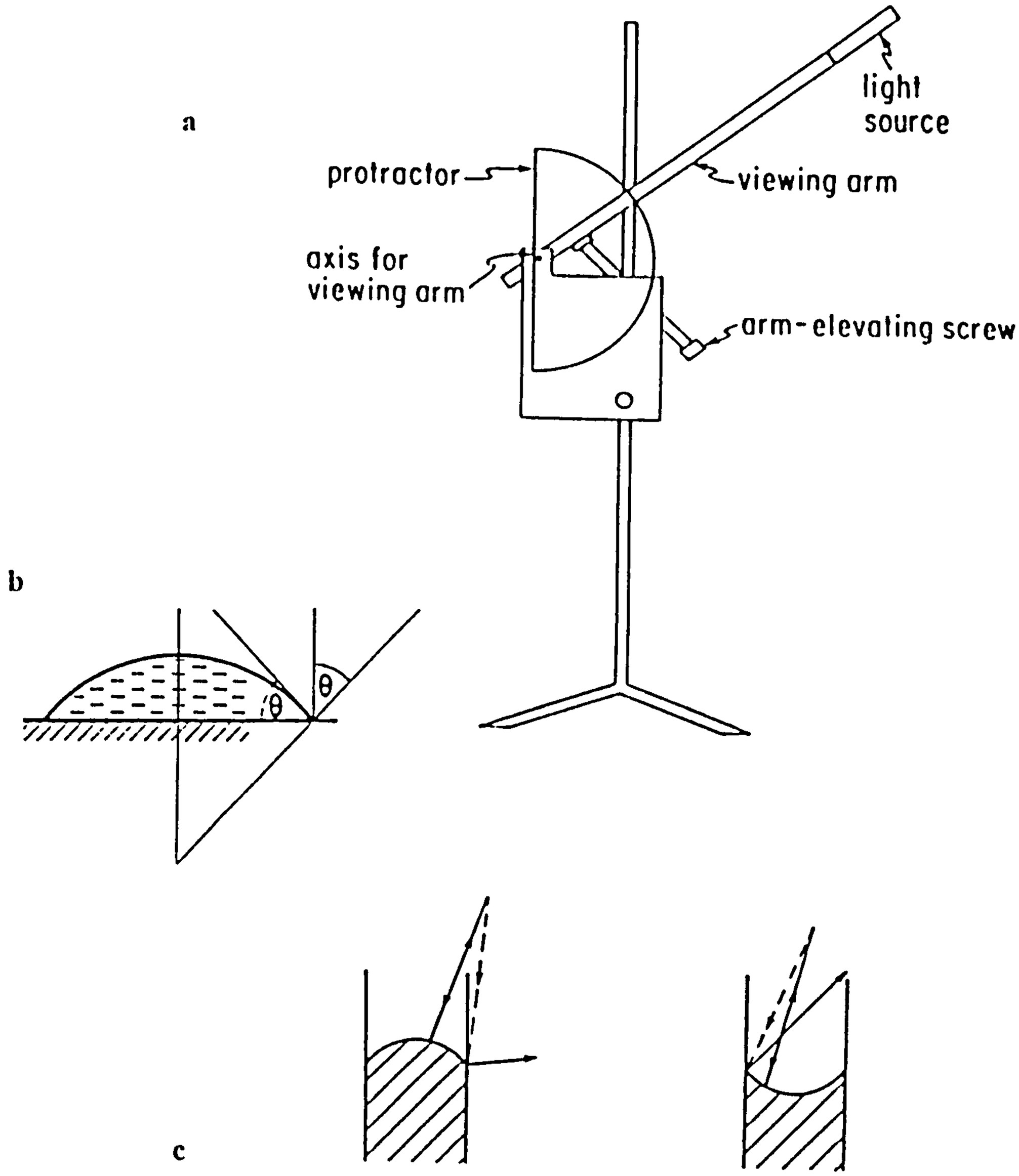


Figure 3.8. **a** Apparatus for measuring the contact angle by the Langmuir-Schaefer reflecting method, **b** reflection from a drop and from a flat surface shows the wetting angle θ, and **c** the wetting angle of a meniscus of a tube.

3.3. Bubble Methods

3.3.1. Captive Bubble Method

In the captive bubble method, the material or contact lens is submerged in water with the apex down. A small bubble formed at the tip of a hypodermic needle just below the apex is allowed to float upwards and, hopefully, adhere to the lens. The angle measured in the water at the perimeter where the bubble is in contact with the lens is the contact angle, while the solid-water-air contact angle is then measured directly using a telemicroscope with a goniometer (protractor) eyepiece or indirectly from a photograph of the bubble or bubble dimensions (Figure. 3.9, 3.10 and 3.11, Holly et al 1975). The use of a sample chamber requires at least two of the walls to be transparent and preferably of optical quality glass. For accuracy, constant bubble volumes should be employed and duplicate measurements made.

This method was used by Huntington (1906), improved by Del Giudice (1936) and modified by Gaudin et al (1963) for the investigation of contact angle hysteresis (see 3.6). Taggart et al (1930) and Shuttleworth et al (1948) originally used a bubble machine for investigating of flotation systems, a technique that is widely used and has been accepted by the Contact Lens Manufacturers Association (CLMA) [Gaudin et al (1963), Poster et al (1978a and 1978b), Cappelli (1979), NIH (1980), King (1980), Gregonis et al (1982), Andrade et al (1982), Benjamin et al (1983), Fitzgerald (1983), Cordrey (1983), Jho (1983), Poster et al (1984), Sarver et al (1984), Keates et al (1984), Derjaguin et al. (1987) and NIH (1989).

The captive bubble method has several problems (Fatt 1984), in addition to the fundamental problem of the possible presence of a water film between the bubble and the sample. A review of the surface science literature and some laboratory experiments indicate that the captive bubble method may be invalid unless precautions are taken when performing measurements (Fatt 1990). Eriksen et al (1982) and Gregonis et al (1982) stated that the wetting angle and measurement methods were debatable, although Andrade et al (1979) utilised this method to analyse the fully hydrated polymer surface, reporting that the hydrogel-water interface is more diffuse than an un-wettable polymer interface.

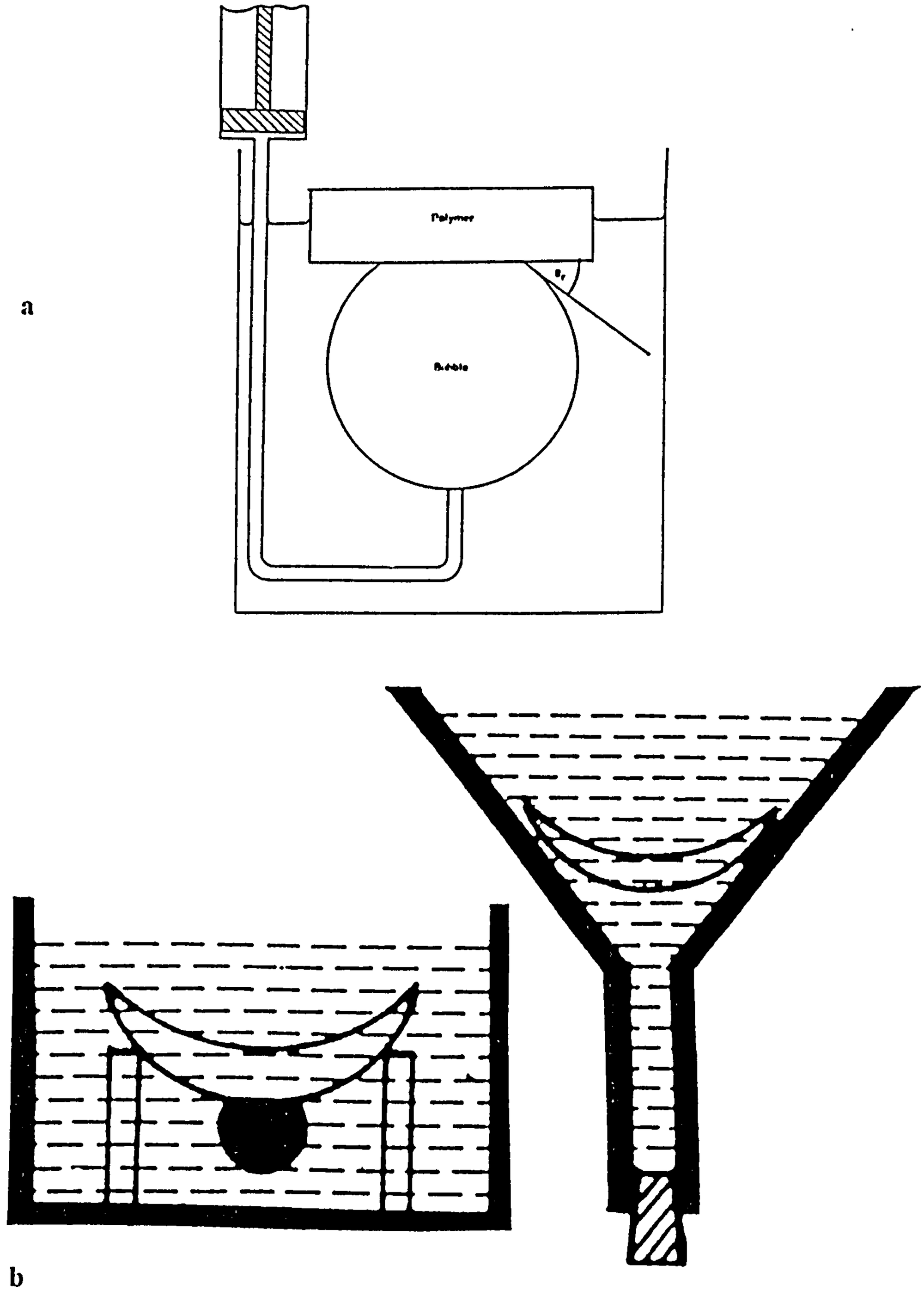


Figure 3.9. The Captive bubble technique. **a** The bubble delivery apparatus, **b** Bubble chamber for wetting angle measurement.

Nevertheless, there are virtues in a bubble method, the main one being that the sample is always wet. The disadvantages are the difficulty in measuring because the discontinuous light path that passes from the air to the liquid and back to the air and the fact that the large liquid volume required precludes the use of human tears. Dabezies (1989) stated that it was difficult, however, to accurately measure the sessile drop on a soft lens because the surface tends to dry if it is not in an atmosphere of 100 per cent relative humidity. For soft contact lenses, therefore, the air-in-water technique may be used.

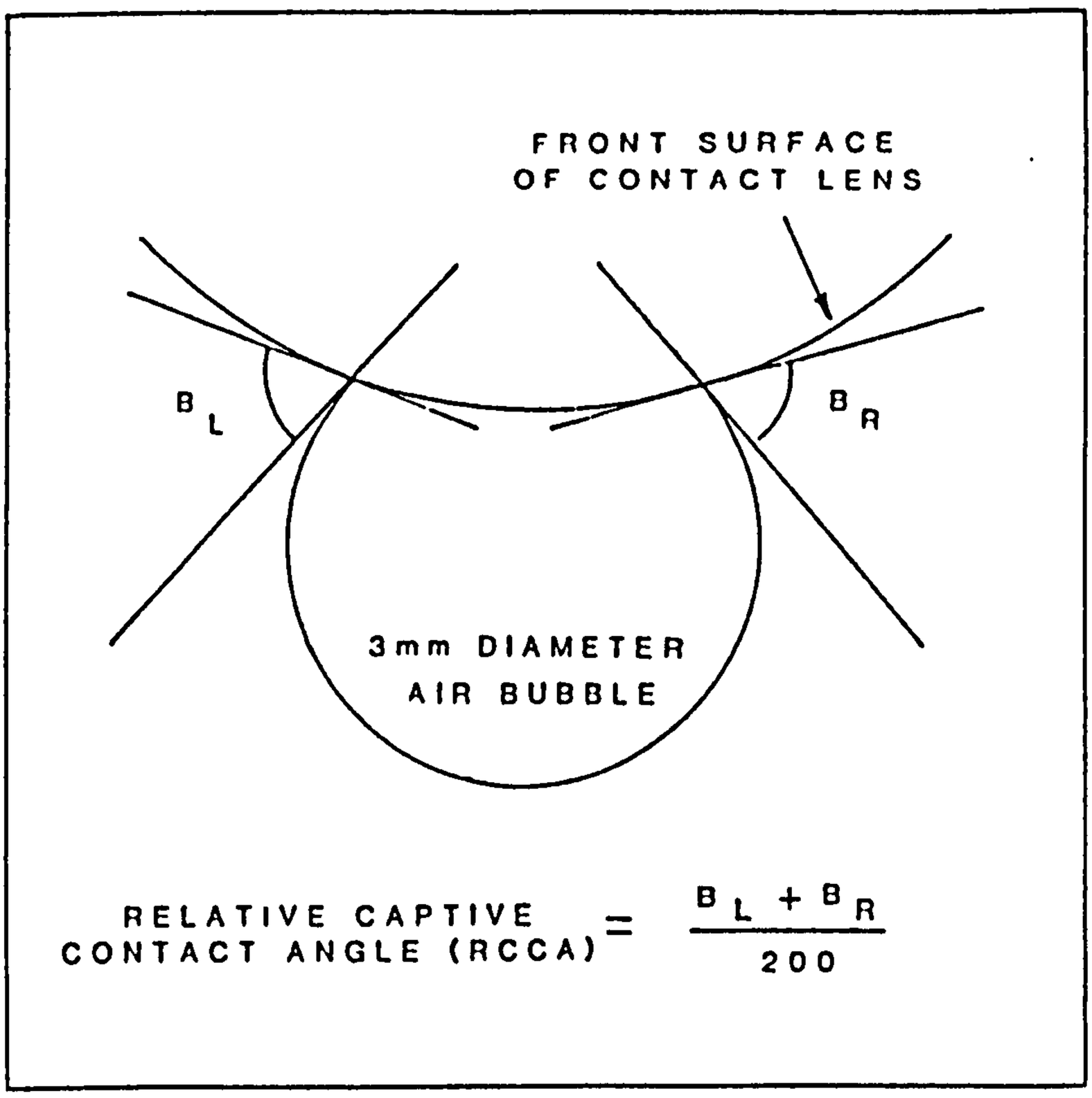


Figure 3.10. The relative captive contact angle.

Octane bubbles have been used by many investigators, such as Holly et al (1976a and 1976b) and Hamilton (1972) with the latter estimating the polar character of unknown polymers (Figure 3.11). The results with air bubbles have lower angles than when octane was used. It was concluded that the wetting angle represented by the polar component was not as good a parameter to predict the wettability, which is a net balance of all the interfacial free energies (Jho 1983). Baszkin et al (1979)

used tear solution and found zero receding contact angle for the tear liquid on all surfaces.

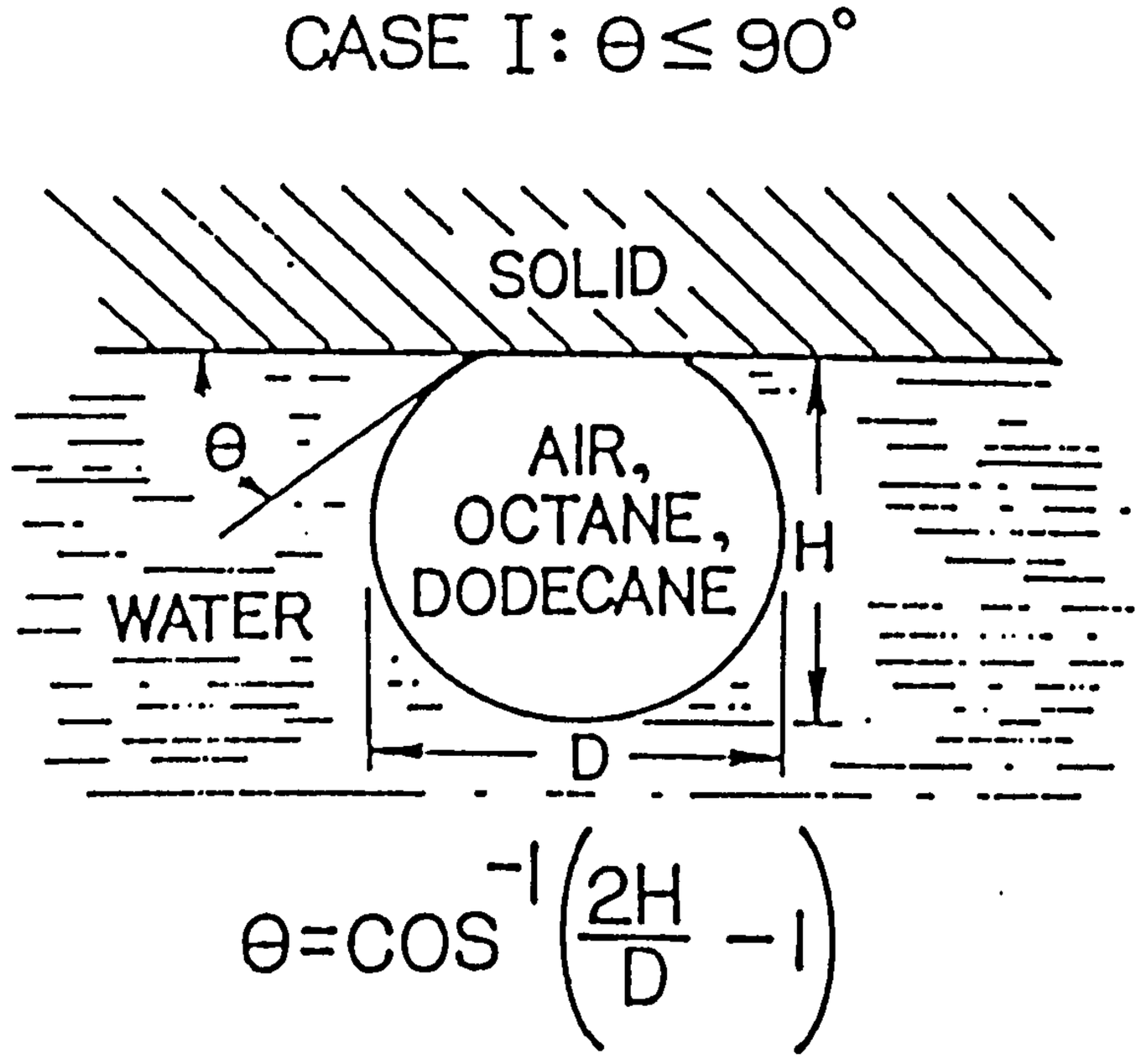


Figure 3.11. The geometrical dimension contact angle measurement of captive bubble.

3.3.2. Adherent Bubble Method

Fatt (1990) introduced a new bubble method, called 'the adherent bubble method'. The contact angle was measured by either a goniometer in the microscope or on photographic prints. The apex of the contact lens was viewed in profile either by a single lens reflex 35 mm camera or by the prism and microscope. The procedure involved filling the plastic box with distilled water so that the apex of the lens was covered to a depth of about 5 mm. The lens was allowed to remain under water from 1 to 12 or 24 hours. The barrel in the syringe connected to the lower port was then very slowly withdrawn to lower the water level. The water film on the lens broke at the apex when the water film over the lens was very thin and the interface retreated to the edge of the lens. It was only necessary to observe that

after the film was broken a water-solid-air interface was created (Figure 3.12). The syringe barrel is now pushed slowly inwards, raising the water level in the box and advancing the interface on the surface of the lens. The advancing angle is high when the circular interface moves towards the apex, and the cylinder of air within the water reaches from the apex of the lens to the air space above the water surface. On further advance of the interface, the cylinder collapses to form a complete, thick layer of water over the lens, but a bubble of air adhering to the lens apex is usually left behind. The only cases in which a bubble could not be formed were after an RGP lens had been treated with a wetting solution to give a zero contact angle or on a fresh, clean hydrogel lens.

After the water film breaks at the apex of an RGP lens, the water-air interface retreats rapidly until it comes to rest near the edge of the lens. The contact angle at this point is clearly a result of a receding interface on a previous wet surface. When the apex of the contact lens emerges from the water, the film breaks on an RGP lens surface treated with a wetting agent and the receding contact angle

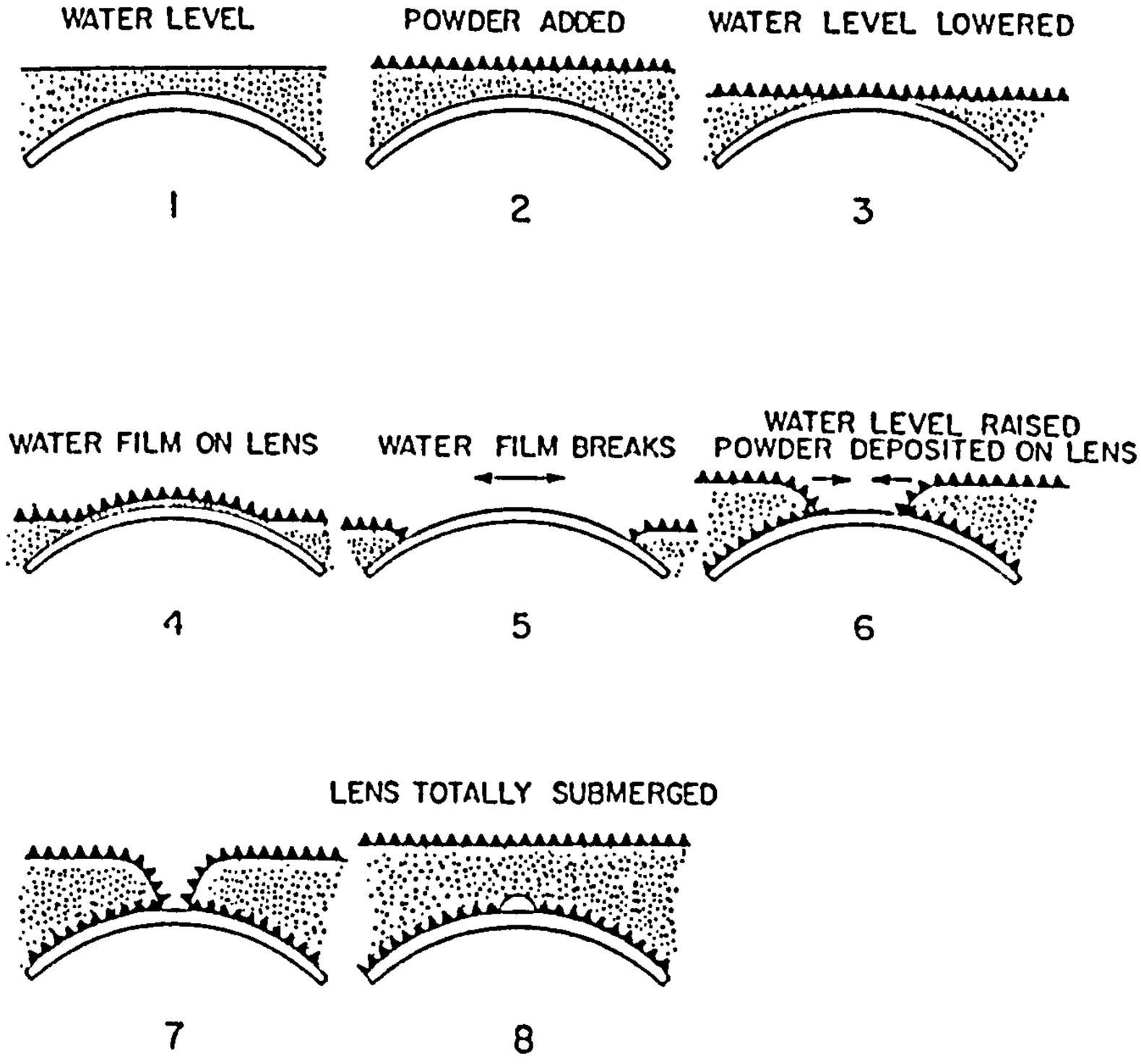


Figure 3.12. Adherent bubble method (Fatt 1990).

will be zero or near zero. Film break up on a hydrogel lens will give a zero receding angle, while on raising the water level to re-submerge the lens the advancing contact angles on PMMA, RGP or hydrogel lenses are very high, approaching 90° as the advancing film nears the apex. On RGP lenses, an adherent bubble is left behind on the apex when the advancing film coalesces, while, on a hydrogel lens that has not been allowed to dry after the break up of the film, the air bubble does not adhere to the apex.

3.4. Meniscus Methods

3.4.1. Wilhelmy Balance Technique

The Wilhelmy balance technique is also variously referred to as the Wilhelmy gravitation, Wilhelmy-plate or Dynamic contact angle method. In this method, a rectangular sample is slowly immersed into, or withdrawn vertically from, a liquid and a precision balance is used to measure the force in the course of immersion and withdrawal. An advancing angle is measured during the immersion and a receding angle is calculated during the removal of the specimen from the liquid. Electrical

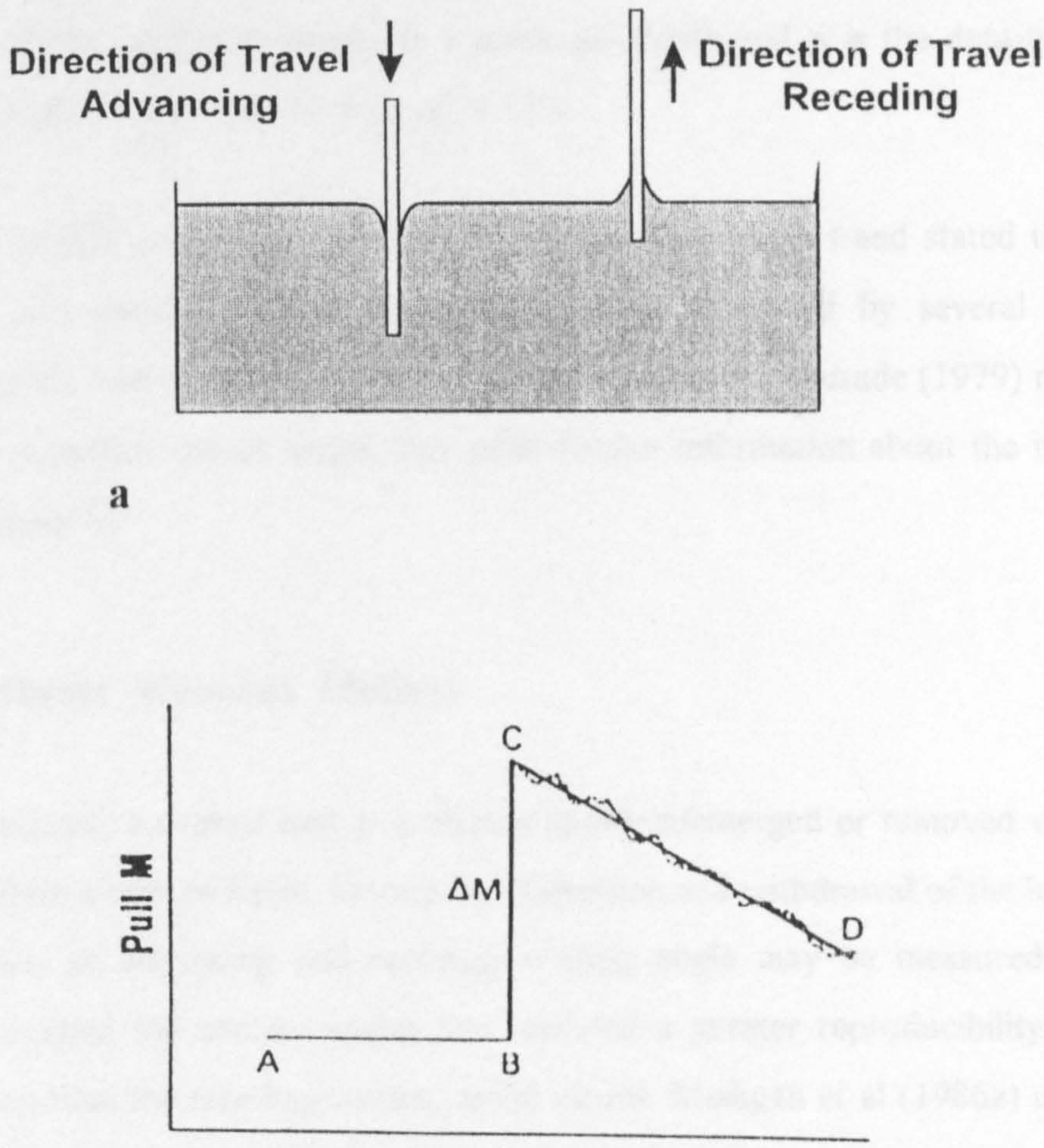


Figure 3.13. The Wilhelmy plate method can be used to determine both advancing and receding contact angles from the forces monitored during the immersion (advancing) or removal (receding) of the polymer from solution.

signals from the balance are fed to a recorder (Figure 3.13a, Wenzel 1936, Gaudin et al 1963, Wilhelmy 1863, Burley et al 1976, Holly 1976, Andrade et al 1979, Adamson 1982, Gregonis et al 1982, Smith et al 1982a and Sarver et al 1984). The advancing and receding angles were then calculated (Figure 3.13b):-

$$\cos\theta = \frac{m\,g}{p\,\gamma} + \frac{V\,p\,g}{p\,\gamma} \qquad (11)$$

Where **V pg / pγ** is buoyancy factor, **m** is mass of slide sample as measured by electrobalance, **g** is local gravitational force (979.3 dynes/g), **p** is perimeter of the slide (cm), γ is surface tension of wetting liquid (water = 72.6 dynes/cm, **V** is the volume of the immersed sample at a particular depth and **p** is the density of the wetting liquid (water = 0.998 g/cc at 20 ° C).

Pearson (1987) compared two sets of data from two studies and stated that it is possible the measurement of wetting angles is influenced by several factors, including the rate of movement of the sample. However, Andrade (1979) reported that the dynamic contact angles may offer further information about the interface (see Chapter 6).

3.4.2. Direct Meniscus Method

In this method, a contact lens or a plate is slowly submerged or removed vertically into or from a bath of liquid. During the immersion and withdrawal of the lens from the liquid, an advancing and receding wetting angle may be measured. Elliott (1962) studied the contact angles and reported a greater reproducibility for the advancing than the receding wetting angle values. Madigan et al (1986a) used this method to measure the wetting angle of a rigid contact lens utilising a Nikon profile projector, in which a saline-filled container was placed on the projector platform, the contact lens was mounted vertically above the container and the liquid is moved to the lens to view and measure the formed meniscus. The advancing wetting angle was measured while the meniscus passed over the dry lens

surface, and the receding angle was observed as the meniscus moved over a previously wet surface. The wetting angle was then measured by a goinometer through drawing a tangent to the meniscus. Madigan et al (1986a and 1986b) suggested that wetting angles measured after wear were the most appropriate way to predict in vivo material wettability characteristics. This can assess a surface wettability that is created with tear film components, although Shirafkan et al (1994) found several problems in the creation of the meniscus (see Chapter 6).

3.4.3. The Tilting Plate Method

The tilting plate method was originally used by Adam et al (1925). A test plate of approximately 2 cm wide is dipped into the test liquid, and the plate tilted until the meniscus becomes flat, with the wetting angle being the measured angle between the plate and the liquid horizontal (Huntington 1906, Adam et al 1934, Fowkes et al 1940, Gaudin et al 1963 and Aveyard et al 1973). The solid is held in an adjustable holder that can tilt the solid to any angle, with the axis of rotation at the solid-liquid interface. The plate is tilted until a position is found at which the water surface remains undisturbed up to the line of contact with the solid. The apparatus also contains provision for raising or lowering the plate in the liquid, so that the contact angle can be measured either on a portion of the plate that has been immersed in the liquid or on an unexposed portion of the plate (Figure 3.14).

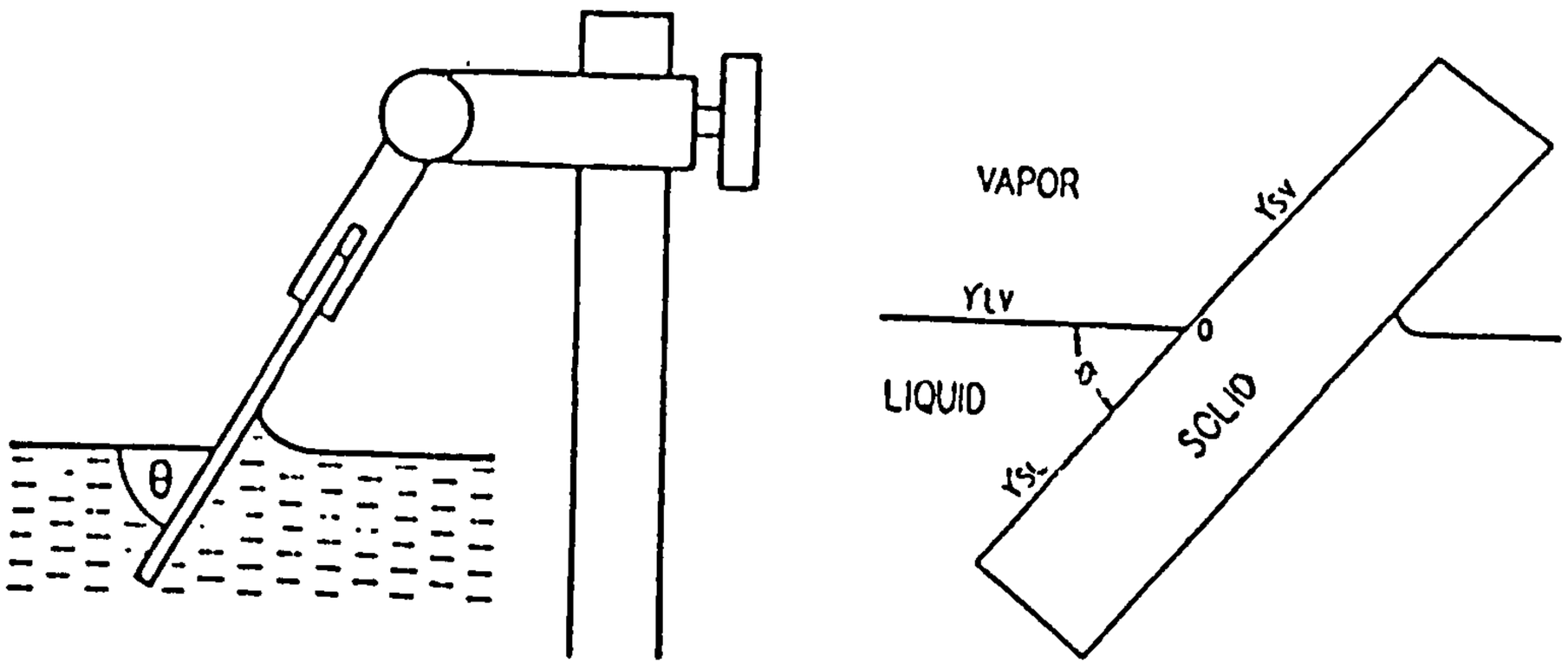


Figure 3.14. The tilting plate wetting angle method.

When the tilting plate is lowered to expose a fresh portion to the liquid, the angle measured is known as the advancing contact angle, and when the plate is raised partially out of the liquid the receding contact angle is measured, with the plate being set to the required angle before, and not after, the raising or lowering of the plate, this requires several trials. The more important additions to the tilting plate apparatus were the use of glass barriers to clean the surface of the liquid, a film balance to detect the presence of impurities on the surface of the liquid and the use of a tight cover to achieve equilibrium between the liquid and vapour. Adam (1941) emphasised the necessity for clean solid surface, while Fowkes et al (1940) reported that the main requirements of an accurate instrument for measuring of contact angles by the tilting plate method were three-fold:-

a. The surface of the liquid must be kept clean during measurement.

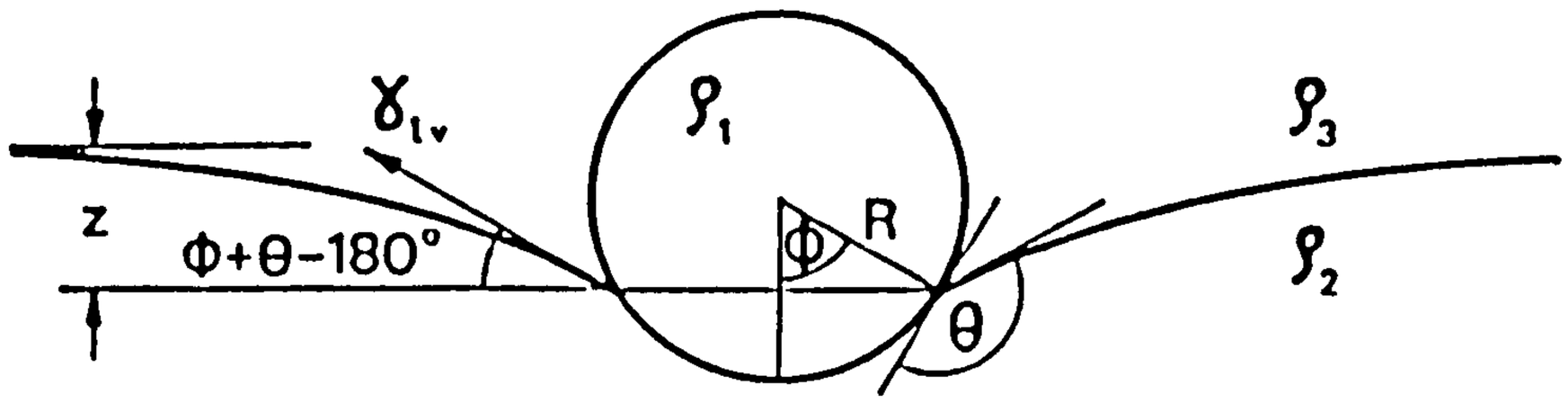
b. The observed edge of the solid-liquid intersection must lie on the axis of rotation of the solid surface.

c. There should be a mechanism to move the slide up and down in the liquid and in a direction parallel to the length of the slide.

3.4.4. Rotating-rod Method

The rotating plate method can be considered to be an improved tilting plate method, with the fluid-fluid interface being contained within a cylindrical glass and the cuvette having optically flat end windows (Figure 3.15). The cuvette has an opening on the upper side that allows the cell to be filled with fluid phases and introduces the rod to be investigated and is encased in a hollow aluminium cylinder that is mounted on ball bearings so it may be rotated around its axis. The rod that is made of the material to be investigated is driven in and out through the fluid-fluid interface in the cuvette by a hydraulic piston mounted on the aluminium casing. The glass cylinder with the mounted rod can be rotated so that the fluid-fluid interface meets, horizontally, the surface of the rod (or plate) that is simultaneously moving either in or out. The three-phase interline can be directly

observed with a microscope, and the contact angle measured with a protractor that is attached to the aluminium casing, or, alternatively, the system can be filmed as previously indicated (Adam et al 1934).



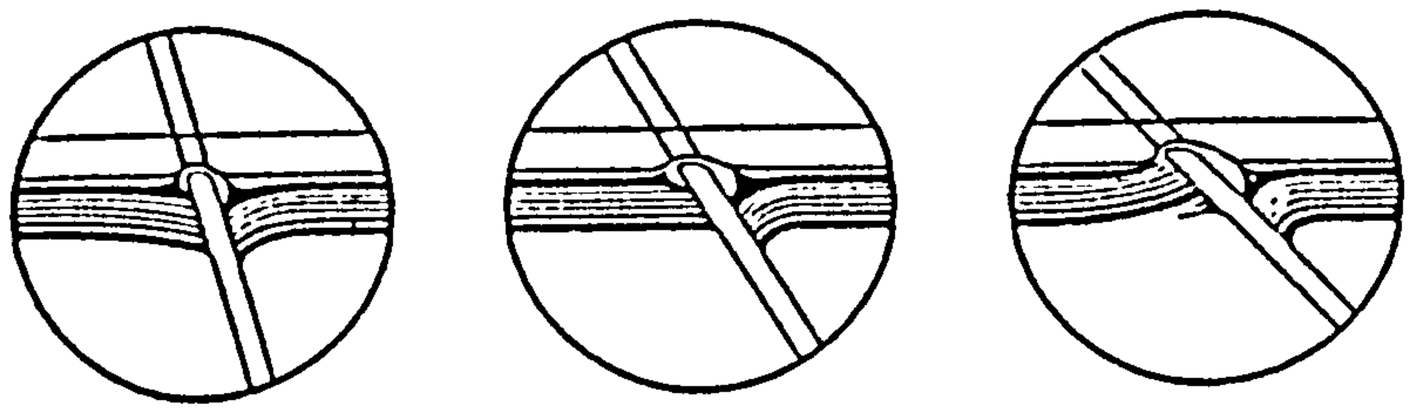


Figure 3.15. Change of curvature of the water surface with rotation of the plate.

The main advantages of this method were claimed to be:

1. Precisely controlled motion of the specimen relative to the fluid-fluid interface over an unlimited range of speeds.
2. Highest reading accuracy over the range from 0° to 180°.
3. Absence of any vibrations because of the hydraulic driving system.
4. The construction material of the cuvette and the driving mechanism is glass and Teflon. This allows the system to be cleaned by all available methods. The airtight sealing eliminates any possibility of contamination by the ambient atmosphere.
5. The contact angle (advancing and receding) can be read directly.

Ablett (1923) and Wenzel (1936) studied the solid surface energy by measuring the contact angle (θ) by immersing and rotating a cylinder:

$$\text{Cos}\theta = (2\frac{h}{d} - 1) \qquad (12)$$

h is the height of the free liquid surface above the lowest generator of the cylinder and **d** is the diameter of the cylinder.

3.4.5. Capillary Rise Method

The tendency of liquids to rise up a capillary tube or a flat material is called capillary rise or adherent action and is a result of surface and interfacial tension. When a tube or a flat material is moved into the liquid, the rise of a liquid in a capillary tube depends on the contact angle and the curvature of the tube, which in turn determine the curve of the liquid surface (Figure 3.16). The pressure difference across the curved surface depends on the free energy of the surface and provides the hydrostatic pressure under which the liquid flows up the tube (Holly 1983b, Bartell et al 1953 and Atkins 1994). If the radius **r** of a cylindrical tube is so small that the liquid meniscus is essentially spherical, the height of the rise (**h**) of the meniscus is given by:-

$$\frac{2\gamma\cos\theta}{r} = gh(p_1 - p_2) \qquad (13)$$

where γ is the surface tension, θ is the contact angle, g is the gravitational constant and $p_1 - p_2$ is the difference in pressure between the rising liquid and the surrounding fluid. Neumann et al (1971 and 1970) reported on the dependence of the advancing and receding contact angle on temperature in this method.

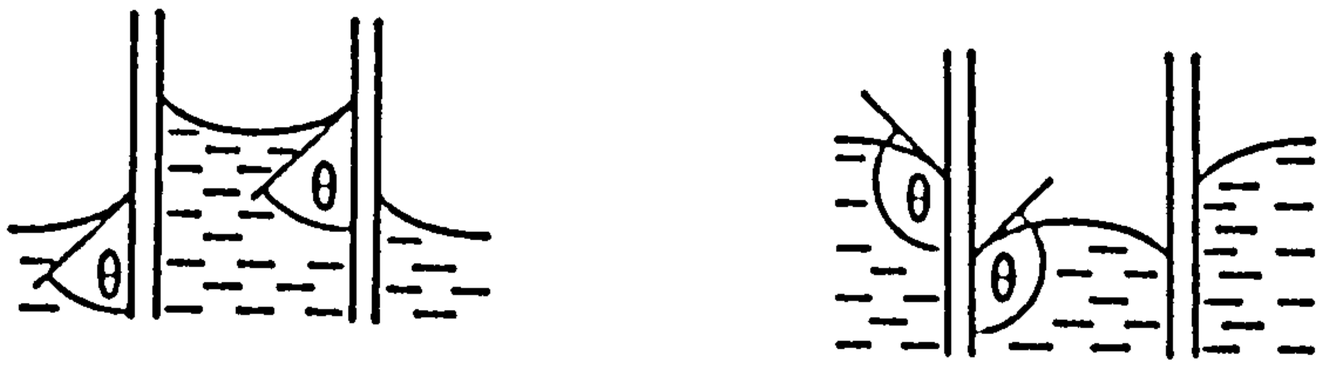


Figure 3.16. Meniscus of a liquid in a capillary.

3.5. In vitro Interferometer Wetting Angle Method

The wettability of contact lenses may be indirectly determined macroscopically using the interferometer method (Garner 1981, Doane 1989a and b, Forst 1989, and 1990). The water layers were observed using a Nomarski differential interference contrast microscope with a magnification of approximately 23X and then located in a perpendicular standing position on a convex holder. The contact lens was submerged in the water and withdrawn. The behaviour of the thin water layer on the contact lens was shown as interference, and the photograph was taken to measure the contact lens wettability. The microscopic method observes the behaviour of water layers on the contact lens surfaces up to a thickness of 0.1μm - 0.2μm, and by elevating the interference phenomena a water profile can be determined and the microscopic contact angle between the water and surface of the contact lens calculated (Figure 3.17a). It was claimed that this method allows a great influence of surface deposits to be recognised.

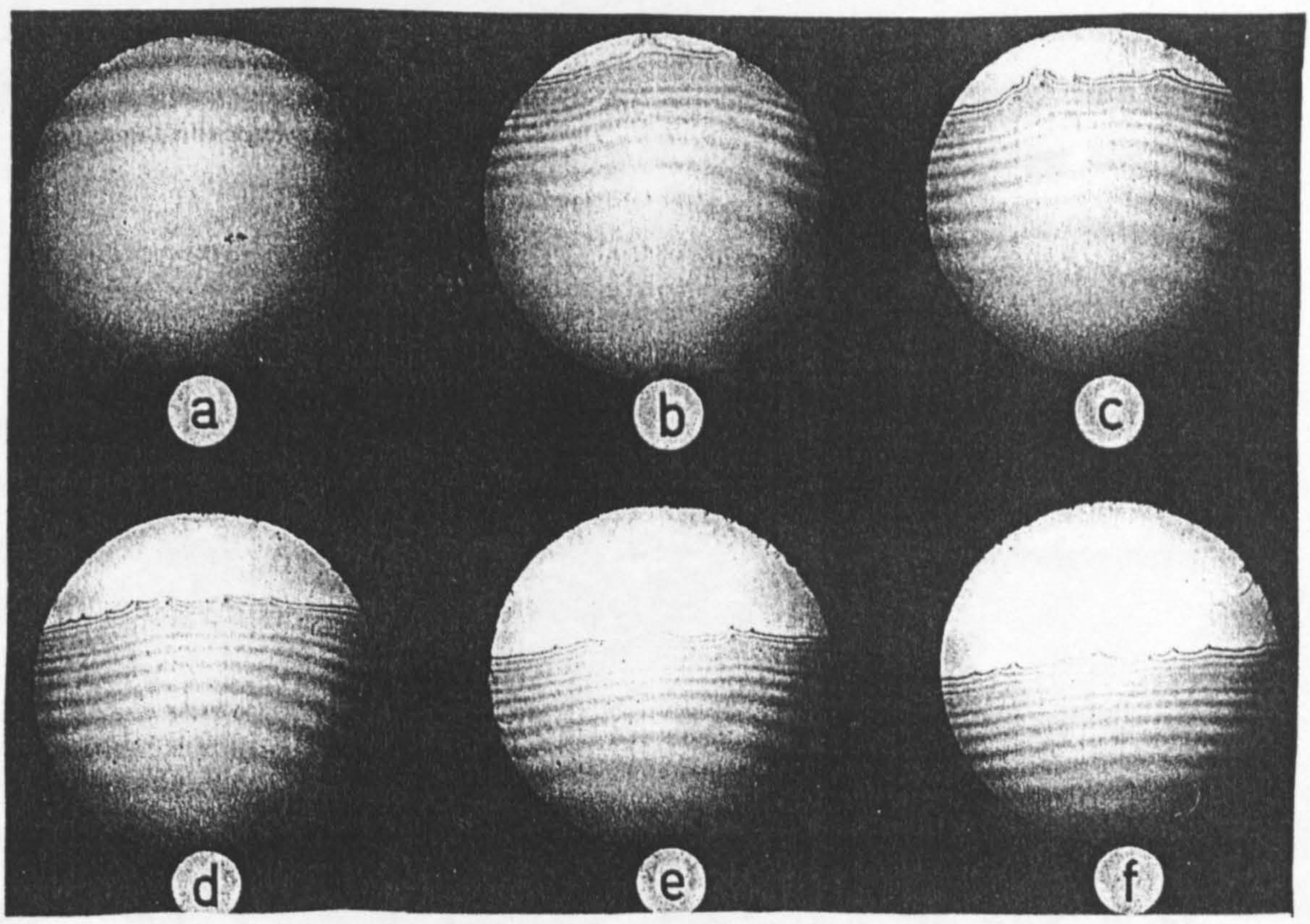


Figure 3.17a. In-vitro interference to measure contact lens wettability.

3.6. Wetting Angle Hysteresis

The difference between the maximum (advancing) and the minimum (receding) contact angle was termed hysteresis, Taggart et al (1930), Del Giudice (1936), Gaudin et al (1963) and Andrade (1976) while Holly (1978 and 1983b) defined relative contact angle hysteresis (H_R) as the difference between the advancing and receding contact angle values divided by the advancing contact angle. Hysteresis also refers to phenomena in which two different values are obtained in a measurement, depending on whether the drop is expanding or receding, such as contamination of a liquid or solid that gives rise to hysteresis.

In 1920, Sulman investigated the cause of discrepancies between recorded values of contact angles, and there are several possible causes of wetting angle hysteresis. One involves chemical changes on the surface of the solid. On the surface of a material (especially hydrogels), the various groups of polymer chains are mobile as they can rotate, and when the surface of the polymer is exposed to air the un-wettable groups tend to be oriented towards the out side. In measuring the advancing angle, since more of the un-wettable groups of the polymer chain are oriented towards the surface, there is less wettability and thus a larger contact angle is obtained. When the surface of the un-wettable groups is in the bulk, the wettable groups come to the surface. In measuring the receding angle, since more of the wettable groups of the polymer chain are oriented towards the surface, there is greater wettability and thus a lower contact angle is obtained (Holly 1983). The other cause can involve the work of adhesion (W_A) between the liquid-dry solid and liquid-previously wetted solid. In this case, penetration and absorption were recorded as the most frequent causes of hysteresis (Cassie 1944).

There has been an attempt in the literature to correlate hysteresis with lens material wettability (Holly 1978), but the results indicate that hysteresis is not a good indicator for advancing or receding contact angle (Fitzgerald 1983). Accurate measurement below 10° was impossible, and the receding contact angle of the treated silicone material is recorded as <10°. Thus, he concluded it was not possible to calculate precise hysteresis.

Bartell et al, (1953) and Grohe et al, (1989) ascribed "advancing and receding" wetting angles to improper preparation of the surface and poor measuring techniques, with the three factors responsible for hysteresis appearing to be surface roughness, contamination and adsorption effects. Similarly, Guastalla (1957) have listed several causes of contact angle hysteresis: hydration; dissolution; deposition and chemical interaction between the liquid and solid.

3.7. In vivo Wettability

Clinical observations showed that tear spreading is a factor in determining the wearability of a contact lens surface (Dohlman et al 1976, Doane 1980a, Guillon et al 1989, Shiobara et al 1989, MacMillan 1992).

Jones et al (1994) and Doane (1988 and 1989) studied in vivo wettability, using an interferometric method, demonstrated that a thin lipid layer is usually present on the front surface of the pre-soft lens tear film, although, in the case of standard PMMA corneal lenses, a lipid layer in the pre-lens tear film was rarely detected. Guillon et al (1989) stated that tear film on thicker soft contact lenses are more stable than the ultrathin lenses. Tears contain a significant amount of calcium, the precipitation of which can be examined by rapid tear film break-up. If tear film composition, quantity or quality is significantly found outside accepted values, an increase in the level of deposition is to be expected. The fatty acids lipids come into contact with the contact lens surface, which produces areas of non-wettability.

Tomlinson (1984) investigated the contrast sensitivity function of subjects wearing rigid contact lenses, the contact angles were between 46.9° and 66.9° using the captive bubble method and subjects varied in their response, with the visual performance of one being severely affected by the material with the highest contact angle while another subject showed no relation between performance and contact angle. He concluded that for some patients visual performance is affected adversely by contact angles exceeding 60°, but felt that angles lower than 60° were not necessary for establishing stable mucin.

On-eye wetting was assessed using a slit-lamp biomicroscope. A qualitative grading system from 0° (very good) was adopted, which was based on the number and size of non-wetting areas on the lens front surface and the evaporation time of the film on the lens front surface immediately following a blink (front surface tear break-up time). In vivo wettability was correlated with the advancing angle after seven days of soak and 20 minutes of wear (Benjamin 1984). In-eye wetting characteristics are markedly influenced by the lens manufacturing procedures, with variables, such as the polishing media, polishing compounds and solvent exposure

(duration and type), altering surface wettability (Bennett, 1990). Clinical experience has demonstrated that gas permeable hard contact lenses are more susceptible to deposit formation than those made from PMMA. In the case of CAB, the deposit is essentially lipid in nature, while siloxane-methacrylate adsorbs both lipid and protein. The deposits block the wettable groups of the polymer surface and produce an un-wettable surface.

3.7.1. In vivo Sessile Drop Method

Although contact angles can be measured on contact lens surfaces, there is still the problem of interpreting the observed angle in terms of a surface property of interest to a contact lens practitioner (Fatt 1990). Experience shows that the observed contact angle on RGP lens surfaces is sensitive to the history of the surface, while the in vivo study (Benjamin et al, 1984a and 1989) illustrated that a sessile drop contact angle ranged from the maximum observed for a fresh lens, about 65°, to as low as 12° after a few blinks.

Benjamin et al (1984a), Benjamin et al (1984b) Yeager et al (1987) and Benjamin (1987) measured in vivo RSCA: after five blinks and following five, ten, and fifteen minutes of lens wear. They concluded that the wetting effect of rigid lens "wetting solutions" is short lived after five blinks, one wetting regime started to reduce the wetting angle and then after five minutes of wearing began to increase the wetting angle, the contact angles of the lenses treated with various care regimens were not significantly different ($P<0.05$) from those found with the saline control within the first 10 minutes of wear and were certainly not different after one minute. Therefore, they concluded that the factors determining patient acceptance of most solutions did not include major differences in the initial surface wettability on insertion. In vivo wettability was also investigated by Benjamin et al (1986), Bourassa at al (1987 and 1992), Cooke (1991) and Owen (1990), Benjamin (1992a and b), who showed a variation of tear on contact lens wettability. The slit-lamp biomicroscope was also used to observe the various aspects of the anterior lens surface, including wettability by Josephson et al (1989).

3.7.2. Tear Break Up Time

The tear film break up time method (TBUT, Norn 1969, Holly 1973, Lemp et al 1973, Koetting 1977, Holly 1981, Gleason et al 1987) and tearscope were used in vivo to evaluate tear film structure and tear film stability to measure the wettability of rigid and soft contact lens surfaces (Holly et al 1977, Guillon 1987, Guillon et al 1988 Guillon et al 1989 and Tighe et al 1990, Figure 3.17b). There were marked differences between some of the lenses in the rate of tear film break up and tear film thickness on the lens surfaces, with the surface chemistry of rigid gas permeables (RGP) being reported as the cause of lens surface drying, the accumulation of debris on the surface, peripheral corneal staining and lens discomfort visual problems (Lemp et al 1970a). Subjective responses about comfort, vision and lens preference were also the subject of contact lens wettability in vivo. But Tomlinson at al (1991) stated that pre-lens tear film, lens wettability and deposit resistance did not vary significantly with the fluorine content in vivo initially and after three days of wear.

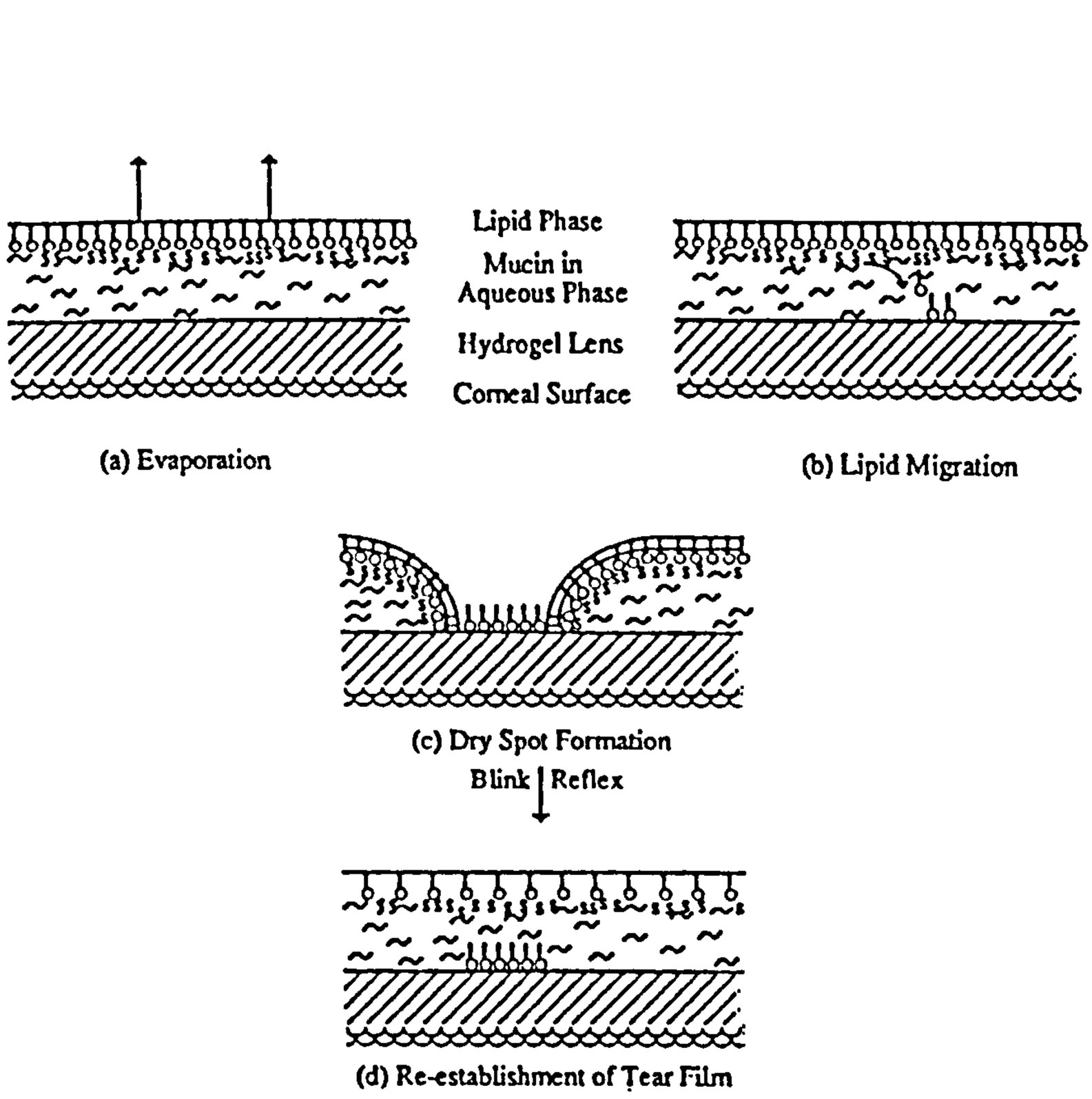


Figure 3.17b. Schematic presentation of tear film on a hydrogel contact lens (Tighe et al 1990).

