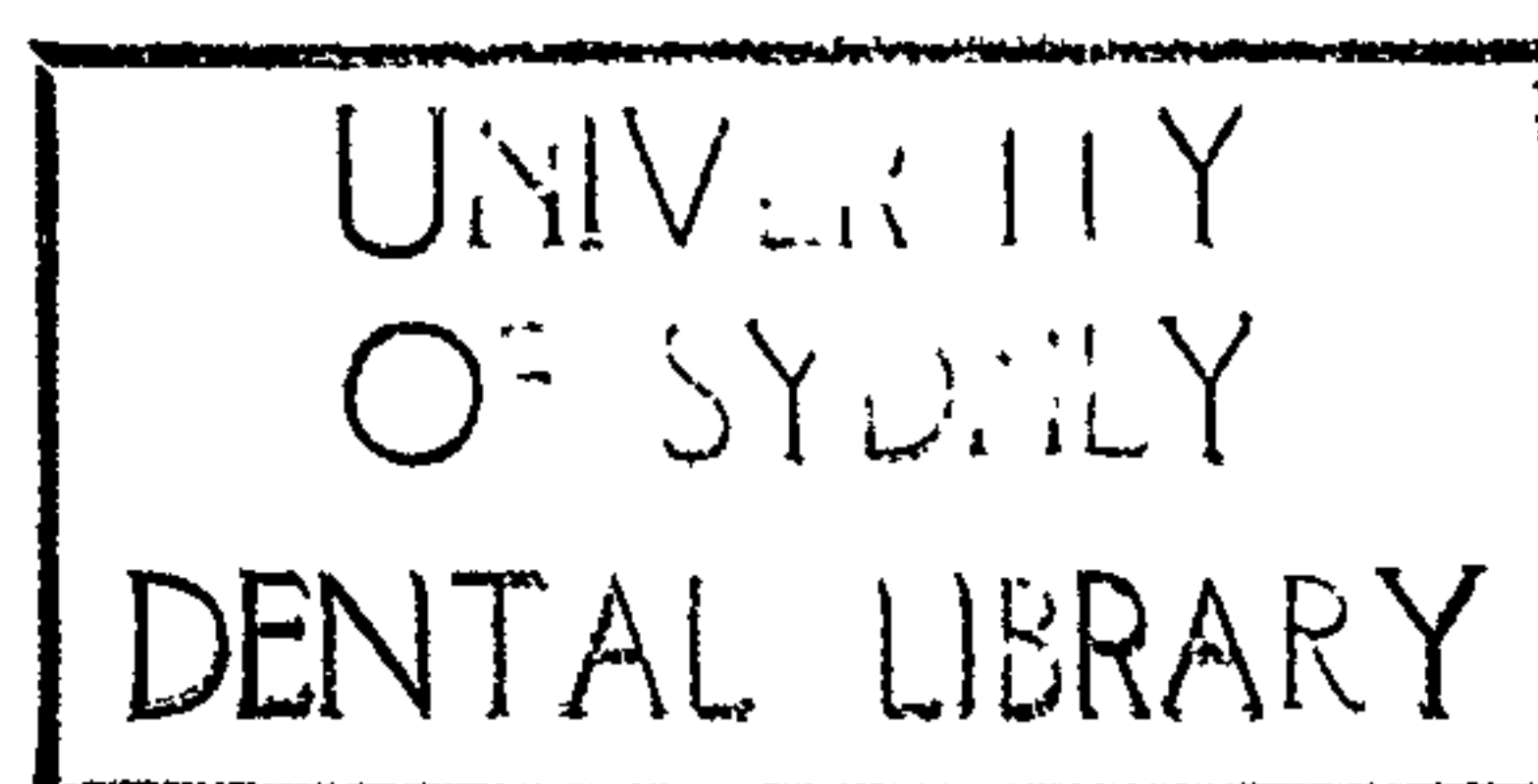


**ORTHODONTIC BONDING TO
DENTAL GOLD ALLOY**

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SUMMARY

To test the effectiveness of bonding orthodontic attachments to dental gold alloy, orthodontic lingual buttons were bonded to 80 roughened flat gold alloy surfaces by means of three commercially available gold bonding agents and a conventional composite restorative material. Bonding to gold was found to be effective, when compared with acceptable shear strength values for adhesives resisting orthodontic forces. Gold bonding however produced bond strength values of only one half of comparable enamel bonding techniques. Of the four materials used in this experiment none exhibited a significantly higher bond strength value. Electron microscopic examination of debonded gold surfaces produced little evidence of a true joint between adhesive and substrate. There appears little justification for the use of specific gold bonding agents in place of conventional bonding agents when adhesion is desired to dental gold alloys.

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DEDICATION

This thesis is dedicated to my wife, Pam, who during the past two years has had to manage a full-time dental practice, cope with an additional part-time job, maintain a household, adopt the role of both parents to Amanda and James, and somehow still found to find time to encourage and motivate me.

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1. INTRODUCTION

"The search for hard tissue adhesives should utilize knowledge gained from available sources and comprise studies of idealized systems and the Edisonian trial and error approach"
(Buonocore 1970).

Until this century the selection of suitable adhesives and application techniques was an art depending on the use of glue formulations made from fish and animal products or cements made from inorganic slurries or solutions (Zisman 1963). Since 1955, when Buonocore first developed a direct bonding system there have been many materials produced which claim direct-bonding success. The difficulty in evaluating these materials is that firstly, much of the product research has been conducted by the manufacturers of the product and the results might conceivably be biased. Secondly, there has been no standardization of techniques for testing the products (Johnson, Hembree & Weber 1976) and, therefore it is hard to compare results from different studies. Finally, new products are being developed all the time making it difficult to compare these to products previously marketed.

It is the aim of this study to measure and compare shear bond strengths, at different times, of orthodontic attachments bonded to a roughened dental gold alloy surfaces using a variety of commercially available gold bonding agents, and to examine, with the aid of a scanning electron microscope, the extent of the bond obtained.

Dietz and Gianelly (1975) point out that for an orthodontic bonding system to achieve acceptance it must be able to support shear and tensile forces of the magnitude of currently available orthodontic materials as well as being able to maintain this strength for the duration of treatment in the oral environment.

In recent times, banded orthodontic attachments have been replaced by bonded attachments. The advantage of bonded brackets is that they are easier to place, and placement can be done more rapidly and more comfortably than can be done with banded attachments (Gorelick 1977). There is no need for separation of the teeth, band spaces are eliminated, oral hygiene is easier to maintain (Khowassah, Bishara, Francis & Henderson 1975; Zachrisson 1977), and bond strength does not deteriorate with time (Zachrisson 1977). In addition, if a bracket comes loose the patient is immediately aware and can notify the orthodontic office (Maijer 1982).

Maijer (1982) notes that the disadvantage of bonding is that it is difficult to place brackets on teeth that have received large ceramic crowns or lingual restorations.

In the past twelve years, orthodontics has been increasingly applied to the adult dentition (Newman, Dressler & Grenadier 1984). With adult orthodontics comes the problem of bonding to esthetic restorative materials such as composite, porcelain and gold. Whilst a stainless steel band is still suitable for a posterior tooth, it is unsightly in the anterior region and cannot be used on the abutment teeth of fixed bridges. The adult patient is more

likely to request lingual orthodontic appliances and this further increases the need to be able to bond to gold alloy surfaces.

Several authors have already investigated the uses of coupling agents and bonding to metal in restorative dentistry (Paffenbarger, Sweeney & Bowen 1967; Marshall 1977; Eames & Rogers 1979; Dent 1979; Highton, Caputo & Matyas 1979; Jones 1982; Shaw & Tay 1982; Calamia 1983; Milhauser 1983; Heymann 1984). Wood, Jordan, Way and Galil (1986) commented that new dental materials have recently been produced which provide a silane coupling bond between resins and porcelain. They noted that little research work has been done in the field of orthodontically bonding to porcelain and that none has been done in the area of bonding orthodontic attachments to gold alloy surfaces.

2. GOLD

In 1907, Taggart introduced the technique of casting gold inlay restorations. He made use of the ancient, lost wax process and developed an air pressure device for forcing a small amount of pure gold into the investment mold (Phillips 1982).

2.1. COMPOSITION OF DENTAL GOLD ALLOYS

According to the requirements of the American Dental Association specification number 5, the table reproduced below from Phillips (1973), reflects the composition of modern casting gold alloys.

ALLOY TYPE	COMPONENT (%)					
	Gold	Silver	Copper	Palladium	Platinum	Zinc
I (A)	80-96	2-12	2-6	0-4	0-1	0-1
II (B)	73-83	7-15	6-11	0-6	0-4	0-1
III (C)	71-80	5-13	7-13	0-6	0-7	0-2
IV (D)	62-72	8-17	9-15	0-10	0-8	0-3

The basic alloy is a ternary type of gold, copper and silver. Platinum is rarely used in a type I alloy. As greater strength and hardness are required, platinum and palladium are added to the

alloy. In 1927 the Bureau of Standards defined the functions of the different types of dental gold alloys as:

Type I (soft) - small inlays subject to slight stress only

Type II (medium) - inlays subject to moderate stress,
abutments, pontics, and full crowns.

Type III (hard) - inlays subject to high stress, thin cast
backings, pontics, full crowns and
abutments.

Type IV (extra hard) - inlays subject to very high stress,
partial denture framework and long
span bridgework.

In the late 1950's a method was developed for obtaining a compatible combination of a dental alloy and porcelain (Phillips 1982). The addition of less than 1% of oxide forming elements such as iron, indium and tin to the gold, palladium and platinum alloy was all that was needed to obtain a slight oxide film on the surface of the metal in order to achieve a bond strength superior to the strength of the porcelain itself (Nally 1968; Driessens 1977).

2.2. PROPERTIES OF DENTAL GOLD ALLOYS

The noble metals are classified by their position in the periodic table and include gold, platinum, palladium, and iridium. Oxides of these metals are not stable at room temperature, unlike those of base metals which are stable. The precious metals are determined by their monetary value and in addition to the noble metals, also include silver (Asgar 1977).

The properties of dental alloys may be summarised by examining their constituent parts;

Gold- conveys ductility and tarnish resistance to the alloy (Phillips 1982). Dental gold alloys containing a noble metal content below approximately 40% by weight will be susceptible to rapid tarnish (Treacy & German 1984).

Platinum- acts as a hardener, raises the melting temperature increases tarnish resistance (McLean 1974), and decreases the co-efficient of expansion (Craig 1985a).

Palladium- strengthens and hardens the gold alloy, increases tarnish resistance, raises the melting temperature (McLean 1974) and decreases the co-efficient of expansion (Craig 1985a).

Silver- contributes to the ductility of the alloy but reduces resistance to corrosion (Phillips 1982).

Iridium- reduces grain size and allows the development of a more homogenous casting. It increases tarnish resistance and acts as an oxide producer for bonding with porcelain (Phillips 1982).

Iron- hardens the alloy and aids in oxide formation (McLean 1974).

Tin- also hardens the alloy and aids in oxide formation (McLean 1974).

Zinc- acts as an oxide scavenger during casting procedures (Phillips 1982).

2.3. METAL-CERAMIC

2.3.1. PHYSICAL PROPERTIES OF METAL-CERAMIC

The metal-ceramic alloys must have a higher melting range than traditional crown and bridge alloys (Craig, O'Brien & Powers 1983), so that the metal is solid well above the porcelain baking temperature to minimize distortion during porcelain firing procedures (Phillips 1982). The melting range of white gold metal-ceramic, such as Degudent U, is in the range 1271-1304°C.

These alloys also have the highest yield strength at 572 MPa of any of the dental alloys and a Vickers Hardness Number of 220. The noble metal castings are sufficiently stable that they can be recast two to three times without appreciable changes in properties. Compositional loss can be remedied by the addition of at least equal amounts of new alloy to the scrap when recasting (Phillips 1982).

2.3.2. TYPES OF METAL-CERAMIC

Due to the increasing cost of gold more economic alternatives have been sought to replace high gold metal-ceramic alloys. These include the white coloured alloys, having a gold content of about 50% and consisting primarily of palladium and silver. These alloys have a much higher melting temperature than gold alloys.

Even less costly are the base metal alloys, consisting principally of nickel and chromium without any gold content. These alloys are harder and stronger than the gold alloys but are difficult to cast with accuracy (Anderson 1977).

3. ADHESION

3.1. INTRODUCTION

The use of adhesives can be traced back to 3500B.C. when the ancient Egyptians used a type of glue to stick decorations onto wooden coffins (Parker & Taylor 1966). However, the development of synthetic adhesives is a relatively recent occurrence dating back only to the early part of this Century.

This development of synthetic adhesives is paralleled by the advent of the polymer industry since many adhesives are polymer materials.

3.2. DEFINITION

Several authors have offered definitions of "adhesion".