3.8. Variables Which May Influence Wettability

3.8.1. Conditioning

Hydration, dehydration, contact lens wearing time, wetting and soaking solutions generally influence on the lens surface wettability. Several methods have been used to hydrate and dehydrate a material surface to measure the wettability, and some workers have dried the contact lenses with a paper tissue before each measurement [Poster et al (1978), Bush et al (1988), Huff et al (1988) and Knick et al (1991)]. Fitzgerald (1983) and Madigan et al (1986) dried the contact lenses with lint free cloths, while Harris et al (1973), Cappelli (1979) and Sunny et al (1991), measured the wetting angle after several hours of dehydration in air and Fakes et al (1987) dried the lenses in Nitrogen. Many investigators rinsed lenses with distilled water and dehydrated them over night in a desiccator containing $CaSO_4$ palates [Anan (1979), Benjamin et al (1983), Madigan et al (1986), Huff et al (1988) and Sunny et al (1991)]. Shirafkan et al (1994, see 4.2.1.1 and 5.1.2) introduced a reliable and easy method to remove water from the hydrated, both rigid and soft contact lens surfaces.

Bush et al (1988) stored the contact lenses in wetting and soaking solution, rinsed them with distilled water and dried them with a tissue before each measurement. Knick et al (1991) stored the lenses in saline for three days and in a Boston conditioner for seven days, reporting that all lenses returned to their baseline wettability by the third day. Huff et al (1988) stored the lenses in Soaclens, rinsed them with saline and dried them with tissue, Sarver et al (1984) soaked the lenses in Bausch and Lomb saline solution for two weeks and Benjamin et al (1983) measured the wetting angle in the dried and soaked state for 0-20 hours in Flex-Care solution.

Madigan et al (1986) measured the contact lenses' wetting angle in a dry state which had been hydrated in saline for one day and seven days, reporting the advancing wetting angles of 65°, 24° and 20° and the receding angle values of 34°, 16° and 12° (±3) respectively. Gregonis et al (1982) reported the wetting angle value of 59° (±2) for soaking the lenses for 24 hours, while Poster (1984) and

Fakes et al (1987) compared the wetting angle values of PMMA Glass flex clear in the different soaking solutions of normal saline and Soaclens for 24 hours, which were 45.25° and 20.16° respectively. They also measured the wetting angle values for blue PMMA with different soaking solutions, as before, finding that the values were 41.60° and 18.73° and concluding that the preconditioned lenses in Soaclens appeared to have the lowest wetting angle. Hydration and dehydration in a room air temperature of 22°C and humidity of 50 per cent did not significantly alter (71.2° and 72.3°) the wetting angle of PMMA lenses (Benjamin et al 1983).

Distilled water has been used to hydrate contact lenses by many investigators [O'Brien (1965), Poster et al (1978), Cappelli (1979) Gregonis et al (1982), Jho (1983), Fakes et al (1987) and Sunny et al (1991)]. Keates et al (1984) soaked the lenses in de-ionised water, and Rosenthal et al (1986) reported that Benzalkonium chloride reduced the surface wettability of materials. In contrast, Chlorhexidine Gluconate (CHG) was less strongly bound to the lens polymers and did not create an un-wettable lens surface.

Davidson et at (1971) and Dexter (1979) argued that there was a need to standardise surface preparation techniques to minimise fluctuations in the interaction parameters and make precise measurements of the wettabilities by organic liquids. The wettability of water by non-polar organic liquids has been measured experimentally by Shafrin et al (1967), while Hill et al (1981) studied the wettability of 10 different wetting solutions on PMMA material and reported the advancing and receding wetting angle values of 60° and 36° respectively for the distilled sessile drop.

Most wetting solutions on the market contain water-soluble polymers, such as methyl cellulose, hydroxyethylcellulose and hydroxypropylmethylcellulose. These components impart high viscosity, and increase the break-up time, and, therefore, these solutions appear to form an aqueous layer over the surface that is applied to an un-wettable solid surface. Polyvinyl alcohol is also used as a wetting solution ingredient, the aqueous solutions of polyvinyl alcohol at one to two per cent concentration are nonviscous. The higher the residual acetate content, the more

surface activity (Holly 1983a). The wettability of rigid lenses with respect to the actions of lens care solutions has been tested by in vitro methods [Krishner et al (1964), Benjamin et al (1984), Poster et al (1987) and Holden et al (1992)]. The use of one day conditioning solution on Boston contact lenses showed reductions of 51 per cent and 65 per cent respectively for advancing and receding angles, but after, seven days soaking, the advancing and receding angles had either stabilised or declined further (Madigan et al 1986). Hill et al (1981) stated that every wetting solution must have relative acidity (pH) and equivalent osmolarity to produce a good wettability. Knick et al (1991) compared the wettability of PMMA lenses that had been hydrated in saline for three days and in the Boston solution for seven days, reporting a temporarily lower wetting angle of 20° to 12° for the Boston conditioning solution. Poster (1984) compared the wettability of clear PMMA in normal saline (45.3°) and in Soaclens solution (20.2°) for 24 hours and reported on the wetting angle values for the blue PMMA with different soaking solutions, which were the same as before (41.60° and 18.73°), and concluded that the preconditioned lenses in Soaclens appeared to have the best wetting angle. Fatt (1984) reported different wetting angle values of PMMA when:-

1. The contact lenses were stored in Contique soaking solution for 14 hours and rinsed with distilled water (73°).
2. Cleaned by rubbing the lenses with fingers using Contique cleaning solution and rinsing in distilled water (13°).
3. After two hours of wearing (44°).
4. After being worn for 12 hours (about 44°).

He concluded that those lenses cleaned by rubbing using Contique cleaning solution, even after being rinsed with distilled water, lowered the wetting angles substantially from 73° to 13°. Fatt also found that wearing the lens changed the wetting angle from 13° to 44° in two hours and additional hours of wearing did not raise the contact angle.

3.8.2. Wetting Angle Interface Solution

The presence of dissolved substances in the liquid, as well as un-dissolved particles on the surface of the drop, can markedly affect the contact angle. The purity of the liquid may be checked with published physical constants, as well as the use of instrumental methods of gas-liquid chromatography and spectrophotometric techniques (Bikerman 1970). Various solutions have been used in the sessile drop method: distilled water [O'Brien (1965), Lin et al (1973), Harris et al (1973), Ong et al (1976), Benjamin et al (1983), Fatt (1984), Fakes et al (1987), and Sunny et al (1991),]; unpreserved saline [Lemp et al (1972) and Knick et al (1991)]; and preserved saline [Sarver et al (1984); Huff et al (1988) and Bush et al (1988)]. The latter also used 0.8 per cent Mucin and stated that this significantly decreased wetting angles by 8° to 15°, although to acquire explicit data amenable to analysis it is essential that only pure solutions are used (Good 1979 and Zekman et al 1972).

3.8.3. Temperature

Most workers have measured contact lens contact angles between 20°C and 25° C [Brophy et al (1951), Tomlinson et al (1963), O'Brien et al (1965), Ong et al (1976), Cain et al (1982), Gregonis et al (1982), Jho (1983), Benjamin et al (1983), Fitzgerald (1983), Sarver et al (1984), Benjamin et al (1984) and Sunny et al (1991)]. While several researchers suggested that strict temperature control is not necessary [Neumann et al (1970), Neumann et al (1971) and Neumann (1979)], Staicopolu (1962) and Petke et al (1969) argued that contact angles were dependent on temperature.

Knick et al (1991) measured the wetting angle of contact lenses at the corneal value of 34.3°C (Efron et al 1989), discovering that the wetting angles decreased slightly with temperature and the increased temperatures failed to improve wettability, concluding that the wetting angles were independent of temperature. Fowkes et al (1940) stated that temperature control of plus or minus two degrees is satisfactory while taking measurements for calculations at 25° C.

3.8.4. Humidity

In general, wetting angles have been measured at humidities of between 29 to 76 per cent [Tomlinson et al (1963), Poster et al (1978), Gregonis et al (1982), Benjamin et al (1983) and Sarver et al (1984)], although Huff et al (1988), Bush et al (1988) and Knick et al (1991) used calcium chloride, magnesium nitrate and sodium acetate to measure the wetting angle at humidities of 31 per cent , 56 per cent and 76 per cent. They calculated that the wetting angle of hydrated and dehydrated lenses at the ranges tested were not affected by humidity and suggested that, if a moderate range of humidity was the only environmental variable, lens wettability would be unaffected by dry or humid environments. Poster et al (1978) measured the wetting angles in ambient relative humidities of 29 per cent to 60 per cent, Benjamin et al (1983) measured the wetting angle in 50 per cent humidity. Sarver et al (1984) measured the wetting angles at ambient room temperature, Gregonis et al (1982) measured the wetting angle in humidity of 30 per cent and Tomlinson et al (1963) measured the wetting angle of liquids by the reflecting method at relative humidity of 65 per cent.

Kneen et al (1937) reported that in the projection method careful control of humidity or temperature is not essential, with the measurement being carried out in less than 30 seconds after the drop has come into contact with the surface. Under such conditions, evaporation can be neglected for water and aqueous solution, with the contact angle showing no appreciable change over two to three minutes.

3.8.5. Surface Modification and Manufacturing

Several manufacturing processes have been recorded that affect lens surface wettability (Walker 1990) :-

1. Special soaking solutions (Kokoski et al 1963, Dabezies et al 1966, Benedetto et al 1975 and 1978, Doell et al 1986).
2. Special coating on hard contact lenses (O'Brien et al 1965 and Blue 1967).

3. Polishing (Lowther 1984; Dent 1986; Clompus 1987; Grohe 1988; Zantos 1990 and Morgan et al 1992).

4. Lens surface treatment [Gesser et al (1965 and 1967), Blue (1966), Fakes (1987)]. Sunny et al (1991) reported wetting angle values of 12.6° (±0.8) for treated and 78.7° (±2.25) for untreated PMMA materials.

5. Roughness. The surfaces appear to be more wettable when the surface is roughened (Wenzel 1936, Larke et al 1973, see later).

3.8.6. Surface Density

Surface characterisation of biomedical polymers is obviously important because the surface of the material interacts with the biological milieu (Hosaka et al 1983, Ratner 1983 and Castillo et al 1984). PHEMA 38 per cent water content is a cross linked polymer that can be lathe cut, spin cast or moulded into contact lenses, while the concentration of the ester group increases slightly from the surface (0.35 μm) to the bulk (2μm). The data suggest that the surface of the lens is less dense than its bulk, which is probably due to the lathe manufacturing technique.

In the spin cast process, the monomers are polymerised in a concave spinning mould, providing a better surface finish (Castillo et al 1983 and 1984) and a smoother surface without the lathe markings, pits and grooves associated with the lathe cut method. A small, but statistically significant difference was recorded when comparing the manufacturing process. The spin cast lenses are more compact than those of either the other two methods (Holly 1977), although the latest work by Shirafkan et al (see 5.3) showed that the wetting angle was inversely related to the material's bulk density.

3.8.7. Front Surface Radius

Bush et al (1988) measured the wetting angle of different front contact lens surface radii (7.00mm to 8.30mm) and reported that the wetting angle was independent of the radius. Huff et al (1988) measured the wetting angle of different

radii between 7.9mm to 8.1mm and stated that the wetting angle's values and front surface radius did not significantly correlate for the PMMA material.

3.8.8. Surface Roughness

Bartell et al (1953) defined roughness in terms of the average height **h** to which the asperities rise above the horizontal surface plane and the mean angle of inclination of the sides. **(a)** If, at the solid-liquid-air interface, the stable contact angle, with respect to the pyramid face, is formed, the curvature of the liquid-air interface will be distorted, which tends to cause the liquid to advance. **(b)** If the curvature of the liquid-air interface is constant, the angle made by the liquid with the solid on this pyramid face will be greater than the stable angle and the liquid will tend to advance the asperities with respect to the horizontal plane of the solid surface. The effect of such roughening to the surface is best understood in terms of the Wenzel (1936) equation through the Young equation, that modified by multiplying the energy change by a roughness factor, which is the ratio of the actual surface area to the geometrical surface area:

$$r\,(\gamma_s\,\gamma_{sl}) = \gamma_L \cos\theta' \tag{14}$$

where θ' is the contact angle on the roughened surface. The roughness factor **r** is always greater than one, except on an ideally smooth surface, when it is equal to one. The contact angle observed on a smooth surface is related to the angle observed on a roughened surface:

$$r\,(\cos\theta) = \cos\theta' \tag{15}$$

From this relationship, it follows that, if a contact angle on a smooth surface is less than 90°, roughening the surface will reduce the observed contact angle. If the angle on a smooth surface is more than 90°, roughening the surface should increase the observed contact angle. The contact angle depends on whether the interface at the periphery of the drop is roughened (Blake 1968 . Eick et al 1975 and Sammons 1985). Hoffman (1983b) discussed the nature of surface properties and stated that

a roughness that is greater than 0.1μm can be readily detected by contact angle measurement, so it is important that all lens manufacturers use the same techniques in machining and polishing.

Bikerman (1970) stated that grooves, valleys and scratches act as capillary tubes, in which a liquid rises if the angle is less than 90° or descends if the angle is greater than 90°. Lin et al (1973) reported that a rough surface is usually more effected on wettability than a smooth surface by a 'well wetting' liquid, while a 'poor wetting' liquid should spread on a smooth surface better than on a rough one. A rougher surface, therefore, would be more readily wet by water than a smoother one. Li et al (1992) and Cordrey (1983) studied the wetting angle on a surface that had less than 0.1μm roughness, reporting that contact angle measurements are very sensitive to surface roughness and all samples should be smooth to the 0.1μm level to improve wettability.

3.8.9. Surface Preparation

The presence of foreign materials on the solid surface can have a marked effect on the contact angle, according to Bikerman (1970). Lin et al (1973) stated that care must be taken in preparing and maintaining clean surfaces, while Ellison and Zisman (1954) used a procedure in which the samples, after polishing with silk, were rinsed. Tomlinson (1984) cleaned contact lenses by a solution and a hot ultrasonic cleaning device, Gleason (1987) stated that if the surface preparation was poor, the lenses would not wet properly and Dexter (1979) stated that there was a need to standardise surface preparation techniques to minimise fluctuations in the interaction parameters. Contact lens surface preparation was found to be an important factor (Shirafkan et al 1994, see 4.2.1), which could change the values of wetting angles.

3.8.10. Deposit

Bagnall et al (1980) evaluated the quality and quantity of deposits of PMMA materials before and after implantation in animals and measured the contact angle by the sessile drop/photograph method to determine the effect of adsorption of

proteins on contact angle values, concluding that in-vitro PMMA absorbs more protein than the other polymers on the surface. A similar report was documented by Wilsher (1982) and Anderson et al (1991), who also stated that in vivo contact angle measurement is not sufficient to justify and consider the protein absorption. High water content lenses have a greater pore size and/or number of pores and are, therefore, more susceptible to tear film constituents entering the lens matrix (Ong et al 1976 Minarik et al 1989, Smiddy et al 1990).

Feldman et al (1987) reported that a 'fluorinated' monomer enables the Equalens to resist surface deposition through its superior wetting on the eye. Tears contain a significant amount of calcium, the precipitation of which can be favoured by rapid tear film break-up, and if tear film composition, quantity or quality is found to be significantly outside the expected range then an increased level of deposition is to be expected. The fatty acids lipids coming into contact with the contact lens surface produce areas of non-wettability (Jones 1992). Deposit formation on various types of contact lenses are reported by many investigators, including Eggink et al (1988) and Allary et al (1989), while lathe-cut lenses may attract more surface deposits than lenses fabricated by either spin-casting or moulding because of their surface quality and lathing marks. Peppas et al (1981) and Jones (1992) stated that contact lens' manufacturing techniques are contributory factors in this respect.

The anterior surface of contact lenses examination showed that the continuously worn lenses had thicker coats, but more even surfaces than those worn daily, and the coatings on the two type of lenses seemed to be composed of the same elements, trabecular and granular mucus-like material and some bacterial forms. When one observes contact lens coatings by comparing new lenses worn for only 30 minutes, new lenses worn for only eight hours, routinely worn cosmetic lenses and continuously worn therapeutic lenses, the following hypothesis arises: in the first few minutes and hours of wear, cells and scattered bits of mucus adhere to the contact lens surface. As wear continues, more mucus is deposited and is ground to a more amorphous coating by the action of the upper lid on continuously worn lenses (Fowler et al, 1980).

The contact angle of water on PMMA is 65°-70° and on Silicone lenses is 103° and the problem of lipid adsorption for PMMA was not severe with a silicone lens (Holly 1983). In fact, the absorbed lipid clings more tenaciously to a hydrogel lens than to a hard lens and becomes insoluble in water, which appears to defeat the purpose of the attempts to make the surface of silicone or hard lenses permanently wettable either by ion or electron bombardment or by the deposition (Fowler et al, 1980) of a thin coat of wettable material. Such a wettable surface absorbs lipids tenaciously in a short time, resulting in a short lens life.

3.8.11. Ageing

Ageing of contact lenses has been reported to decay the wettability of contact lenses, particularly the treated polymer surfaces (Yasuda et al 1981, Guillon et al 1990, Figure 3.18)

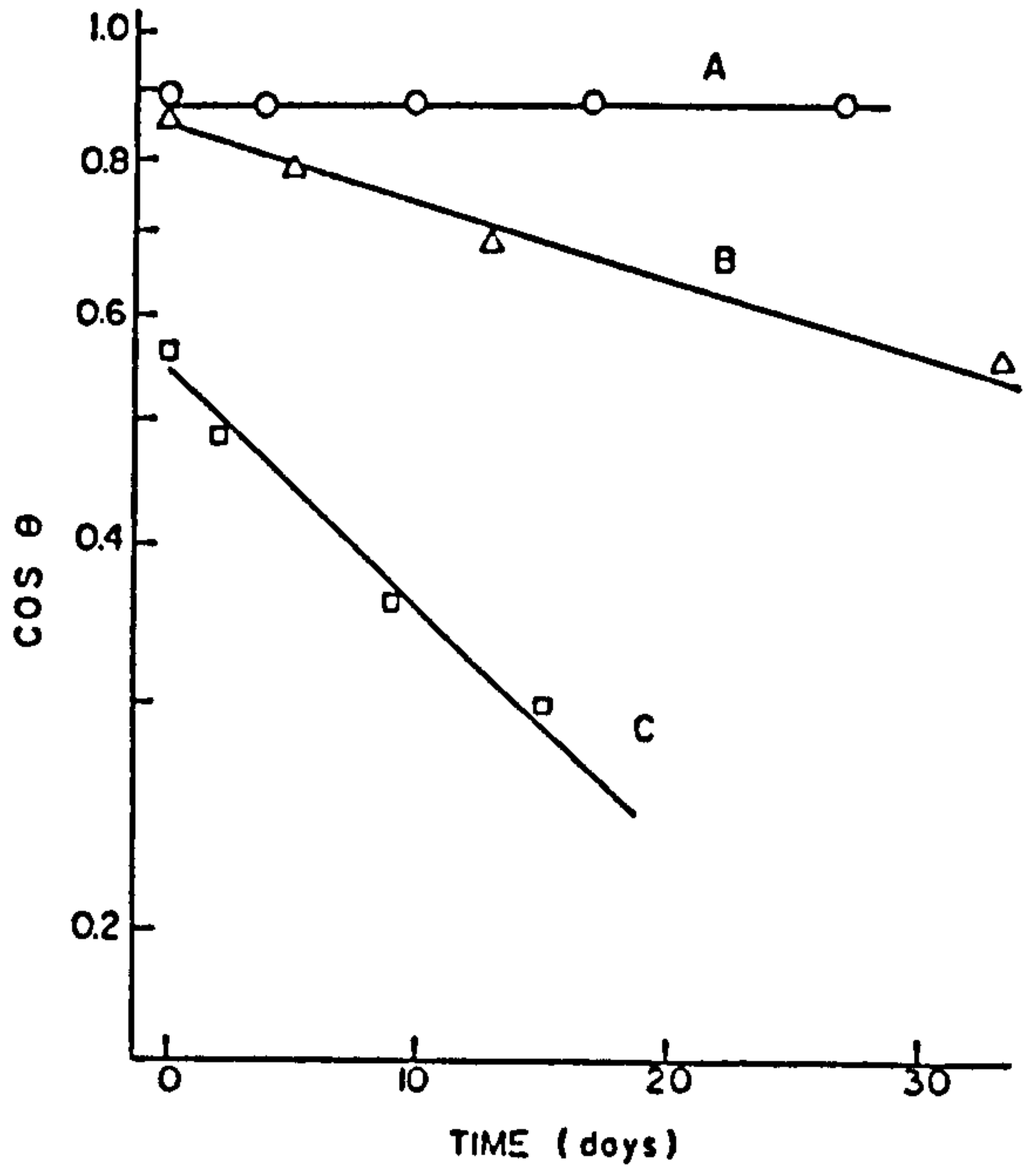


Figure 3.18. Variation of wetting angle as a function of ageing time for different plasma-treated surfaces. **A** Glow-discharge-polymerised methane, **B** glow-discharge-polymerised propylene and **C** conventional polypropylene (Yasuda et al 1981).

Chapter 4. Contact Lens Sessile Drop Wetting Angles

4.1. Introduction

The sessile drop wetting angle technique is one of the oldest methods used to measure rigid contact lenses' wettability. Despite disagreement over the repeatability values and reliability of the method (Hoffman 1983), it is still valid for scientific investigation and was, for example, recently used to measure the wettability of soft contact lenses (Jones et al 1994).

To produce a sessile drop on a hydrated contact lens surface, several techniques have been used by investigators to remove liquid from the hydrated contact lenses. It was suggested that the only method that could prevent extrinsic factors influencing the surface was to break the polymer material in to two pieces (Figure 4.1), although the produced surface is not like a contact lens surface. Contact lens preparation methods, however, produce either surface dehydration or surface contamination that can affect the measurement.

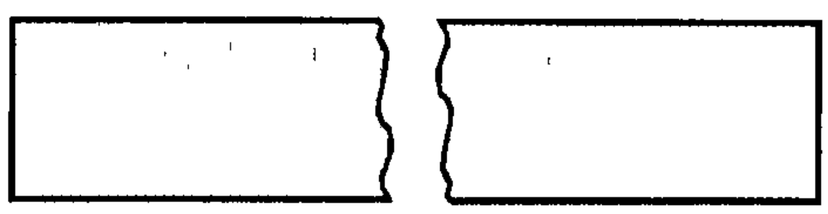


Figure 4.1. Polymer wettability can be measured when it is broken.

This Chapter will discuss a series of experiments, for the first a novel method was used to clean and remove liquid from hydrated rigid contact lens surfaces to produce a solid-liquid-air interface to measure wettability (experiment 4.2.1). The aim of the next two experiments was to find a repeatable sessile drop delivery system (4.2.2) and investigate the influence of the front lens surface radius on the contact lens wetting angle (4.2.3). Both attempted to standardise the sessile drop technique.

In 4.3.1, the sessile drop was used to measure contact lens wettability influenced by solutions, while 4.3.2 revealed the wettability of rigid lenses when influenced by

the tear film. Finally, the receding sessile drop on a rigid contact lens was monitored by measuring the wetting angle and diameter of a sessile drop every two minutes (4.4).

4.2. Pilot Studies

4.2.1. Contact Lens Surface Preparation Method

4.2.1.1. Aims, Material and Method

A contact lens in vivo would be in hydrated state, hence the wettability values of hydrated contact lens surface has close relationship to the actual usage of a lens. The literature search showed that the two methods of evaporation and wiping have been used to remove liquid from the hydrated contact lens surfaces which can partially or completely made the lens surface to be dehydrated. In order to use sessile drop method to measure contact lens surface wettability a novel method is used to clean and remove a liquid from hydrated rigid contact lens surface to produce a solid-liquid-air interface. The result were compared with the established methods of evaporation and wiping methods.

A PMMA contact lens from the contact lens clinic at City University was cleaned with a L.C. 65 surfactant cleaner using a brush (Prolene by Proarte UK 106-50739455) for 30 seconds. To prevent lens surface contamination from the fingers, it was held by a contact lens holder. After cleaning, the lens was repeatedly washed with distilled water and soaked for 24 hours in de-ionised distilled water (pH 6.6 ±0.2; γ= 72.5 ±0.4). The following methods were used to remove liquid from the lens surface.

a. **Evaporation Method.** The rigid contact lens, after cleaning and hydration, had warm air blown over it for three minutes to remove liquid from the lens surface. The temperature at the contact lens surface was adjusted to 40° C (±2).

b. Wiping Method. A medical paper tissue (Kleenex 3020) was rubbed on the rigid contact lens front surface five times.

c. Surface Tension Removing Liquid Technique. Surface tension was used to remove liquid from the hydrated contact lens surface. The hydrated rigid contact lens was withdrawn vertically about 1mm from the liquid surface of a container using two tweezers (Figure 4.2) and then tilted and elevated to remove water from the contact lens surface without touching or damaging it. The small amount of saline remaining on the edge of the lens was removed by a corner of the paper tissue. The equilibrium sessile drop/laser assisted method was utilised to measure contact lens wettability (see 3.2.3.5, Bush et al 1988).

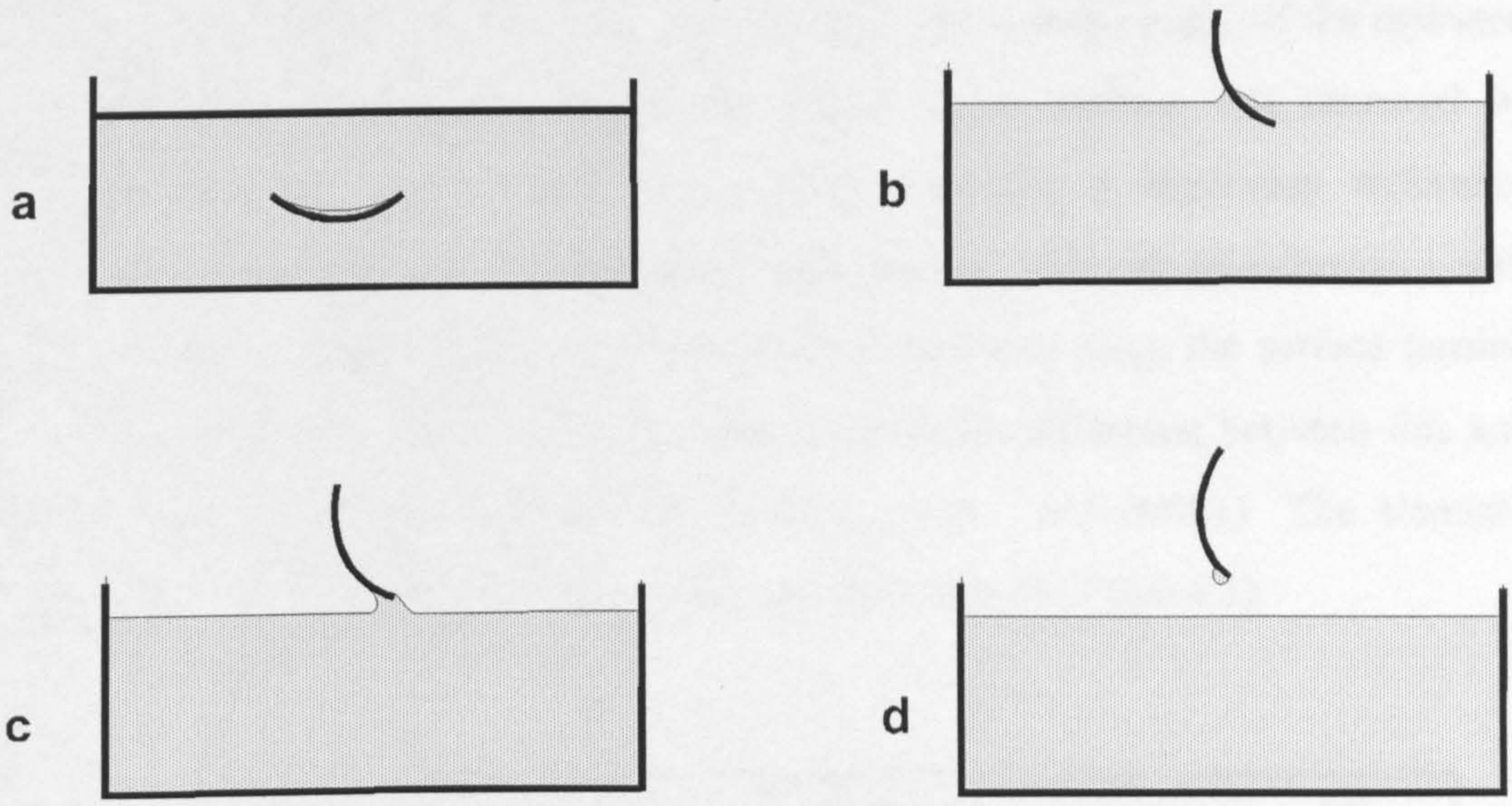


Figure 4.2. The use of the surface tension function to remove liquid from the hydrated contact lens surface: **a**. hydrated contact lens; **b** withdrawing the contact lens from the liquid; **c** removing liquid from the contact lens surface; and **d** the remaining liquid was removed by a paper tissue without touching the contact lens surface.

A Hamilton micrometer syringe with a circular modified needle tip (0.46mm diameter, see 3.2.1 and Figure 3.1) was used to place a sessile drop of de-ionised distilled water on the lens surface to produce a solid/liquid/air interface, while the contact drop delivery method (see later) was employed to place a sessile drop. Within 60 seconds of drop delivery, the laser was adjusted at the interface to

measure the wetting angle. To produce the wetting angle on the protractor quickly, the light was adjusted on the contact lens surface and then directed at the interface area. Two measurements were read for the left and right side of the drop and the average of two readings was calculated as the wetting angle. Ten independent measurements were taken for each contact lens preparation method.

4.2.1.2. Results

The effects of surface preparation on the wetting angle measurements are illustrated in Figure 4.3 and Table 4.1. The wetting angle values of the hydrated rigid contact lenses varied with the surface preparation methods and there was a significant difference between the wetting angle of the various contact lens surface preparations (ANOVA, $F= 47.01$, $p<0.00001$). The wetting angle of the hydrated PMMA contact lens, from which the liquid of the surface was removed by evaporation, had the greatest value. There was also a significant difference between the values of the "evaporation" and "wiping" methods (Bonferroni, t-test, $P<0.001$). The mean wetting angle of the hydrated lens using the surface tension technique was the lowest and there was a significant difference between this and the other preparation methods (Bonferroni, t-test, $p<0.00001$). The standard deviation of the surface tension method was the smallest (Table 4.1).

Removing liquid techniques	Wetting angle mean	SD
Evaporation	73.2	2.4
Wiping	70.2	4.8
Surface tension	62.8	1.8

Table 4.1. The mean and standard deviation of the wetting angle values of the hydrated PMMA lens using different methods to remove liquid from the hydrated contact lens surface.

4.2.1.3. Discussion

Several methods have been used, apart from the surface tension technique, to remove liquid from the surface of hydrated contact lenses, which led to the lens

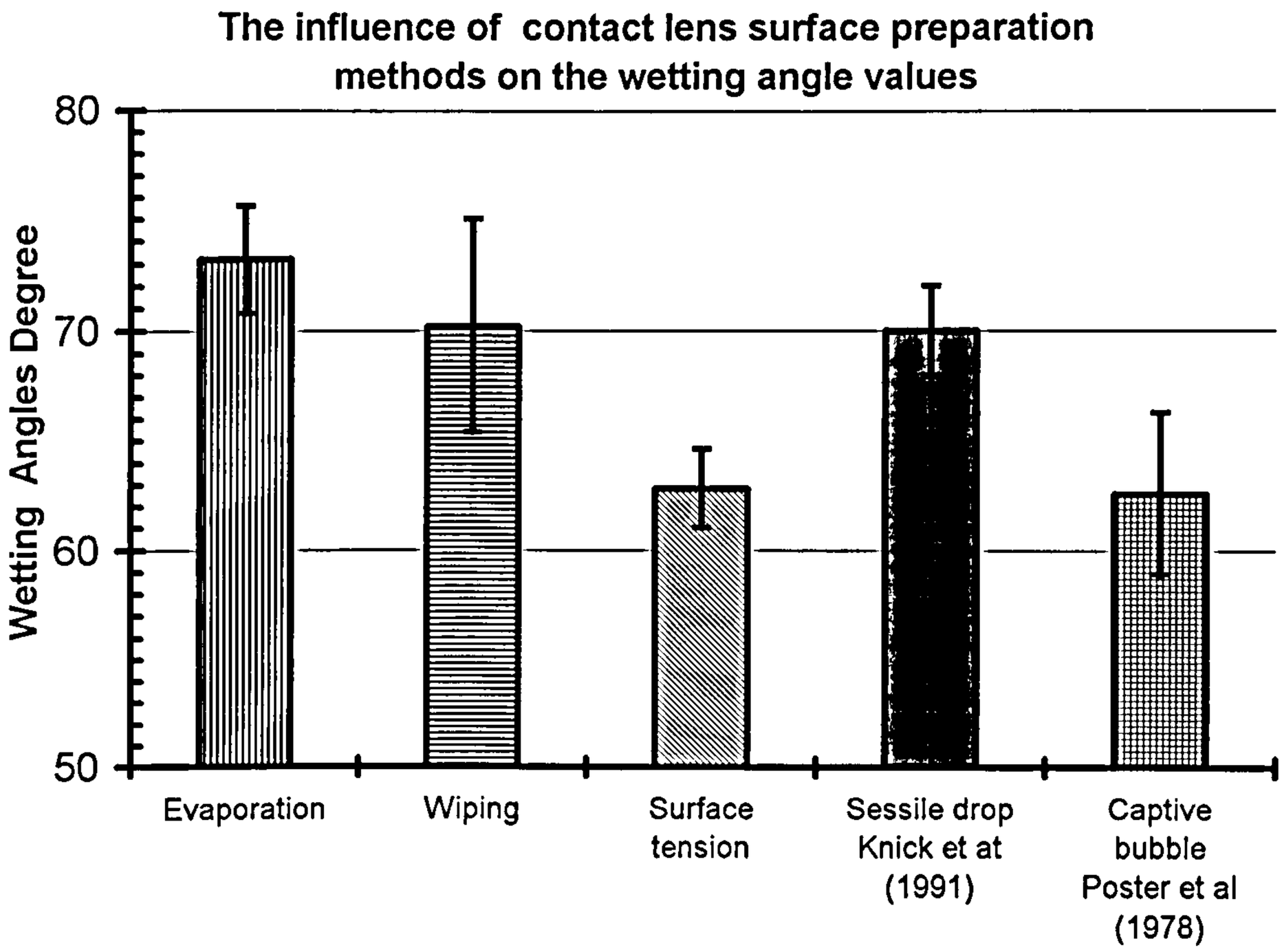


Figure 4.3. The wetting angle values following different contact lens surface preparation methods: evaporation, wiping and surface tension compared with the two the established values (PMMA)..

surfaces becoming partially or totally dehydrated. As the use of contact lenses in vivo would be in a hydrated condition, it is logical to measure the contact lens surfaces' wettability in vitro whist they are hydrated (see 3.9).

Contact lens surface wettability can be influenced by manufacturing processes and wetting solutions (see later). When they were measured using wiping and evaporation methods to remove liquid from the contact lens surface, the surfaces dehydrated partially or completely, causing the values to increase towards a dehydrated condition.

When the lens surface was wiped by the tissue and the pendant drop delivery used, measurement values increased. Because the drop at the tip of the needle became unstable and shook when the lens surface approached the droplet, it suddenly fell

on a contact lens peripheral area (not at the contact lens centre as expected). This was because the electrostatic charges were produced on the lens surface by wiping the tissue. As a result, a greater standard deviation was calculated from the measurement values (± 4.8).

Figure 4.3 compares the established captive bubble method value with the experiment values which the standard method (captive bubble) shows a greater variation. One of the main reason to accept the captive bubble was because the measurement could be obtained in hydrated condition, otherwise there were no advantages over other methods. The only remaining method without any problem, therefore, was the surface tension technique, in which the molecules of water on the contact lens were removed by surface tension forces and, therefore, the molecules that were absorbed by the polymer bulk were not removed. The advantages of this method are that:

- it does not affect lens surface hydration;
- it gives low-standard deviation; and
- it produces and incurs minimum surface contamination.

4.2.2. The Influence of Sessile Drop Delivery Methods on Contact Lens Surface Wettability

4.2.2.1. Aims, Material and Method

A Literature search showed that to measure contact lens surface wettability a sessile drop can be used either in the state of dripping or contacting the lens surface to a pendant drop for placing the droplet. There was also a dilemma on reproducibility of methods, hence both methods were explored.

A rigid contact lens made from PMMA with a front surface radius of 8.00mm and a total diameter of 9.50mm was manufactured by the City University contact lens laboratory. It was cleaned with L.C 65 using a brush, as described in 4.2.1.1. It was hydrated in de-ionised H_2O (pH=6.6 ±0.2, γ=72.6 dynes ±0.4) for 24 hours

and the water on the hydrated lens surface was removed by the surface tension method. Two drop delivery techniques were used.

a. Dripping Drop

In this method, an equilibrium sessile drop freely fell from the tip of a syringe needle on to a contact lens surface. The distance between the droplet and the lens surface was adjusted to less than 1mm and the volume of the drop was controlled by modifying the tip of the syringe needle. An initial study showed that the larger the syringe needle diameter and the more rough and unsharpened the needle tip, the larger the droplet volume. A 0.46mm syringe needle tip diameter was modified to produce a 3μl volume drop.

b. Contact Drop (pendant drop)

The contact lens was elevated slowly towards a prepared drop on the tip of a syringe. To deliver a sessile drop to the centre of the contact lens surface, the centre of the platform was adjusted towards the tip of the needle. The platform was then moved 5mm away from the tip of the needle while the syringe was filled with de-ionised water. A drop was created at the tip of the needle and the platform was slowly elevated until the front surface of the contact lens touched the drop.

The laser wetting angle method was used to measure wetting angles. The laboratory temperature and relative humidity were 23° C (± 2) and 40 per cent (±5), and ten independent measurements were calculated for each drop delivery method.

4.2.2.2. Results

The results are illustrated in Figure 4.4, with the Student t test revealing that there was a significant difference between the mean wetting angle values of 'the contact drop delivery (63.8°, SD=±0.9) and the dripping drop delivery (62.20°, SD=±1.8, $p<0.045$) methods.

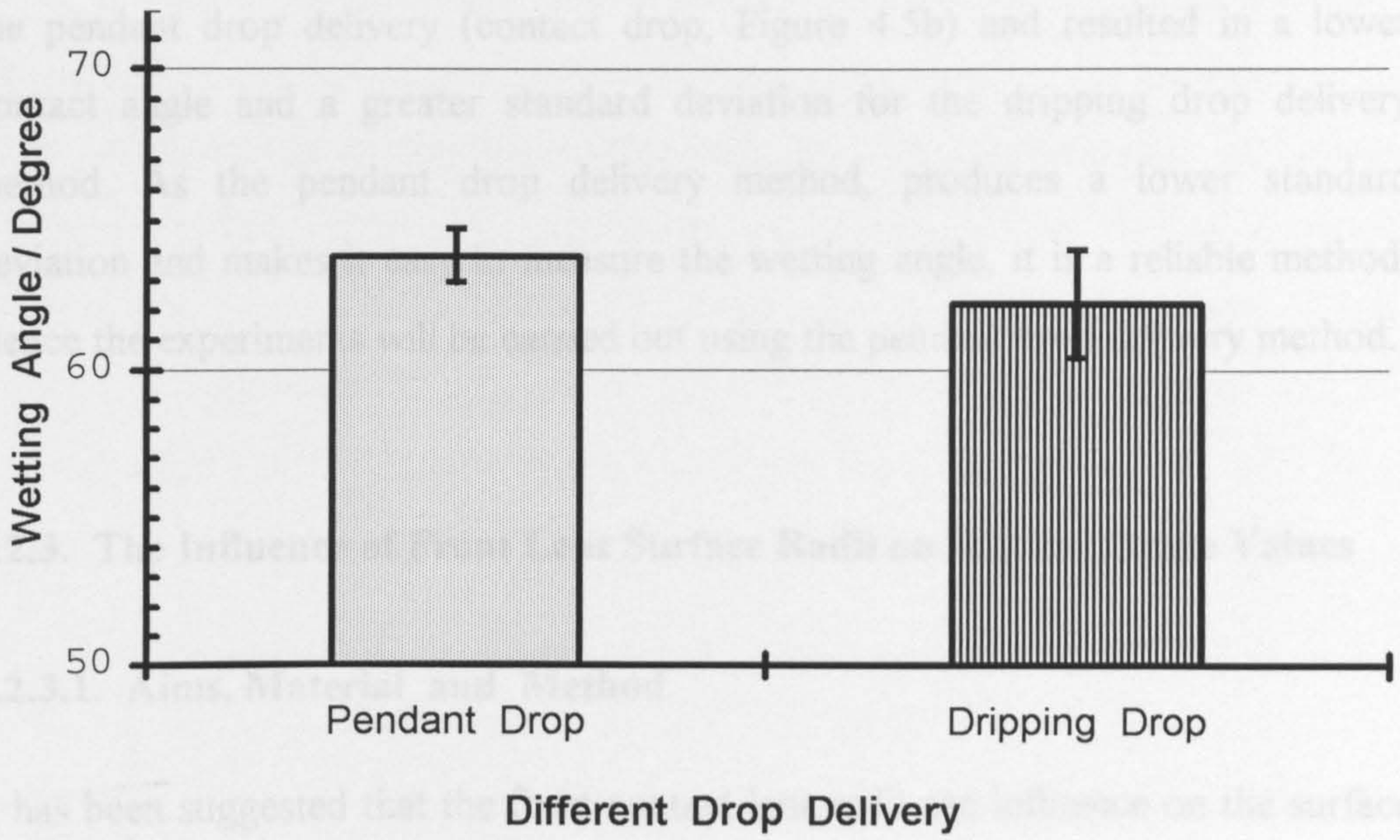


Figure 4.4. The wetting angle values of different drop delivery methods of the dripping and pendant sessile drops on hydrated PMMA contact lens surfaces.

4.2.2.3. Discussion

The dripping drop had kinetic energy at the drop delivery point (Figure 4.5a) that

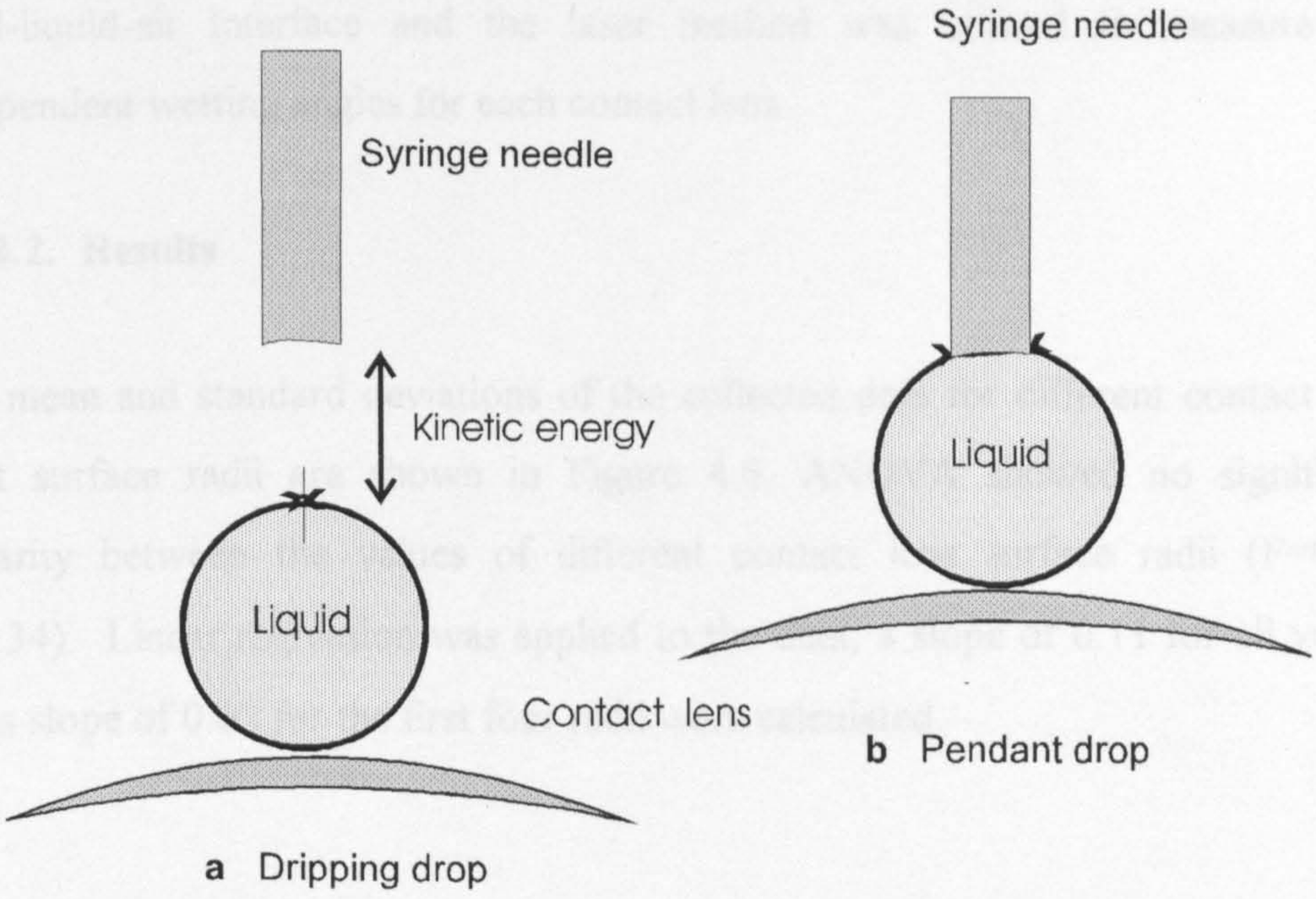


Figure 4.5. **a** Kinetic energy for the dripping drop delivery method; and **b** adhesion force for the pendant drop delivery method.

affected the sessile drop, which expanded to a greater area on the contact lens surface. This can lead to the dripping drop delivery producing a flatter droplet than the pendant drop delivery (contact drop, Figure 4.5b) and resulted in a lower contact angle and a greater standard deviation for the dripping drop delivery method. As the pendant drop delivery method, produces a lower standard deviation and makes it easy to measure the wetting angle, it is a reliable method. Hence the experiments will be carried out using the pendant drop delivery method.

4.2.3. The Influence of Front Lens Surface Radii on Wetting Angle Values

4.2.3.1. Aims, Material and Method

It has been suggested that the front contact lens radii can influence on the surface wettability values, hence it was necessarily to establish if this factor implemented wetting angle values.

Six contact lenses, made of PMMA, had front surface radii of 7.00mm, 8.00mm, 9 mm, 10 mm, 11 mm and 12 mm and a total diameter of 9.5mm. The front lens surfaces were manufactured at the City University contact lens laboratory and polished for three minutes and cleaned, hydrated and prepared in the method described in 4.2.1.1. A 3μl pendant drop of distilled water was used to create a solid-liquid-air interface and the laser method was utilised to measure ten independent wetting angles for each contact lens.

4.2.3.2. Results

The mean and standard deviations of the collected data for different contact lens front surface radii are shown in Figure 4.6. ANOVA showed no significant disparity between the values of different contact lens surface radii ($F=0.34$, $P>0.34$). Linear regression was applied to the data, a slope of 0.11 for all values and a slope of 0.02 for the first four radii were calculated.

4.2.3.3. Discussion

A flat surface shape material is ideal to create a solid-liquid-air interface through a sessile drop method because it prevents gravity from changing the geometry of the drop and hence its wetting angle. Choosing front lens surface radii of between 7.00mm and 9.00mm for analysing was logical because 98 per cent of laboratory contact lens production is within this range. For this range the slope of 0.02 showed no significant dependence on the contact lenses' front surface radii, the wetting angle (ANOVA, $F=0.34$, $p>0.87$) and the mean of the data was 63.9° (SD=±1.02), which showed the repeatability of the values.

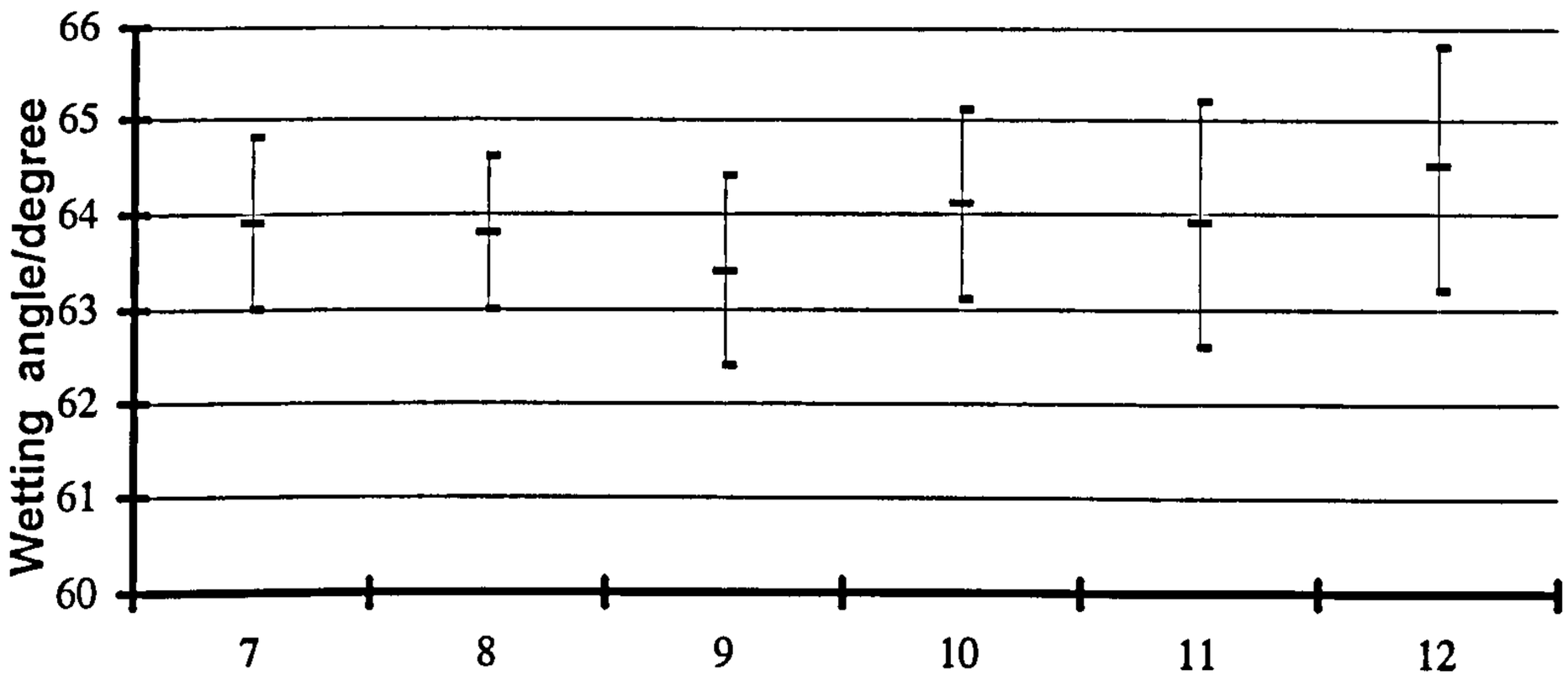


Figure 4.6. Correlation of the wetting angle values to the front lens surface radii ($p>0.1$).

4.3. Rigid Contact Lens Wettability

4.3.1. The Influence of Wetting Solutions on Contact Lens Surface Wettability

4.3.1.1. Aims, Materials and Methods

The effect of wetting solutions on the wettability of different rigid contact lens surfaces was investigated in this study. Three sets of nine contact lenses made of PMMA, Boston IV and Equalens, were lathe cut to the same specification: 8.00mm front surface radius and a total diameter of 9.5mm. The front lens surfaces were polished for three minutes and then cleaned and soaked in de-ionised distilled water for 24 hours. They were soaked for 12 hours in five contact lens solutions: Bausch and Lomb wetting and soaking solution (B&L.W&S.S), wetting and soaking solutions of both Delta and Renu; Allergan wetting solution; and Prymesoak (Table 4.2).

Contact Lens Solutions		
Solutions	**Function**	**Formula**
De-ionised H_2O	-	pH=6.6, γ=72.6
Bausch and Lomb	Wetting Soaking Disinfecting	Chlorhexidine Gluconate 0.006 per cent Disodium edetate 0.05 per cent
Delta (B&L)	Disinfecting Wetting Soaking	Benzalkonium chloride 0.005 per cent Disodium edetate 0.128 per cent
Liquifilm (Allergan)	Wetting Soaking	Polyvinyl alcohol Hydroxypropyl methylcellulose Edetate disodium Sodium chloride Potassium chloride Benzalkonium chloride 0.004 per cent
Renu (B&L)	Cleaning Disinfecting	Boric acid Edetate disodium Sodium borate Sodium chloride Polyhexanide 0.0006 mg Poloxamine 1 per cent
Prymesoak	Disinfecting	Chlorhexidine Gluconate 0.002 per cent

Table 4.2. Contact lens solution ingredients.

The contact lenses were rinsed with de-ionised distilled water, the surface tension method removed the liquid from the hydrated lens surface and the pendant drop placed a sessile drop on the contact lens surface. Five independent wetting angle measurements were taken for the hydrated and soaked lenses in solutions.

4.3.1.2. Results

The wetting angle values are shown in Figure 4.7 and Table 4.3. Hydrated PMMA with H_2O had the highest wetting angle values, which was expected, with the lowest being Boston IV and Equalens. There was a significant difference between the hydrated contact lenses (ANOVA, $F=9.1$ $P<0.01$) because contact lens solution influenced the contact lenses' wettability and produced a greater wettability. An example was PMMA for which different solutions produced various wettability values (ANOVA, $F=260.8$, $P<0.00001$).The B&L wetting solution significantly influenced the materials ($P<0.0001$) and increased their wettability to 30° with no significant difference between the three material's values (ANOVA, $F=0.36$, $P>0.7$).

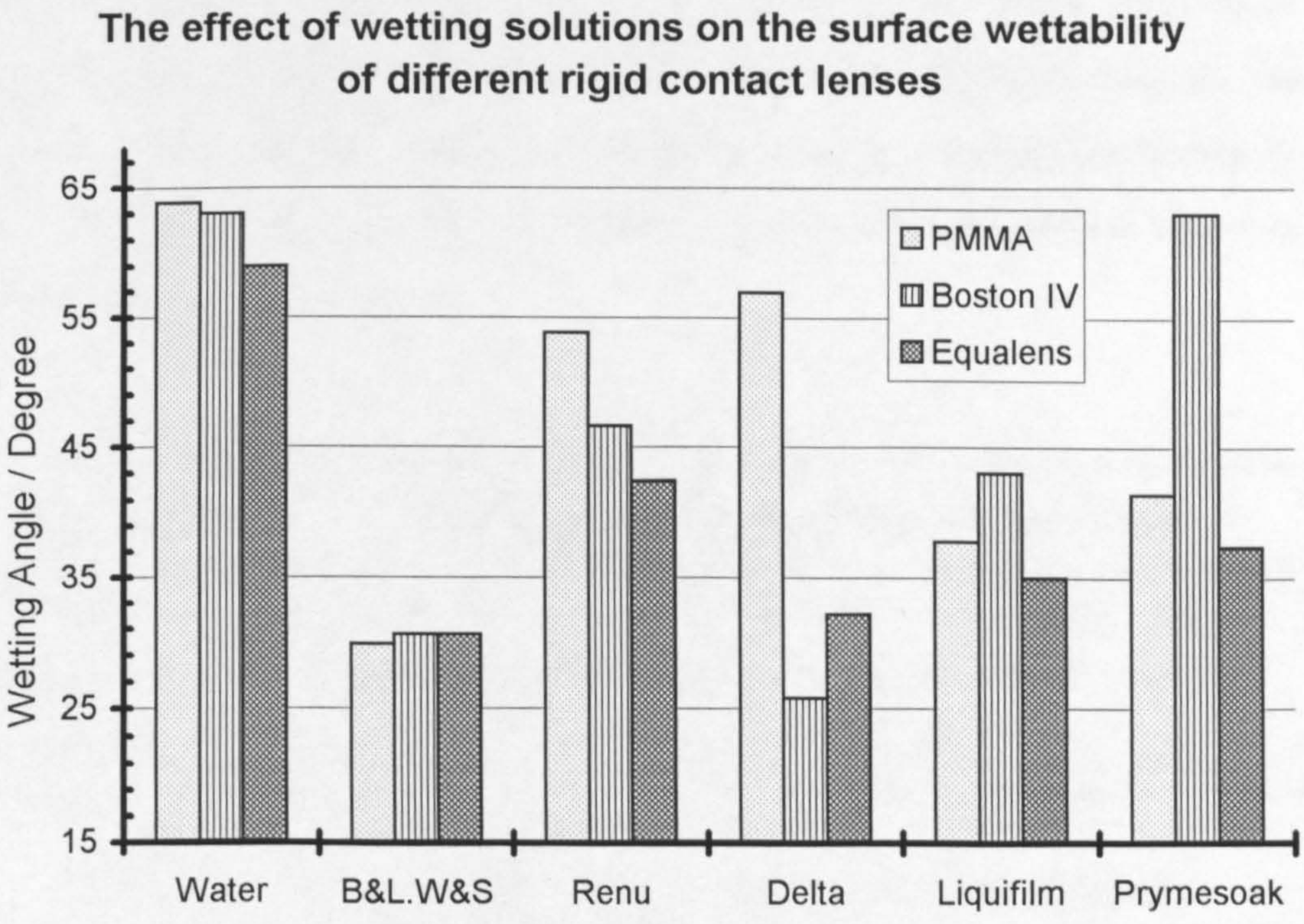


Figure 4.7. The surface wettability of PMMA, Boston IV and Equalens contact lenses when soaked in various solutions.

Wetting angle of different contact lens materials after soaking in various solutions						
Materials →	**PMMA**		**Boston IV**		**Equalens**	
Solutions ↓	Mean	SD	Mean	SD	Mean	SD
Water	63.8	1.4	63.0	1.7	59.0	1.3
B&L.W&S	29.8	1.3	30.6	1.2	30.6	1.2
Renu	53.8	1.3	46.6	1.7	42.4	1.8
Delta	57.0	1.6	25.8	1.6	32.2	1.7
Liquifilm	37.8	1.5	43.0	1.2	35.0	0.7
Prymesoak	41.4	1.2	63.0	1.6	37.4	1.9

Table 4.3. The wetting angle' mean and standard deviation values for the rigid contact lenses of PMMA, Boston IV and Equalens' which were influenced by various solutions of water, B&L, Renu, Delta, Liquifilm and Prymesoak.

Delta solution had the greatest effect on Boston IV (25.8°), while Prymesoak had the least influence (63°). There was no significant difference between the values of hydrated lenses with distilled water and Sauflon solution (Bonferonni: t-test, P=1), and the influence of different solutions on rigid contact lenses is ranked in Table 4.4.

Materials ↓	**Wettability order of various CL materials**
PMMA	Water < Delta <Renu < Prymesoak < Liquifilm < B&L
Boston IV	Water = Prymesoak <Renu < Liquifilm< B&L < Delta
Equalens	Water < Renu < Prymesoak < Liquifilm< Delta < B&L

Table 4.4. The wettability of various contact lens materials that were influenced by different solutions.

4.3.1.3. Discussion

As a contact lens in vivo is hydrated, the most meaningful wettability value is related to its use in vivo. The wettability values could be affected by a number of factors, such as the manufacturing process (see later). The results show a high-wetting angle for the hydrated materials between 59°-63.8°. In this experiment, when a contact lens was influenced by the wetting solutions, a wettable surface was stabilised on the contact lens surface. The B&L wetting solution increased the wettability of all materials to one level, while other solutions produced different wettability values for a given material. Different wetting solutions may be recommended, therefore, for different materials. A moderate contact lens wettability of 40° (±5) would be enough for most patients while a high-wettable material is not always necessary (Tomlinson 1991). The use of wetting solutions in general increases the surface wettability to a moderate level, enabling the subject to feel more comfortable at the time of wearing, although later in vivo the individual tear film (Bright and Tighe 1993, Tomlinson et al 1993) and deposit affect contact lenses wettability and produce a different value for the contact lens surfaces' wettability (see Chapter 7).

4.3.2. Post-wear Contact Lens Wettability

4.3.2.1. Aims, Materials and Method

The tear film can influence contact lenses' wettability (Guillon 1988, Guillon et al 1991 and Tomlinson 1992). The quality varies from one person to another (Hill 1977) and is influenced by several systemic mechanisms, like hormones and non-systemic factors such as cells and fatty components. It was, therefore, suggested that the wettability of materials would only be ascribable to an individual tear film and could differ for another.

Contact lenses made from PMMA, Polycon II, Boston IV, Equalens and Fluoroperm were manufactured at the City University contact lens laboratory. They were prepared using the method explained in 4.2.1.1, hydrated for 24 hours and the liquid on the lens surface was removed through the surface tension

technique. The contact lenses were then fitted on one male subject for 30 minutes and removed using a suction holder that did not touch the area of the lens to be measured. The remaining tear film on the lens surface was removed using the surface tension method. A 3µl pendant sessile drop of de-ionised distilled water (pH=6.6 ±0.2, γ=72.6 dynes ±0.4) was placed on the contact lens surface to form a solid/liquid/air interface and the laser method was used to measure the wetting angle. Ten independent measurements were taken for each material.

4.3.2.2. Results

The mean wetting angle values for the tested materials declined from the hydrated condition values 57°-63.8° to 11°-13° and an ANOVA revealed there was no significant difference between the values of various materials after 30 minutes of wearing contact lenses (F=3.47, P>0.47).

4.3.2.3. Discussion

In 1977 Hill reported the mean wetting angle of 55° for contact lens post-wear. The results of this experiment showed that the tear film significantly affected contact lens surfaces and produced wettable surfaces, when using both the sessile drop method and the novel contact lens surface preparation method. A similar result was also reported by Benjamin (1986) who found values of less than 10°. The sessile drop results showed no difference between materials after wear (see 4.5 and Chapter 7).

4.4. Receding Wetting Angle

4.4.1. Aims, Materials and Method

The aims of this study were:

a. to evaluate the reliability of the traditional sessile drop/receding wetting angle method; and

b. to introduce a new method to monitor the diameter of a sessile drop in relation to the contact lens wetting angle, in which an equilibrium sessile drop is monitored until the solid/liquid/air interface is terminated.

For the first part of the study, rigid contact lenses made of PMMA, Boston IV, Equalens and Aquasil were investigated, after which two RGP Scleral lenses of 115 Dk (Fluoroperm) were used. One was from a patient who had dry patches on the contact lens surface and found the lenses uncomfortable. The wearing time was reduced to about five hours. The other RGP lens was made from the same material but was only used to compare wettability.

A 3μl de-ionised distilled pendant drop of water (pH=6.6 ±0.2, γ=72.6 dynes ±0.4) was used to create a solid/liquid/air interface. The receding sessile drop/laser wetting angle method was used, in which, after delivering the sessile drop, the laser was adjusted at the solid/liquid/air interface to measure and monitor the changes in wetting angle and diameter of the sessile drop with evaporation time which receded with evaporation. The shape of the sessile drop was changed by increasing the evaporation time, which altered the wetting angle and the diameter of the solid/liquid/interface. At every two minutes, two independent wetting angle measurements were calculated on both the left and right sides of the sessile drop, with the average of the two readings being recorded as the wetting angle. The diameter of the sessile drop was also measured using a digital micrometer by moving the laser from one side of the sessile drop to the other.

4.4.2. Results

Figure 4.8 illustrates the variation in the sessile drop diameter with the wetting angle and the time that the sessile drop receded with evaporation. The PMMA contact lens had the lowest sessile drop diameter, while Aquasil had the largest value. Even though the sessile drop diameter on Boston IV (2.67mm) was the same as on PMMA (2.65mm), the wetting angle reached 0° at a diameter of 2.00mm while PMMA the wetting angle reached 0° at 1mm diameter.

Equalens had a sessile drop diameter of 3.06mm, and when the wetting angle reached 0° the interface diameter was 3.00mm. This material also showed the lowest reduction in its wetting interface diameter 0.06mm in which the wetting angle reached 0°. The Aquasil lens had the largest wetting diameter (3.15mm), while the wetting angle declined to 0°, the wetting interface diameter only declined to 0.15mm and the wetting diameter reduced to 3.00mm (Figure 4.8).

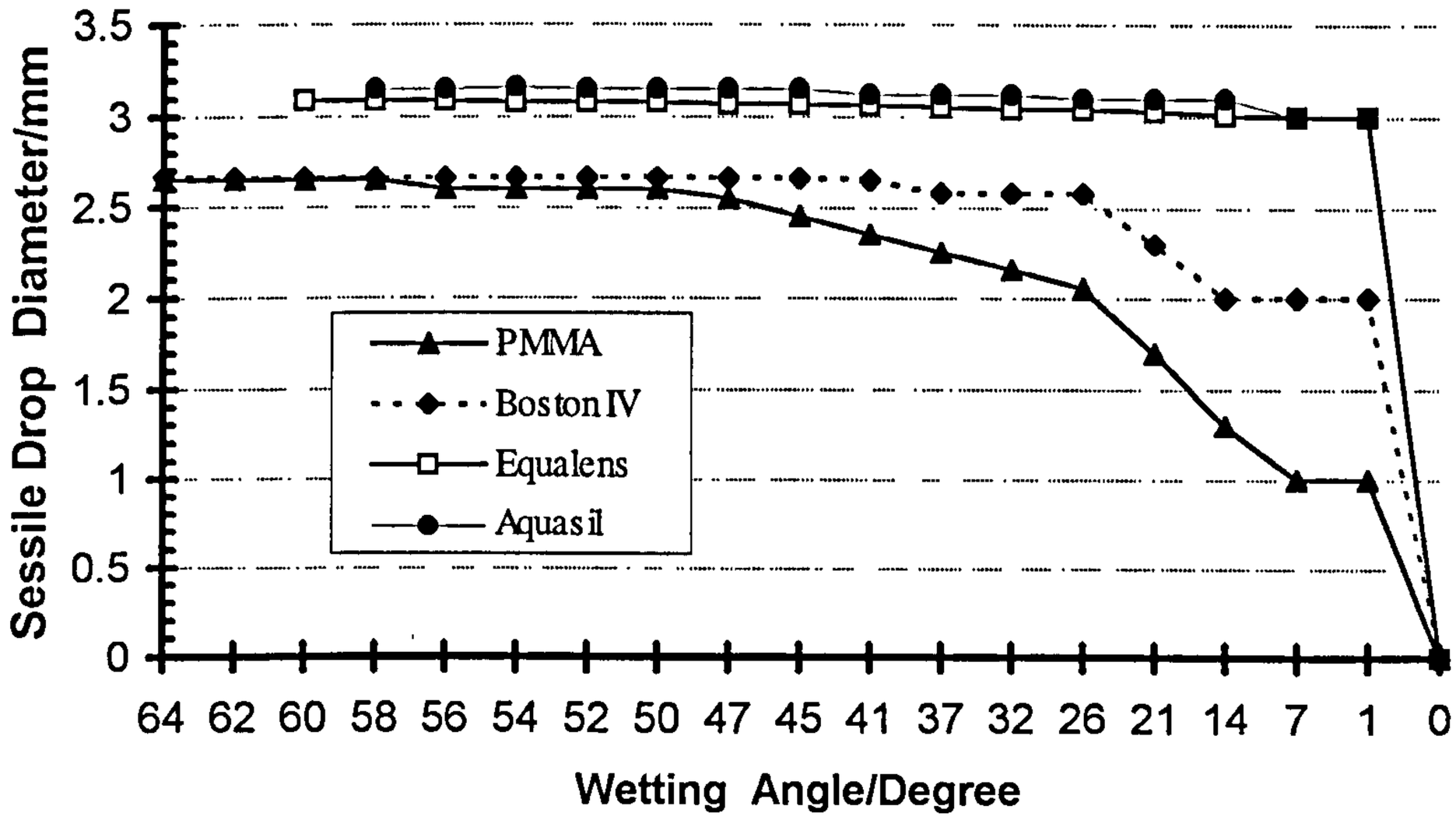


Figure 4.8. The variation in the sessile drop diameter (interfacial tension area diameter) and wetting angles on different contact lens materials with evaporation of droplet.

The scleral contact lenses had the same wetting interface diameter 2.45mm. The wetting interface diameter of un-worn lenses declined to 1mm (a reduction of

1.45mm) when the wetting angle fell to 0°, although, for the patient contact lens, the wetting diameter reached 0.6mm (quantity of reduction 1.95mm), in which the wetting angle declined to 0° (Figure 4.9).

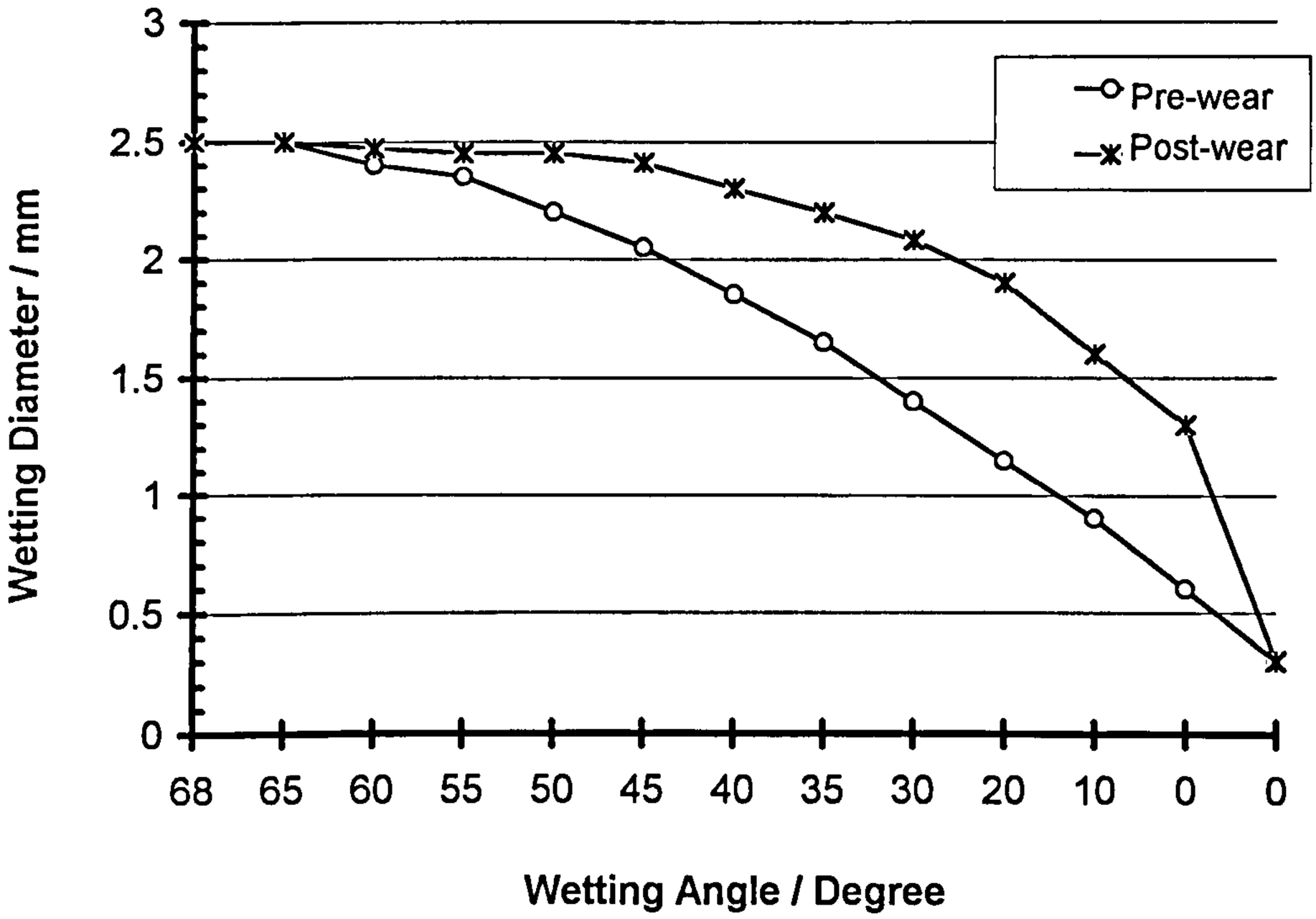


Figure 4.9. The variation in the sessile drop diameter (interfacial tension area diameter) with wetting angles on pre- and post-wear rigid contact lenses.

4.4.3. Discussion

The variation of the sessile drop diameter on the contact lens materials may be explained in relationship to the spreading coefficient (S) which Tadros (1978) defined as: $S=\gamma_{LV}(\cos\theta - 1)$. Where the sessile drops at the receding state had 2.3mm diameter the wetting angles for Equalens, Aquasil, Boston IV and PMMA were 0°, 0°, 21° and 43° (Figure 4.8) giving a calculated spreading coefficient as 0, 0, -4.7 and -19 respectively (γ= 72.6 Dynes/cm). This clearly indicate that PMMA has the lowest surface spreading coefficient to liquid than the other materials. Spreading coefficient for the pre- and post-wear were calculated when the sessile drops had 2.3mm diameter (Figure 4.9) which the wetting angle were 47° and 26° respectively. Pre-wear Fluoroperm lens had -24.1 and the post-wear one had the S

values of -7.7 which show wearing contact lenses produce a greater spreading ability on the lens surface (see also 1.4).

Paddy (1978) stated that spreading can only occur when the effective work of adhesion W_A is greater than the work of cohesion Wc of the liquid ($Wc < W_A$). In this experimental work the liquid surface tension was constant but material variable producing different work of adhesion. The greater adhesion sessile drop diameter produced a greater work of adhesion for Equalens than the other materials.

While the sessile drop shape changes, the liquid surface tension pulls surface molecules into the liquid to produce a minimum surface area for the given liquid volume, according to the surface tension definition. An example is a sessile drop on a contact lens, in which the liquid molecules produce interfacial tension with the contact lens surface molecules. The edge molecules of the liquid play an important role at the air/solid/liquid interface and are affected by three different forces in comparison with the molecules inside the liquid. One force is from the interior molecule of the liquid because of the un-opposed force that is called surface tension, while the second force is between the liquid and solid surface that, produces interfacial tension. The third is from the side of the liquid molecule, that have ordinary bond.

The liquid and contact lenses' material can make an interface bond and wettability, which is dependent on the quantity of the bonds that produce interfacial forces. Consequently, a variation in the wetting angle and interface area diameter is created by the same liquid on different contact lens materials.

As can be seen in Table 4.5, Aquasil and Equalens had the largest sessile drop interface diameter at 0°, which could lead these materials having a greater tendency to keep the liquid on the surface. The interfacial forces were thus higher than for Boston IV and PMMA and the values revealed that the liquid on the Equalens and Aquasil did not coalesce, showing these materials were more wettable than the others.

The results of the second part of the study revealed the ability of the scleral contact lens surface to coalesce the liquid. The quicker the liquid coalesces on the material,

the lower the interfacial forces. The greatest coalescent liquid from contact lenses was found with diminishing sessile drop diameter on the lens of the patient with dry patches on the surface. It was suggested, therefore, that either the contact lens surface of the patient was damaged or the material was contaminated and or tear film was abnormal.

Contact Lens Wettability		
Materials	Interface Area Diameter at Equilibrium/mm	Interface Area Diameter at Receding 0°/mm
PMMA	2.65	1.00
Boston IV	2.67	2.00
Equalens	3.06	3.00
Aquasil	3.15	3.00
Fluoroperm, 115 Dk, Patient	2.45	0.60
Fluoroperm, 115 Dk, Sample	2.45	1.00

Table 4.5. Interface area diameter values for equilibrium and receding 0° wetting angle.

4.5. Sessile Drop Discussion

One of the aims of Chapter 4 was to standardise and validate the sessile drop wetting angle. The equilibrium and receding sessile drop methods have been used to measure the wetting angle of rigid contact lenses. Several investigators attempted to standardise the sessile drop wetting angle methods by controlling the humidity, temperature, liquid drop size, front lens radii, asperity and measurement technique (see Chapter 3). The preparation of hydrated contact lens surface and a method to control the receding wetting angle were found to be important. Thus removing the liquid from the hydrated contact lens surface through the surface tension method and monitoring the receding wetting angle and diameter of the sessile drop methods that have not been previously reported before are introduced.

In introducing a liquid to polymer molecules, an essential requirement is the purity of the polymer surface. Cleaning the contact lens surface using surfactant agents (30 seconds) may not remove all contact lens surface contamination (Tang et al 1977), while a preliminary study demonstrated that using fingers to clean a contact lens affects the lens surface wetting property. One of the basic requirements for measuring surface wettability, therefore, is to keep the polymer surface clean and keep it away from further contamination. Using tweezers and brushes helps not only to remove the contact lens surface contamination, but also, unlike fingers, does not contaminate the contact lens surface.

As contact lenses in the eye are hydrated, they logically should be measured when hydrated. One factor prompting researchers to use the captive bubble method for measuring wettability was the hydration condition, although the values were un-repeatable when measured by various investigators (see 3.3). Removing liquid from the hydrated contact lens surface by evaporation and wiping, dehydrates the contact lens surfaces because wiping contaminates the contact lens surface with electrostatic charges. It is clear that the only remaining technique for removing liquid from the hydrated contact lenses is surface tension. The lens surface will not, therefore, be dehydrated and will not be contaminated, this technique is also quick and easy to use.

In a solid/liquid/air interface, the rigid contact lens shape is a constant,. Expanding or coalescing liquid on contact lens occurs as a result of interface forces and liquid surface tension. In these experiments, the liquid surface tension was constant (de-ionised water γ= 72.6; pH=6.6) and the variable factors were therefore either the contact lens materials or the lens surfaces that were influenced by tear film.

Hydrated rigid contact lenses wettability can be measured by the sessile drop technique. When they were influenced by solutions and tear film, the wettability increased as this method reveals. The sessile drop method values can distinguish between different materials' wettability but not when they were influenced by a tear film (see 4.4.3). One possible explanation could be the existence of tear film ingredients on the lens surfaces which make the surfaces wettability indistinguishable. An investigation on the wettability, therefore, needs to be carried out by a new measurement method (see Chapter 5).

Monitoring the wettability through the changes in sessile drop area diameter and wetting angle during receding conditions reveals the interfacial forces between the contact lens surface and the liquid. If the forces are high, the liquid does not coalesce on the lens surface, the wetting angles change quickly and the drop diameter remains constant. But, if the interface forces are low, the surface tension pulls the liquid from the solid/liquid/air interface into the liquid, which causes the sessile drop diameter to decline the drop coalesces while the wetting angle remains constant. These findings can help to reveal the variation in contact lenses' wettability due to different materials and when they are affected by the tear film (see Chapter 7).

Chapter 5. Wettability of Contact Lenses Using Un-separated Adherent Liquid/Laser Method

5.1. Un-separated Adherent Liquid/Laser Method

5.1.1. Introduction

Producing an interface between a liquid and a material is one of the basic requirements when measuring contact lens surface wettability. This can be influenced by several factors, such as polymer contamination. The sessile drop, captive bubble, vertical contact lens/adherent meniscus and adherent bubble meniscus (see Chapter 3) methods have been used to measure the wettability of contact lens surfaces, with the results differing even when the same method has been used. The most measurement values have been determined the flat and rigid contact lens materials wettability.

In this Chapter, a new method called un-separated adherent liquid is used to produce the solid/liquid/air interface on rigid and soft contact lenses and the wetting angle is measured using the laser method. The liquid at the interface is in a receding state, which, as has been documented, is a measure of contact lens surface wettability. As it is a new method, a primary investigation to determine the influencing factors is necessary (see later).

Hydrated rigid contact lens materials can be influenced by wetting solutions and tear films which have been investigated in 5.2. The important advantage of this method is that it can measure the wettability of both soft and rigid contact lens surfaces at hydrated condition (5.3).

5.1.2. The Un-separated Adherent Liquid/Laser Technique

a. Soft Contact Lenses Preparation

Rigid contact lenses were prepared using the method described in 4.2.1. For the soft contact lens surface preparation, however, a convex ended rod surface of 8.7mm radius was lathe cut from a cylindrical shaped material to act as a soft contact lens holder. The convex rod surface was then lowered through saline to the back surface of the soft contact lens (Figure 5.1) and moving the holder close to the contact lens back surface, the lens was attached to the holder (Figure 5.1b). A spatula supported the contact lens on the rod and was then withdrawn vertically 1mm from the container liquid surface (Figure 5.1c). The rod was tilted and elevated to move the liquid from the contact lens surface to the lens edge (the surface tension removing liquid method (Figure 5.1d) without touching or damaging the prepared contact lens surface. A small amount of the liquid that remained on the edge of the lens (Figure 5.1e) was removed by a corner of a paper tissue and the rod was then fixed to the adherent liquid/laser apparatus.

b. Adherent Liquid/Laser Apparatus

The apparatus used in the un-separated adherent liquid/laser method (UALLM) comprised (Figure 5.2):

1. Two manually adjustable micrometer stages.
2. An adjustable rotatable large protractor.
3. A +7.00D convex lens fitted on an adjustable stand.
4. A Helium-Neon laser with 2m Watt power.
5. A rigid contact lens holder.
6. A soft contact lens holder with an 8.7mm radius.

The laser beam was incident at the centre of a convex lens that was placed on an X, Y and Z adjustable stand 80cm away from the laser and was focused 14.3cm from the convex focusing lens at the solid/liquid/air interface. The lower stage was able to move vertically and had a platform for holding a solution container.

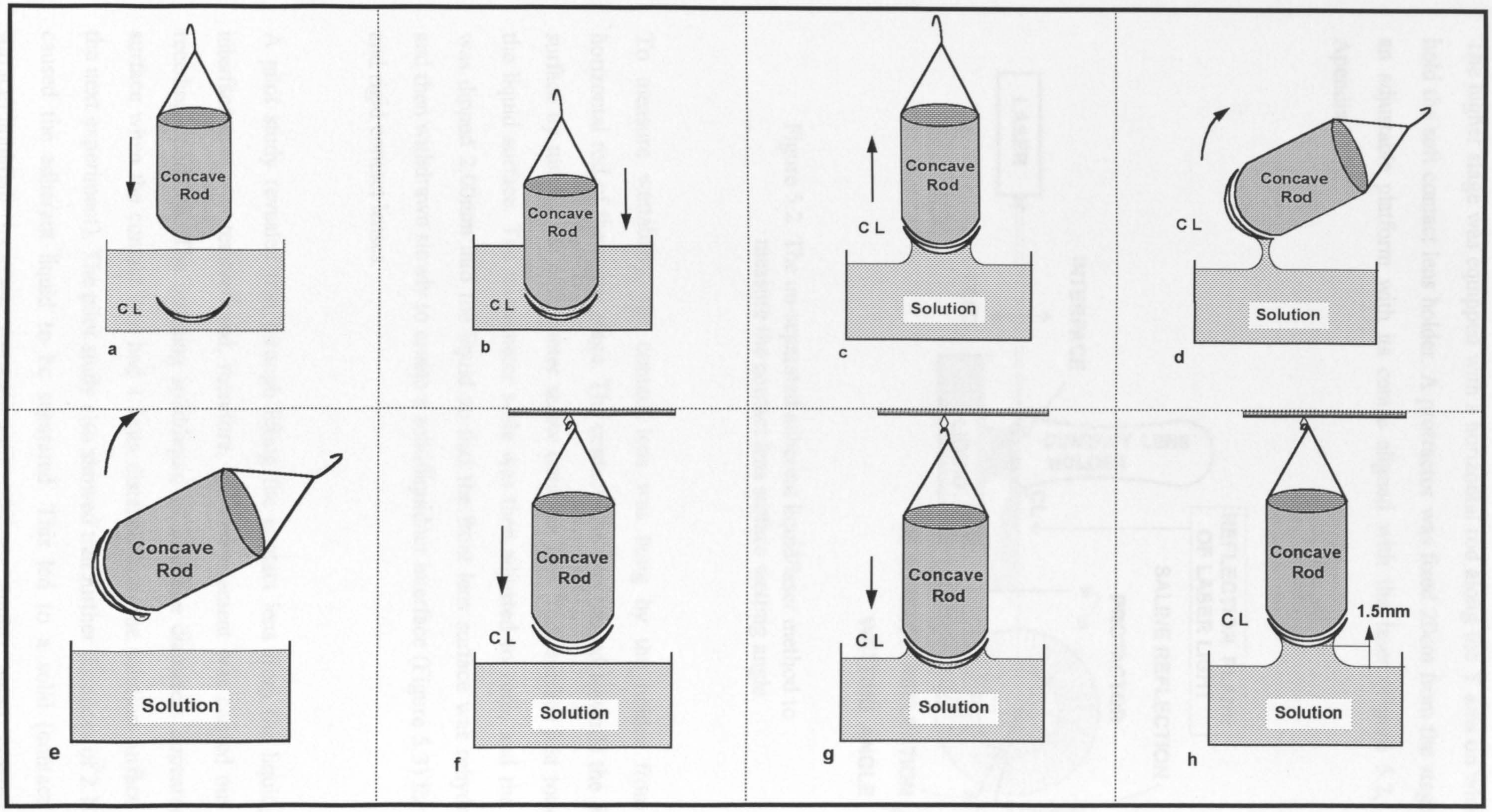


Figure 5.1. **a, b, c, d** and **e** illustrate the method for mounting a soft contact lens on the concave surface rod. **F, g** and **h** create an un-separated adherent liquid to measure the wetting angle using the laser method.

The higher stage was equipped with a horizontal rod along the Y axis on which to hold the soft contact lens holder. A protractor was fixed 20cm from the stages on an adjustable platform with its centre aligned with the laser (Figure 5.2, see Apendix 1).

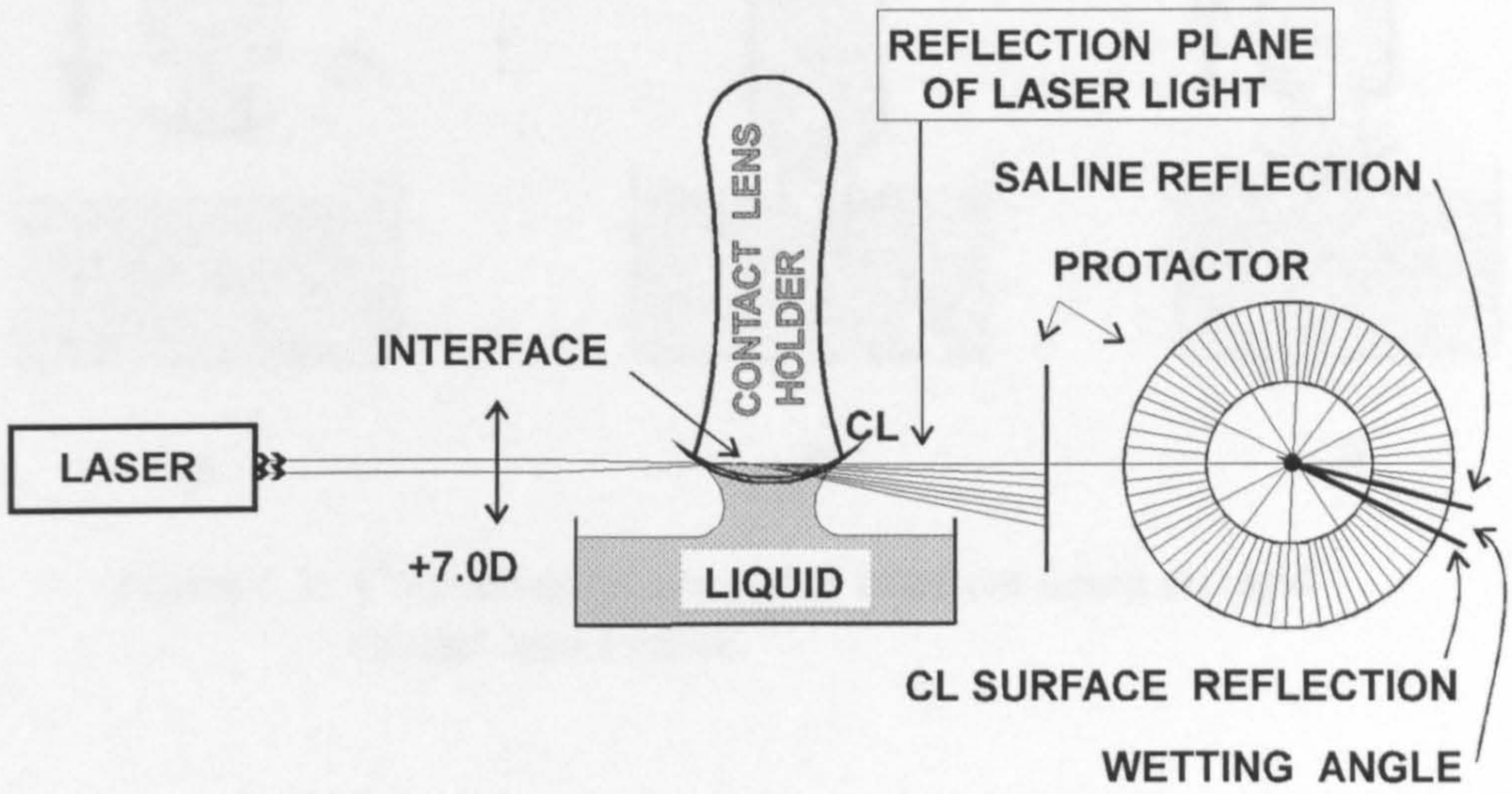


Figure 5.2. The un-separated adherent liquid/laser method to measure the contact lens surface wetting angle.

To measure wettability, the contact lens was hung by the holder from the horizontal rod of the upper stage. The contact lens was moved towards the liquid surface by turning the micrometer screw until the lens front surface just touched the liquid surface. The micrometer scale was then adjusted to zero, and the lens was dipped 2.00mm into the liquid so that the front lens surface was rehydrated and then withdrawn slowly to create a solid/liquid/air interface (Figure 5.3) for soft and rigid contact lenses.

A pilot study revealed that through lifting the contact lens from the liquid, the interface area was reduced and, therefore, the measurement was carried out in a receding condition. The receding solid/liquid/air interface diameters appeared on surface when the contact lens had 1.5mm distance from the solution surface (see the next experiment). The pilot study also showed that further distances of 2.10mm caused the adherent liquid to be separated. This led to a solid (contact lens surface)\liquid\air interface (un-separated adherent liquid) being created for

measuring the wetting angle by laser. To measure the rigid contact lens surface, a contact lens suction holder was used, as shown in Figure 5.3.

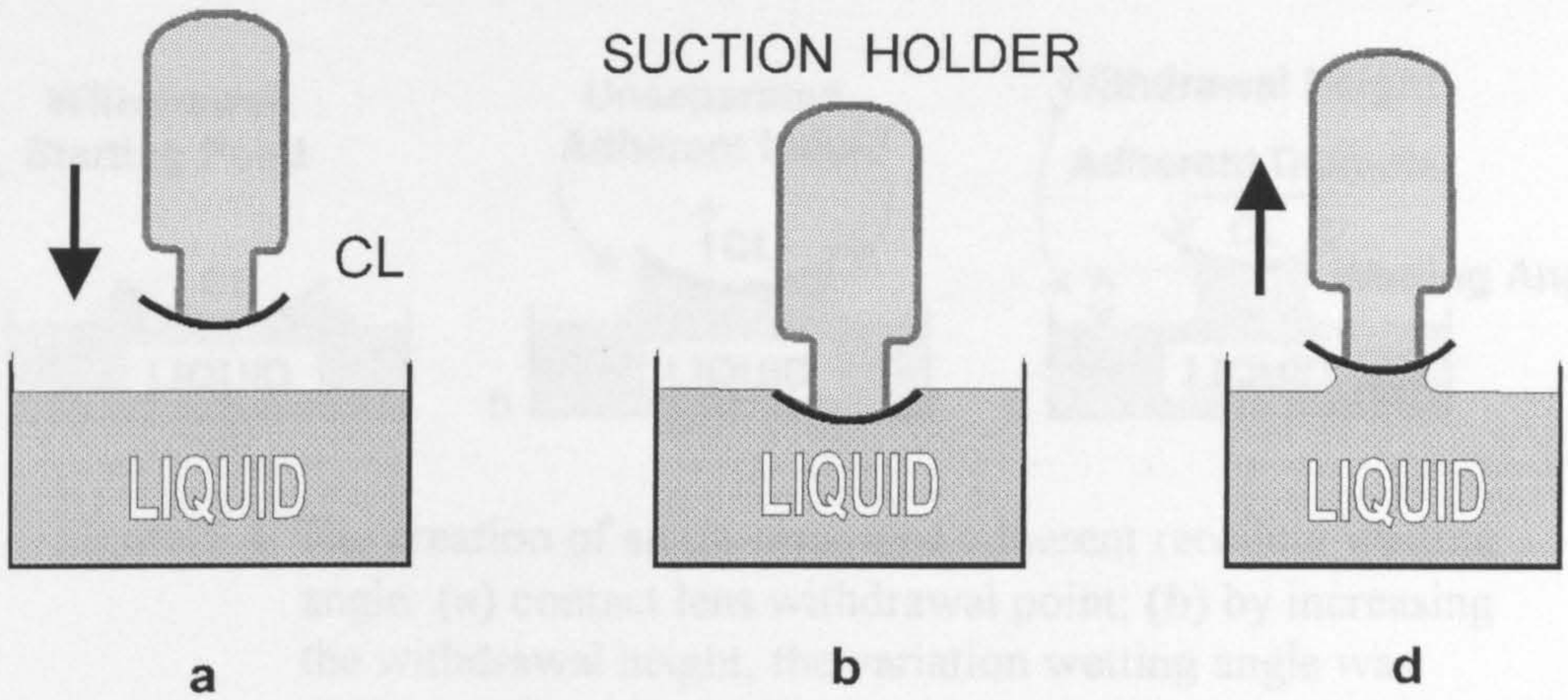


Figure 5.3. Creation of un-separated adherent liquid on rigid contact lens surface.

The laser beam was adjusted on the contact lens surface and then moved to the contact angle of the solid/liquid/air interface, which produced two reflection strip pattern lines representing the wetting angle on the protractor (Figure 5.2). Two readings were taken, one from the left and one from the right side of the interface, and the average of the two readings was calculated as the contact lens adherent wetting angle.

5.1.3. The Influence of Withdrawal Distance

5.1.3.1. Aims, Materials and Method

The aim of this experiment was to investigate the influence of the withdrawal height on the adherent liquid wetting angle values. As a pilot study suggested the contact lens withdrawal heights from the liquid surface might change the wetting angles (Figure 5.4), they were measured at the point at which the receding liquid/contact lens/air interface started (Figure 5.4b), although in practice they were measured where the diameter of the solid/liquid/air meniscus was at the receding condition which the solid/liquid/air interface was obvious. This point began where the contact lens surface was 1.4mm from the solution surface (de-

ionised distilled water, pH=6.6 ±0.2, γ=72.6 dynes ±0.4), when the contact lens surface first touched, the liquid surface and withdrawn.

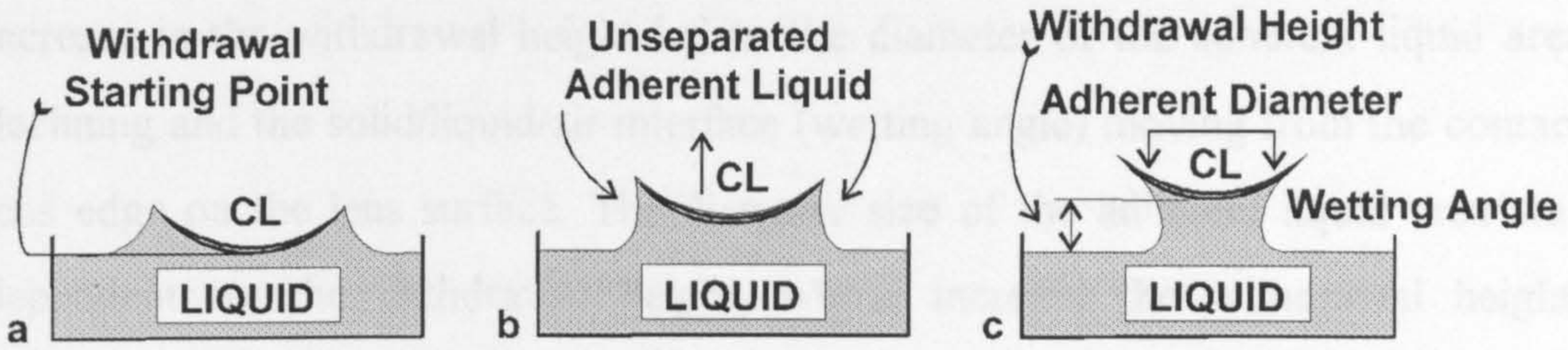


Figure 5.4. The creation of an un-separated adherent receding wetting angle: **(a)** contact lens withdrawal point; **(b)** by increasing the withdrawal height, the variation wetting angle was visible; **(c)** by a further increasing in the withdrawal height, the diameter area of the un-separated adherent liquid declined and the wetting angle moved on to the contact lens surface.

Withdrawal heights of 1.5, 1.6, 1.7, 1.8, 1.9, 2.00 and 2.10mm were investigated, and ten independent wetting angle measurements were carried out for each selected withdrawal height for the PMMA contact lens using the un-separated adherent liquid/laser method.

5.1.3.2. Results

Figure 5.5 shows the mean, standard deviation and linear regression of the un-separated adherent liquid wetting angle values. Despite a negative correlation between various withdrawal heights and wetting angle values (Slope=−0.26), there was no significant difference between the wetting angles measured at various withdrawal distances (ANOVA, F=0.96, P>0.5).

5.1.3.3. Discussion

As the contact lens was lifted from the withdrawal point, the shape of the liquid meniscus on the contact lens surface changed without varying the adherent liquid diameter on the contact lens surface until it reached to a height at which the

diameter started to decline (Figure 5.4). The changes meniscus shape from the withdrawal point to a height at which the diameter started to decline were obvious, although no liquid/contact lens surface/air interface (Figure 5.4) enables the adherent wetting angle values to be measured at the edge of lens surface. A further increase in the withdrawal height led to the diameter of the adherent liquid area declining and the solid/liquid/air interface (wetting angle) moving from the contact lens edge on the lens surface. The diameter size of the adherent liquid area was dependent on the withdrawal height, whose increase the withdrawal height, changed the meniscus mechanically, although, because of the presence of the liquid surface tension function, the liquid meniscus was re-shaped.

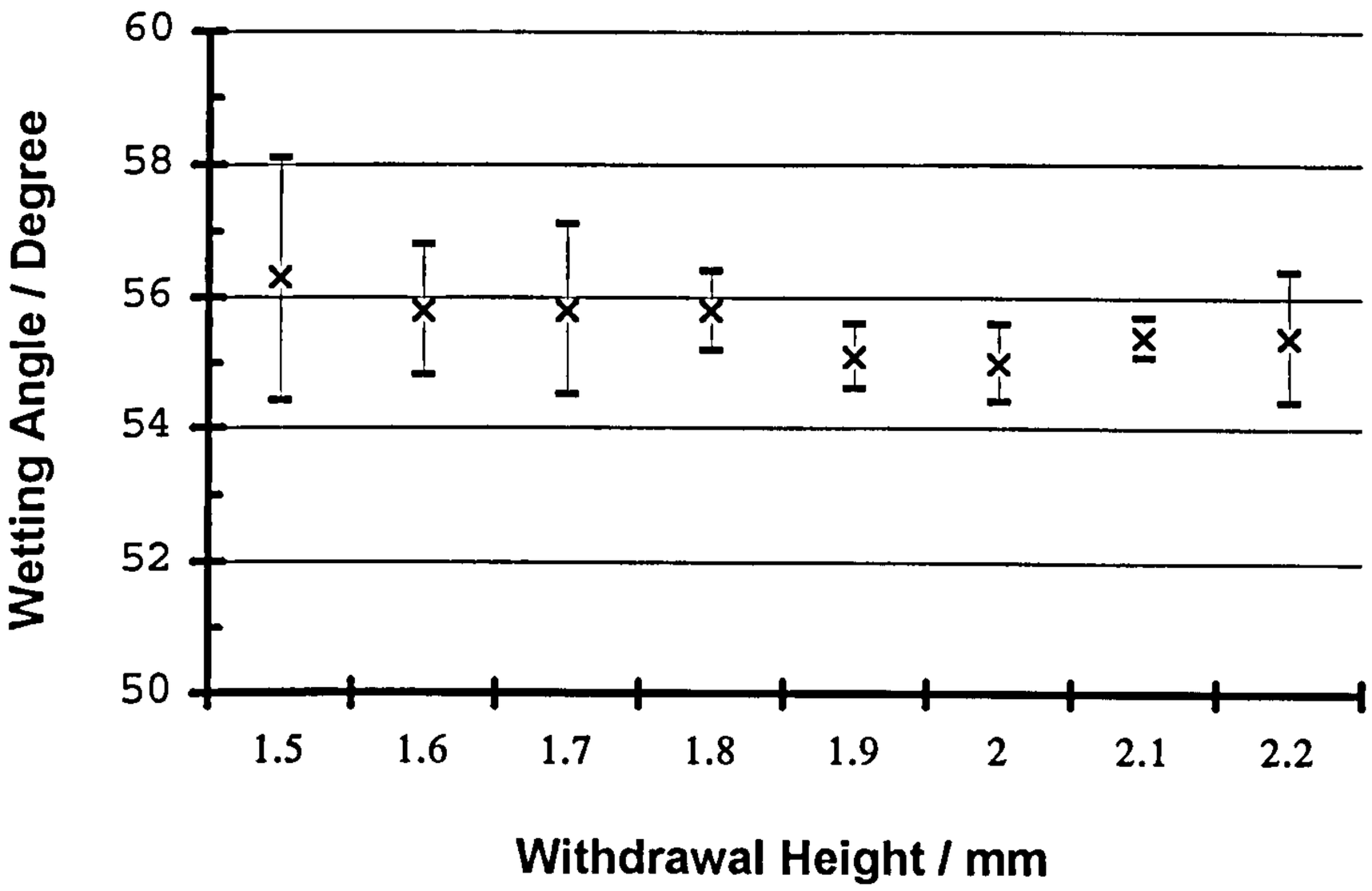


Figure 5.5. The influence of the withdrawal height on the adherent wetting angle of the PMMA contact lens.

Surface tension at a new withdrawal height pulled, as much as possible, the liquid molecules from the surface into the liquid. By increasing the withdrawal height, the surface area of the liquid expanded, which caused the molecules involved in the surface tension to increase. Through a further increase in the withdrawal height, the liquid surface area expanded, resulting in a greater number of liquid molecules involved in the surface tension until a height at which, by increasing the surface area, the interface diameter declined. At this point, the molecules involved in the

surface tension had reached a maximum level and a further increase the withdrawal height caused the molecules at the interface to be pulled into the liquid, leading to a reduction of the solid/liquid/air interface diameter.

This experiment was carried out on one rigid contact lens, and the interface liquid was de-ionised distilled water, with the only variation being the withdrawal height. The results revealed that, while the solid/liquid interface area declined on the contact lens, the wetting angles had a similar range to various withdrawal heights, and, therefore, the method was consistent in producing a solid/liquid/air interface and in measuring contact lens wettability.

The values of 1.8mm to 2.1mm had a lower standard deviation (±0.2°) than the first three values, which gave a more repeatable value to measure the wetting angle. It can, therefore, be concluded that measuring the wetting angles using un-separated adherent liquid not only provides the wettability values of hydrated contact lenses, but is also repeatable. This method can evaluate the contact lens surface wettability through the un-separated solid/liquid/air interface at the receding condition.

5.1.4. The Influence of Front Rigid Contact Lens Surface Radii

5.1.4.1 Aims, Material and Method

The objective of this procedure was to investigate the influence of the front surface radii on the contact lens surface wetting angle. Six contact lenses made of PMMA were used with differing front surface radii of 7, 8, 9, 1, 11.00 and 12mm, which were manufactured by the same technique. The front surface of each lens was polished for one minute, cleaned and prepared in a hydrated state using de-ionised water ((pH=6.6 ±0.2, γ=72.6 dynes ±0.4), while the un-separated adherent liquid/laser method was used to measure the wetting angle.

5.1.4.2. Results

Figure 5.6a shows the mean and linear regression of wetting angle values for various front contact lens surface radii. The lens with the 12mm front surface radius had the highest wetting angle of 57°, while ANOVA indicated there was a significant difference between the wettability of various contact lens surface radii ($F=10.2$, $P<0.00001$) while linear regression analysis revealed a positive correlation between the wetting angle and the contact lens front surface radii, more than 97 per cent of contact lens production was within the front surface radii of 7.00-9.00mm and ANOVA showed no significant difference between the values ($F=1.6$, $P>0.21$).

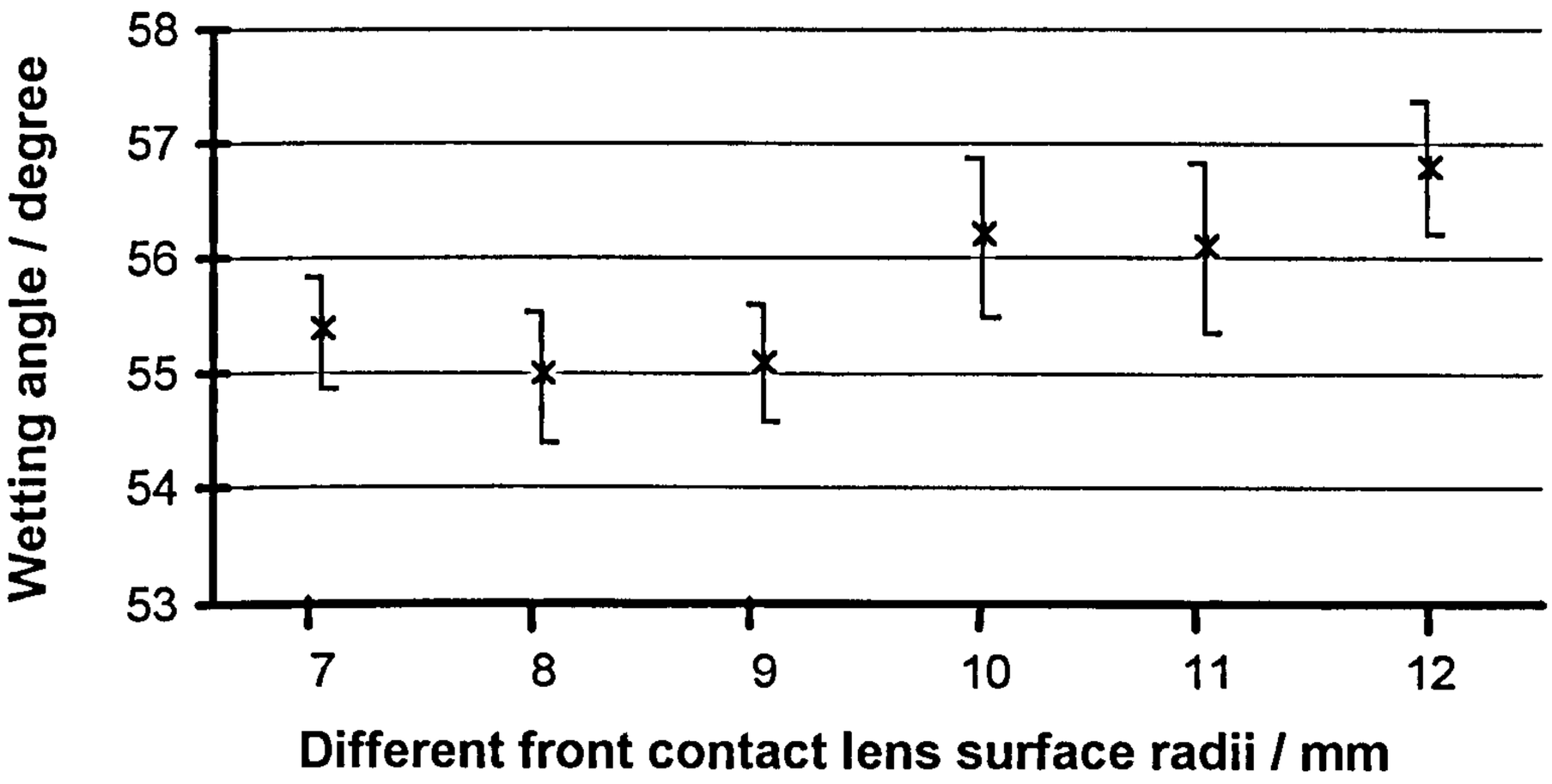


Figure 5.6a. The influence of PMMA front lens surface radii on the wetting angle of an un-separated adherent liquid.

5.1.4.3. Discussion

A perfect method to measure the influence of front lens surface radii on the wetting angle values would be a plate at various angles to a liquid (Tighe 1997, Figure 5.6b), but the laser method is not applicable to the solid/liquid/air interface produced, possibly a goniometer could be used. However during withdrawal a contact lens surface from a liquid the angle of contact lens surface to liquid would

change due to the area of interface, hence it was decided to investigate the influence of the lens surface on the contact lenses rather than a flat material.

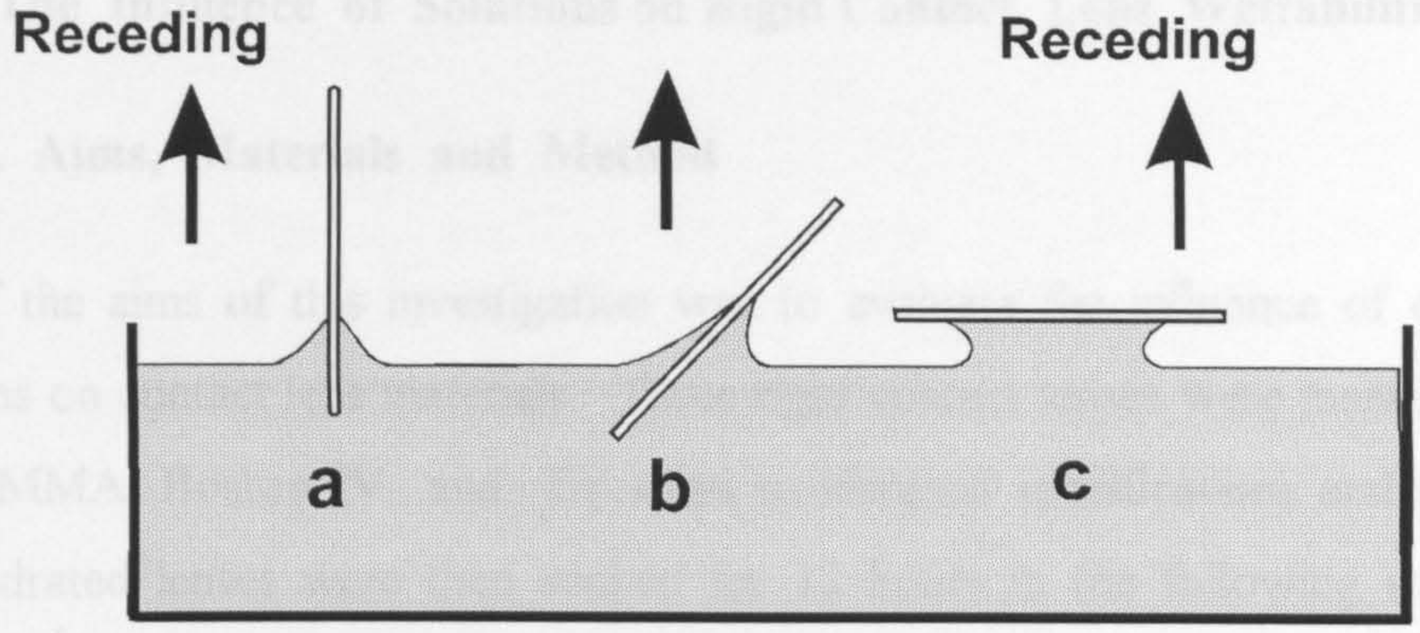


Figure 5.6b. A flat material at three different angles to a liquid, demonstrating the influence of front lens surface radii on the wetting angle values.

The results revealed that the values of un-separated adherent liquid wetting were dependent on the front lens surface radii from 7mm to 12mm. As the shapes of liquid meniscus on both flat and steep front contact lens surfaces were the same, they produced similar reflecting patterns. But the reflected lines from the different contact lens front surfaces were not the same because varying front contact lens radii produced different wetting angles, with the greater the lens front surface radii, the greater the wetting angle.

A high percentage (97%) of contact lens front surface radii were in the 7.00mm to 9.00mm range, with results revealing there was no significant difference (at the level of 95 per cent) between the values in this range. The wetting angle of the typical range of contact lenses used in practices can be consistently measured by using the un-separated liquid/laser method.