Buonocore (1963, 1975) defined it as the molecular attraction exerted between the surfaces of bodies in contact, in other words, the attraction between molecules at an interface. He noted that if adhesion depends essentially on these forces of molecular attraction then true adhesion exists at only short distances of separation, no more than 1 to 2 Ångström units.

Parker and Taylor (1966) felt that adhesion may be termed the process by which materials are joined by application of an external material not involving a molten state.

Retief (1970, 1975) adopted Buonocore's definition and added that the force is called "adhesion" when unlike molecules are attracted and "cohesion" when molecules of the same kind are attracted. The material added to produce adhesion is known as the adhesive and the surface to which it is applied, the adherend or

substrate. The interface is the zone between the interacting substances.

Reynolds (1975) simply defined an adhesive as a substance capable of holding materials together. Beech (1977, 1982) stated that in its broadest and most general sense adhesion is just surface attachment, and Kinloch (1980) echoed this thought when he defined an adhesive as a material which when applied to substrate surfaces can join them together and resist separation.

Buonocore (1975) points out that the term adhesion refers to a special means of joining substances and cannot, by definition, apply to any other means of joining materials such as bonding. De Lollis (1980) states that a substance functions as an adhesive only when it holds two or more materials together by attaching purely to the surface of the materials. Beech (1982) notes that whilst mechanical interlocking cannot be considered as adhesion under the definitions which specify intermolecular attraction, the term bonding is generally accepted to have the broader connotation of surface attachment. Smith (1982) feels that both mechanisms probably contribute to the strength of a joint and prefers the general term bonding to describe all the various mechanisms of surface attachment.

The American Council on Dental Materials, Instruments, and Equipment (1974, 1981) took the easy option and defined adhesion as simply "sticking " things together. It did, however, emphasize that the term implies that the use of the usual mechanical means of retention is unnecessary. The Council notes that for an adhesive to be clinically acceptable it must be sufficiently strong to withstand the functional stresses of mastication without relying on interlocking effects. By 1981 only two types

of dental materials - glass ionomers and polycarboxylates - have met the Council's criteria.

3.3. THEORIES OF ADHESION

Kinloch (1980) notes that the mechanisms of adhesion are still not fully understood. De Lollis (1980) comments that whilst the theories of adhesion are relatively few in number this lack of numbers has not necessarily simplified understanding or encouraged agreement.

Some of the main mechanisms of adhesion which have been proposed are:

- a) mechanical interlocking,
- b) weak boundary layer theory,
- c) diffusion theory,
- d) electronic theory,
- e) adsorption theory.

3.3.1. MECHANICAL INTERLOCKING

This theory proposes that mechanical keying of the adhesive into the irregularities of the substrate surface is the major source of intrinsic adhesion. Kinloch (1980) points out that the attainment of good adhesion between smooth surfaces exposes this theory as not being of general applicability although it is certain that mechanical interlocking will contribute to increased joint strength.

3.3.2. WEAK BOUNDARY LAYER

Bickerman (1968) points out that a proper joint which lacks a weak interfacial boundary layer must fail cohesively. In other words, interfacial failure does not take place in the absence of weak boundary layers. Bickerman states that if a material "does

not stick to anything" and "nothing sticks to it" it is highly probable that this material is a carrier of a weak boundary layer. In other words, it contains a soft or nearly liquid ingredient which tends to accumulate at the specimen surface and to form there a soft or nearly liquid stratum.

De Lollis (1980) uses an unpolymerized liquid fraction in an adhesive as an example of a weak boundary layer.

3.3.3. DIFFUSION THEORY

Kinloch (1980) states that Voyutskii (1963) is the chief advocate of this theory which claims that the intrinsic adhesion of high molecular weight polymers to themselves, and to each other, is due to mutual diffusion of polymer molecules across the interface. This type of adhesion probably occurs in certain situations. However, where one polymer is highly cross-linked, crystalline, or insoluble, then diffusion is an unlikely mechanism (Kinloch 1980).

3.3.4. ELECTRONIC THEORY

If the adhesive and adherend have different electron band structures there is likely to be some electron transfer on contact resulting in the formation of a double layer of electrical charge at the interface. Kinloch (1980) attributes this theory to Deryaguin (1955) who suggested that the electrostatic forces arising from such contact, or junction potentials, may contribute significantly to the intrinsic adhesion.

Deryaguin's theory essentially treats the adhesive-adherend system as a capacitor, which is charged due to the contact of the two different materials. Separation of the parts of the capacitor, as during interface rupture, leads to a separation of charge and to a potential difference which increases until a discharge occurs.

Adhesion is presumed to be due to the existence of these attractive forces across the electrical double layer.

This theory appears to be well accepted. However, the chief reservation seems to be over the possible degree of contribution to adhesion, as compared with van der Waal's forces, by this electrostatic force.

3.3.5. ADSORPTION THEORY

According to Kinloch (1980) this is the most generally accepted theory of adhesion and is attributed to Zisman. The adsorption theory proposes that, provided sufficiently intimate intermolecular contact is achieved at the interface, the materials will adhere because of the surface forces acting between the atoms in the two surfaces; the most common such forces are van der Waal's forces which are referred to as secondary forces. In addition, chemisorption may also occur and thus ionic, covalent and metallic bonds may operate across the interface. These types of bonds are referred to as primary bonds (Kinloch 1980). Beech (1982) is not in complete agreement with Kinloch and points to the major shortcoming of this theory as being its exclusive emphasis on short-range intermolecular forces of interaction at the expense of the long-range forces. It must be noted that there does appear to be a difference in interpretation of this theory by the two authors.

3.4. FORCES OF ADHESION

The molecular forces involved in adhesion can be divided into chemical or primary forces and physical or secondary attractive forces. The chemical attractive forces include those arising from electrovalent or ionic, polar and nonpolar covalent

and metallic bonds. The physical or secondary molecular attractive forces arise from the Van der Waals forces which include Keesom forces (orientation effect), Debye forces (induction effect) and London forces (dispersion effect) as well as hydrogen bonding (Retief 1970). These secondary forces are weaker than primary forces and are intermolecular rather than intramolecular, since no electron sharing or exchange takes place (Beech 1977).

3.4.1. CHEMICAL FORCES

These are the intramolecular attractive forces.

3.4.1.1. The Electrovalent or Ionic Bond

The bond is formed by the electron transfer from the valency orbit of one atom to the valency orbit of another atom. This transfer results in the formation of positively and negatively charged ions, and the attractive forces arise from the electrostatic attraction between these ions. An example of this type of bond is sodium chloride (Retief 1970). Parker and Taylor (1966) note that ionic bonding is extremely stable to heat, but is readily dissociated by polar solvents such as water.