5.2. Rigid Contact Lens Wettabilities

5.2.1. The Influence of Solutions on Rigid Contact Lens Wettabilities

5.2.1.1. Aims, Materials and Method

One of the aims of this investigation was to evaluate the influence of different solutions on contact lens materials. Three rigid contact lenses were manufactured from PMMA, Boston IV and Equalens to identical specifications and cleaned. The hydrated lenses were then soaked for 12 hours in the following solutions: B&L.W&S, Delta-Sauflon, Allergan Liquifilm, Prymesoak and Renu (Table 4.2), while the contact lenses were repeatedly washed with de-ionised distilled water before being measured using the un-separated adherent liquid method. The process repeated five times to collect five independent data.

5.2.1.2. Results

Figure 5.7. shows the un-separated adherent liquid wetting angle values for PMMA, Boston IV and Equalens when influenced by the Bausch and Lomb, Delta, Allergan liquifilm, Prymesoak and Renu solutions. An analysis of variance revealed there was a significant difference between the values for PMMA ($F=173.6$, $P<0.00001$), Boston IV ($F=48$, $P<0.00001$) and Equalens ($F=56.6$, $P<0.00001$) using the various wetting solutions.

The Delta and Renu-multi solutions had less influence on PMMA material and there was no significant difference between them (Bonferroni: t-test, $P=0.6$). Prymesoak had the greatest effect on PMMA, although there was no significant difference between Prymesoak and the next wetting value of B&L.W&S (Bonferonni: t-test, $P=0.47$). For Allergan liquifilm, however, compared with the next highest wetting angle, which was Delta, there was a significant difference between their values (Bonferroni: t-test, $P<0.00001$). The value of Allergan Liquifilm was compared with the next lowest wetting angle, which was B&L.W&S, there was a disparity between their wettability (Bonferonni: t-test, $P<0.01$).

There was also a contrast between the values of Delta and B&L.W&S on Boston IV (Bonferonni: t-test $P<0.001$), although there was no significant difference between the values of Renu, Allergen, Prymesoak and B&L.W&S solutions (ANOVA, $F=0.25$, $P=0.85$).

The Allergan liquifilm had less effect on Equalens' wettability than PMMA and Boston IV. And while there was a significant difference between Equalens and the next less influenced one (Delta, Bonferonni: t-test, $P<0.02$), there was no great disparity between the wettability of B&L, Prymesoak and Renu solutions (ANOVA, $F=1.68$, $P=0.22$).

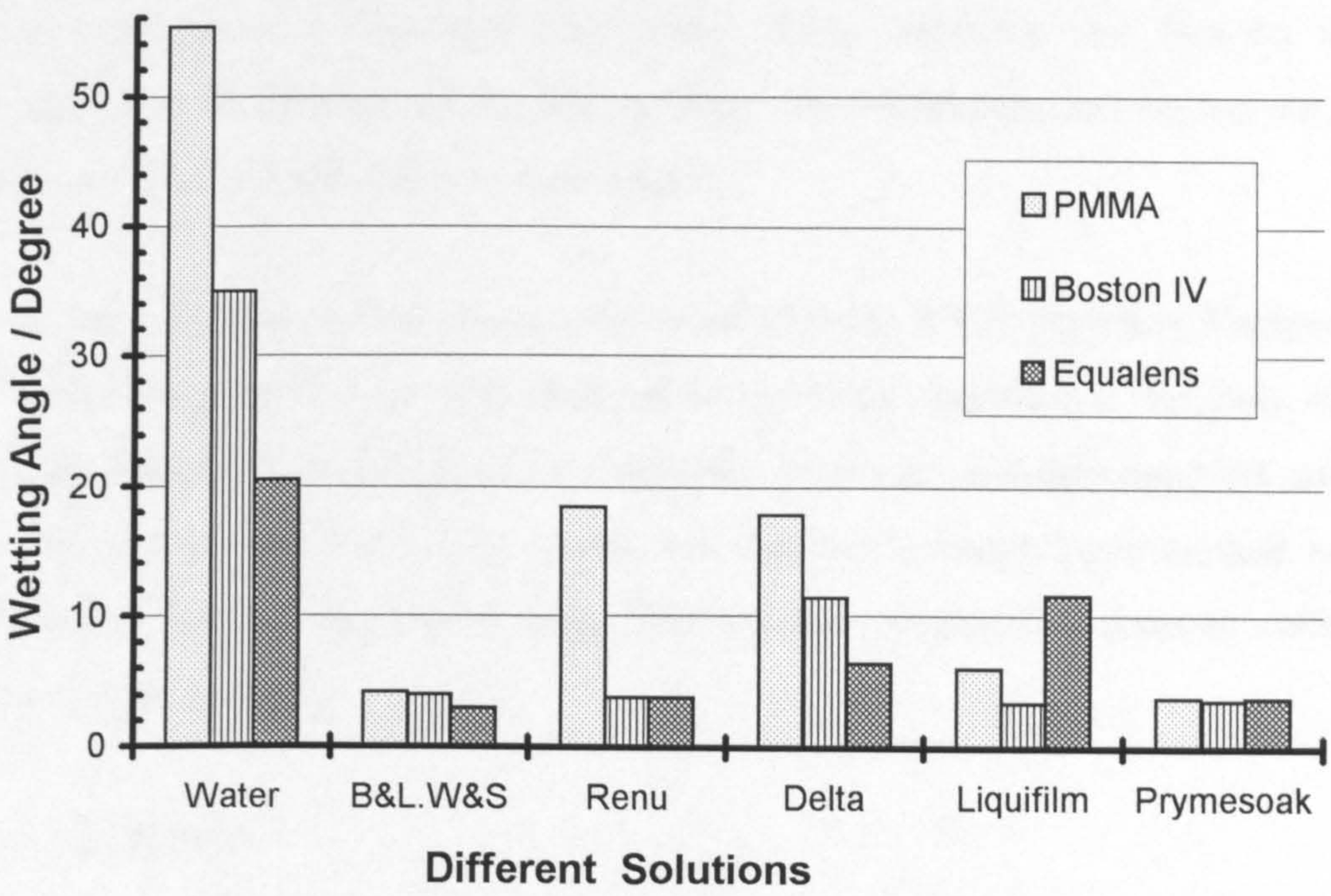


Figure 5.7. Un-separated adherent liquid wetting angles of different contact lenses of PMMA, Boston IV and Equalens when influenced by various solutions.

5.2.1.3. Discussion

The influence of solutions on contact lens wetting properties has been reported by many investigators. Contact lens solutions generally reduce the wetting angle of a lens. Prymesoak and Bausch and Lomb wetting solutions, which include Chlorhexidine Gluconate, produced excellent wettability for all three materials,

while others had a selective influence on the materials' wettability. These may prompt practitioners to use a particular solution for a specific material, such as utilising Bausch and Lomb wetting or Prymesoak rather than using Renu or Delta solutions for PMMA contact lenses.

5.2.2. Post-wear Rigid Contact Lens Surface Wettabilities

5.2.2.1. Aims, Materials and Method

Although an individual tear film has a general composition, it can be influenced by nutrition and blood components, such as hormones. The purpose of this experiment, was to investigate the effect of one subject's tear film on the wettabilities of different contact lens surfaces. The experiment was carried out at the same time on each day on a male subject.

Five pairs of rigid contact lenses made from PMMA, RXD, Equalens, Paraperm EX and Polycon II were manufactured to the same specification for only one subject. Pairs of hydrated lenses were worn for 30 minutes and then removed using the method described in 4.4.2.1 and the un-separated adherent liquid method was utilised to measure the wetting angle. The process repeated five times to collect five independent data.

5.2.2.2. Results

Figure 5.8 shows the mean values of the un-separated adherent liquid wetting angle for pre- and post-wear rigid contact lenses. There was a significant difference between the wetting angle of adherent liquid on various hydrated pre-wear contact lenses (ANOVA, $F=305.11$, $P<0.00001$). The wettability of the materials in the hydrated state would be ranked as:

PMMA < Polycon II < RXD < Paraperm < Equalens

The increase in wettability of the post-wear contact lenses can be seen from the plot. The mean of the post-wear wetting angle values (12.16°, SD=±2.5) had an

enhancement in wettabilities compared with the hydrated pre-wear values (35.8°). Despite a significant difference between various contact lenses in pre-wearing materials (ANOVA: $F=27.62$, $P<0.00001$), there was no great disparity between the PMMA, RXD and Equalens contact lenses in post-wear (ANOVA, $F=2.04$, $P>0.21$). The Paraperm Ex-wear contact lens had a greater wetting angle for post-wear, while the next lowest wetting angle was Polycon II. The wettability of post-wear rigid contact lenses were ranked as:-

P=0.09

Paraperm ≤ Polycon II < PMMA ≤ RXD ≤ Equalens

P= 0.11 P=0.02 P=0.23 P=0.5

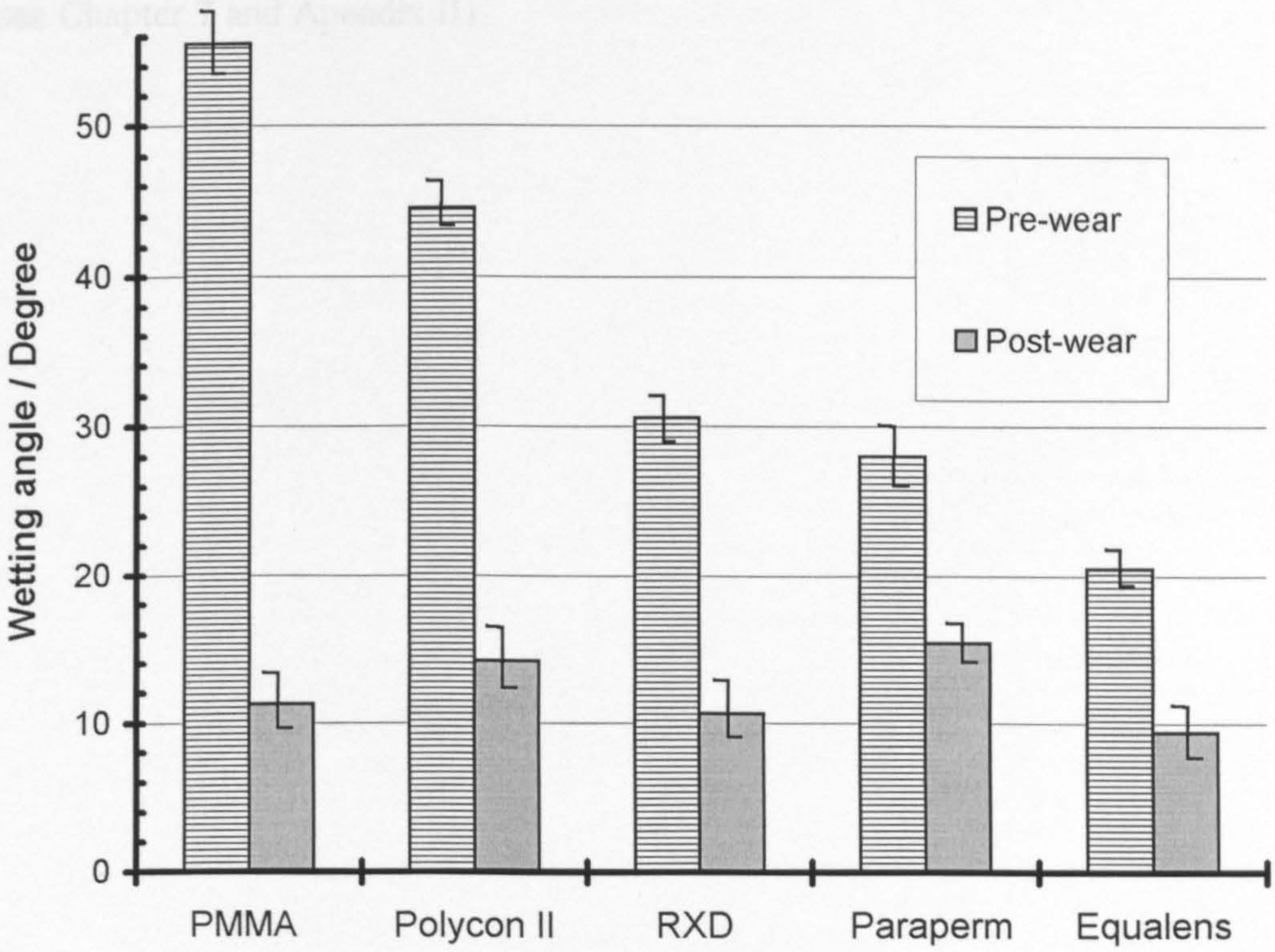


Figure 5.8. Pre- and post-wear un-separated adherent liquid wetting angles of PMMA, Polycon II, Boston RXD, Paraperm EX and Equalens contact lenses.

5.2.2.3. Discussion

Contact lens wettability can be measured either pre- or post-wear in vitro. When contact lens wettability is measured pre-wear using de-ionised distilled water, it evaluates the finished contact lens, but when measured post-wear it evaluates the influence and integration of the individual tear film on a specific contact lens material. The results of the experiment revealed there was a contrast between the wettability of the hydrated pre-wear contact lenses and the post-wear using different materials. When worn, the tear film influenced the contact lens surfaces and increased wettabilities significantly. A similar result was also reported by Shirafkan et al (1995) for the pre- and post-wear soft contact lens surface wettabilities using the method. They showed that the maximum wettability was created on the lens surface after 30 minutes of wearing and further wearing period did not enhance the wettability because surface charge equilibrium was reached (see Chapter 7 and Apendix II).

5.3. Pre- and Post-wear Soft Contact Lens Wettabilities

5.3.1. Aims, Materials and Method

The aim of this experiment was to measure the surface wettability of a range soft contact lenses (Table 5.2) with different water contents, that were manufactured using varying techniques. The tear film can influence wettability, so post-wear was also investigated. The un-separated adherent liquid/laser method measured the wetting angle of pre-wear and 30 minutes post-wear in five subjects (four females and one male), and saline ((pH=7, γ=82.8 dynes/cm) was used to produce the meniscus on the soft contact lenses. The process repeated five times to collect five independent data.

Trade Name	Material	Water Content %	DK	Manufacture
Hydron Z6	pHEMA	38.6	10	Lathed Cut
SeeQuence B&L	pHEMA	38.6	8.5	Spincast
Hydron Z4	pHEMA	38.6	10	Cast Moulded
Elegance	pHEMA	38.6	10	Cast Moulded
Acuvue	Etafilcon A	58	27	Cast Moulded
Wöhlk 55	PAM/NVP	55	23	Lathed Cut
Focus	Vifilcon A	55	20	Cast Moulded
Medalist	Alphafilcon A	66	29.1	Spincast
Wöhlk 70	MMA/VP	70	43	Lathed Cut
Hydron 67	MMA/VP	67	30	Lathed Cut
OmniFlex	MMA/VP	70	32	Lathed Cut

Table 5.1. Soft contact lenses' characteristics.

5.3.2. Results

The mean values and standard deviations of un-separated adherent liquid wetting angles for pre- and post-wear soft contact lenses are plotted in Figure 5.9. There was a significant difference between the wetting angle values of various soft contact lenses (pre-wear, ANOVA, $F=51.42$, $p<0.00001$), but, while they were

worn, wettability increased to 2° (±0.2), although the ANOVA showed no great disparity between them (F=1, p<0.45).

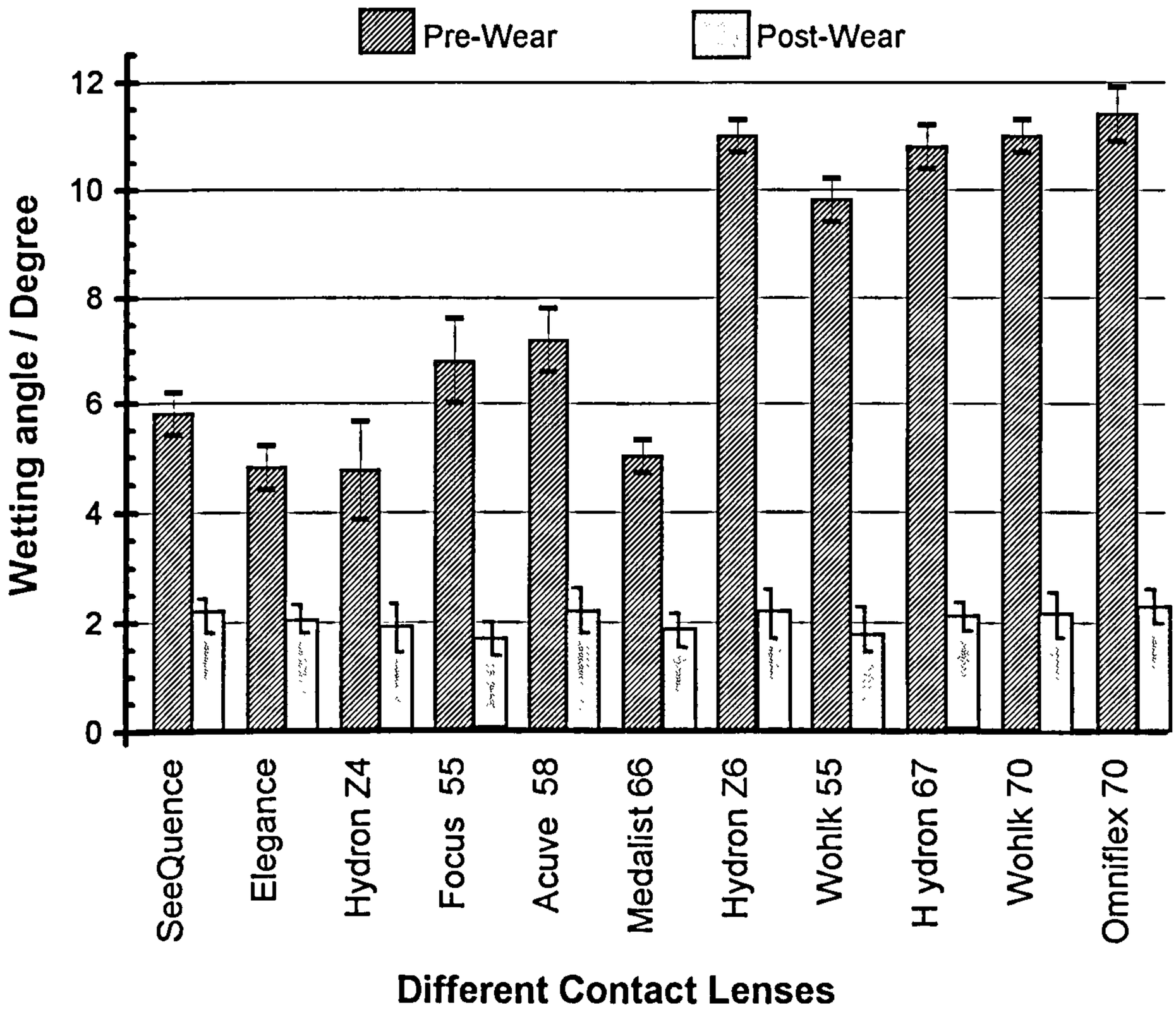


Figure 5.9. The pre and post-wear un-separated adherent liquid wetting angle values for different soft contact lenses.

The analysis was also applied to the soft contact lenses manufactured by lathe cut, cast moulded and spincast. There was a significant difference between the values of those lathe cut and the others (ANOVA: F<109, P<0.00001), which were ranked as follows:

Z4 (Cast moulded, p=0.02)**>SeeQuence** (Spincast, p=0.0001)**>Z6** (Lathed cut)

The lathe cut contact lens of Hydron Z6 had the highest wetting angle (11°, SD=±0.7°) while Hydron Z4 moulded lenses had the lowest (3.8°, SD=±0.83°).

5.3.3. Discussion

The results of the un-separated adherent liquid/laser wetting angle method on soft contact lenses revealed their surface ability to adhere (to prevent coalescence) liquid and that soft contact lens surface wettability is dependent on two main factors:.

- The contact lens materials.
- The contact lens manufacturing methods.

Linear regression showed a positive correlation (slope=0.009) on the wetting angles of various water content lathe cut contact lenses. Cast moulded contact lenses had a very low-wetting angle because of either a higher surface density than the lathe cut lenses of the same material or a greater ionic bond due to manufacturing. The results from post-wear contact lenses showed that the tear film influenced all types of soft contact lenses, resulting in greater wettability. The lower wetting angle resulted in greater comfort for contact lens wearers (Woodward 1984).

These results demonstrate that the technique can assess pre-wear soft contact lens surface wettability, and this discussion may assist practitioners in fitting soft contact lenses on the basis of contact lens manufacturing and the other factors that can influence surface wettability. The significant difference in wettability prompts the questions that if:

a. there was another technique for polishing lathe cut lenses, would wettability be improved?

b. If the material of the mould changed, would wettability alter?

5.4. Adherent Liquid Discussion

The un-separated adherent liquid/laser wetting angle method has a common characteristic with other solid/liquid/air interface techniques used to measure contact lens surface wettability. In the novel method, when the contact lens surface touched the liquid and while it was lifted, the contact lens surface could continually attract liquid until a receding wetting angle was reached. The solid/liquid interface area diameter is dependent on the contact lens wettability. If the molecules of the contact lens surface are wettable, the interface bonds do not break quickly, they resist breaking up. The interface area does not decline, and therefore, the wetting angle is lower. In contrast, if the contact lens surface is unable to keep liquid on the surface, the surface tension separates and pulls the interfaced liquid molecules into the liquid, at which point, the interface area declines, leading to a greater wetting angle.

The experimental results demonstrate that the water adhering to a contact lens surface provides a measurement of wettability which is in agreement with the literature. A justification of the validity of this method is as follows: All materials in this study had the same front surface radius of curvature (8mm) and were immersed 1.5mm (the sagitta of the FS curve) into the water after point of contact. Therefore, the surface area of the contact lens exposed to the water was a constant for all samples. As the lens was lifted from the water, the surface tension, which was constant irrespective of the volume of the water, acts to "sweep" the water molecules from the surface of the lens. Towards the edge of the lens (at the start of removal) the surface tension acted at a large angle (perhaps 70° - 80°) to the adhesion force on the lens surface, the component of the adhesion force opposing the movement was greater and there was less chance of moving the water molecules. When the adhesion force balanced the surface tension, any further upward force led toward breaking the molecular bonds from the surface. Since the surface tension and liquid hydrogen bonds were constant for all samples, the only variable was the contact lens material affecting the adherent liquid, producing different adhesion force, resulting a variation in adherent wetting angle.

To further confirm the above arguments, the shape of the adherent liquid was investigated for the explored contact lens materials in this study. A micrometer was used to measure six different diameters of the adherent liquid on contact lenses. The potential energy is a minimum for any system in equilibrium and hence expects the surfaces of the adherent liquid to be spherical, because of adhesion forces it produced a meniscus in the receding condition.

A measure of how well the adhered liquid laser technique can distinguish between different materials may be obtained by performing a single variable analysis of variance. The values were computed for the hydrated lenses. All the F (ANOVA: Single-factor and F-test) values were significant at the 5% level and therefore indicate a statistically significant difference between the materials. This indicates that the unseparated adherent liquid laser method can more readily distinguish between the material wettabilities.

The wetting angle values for all 3 hydrated materials were in a wide range of 20.5° -55.25°(Table 5.2). Nevertheless, the results determined by the new technique gave comparable orders for wettability to that obtained by current techniques. The advantages of this technique are that as the entire lens surface is immersed, it reproduces more closely the in-vivo situation where the whole of the lens is wetted, unlike the sessile drop method where only a small area of the lens has its wettability measured. The results of the novel approach show less variation than those given in the literature using the captive bubble technique.

In order to reduce the number of confining factors of the new method, the front surface radii of the lenses were constant. However, spherical front lens surfaces, and differing optic radii, may alter the results. It is also suspected that the speed of withdrawing the lens from the liquid, cleaning the lens surface, the liquid container and pH could alter the values. Consideration of these different effects will help to standardise the method and can be a topic for a further investigation.

when rigid contact lens wettability is measured pre-wear, the result represents the finished contact lens, which may be used by the contact lens manufacturer to control lens surface quality. But when it is measured post-wear the result reveals

the influence and integration of individual tear film on specific contact lens materials.

The variation of the adherent liquid wetting angle on contact lens surfaces may be explained in relationship to spreading coefficient: $S=\gamma_{LV}$ **(cos θ - 1)**. In the hydrated condition the wetting angle of PMMA, Boston IV and Equalens were 55.25°, 35° and 20.5° respectively which the spreading coefficients were -31.2, -13.2 and -4.6. The values for the effect of solutions ionisation showed a significant enhancement in wettability close to absolute spreading value of 0. One of the possible explanation would be creation of hydrophilic sites on the lens surfaces.

Wetting Angles and Spreading Coefficients (S)						
Materials	Water	B&L.W&S	Renu	Delta	Liquifilm	Prymesoak
PMMA	55.25°	4.2°	18.4°	17.8°	6°	3.8°
S	-31.2	-0.2	-3.7	-3.5	-0.4	-1.5
Post-wear	11.2°					
S	-1.6					
Boston IV	35°	4°	3.8°	11.4°	3.4°	3.6°
S	-13.2	-0.17	-1.16	-1.4	-0.12	-0.14
Equalens	20.5°	3°	3.8°	6.4°	11.6°	3.8°
S	-4.6	-0.1	-0.16	-0.5	-1	-0.16
Post-wear	9.4°					
S	-1					

Table 5.2. Un-separated adherent liquid wetting angle and spreading coefficient of PMMA, Boston IV and Equalens contact lenses when influenced by various solutions and tear film.

Measuring contact lens wettability through the un-separated adherent liquid/laser method has several advantages:

1. The apparatus used in the UALLM is readily available and inexpensive.

2. Measurement training is short.

3. It can be used on soft and rigid contact lenses. and

4. Measurements can be carried out in the hydrated condition.

(see Chapter 7)

Chapter 6. Contact Lens Surface Hydrophilicity

6.1. Introduction

While the meniscus of a solid/liquid/air interface can be measured using wetting angle methods, the interfacial forces between a liquid and solid can be measured using a balance. The balance of the dynamic contact angle method has been used to measure force between a thin rectangular piece of a material and a liquid. The force values can be converted to wetting angles through several formulae (see Chapter 3). A balance can also be used to measure the chemical bonding forces between the molecules of a liquid and those of a contact lens material, this parameter is known as the surface hydrophilicity. This can be determined by immersing the front surface of the lens and measuring the forces with a balance. The maximum force recorded as the lens is withdrawn and measures the interface molecular binding forces between a contact lens surface and a liquid. The value can be taken as a direct measure the contact lens surface hydrophilicity.

In this Chapter, studies are presented in an attempt to apply the Wilhelmy plate method (dynamic contact angle) to both hard and soft contact lenses (6.2). The first experiment demonstrates the problems associated with a rigid contact lens moving into a liquid and being removed vertically (6.2.1). Then the adherent liquid/maximum force method (ALMFM, 6.3) is explained to measure surface hydrophilicity of rigid and soft contact lenses both for pre-and post-wear (6.3.3, 6.3.4 and 6.3.5). The aim of 6.3.2, is to find the influence of front lens surface radius on the contact lens surface hydrophilicity. In 6.4, the experiments' results of this chapter will be discussed.

6.2. Dynamic Contact Angle Method

6. 2.1. Aims, Material and Method

The aim of this experiment was to investigate whether the Wilhelmy plate method could be adapted to measure contact lens wettability. Four samples made from PMMA material were manufactured to four specifications.

I. A rectangular plate measuring 25 x 10 x 1.5mm (length x width x and thickness).

II. A triangular shape, for which the lengths of the hypotenuse were 25mm with a base length of 20mm. The thickness of the material was 1.5mm, as above.

III. A circular disc with a diameter of 10mm and a thickness of 1.5mm.

IV. A contact lens with specifications TD = 10mm and Tc = 0.2 mm, while the front and back optic radii were cut to 7.3mm and each surface was polished for one minute.

The dynamic contact angle system (DCA-CAHN-312) was used to collect data and calculate the wetting angle. The speed of moving the material into the liquid was adjusted to 40μm/sec because a pilot study discovered that a faster speed did not allow enough time to read the scale and a speed 40μm/sec was found to be repeatable.

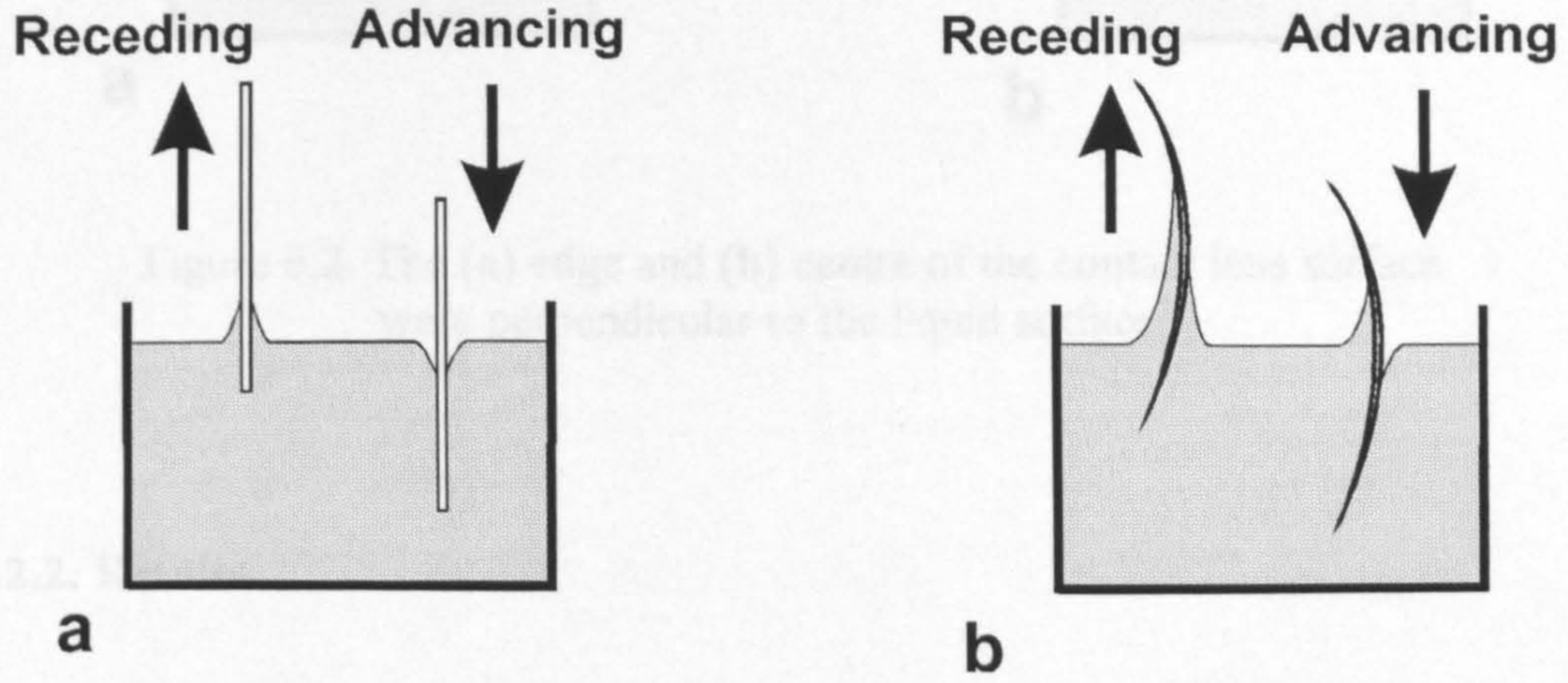


Figure 6.1. A comparison of the liquid meniscuses of PMMA **(a)** on a flat material and **(b)** on a contact lens.

The material was moved into de-ionised distilled water (pH 6.6, ± 0.2; advancing) and then withdrawn (receding), while data were stored automatically in a computer to analyse the wetting angle (Figure 6.1). The contact angle of the central and peripheral area of the contact lens were also measured by (Figure 6.2):

a. Moving the lens perpendicularly into the liquid, and the force data between 4mm to 5mm from the edge of the contact lens were used to calculate the wetting angle.

b. The force values from the periphery of the lens were recorded by tilting the contact lens towards the back lens surface until its peripheral area was perpendicular to the liquid surface. Values were obtained between 0.75 and 1.5mm from the contact lens edge.

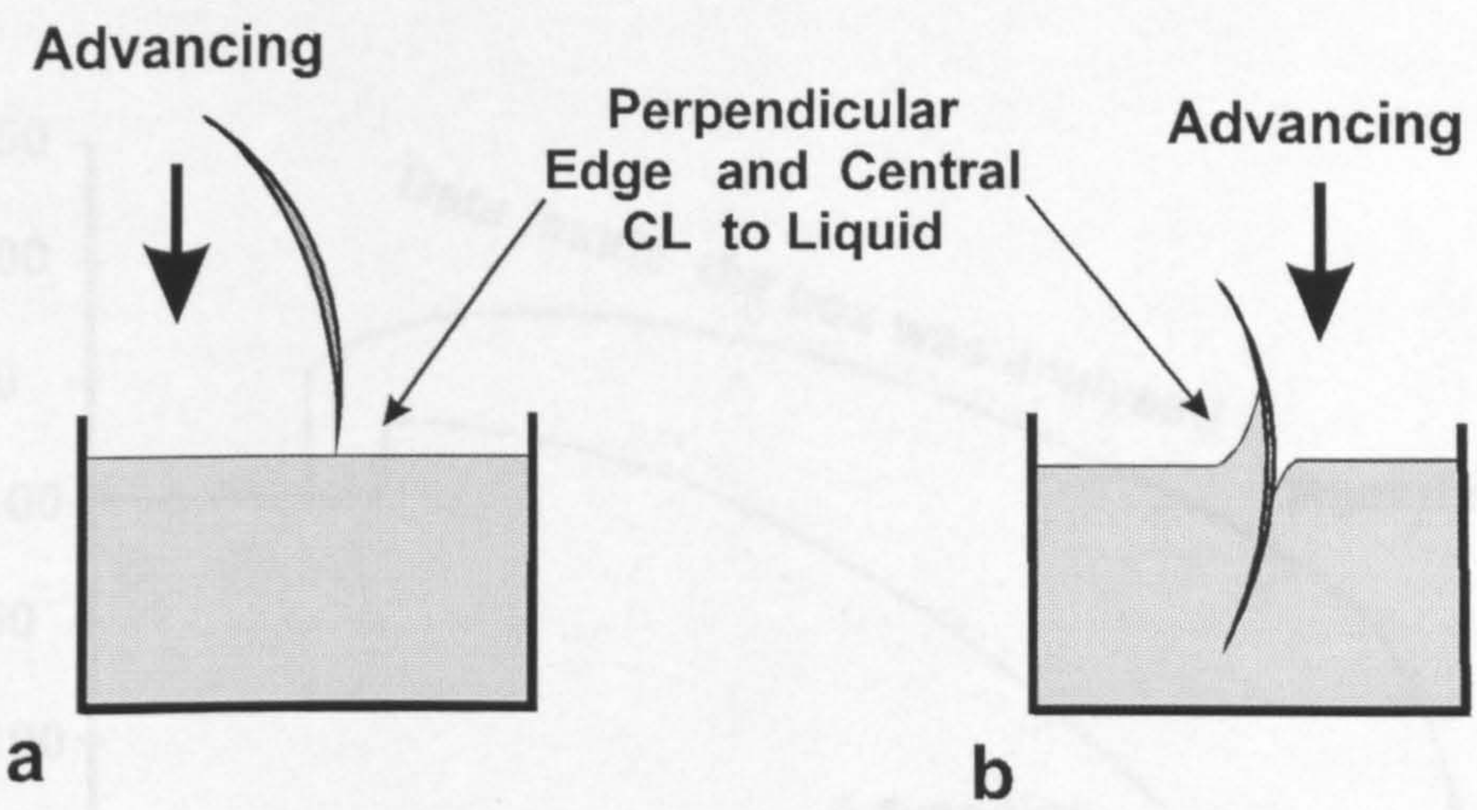


Figure 6.2. The **(a)** edge and **(b)** centre of the contact lens surface were perpendicular to the liquid surface.

6.2.2. Results

The wetting angle values for the samples are shown in Table 6.1, and the changes in the force, measured by the balance are illustrated in Figures 6.3, 6.4, 6.5, 6.6 and

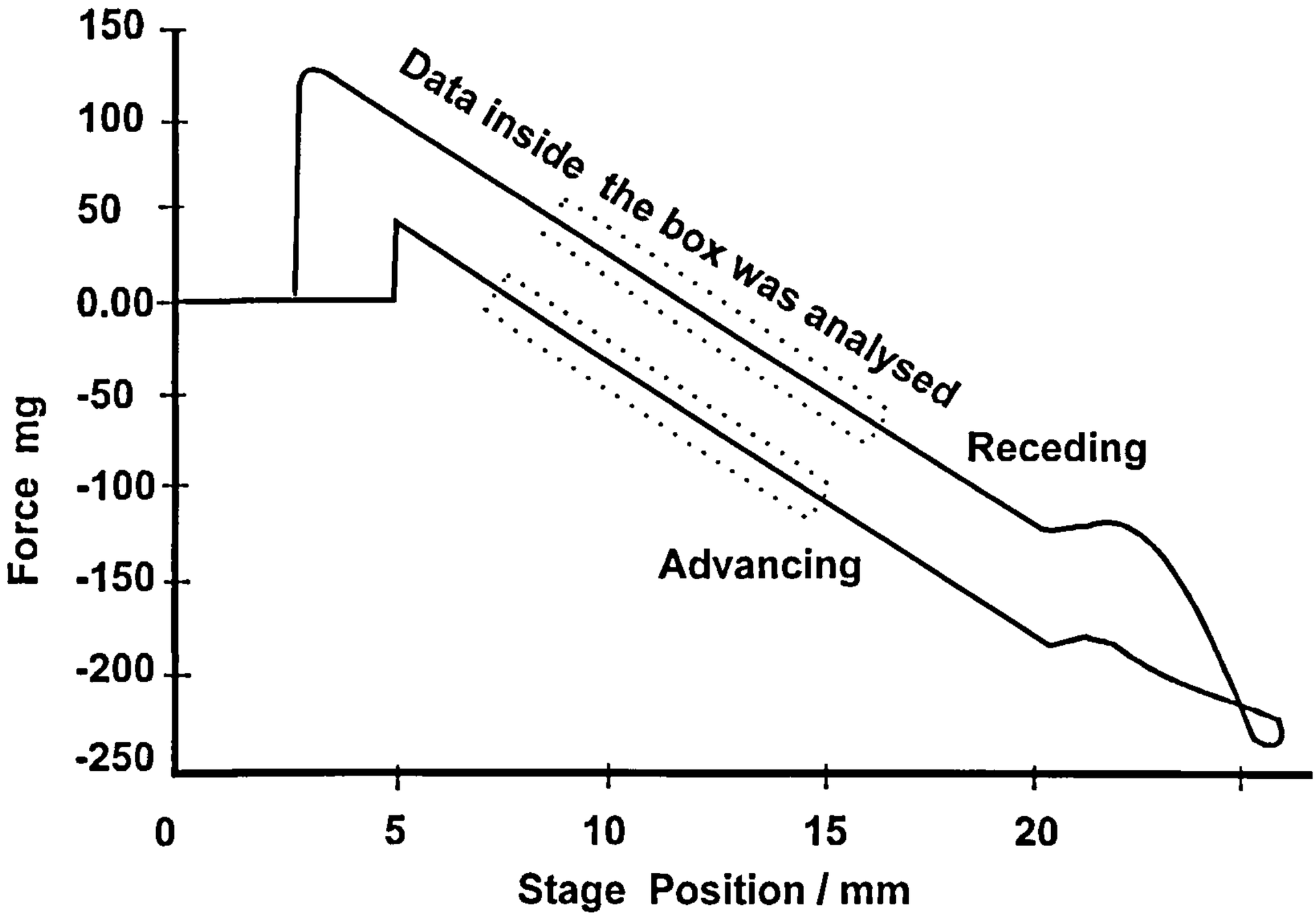


Figure 6.3. Adherent force values of a rectangular flat PMMA material at different immersion positions in the liquid.

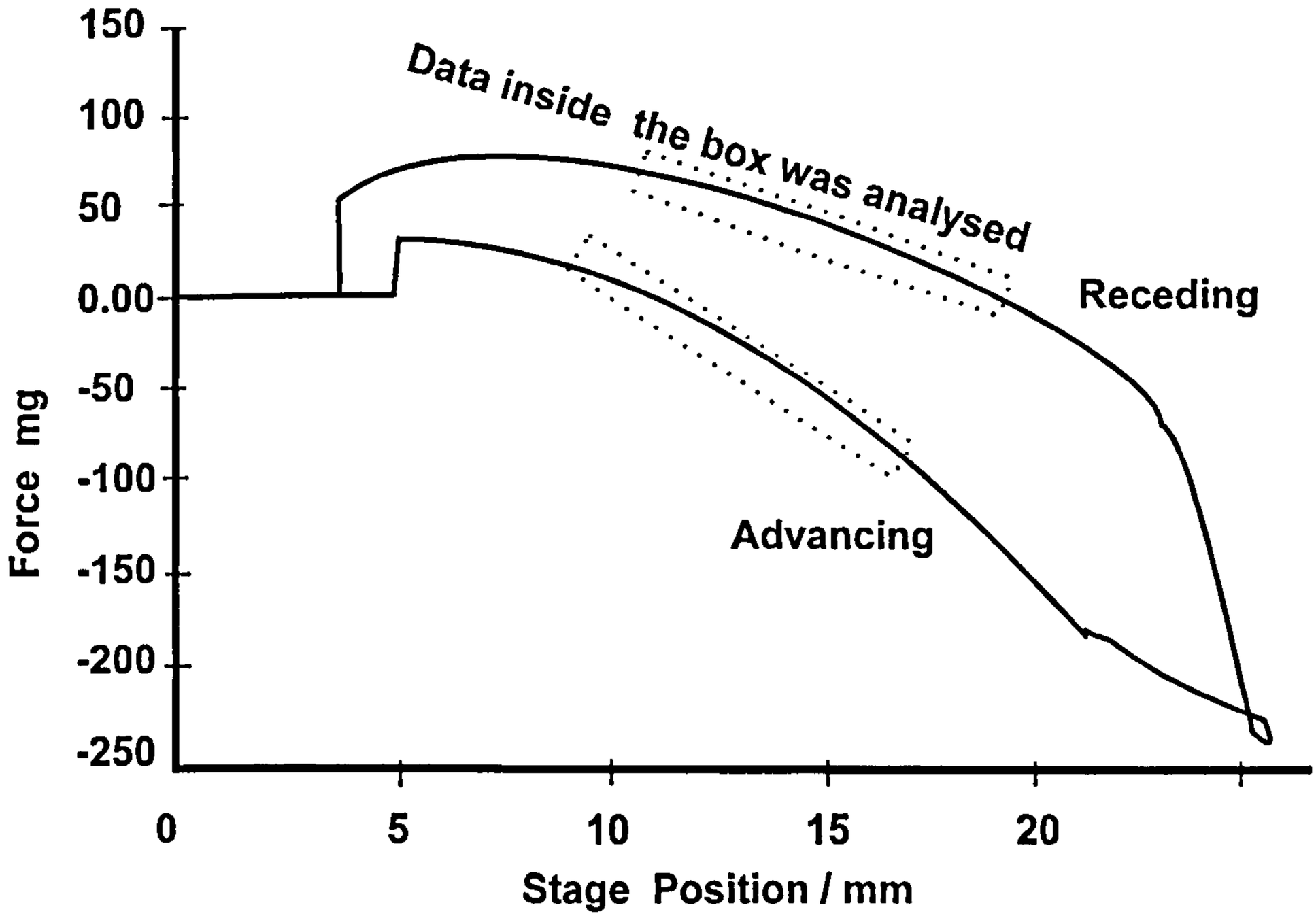


Figure 6.4. Adherent force values of a triangular, flat PMMA material at different immersion positions in the liquid.

6.7. Figure 6.3 shows the force values when using the rectangular shaped PMMA sample, in which the force variation is linear and has the same gradient for both advancing and receding, but the results for the triangular shaped sample produce curved lines due to an increasing (advancing) or declining (receding) solid/liquid/air interface perimeter (Figure 6.4).

The values of the disc-shaped sample produced even greater variations because of changes in the solid/liquid/air interface perimeter during the advancing and receding phase (Figures 6.5).

Figures 6.6 and 6.7 show the values of the contact lens periphery and its central area. As can be seen, the slope of values that were expected to be negative was positive and had greater fluctuation due to front and back contact lens radii and changes to the solid/liquid/air interface perimeter.

PMMA Material Shapes	Contact Angle Conditions		
	Advancing	Receding	Hysteresis
Rectangular	68	54	14
Triangular	72	63	9
Disc	74	61	13
Contact Lens Periphery	81	70	11
Contact Lens Centre	87	72	15

Table 6.1. The contact angles of variously shaped PMMA lenses measured by the dynamic contact angle method.

6.2.3. Discussion

A DCA balance was used to collect data on changes to the forces at the solid/liquid/air interface. The force data depend on several factors, such as the perimeter of the material (length of solid/liquid/air interface), the surface tension, the

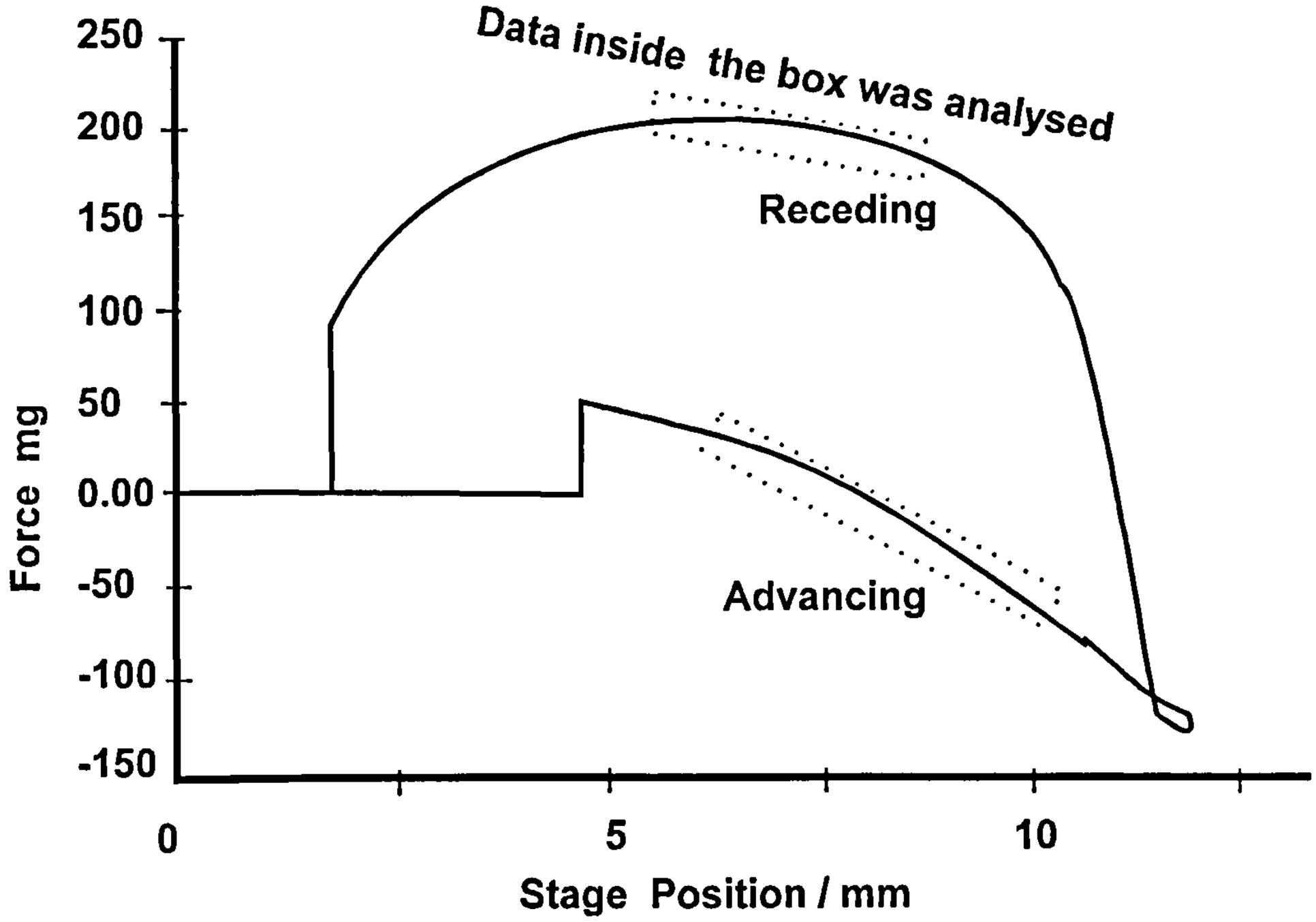


Figure 6.5. Adherent force values of the circular, flat PMMA material at different immersion positions in the liquid.

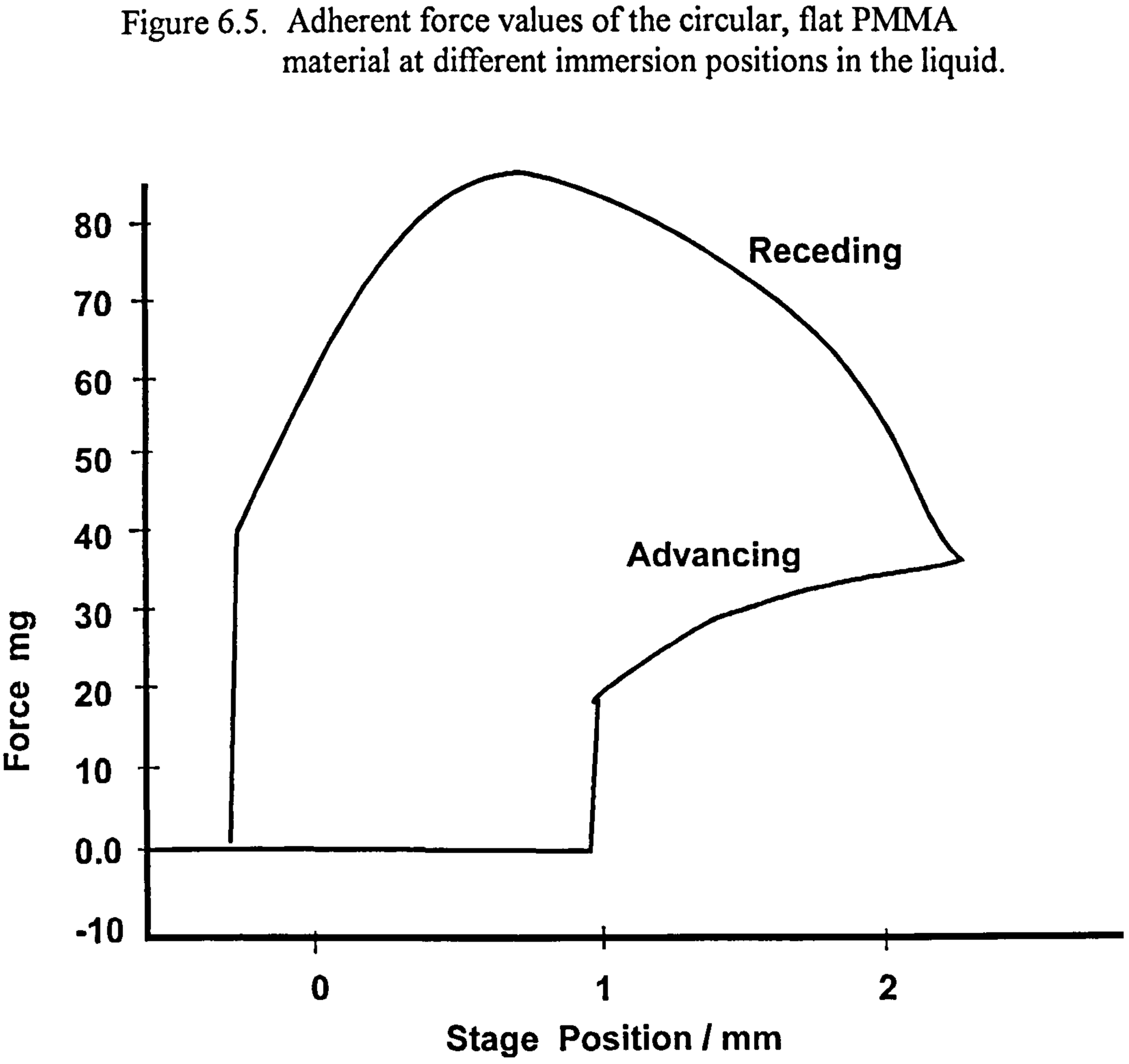


Figure 6.6. Adherent force values of a PMMA contact lens when the edge was immersed perpendicularly into a liquid.

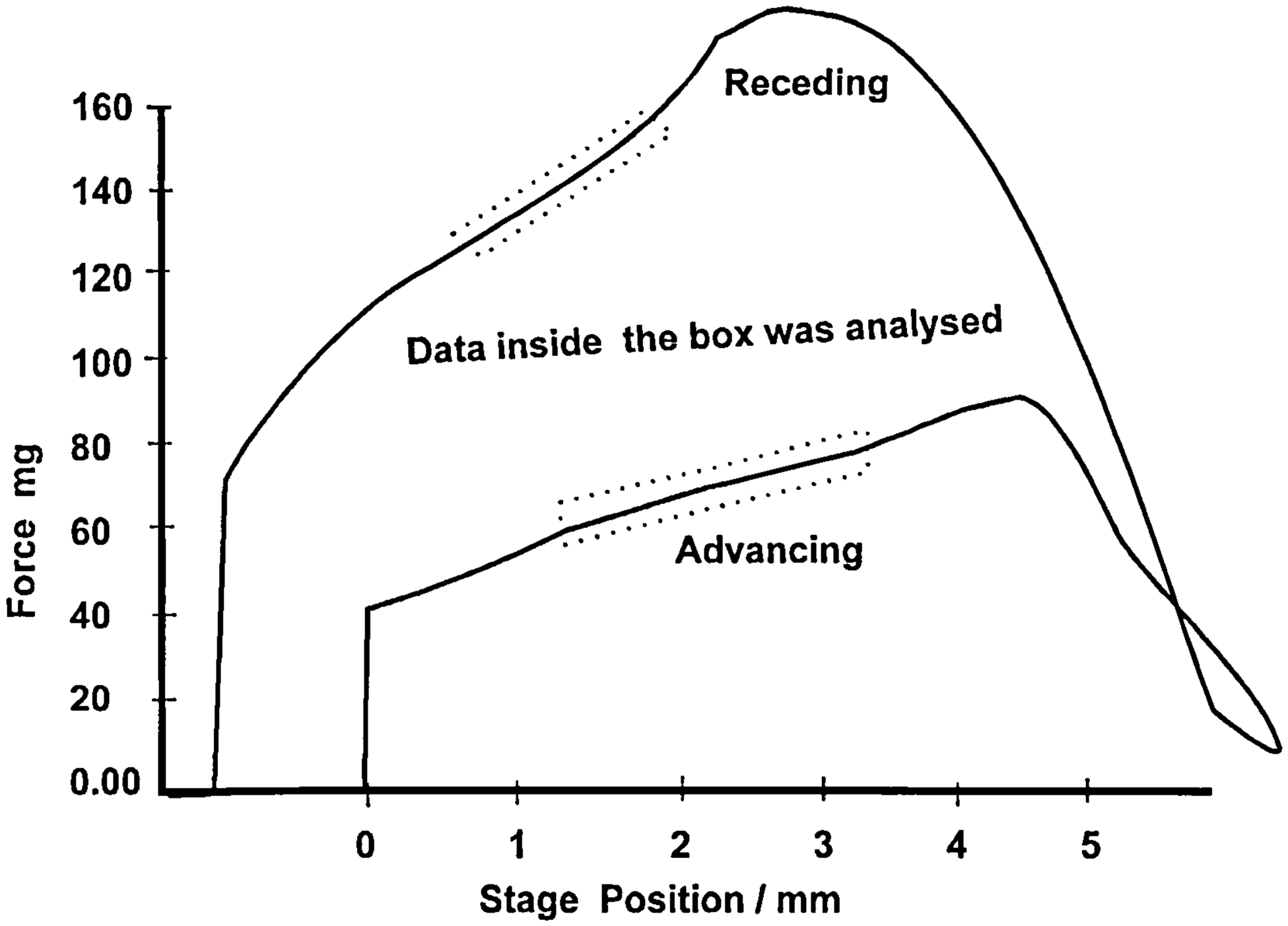


Figure 6.7. Adherent force values of a PMMA contact lens when it was immersed in liquid.

volume of the sample that was immersed and the density of the solid. Figure 6.3 reveals that, when the rectangular material was immersed in water and withdrawn, the force data plot was a straight line (see Chapter 3, Figures 6.3). When the triangular-shaped sample was being immersed from the vertex into the liquid, the contact area between the material and the liquid (perimeter) gradually increased. The enhancement of the perimeter created a greater force on the material and vice versa during withdrawal (receding). The force variations were neither linear, nor a straight line, with great variation being seen on the scale (Figure 6.4). To make the force values linear, the variations of perimeter size were needed to adapt in the main formula (Chapter 3). that were variable with the depth of immersion for advancing and receding conditions, then the data could be converted to wetting angle.

The values for the disc sample were not consistently increased or reduced because of the influence of the solid(disc)/liquid/air interface perimeter on the depth of

immersion (Figure 6.5), which caused greater variation in data in comparison with the triangular sample.