3.4.1.2. The Covalent Bond

This is formed by the sharing of a pair of electrons from the valency orbits (Retief 1970).

A purely covalent or non-polar bond is formed by the equal sharing of electron pairs by similar atoms, an example being Cl_2 . Such a bond has no ionic character. Covalent bonds represent strong bonds which liberate considerable energy in their formation (Buonocore 1975).

If the electron pairs are shared by dissimilar atoms, that is, those which have different degrees of electro-negativity, they

will be displaced closer towards the more electro-negative atom. The bond or bonds between these atoms will have a partly ionic character; as well as a polar characteristic, due to the unequal sharing of the electron pairs (Retief 1970).

A dipole results whenever a covalent bond is formed by the unequal sharing of the electron pairs that go to make up the bonds (Retief 1970). The shared electron pair is displaced towards the most electro-negative atom and the degree of electron displacement is reflected by the dipole moment. Permanent dipoles are found in polar organic compounds and are of considerable importance in adhesion (Retief 1970).

3.4.1.3. The Metallic Bond

The free valence electrons of metals can move about the metal space lattice to form an electron cloud. The movement of these electrons is responsible for some of the properties of metals, such as the conduction of electricity. The movement of the free valence electrons leads to a regular array of positive ion cores being found in the crystal. The electron clouds and the positive ion cores provide the forces of attraction which bond the metal atoms together. The surface of metals when free from oxides will have some free electron deficient sites available for bonding (Parker & Taylor 1966; Retief 1970).

Metallic bonds may be considered as partly ionic and partly covalent (Buonocore 1975).

VAN DER WAALS FORCES.

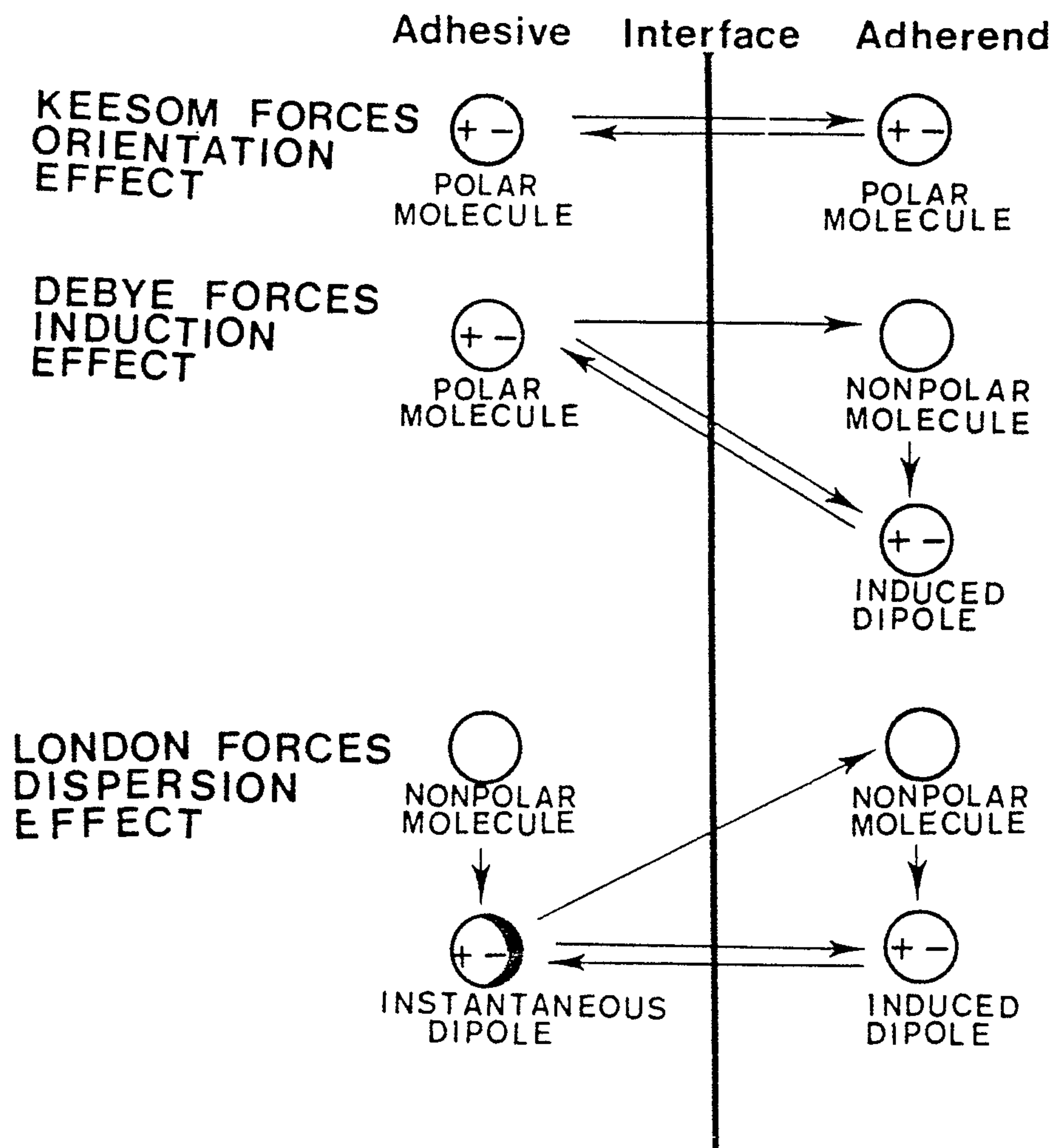


Figure 1 Diagrammatic presentation of Van der Waal's attractive forces (Retief 1975).

3.4.2. PHYSICAL FORCES

3.4.2.1. Van der Waal's Forces (see Figure 1)

As stated these may be divided into: Keesom, Debye and London forces.

3.4.2.1.1 Keesom forces.

These result from the interaction of permanent dipoles in neighbouring molecules of polar compounds (Retief 1970). The greater the number of polar groups, according to Parker and Taylor (1966), the greater will be the adhesive force. Orientation of the dipoles to a head-to-tail or lowest energy configuration will result in molecular attraction across the interface (Retief 1975).

3.4.2.1.2. Debye forces.

These take into account the influence of a dipole moment in a molecule which induces an additional dipole moment in a molecule across the interface. A dipole in a molecule may provide the electrical field to polarize a neighbouring symmetrical or nonpolar molecule (Retief 1975).

The electric dipole moment (μ) is defined as

$$\mu = q l$$

where q = the magnitude of the charges separated.

l = the distance separating the charges (Retief 1970).

Once a dipole has been induced, the two molecules attract each other.

Both the Keesom and Debye forces depend on the existence of permanent dipole moments and, therefore, play no part in a medium consisting of non-polar molecules (Retief 1970). Parker and Taylor (1966) note that Debye forces contribute very little to the total energy of adhesion or cohesion.

3.4.2.1.3. London forces.

These are not dependent on the existence of permanent dipoles. Slight displacement of the electrons or nuclei in an atom or molecule is constantly occurring. It is instantaneous and at random, and results in the formation of a dipole which at any one instant induces another dipole in a neighbouring molecule. Attraction between the dipoles occurs, and gives rise to London forces (Retief 1975).

The Keesom and London forces are by far the most important in adhesion.

3.4.2.2. The Hydrogen Bond

This can be regarded as a special type of dipole-dipole interaction (Buonocore 1975). Retief (1970) cites Good (1967) as describing two special requirements for the establishment of hydrogen bonds:

1. A highly electro-negative atom such as F, O or Cl or strongly electro-negative groups like -CN with a hydrogen atom attached.

2. Another highly electro-negative atom, which may or may not be in a molecule of the same species as the first atom or group, to be in the vicinity.

An example of the hydrogen bond is water, H_2O , which does not exist as such, but as $(H_2O)_3$, where the 3 associated molecules are held together by hydrogen bonds (Retief 1975).

Hydrogen bonds involve relatively strong attractive forces between materials, being greater than those involved in the other van der Waal's forces (Retief 1970).

3.4.3. ROLES OF PHYSICAL AND CHEMICAL FORCES

The physical forces of attraction result in the adsorption of the adhesive on the adherend; that is, they bring the adhesive molecules in close contact with the adherend surface. This is a rapid and reversible process and requires no activation energy as the molecules remain chemically intact on the surface (Retief 1973).

Although weaker than the chemical attractive forces, the physical forces of attraction - principally the London forces - are sufficiently strong to produce good adhesive performance no matter what the chemical nature of the two phases in contact, provided that intermolecular contact is achieved at the interface (Retief 1973). These forces only operate over very short distances. When two attracting molecules are separated by a distance that exceeds their own approximate diameter they no longer have any appreciable interaction (Glantz 1977).

Physical forces of attraction are also responsible for such properties of materials as tensile strength, surface tension, and viscosity (Buonocore 1975).

Chemical bonding or chemisorption occurs after physical adsorption. The rate of this reaction is, however, slower because an activation energy is required for chemical bonding to take place across the interface. The composition of the adhesive and the adherend will have a profound effect on the rate of the reaction (Retief 1973). Chemisorption gives rise to very strong attractive forces and once established is not easy to reverse (Halpern 1981). It also provides greater heat, water, and chemical resistance. With covalent bonds, water is not able to destroy the

adhesion, as it is more likely to do with substances bonded solely by physical forces (Buonocore 1975).

3.5. SURFACE CONTACT (see Figure 2)

Adhesion, depending only on the forces of molecular attraction at the interface, exists at very short distances of separation, in the order of 1 to 2 Ångström units (Halpern 1981). If solid surfaces are naturally smooth on an atomic scale they will adhere spontaneously when brought together. The best surfaces, however, that scientist have been able to produce are flat to only one millionth of an inch, which is about 250 times less flat than is required for molecular attraction (Buonocore 1975). If such rough surfaces are brought into contact the molecular forces of attraction will operate only where the tips of the asperities on the surface meet. These widely spaced attractive forces are so small that poor adhesion will result (Retief 1970).

3.6. FUNCTION OF AN ADHESIVE

In practice, to obtain adhesion between rough surfaces, a liquid adhesive is introduced. Its function is to adapt itself to the irregularities of the surfaces to be joined, thereby establishing close contact with them. The molecular forces of attraction between the solid surfaces operating at the tips of the asperities will be supplemented by those between the adhesive and the adhesive at the interfaces. To maintain this molecular closeness