When the contact lens was moved into the liquid, the front and back surface radii and the angle between the lens surface and liquid surface affected the values, in addition to the previously mentioned factor. In an advancing state, the meniscus for the back lens surface was upward, which needed to be downward to create negative force (see Figure 6.2). The meniscus that created a positive force was acting as a semi-capillary attraction force, which was observed for both advancing and receding conditions. As a result, different contact angle values were calculated for the varying depths of immersion in the advancing condition. Different values were also obtained for the receding condition due to the influence factors that have already been explained (Figures 6.6 and 6.7).

The angle between the contact lens surface and liquid surface was thought to be perpendicular, but, if the contact lens is initially adjusted to be perpendicular to the lens edge surface as it moves down into the liquid, the angle will change. A device was thus required to vary the position of the lens perpendicular to the liquid surface for every level of immersion (both for advancing and receding condition). In addition, the front and back optic radii, total diameter and peripheral radius of the contact lenses are variable, and to change the position from the advancing to receding condition a manoeuvre of a few millimetres was required (4mm), which limited the measurements.

As the four samples were prepared under the same conditions, one solution was used and all samples were perpendicularly moved to the liquid surface, the wetting angle of the materials were expected to be the same, although there was a large and significant variation between them (ANOVA: $p<0.00001$).

When the flat materials were moved to the liquid, the meniscuses of both surfaces had the same shape. The meniscuses of the contact lenses in the advancing position varied: the meniscus of the front optic radius was convex and the meniscus of the back optic radius concave. This created a greater force on the contact lens surface, resulting in larger wetting angles. When the contact lens was withdrawn from the

liquid, the meniscus on the back and front surfaces did not have the same height. The size (height and base) of the meniscus of the front optic radius was smaller than the meniscus of the back optic radius, which led to a greater force on the back surface and a larger receding wetting angle on the contact lens than the receding wetting angle on the flat material. The front contact lens surface radius produced partially capillary force, which elevated the liquid in the advancing condition and enhanced the values.

From the above discussion it may be concluded that measuring the wetting angle of rigid contact lenses through the DCA method is not repeatable and not reliable because:

a. The contact lens/liquid interface perimeter varies.

b. The back and front contact lens radii effect.

c. The lack of perpendicularity of the contact lens to the liquid surface.

For the reasons that were explained earlier, it is suggested that the balance method might only determine the wetting properties of a rectangular flat sample of contact lens materials and not the finished soft and rigid contact lenses (see later).

6.3. The Adherent Liquid/Maximum Force Method

6.3.1. Theory and Method

In the Adherent Liquid/Maximum Force Method (ALMFM), the back surface of both rigid and soft contact lenses were held by a suction holder and a convex ended rod surface respectively (see Chapter 5.2.1). The contact lens holder was then attached to the balance and the lens was moved automatically towards the liquid surface at a speed of 40μm per second until it touched the liquid surface (Figure 6.8). When the convex contact lens surface touched the liquid, the attraction force at the interface, which was monitored by the DCA system suddenly increased. Further downward movement of the lens by 1.5mm reduced the force to zero, with the collected data of time, immersion depth and force being digitised and stored by computer every second. On withdrawing the lens, the force at the contact lens surface increased until, at a certain point, the force started to decline.

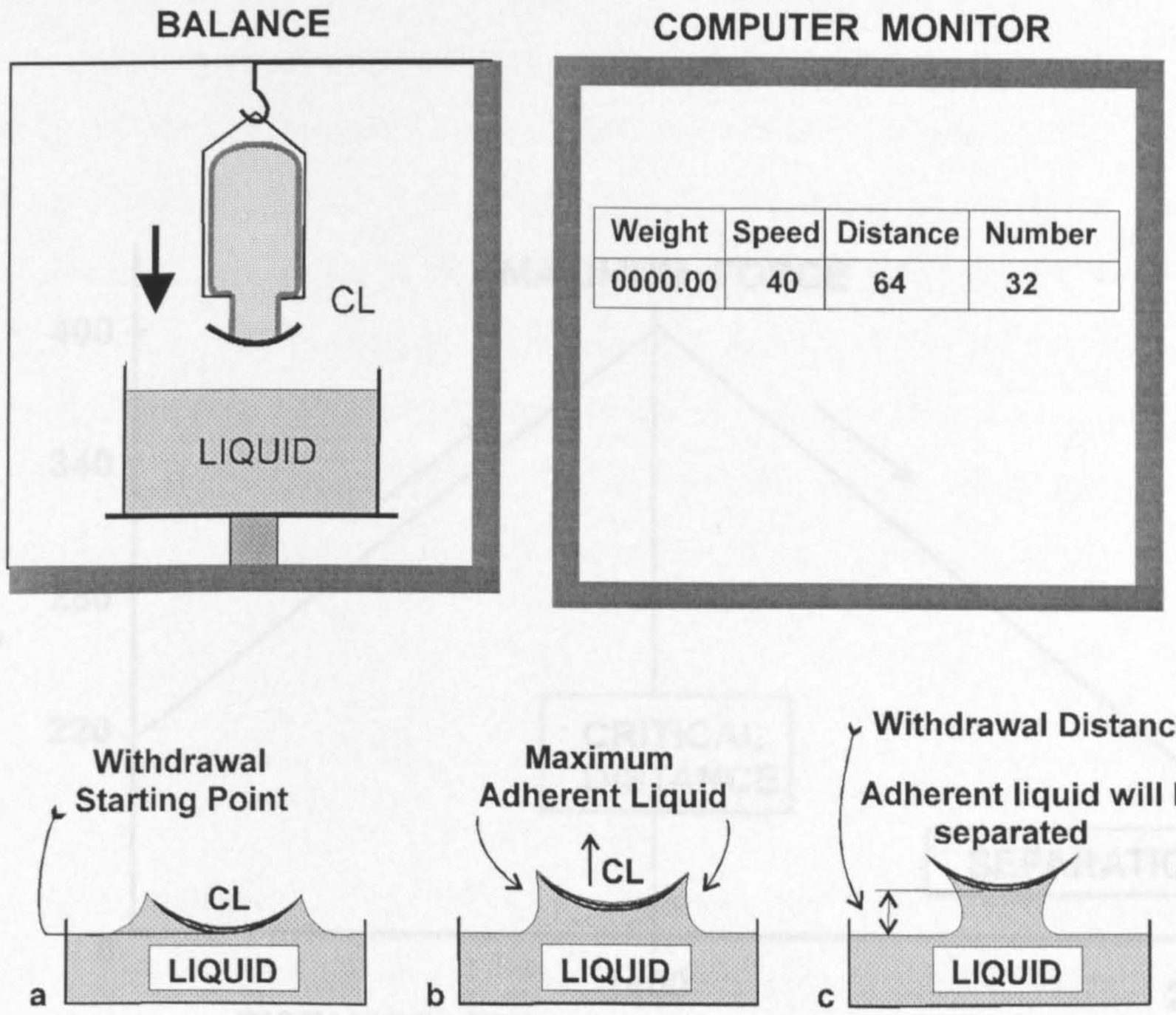


Figure 6.8. The prepared contact lens was moved to the liquid surface and withdrawn. The maximum adherent force, critical distance and separation distance were measured.

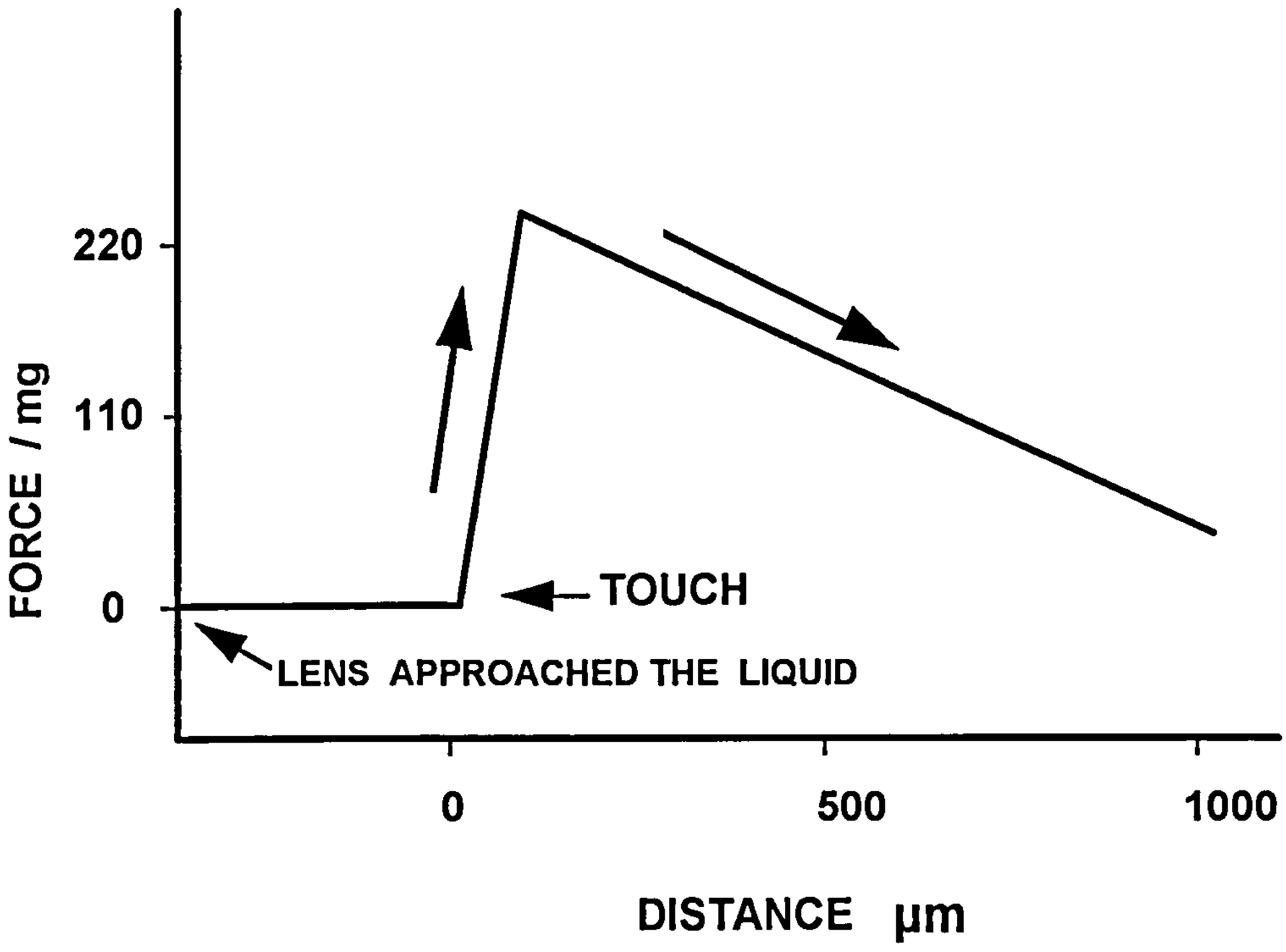


Figure 6.9. A rapid increase in force at the point where the contact lens surface touched the liquid.

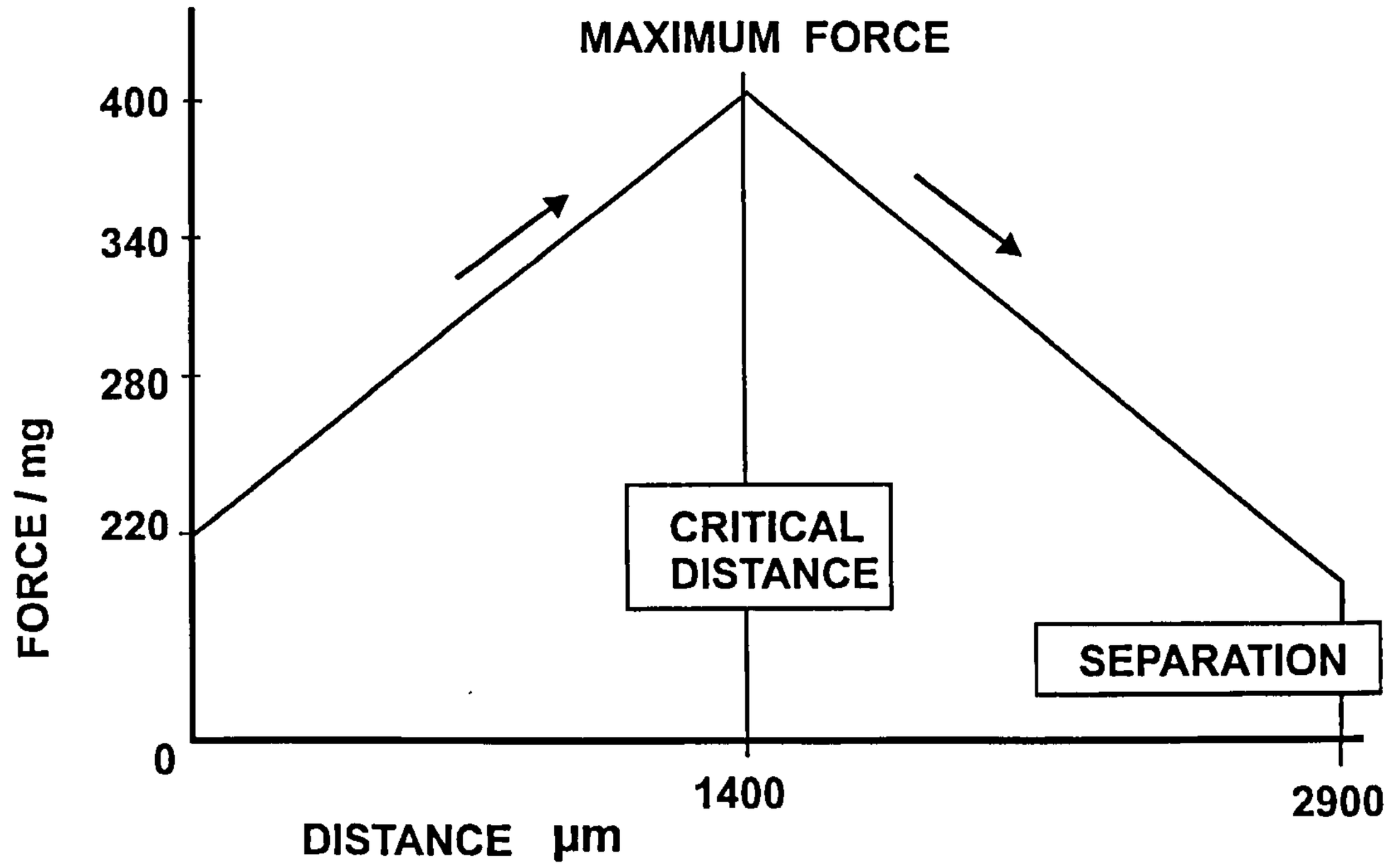


Figure 6.10. The changes in force at different withdrawal distances.

The force at this point is called the maximum force and the withdrawal distance is known as the critical distance. By further withdrawing the lens from the liquid, the liquid separated at a certain distance known as the separation distance (Figures 6.10). As the contact lens surface attracted the liquid and when the interfacial force between the contact lens surface and liquid was at the maximum values of the scale, this measures the phenomenon known as contact lens surface hydrophilicity.

6.3.2. The Influence of Front Lens Surface Radii

6.3.2.1. Aims, Material and Method

The aim of this experiment was to investigate the influence of front lens surface radii on the maximum adherent force. Six rigid contact lenses made of PMMA were used, all of which had the same specification of 0.2mm centre thickness and total diameter of 9.5mm. The front contact lens surfaces (FOZR) were cut on one lathe with the same diamond that had radii ranges of 7.00, 8.00, 9.00, 10.00, 11.00 and 12.00mm. The front lens surfaces were then polished for one minute with Silo-O2-Care and cleaned with Isobar liquid in the final stages of manufacture. The lens surfaces were perpetrated through the method explained in Chapter 4. De-ionised distilled water was used to produce adherent liquid and the DCA balance was utilised to measure the adherent maximum force, which was taken as a measure of contact lens surface hydrophilicity. Ten independent measurements were carried out on each contact lens at a temperature of 23° ±2 and a humidity of 40 per cent ±10.

6.3.2.1. Results

The mean and standard deviation of the maximum adherent force values are illustrated in Figure 6.11, which shows that the maximum force increases with an increasing front surface radius. A linear regression analysis confirmed there was a positive correlation coefficient between the contact lens surface radii and the

maximum force values (slope=+0.15), and an analysis of variance revealed there was a significant difference between the values (ANOVA: F= 14.86, p<0.001).

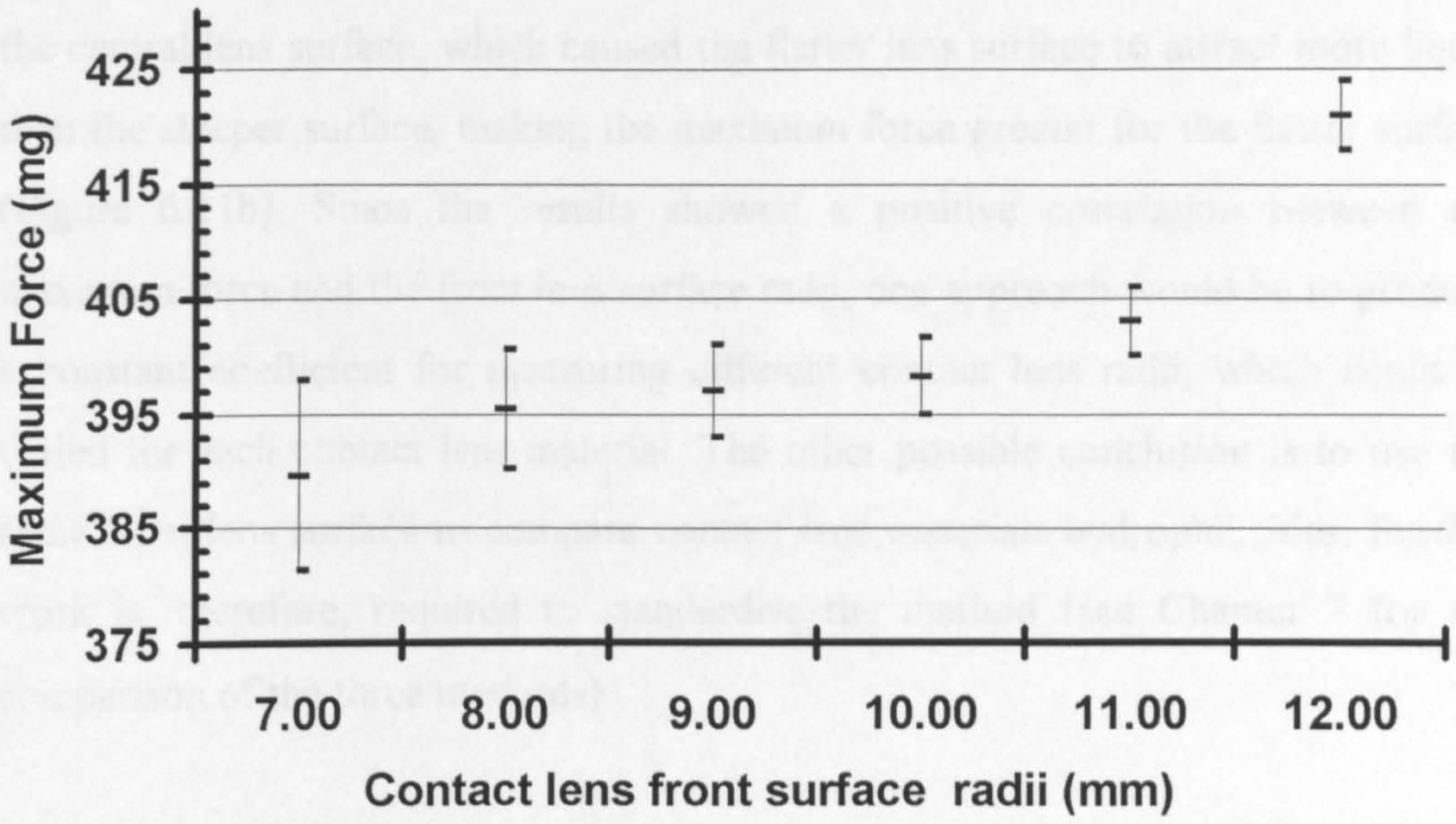


Figure 6.11a. The mean, standard deviation and linear regression of the adherent value for different contact lens surface radii.

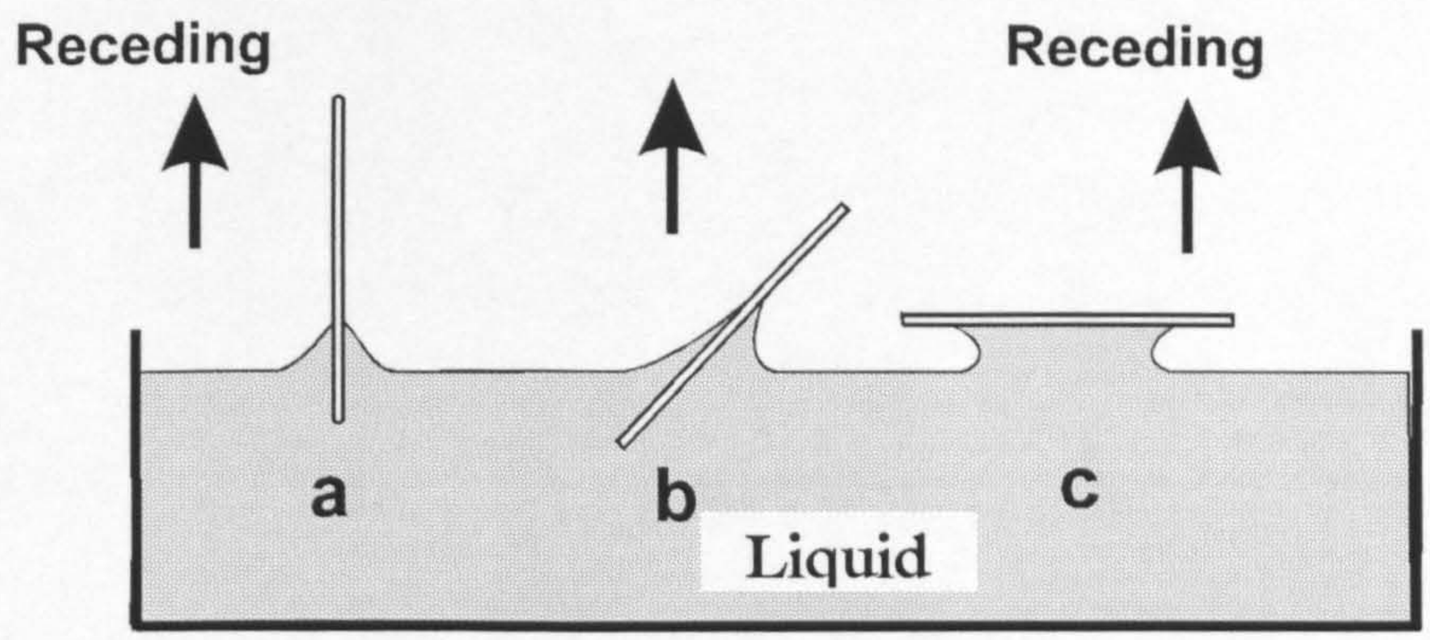


Figure 6.11b. A flat material at three different angles to a liquid, demonstrating the influence of front lens surface radii on the values (Tighe 1997).

6.3.2.3. Discussion

A possible explanation for these results is that the surface molecules of the flatter front radii (at the periphery) were closer to the liquid surface than the molecules of the central lens surface, which caused the flatter lens surface to attract more liquid than the steeper surface, making the maximum force greater for the flatter surface (Figure 6.11b). Since the results showed a positive correlation between the maximum force and the front lens surface radii, one approach would be to produce a constant coefficient for measuring different contact lens radii, which could be varied for each contact lens material. The other possible conclusion is to use the same front lens surface to compare contact lens materials hydrophilicities. Further work is, therefore, required to standardise the method (see Chapter 7 for the comparison of the three methods).

6.3.3. Variation in Hydrophilicity with Contact Lens Manufacturing Methods

6.3.3.1. Aims, Materials and Method

The objective of this experiment was to evaluate the effect of polishing time on the surface hydrophilicities of different lens materials. PMMA, CAB, Boston RXD and Equalens materials were manufactured to the same specification, and samples were produced with polishing periods of one, three and five minutes polished with Silo-O2-Care and cleaned with Isobar liquid in the final stages of manufacture. The contact lenses were cleaned and hydrated for 24 hours, and the ALMFM method was used to record the measurements of the maximum adherent force. The process repeated five times to collect five independent data.

6.3.3.2. Results

The values of the maximum force for all materials are illustrated in Figure 6.12, which shows that one minute polishing on PMMA produces 395mg maximum force. When PMMA was polished for three minutes, the maximum force increased significantly (Bonferonni: t-test, $p<0.0001$), but after five minutes of polishing the maximum force was significantly lower than the value for three minutes polishing time (Bonferonni: t test, $p<0.001$).

Polishing CAB contact lenses had a significant effect on the maximum force values with three minutes of polishing producing a greater maximum force than one minute of polishing (Bonferonni: t test, $P<0.00001$). After five minutes of polishing the maximum force had reduced to a value below that for one minute.

Equalens had similar trends to PMMA, with three minutes of polishing producing a significantly greater maximum force than one minute of polishing ($p<0.00001$). But, five minutes of polishing reduced the maximum force to a value that was still higher than for one minute polishing ($p<0.001$).

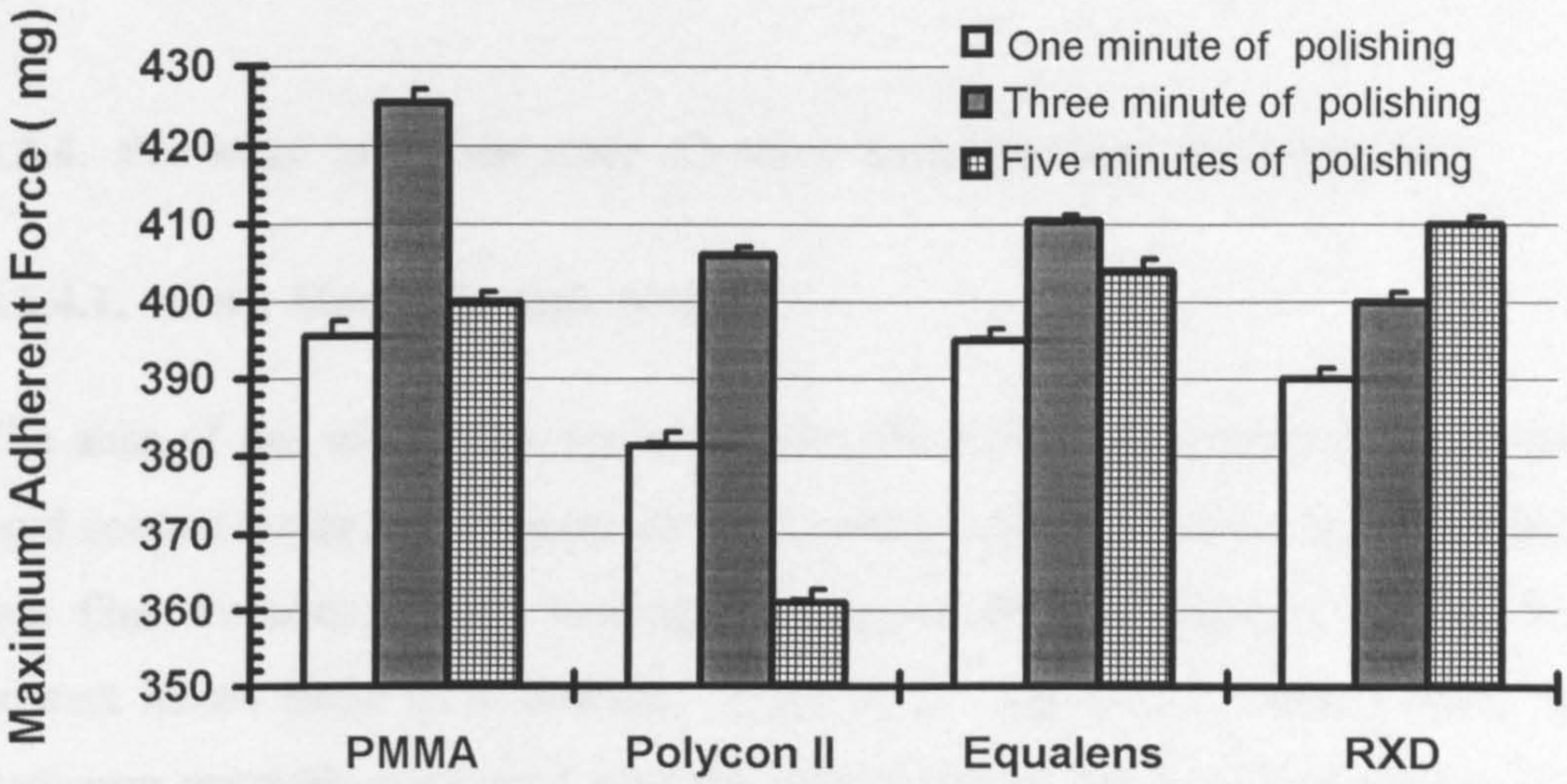


Figure 6.12. Adherent maximum force values for different contact lenses that were polished for three periods of time: one, three and five minutes.

6.3.3.3. Discussion

The lathe cutting of a material produces heat on the contact lens surface and the tip of the diamond, with the amount depending on a number of factors, including material stiffness, the speed of lathe cutting and the sharpness of the tip of the diamond. It has been reported that generated heat can damage material surfaces (Walker 1989), although one and three minutes of polishing required to remove the damaged surface areas of contact lenses for all materials, increased the hydrophilicity. Further polishing produced heat energy that reduced hydrophilicity for all materials, apart from Boston RXD. The conclusions of the experiment are:-

a. Polishing up to three minutes increases contact lens surface hydrophilicity for all materials.

b. For the tested contact lens materials (apart from RXD), excess polishing reduces the hydrophilicity of the contact lens surface when measured using the ALMF method (see 7.3).

c. Contact lens materials have different sensitivities to polishing.

d. Another possible method of increasing lens surface hydrophilicity might be through determining the optimal polishing time and pressure (weight).

6.3.4. Pre-wear and Post-wear Contact Lens Surface Hydrophilicity

6.3.4.1. Aims, Materials and Method

The aims of this experiment were to assess the surface hydrophilicity of various rigid contact lenses for pre-wear condition and to determine the effect of residual tear film components and wearing (post-wear) on hydrophilicity values. Five contact lenses made from PMMA, Polycon II, Equalens, Boston RXD and Paraperm materials were used with the same diameter and front lens surface radii ($\pm$0.1), and the values of the maximum adherent force for pre- and post-wear (30 minutes of wearing) were measured. The lenses were prepared as described in 4.4.2.1 and the process repeated five times to collect five independent data.

6.3.4.2. Results

The mean and standard deviation of the maximum adherent force for pre- and post-wear rigid contact lenses are illustrated in figure 6.13, showing that there are differences in surface hydrophilicity between the contact lenses for pre and post-wear. An analysis of variance showed there was a significant variation between the values of the different materials for both pre-wear (ANOVA: $F=170.32$, $P<0.00001$) and post-wear contact lenses (ANOVA: $F=266.12$, $P<0.00001$) and the mean value of the measurements for post-wear (387.8 mg) was significantly lower than for pre-wear (410.6 mg). These variations were established by using t tests: PMMA $p<0.001$, Polycon II $p<0.0001$, Equalens $p<0.0001$, Boston RXD $p<0.0001$ and Paraperm $p<0.000001$.

6.3.4.3. Discussion

Guillon et al (1994) measured the wettability of rigid contact lenses in vivo using a tear break up method and stated that 'some patients perform similarly with several materials and others show very large inter-material differences'. The pre-wear rigid

contact lens surfaces attracted a greater water than the post-wear surfaces, therefore, pre-wear rigid contact lens surfaces were found more hydrophilic than the post-wear surfaces (see 6.4). It can be suggested that hydrophilic sites on the contact lens surfaces might be blocked by tear film components. PMMA which had a moderate hydrophilicity was influenced the least by the tear film. The post-wear hydrophilicity value of PMMA was greater than any other material, therefore, PMMA had the highest hydrophilicity after 30 minutes of wear among the tested materials. In contrast, Paraperm lens surface had the highest hydrophilicity, but after wear it had the lowest hydrophilicity apart from Polycon 11, which before and after wear had the lowest hydrophilicity.

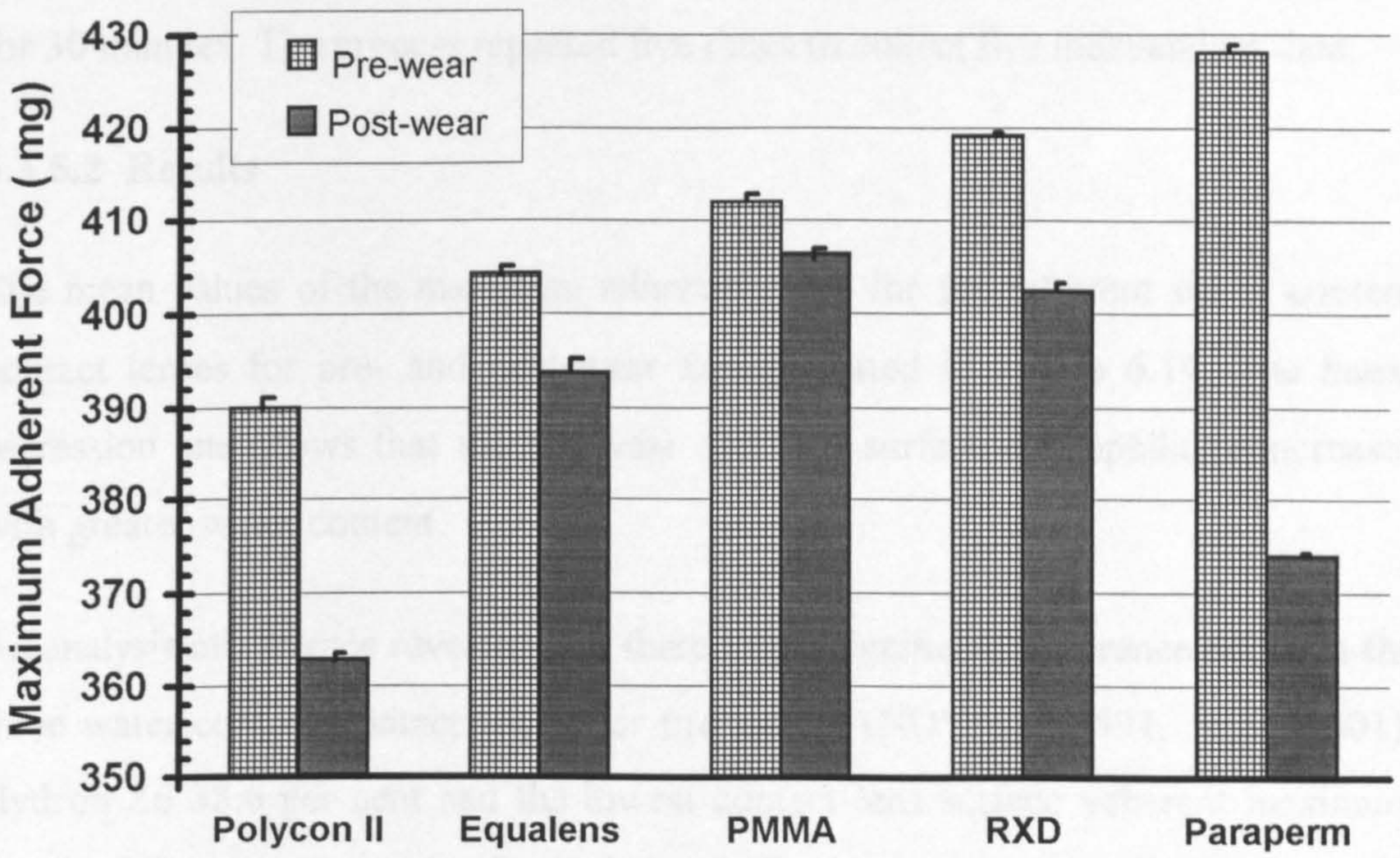


Figure 6.13. The pre- and post-wear adherent maximum force values of different contact lenses.

The influence of the tear film on materials may prompt practitioners to select a contact lens material on the basis of post-wear hydrophilicity, which would make PMMA the first choice and Polycon II the last (see Chapter 7).

6.3. 5. Pre- and Post-wear Soft Contact Lens Surface Hydrophilicity

6.3.5.1. Aims, Materials and Method

The purposes of this experiment, were to determine the influence of water content on the hydrophilicity of soft contact lens surfaces and to investigate the effect of one subject's tear film on different contact lens surfaces. The experiment was carried out at the same time on each day on a male subject. Three contact lenses of low, medium and high-water content (pHEMA Hydron Z6 38 per cent, Wöhlk 55 per cent and Omniflex 70 per cent) were manufactured. Saline (pH=7, γ=82.8 dynes/cm) was used as the liquid and a solid/liquid interface was produced. The ALMF method was then used to measure the maximum adherent force and measurements were carried out for pre-wear lenses and after they had been worn for 30 minutes. The process repeated five times to collect five independent data.

6.3.5.2 Results

The mean values of the maximum adherent force for the different water content contact lenses for pre- and post-wear are illustrated in Figure 6.14. The linear regression line shows that the pre-wear soft lens surface hydrophilicity increases with greater water content.

An analysis of variance revealed that there was a significant difference between the three water content contact lenses for pre-wear (ANOVA: $F=591$, $p<0.00001$). Hydron Z6 38.6 per cent had the lowest contact lens surface adherent maximum force, while there was a significant difference between the values of the low-water content of Hydron Z6 and the medium water content of Wöhlk 55 per cent contact lenses (Bonferonni, t-test, $p<0.0001$) and also disparity between the hydrophilicity of the medium water content of Wöhlk 55 per cent and the high-water content of Omniflex 70 per cent lenses (Bonferonni: t-test, $P<0.0001$).

After wearing the lenses for 30 minutes, the values of the maximum adherent force significantly declined in comparison with the pre-wear values for all three materials (Bonferonni: t-test, $p<0.000001$). ANOVA demonstrated there was a significant difference between the values of post-wear ($F=28.9$, $p<0.001$).

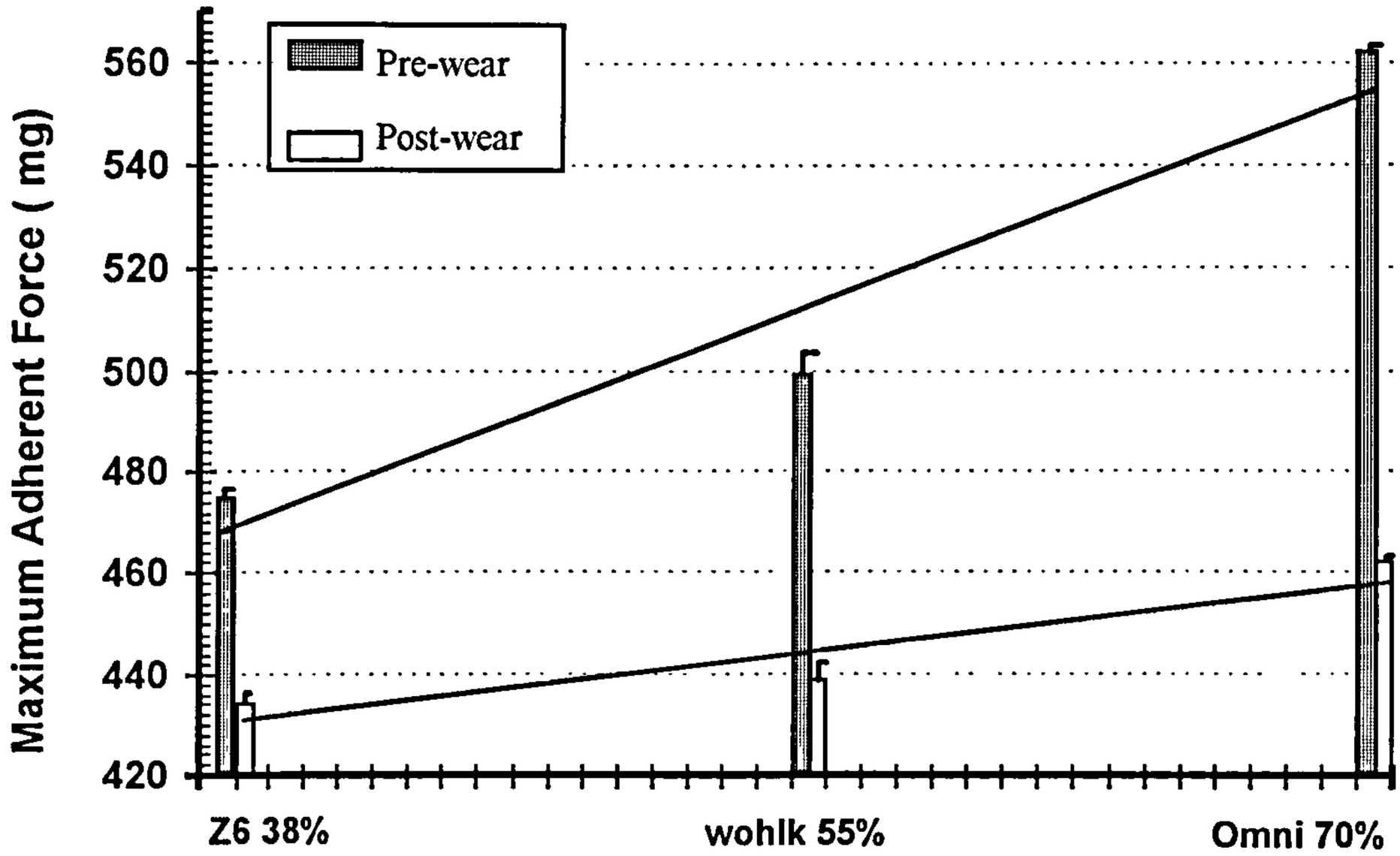


Figure 6.14. Linear regressions for the pre- and post-wear adherent maximum force values for different water content soft contact lenses.

6.3.5.3. Discussion

Water absorption into a polymer depends on a number of factors including hydrophilic sites inside the polymer. Water molecules in the polymers can create a hydrogen bond with water molecules in the liquid outside the polymer (adherent liquid). The greater the water content, the higher the liquid attraction from outside. Linear regression (slope=2.75) revealed a positive correlation between water content and the maximum adherent forces for pre-wear, and after-wear the maximum adherent force values declined significantly. The greater water content contact lenses, lost higher values than the lower water content lenses (slope=0.99). High-water content lenses obviously had greater hydrophilic sites, a number of these sites were blocked by the tear component causing the lens surface to become less hydrophilic due to wearing (see later).

6.4. Hydrophilicity Discussion

Hydrophilicity is a general term that has been used to specify a polymer surface wettability or water absorption into a bulk polymer and swell (Tighe 1989). But contact lens surface hydrophilicity is the ability of a material surface to attract water. The maximum force between water and a contact lens surface was measured by a balance and the method to measure contact lens surface hydrophilicity called adherent liquid maximum force (ALMF) which has been used in this chapter. The values were obtained when the lens surfaces had the highest interaction with the water.

When the front surface of a rigid lens is withdrawn from the liquid, the changes of meniscus shape were clearly visible. The shape can be explained by changes in the surface tension of liquid. The surface energy pulled the surface molecules inside the liquid volume, but the interaction forces between the liquid and contact lens surface resisted which resulted in enhancement in forces until at a level (maximum) that the resistance was broken. This was called maximum force. The hydrophilicity of the contact lens surfaces was found to be dependent on two main factors (excluding external variables such as front lens surface radii): the liquid surface tension and the polymers' hydrophilic sites.

In the experimented samples the γ_L was constant (72.6 dynes/cm). The other factors such as liquid container were constant. The variable factors were the contact lens surface material and polishing time. As explained in Chapter 1 when a covalent bond is formed between two atoms of different electronegativities, the atom with the higher electronegativity attracts the shared electron pair more strongly. Consequently, the electron spends more time around the atom with the higher electronegativity, with this atom acquiring a partial negative charge and the other atom a partial positive charge. The greater the electronegativity difference between the two atoms, the greater the polarity of the bond. An example of such a polar bond is the carboxyl group (C=O) in which the oxygen atom has a higher

electronegativity and therefore takes on a small negative charge. The carbon atom subsequently has a small positive charge which produces forces with a liquid.

In the case water, the oxygen atom has a greater attraction for the electrons, with the oxygen having a relatively negative charge and the hydrogen atom having a relatively positive charge. Since the hydrogen atom has a relatively positive charge, it will be attracted to the oxygen atom (relatively negative) of another molecule, forming a hydrogen bond. This bond is not very strong because it is only a partial charge, but it is very important in surface chemistry and wetting.

The hydrogen bond can be considered electrostatic or ionic in character. The hydrogen is usually attached to an acidic group typically a hydroxyl, carboxyl, amine or amide group. The other group could be basic usually oxygen such as carboxyls, ethers or hydroxyls or nitrogen such as amines and amides. The association of such polar liquid molecules as water, alcohols and hydrofluoric acid results in polar polymers such as nylon, cellulose and proteins because of hydrogen bonding). Only fluorine, nitrogen, oxygen and occasionally chlorine have sufficient electronegativity to form hydrogen bonds.

Varying the length of polishing time up to a maximum of three minutes increased the potential maximum force because possibly increasing the numbers of hydrophilic sites, and further expansion from three minutes to five minutes reduced the hydrophilicity property. It may suggested that, this may caused either by heat damaging the hydrophilic sites on the lens surface or removing the hydrophilic sites and or by penetrating the polishing component into the polymer bulk (Tighe 1997). Hence contact lens manufacturing can, therefore, affect lens surface hydrophilicity (see Chapter 7).

Different contact lens materials have varying surface hydrophilic sites due to the nature of polymerisation ($F=170.32$, $P<0.00001$) and the post-wear results showed even a greater disparity between them ($F=266.12$, $P<0.00001$) but in lower value than the pre-wear (mean of pre-wear 413>385 post-wear). The maximum force results showed a greater differences between the post wear and secondly showed

that for post-wear the hydrophilic sites may be blocked by tear film components resulted in reducing hydrophilicity. It also appears to be logical to assume, therefore, that other factors, such as deposits, could further reduce hydrophilicity, which is being investigated.

Pre-wear soft contact lenses with varying water content gave the maximum force values with increasing water content. But, after being worn for 30 minutes, the hydrophilicities decreased significantly (pre-wear 512.8>445.1 post-wear, F=216, $p<0.04$). The value for the post-wear of the high-water content lens was still greater than for the medium and low-water content lenses. This could imply that the tear film components influence high-water content material more than lower-water content material. One possible the reason for a greater value of soft contact lenses to rigid lenses can explained of the water inside the bulk of soft makes hydrogen bonds with the tested liquid beside of liquid/contact lens material surface ionic bonds (see Chapter 7).

Chapter 7. General Discussion

7.1. Introduction

An ideal contact lens material should have a hydrophilic surface (Refojo 1994), and the more wettable and hydrophilic the lens surface is, the more stable the pre-lens tear film covering it becomes (Holly et al, 1971 and Holly 1973). A stable tear film is important because it affects:

a. the transmission of gases when the contact lens is on the eye;

b. the quality of vision;

c. comfort;

d. deposition.

When a liquid covers a solid surface, the process is known as wetting (Dabezies 1989). A number of definitions have been used to describe contact lens surface wettability that are intrinsically related to the methods of measuring their values (Table 7.1).

Definitions **A contact lens surface will be wettable if:**	**Methods**	**References** (see caption)
It has 0° wetting angle	θ	1
It has low receding wetting angle	θ_R	2
It spreads a liquid on the surface spontaneously	-	3
It produces a long TBUT	TBUT	4
It creates a thick tear film on the surface	Tearscope	5
It produces a good and stable vision	VA	6
It produces comfort	-	7

Table 7.1. Different contact lens surface wettability definitions according to various measurement methods. **1** (Fitzgerald, 1983), **2** (Holly, 1978), **3** (Andrade, 1980; Zisman, 1964), **4-5** (Guillon 1988), **6** (Vaghmaria, 1993) and **7** (Benjamin et al 1984).

The majority of papers (see Chapters 3 and 5) utilised indirect methods to grade the wettability because it was well known that solid-liquid interfacial tension can not be measured directly (Holly, 1983b). Contact lens surface hydrophilicity has been defined as the ability of the surface to attract a liquid, this was measured directly using the ALMF method which determines the force between a liquid and contact lens surface.

When there are no attraction forces between a contact lens surface and a liquid, the phenomenon may be called hydrophobicity, however all the tested contact lens surfaces had attraction forces with the water and hence the contact lens surfaces were found to be hydrophilic (Figure 7.1). An attempt to measure the attraction forces on both soft and hard contact lenses using the DCA system was unsuccessful when the contact lens moved into a liquid and was withdrawn vertically (see 6.2). Madigan et al (1983) and (1986) claimed to have measured the wetting angle of rigid contact lens surfaces when they moved into a liquid (advancing) and withdrawn (receding) vertically. The results were found unreliable because in both advancing and receding conditions the meniscus of the back and front surfaces were influenced by front and back contact lens surface radii such that no resolving method was found (6.2).

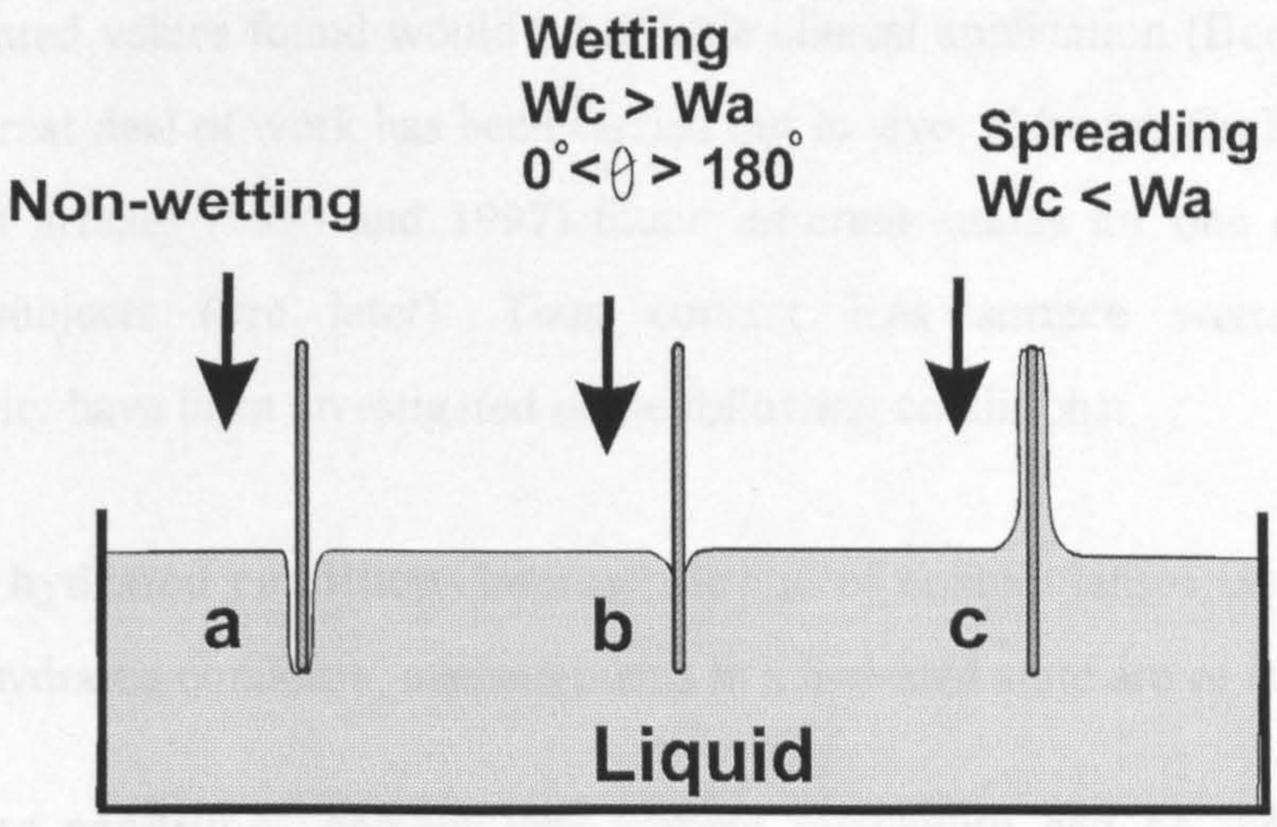


Figure 7.1. Representation of non-wetting and wetting systems (Padday 1978, (See also 1.3.1.2).

There are three main reasons why in vitro measurements have value in assessing contact lens surface wettability:

a. As a quality check of contact lens manufacturing processes, the lens surface may be damaged by heat or be contaminated in such a way that affects the surface wettability and hydrophilicity.

b. Tear film components in vivo can cover damaged or un-wettable surfaces (Holly et al, 1971). The authors stated that 'mucus coating can make practically any material wettable 'even a material with as high a wetting angle as Teflon'.

c. It has been documented that tear film break-up can be influenced by tear deficiency, inadequate mucus, a pathological lipid layer, excessively fast evaporation, pathological blinking reflexes, drugs and hormone imbalance (Marquardt, 1993). In addition, the values in vivo are significantly influenced by lens designs. Thus in vivo measurement of wettability may not be repeatable or universally applicable.

Wetting values in dehydrated and in vivo conditions are not covered in this study because it is obvious that contact lenses would be used in hydrated condition and the dehydrated values found would be of little clinical application (Benjamin et al 1984). A great deal of work has been carried out in vivo, although Guillon et al, in their recent articles (1994 and 1997) found different values for one material on different subjects (see later). Thus contact lens surface wettability and hydrophilicity have been investigated in the following conditions:

1. **Wet or hydrated condition-** because the use of contact lenses in vivo would be in a hydrated condition, measurements in a hydrated state are of interest.

2. **Pre-wear condition-** contact lens surface wettability can be influenced by solutions and therefore, measurements in this state can illustrate the capabilities of wetting agents.

3. **Post-wear condition-** shows the effect of wearing and a tear film on lens surface wettability. The values may be used to evaluate the effect of individual tear film characteristics and wearing period on the contact lens surface wettability.

7.2. Wettability Discussion

In order to study the interaction of materials with liquids, it is necessary to control as many of the variables as possible. The lens surface preparation was deemed important to meet criteria for measuring wettability (Lin et al 1973 and Poster et al 1978). In this study this was partly achieved by standardising contact lens surface preparation and measurement methods. One of the aims of Chapter 4 was to introduce a new method for preparing the lenses in hydrated conditions and to remove the liquid from both soft and rigid contact lenses without contaminating and damaging the prepared surfaces. As contact lenses are hydrated in vivo and absorb a percentage of water, the surface tension method, in which the water molecules are swept from the lens surface using a non-mechanical method, would appear to be the most appropriate. In a controlled study, this method produced the highest repeatability and was, therefore, chosen as the preparation method for this work.

The second aim of Chapter 4 was to show that the equilibrium sessile drop delivery method could be made repeatable through the liquid delivery system, in which the tip of the syringe needle was modified (sharpened and softened). When the syringe needle was made rougher the suspended drop at the tip of the needle was spread over a greater area of the needle body, and thus a rough needle surface produced a greater variability in results. The reduced variability with the pendant drop delivery method showed a greater repeatability (4.2.2).

A comparison study on influencing factors of front lens surface radii (Figures 4.6 , 5.6 and 6.11) demonstrated that the sessile drop method is reliable, but on the other hand does not explain the influence of varying front surface radii. One possible explanation could be that in the sessile drop method the explored diameter

area would be less than 3mm which has 1.5mm distance from the lens surface centre. If the liquid volume increased the interface area diameter will be increased, hence the air/liquid/contact lens surface interface will be moved to the lens peripheral which has a greater slope. At this area the values will be influenced by radii.

The de-ionised distilled water had the hydrogen bonds and γ_L energies (72.6 dynes/cm, pH=6.6). When a sessile drop was delivered on to a contact lens surface, the polar-covalent bonds of H_2O (see 1.2.2, the partial positive charge on hydrogen and a partial negative charge on the oxygen) produced interface bonds with the contact lens surface. If the contact lens surface is ionic, the bonds produce a greater interface area diameter (solid/liquid interface) for the sessile drop. The greater interface area diameter means the liquid spreads more on the contact lens surface, resulting in a lower-wetting angle.

In the sessile drop experiments, the liquid surface tension was constant, contact lenses were hydrated and the surfaces were cleaned and prepared using the same method avoiding any contamination. The experimental variables were restricted to:

a. Differing materials,

b. Differing contact lens manufacturing processes,

c. Solutions and tear films.

The results revealed wetting angles between 59°-64° (S=-35 to -40.7) for the hydrated rigid contact lens materials tested. The majority of the literature recommended low-wetting angle values for contact lenses, apart from when they are influenced by the tear film and become more wettable. However, measuring the pre-wear wettability, using the sessile drop method in the hydrated condition helps to evaluate unworn contact lens wettability that could be influenced by a number of factors as explained earlier.

The application different solutions on contact lens surfaces resulted in a significant enhancement of contact lens wettability ($p<0.001$) due to creation of hydrophilic

sites on the surfaces. The extent of the interaction varied because of the effect of solution contents on contact lens materials. The effect of different solutions on various contact lenses indicated that different contact lens materials have differing ionic charges altering surface wettability. The use of solutions on contact lenses were found to be important because they may increase or reduce deposits and wettability on contact lens surfaces (Benjamin et al 1984). However, Rosenthal et al (1986), stated that the increase in wettability was due to the adsorption of a wetting agent by polymers.