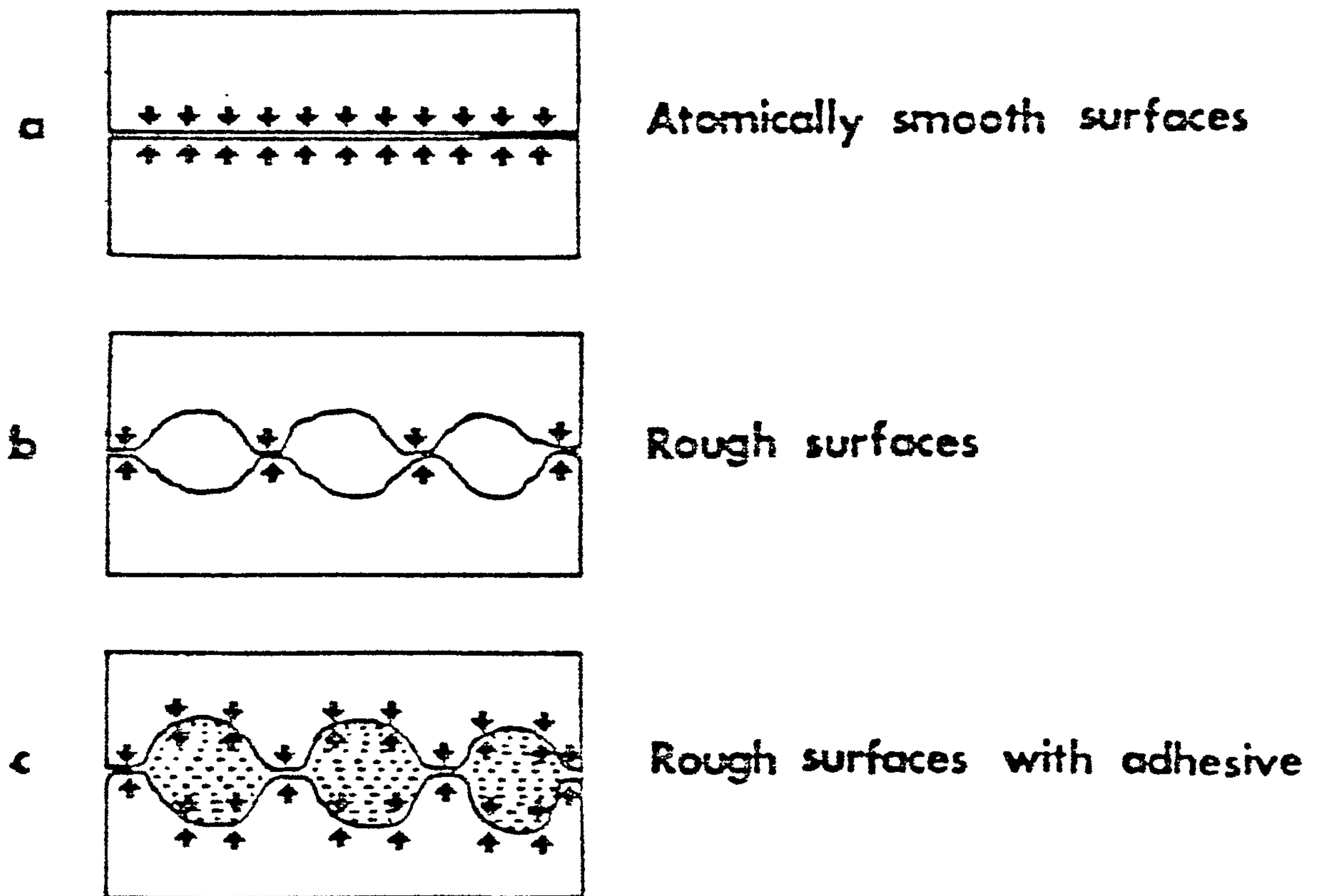


Figure 2 a) Adhesion between atomsically smooth surfaces.
b) Adhesion between rough surfaces.
c) Adhesion with adhesive between rough surfaces.
(Retief 1970)

a liquid adhesive that solidifies either by evaporation or cross-linking is used (Retief 1973).

3.7. WETTING

A liquid adhesive will bond to an adherend surface or unite two solid surfaces only if the adhesive is able to wet the surface of the materials. Wetting is a manifestation of the attractive forces between the molecules of an adhesive and an adherend and may be defined as the process of obtaining molecular nearness or establishing interfacial contact (Buonocore 1975).

Huntsberger (1964) used the term wetting in reference to a process and a state. The wetting process is described as the establishment of interfacial contact. The wetting state is defined as the number of interfacial contacts between the phases at the interface in relation to the maximum number possible for the system when wetting is complete.

Only when the attractive forces between the molecules of the adherend and the molecules of the adhesive are stronger than the attractive forces within the adhesive itself will wetting occur. When the maximum possible number of interfacial contacts is achieved, the adhesive completely wets the substrate (Brauer 1975). Kinloch (1980) cites Sharpe and Schonhorn (1964) who emphasize wetting as the single, most important factor influencing adhesive strength.

The extent to which an adhesive will wet a surface depends on the viscosity of the adhesive (Driessens 1977), the shape of the irregularities on the surface (De Bruyne 1962), and the contact angle at which the adhesive meets the surface of the adherend (Zisman 1963).

Rates of wetting will be proportional to the viscosity of the adhesive (Brauer & Huget 1972).

3.8. VISCOSITY

Viscosity is the property of a liquid which opposes the relative motion of adjoining portions of the liquid and can be regarded as a type of internal friction. Liquids which have low co-efficients of viscosity are said to be mobile since they flow readily (Retief 1975).

Buonocore (1975) points out that viscosity interferes with establishing maximum wetting in spite of the fact that strong attraction may exist between molecules of a viscous adhesive and those of the adherend surface. A thick pasty adhesive cannot be expected to flow readily over a surface nor to fill surface irregularities to the same extent as a more fluid adhesive. If surface irregularities are not completely filled, the contact area will be reduced and areas of stress concentration may develop which can lead to early failure (Buonocore 1975).

The polymerization of a liquid adhesive may be considered as a continuous process of viscosity increase until a rigid state is reached. Hence as an adhesive undergoes polymerization, the assembly undergoes a continuous increase in shear strength, providing internal stresses are not induced (Buonocore 1975).

3.9. CONTACT ANGLE (see Figure 3)

The contact angle θ , is the angle formed between the surface of the adhesive drop and the surface of the adherend upon which it is resting (Retief 1970), measured at equilibrium. It is a