Results from post-wear contact lens surfaces demonstrated increased wettability, probably because of tear film component interactions with the contact lens surface. A similar result was also reported by Kokoski et al (1963) and Benjamin et al (1989). The measurements were carried out after 30 minutes of wearing, for longer wearing times, a greater deposition may appear on the lens surface reducing contact lens surface wettability. But Shirafkan et al (1995b) showed no changes in wettability after 30 minutes of wear up to two hours wearing.

Variation of the sessile drop wetting angle and interface area diameter with evaporation time caused the sessile drop to be in a receding condition. These changes, therefore, have a relationship with contact lens surface wettability. If a contact lens has a low-surface attraction force to adhere liquid, the liquid surface tension coalesces the liquid and reduces the liquid diameter, leading to a high and constant wetting angle. If, however, a contact lens has a large surface attraction force, the diameter of the interface area does not decline, and the wetting angles change during evaporation.

The results of wetting angle and interface area diameter showed a greater attraction by the Aquasil contact lens surface. In general, the greater sessile drop diameter in the receding condition shows that the surface is more wettable. This method can, therefore, determine whether a thick film of liquid will be present on the lens or whether it spreads to form a thin film on a surface, such as Aquasil, for which the sessile drop area diameter was large.

If the wettability is defined as a material property, in that a liquid spreads on a surface, then Aquasil contact lens material is wettable. However, if the thickness of the liquid film on the contact lens is used as a measure of wettability, then Aquasil is a less wettable material than PMMA, because the liquid on the PMMA surface had a lower interface area diameter (a greater liquid thickness) than the Aquasil according to Lin et al (1973, $\frac{2h}{d} = \frac{\tan\theta}{2}$).

Aquasil and Equalens had the greatest sessile drop interface area, which indicates that these materials are able to keep the liquid spread on the surface. The interface area diameter values of the sessile drop showed that the liquid on these lenses did not coalesce, the mean values for these materials were found to be greater than PMMA values. It can be clinically concluded that if tear break up occurs in these materials the dry patches do not advance quickly on Equalens, but PMMA may produce a greater tear film thickness that theoretically produces a greater TBUT. If however tear break up occurs on the PMMA the dry patches advance quickly on the lens surface. Thus the equilibrium, receding and monitoring the wetting angle/diameter of the sessile drop values demonstrated different information about wettability.

When the height of an un-separated adherent liquid increased (Chapter 5), the liquid surface tension acted to minimise the surface interface area for a given volume. If the surface is wettable, the attraction forces would be high and the liquid would be kept spread by the lens surface. However, if the contact lens surface attraction force is low, the liquid will coalesce due to liquid surface tension and the wetting angle would be high. One of the advantages of this method is that the lens surface does not become dehydrated or un-wetted. The results showed differing wetting angles for different contact lens materials, such as the liquid on Equalens ($\theta = 20.50°$, $S = -4.6$) or the liquid coalescing on a surface such as PMMA ($\theta = 55°$, $S = -31.2$). When the hydrophilic sites at the surface increased, due to the influence of wetting solutions the contact lens surface maintained the liquid spread, resulting in a lower wetting angle. When the lens was worn for 30 minutes, the influence of the tear film produced even lower wetting angles between

9.5°-12° (S=-1 to -1.6) for the tested rigid contact lenses. The method thus supports lower interfacial forces for PMMA than Equalens. The clinical consequence of this is: if tear breaking occurs on Equalens, the thickness of broken tear film would be stable or increased which could means that the lens surface is damaged or contaminated. If however the broken tear film thickness decreases it could means that the lens surface is not damaged, but the problem caused by tear film quality.

7.3. Contact Lens Surface Hydrophilicity Discussion

a. Rigid contact lenses: In Chapter 6, the adherent liquid/maximum force method was introduced to measure interfacial forces between liquid and the contact lens front surface directly, known as lens surface hydrophilicity. Hence when the wetting angle was measured, the distribution of liquid on the surface is measured. Hence the results of this study indicate that the surface wettability and hydrophilicity were two different surface properties. The results revealed a difference in the attractive forces between liquid and both the soft and rigid contact lens surfaces.

Surface hydrophilicty was also found to be different when the contact lenses were polished for one, three and five minutes. The results revealed that polishing time can increase contact lens surface hydrophilicity and over-polishing can lead the hydrophilic sites at the surface being blocked and reducing hydrophilicity. These results depend on many factors including the material's rigidity (Meszaros 1986). When these lenses were over polished the hydrophilicity decreased due to heat produced at the surface or the polishing component penetrated into the bulk polymer (Tighe 1997). This provides a possible explanation as to why there have been some conflicting results on the asperity/wettability issue (see 3.9.8).

The post-wear results revealed that, in general, contact lens surface hydrophilicity declines with wearing and it is possible to suggest that the tear film components may block the lens surface hydrophilic sites. PMMA surface hydrophilicity was influenced less than Paraperm by wearing time, even though the pre-wear surface

hydrophilicity of Paraperm was greater than PMMA (see Figure 6.13). In this case it was found that for 30 minutes wearing, PMMA had a greater surface hydrophilicity than Paraperm.

b. Soft contact lenses: The surface wettability of soft contact lenses using un-separated adherent liquid laser method for pre-wear was significantly higher than the mean of rigid contact lenses ($p<0.00001$). The low-water content soft lenses had a greater tendency to keep the liquid spread over the surface, for the pre-wear situation. After wear, the wetting angle values decreased significantly. A similar result was also reported recently by Guillon et al (1997).

The results of the adherent liquid/maximum force revealed that soft contact lenses with a higher water-content have a greater surface hydrophilicity due to an increase in hydrophilic sites. The results (Figure 6.14, Table 5.1) also showed that high Dk materials have a greater surface hydrophilicities than the low Dk polymers. Holly (1979) suggested the changes in hydrophilicities were due to the segmental mobility of hydrophilic-hydrophobic transition of the surface polymeric chains. Despite a decrease in surface hydrophilicity with wearing time, the surface hydrophilicity of the high-water content lens was higher than low-water content. This change could be due to the deposition of the tear film component on the lens surface and also into the high water content polymers (Tighe 1994).

7.4. Wettability and Surface Hydrophilicity General Discussion

Throughout the work described in this thesis, wetting angles were taken for the equilibrium and receding conditions. The use of each method resulted in a value that related to a specific wettability definition. In contact lens practice, a lens surface is required to maintain a stable tear film doing the normal inter-blink period. A combination of the adherent liquid/maximum force with sessile drop wetting angle and adherent liquid/wetting angle can help to determine the requirement of wettability in the contact lens industry and also in practice. An example is shown in Table 7.2. The sessile drop wetting angle on pre-wear PMMA was measured at 63.7° which was greater than the Equalens wetting angle (59°).

After wear the materials demonstrated an equal surface wettability (11°-13°). On the basis of the post-wear values, it can be concluded that when worn there is no clinical difference between these two lenses.

Materials →	PMMA		Equalens	
Wettability methods ↓	Pre-wear	Post-wear	Pre-wear	Post-wear
Sessile drop	63.7°	11°-13°	59°	11°-13°
Adherent liquid/wetting angle	55°	12°	20.5°	9.5°
Adherent liquid/maximum force	412mg	407mg	404mg	393mg

Table 7.2. The wettability values of PMMA and Equalens when measured by different methods of sessile drop, adherent liquid/wetting angle and adherent liquid/maximum force (4.3.1, 4.3.2, 5.2.2 and 6.3.4, see Table 5.2).

The adherent liquid/wetting angle revealed a difference between pre-wear PMMA (55.0°) and Equalens wettability (20.5°). The post-wear values demonstrated an increase in surface wettability and a reduction in the disparity between their values (12.0°, 9.5°).

The values of the adherent liquid/maximum force for pre-wear showed different, surface hydrophilicity between PMMA (412mg) and Equalens (404mg), and when worn, both values decreased (404mg, 393mg). The results suggested that hydrophilic sites on the Equalens had greater blockage than the PMMA with the tear film component. It can be concluded that the PMMA surface has a greater resistance to tear film component blocking the hydrophilic sites than the Equalens.

Results obtained indicate that Equalens has a greater surface wettability than PMMA, and on the basis of surface hydrophilicity values, PMMA has a greater hydrophilicity surface than Equalens. Therefore, the contact lens wettability and surface hydrophilicity defined in this thesis are two different properties. On the basis of this discussion the selection of contact lens material would be in the hands

of practitioners to select the lens either on wettability or surface hydrophilicity values. If the lens is selected on the basis of surface hydrophilicity, a material that influenced less by tear film such as PMMA would be the first choice among the possible materials which some still believe is superior to RGP lenses in some cases, but the long term effects on the corneal epithelium needs to be considered as pointed out by Stevenson (1993).

In developing contact lens materials a difference between these two properties needs to be understood and considered by the polymer designers, so that they informing the practitioners about materials. Tear composition changes with the ageing, the different materials may be appropriate with age changing.

Chapter 8. Conclusions

8.1. General Conclusion

A series of techniques has been developed to determine the wettability and surface hydrophilicity of both rigid and soft contact lenses:

a. Sessile drop/wetting angle method.

b. Sessile drop, monitoring the receding wetting angle/interface area diameter.

c. Un-separated adherent liquid/laser method (UALLM).

d. Adherent liquid/maximum force method (ALMFM).

The first three methods were indirect techniques used to measure the contact lens surface wettability. Knowing the wetting angle is not enough to define the wettability in scientific terms (Fatt (1984). However, the use of the ALMF method is a possible way to measure contact lens surface hydrophilicity directly. The outcome of this research is that the results of a variety of tests help in the understanding of biocompatibility in relation to contact lens surfaces. No single test can fully describe the surface properties of contact lens surface materials, but it is proposed that information from a series of tests provides the most useful clinical description.

The conclusions of this research are as follows:

I. The un-separated adherent liquid laser method enabled one to measure rigid and soft contact lens surface wettability in a hydrated condition. A significant disparity between pre-wear values and no significant difference between the post-wear results, demonstrated that tear film has a very great effect on contact lens wettability. The method was reliable and easy to use both for rigid and soft contact lens surfaces.

II. The distributions of sessile drop at equilibrium and receding conditions were investigated when liquid coalesced on different contact lens material surfaces. There was a significant disparity between the wettability values for different contact lens materials. Contact lens materials such as Equalens and Paraperm had a wettable surface, because of a greater interface area diameter and a low wetting angle. A similar result was also obtained using un-separated adherent liquid laser method. The results showed that these materials were able to keep the liquid spread over the surfaces (not coalescing), but the liquid on PMMA was coalesced. It thus can be concluded that if liquid or tear film breaks on the PMMA, the dry area will be expanded quicker than those on Equalens and Paraperm lenses.

III. Because PMMA surface hydrophilicity was less influenced by tear film than the other contact lens materials, it can be concluded that the PMMA surface is more acceptable in vivo than the others.

IV. Wetting solutions and tear films affect contact lenses, leading to liquid spread on the surfaces and preventing the liquid from coalescing, which means the surface was made more wettable.

V. In general polishing the contact lens surfaces increased surface hydrophilicity, but over polishing decreased these values.

VI. A high- water content soft contact lens had the greater surface hydrophilicity than the low- water content materials, but high- water content contact lens surfaces were influenced more by tear film components, so the difference between high and low- water content contact lenses decreased with wearing time. The surface hydrophilicity values could provide a base line by contact lens manufacturers to help practitioners.

8.2. Suggestions for Further Research

The work described in this thesis has highlighted a number of areas with potential for future research. A brief resum'e of these areas follows.

1. The wettability and surface hydrophilicity of a contact lens could be investigated when different artificial tears on a standard flat material, interfere with different contact lens surfaces (Figure 8.1). These may help one to evaluate different tear compositions with contact lens surfaces

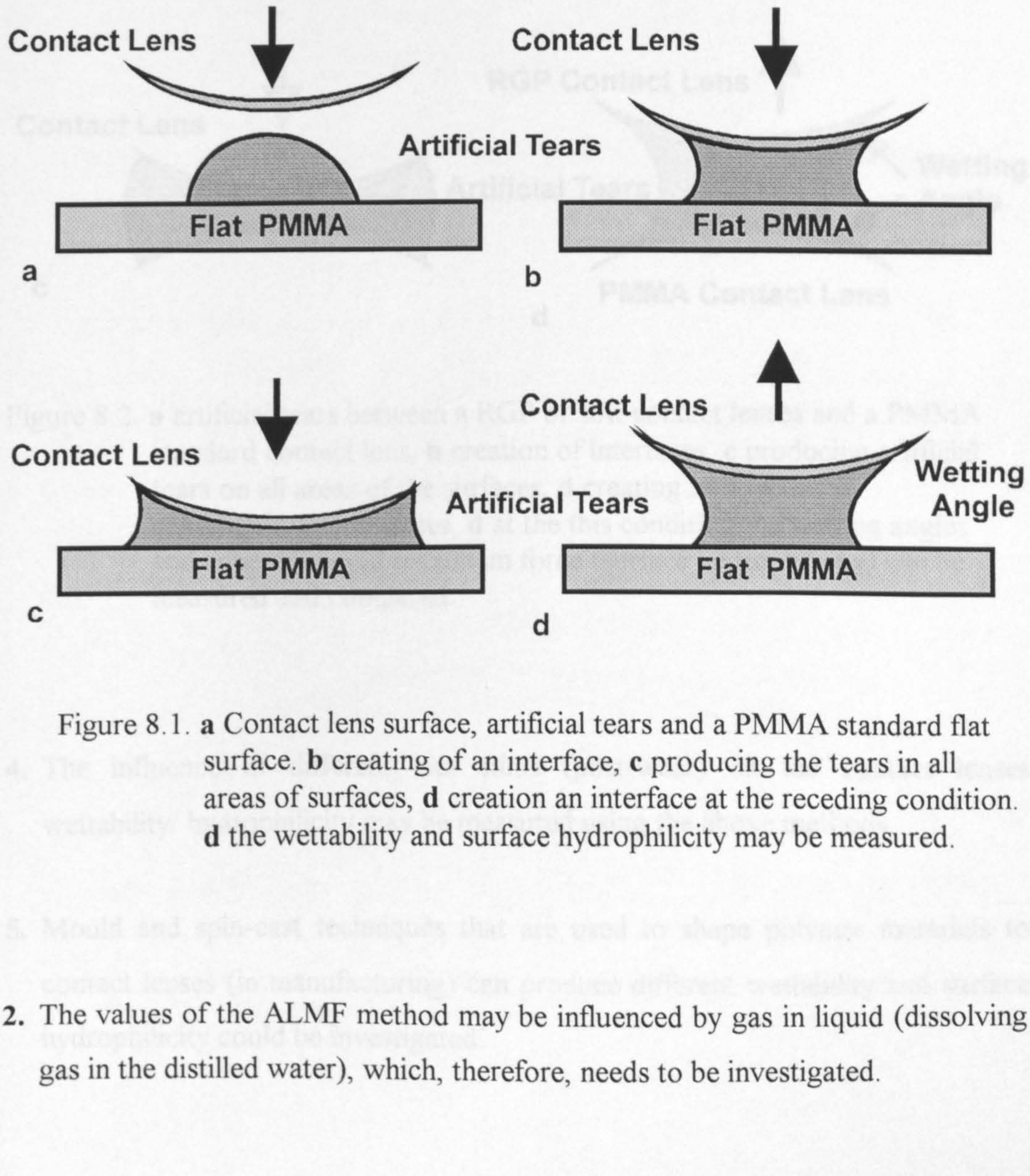


Figure 8.1. **a** Contact lens surface, artificial tears and a PMMA standard flat surface. **b** creating of an interface, **c** producing the tears in all areas of surfaces, **d** creation an interface at the receding condition. **d** the wettability and surface hydrophilicity may be measured.

2. The values of the ALMF method may be influenced by gas in liquid (dissolving gas in the distilled water), which, therefore, needs to be investigated.

3. The wetting angle of two contact lens surfaces could be compared when the adherent artificial tears are created between the two contact lens surfaces (Figure 8.2).

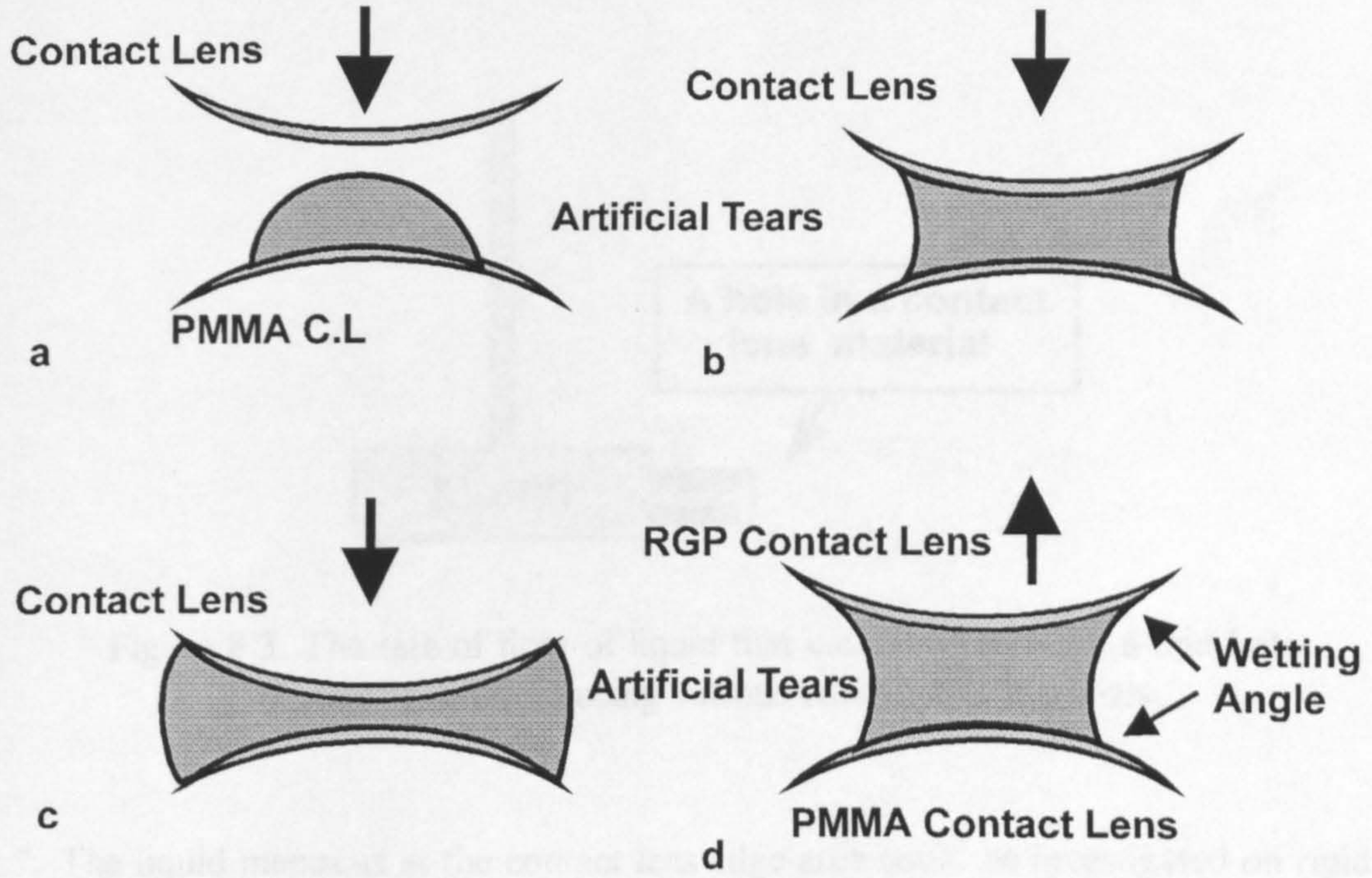


Figure 8.2. **a** artificial tears between a RGP or soft contact lenses and a PMMA standard contact lens, **b** creation of interfaces, **c** producing artificial tears on all areas of the surfaces, **d** creating two receding solid/liquid/air interfaces, **d** at the this condition the wetting angles and adherent liquid maximum force (surface hydrophilicity) can be measured and compared.

4. The influence of different tear films (post-wear) on the contact lenses wettability/ hydrophilicity may be measured using the above methods.

5. Mould and spin-cast techniques that are used to shape polymer materials to contact lenses (in manufacturing) can produce different wettability and surface hydrophilicity could be investigated.

6. The rate of flow of liquid across different contact lens materials can be measured by making a hole in a material and measuring the rate of liquid that flows through it. This work could be extended when a liquid passing through a gap between two contact lenses. This can help to assess frictional forces caused by surface effects, and demonstrating the changes of the hydrogen bonding between molecules of liquid and a polymer surface (Figure 8.3).

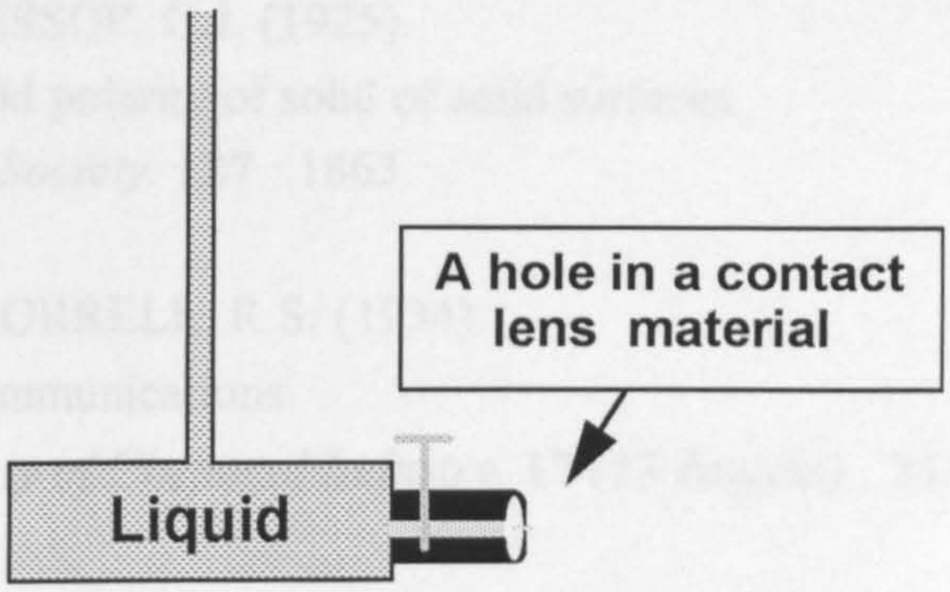


Figure 8.3. The rate of flow of liquid that can flows through a thin hole may be different using various contact lens materials.

7. The liquid meniscus at the contact lens edge area could be investigated on rigid and a model eye (Figure 8.4). The influence of lens design on the tear film meniscus (pump efficiency) associated with plus and minus power rigid contact lenses may be also investigated on single cut, lenticular and minus-carrier designs on different materials.

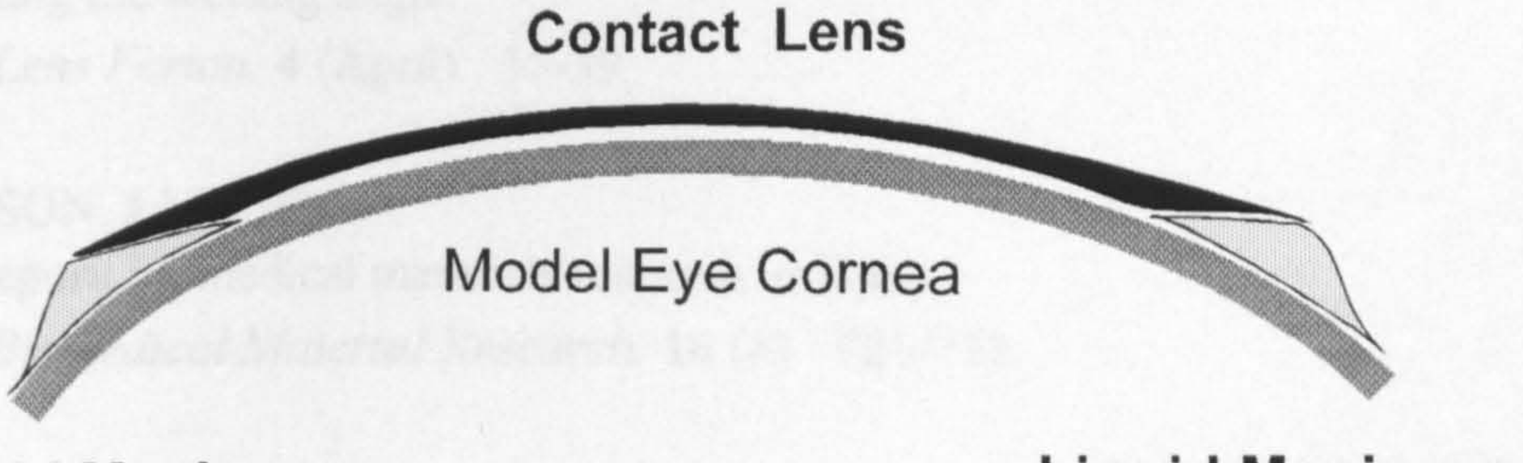


Figure 8.4. The liquids at peripheral area of contact lenses produce meniscus that may be varied using different materials on the a PMMA model eye.

REFERENCES

ABLETT, R. (1923).
The angle of contact.
Philosophical Magazine. **46** : 244-257.

ADAM, N.K. (1941).
The physics and chemistry of surfaces. University Press, Oxford London : 182

ADAM, N.K and JESSOP, G.J. (1925).
Angles of contact and polarity of solid of solid surfaces.
Journal. Chemical. Society. **127** : 1863.

ADAM, N.K and MORRELL, R.S. (1934).
Transactions and communications.
Journal of the Society of Chemical Industry. **17** (53 August) : 234-261.

ADAMSON, A.W. (1982).
Physical chemistry of surfaces. 4th edition. Wiley, and Sons, New York.

ALLARY, J.C. MAPSTONE, V. GUILLON, J.P and GUILLON, M. (1989).
Rigid gas permeable lens surface evaluation.
Transaction of the British Contact Lens Association Annual Clinical Conference, Birmingham : 18-19.

AMBWANI, D.S and TOMLINSON, F.J. (1979).
Surface and Colloid Science. London Plenum Press, **2** : 93-119.

ANAN, N. (1979).
Determining the wetting angle.
Contact Lens Forum. **4** (April) : 35-39.

ANDERSON, J.M. (1982).
Special report; biomedical materials research in Japan.
Journal Biomedical Material Research. **16** (5) : 721-733.

ANDERSON, D.M and STROM, P. (1991).
Polymerised lyotropic liquid crystals as contract lens materials.
Physica. **176** (1) : 151-167.

ANDRADE, J.D. (1980).
Surface analysis of materials for medical devices and diagnostic products.
Medical Device & Diagnostic Industry. **2** (6. June) : 22-33.

ANDRADE, J.D. KING, D.N and GREGONIS, D.E.(1976).
Probing the hydrogel/water interface.
Hydrogels for Medical and Related Applications. **16** : 206-224.

ANDRADE, J.D. KING, D.N. GREGONIS, D.E and COLEMAN, D.L. (1979).
Surface characterisation of poly hydroxyethyl methacrylate and related polymers. I contact angle method in water.
Journal of polymer Science. **66** : 313-336.

ANDRADE, J.D. BOWMAN, L and SMITH, L.M. (1982).
Contact angle analysis of hydrated contact lenses.
Biomedical Polymers and Procedures. International Symposium of Contact Lenses and Artificial Eyes. July **:** 12-15.

ANDRASKO, G and SCHOESSLER, J.P. (1980).
The effect of humidity on the dehydration of soft contact lenses on the eye.
International Contact Lens Clinic. September : 30-32.

ANDRASKO, G and HERSKOWITZ, R. (1988).
Fitting and patient management with the Boston Equalens.
Contact Lens Symposium. **3** (4) : 53-58.

AQUAVELLA. J.V. (1976).
New aspects of contact lenses in Ophthalmology.
Adv Ophthal. **32** : 2-34.

ATKINS, P.W. (1994).
Physical Chemistry. Fifth Edition. Oxford University Press, Oxford, Melbourne, Tokyo.

AVEYARD, R and HAYDON, D.A. (1973).
An introduction to the principles of surface chemistry. Cambridge University Press.

BAGNALL, R.D. ANNIS, J.A.D and SHERLIKER, S.J. (1980).
Adsorption of plasma proteins on hydrophobic surfaces. IV. Contact angle studies on implanted polymers.
Journal of Biomedical Materials Research. **14** : 1-10.

BAILEY, N. J. (1960).
Contact lenses must be kept wet.
Journal of the American Optometric Association. **31** (July) : 985.

BAKER, D and TIGHE, B.J. (1977).
Polymers in contact lens applications (V III). The problem of biocompatibility.
Contact Lens Journal : 3-14.

BARNES HINT (1982).
GP-II T M (Parafocon B) Contact lens for daily wear,
Hydrocurve Package Insert. October.

BARR, J.T. (1981).
Silicone lenses are elastic and permeable.
Review Optometry, **118** : 59-62.

BARR, J.T. (1988).
The Fluoroperm RGP materials.
Contact Lens Spectrum. **3** (11) : 68-75.

BARR, J.T. and HETTLER, D. H. (1984).
Effects of emulsion cleaners on silicone lenses.
Contact Lens Forum. **9** (11 November) : 45-49.

BARR, J.T and BAILEY, N.J. (1989).
Disposable contact lenses.
Contact Lens Spectrum. **4** (1) : 39-47.

BARTELL, F.E and ZUIDEMA, H.H. (1936).
Wetting characteristics of solids of low surface tension such as talc, waxes and resins.
Journal of American Chemical Society. **58** (August): 1449-1454.

BARTELL, F.E and BJORKLAND, C.W. (1952).
Hysteresis of contact angles. A study of interfacial contact angle in the mercury benzene water system.
Journal of Physical Chemistry. **56** : 453-457.

BARTELL, F.E and SHEPARD, J.W. (1953).
Surface roughness as related to hysteresis of contact angles.
Journal Phys-Chemical. **57** : 211-216.

BASZKIN, A and SARAGA, L.T. (1971).
Chemical structures of surface-oxidized and crafted polyethylene: Adsorption and Wetting studies.
Journal of Polymer Science. **C** (34) : 243-252.

BASZKIN, A. BOISSONNADE, M.M. PROUST, J.E and TCHALIOVSKA, S. (1978).
Silicone grafted with poly (vinyl pyrrolidone) for contact lenses. Surface properties and stability of thin tear film.
Journal of Bioengineering. **2** (6) : 527-538.

BASZKIN, A. LYMAN, J and MELTZER, T.H. (1979).
Theoretical considerations of bubble-point. Solid/liquid/ wetting interaction.
Pharmaceutical technology international. (January) : 23-25.

BENEDETTO, D.A. SHAH, D.D and KAUFMAN, H.E. (1975).
Instilled fluid dynamics and surface chemistry of polymers in the pre ocular tear film.
Investigative Ophthalmology and Visual Science. **14** : 887-902.

BENEDETTO, D.A. SHAH, D.D and KAUFMAN, H.E. (1978).
The dynamic film thickness of cushioning agent on contact lens materials.
Annuals of Ophthalmology. **10** (4) : 437.

BENJAMIN, W.J (1987).
Care regime and initial wetting of Silicone / acrylate surfaces in vivo.
Transaction, The Journal of the British Contact Lens Association Conference. **4** : 55-56.

BENJAMIN, W.J. (1992a).
The patient's first impressions of high-Dk RGP lenses.
International Contact Lens Clinic. **19** (Nov / Dec) : 273-275.

BENJAMIN, W.J. (1992b).
In eye wettability of new rigid gas permeable lenses: worst-case scenario.
The Journal of the British Contact Lens Association. **15** (4) : 139-142.

BENJAMIN, W.J and GHORMLEY, N.R. (1983).
Wettability of silicone and silicone-acrylate contact lens materials.
International Contact Lens Clinic. **10** (2) : 94-99.

BENJAMIN, W.J. PICCOLO, G and TOUBIARA, H. (1984a).
Wettability a blink by blink account.
International Contact Lens Clinic. **11** (8) : 492 497.

BENJAMIN, W.J and SIMONS, M.H. (1984b).
Contact angle update: Care regimens and their effect on a rigid silicon-acrylate surface.
International Contact Lens Clinic. **11** (18) : 500-507.

BENJAMIN, W.J and HILL, R.H. (1986).
Tear osmotic differences across the ocular surface.
Archives Clinical Experimental Ophthalmology. **224** : 583-586.

BENJAMIN, W.J. YEAGER, M.Y. DESAI, N.N and CARMICHAEL C.A. (1986).
In-vivo analysis of contact angles.
International Eyecare. **2** (3) : 163-170.

BENJAMIN, W.J and BOURASSA, S. (1989).
Comparison of two contact lens storage solution preservatives with respect to in eye wetting of rigid oxygen-permeable lens surface and related factors.
International Contact Lens Clinic. **16** (9, 10) : 273-281.

BENNETT, E.S. (1990).
How important are lens oxygen ratings? They are one of many performance factors.
Cornea. **9** (Suppl 1) : 54-57.

BENNETT, S. ELLEFSON, B.S and TAYLOR, W.N. (1938).
Surface properties of fused salts and glasses: (I) Sessile drop methods for determining surface tension and density of viscous liquids at high temperatures.
Journal of American Ceram Society. **21** :193-205.

BENNETT, E.S. TOMLINSON, A. MIROWITZ, M.C. MOSER, L. NELSON, J.M and HENRY, V.M. (1988).
Comparison of overnight swelling and lens performance in RGP extended wear.
International Contact Lens Clinic. **14** (2) : 94-100.

BERMAN, M.R and DELAWARE, D. (1963).
Some comments on the Erb method of contact lens wetting.
American Journal of Optometry & Physiological Optics. **40** : 148-149.

BIER, N and LOWTHER, G.E. (1980).
Contact Lens Correction. London and Boston: Butterworths.

BIKERMAN, J.J. (1970).
Physical surfaces. New York. Academic Press.

BILLMEYER, J.R. (1971).
Textbook of polymer science. Second Edition. **76** : 4055. New York Wiley.

BLAKE, T.D. (1968).
The Contact angle and two-phase flow. PhD Thesis. Department of Physical Chemistry. University of Bristol UK.

BLUE, H.D. (1966).
Method of producing permanent wettability on plastic contact lenses.
Journal of the American Optometric Association. **37** : 678-681.

BLUE, H.D. (1967).
Contact lens coating.
Journal American Optometric Association. **38** (3) : 195-199.

BONTEMPO, A.R and RAPP, J. (1994).
Lipid deposition on hydrophilic and rigid gas permeable contact lenses.
Journal of the British Contact Lens Association. **20** (4) : 242-244.

BOURASSA, S and BENJAMIN, W. (1987).
In-eye wettability: The in-vivo "RSCA" technique.
American Journal of Optometry Physiological Optics. **64** : 108

BOURASSA, S and BENJAMIN, W.J. (1989).
Rigid lens surface wettability: The first day is the worth day.
Optometry and Vision Science. **67** (10) : 48.

BOURASSA, S and BENJAMIN, W.J. (1989).
Clinical findings correlated with contact angles on rigid gas permeable contact lens surface in-vivo.
Journal of the American Optometric Association. **60** (8) : 584-590.

BOURASSA, S and BENJAMIN, W.J. (1992).
RGP wettability: The first day could be the worst day!
International Contact Lens Clinic. **19** (February) : 25-34.

BRAUDO, E.E. TOLSTOGUZOV, V.B and NIKITINA, E.A (1974).
Investigation of the wettability of gelatin gels.
Journal of Colloid. **36** : 191-195.

BRENNAN, N.A. (1983).
A simple instrument for measuring the water content of hydrogel lenses.
International Contact Lens Clinic. 10 (6) : 357-362.

BRENNAN, N.A. EFRON, N and HOLDEN, B.A. (1986).
Oxygen permeability of hard gas permeable contact lens materials.
Clinical Experimental Optometry. **59** (3) : 82-89.

BRIGHT, A.M and TIGHE, B.J. (1993).
The Composition and interfacial properties of tears, tear substitutes and tear models.
Journal of The British Contact Lens Association. **16** (2) : 57-66.

BROPHY, J.E and ZISMAN, W.A. (1951).
Annals New York Academy Sciences. **53** : 836-861.

BROWN, J. (1992).
A year with Aquasil.
Contact Lens Journal, **20** (4) : 20-22.

BRUUN, H.H and JULSRUD, E. (1965).
A study of the contact angles of water on solid surfaces of rosin acids of the abietic and pimaric series and technical rosin acids.
Proceedings of 2nd Scandinavian Symposium on Surface activity. Surface Chemistry. 54-70.

BURLEY, R and KENNEDY, B.S. (1976).
A study of the dynamic wetting behaviour of poly-ester tapes.
British Polymer Journal. **8** : 140-143.

BUSH, J.F. HUFF, J.W and MACKEEN, D.L. (1988).
Laser assisted contact angle optics measurements.
American Journal of Optometry and Physiological Optics. **65** (9) : 722-728.

CAFFERY, B. (1989).
The influence of diet on the tear film.
Transaction of Journal of the British Contact Lens Association Annual Conference. Birmingham (6) : 14-17.

CAIN, J.B. FRANCIS, R.D. VENTER, R.D and NEUMANN, A.W. (1982).
Dynamic contact angles on smooth and rough surfaces.
Journal of Colloid and Interface Science. **94** (1) : 123-130.

CAPPELLI, A. (1979).
Determining the wetting angle.
Contact Lens Forum. **4** : 35-39.

CAPPELLI, A. (1982).
The manufacture of contact lenses from cellulose Acetate Butyrate.
Contact Lens Journal. **10** (10) : 2-4.

CAROLINE, P.J. (1988).
Soft Contact Lenses (daily wear).
Annual Contact Lens Association Ophthalmologist. Las Vegas.

CARROLL, A. GUILLON, M. FONN, D. GUILLON, J.P and LEAHY, C.D. (1994).
Effect of polymeric composition on the in vivo wettability of RGP contact lenses
Investigative Ophthalmology and Visual Science. **35** : 1778.

CASSIE, A.B.D and BAXTER, S. (1944).
Wettability of porous surfaces.
Transaction Faraday Society. **40** : 546-551.

CASSIE, A.B.D. (1948).
Contact angle.
Faraday Society. **3** (11): 11.

CASTILLO, E.J. BROWN, C., KOENIG, J.L. and ANDERSON, J. (1983).
Report to CAPRI and national patent development corporation (February).

CASTILLO, E.J. KOENIG, J.L and ANDERSON, J.M (1984).
Surface analysis of biomedical polymers by attenuated total reflectance-Fourier transform infra-red.
Biomaterials. **5** (4) : 186-193.

CKARK, S.A. BENNETT, E.S. HENRY A.V and CAROLINE, P.J. (1993).
The effect of contact lens cleaners on lens parameters and surface quality of the Novalens.
Journal of the American Optometric Association. **64** : 333.

CLOMPUS, R. (1987).
How to polish and modify rigid lenses.
Review Optometry. **124** (4) : 106-113.

COOKE, S.P. (1991).
Variation of contact lens wetting angle with menstrual cycle. BSc Project, Department of Optometry and Visual Science, City University.

COOMBS, W.F. (1982).
Spin casting of HEMA lenses.
Contact Lens Journal. **10** (10) : 25-29.

CORDREY, P. (1983).
What the papers say.
Journal of the British Contact Lens Association 7 (1) : 48-51.

DABEZIES, O.H. NAUGLE, T and REICH, L. (1966).
Evaluation of a stronger concentration of preservative (benzalkonium chloride) in contact lens soaking solution.
Eye, Ear, Nose and Throat Monthly. **45** : 78-84.

DABEZIES, O.H.J. CAVANAGH, D. FARRIS, R.L and LEMP, M.A (1989).
Contact lenses.
Grune and Stratton. Inc. London.

DANN, J.R. (1970).
Forces involved in the adhesive process. 1 Critical surface tensions of polymeric solids as determined with polar lipids.
Journal of Colloid and Interface Science. **32** (2) : 302-320.

DAVIDSON, T and LEI, G. (1971).
Preparation of polymer film for contact angle measurement.
British Polymer Science Journal. **9** : 569-573.

DAVIS, L.J. (1994).
Rigid gas permeable extended wear (RGPEW) for the postoperative patient: a review and clinical observations.
Journal of the American Optometric Association. **65** (3) : 179-186.

DEL-GIUDICE G.R.M. (1936).
The bubble machine for flotation testing.
Engineering & Mining, Journal. **137** (6) : 291-294.

DERJAGUIN, B.V. CHURAEV, N.V and MULLER, V.M. (1987).
Surface forces, Wetting film. Consultants Bureau (Plenum press). New York. : 327-367.

DENT, M. (1986).
Scanning the contact lens surface. A comparison of results between lathes requiring operator skills and those with sophisticated control systems and proven mechanical characteristics.
Contact Lens Spectrum. **1** (12 December) : 29-34.

DESCARTES (1636).
See MANDELL (1953) and ENOCH (1956).

DEXTER, S.C. (1979).
Influence of substratum critical surface tension on bacterial adhesion in-situ studies.
Journal of Colloid and Interface Science. **70** (2) : 346-354.

DOANE, M.G. (1980).
Interaction of eyelids and tears in corneal wetting and the dynamics of the normal human eyeblink.
American Journal of Ophthalmology. April : 507-516.

DOANE M.G. (1988).
In vivo measurement of contact lens wetting.
Transaction the British Contact Lens Association International Conference. 110-111.

DOANE, M.G. (1989a).
An instrument for in vivo tear film interferometry.
Optometry and Vision Science. **66** (6) : 383-388.

DOANE, M.G. (1989b).
Interferometric measurement of in vivo contact lens wetting.
Proceeding of the SPRE The International Society for Optical Engineering. **1161** : 320-326.

DOELL, G.B. PALOMBI, D.L. EGAN, D.J and HUFF, J.W. (1986).
Contact lens surface changes after exposure to surfactant and abrasive cleaning procedures.
American Journal of Optometry & Physiological Optics. **63** (6) : 399-402.

DOHLMAN, C.H. FRIEND, J. KALEVAR, V. YAGODA, D and BALAZS, E. (1976).
The glycoprotein (mucus) content of tear from normals and dry eye patients.
Experimental Eye Research. **22** : 359-365.

DOUTHWAITE, W. (1992).
Tear break-up time and the effect of lifting the eyelid during its measurement.
Clinical and Experimental Optometry. **75** (6) : 231-235.

DUBOW, B. (1992).
Personal experience with Fluoroperm.
Contact lens Journal. **20** (6) : 20-21.

DUSSAN, V.E.B. (1976).
The moving contact line: the slip boundary condition.
Journal of Fluid Mechanics. **77** : 665-84.

DUSSAN, V.E.B. (1976b).
On the difference between a bounding surface and a material surface.
Journal of Fluid Mechanics. **75** : 609-623.

DUSSAN, V.E.B. (1979).
On the spreading of liquids on solid surfaces: static and dynamic contact lines.
Annual Review of Fluid Mechanics. Edited by Dyke, M.V. Wehausen, J.V. Lumley, J.L. **11** : 371-400.

DZIABO, A.J. HALL, M. KIRAL, R.M and RICH, W.J. (1987).
Preservative effect on the wettability of rigid gas-permeable lenses.
International Contact Lens Clinic. **14** (2) : 62-67.

EFRON, N. YOUNG, G and BRENNAN, N.A. (1989).
Ocular surface temperature.
Current Eye Research. **8** (9) : 901-906.

EGGINK, F.A and PINCKERS, A.J. (1988).
Problems with siloxanyl-alkyl-methacrylate and fluro-silico-acrylate contact lens materials.
Contactologica. **10 :** 169-171.

EICK, J.D. GOOD, R.J and NEUMANN, A.W. (1975).
Thermodynamics of contact angles II rough solid surface.
Journal of Colloid Interface Science. **53** (2) : 235-248.

ELLIOTT, G.E.P. (1962).
Some studies of contact angles. PhD Thesis. Department of Chemistry. University of Southampton.

ELLIOTT, G.E.P and RIDDIFORD, A.C. (1964).
Contact angles.
Recent Progress Surface Science. **2** (11) : 111-128.

ELLISON, A.H and ZISMAN W.A. (1954a).
Wettability studies of Nylon, Polyethylene terephthalate and Polystyrene.
Surface Chemistry. **58** : 503-506.

ELLISON, A.H and ZISMAN, W.A. (1954b).
Wettability of halogenated organic solid surfaces.
Journal of Physical Chemistry. **58** : 260-265.

ENOCH, J.M. (1956).
Descartes' contact lens.
American Journal of Optometry. **33** (2) : 77-85.

ERIKSON, S. (1984).
A look at the lens surface and how wearing affects it.
Journal of the British Contact lens Association. 7 (4) : 204-206.

ERIKSEN, S.P. and OLSON, A.P. (1982).
Letters to the editor.
Optometry Monthly. (December) : 691-692.

ESPY, J.W. (1978).
A new gas permeable hard contact lens.
Annals of Ophthalmology. June : 761-765.

EWBANK, A. (1992).
Making an informed choice.
Optician. **204** (5363) : 25-29.

FAKES, D.W. (1986).
Surface characterisation of contact lens materials. Ph.D., Thesis. Faculty of Medicine, Department of Pharmacy, King's College, University of London.

FAKES, D.W. NEWTON, J.M. WATTS J.F and EDGELL. M.J. (1987).
Surface modification of a contact lens co-polymer by plasma-discharge treatments.
Surface and Interface Analysis. **10** (8) : 416-423.

FARNARIERE, C. CAPO, C. BALLOY, V. BENOLIEL, A.M and BONGRAND, P. (1984).
Simple microscopical measurement of contact angles on transparent substrates.
Journal Colloid Interface Science. **99** (1) : 164-167.

FATT, I. (1984a).
Contact lens wettability-Myths, mysteries, and realities.
American Journal of Optometry and Physiology Optics. **61** (7) **:** 419-430.

FATT, I. (1984b).
Oxygen transmissibility and permeability of gas permeable hard contact lenses and materials.
International Contact Lens Clinic. **11** (3) : 175-187.

FATT, I. (1990).
Observation of film breaking on model eyes.
British Contact Lens Association Transaction. Annual Clinical Conference. Glasgow. 20-32.

FEINBLOOM, W. (1936).
A plastic contact lens.
Transaction of American Academy of Optometry. **10** : 37-44.

FELDMAN, G.L. (1977).
Chemical and physical properties of cellulose acetate butyrate as related to contact lenses.
Contact Lens Journal. **11** (1) : 25-31.

FELDMAN, G.L. (1981).
Contact lens materials.
International Ophthalmology Clinic. **21** (2) : 155-162.

FELDMAN, G. YAMANE, S.J and HERSKOWITZ, R. (1987).
Fluorinated materials and the Boston Equalens.
Contact Lens Forum. **12** (June) : 57-59.

FICK (1887).
See MANDELL 1953.

FINK, B.A. CARNEY, L.G and HILL, R.M. (1993).
Influence of lens design on the tear pump efficiency associated with plus-power rigid contact lenses: A comparison of single-cut, lenticular, and minus-carrier designs.
Optometry and Vision Science. **70** (1) : 2-8.

FINNEMORE, V.M and KORB, J. (1980).
Corneal oedema with polymethylmethacrylate versus gas-permeable rigid polymer contact lenses of identical design.
Journal of the American Optometric Association. **51** : 271-274.

FINNEMORE, V.M. (1984).
Drying phenomenon with rigid lenses: Exacerbation with gas-permeable materials?
Journal of the American Optometric Association. **55** (3) : 179-180.

FITZGERALD, J.K. (1983a).
Understanding permeability and wettability.
Contact Lens Journal. **11** (4) : 2-9.

FITZGERALD, J.K. (1983b).
A comparison of selected rigid gas permeable contact lens material properties.
Contact Lens Association Ophthalmologist Journal. **9** (3) : 245-248.

FLORY, P.J. (1953).
Principles of polymer chemistry. Cornell University Press. Ithaca New York. 29-70.

FONN, D and HOLDEN, B.A. (1988).
Rigid gas permeable vs. hydrogel contact lenses for extended wear.
American Journal of Optometry and Physiological Optics. **65** (7) : 536-544.

FORST, G. (1989).
The contact angle - a measure of wettability.
Contact Lens Journal. **17** (3) : 73-79.

FORST, G. (1990).
Assessment of the wettability of contact lenses in vitro and on the eye.
Contact Lens Journal. **18** (10) : 271-281.

FORT, T.J and PATTERSON, H.T. (1963).
A simple method for measuring solid-liquid contact angles.
Journal Colloid Science. **18** : 217-222.

FOWKES, M.F. (1968).
Calculation of work of adhesion.
Journal of Colloid Interface Science. **28** (314) : 493.

FOWKES, F.M and HARKINS. W.D.(1940).
The state of monolayers adsorbed at the interface solid-aqueous solution.
American Journal of Chemical Society. **62** (December) **:** 3377-3386.

FOWLER, S.A and ALLANSMITH, M.R. (1980).
Evaluation soft contact lens coatings.
Archives Ophthalmology. **98** (July) : 95-99.

FOWLER, S.A. KORB, D.R. FINNEMORE, V.M. ROSS, R.N and ALLANSMITH, M.R. (1984).
Surface deposits on worn hard contact lenses.
Archives Ophthalmology. **102** (5) : 757-759.

FOWLER, S.A. KORB, D.R. FINNEMORE, V.M. ROSS, R.N and ALLANSMITH, M.R. (1987).
Coating on the surface of siloxane gas permeable lenses worn by keratoconic patients.
The Contact Lens Association Ophthalmologist Journal. **13** (4) : 207-210.

FOWLER, A.S and GAERTNER, K.I. (1990).
Scanning electron microscopy of deposits remaining in soft contact lens polishing marks after cleaning.
The Contact Lens Association Ophthalmologist Journal. **16** (3) : 214-218.

FOX, H.W and ZISMAN, W.A. (1946).
Contact angle.
Journal Colloid Science. **1** : 513.

GARNER, L.F. (1981).
A simple interferometer for hard contact lenses.
American Journal of Optometry and Physiological Optics. **58** (11) : 944-950.

GASSON, A. (1981).
Further clinical experience with CAB.
The Journal of the British Contact Lens Association. **4** : 113-120.

GAUDIN, A.M. WITT, A.F and DECKER, T.G. (1963).
Contact angle hysteresis-principles and application of measurement methods.
Transaction of Society of Mining Engineers. (226) : 107-112.

GAYLORD, N.G. (1974).
Oxygen-permeable contact lens composition, methods and article of manufacture.
United States Patent. (3808) 179 : 1-6.

GEER, M.R. SOKASKI, M. JACOBSEN, P.S and YANCEY, H.F. (1961).
Performance of Dense-Medium Cyclone in cleaning fine coal.
USBM report of investigations 5732.

GELNER, P.V and BEHNKEN, B.H. (1989).
Paraperm EW1 vs fluoroperm 90 gas permeable contact lens study.
Contact Lens Journal. **17** (1) : 15.

GESSER, H.D. FUNT, B.L and WARRINER, R.E. (1965).
A method of improving the wettability of contact lens by free radical treatment.
American Journal of Optometry and Archives American Academic Optometry. **42** (1) : 321-324.

GESSER, H.D. WARRINER, R.E and FUNT, B.L. (1967).
The wettability of contact lenses with hydroxyl free radicals.
Journal. American Optometric Association. **38** (3) : 191.

GLEASON, W.J and DOANE, M.G. (1987).
Contact angle vs in-vivo lens wetting evaluation.
Transactions British Contact Lens Association Conference. **4** : 51-52.

GOLDBERG, J. (1979).
Gas permeable contact lenses. How good are they?
International Contact Lens Clinic. (November) : 281.

GOOD, R.J and FERRY, G.V. (1963).
The wettability of solids by liquid hydrogen.
Advan Cryogen Engineering. **E10** (8) : 306-310.

GOOD, R.J. (1977).
Surface free energy of solids and liquids: Thermodynamic molecular forces and structure.
Journal of Colloid Interface Science. **59** (3) : 398-419.

GOOD, R.J. (1979).
Contact angles and the surface free energy of solids.
Surface and Colloid Science. **11** : 1-31.

GOOD, R.J and STROMBERG, R. (1979).
Surface and Colloid Science. Plenum Press. **2** : 1-31.

GRAY, V.R. (1966).
Contact angles, surface tensions and adhesion. Aspects of adhesion. University of London. Press **2** : 42-48.

GREGONIS, D.E. HSU, R. BUERGER, D.E. SMITH, L.M. and ANDRADE, J.D. (1982).
Wettability of polymers and hydrogels as determined by Wilhelmy plate technique. Solvent property relationships to polymers. WHITTAKER'S BOOKBANK, PERGAMON : 120-130.

GROHE, R.M. COT, P.J and COT, C.W. (1988).
The role of in office modification for RGP surface defects.
Contact Lens Spectrum. (October) : 52-60.

GROHE, R.M and COT C.P.J. (1989).
RGP non-wetting syndrome.
Contact Lens Spectrum. **4** (3): 32-44.

GP-US/6039 (1989).
Guidelines for physicochemical characterisation of biomaterials. Report of the National Heart, Lung and Blood Institute working Group. US, Department of Heath and Human Services.

GUASTALLA, J. (1957).
Wetting angle balance method and its applications.
Proc 2nd International Congress on surface Activity. **3** : 143-153.

GUILLON, J.P. (1988).
Tear film structure of the contact lens wearer Ph.D. Thesis. The City University, London England.

GUILLON, M and GUILLON, J.P. (1987).
In-vivo wettability of rigid gas permeable lenses during extended wear.
Optometry and Vision Science. **67** : (10) : 49.

GUILLON, J.P and GUILLON, M. (1988).
Tear film examination of the contact lens patient.
Contax. May : 14-18.

GUILLON, M and GUILLON, J.P. (1988).
Pre-lens film characteristics of high Dk rigid gas permeable lenses.
American Journal of Optometry and Physiological Optics. **65** : 73.

GUILLON, M and GUILLON, J.P. (1989).
Hydrogel lens wettability during overnight wer.
Ophthalmic and Physiological Optics. **9** (4) : 355-359.

GUILLON, J.P. GUILLON, M. DWYER S and MAPSTONE V. (1989).
Hydrogel lens in vivo wettability.
Transaction of The British Contact Lens Association Conference Birmingham : 44-45.

GUILLON, M. GUILLON, J.P. MAPSTONE, V and DWYER, S. (1989).
Rigid gas permeable lenses in vivo wettability.
Transaction of the British Contact Lens Association. Annual Clinical Conference Birmingham. **6** : 24-26.

GUILLON, J.P and GUILLON, M. (1990).
How to predict tear related contact lens problems.
Transaction of the Journal of the British Contact Lens Association. Annual meeting Glasgow. 33-35.

GUILLON, J.P. GUILLON, M and CROIN, F. (1990).
Hydrogel lens in vivo wettability during sleep.
Optometry and Vision Science. **67** (10) : 170.

GUILLON, M. GUILLON, J.P and ALLARY, C.J. (1990).
In-vivo wettability of rigid gas permeable lenses during extended wear.
Optometry and Vision Science. **67** (10) : 49.

GUILLON, M. GUILLON, J.P. SHAH, D. BERTRAND, S and GRANT, T. (1994).
In vivo wettability of high Dk RGP materials.
Journal of the British Contact Lens Association. **18** (1) : 9-15.

GUILLON, M. MC GROGAN, L. GUILLON, J.P. STYLES, E. and MAISSA, C. (1997).
Effect of material ionicity on the performance of daily disposable contact lenses.
Contact Lens and Anterior Eye Journal. **20** (1) : 3-8.

GUMPELMAYER, T.F. (1972).
The first decade of hydrophilic contact lenses.
Journal of the American Optometric Association. **43** (3) : 253-255.

HALES, R.H. (1982).
Contact lenses, a clinical approach to fitting, 2nd Edition, William & Wilins London, Baltimore.

HARRIS, M.G. OYE, R. HALL, K and FATT, I. (1973).
Contact angle measurements on hard contact lenses.
American Journal of Optometry and Archives. American Academic Optometry. **50** : 446-451.

HAMILTON, W.C.J. (1972).
A technique for the characterisation of hydrophilic solid surfaces.
Journal of Colloid Interface Science. **40** (2) : 219-222.

HAN, D. (1991).
The wettability of silicone carbide by liquid pure aluminium and aluminium alloys.
MSc. Thesis. School of materials. University of Sheffield.

HANSEN, R.L and TOONG, T.Y. (1971).
Dynamic contact angle and its relationship to forces of hydrodynamic origin.
Journal of Colloid Interface Science. **37** (1) : 196-207.

HANCOCK, B.C. (1991).
Material interactions and surface phenomena in size enlargement processes. Ph.D. Thesis. Department of pharmaceutical technology, University of Bradford.

HATFIELD, R.O. JORDAN, D.R. BENNETT, E.S. HENRY, V.A. MAROHN, J.W and MORGAN, B.W. (1993).
Initial comfort and surface wettability: A comparison between different contact lens materials.
Journal of the American Optometric Association. **64** (4) : 271-273.

HATTORI, S. KING, R.N and ANDRADE, J.D. (1978).
Surface tension measurements on methacrylate monomer solutions, selected solvents and gel extracts.
Journal of Bioengineering. **2** : 113-118.

HERSCHEL (1823).
See MANDELL 1953.

HERSKOWITZ, R. (1989).
The effect of manufacturing variability on fluorinated contact lens material performance.
Optician. **197** (5189) : 32-35.