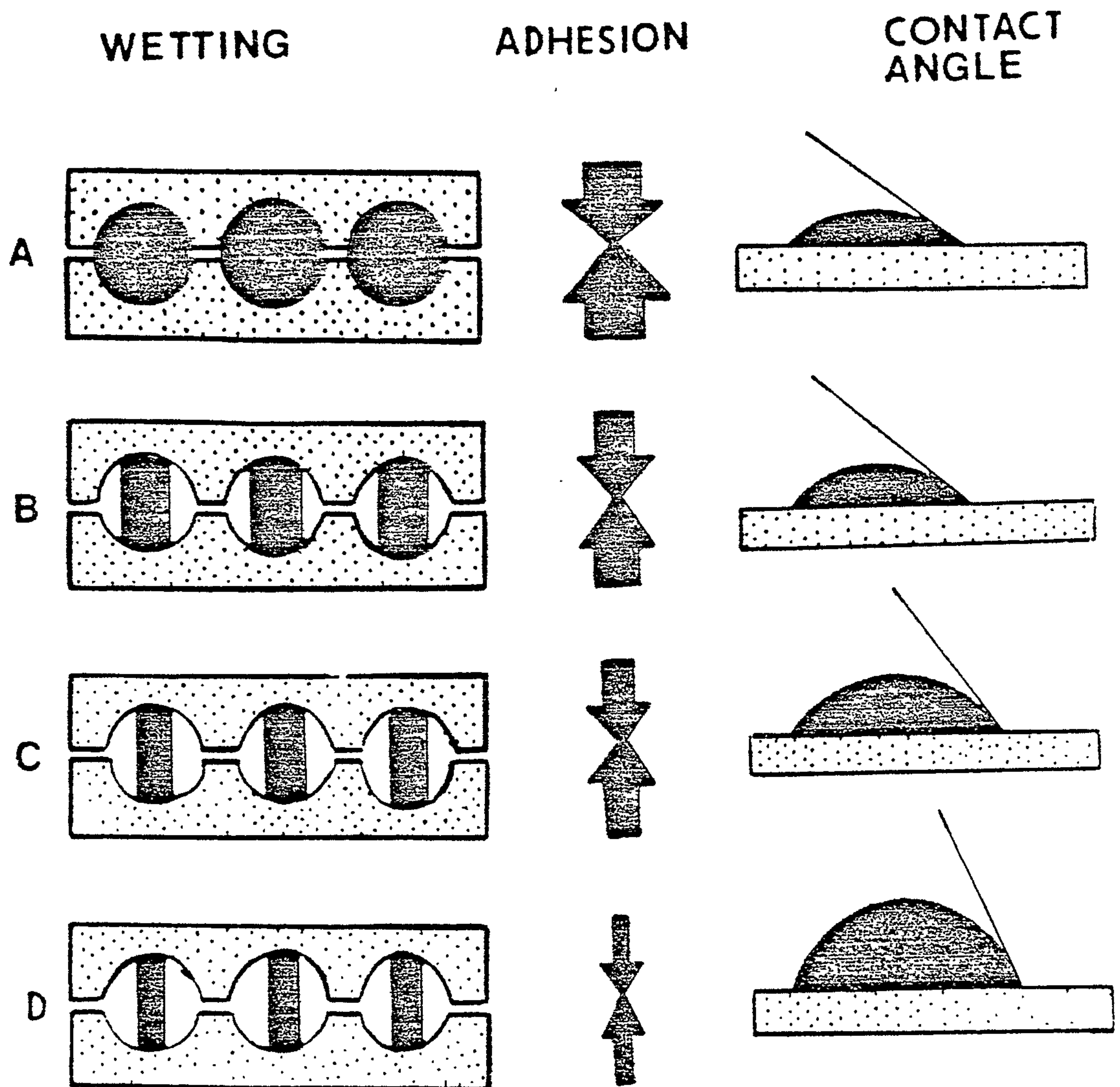


Figure 3 Diagrammatic representation of the relationship between contact angle, wetting, and adhesion (Retief 1975).

measure of the degree of wetting by the adhesive.

The contact angle is small if the attraction between the molecules of the adhesive and the adherend is greater than the attractive forces between the molecules of the adhesive itself (Buonocore 1963). When this angle is small the adhesive will wet the adherend surfaces, and the molecular forces of attraction will operate along the entire interface and strong adhesion will result. Conversely if the angle is large, adhesion will be poor (Retief 1970,1973).

If the angle is zero the adhesive will wet the adherend completely and spontaneously and spread over the surface at a rate depending on the liquid viscosity and surface roughness (Brauer 1975, Kinloch 1980). Baier (1970) emphasizes that when a liquid makes a zero contact angle with a substrate, the adhesive strength will always be much greater than the tensile or shear strength of the substrate. If the angle is greater than 60° the degree of penetration of the adhesive into the pores of the adherend will be primarily dependent on applied pressure (Parker & Taylor 1966).

In geometric terms, the cosine of θ is a direct measure of the wettability of the surface in that, as the value of $\cos \theta$ increases towards unity, the wettability also increases (Baier 1970).

3.10. SURFACE TENSION

Retief (1970) points out that in liquids there is a tension in the surface region. A molecule in the bulk of a liquid is surrounded by neighbouring molecules and is attracted equally from both sides. The attractive forces always include the London

dispersion forces but additional forces such as dipole and ionic interactions will operate in polar or ionic liquids respectively. A molecule in the surface of a liquid will be attracted from below and from the sides but not from above. As a result molecules in the surface are in a one-sided field of force, pulling them downward into the bulk of the liquid. The surface tension results from this one-sided field force exerted on surface layers. The stronger this force, the greater the surface tension. Since the range of these forces is short, most of the tension is in the outer layer of the liquid (Retief 1970). Kinloch (1980) accredits surface tension as being a direct measurement of intermolecular forces.

The rate and extent to which the adhesive will fill the microscopic and submicroscopic irregularities of an adherend, many of which may be considered as capillaries, will depend on a number of factors. Other things being equal, a relatively free-flowing liquid adhesive with a high surface tension would tend to fill the surface irregularities of an adherend more rapidly than one with a lower surface tension. This is due to the fact that a liquid of high surface tension exerts a greater driving force in filling a capillary than one of low surface tension (Buonocore 1975).

Surface tension (γ), is defined as the force in newtons acting at right angles to any line of 1 metre length in the surface. The work done in extending the area of a surface by 1 square metre is equal to the surface tension (Beech 1982).

The difficulty in measuring small contact angles was offset by Zisman's (1963) concept of critical surface tension (γ_c), which is the maximum surface tension of a liquid that will form a zero

contact angle with the surface. Specific values of the critical surface tension are characteristic of the chemical groups forming the surface i.e. the critical surface values are characteristic of the solid only (Baier 1970). Provided the molecules in the solid surface do not form hydrogen bonds, or otherwise associate strongly with the liquid, a rectilinear relationship is shown to exist between the cosine of the contact angle and the surface tensions of a homologous series of organic liquids (Brauer & Huget 1972). The critical surface tension for wetting was defined as the intercept of the horizontal line where $\cos \theta$ was equal to one (Brauer 1975).

Surface tension is a property of the adhesive and is similar to surface free energy, which is a property of the adherend. To obtain strong adhesion, it is best to use an adhesive with a surface tension slightly less than the critical surface tension of the adherend (Brauer & Huget 1972).

3.11. THERMODYNAMICS OF SURFACE TENSION (see Figure 4)

Retief (1970) accredits Thomas Young (1805) with enunciating that the relationship between the three surface tensions γ_{SV}^0 , γ_{SL} and γ_{LV}^0 existing at the phase boundaries of a drop of liquid at rest on a solid surface must form a system in static harmony.

He formulated what is now known as the Young equation, which is...