HILL, R.M. (1977a).
PMMA contact lenses.
International Contact Lens Clinic. **3 :** 34-36.

HILL, R.M. (1977b).
How wet are your patient's tears?
International Contact Lens Clinic. **4 :** 46-49.

HILL, R.M.(1995).
Contact lenses, beyond refractive error.
Journal of the British Contact Lens Association. **18** (4) : 109-114.

HILL, M.R. (1981).
Laboratory studies.
International Ophthalmology Clinic. **21** : 223-239.

HILL, R.M and CARNEY, L.G. (1975).
pH profile II.
Journal of the American Optometric Association. **46** : 1146.

HILL, R.M and CARNEY, L.G. (1976).
The closed eye environment.
Journal of the American Optometric Association. **53** : 718.

HILL, R.M and MAUGER, T.F. (1981).
The solution label's phantom features.
Contact Lens Forum. **6** (4) : 115-117.

HIND, H. and SZEKELY, I. (1959).
Wetting and hydration of contact lenses.
Contacto. **3** (3) : 65-68.

HIND, H.W. (1963).
Contact lens wetting and comfort.
Encyclopaedia of Contact Lens Practice. **30** (21) supplement. 32-42.

HO, C.P and YASUDA, H. (1988).
Ultra coating of plasma polymer of methane applied on the surface of silicone contact lenses.
Journal Biomedical Material Research. **22** : 919-937.

HOFFMAN, R. (1975).
A study of the advancing interface. Interface shape in liquid-gas-interface.
Journal of Colloid Interface Science. **50** (2) : 228-241.

HOFFMAN, W.C. (1983a).
Surface properties of polyacrylate silicone contact lenses.
Contacto. **27** (4) : 3-6.

HOFFMAN, W.C. (1983b).
Mechanical and viso-elastic properties vs machining scratch. Resistance and optical performance.
Contact Lens Journal. **10** (10) : 8-10.

HOLDEN, B. TIGHE, B. YOUNG, G and BRABANDE, J. (1992).
Back to the future.
British Contact Lens Association Journal. Harrogate Conference, Session 1: **15** (4) : 181-194.

HOLLY, F.J. (1973).
Formation and stability of the tear film. In Holly, F. J. and Lemp, M. A. The preocular tear film and dry eye syndromes.
International Ophthalmology Clinic. Little Brown, Boston, **13** (1) : 73-96.

HOLLY, F.J. (1977).
Contact angle of sessile drops as an indicator of surface polarisation 1.
Journal of Colloid Interface Science. **61** (3) : 435-437.

HOLLY, F.J. (1978).
Surface chemical evaluation of artificial tears and their ingredients. 1. Interfacial activity at equilibrium.
Contact and Intraocular Medical Journal. 4 (2 April/June) : 15-31.

HOLLY, F.J. (1979).
Protein and lipid adsorption by acrylic hydrogels and their relation to water wettability.
Journal of Polymer Science Symposium. **66** : 409-417.

HOLLY, F.J. (1981a).
Tear film physiology and contact lens wear I. pertinent aspects of tear film physiology.
American Journal of Optometry & Physiological Optics. **58** (4) : 324-330.

HOLLY, F.J. (1981b).
Tear film physiology and contact lens wear II.
Contact lens tear film interaction.
American Journal of Optometry & Physiological Optics. **58** (4) : 331-341.

HOLLY, F.J. (1983a).
Surface chemistry of contact lens wear.
International Ophthalmology Clinic. **13** (1) : 279-286.

HOLLY, F.J. (1983b).
Novel methods of studying polymer surface by employing contact angle goniometry.
Physio-Chemical Aspects of Polymer Surfaces. New York, Plenum.**1 :** 141-154.

HOLLY, F.J and LEMP, M.A. (1971a).
Surface chemistry of the tear film implications for dry eye syndromes, Contact lenses and ophthalmic polymers.
Contact Lens Society American Journal. **5** (1) : 12-19.

HOLLY, F.J and LEMP, M.A. (1971b).
Wettability and wetting of corneal epithelium.
Experiment Eye Research. **11** : 239-250.

HOLLY, F.J and REFOJO, M.F. (1975).
Wettability of hydrogels I. Poly (2 hydroxyethyl methacrylate).
Journal Biomed Material Research. **9** (3) : 315-326.

HOLLY, F.J. and REFOJO, M.F. (1976).
Water wettability of hydrogels.
Symposium, Hydrogels for Medical and Related Applications in Chemistry. **19,** (31). 252-266.

HOLLY, J.F and REFOJO, M.F. (1976).
Water wettability of protein adsorbed at the hydrogel water interface.
American Chemical Society Symposium. **31** : 267-282.

HOLLY, F.J and LEMP, M.A. (1977).
Tear physiology and dry eyes.
Survey of Ophthalmology. **22** (2) September-October **:** 69-87.

HOSAKA, S. OZAWA, H. TANZAWA, H. ISHIDA, H., YOSHIMURA, Y. MOMOSE, T, MAGATANI, H and NAKAJIMA, A. (1983).
Analysis of deposits on high water content contact lenses,
Journal Biomedical Materials Research. **17** : 26.

HOUGH, D.A. and PATEL, K.D. (1986).
Plasma modification of GPH lenses- an unexpected clinical result.
Journal of the British Contact Lens Association. **9** (1) : 38-40.

HOUGH, D.A. (1989).
Quantifying the surface characteristics of rigid gas permeable lenses.
Transactions of the British Contact lens Association. Annual Clinical Conference Birmingham. **6** : 27-28.

HUFF, J.W. EGAN, D.J and KATICH, M.J. (1988).
Parameter and wettability influences on rigid contact lens wettability.
American Journal of Optometry & Physiological Optics. **65** (9) : 717-721.

HUNTINGTON, A.K. (1906).
Tilting wetting angle.
Transaction. Faraday Society. **1** : 345-361.

ISAACSON, W.B and RODRIGUES, O.P. (1989).
Flexible Fluoropolymer. A new category of contact lenses. A completely new contact lens material with unique characteristics is discussed.
Contact Lens Spectrum. **4 (1)** : 60-62.

ISAACSON, W.B and RICE, D.E. (1989).
Allergan advent: A Fluoropolymer contact lens in a new classification.
Contact Lens Forum. February : 49-51.

JARVIS, N.L. FOX, R.B and ZISMAN, W.A. (1964).
Surface activity at organic liquid-air interfaces: V. The effect of partially fluorinated additives on the wettability of solid polymers. In Fowkes, F.M. contact angle. Wettability and adhesion.
Advances in chemistry. Series **43**. Washington D.C. American Chemical Society.

JHO, C. (1983).
Water wettability of polymer materials for contact lenses.
Journal of Colloid and Interface Science. **94** (2) : 589-592.

JACOB, R. (1989).
Contact lens material.
Contact Lens Journal. **17 (7)** : 217-219.

JOHNSON, R.E and DETTRE, R.H. (1969).
Wettability and contact angle.
Surfaces and Colloid Science. Wiley-Interscience. **2** : 85-115.

JONES, L.W.J. (1992).
Contact lens deposits: Their causes and control.
Contact Lens Journal. **20** (1) : 6-13.

JONES, R.A. (1994).
The wetting transition for polymer mixture.
Polymer Journal. **35** (10) : 2160-2166.

JONES, L. MA, L. FRANKLIN, V and TIGHE, B. (1994).
In-vivo versus in-vitro wettability of hydrogel materials.
The British Contact Lens Association. 18th annual clinical conference and exhibition. In Torquay. UK. 3-5 June. *Journal of the British Contact Lens Association.* **17** (4).

JOSEPHSON, J.E and CAFFERY. B.E. (1989).
Classification of the surface appearance characteristics of contact lenses in vivo.
Optometry and Vision Science. **66** (2) : 130.

KEATES, R.H. IHLENFELD, J.V and ISAACSON, W.B. (1984).
An introduction to Fluoropolymer contact lenses: A new class of materials.
The Contact Lens Association Ophthalmologist Journal. **10** (4) : 332-334.

KELLER, K.H. (1980).
Guidelines for physicochemical characterisation of biomaterials.
National Institutes of Health Publication. (80- 2168) : 1-32

KING, R.N. (1980).
Protocol for contact angle measurements at the polymer-water interface. Guidelines for physicochemical characterisation of biomaterials. September.
National Institutes of Health Publication. (80-2186) : 105-106.

KING, R.N. GREGONIS, D.E and COLEMAN, D.L. (1979).
Surface characterisation of Poly-hydroxyethyl-methacrylate and related polymers.
Journal of Colloid Interface Science. 72 : 488.

KIRKWOOD, J.G and HUFF. F.P. (1949).
The statistical mechanical theory of surface tension.
Journal of *Chemical Physics.* **17** (3) : 338-343.

KNEEN, E and BENTON, W.W. (1937).
A simplified technique for the determination of contact angles and its application to studies on wetting.
Journal Phys Chem. **41** (1531) : 1195-1203.

KNICK, P.D and HUFF, J.W. (1991).
Effects of temperature and conditioning on contact lens wetting angles.
Contact Lens Association Ophthalmology Journal. **17** (3) : 177-180.

KNOP, E and BREWITT, H. (1992).
Morphology of the conjucntival epithelium in spectacle and contact lens wearers. A light and Electron Microscopic study.
Contactologica. **14** (E) : 108-120.

KOETTING, R.A. (1977).
Tear film break-up time on hydrophilic lens surfaces.
International Contact Lens Clinic. **4** : 30-37.

KOKOSKI, C.S and SCHWARTZ, S.M. (1963).
A study of the effects of various soaking solutions on the wettability of plastic lens surfaces.
Contacto. **7** (5) : 15-21.

KOSSMEHL, G. NEUMANN, W. VOLKHEIMER, J. REZAII-DJAFARI, M and SCHAEFER, H. (1988).
New polymers and hydrogels for contact lenses.
First International Conference. Electrical Optical and Acoustic Properties of Polymers. London.

KOZIOL, J.E. PEYMAN, G.A and YASUDA, H. (1983).
Evaluation of new silicone methane polymer contact lens.
Archives Ophthalmology. **101** (11) : 1779-1781.

KREZANOSKI, J. (1963).
What is wetting.
Contacto. **7** (4) : 20-22.

KRISHNER, N and BROW, F. (1964).
Methylcellulose solution for ophthalmic use.
American Journal Ophthalmology **57** : 99.

LAFERLA, J. (1991).
Looking at Novalens.
Contact Lens Forum. **16** (1) : 37-38.

LAKKIS, C. LINDSAY, R.G. HARRIS, M and BRENNAN, N.A. (1993).
RGP lenses: manufacturer and practitioner perspectives.
Clinical and Experimental Optometry. **76** (1 January/February) : 4-7.

LAMBERTS, S and DABEZIES O.H. 1984).
Wetting in contact lenses. The Contact lens Association Ophthalmologist. Guide to Basic Science and Clinical practice. Edited by Dabezies O.H. .

LANGMUIR, I and SCHAEFER, V.J. (1937).
The effect of dissolved salts on insoluble monolayer.
American Chemistry Society Journal. **59** (November) : 2400-2415.

LARKE, J.R. PEDLEY, D.G and TIGHE, B.J. (1973).
Polymers in contact lens applications, part IV wettability phenomena: critical surface tension criteria and contact lens materials.
Optician. **166** (4301) : 21-30.

LARKE, J.R. PEDLEY, D.G. SMITH, P.J and TIGHE, B.J. (1973).
Contact angle its measurement and significance. Polymers in contact lens applications.
Optician. **166** (October) : 32-39.

LARKE, J.R. PEDLEY, D.G. SMITH, P.J and TIGHE, B.J. (1973).
A semi-rigid contact lens.
Ophthalmic Optician. **166** (September) : 32-39.

LEMBACH, R.G. (1990).
Rigid gas permeable contact lenses.
Contact Lens Association Ophthalmologist Journal. **16** (3) : 129-137.

LEMP, M.A. (1973).
Surfacing the precorneal tear film.
Annals Ophthalmology. **5** (7) : 819-826.

LEMP, M.A. (1973).
Surfacing abnormalities.
International Contact Lens Clinic. **13** (1) : 191-197.

LEMP, M.A and HOLLY, F.J. (1970a).
Corneal desiccation despite, normal tear volume.
Annals of Ophthalmology. June : 258-284.

LEMP, M.A. HOLLY, F.J. (1970b).
Recent advances in ocular surface chemistry.
American Journal of Optometry and Archives of American Academic of Optometry. **47** (9) : 669-672.

LEMP, M.A. HOLLY, F.J. SHUZO, I and DOHLMAN, C.H. (1970).
The precorneal tear film, 1. factors in spreading and maintaining a continuous tear film over the corneal surface.
Archives Ophthalmology. **83** (January) : 89-94.

LEMP, M.A and HOLLY, F.J. (1972).
Ophthalmic polymers as ocular wetting agents.
Annals of Ophthalmology. **14** : 15-20.

LEMP, M.A and HAMILL, J.R. (1973).
Factors affecting tear film break-up in normal eyes.
Archives Ophthalmology. **89** (July) : 103-105.

LI, J.G and HAUSNER, H. (1992).
Wetting and adhesion in liquid silicon/ceramic systems.
Materials Letters. **14** : 329-332.

LIN, S.T. MANDELL, R.B. LEATHY, C.D and NEWELL, J.O. (1991).
Protein accumulation on disposable extended wear lenses.
The Contact Lens Association Ophthalmologist Journal. **17** (1) : 44-50.

LIN, H.W and PINKUS, A.G. (1973).
Assessment of hydrophilicity by contact angle measurement.
Optometry Weekly. **64** (January): 56-60.

LINDRIDGE, C. (1989).
Material differences, a profile of the contact lens materials industry.
Contact Lens Journal. **17** (1) : 24-26.

LIPPMAN, J.I. (1981).
Gas permeable contact lenses: An overview.
Contact Intraocular Lens Medical Journal. **4** (1) : 15-25.

LIPPMAN, J.I. (1989).
Rigid gas permeable contact lenses.
Ophthalmology Clinic of North America. **2** (1) : 261-265.

LIPPMAN, J.I. (1990).
Contact lens materials. A critical review.
The Contact Lens Association Ophthalmologist Journal. **16** (4) : 287-291.

LOVERIDGE, R. (1993).
Breaking up is hard to do?
Journal of The British Contact Lens Association. **16** (2) : 51-55.

LOWTHER, G.E. (1984).
Contact lens preparations. Chapter 12 of Clinical Ocular pharmacology. BARTLETT, J.D. AND JOANUS, S. D. (Eds) Butterworth Publishers, Boston Massachusetts, 327-361.

LYDON, D.P.M and GUILLON, J.P. (1984).
The integrity of the pre-lens tear film.
Transactions of the first international congress, The British College of Ophthalmic Opticians (Optometrists). London. April : 106-135.

MACDOUGALL, G and OCKRENT, C. (1941).
Surface energy relations in liquid/solid systems. 1. The adhesion of liquids to solids and a new method of determining the surface tension of liquid.
Proc Royal Soc Med. **180A** : 151-173.

MACK, G.L and LEE, D.A. (1936).
Measurements of the dimensions of small bubbles and drops II.
Journal Physical Chemistry. 40 : 169-177.

MACK, G.L and LEE, D.A. (1936).
Measurements of the dimensions of small bubbles and drops II.
Journal Physical Chemistry. 40 : 169-177.

MACKEEN, D.L. SACHDEV, M. BALLOU, V and CAVANAGH, H.D. (1992).
A prospective multicenter clinical trial to assess safety and efficacy of Menicon SF-P RGP lenses for extended wear.
International Contact Lens Clinic. **18** (3) : 183-186.

MACMILLAN, B.A and BENJAMIN, W.J. (1992).
Cleaning and storage of rigid contact lenses prior to dispensing.
Journal of the American Optometric Association. **63** (5) : 333-342.

MADIGAN, M. FONG, D and HOLDEN, B.A. (1983).
Wettability: an old method reapplied.
Presented to the American Academy of Optometry Houston.

MADIGAN, M and HOLDEN, B.A. (1986).
Preliminary report: Lens wear and its effect on wetting angle.
International Eye Care. **2** (1) : 36-44.

MADIGAN, M. HOLDEN, B.A and FONG, D. (1986).
A new method for wetting angle measurement.
International Eye Care. **2** (1) : 45-48.

MANDELL, R.B. (1953).
Contact lens practice. Charles Thomas Publisher USA.

MANDELL, R. (1984).
Is there an angle to wetting?
Contact Lens Forum. 45-51.

MANN, I. (1938).
History of contact lenses.
Transaction of Ophthalmology Society. UK. **58** : 109-136.

MARK, H.F and BIKALES, N.M. (1979).
Encyclopaedia of polymer science and technology. Interscience Publishers. New York London Sydney. Toronto.

MARQUARDT, R. (1993).
Tear film stability and the immune barrier.
Contactologica. **15E** (4) : 174-176.

MASKELL, R.W. (1981).
Interesting clinical reaction associated with the clinical surface characteristics and spoilage gas permeable contact lenses.
Journal of the British Contact Lens Association. **6** (4).162-165.

MASKELL, R.W. (1995).
Comments and experience with semi rigid gas permeable contact lenses.
Journal of the British Contact Lens Association. **6** (4).32-35.

MATIJEVIC, E. (1969).
The Equilibrium shape of interfaces, drops and bubbles.
Surfaces and colloid science. Wiley-Interscience. **2** : 3-25.

MCBRIAR, N. (1991).
The plasma treatment of contact lenses. Ph.D. Thesis Durham University.

MCLAUGHLIN, R. (1989).
Fluorosilicone acrylate RGPs vs. silicone acrylate RGPs.
Contact Lens Spectrum. **4** (April) : 74-75.

MCMONNIES, C.W. (1991).
Surface deposit theory and practice.
Journal of the British Contact Lens Association. **14** (4) : 179-182.

MESZAROS, G.K. (1986).
Lens polishes not all created equal. Today's polymers require a unique combination of abrasives.
Contact Lens Spectrum. September : 49-50.

MINARIK, L. and RAPP, J. (1989).
Protein deposits on individual hydrophilic contact lenses: effects of water and ionicity.
Contact Lens Association Journal. **15** (3) : 185-188.

MORGAN, B.W and BENNETT, E.S. (1992).
Modification of RGP lenses.
Contact Lens Spectrum. (July) : 33-52.

MORGAN, B.W. HENRY, A.V. BENNETT, E.S and CAROLINE, P.J. (1992).
The effect of modification procedures rigid gas permeable contact lenses.
Journal of the American Optometric Association. **63** (3) : 201-214.

MORRISON, R.J. (1963).
Contact lens coating.
Optical Journal Review. (July 15) : 38-40.

NEUMANN, A.W. (1974).
Contact angles and their temperature dependence thermodynamic status measurement, interpretation and application.
Advances in Colloid and Interface Science. **4** : 105-191.

NEUMANN, A.W and TANNER. W.J. (1970).
Temperature dependence of contact angles.
Journal of Colloid Interface Science. **34** (1) : 1-9.

NEUMANN, A.W. HAAGE, G. and RENZOW, D.J. (1971).
The temperature dependence of contact angles.
Journal of Colloid Interface Science. **35** : 379-385.

NEUMANN, A.W and GOOD, R.J. (1979).
Techniques of measuring contact angles.
Surface and Colloid Science. **11** : 31-91.

NIH. National Institutes of Health Publication. (1980).
Guidelines for Physicochemical Characterisation of Biomaterials. September 80-2186 : 37-50.

NIH. National Institutes of Health. GP-US/6039 (1989).
Guidelines for physicochemical characterisation of biomaterials.
Report of the National Heart, Lung, and Blood Institute Working Group. U.S. Department of Health and Human Services.

NORN, M.S. (1969).
Desiccation of the pre-corneal tear film: 1. Corneal wetting time.
Acta Ophthalmology. **47** : 865-880.

O'BRIEN, J.W and RYGE, G. (1965).
Wettability of poly methylmethacrylate treated with silicone tetrachloride.
Journal Prosthetic Dentistry. **15** (2) : 304-308.

O'KANE, W.C. (1930).
New Hampshire Agricultural Experiment Station. Bulletin. **39**.

OLSON, A.P. (1982a).
Surface properties, wettability and adsorption..
Contact Lens Journal. **10** (10) : 11-15.

OLSON, A.P. (1982b).
Contact lens surface properties: wettability and adsorption.
Optician Monthly. **73** (7) : 376-380.

ONDARCUHU, T. (1992).
Relaxation modes of the contact line in situation of partial wetting.
Modern Physics Letters B. **6** (15) : 901-916.

ONG, C. (NG, C.O) and TIGHE, B.J. (1976a).
Polymers in contact lens applications V. Design and calibration of a technique for "Dissolved" Oxygen permeability measurements.
British Polymer Journal September : 78-82.

ONG, C. (NG, C.O), PEDLEY, D.G and TIGHE, B. (1976b).
Polymers in contact lens applications VII. Oxygen permeability and surface hydrophilicity of polymers.
British Polymer Journal. (December) : 124-130.

ONG, C (NG, C.O) and TIGHE, B.J. (1976c).
Polymers in contact lens applications VI, the "Dissolved" Oxygen permeability of hydrogels and the design of materials for use in continuous wear lenses measurements.
British Polymer Journal. (December) : 118-123.

OSIPOW, L.I. (1962).
Surface chemistry, theory and industrial applications. Surface energy and surface tension. Reinhold, New York, : 7-23 and 232-294.

OWENS, N.F. RICHMOND, D. GREGORY, J. MINIGINS J and CHAN, D. (1978).
Contact angles of pure liquids and surfactants on low-energy surfaces.
Wetting and Spreading Adhesion, by Padday. Academic Press. London, New York, 127.

PADDAY, J.F. (1963).
Heights of sessile drops and meniscus properties.
Nature. **198** (27) : 378.

PADDAY, J.F. (1978).
Wetting, Spreading and Adhesion.
Academic Press, London, New York.

PEARSON, R.M. (1977).
Dimensional stability of several hard contact lens materials.
American Journal of Optometry and Physiological Optic. **54** (12) : 826-832.

PEARSON, R.M. (1979).
Dimensional stability of two gas permeable, hard contact lens materials.
Journal of the British Contact Lens Association. **2** (1) : 15-17.

PEARSON, R.M. (1986).
The clinical performance of hard gas permeable lenses.
Clinical & Experimental Optometry. **69** (3) : 98-102.

PEARSON, R.M. (1987).
Rigid gas permeable wettability and maintenance.
Contax. (September) : 8-16.

PEARSON, R.M. (1988)
Choosing the best gas permeable hard material.
Optician, Contact Lens Seminar : 22-30.

PEARSON, R.M. (1989).
Stability of hydrated curvature of Quantum lenses.
International Contact Lens Clinic. **16** (6) : 178-181.

PEPPAS, N.A and YANG, H.M.(1981).
Properties-based optimisation of the structure of polymers for contact lens applications.
Contact lens Journal. **7** (4) : 300-314.

PETHICA, B.A. (1961).
Contact angles.
Reports on the Progress of Applied Chemistry. **46** : 14-17.

PETKE, F.D and RAY. B.R. (1969).
Temperature dependence of contact angles of liquids on polymeric solids.
Journal of Colloid and Interface Science. **31** (2) : 216-227.

PHILLIPS, A.J. (1969).
Contact lens plastics, solution and storage, some implications.
Ophthalmic Optician. **9** (January) : 65-79.

PHILLIPS, M.C. (1965).
Some studies of contact angles. Ph.D. Thesis University of Southampton.

PHILIPP, G and SCHMIDT, H. (1984).
New materials for contact lenses prepared from Si and Ti alkoxides by the gel process.
Journal of Non Crystaline Solids : 283-292.

PLAMBECK, L. (1978).
Hydrophilic, oxygen permeable contact lens.
United States Patent 4 130 706 : 1-10.

POLE, J. LOWTHER, G.E. and HAMMACK, G.G.(1987).
Clinical evaluation of RGP contact lens surface qualities and subjective lens comfort.
International Contact Lens Clinic. **14** (4 May) **:** 185-201.

PORT, M.J.A. (1985).
Exploring prolonged wear, Clinical experience with Menicon SP.
Optician. **189** (5002) : 25-26.

POSTER, M.G. (1984).
The wetting angle.
Journal of the American Optometric Association. **55** (3) : 167-168.

POSTER, M.G. GELFER, D.M and GOODERMAN, S. (1978a).
Measuring the contact lens wetting angle in a simulated in vivo environment.
International Contact Lens Clinic. **5** (1) : 51-55.

POSTER, M.G. GELFER, D.M and GOODERMAN, S. (1978b).
Wetting angles of hard contact lenses as related to soaking solutions.
International Contact Lens Clinic. **5** (July) : 166-170.

POSTER, M.G. GELFER, D.M and FERNANDEZ, N.D. (1986).
Wetting angles of rigid contact lens plastics: The effect of contact lens wear.
Journal of the American Optometric Association. **57** : 452-454.

RANKIN, F.B and TRAGER, S.F. (1970a).
Surface wettability and the contact lens.
Contact Lens Society of America Journal. **4** (3) : 5-7.

RANKIN, B.F and TRAGER, F.S. (1970b).
Wetting of contact lenses.
American Journal of Optometry and Archives. American Academic Optometry. **47** (9) : 698-702.

RATNER, B.D. (1983).
Surface characterisation of biomaterials by electron spectroscopy for chemical analysis.
Annals of Biomedical Engineering. **11** : 313-336.

RAYLEIGH, R.S. (1890).
Proc Soc. **30** (March) : 386-400.

REFOJO, M.F. (1965).
'Glyceryl Methacrylate hydrogels. 'applications of soft hydrogel contact lenses'.
Survey. Ophthalmology. **16** : 233.

REFOJO, M.F. (1978).
The chemistry of soft hydrogel lens materials. In Soft Contact lenses. Edited by RUBEN, M. Wiley and Sons, New York.

REFOJO, M.F. (1984).
Materials characteristics. Relevant properties and the chemists rationale.
Journal of the American Optometric Association. **55** (3) : 164-165.

REFOJO, M.F. (1994).
Chemical composition and properties. In contact lens Practice. Edited by RUBEN, M. and GUILLON, M. Chapman and Hall Medical. London.

REFOJO, M.F. and YASUDA, H. (1965a).
Hydrogels from 2-Hydroxyethyl Methacrylate and Propylene Glycol Monoacrylate.
Journal Apply Polymer Science. **9 :** 2425-35.

RIDDIFORD, A.C. (1964).
Contact angle.
Recent Progress Surface Science. 2 : 111.

ROCHER, P. (1975).
Surface phenomena and contact lenses.
Contacto. September : 10-16.

ROSENBERG, M. BARTE, P and LASKO, J. (1960).
Journal of Ultrastructure Research. **4 :** 298.

ROSENTHAL, P. CHOU, M.H. SALAMONE, J.C and ISRAEL, S.C. (1986).
Quantitative analysis of chlorhexidine gluconate and benzalkonium chloride adsorption on silicone acrylate polymers.
Contact Lens Association Ophthalmologist Journal. **12** (1) : 43-50.

SACK, R.A. JONES, B. ANTIGNANI, A. LIBOW, R. and HARVEY, H. (1987).
Specificity and biological activity of the protein deposited on the hydrogel surface.
Investigation Ophthalmology Vision Science. **28** : 842-849.

SAMMONS, W.A. (1985).
Contact lens surface texture.
Journal of the British Contact Lens Association. **8** (1) : 31-41.

SARVER, M. (1984).
Why use a rigid lens?
Journal of the American Optometric Association. **55** (3) : 168-169.

SARVER, M. BOWMAN, L. BAUMAN, E. DIMARTINO, R. LAU, D and UMEDA, W. (1984).
Wettability of some gaspermeables hard contact lenses.
International Contact Lens Clinic. **11** (8) : 479-490.

SARVER, D and STAROBA, J.E. (1978).
Corneal oedema with contact lenses under closed eye conditions.
American Journal of Optometry & Physiological Optics. **55** (11): 739-743.

SCHEER, V.D and SMOLDERS, C.A. (1978).
Dynamic aspects of contact angle measurements on adsorbed protein layers.
Journal of Colloid and Interface Science. **63** (1) : 7-15.

SCHWARTZ, C.A. (1987).
Solutions update 87, beyond compliance.
Contact Lens Forum. (October) : 22-47.

SEIDNER, L. (1987).
Wettability vs surface deposits: searching for a solution.
Contact Lens Forum. 50-52.

SHAFRIN, E.G. ZISMAN, W.A.J. (1967).
Critical surface tension for spreading on a liquid substrate.
Journal of Physical Chemistry. **71** (6) : 1309-1315.

SHARMA, C.P. CHANDY, T and SUNNY, M.C. (1987).
Inhibition of platelets adhesion to glow discharge modified surfaces.
Journal Biomat. **1** April : 533.

SHIOBARA, M. SCHNIDER, C.M. BACK, A. HOLDEN, B.A. (1989).
Guide to the clinical assessment of on eye, wettability of liquid gas permeable lenses.
Optometry and Vision Science. **66** (4) : 202-206.

SHIRAFKAN, A. WOODWARD, E.G. PORT, M.J.A and HULL, C.C. (1994).
Wettability of rigid contact lens materials measured by adherent liquid approaches. 18th Annual Clinical Conference and Exhibition. In Torquay. UK. 3-5 June.
Journal of the British Contact Lens Association. **17** (4) **:** 14.

SHIRAFKAN, A. WOODWARD, E.G. PORT, M.J.A and HULL, C.C. (1995).
Surface wettability and hydrophilicity of soft contact lens materials, before and after wear' British College of Optometry Centenary Conference April 1994.
Ophthalmic and Physiological Optics Journal. **15** (5) : 529-532.

SHIRAFKAN, A. WOODWARD, E.G and HULL, C.C. (1995).
A novel approach to measuring the wettability of rigid contact lenses. Mass measurement of the adherent liquid on the rigid lens surface.
Ophthalmic and Physiological Optics Journal. **15** (6) : 575-583.

SMIDDY, W.E. HAMBURG, T.R. KRACHER, G.P. GOTTSCH, J.D. STARK, W.J. (1990).
Therapeutic contact lenses.
Ophthalmology. **97** (3) : 291-295.

SHUTTLEWORTH, R and BAILEY, G.L.J. (1948).
The spreading of a liquid over a rough solid.
Faraday Society Journal. **3** : 16-22.

SMITH, L. BOWMAN, L and ANDRADE, J.D. (1982).
Contact angle analysis of hydrated contact lenses-in international conference: Biomedical polymers: International symposium: Contact lenses and Artificial eyes: University of Durham. London.
Biological Engineering Society. (July) : 279-284.

SMITH, L. DOYLE, C. GREGONIS, D.E and ANDRADE, J.D. (1982).
Surface oxidation of cis-trans polybutadiene.
Journal of Applied Polymer Science. 26 : 1269-1276.

SOUHENG, W.U.S. (1971).
Calculation of interfacial tension in polymer systems.
Journal Polymer Science. **33** (Part C) : 19-30.

STAHL, O.S. REICH, L.A and IVANI, E. (1974).
Report on laboratory studies and preliminary clinical application of a gas permeable plastic contact lens.
Journal of the American Optometric Association. **45** (3) : 302-307.

STAICOPOLU, D.N. (1962).
The Computation of surface tension and of contact angle by the sessile drop method.
Journal Colloid Science. **17** : 439-447.

STEVENSON, R.W.W. (1993).
An evaluation of gas permeable contact lens polymers and the effects on the corneal endothelium of long term PMMA contact lens wear. Ph.D. Thesis, Tennent Institute of Ophthalmology, December 1993.

STONE, J. PHILLIPS, A.J. (1989).
(Chapter 3 Tighe, B.J. Contact Lens Materials) Butterworths. London. 72-125.

SULMAN, L.H. (1920).
A contribution to the study of flotation.
Transaction Institute of Mining and Metallurgical Engineers. **29** : 44-203.

SUNNY, M.C and SHARMA, C.P. (1991).
Surface modification of corneal contact lens with phosphoryl choline by GLOW discharge.
Biomat Art Cells & Immob Biotech. **19** (3) **:** 599-612.

TADROS, T.F. (1978).
Spreading and retention of aqueous solution droplets of fluorocarbon and hydrocarbon surfactants and their mixtures on wheat leaves.
Wetting and Spreading Adhesion, by Padday. Academic Press. London, New York, 127.

TAGGART, A.F. TAYLOR T.C and INCE, C.R. (1930).
Experiments with flotation reagents.
Aime Transactions. **87** : 285-291.

TAYLOR, A.S. (1979).
In-vitro studies of corneal wetting. Ph.D. Thesis. University of Strathclyde.

TERRY, J.E and HILL, R.M. (1978).
Human tear osmotic pressure.
Archives Ophthalmology. **96** : 120.

TIGHE, B.J. (1976).
Design of polymers for contact lens applications.
British Polymer Journal. **8** (September) : 71-77.

TIGHE, B. (1990).
Blood, sweat and tears or some problems and in the design of biomaterials.
Transactions of the British Contact Lens Association. 13-20.

TIGHE, B. (1994).
Deposits on rigid and soft contact lenses, North West England, South East London and Kent Optometrist Association.

TIGHE, B. (1997).
Personal communication.

TIGHE, B and TREVETT, A. (1990).
The characterisation of mechanical properties of soft contact lenses.
Transactions of the British Contact Lens Association. Annual Clinical Conference Glasgow. 57-61.

TOMLINSON, F.J and PATTERSON, H.T. (1963).
A simple method for measuring solid/liquid contact angles.
Journal of Colloid Science. **18** : 217-222.

TOMLINSON, A. (1984).
Relation between surface wettability and visual performance with gas permeable hard contact lenses. Transactions of the first international congress.
British College of Ophthalmic Optician. April **:** 91-97.

TOMLINSON, A. (1990).
Choice for RGPs-a material issue.
Contact Lens Forum. **9** : 27-36.

TOMLINSON, A. COT, C.P.J and GUILLON, J.P. (1991).
Effect of fluorine contact of RGP contact lens polymers on tear film, lens wettability, and deposit resistance.
International Contact Lens Clinic. **18** (March / April) : 53-57.

TOMLINSON, A and CEDARSTAFF, T.H. (1992).
Diurnal variation in human tear evaporation.
Journal of the British Contact lens Association. **15** (2) : 77-79.

TOMLINSON, A and GIESHRECH, C. (1993).
The ageing tear film.
Journal of the British Contact Lens Association. **16** (2) : 67-69.

TREIBER, A. (1988).
Highly gas permeable contact lenses-surface properties and care.
Optician, Contact Lens Monthly. (April) **:** 29-36.

VAGHMARIA, R.B. (1993).
A study of surface treated rigid gas permeable lenses. BSc project, Department of Optometry and Visual Science. The City University.

WADE, W.L. MAMMONE, R.J and BINDER, M. (1991).
Surface properties of commercial polymer films. Following various gas-plasma treatments.
Journal of Applied Polymer Science. **43** : 1589-1591.

WALKER, P.J.C. (1982).
But what about the other properties of oxygen permeable hard lens materials?.
Journal of the British Contact Lens Association. **5** (3) : 98-104.

WALKER, J. (1988).
A clinical and laboratory comparison of the deposition characteristics of both Silicone/Acrylate and Fluoro-Silicone/Acrylate lenses.
Transactions of British Contact lens Association. International Conference. 83-86.

WALKER, J. (1989).
Over-polishing Fluorosilicone/acrylates: The consequences and the cure.
Transactions of British Contact Lens Association. Annual Clinic Conference Birmingham. **6** : 29-32.

WALKER, J. (1990).
High Dk RGP's: the lens of first choice.
Contact Lens Forum. 26-31.

WALTERS, K.A. GEE, H and MEAKIN, B. (1983).
The interaction of benzalkonium chloride with Boston contact lens material. Part 1 basic interaction studies.
Journal of British Contact lens Association. **6** (2) : 42-52.

WATT, T.J. (1993).
Improved wettability and deposit resistance from surface treated gaspermeable lenses-fact or fiction.
Contact Lens Journal. **20** (8) : 6-9.

WEINCHENK, J.I. (1989).
A look at the components in Fluorosilicone acrylates.
Contact Lens Spectrum. (October) : 61-64.

WENZEL, R.N. (1936).
Resistance of solid surfaces to wetting by water.
Industrial and Engineering Chemistry. **28** (8) : 988-994.

WICHTERLE, O and LIM, D.(1960).
Hydrophilic gels for biological usage.
Nature. **185** : 117-227.

WICHTERLE, O and LIM, D. (1961).
USA. Patent. 2 976 576.(March , 28).

WILHELMY, L. (1863).
Wilhelmy contact angle method.
Ann Physik. **119** : 117.

WILSHER, R.S. (1982).
Chemistry of silicone polymers.
Contact Lens Journal. **10** (10) : 5-7.

WOODWARD, E.G. (1984).
Therapeutic silicone rubber lenses.
Journal of British Contact lens Association. 7 (1) : 39-41.

WYCKOFF, P. (1980).
Experience with new hard contact lens materials.
Contacto. March : 16-19.

YANG, H.M. and PEPPAS, N.A. (1983).
Gas-to liquid permeation in silicone containing crosslinked glossy copolymers of Methylmethacrylate.
Biomaterials. **4** (October) : 281-284.

YASUDA, H. (1976).
Plasma for modification of polymers.
Journal Macromolec Science Chemistry. **10** (3) : 383-420.

YASUDA, H. (1981).
Glow discharge polymerisation.
Journal Polymer Science, Macromolecular Reviews **(16)** : 199-293.

YASUDA, H. BUMGARNER, M.O. MARSH, H.C. YAMANASHI, B.S. DEVITO, D.P. WOLBARSHT, M.L. REED, J.W. BESSLER, M. LANDERS, M. B. HERCULES, D.M and CARVER, J. (1975).
Ultrathin coating by plasma polymerisation applied to corneal contact lens.
Journal of Biomedical Materials Research. **9** (6) : 629-643.

YASUDA, H. GOCHIN, M. and STONE, W. (1966).
Hydrogels of poly (hydroxyethyl) methacrylate-glycerol mono-methacrylate copolymers.
Journal of Polymer Science. Part A-1. **4** : 2913.

YASUDA, H and GAZICKI, M. (1982).
Biomedical application of plasma polymerisation of plasma treatment of polymer surfaces.
Biomaterials. **3** (April) : 68-77.

YASUDA, H. SHARMA, A.K and YASUDA, T. (1981).
Effect of orientation and mobility of polymer molecules at surface on contact angle and its hysteresis.
Journal of Polymer Science. Polymer Physics Edition. **19** : 1205-1291.

YEAGER, M.Y. and BENJAMIN, W.J. (1987).
Care regimens and initial wetting of a Silicone/Acrylate surface in vivo.
International Contact Lens Clinic. **14** (2, February) : 58-61.

YORAV, V.S. RONNEN, M and SUSTER, S. (1987).
Eyelid contact dermatitis due to liquifilm wetting solution of hard contact lenses.
Contact Dermatitis. **17** (5) : 314-315.

YOUNG, T. (1801).
See MANDELL 1953.

YOUNG, T. (1805).
An easy on the cohesion of fluids.
Philos Trans R Soc. London. **95** : 65-87.

ZISMAN, W.A. (1964).
Relation of the equilibrium contact angle to liquid and solid constitution.
Advances in Chemistry Series. American Chemical Society. **43 :** 1-51.

ZEKMAN, R.N and SARNAT, L.A. (1972).
Clinical evaluation of the silicone corneal contact lens.
American Journal of Ophthalmology. **74** (3) : 534-537.

ZANTOS, S.G. (1990).
Some new developments in contact lens materials.
Transaction of *the British Contact Lens Association.* 24-25.

APPENDIXES

Apendix I

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BUTTERWORTH HEINEMANN

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A novel approach to measuring the wettability of rigid contact lenses. Mass measurement of the adherent liquid on the rigid lens surface (1)

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Summary

A novel approach and the equilibrium sessile drop (laser assisted) method were used to determine the wettability of hydrated and unhydrated PMMA, Polycon II, Boston IV, Equalens and Boston RXD rigid contact lens materials. In the new method the ability of the contact lens surface to attract the liquid is evaluated by measuring the adhered mass of liquid on the front lens surface. The mass has a direct relationship to contact lens wettability, so the greater the lens surface hydrophilicity the more liquid adheres to the contact lens surface. In the hydrated state, Equalens and Boston IV showed the greatest hydrophilicity of all five materials, although there was no significant difference between them ($P > 0.9$). Boston RXD had a lower ability to attract liquid and there was a significant difference between it and the next higher material which was Boston IV ($P < 0.005$) and also the next lowest Polycon II ($P < 0.00001$). PMMA had the lowest capability to adhere liquid and there was a significant difference between PMMA and Polycon II ($P < 0.00001$). The new method is simple and quick to use and gives greater discrimination and repeatability than other current methods.

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An optimum contact lens surface wettability is necessary to maintain an unbroken tear film and to minimise greasing and deposition. One of the relevant methods for evaluating surface properties is to measure the wettability (hydrophilicity) of the material surface. The most widely used method for assessing hydrophilicity of a material surface is to measure the wetting angle[1,2]. Only with consistent wettability can the practitioner predict the success from diagnostic lens to dispensed lens and from one dispensed lens to another.

Adequate wettability is defined as the ability of the material to support a stable tear film across its entire surface[3]. It is generally assumed that a low wetting angle is preferred to a high wetting angle. *In vitro* measurement of materials are thus not only necessary for research and development, but are also important for predicting clinical, on-eye performance[4]. The wettability of contact lenses is thus recognised to be an important property of material development possibly as significant as oxygen permeability[5,6].

There is a significant variation in wetting angle obtained with each method of measurement and it is not clear which result best describes the wettability of the various lens materials[7]. It has been believed that because the surfaces of contact lenses in the eye are hydrated, the receding angle is the best indicator of a material's clinical performance on the eye. Furthermore, Ng *et al.*[8] concluded that the sessile drop receding angle values are similar to the captive bubble contact angles[9] which is the method that has been accepted by the Contact Lens Manufacturers Association (CLMA)[4,7,10–14]. Unfortunately, the captive bubble method gives a very wide range of values (90–18°) on the same material in the hands of different investigators (*Table 1*). Notwithstanding this, there is broad agreement among different workers, on average values. The large variation among different laboratories is understandable since procedures and conditions used by different investigators have not been uniform. The main methods used to measure the

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Table 1. Wetting angle values of hydrated PMMA materials using the captive bubble technique (various authors)

No.	*Variations*	*Wetting angle (degrees)*	*SD*	*Reference*
1	24 h in distilled water	90.0	—	19
2	24 h in distilled water	59.0	2.0	14
3	Air in water, receding	49.0	2.0	16
4	7 days in distilled water	45.5	0.5	17
5	PMMA C, in saline	45.3	3.6	10
6	PMMA Blue, in saline	41.6	2.9	10
7	PMMA 4, Lab E	28.0	0.5	12
8	PMMA 4, Lab B	25.3	1.2	12
9	PMMA 4, Lab F	24.8	1.0	12
10	PMMA 4	24.3	3.8	13
11	PMMA 4, Lab A	19.0	0.7	12
12	PMMA Clear	18.3	0.5	13

SD, standard deviation.

surface wettability of the materials are as follows (see also *Table 2*).

(i) Sessile drop method. This is carried out in air; *advancing*, *receding* and *equilibrium* wetting angle $<^{c}$ can be determined[4,7–9,20–27].
(ii) Captive bubble method[7,10,13,14,16–18].
(iii) Meniscus methods[7,14,22,29–33].

The contact lens wetting angle can be determined by several ways. The angle can be measured directly from *photographs*[33,42] or from a *projected image*[8,22,29,34,43]. The angle is commercially measured with a *goniometer* or *protractor*[4,8,23,24,27,39–41] but can also be calculated from the dimensions of the *sessile drop*[31–35] or *captive bubble*[34,48]. The *laser assisted* method[26,27] has also been utilised to measure the wetting angle of a sessile drop in *equilibrium*. Other methods have been used in material property assessments but not in the contact lens field[44–46].

An alternative, and we believe novel, approach would be to assess the wettability of a rigid contact lens by measuring the mass of liquid adherent to a surface. This may be measured by a relatively simple and reliable system. After one of the lens surfaces has been wetted, the retained mass of liquid on the surface is weighed. The mass of liquid adhering to the surface is proportional to its wettability (see discussion).

Table 2. Wetting angle methods and measurement technique used to determine the wettability of the contact lens and materials (various authors)

Measurement techniques	*Sessile drop*	*Captive bubble*	*Meniscus*
Dimensions	34–38	37,48	32
Goniometer	4,7,8,23–26, 39–41	7,10,13,14, 16,18,41	29,32
Photographic	36,42	19	19
Projection	27,28,34,43	—	18,20,22
Laser assisted	26,27	—	—
Reflecting	41	—	43

Reference numbers shown.

Despite a plethora of papers in the literature and opinions such as those given by Lakkis *et al.*[47] who stated that 'wettability is among the most important properties of RGP materials to be followed by Dk in the order of importance', there is much confusion and little consistent information available to the contact lens practitioners on this subject[49,50]. The aim of this paper is to introduce the novel approach for measuring the ability of the rigid contact lens surfaces to attract the liquid.

Methods

A novel approach and the equilibrium sessile drop (laser assisted)[26] method were both employed to determine the wettability of hydrated and unhydrated rigid contact lenses. The apparatus utilised to apply the adherent drop and measure *the mass of liquid adhered* to the surface of contact lenses was as follows.

(1) A digital balance scale (Mettler AE50) with a resolution of ±0.01 mg. The balance was able to measure positive and negative weight changes between 0.1 mg and 15 g.
(2) Two micrometer manual positioning components with two platforms in one device. A set of tweezers on the upper platform, to hold the contact lens suction holder. This could be manoeuvred vertically into a container which was positioned on the lower platform (*Figures 1–4*).
(3) Thermometer and humidity indicator to measure ambient air conditions.

Five lenses for each of five different rigid contact lens materials (PMMA, Boston IV, Boston RXD, Equalens and Polycon II) were measured. All lenses had the same specification of 8 mm FOZR, 0.2 mm centre thickness and a total diameter of 9.5 mm and were manufactured at City University contact lens laboratory. The front lens surfaces were cut by one lathe with the same set of diamonds. Both front and back lens surfaces were polished for 1 min with Silo-O2-Care. The lenses were cleaned with Isobar liquid in the last stages of manufacture. Before measurement the lenses were cleaned with L.C.65 surfactant cleaner and washed repeatedly with distilled water; they were then soaked for 24 h in distilled water. The hydration process was reversed by leaving the lenses for 24 h in a room temperature of 23°C (±2) with a humidity of 30–50%.

The lens was first weighed prior to wetting the front surface. It was then lowered until it just touched the liquid using the micrometer screw, and then lowered a further 1.5 mm to wet the front surface completely (*Figures 1* and *2*).

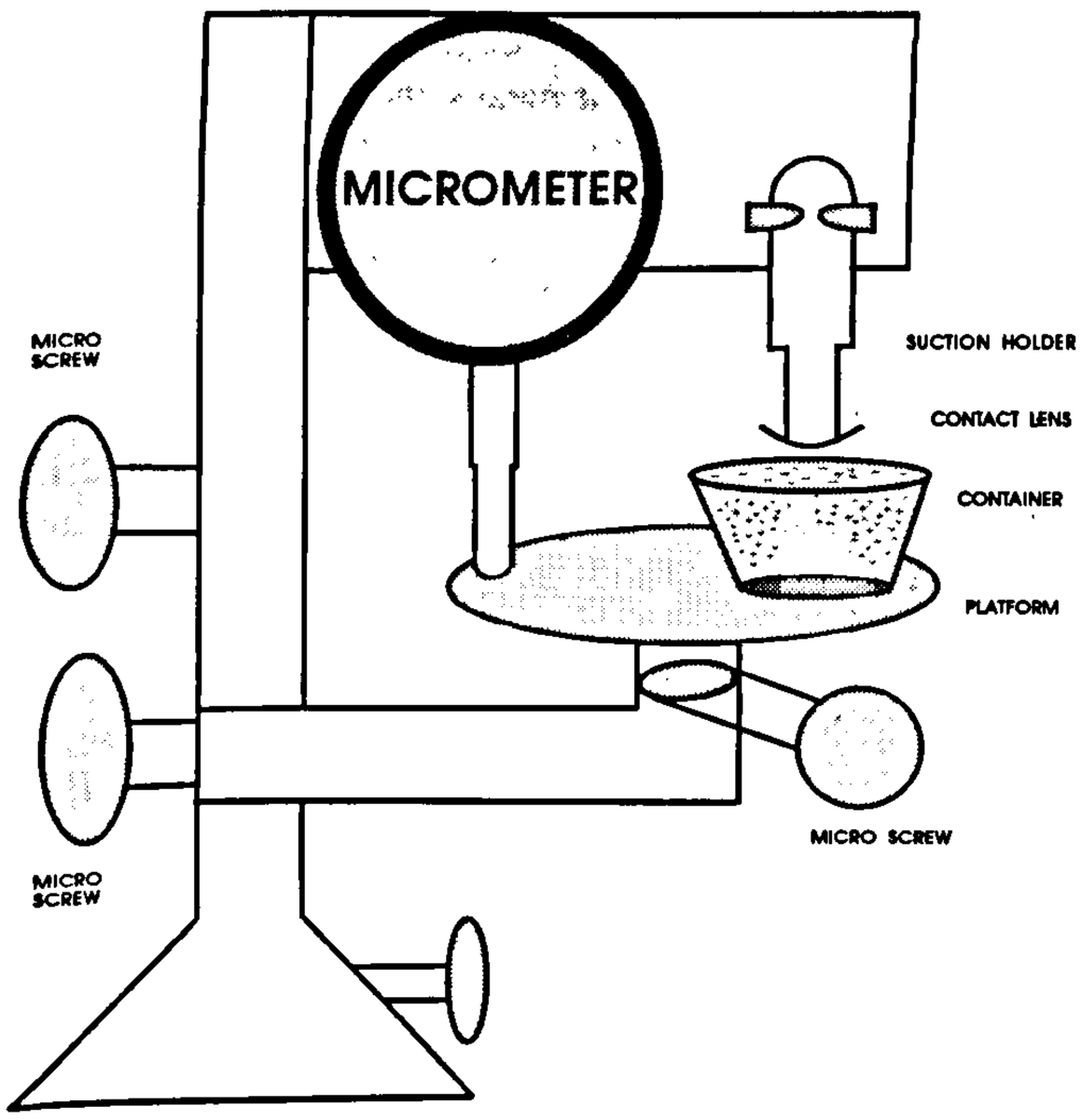


Figure 1. The adherent mass of liquid device diagram.

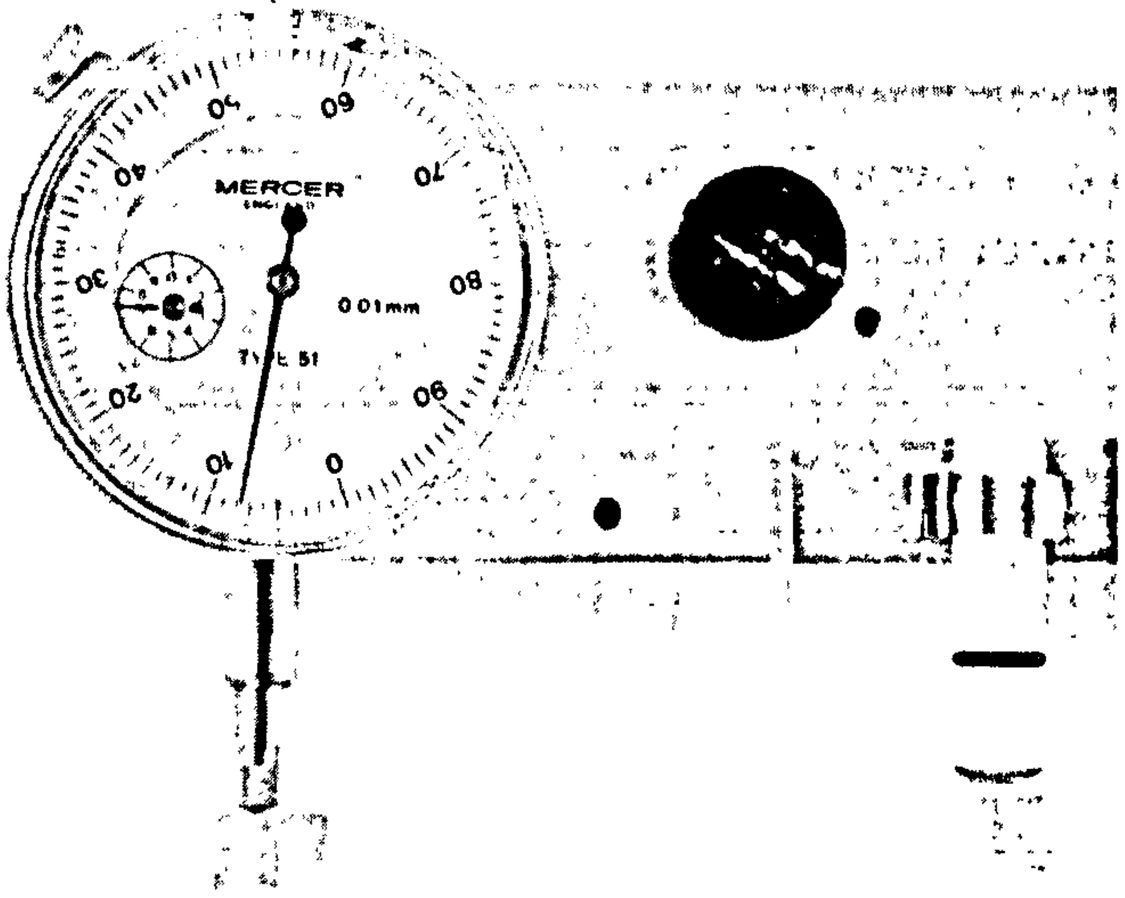


Figure 2. The device to create the adhered mass of liquid on contact lens surface.

After 30 seconds the wetted lens was removed and placed on the balance (*Figures 3* and *4*). The weight of adhered liquid was obtained by subtracting the total weight of the contact lens and adhered liquid from the original lens weight. This procedure was repeated four times for each contact lens.

The laser assisted method is based on reflection of a laser

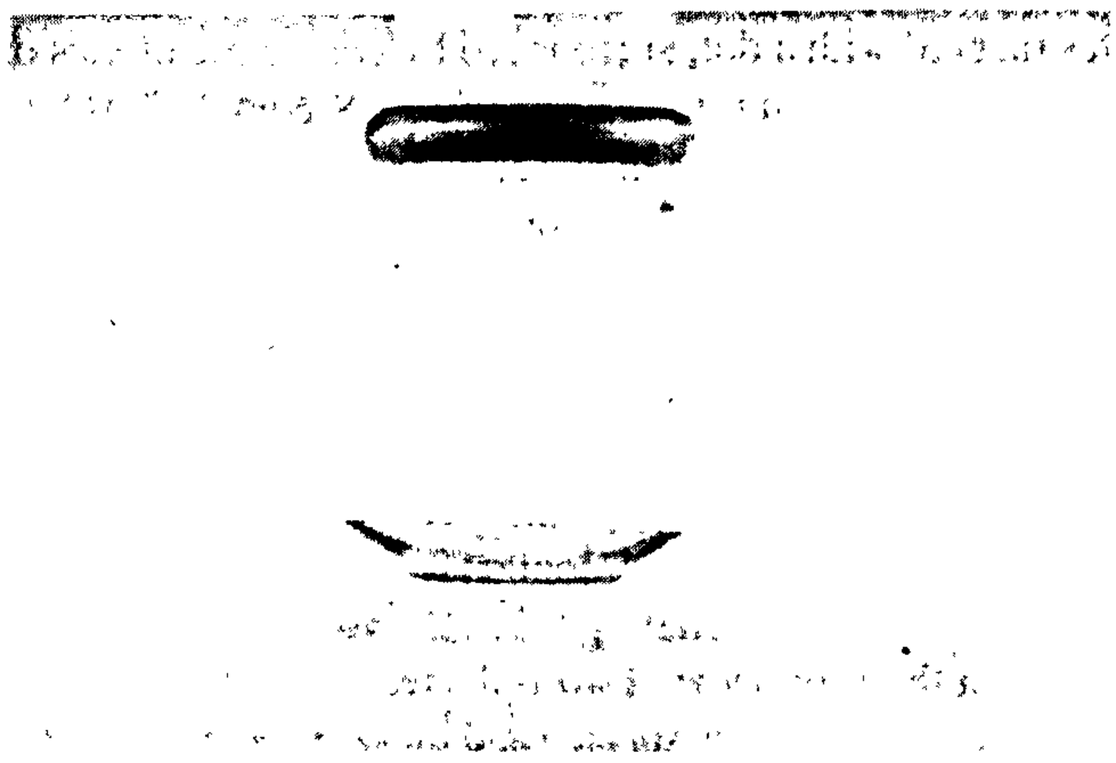


Figure 3. Surface tension, adhesion force and air–liquid–PMMA interface.

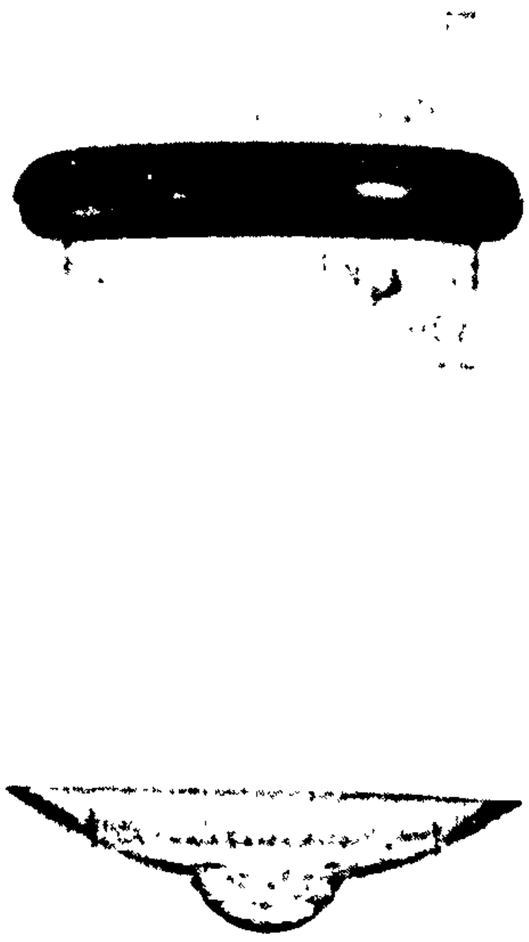


Figure 4. Adhered mass of liquid on the rigid lens.

beam at the point of *solid–liquid–air interface* and is suggested to be less subjective, and superior to goniometry[26,27]. A helium–neon laser with a maximum power of 1 mW, was clamped to the left side of an optical triangular bench. The laser beam travelled parallel to the optical bench and was incident at the centre of a wetting angle indicator (a paper protractor drawn by a computer), which could read both 120° clockwise and anticlockwise. The anticlockwise and clockwise sections were separated by a zero central line. The protractor was mounted 155 cm away from the laser on the optical bench and could be rotated about the axis of the laser beam. The contact lens platform was mounted on a manual positioning component for horizontal,

vertical and rotary movement. The centre of the platform was marked with a dot, surrounded by concentric circles of 1, 2, 3, 4 and 5 mm radii. A +7.00 DS convex lens was fixed 120 cm away from the laser in order to focus the laser beam on to the centre of the contact lens surface which was placed at the centre of the platform. A 10 μl syringe with a needle diameter of 0.46 mm was fixed vertically above the platform to deliver a 3 μl saline sessile drop on to the front surface apex of the contact lens.

By moving the Z and Y translators, the laser beam was directed to the sessile drop/contact lens interface. The laser beam at the contact angle produced two reflection pattern strips on the protractor. Two reflected lines are produced, one by the contact lens surface and the second by the sessile drop of the solid–liquid–air interface. In order to have the narrow laser strips on the protractor, the laser beam was focused on the interface. The zero line of the protractor was aligned with the first reflected line then the second reflected line showing the liquid–contact lens interface wetting angle was measured on the protractor. The measurements were made in dim light within 1 min of drop delivery. The procedure was also repeated four times for each contact lens.

Results

The means and standard deviations of the adhered mass of liquid for hydrated and unhydrated states on each set of the rigid contact lenses are illustrated in *Figure 5*. The means and standard deviations of sessile drop wetting angle for hydrated and unhydrated contact lenses are plotted in *Figure 6*. An analysis of variance (ANOVA: single-factor, t-test: paired two-sample for means and F-test: two-sample for variances) at the $P < 0.05$ level of significance were performed on the results of the studies.

There was a significant difference between the mass of adhered liquid on different materials for both hydrated and unhydrated contact lenses (ANOVA: single-factor, $P < 0.00001$). In the unhydrated state, PMMA (12.1 mg × 10, SD = 1.3) attracted the lowest mass of adhered liquid on the surface, hence showing the least hydrophilicity and there was a significant difference between it and the next higher lens which was Polycon II (15 mg × 10, SD = 1.1, t-test, $P < 0.00001$). Equalens (25.7 mg × 10, SD = 1.7) attracted the highest quantity of liquid and showed a significant difference from the other materials (t-test, $P < 0.00001$). There was no significant difference between the values of Boston RXD (19.9 mg × 10, SD = 1.6) and Boston IV (20.2 mg × 10, SD = 1.9, t-test, $P < 0.6$). However, there was a significant difference between them and Polycon II (t-test, $P < 0.00001$). The hydrophilicity values of unhydrated materials and the rank order of wettability are illustrated in *Tables 3* and *4*, which would be summarised as:

Equalens > Boston IV ⩾ Boston RXD > Polycon II > PMMA.

There were significant (ANOVA: single-factor, $P < 0.00001$) increases in the adhered mass of liquid on all

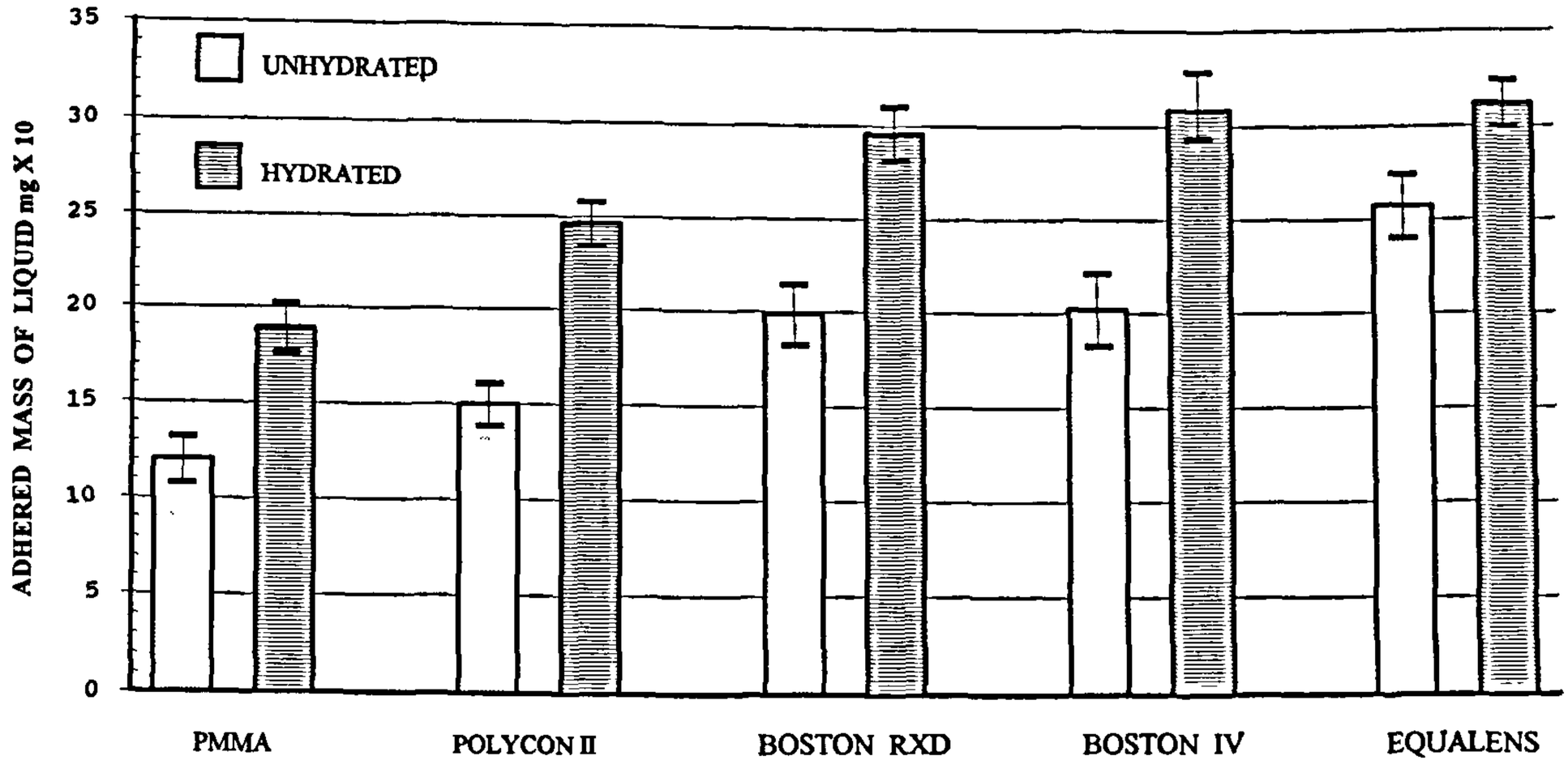


Figure 5. Mean values of adhered mass of liquid of five different hydrated and unhydrated rigid contact lenses are plotted to show the hydrophilicity of materials.

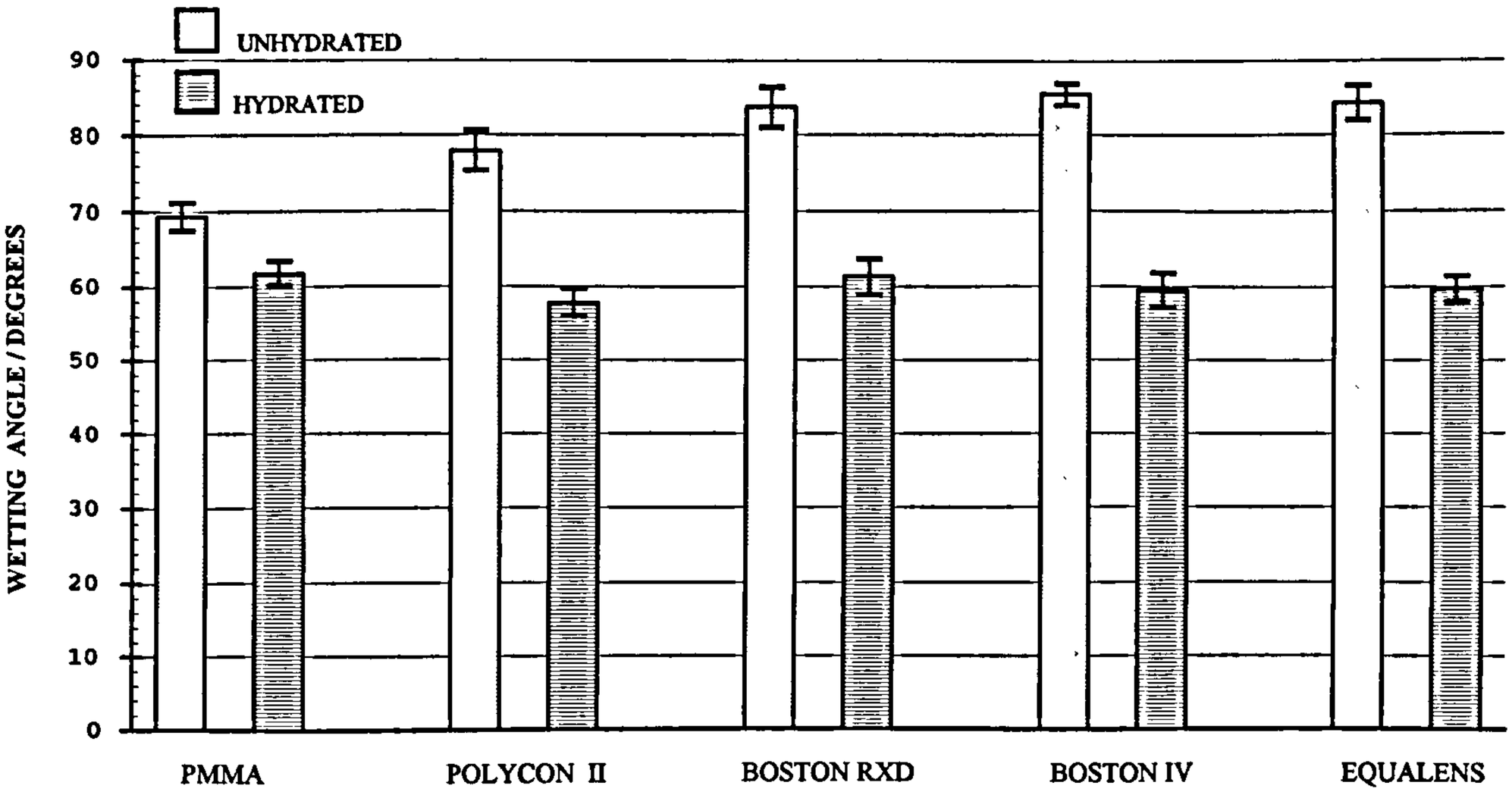


Figure 6. Mean values of wetting angle of five different and hydrated and unhydrated rigid contact lenses are plotted using the laser assisted method.

Table 3. Comparison of the wettability of Boston IV, Equalens, Boston RXD, Polycon II and PMMA lenses using adhered liquid balance, sessile drop laser assisted equilibrium and captive bubble methods (literature values)

Adhered mass of liquid and wetting angle

Methods	*Adhered mass*				*Sessile drop*				*Captive bubble*
Material	*Unhydrated (mg × 10)*	*SD*	*Hydrated (mg × 10)*	*SD*	*Unhydrated (mg × 10)*	*SD*	*Hydrated (mg × 10)*	*SD*	*Hydrated (mg × 10)*
Equalens	25.7	1.7	31.2	1.2	84.3	2.3	59.6	1.7	30
Boston IV	20.2	1.9	31.15	1.7	85.5	1.5	59.4	2.3	16
Boston RXD	19.9	1.6	29.6	1.4	83.7	2.6	61.3	2.4	–
Polycon II	15.0	1.1	24.6	1.2	78.0	1.3	58.0	2.0	20–46
PMMA	12.1	1.3	18.9	1.3	69.3	2.6	61.7	1.6	19–90

SD, standard deviation.

Table 4. Comparison of the wettability of Boston IV, Equalens, Boston RXD, Polycon II and PMMA lenses using the values of the adhered mass of liquid, sessile drop laser assisted equilibrium and captive bubble methods (from the literature) in ranking order

Wetting angle	*Adhered mass of liquid*		*Sessile drop*		*Captive bubble*
Material	*Unhydrated*	*Hydrated*	*Unhydrated*	*Hydrated*	*Hydrated*
Equalens	4	4	1	2–3	3
Boston IV	4	4	1–2	2–3	4
Boston RXD	3	3	2	1	–
Polycon II	2	2	3	4	2–3–4
PMMA	1	1	4	1	1–2–3–4

hydrated contact lens materials as compared to the unhydrated contact lenses: 21.4% Equalens; 48.7% Boston RXD; 56.8% PMMA; 54.6% Boston IV; and 64% Polycon II. Equalens (31.2 mg × 10, SD = 1.2) and Boston IV (31.15 mg × 10, SD = 1.7) showed the greatest hydrophilicity of all five materials although there was no significant difference between them (*t*-test, $P < 0.9$). Boston RXD (29.6 mg × 10, SD = 1.4) had a lower ability to attract the liquid and there was a significant difference between it and the next higher material which was Boston IV (*t*-test, $P < 0.005$) and also a significant difference to the next lower lens that was Polycon II (24.6 mg × 10, SD = 1.2, *t*-test, $P < 0.00001$). PMMA (18.9 mg × 10, SD = 1.3) had the lowest capability to adhere liquid and there was a significant difference between PMMA and Polycon II (*t*-test, $P < 0.00001$). The hydrophilicity of hydrated contact lens materials would be ranked as (*Tables 3* and *4*):

Equalens ⩾ Boston IV > Boston RXD > Polycon II > PMMA.

The wetting angle values of unhydrated contact lens materials measured with the laser assisted method showed a significant difference between them as we expected (ANOVA: single-factor, $P < 0.00001$). PMMA (69.3°, SD = 2.6) had the lowest wetting angle and there was a significant difference to the next material which was Polycon II (78°, SD = 1.3, *t*-test, $P < 0.00001$). Boston IV (85.5°, SD = 1.5) had the highest wetting angle value and there was no significant difference between it and Equalens (84.3°, SD = 2.3, *t*-test, $P < 0.1$). There was a significant difference between Boston RXD (83.7°, SD = 2.6) and Boston IV (*t*-test, $P < 0.02$).

The wetting angle values on the 24 h hydrated contact lenses showed a significant decrease in wetting angle for all the materials, which indicated an increase in the wettability in comparison with the unhydrated state (ANOVA: single-factor, $P < 0.00001$). The decrease in wetting angles varied: 9.9% PMMA; 25.2% Polycon II; 26.7% Boston RXD; Equalens 29.3%; and 29.4% Boston IV. There was no significant difference between Boston IV (59.4°, SD = 2.3) and PMMA (61.7°, SD = 1.6, *t*-test, $P < 0.6$) and also no significant difference between Equalens (59.6°, SD = 1.7) and Boston RXD (61.3°, SD = 2.4, *t*-test, $P < 0.8$). There was, however, a significant difference between Polycon II (58°, SD = 2) and Boston IV (*t*-test, $P < 0.02$). The wetting angle of all five materials after 24 h soaking stabilised at a close range level of (58–61.7°) which suggested little difference between the wettability of the five hydrated lens materials.

Discussion

The experimental results demonstrate that the mass of water adhering to a contact lens surface provides a measurement of wettability which is in agreement with the literature. However, it is perhaps not obvious why the mass of water is a suitable measure of wettability and so we present a qualitative explanation as to why the method reported here is valid. All materials in this study had the same front surface radius of curvature (8 mm) and were immersed 1.5 mm (the saggita of the FS curve) into the water after point of contact. Therefore, the surface area of the contact lens exposed to the water is a constant for all samples. As the lens is lifted from the water, the surface tension, which is constant irrespective of the volume of the water, acts to 'sweep' the water molecules from the surface of the lens. Towards the edge of the lens (at the start of removal), the surface tension acts at a large angle (perhaps 70–80°) to the adhesion force and it is relatively easy for the molecules to be moved towards the lens apex (*Figure 7a*). Nearer the lens apex, the component of the adhesion force opposing the movement is greater and there is less chance of moving the water molecules (*Figure 7b*). When the adhesion force balances the surface tension, any further upward force goes to break the molecular bonds in the surface at which point the water drop on the lens separates from the main body of the water (*Figure 7c*). Since the surface tension and the intermolecular spacing are constant for all samples, the only variable affecting the mass of water adhering to the surface is the adhesion force.

To further confirm the above arguments, the shape of the adhered mass of liquid was investigated for the five contact lens materials in this study. A travelling microscope was used to locate nine points on the air–water–contact lens interface of hydrated contact lenses (*Figures 7* and *8*). The potential energy is a minimum for any system in equilibrium and hence we would expect the surfaces of the drops to be spherical. (It can be shown mathematically that a sphere has minimum surface area for a given volume.) Best fit spherical surfaces were calculated from the data (coefficient of variation, 3.86–8.66%) and are shown, together with the lens surface, in *Figure 8* (data points and error bars not shown for clarity). The drops are all spherical (within error), and have approximately the same thickness between the lens surface vertex and the drop apex (*Figure 8*). This is expected since the distance between these apices primarily depends upon the surface tension and the intermolecular forces holding the water molecules together, both of which are constant. However, evaporation and gravity can act to distort the shape and it is these factors which contribute to the errors.

A measure of how well the adhered mass technique and the laser assisted sessile drop method can distinguish between different materials may be obtained by performing a single variable analysis of variance. The values were computed for both unhydrated and hydrated lenses and for both measurement techniques. All the *F* (ANOVA: single-factor and *F*-test) values were greater than the 5% critical level (2.47) and therefore indicate a statistically significant

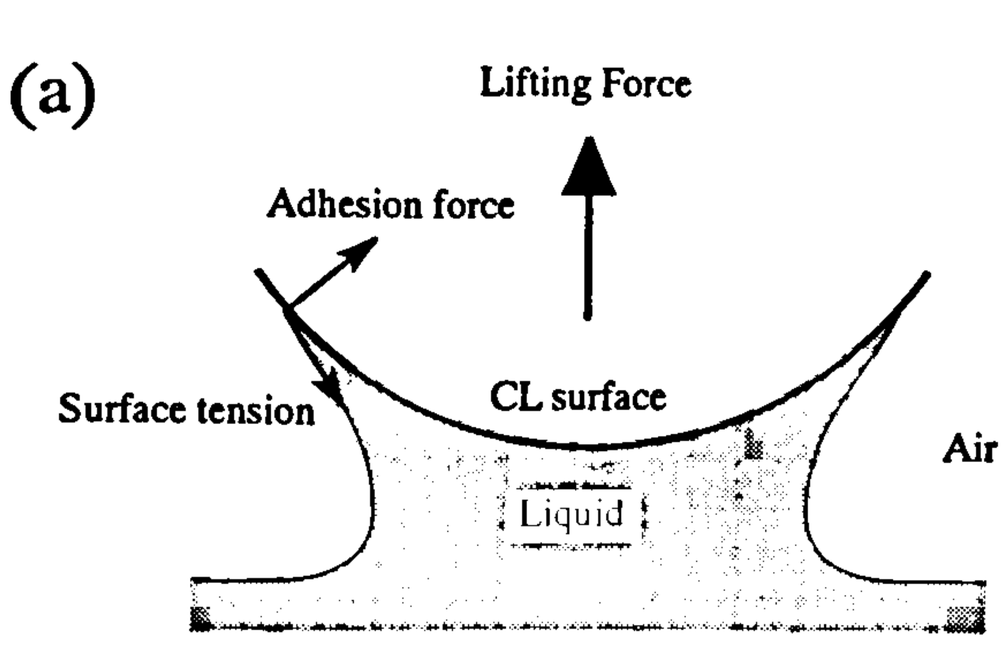


Figure 7. Explanation of drop size on the contact lens surface. (*a*) Surface tension acting at a large angle to the adhesion force; any water molecules are easily moved at this stage. (*b*) The adhesion force is now more strongly opposing any further movement of water. (*c*) Any further lifting provides the energy to break the surface tension and then separates from the main body of the water.

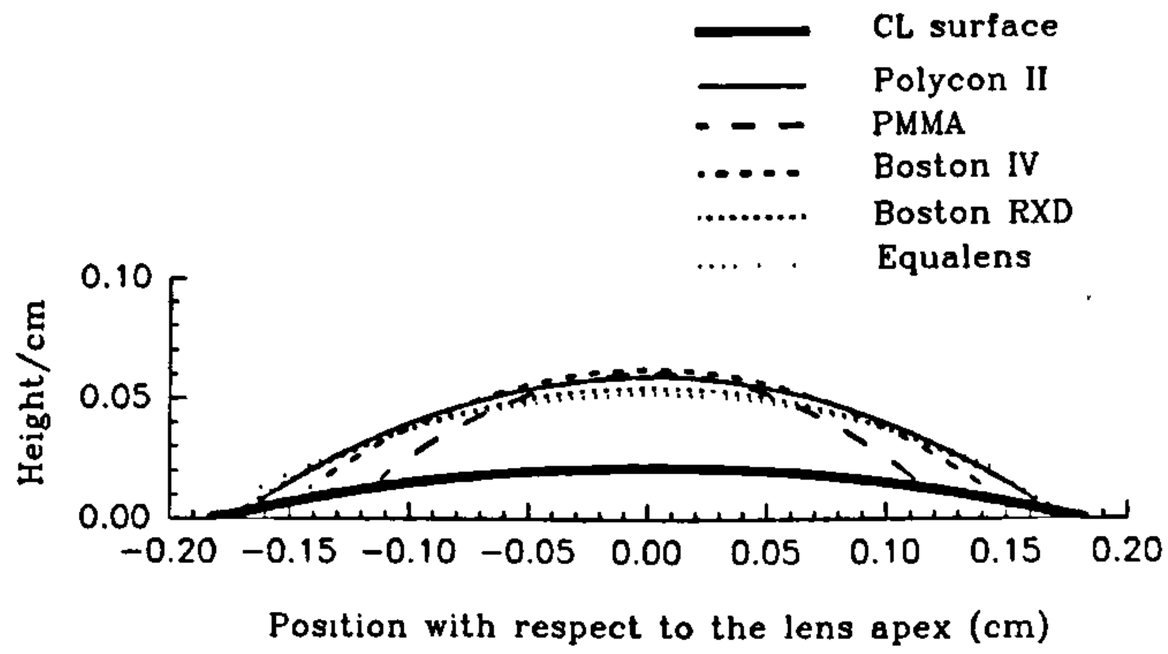


Figure 8. Disposition of adherent liquid on the contact lens materials.

difference between the materials. However the F values obtained using the laser assisted sessile drop method ($F = 180.7$ unhydrated and $F = 7.8$ hydrated) are significantly lower than the values for the adhered mass method ($F = 222.6$ unhydrated and $F = 289.8$ hydrated). This indicates that the adhered mass method has a greater ability to distinguish between types than the laser assisted method.

It has been suggested that wetting angle measurement *in vitro* gives the best rank order description of lens wettability *in vivo*[7]. Thus, from parametric results and statistical significance of the adherent mass of liquid, we were able to rank the wettability by non-parametric ranking order. The higher the number, the greater the lens wettability using this system. Four different groups of contact lens wettability were identified for both hydrated and unhydrated materials (*Table 4*).

Contact lenses *in vivo* are hydrated so the wettability *values and* ranking order of hydrated lenses are likely to be more relevant. The wetting angle values for all five hydrated materials were in a small range of 58–61.7°. The ranking order of wetting angle values showed three with a significant difference and two with no significant differences both for the hydrated and unhydrated state, which indicated a low hydrophilicity. However, the ranking order for the *adhered mass of liquid* method resulted in four with a significant difference and one with no significant difference. Furthermore, on comparison of the two methods, the adhered mass of liquid provided 25% more confidence than the sessile drop wetting angle which is confirmation of the reliability of the new method. Nevertheless the results determined by the new technique gave comparable orders of ranking for wettability to that obtained by current techniques (*Table 4*). The advantages of this technique are that as the entire lens surface is immersed, it reproduces more closely the *in vivo* situation where the whole of the lens is wetted, unlike the sessile drop method where only a small area of the lens has its wettability measured.

The ranking system of the results, which is given in *Table 4*, is more likely to be of value in clinical decision making. However, if it is wished to make a comparison with results from other techniques, the most appropriate comparison would be with the receding angle.

A significant increase of adhered mass of liquid on all hydrated materials indicated that all lens surfaces became more hydrophilic (46%), while the increase of hydrophilicity measured by sessile drop laser assisted equilibrium in hydrated state was less than the new method (25%). The results of the novel approach show less variation than those

given in the literature using the captive bubble technique (*Table 1*).

Unhydrated values have been given as they are widely quoted in the literature. However, we feel they have little relevance to the *in vivo* situation and should be treated with caution. We appreciate that the unhydrated values are in opposition to the accepted view that a low wetting angle equates to better wettability, in that we found samples with a low wetting angle and a high adherent mass. However, this does not invalidate the technique when used on hydrated samples. The variation could well be due to significant changes in surface properties produced by hydration. The technique offers the advantage of simulating the *in vivo* situation, but avoiding the inter-patient variation produced by differences in the subjects biofilm production. The technique is simple and quick and reliable, it may be replicated and utilised by laboratories.

In order to reduce the number of confining factors of the new method, the front surface radii of the lenses were constant. However, aspherical front lens surfaces and differing optic radii may alter the results. It is also suspected that the speed of withdrawing the lens from the liquid, polishing, cleaning, lens surface charge and ionisation of the solution could alter values. Consideration of these different effects will be the topic for a further investigation. The intention of the authors is to utilise the technique on lenses before and after wearing to investigate variation of the lens surface characteristics.

References

1 Pethica, B. A. Contact angles. *Progress Appl. Chem.* **46**, 14 (1961)
2 Elliott, G. E. P. and Riddiford, A. C. Contact angles. *Recent Progr. Surface Sci.* **2**(11), 111–128 (1964)
3 Poster, M. G., Gelfer, D. M. and Fernandez, N. D. Wetting angles of rigid contact lens plastics: the effect of contact lens wear (a). *J. Am. Optom. Assoc.* **57**, 452–454 (1986)
4 Fitzgerald, J. K. A. Comparison of selected rigid gas permeable contact lens material properties. *CLAO J.* **9**(3), 245–248 (1983)
5 Benjamin, W. J. and Simons, M. H. Contact angle update: care regimens and their effect on a rigid silicon–acrylate surface. *ICLC* **11**(18), 500–507 (1984)
6 Benjamin, W. J. Care regime and initial wetting of silicone–acrylate surfaces *in vivo*. *Trans. JBCLAB Con.* **4**, 55–56 (1987)
7 Sarver, M., Bowman, L., Bauman, E., Dimartino, R., Lau, D. and Umeda, W. Wettability of some gas permeable hard contact lenses. *ICLC* **11**(8), 479–490 (1984)
8 Ng, O. C. and Tighe, B. J. Polymers in contact lens applications V. Design and calibration of a technique for 'dissolved' oxygen permeability measurements. *Br. Pol. J.* September, 78–82 (1976)
9 Ng, O. C., Peddle, D. G. and Tighe, B. J. Polymers in contact lens applications VII. Oxygen permeability and surface hydrophilicity of polymers. *Br. Pol. J.* December, 124–130 (1976)
10 Poster, M. G. The wetting angle. *J. Am. Optom. Assoc.* **55**(3), 167–168 (1984)
11 Holly, F. and Refrojo, M. F. Water wettability of hydrogels. *Sym. HMRA Chem.* **19**(31), 252–266 (1976)
12 Poster, G. M., Gelfer, D. and Gooderman, S. Measuring the contact lens wetting angle in a simulated *in vivo* environment. *ICLC* **5**, 51–55 (1978)
13 Anon, N. Determining the wetting angle. *CLAO J.* **4**, 35–39 (1979)
14 Gregonis, D. E., Hsu, R., Buerger, D. E., Smith, L. M. and Andrade, J. D. Wettability of polymers and hydrogels as determined by Wilhelmy plate technique. *Solvent Property.* Pergamon, New York, pp. 120–130 (1982)
15 Cordrey, P. What the papers say. *J. BCLA* **7**(1), 48–51 (1983)
16 Jho, C. Water wettability of polymer materials for contact lenses. *J. Col. Inter. Sci.* **94**(2), 589–592 (1983)
17 Keates, R. H., Ihlenfeld, J. V. and Isaacson, W. B. An introduction to fluoropolymer contact lenses: a new class of materials. *CLAO J.* **10**(4), 332–334 (1984)
18 Madigan, M., Fonn, D. and Holden, B. A. Wettability: an old method reapplied. *Presented to American Academy of Optometrists, Houston, TX, USA* (1983)
19 Fatt, I. Observation of film breaking on model eyes. *BCLA Trans.*, Annual Clinical Conference, Glasgow, pp. 20–32 (1990)
20 Davidson, T. and Lei, G. Preparation of polymer film for contact angle measurement. *Br. Pol. Sci. J.* **9**, 569–573 (1971)
21 Lemp, M. D. and Holly, G. J. Ophthalmic polymers as ocular wetting agents. *Arch. Ophthalmol.* **14**, 15–20 (1972)
22 Madigan, M., Holden, B. A. and Fonn, D. A new method for wetting angle measurement. *IEC* **2**(1), 45–48 (1986)
23 Huff, J. W., Egan, D. J. and Katich, M. J. Parameter and wettability influences on rigid contact lens wettability. *Am. J. Optom. Physiol. Opt.* **65**(9), 717–721 (1988)
24 Hill, M. R. How wet are your patient's tears? *ICLC* **4**, 46–49 (1977)
25 Sunny, M. C. and Sharma, C. P. Surface modification of corneal contact lens with phosphoryl choline by glow discharge. *Biomat. Art. Cells Immob. Biotech.* **19**(3), 599–612 (1991)
26 Bush, J. F., Huff, J. W. and MacKeen, D. L. Laser assisted contact angle optics measurements. *Am. J. Optom. Physiol. Opt.* **65**(9), 722–728 (1988)
27 Knick, P. D. and Huff, J. W. Effects of temperature and conditioning on contact lens wetting angles. *CLAO J.* **17**(3), 177–180 (1991)
28 Madigan, M. and Holden, B. A. Preliminary report: lens wear and its effect on wetting angle. *IEC* **2**(1), 36–44 (1986)
29 Bikerman, J. J. *Physical Surfaces*, Academic Press, New York, USA (1970)
30 Smith, L., Doyle, C., Gregonis, D. E. and Andrade, J. D. Surface oxidation of *cis–trans* polybutadiene. *J. A. Pol. Sci.* **26**, 1269–1276 (1982)
31 Smith, L., Bowman, L. and Andrade, J. D. Contact angle analysis of hydrated contact lenses. *Biomed. Pol. Int. Sym. Contact Lenses and Artificial Eyes*, University of Durham, July, pp. 279–284 (1982)
32 Blodgett, K. B. Film built by depositing successive monomolecular layers on a solid surface. *J. Am. Chem. Soc.* **57**, 1007–1022 (1935)
33 Adam, N. K. and Jessop, G. J. Angles of contact and polarity of solid surfaces. *J. Chem. Soc.* **127**, 1863 (1925)

34 Lin, H. W. and Pinkus, A. G. Assessment of hydrophilicity by contact angle measurement. *Opt. Weekly* **64**, 56–60 (1973)

35 Bartell, F. E. and Zuidema, H. Wetting characteristics of solids of low surface tension such as talc, waxes and resins. *J. Am. Chem. Soc.* **58**, 1449–1454 (1936)

36 Harris, M. G., Oye, R., Hall, K. and Fatt, I. Contact angle measurements on hard contact lenses. *Am. J. Optom. Assoc.* **50**, 446–451 (1973)

37 Mack, G. L. and Lee, D. A. Measurements of the dimensions of small bubbles and drops II. *J. Phys. Chem.* **40**, 169–177 (1936)

38 Farnarier, C., Capo, C., Balloy, V., Benoliel, A. M. and Bongr, P. Simple microscopical measurement of contact angles on transparent substrates. *J. Col. I. Sci.* **99**(1), 164–167 (1984)

39 Fatt, I. Contact lens wettability—Myths, mysteries and realities. *Am. J. Optom. Physiol. Opt.* **61**, 419–430 (1984)

40 Benjamin, W. J. and Ghormley, N. R. Wettability of silicon and silicone–acrylate contact lens materials. *ICLC* **10**(2), 94–99 (1983)

41 Neumann, A. W. and Good, R. J. Techniques of measuring contact angles. *Sur. Col. Sci.* **11**, 31–91 (1979)

42 Li, J. G. and Hausner, H. Wetting and adhesion in liquid silicon/ceramic systems. *Mat. Let.* **14**(5,6), 329–332 (1992)

43 Osipow, L. I. *Surface Chemistry, Theory and Industrial Applications*. Reinhold, New York, USA, pp. 7–23, 232–294 (1962)

44 Langmuir, I. and Schaefer, V. J. The effect of dissolved salts on insoluble monolayer. *J. Am. Chem. Soc.* **59** (November), 2400–2415 (1937)

45 Tomlinson, F. J. and Patron, H. T. A simple method for measuring solid–liquid contact angles. *J. Col. Sci.* **18**, 217–222 (1963)

46 Good, R. J. and Ferry, G. V. The wettability of solids by liquid hydrogen. *Adv. Cry. Eng.* **8**, 306–310 (1963)

47 Lakkis, C., Lindsay, R. G., Harris, M. and Brennan, N. A. RGP lenses manufacture and practitioner perspectives. *Clin. Exp. Optom.* **76**, 14–17 (1993)

48 Andrade, J. D. Surface analysis of materials for medical devices and diagnostic products. *Med. Dev. Diag. Ind.* **2**(6), 22–33 (1980)

49 Benjamin, W. J. In-eye wettability of new rigid gas permeable lenses: worst-case scenario. *JBCLA* **15**(4), 139–142 (1992)

50 Benjamin, W. J. and Bourassa, S. Comparison of two contact lens storage solution preservatives with respect to in-eye wetting of rigid oxygen-permeable lens surface and related factors. *ICLC* **16**(9,10), 273–281 (1989)

Apendix II

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Surface wettability and hydrophilicity of soft contact lens materials, before and after wear

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Summary

Surface wettability and hydrophilicity of pHEMA soft contact lenses were investigated utilising adherent liquid/laser method (ALLM) and adherent liquid/balance method (ALBM). The measurements were carried out before and after periods of 15 min to 2 h contact lens wear. Following the lens removal, the wetting angle of the contact lens of the left eyes and hydrophilicity (maximum force) of the contact lens of the right eyes of the five subjects were immediately measured, respectively, without cleaning (one value for pre-lens wear and eight values for post-lens wear). The wettability of soft contact lenses significantly increased after 15 min of wearing and stabilised at a maximum level after 30 min *in vivo*. Contact lens hydrophilicity was found to decrease as the lens was worn. The reduction continued for up to 1.5 h of wearing, for male cases, and for the female cases, the reduction continued until the end of the experiment.

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Introduction

Several methods have been introduced to create a solid–liquid–air interface. To measure the angle of interface, various techniques were utilised by several investigators, most of which were used on rigid materials[1]. The Wilhelmy balance method is the only method which has been used on soft, hydrophilic, flat materials. However the method has limitations when used on soft contact lenses. On the other hand there are no reports of the sessile drop techniques being used successfully on hydrophilic contact lenses. The manufacturing techniques of soft contact lenses have been found to be important in the final wettability of the material, but there are few reports in the literature. However, a recent study by Shirafkan *et al.*[1] provided a new method to measure the wettability and a novel technique to create a meniscus[2] of solid–liquid–air interface for actual soft contact lenses. They also reported a new method[3] to remove water from a hydrophilic lens surface prior to surface wettability measurements.

The difference between the wettability and hydrophilicity of contact lenses has been discussed by Shirafkan *et al.*[4]. Contact lens surface wettability depends on the ability of a polymer surface to spread and maintain liquid on the lens surface. The wettability of the contact lens surface may be measured when there is a creation of a solid–liquid–air interface on the lens surface. Hydrophilicity is a term which is used to specify the ability of a contact lens material to attract water. This sort of attraction force into the polymer depends on the polymer structure. The aim of this study was to determine the effect of wear on the wettability and hydrophilicity of soft contact lenses.

Methods

Five pairs of unworn soft contact lenses of pHEMA (Hydron Z6, lathe cut, WC 38%, $Dk = 10$) were used for five subjects, two males and three females. The lenses were cleaned with LC 65 surfactant cleaner for 30 s using a brush and tweezers. They were then washed repeatedly with saline and soaked in saline for 24 h.

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Unseparated adherent liquid/laser method (UALLM)

A convex shape stage with a radius of 8.7 mm was utilised for holding the soft contact lens. It was lowered to the back surface of the contact lens which was prepared in the saline container and then adhered to the stage. It was subsequently withdrawn vertically about 1 mm from the container (*Figure 1a*), then tilted and elevated in order to remove the liquid from the contact lens surface (*Figure 1b*). The small amount of saline which remained on the periphery of the lens surface (*Figure 1c*) was removed with a tissue. The stage was then connected to the rod of an adjustable *X*, *Y* and *Z* component. The contact lens was moved towards the saline surface by turning the micrometer screw until the front lens surface just touched the liquid surface (*Figure 2a*). The micrometer scale was adjusted to zero. The lens was then submerged to a depth of 2.5 mm in order to re-wet the lens surface completely (*Figure 2b*) and the lens was withdrawn slowly 1.4 mm from the solution surface (*Figure 2c*). This action caused a solid–liquid–air interface to be created for measuring the wetting angle.

A laser beam[5] was adjusted on the periphery of the lens. It was then further adjusted to produce a reflection from the solid–liquid–air interface. The reflected laser was incident on a protractor which can directly measure the contact angle (*Figure 3*). For the post-wear measurements, the

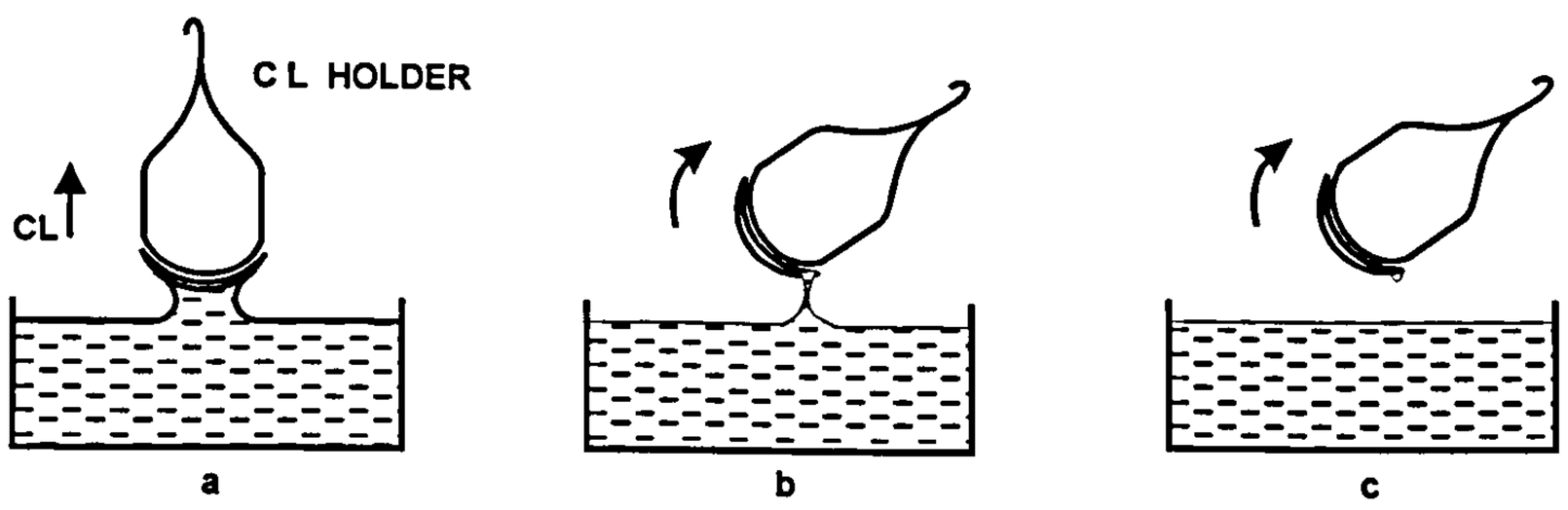


Figure 1. Wetting and removing liquid from hydrated soft contact lens surface.

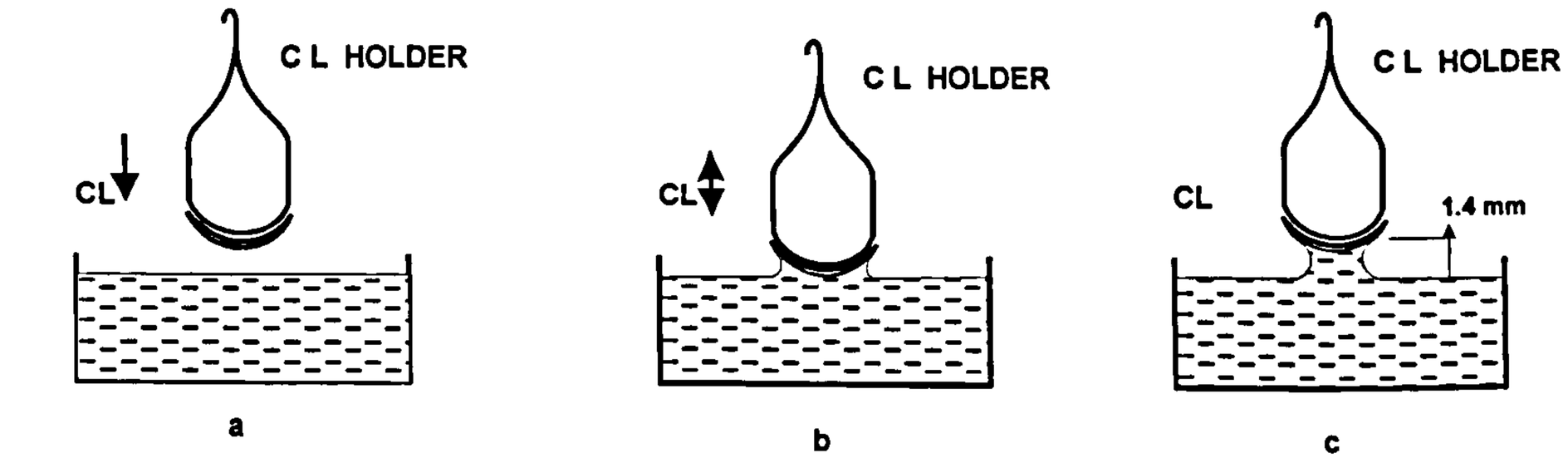


Figure 2. Creation of solid–liquid–air interface.

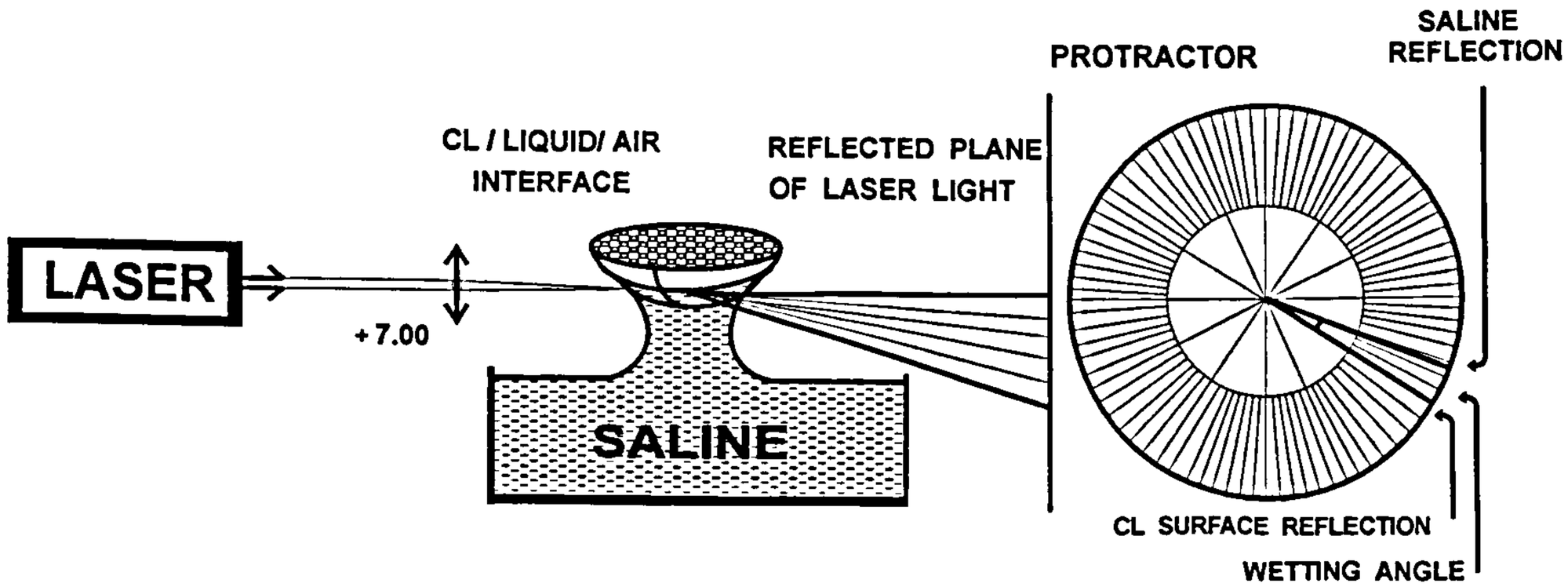


Figure 3. Adherent liquid/laser assisted method, to measure the wetting angle of solid–liquid–air interface.

lenses were directly mounted on the contact lens holder by a suction holder. One pre-wear and eight post-wear (with an interval of 15 min) independent wetting angle measurements were carried out for the right eyes of the five subjects.

Adherent liquid/maximum force (ALMF)

A Cahn (312) balance was utilised in the second part of the study to measure the hydrophilicity of the bulk material. The device consisted of a balance and two stages in a glass cubical box. The upper stage was connected to a balance and was able to move vertically[2]. The speed of movement was 40 μm/s. The container was placed on the lower stage. The position (force and distance) of the upper stage was stored automatically into a computer every second.

The soft contact lens, after preparation, was mounted on the holder as before and attached to the balance. A container of saline solution was placed on the lower platform and the level of the saline surface adjusted to be about 4 mm distance from the contact lens. The lens was moved towards the container until it just touched the liquid. A further movement of 2.5 mm enabled the lens surface to wet completely. After 30 s the lens was withdrawn from the saline until the liquid on the lens surface separated from the liquid of the container. During withdrawal, the force at the contact lens surface increased until, at the critical distance, it started to decrease (maximum force). One pre-wear and eight post-wear (with an interval of 15 min) independent measurements were carried out to determine the hydrophilicity of the material surface for the left eyes of the subjects.

Results

Wettability (unseparated wetting angle)

The mean wetting angle value of the contact lenses for pre-wear measurements was 10.40° (±1.1°) (*Figure 4*). After

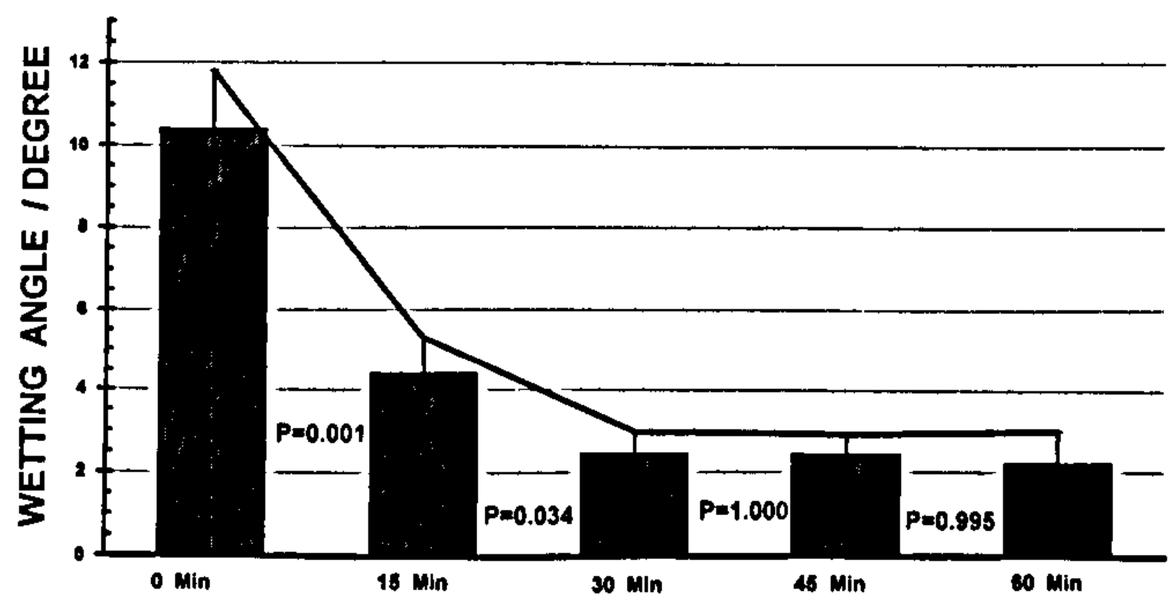


Figure 4. Wettability of the soft contact lenses before and after wear. After 15 min of wearing, the wettability significantly increased. The enhancement of wettability continued to an optimum level, when the lenses were worn for 30 min. Further wearing up to 2 h did not show a significant variation in wettability.

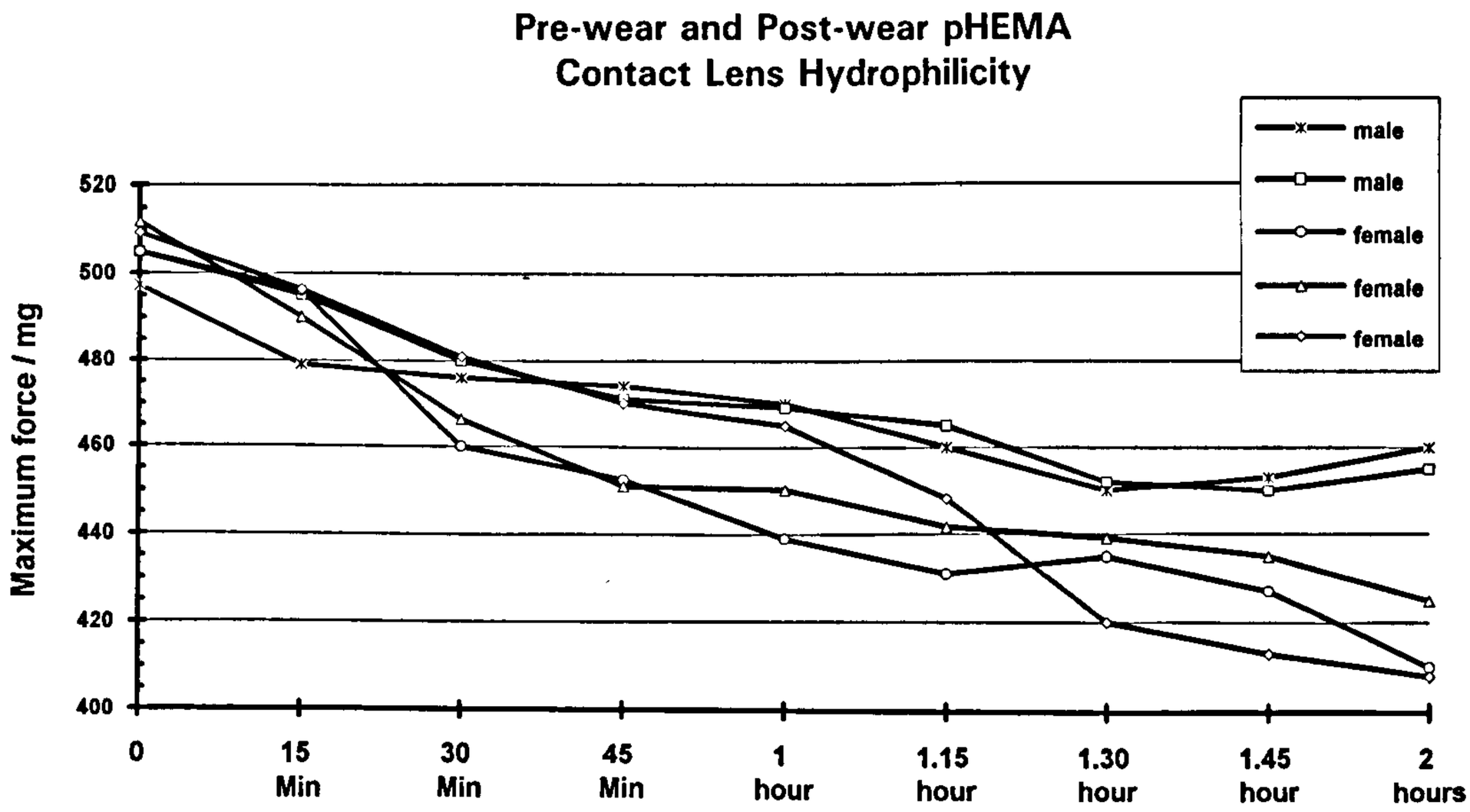


Figure 5. The figure shows that the pre-wearing contact lens hydrophilicity was higher than that after wear. When the lenses were worn for 15 min, the wettability significantly decreased for all subjects. The reduction was continued for up to 1.5 h of wearing, for male cases and, for the female cases, the reduction continued until the end of the experiment.

15 min of wearing, the wettability significantly increased (4.4°, SD = ±1.4°, $P = 0.001$). The enhancement of wettability continued to a maximum level of 2.2° (SD = 1.00°) when the lenses were worn for 30 min. Further wearing for up to 2 h did not show a statistically significant variation in wettability.

Hydrophilicity (maximum force)

Pre-wearing contact lens values of hydrophilicity (maximum force) were higher than the other values (mean = 504 mg, SD = ±6.6 mg) (*Figure 5*). When the lenses were worn for 15 min, the values significantly decreased for all subjects (mean = 489 mg, SD = ±7 mg, $P = 0.008$). The reduction was continued for up to 1.5 h of wearing, for male cases (450 mg) and then appeared to increase slightly. For the female cases, the reduction continued until the end of the experiment.

Discussion

The results of wetting angle measurements showed the ability of the lens surface to prevent coalescence of the liquid. In pre-wear, the mean wetting angle was 10.40° when the lens was worn; the tear film components varied the surface charges, causing a reduction of the contact lens surface tension, which resulted in a lower wetting angle. Further contact lens wear enhanced these effects further, lowering the surface tension. After 30 min of wearing, the wetting angle showed no further reduction, possibly because surface charge equilibrium was reached. The clinical consequence of this is that the wettability of this type of contact lens after 30 min of wearing would be at a maximum level.

The second experiment showed that after wear, lenses attracted water with lessening forces compared to unworn lenses. Possible causes of this reduction in hydrophilicity could include absorption of protein or lipid to the surface of lens. The inter-subject variability suggested that the selection of an appropriate material for a particular patient might be assisted by such measurements.

Acknowledgement

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References

1 Shirafkan, A., Woodward, E. G. and Hill, C. C. A novel approach to measuring the wettability of rigid contact lenses. Mass measurement of the adherent liquid on the rigid lens surface. *Ophthal. Physiol. Opt.* (in press)
2 Shirafkan, A., Woodward, E. G., Port, M. J. A. and Hill, C. C. Wettability of rigid contact lens materials measured by adherent liquid approach. *18th Annual Clinical Conference and Exhibition*, 3–5 June, Torquay, UK. *Br. C. L. Assoc.* **17**, 4 (1994)
3 Shirafkan, A., Woodward, E. G., Port, M. J. A. and Hull, C. C. Wettability of rigid contact lens material utilising adherent liquid. *Optom. Vision Sci.* (in press)
4 Shirafkan, A., Woodward, E. G., Hull, C. C. and Port, M. J. A. Variation in wettability and hydrophilicity of soft contact lenses with differing techniques of manufacture. *Optom. Vision Sci.* (in press)
5 Bush, J. F., Huff, J. W. and MacKeen, D. L. Laser assisted contact angle measurements. *Am. J. Optom. Physiol. Opt.* **65**, 722 (1988)