$$\gamma_{SL} + \gamma_{LV} \cos \theta = \gamma_{SV}$$

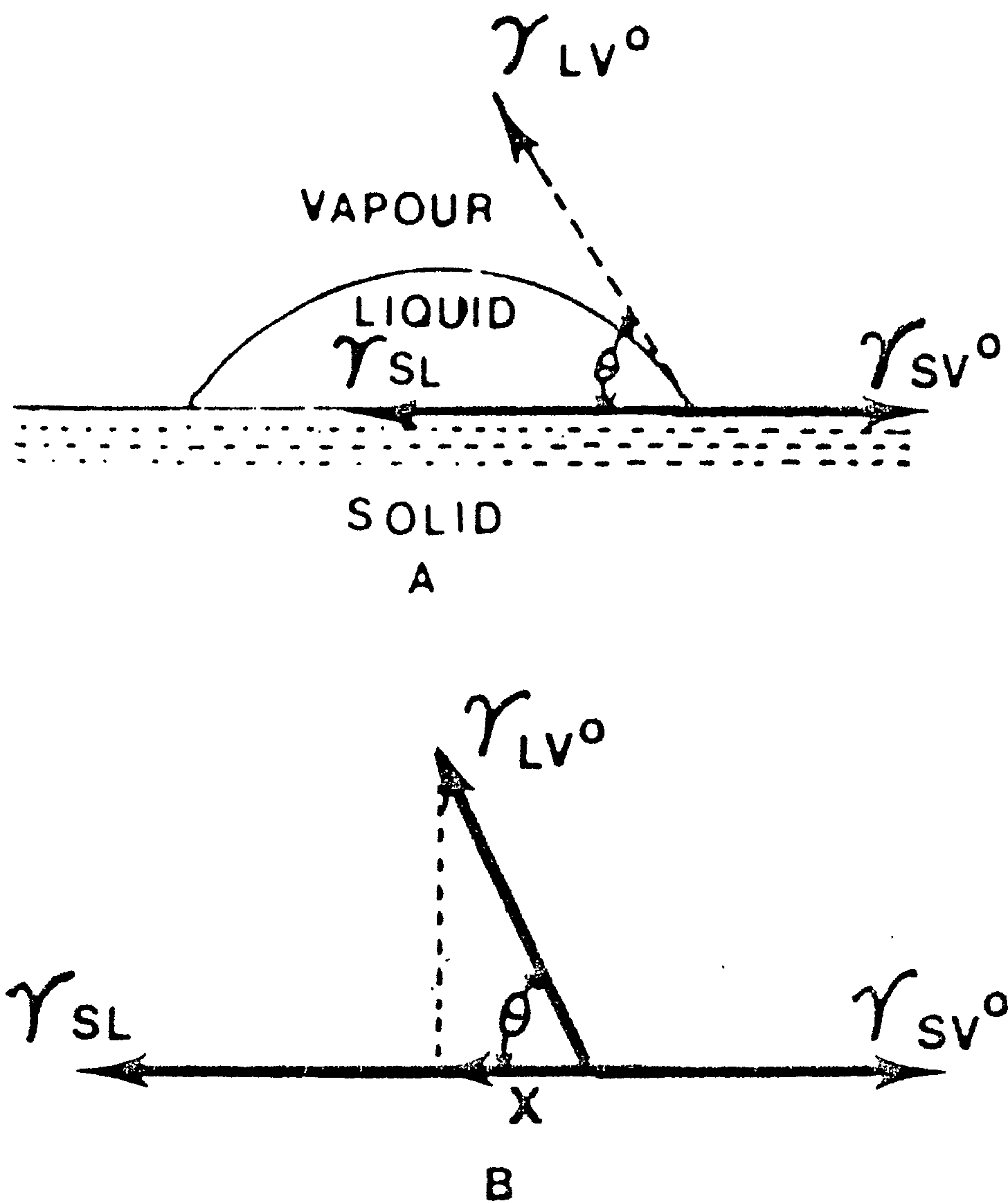


Figure 4 The relationship between contact angle and surface tension. a) The surface tensions at the phase boundaries of a liquid at rest on a solid surface.

b) Resolution of forces at the point where the phases meet. (Retief 1970)

Where: γ_{SV} = the surface tension of the solid in
equilibrium with the vapour.

γ_{LV} = the surface tension of the liquid in
equilibrium with the vapour.

γ_{SL} = the surface tension of the solid/liquid
interface.

In other words the cosine of the contact angle formed between a liquid drop and the plane surface of a solid on which the drop is resting has, at equilibrium, a definite relationship to the surface tensions of the liquid and the solid in contact with the saturated vapour.

Brauer and Huget (1972) point out that enthalpies of adhesion can give a direct measure of the forces of chemical interaction. Enthalpy is defined as the amount of heat energy of a chemical substance. When chemicals react there is a change in heat energy which can be measured.

3.12. SURFACE FREE ENERGY

Surface free energy is directly related to the composition of the adherend. An adherend having polar groups will have a higher surface free energy than a substance not possessing such groups (Buonocore 1975). Under normal conditions a high-energy surface seldom retains its hydrophilic properties as it attracts, and is covered, by low-energy substances (Brauer & Huget 1972).

Solids may be broadly classified in two groups according to their surface free energies:

1. Hard, high melting point, generally inorganic materials with strong intermolecular forces, having a high surface energy, typically greater than 500 mJm^{-2} e.g., tooth enamel, metals, gold.

2. Soft, low melting point organic solids, having weak intermolecular forces, with a low surface energy, usually less than 100 mJm^{-2} e.g., protein, acrylic resin (Kinloch 1980, Beech 1982).

Buonocore (1975) notes that it is generally agreed that the surface free energy of the adherend must be greater than the surface tension of the adhesive for suitable wetting to occur. In other words, liquids will generally spread freely on solids of high energy but may show non-spreading behaviour on low surface energy solids (Baier 1970).

Buonocore (1975) further states that the process of molecular attraction, resulting in adhesion, releases energy, and the energy release is greatest, the higher the surface free energy of the solid. This energy release, which is measurable as heat of adsorption, is called the work of adhesion. To cleanly separate the joined surfaces an equivalent amount of energy would have to be applied to the system. Therefore, it can be said that the greater the work of adhesion, the greater the strength of the adhesive bond.

3.13. SURFACE ROUGHNESS

Most solid surfaces, as previously discussed, are not smooth, but rather contain pores, crevices, capillaries, etc. Certain types of surface roughness can promote spreading and wetting better than other types (Buonocore 1975).

3.13.1. ADVANTAGES OF ROUGHNESS

The presence of surface irregularities is beneficial if they can be properly filled by an adhesive, since the surface area would be increased (Eick, Johnson, Fromer, Good & Neumann 1972), which would in turn increase the work of adhesion resulting in greater overall strength of the adhesive joint (Buonocore 1975). Kinloch (1980) cites Bascom et al. (1964) who reported that random surface scratches increased the spreading rate of some liquids by as much as 50 %, and that open capillaries filled well ahead of the diffusional advance of the primary film.

Roughening the surface will also alter the contact angle that a liquid makes with the smooth surface. If θ is less than 90° , roughening the surface will result in θ becoming even smaller, which will in turn increase the wettability of the surface (Baier, Shafrin & Zisman 1968).

3.13.2. DISADVANTAGES OF ROUGHNESS

Surface roughness may, however, present certain problems, particularly if the contact angle which an adhesive makes with the adherend surface becomes greater than 90° (Wenzel 1963). In this case, incomplete filling of such surface irregularities with air entrapment is more likely, especially if these irregularities are of the "ink-bottle" shape with increasing distance between the lateral walls (Retief 1970). With viscous adhesives this problem is further magnified since the formation of voids, air pockets, and other surface defects is enhanced. These act as stress concentrators to cause fracture of the adhesive (Buonocore 1975).

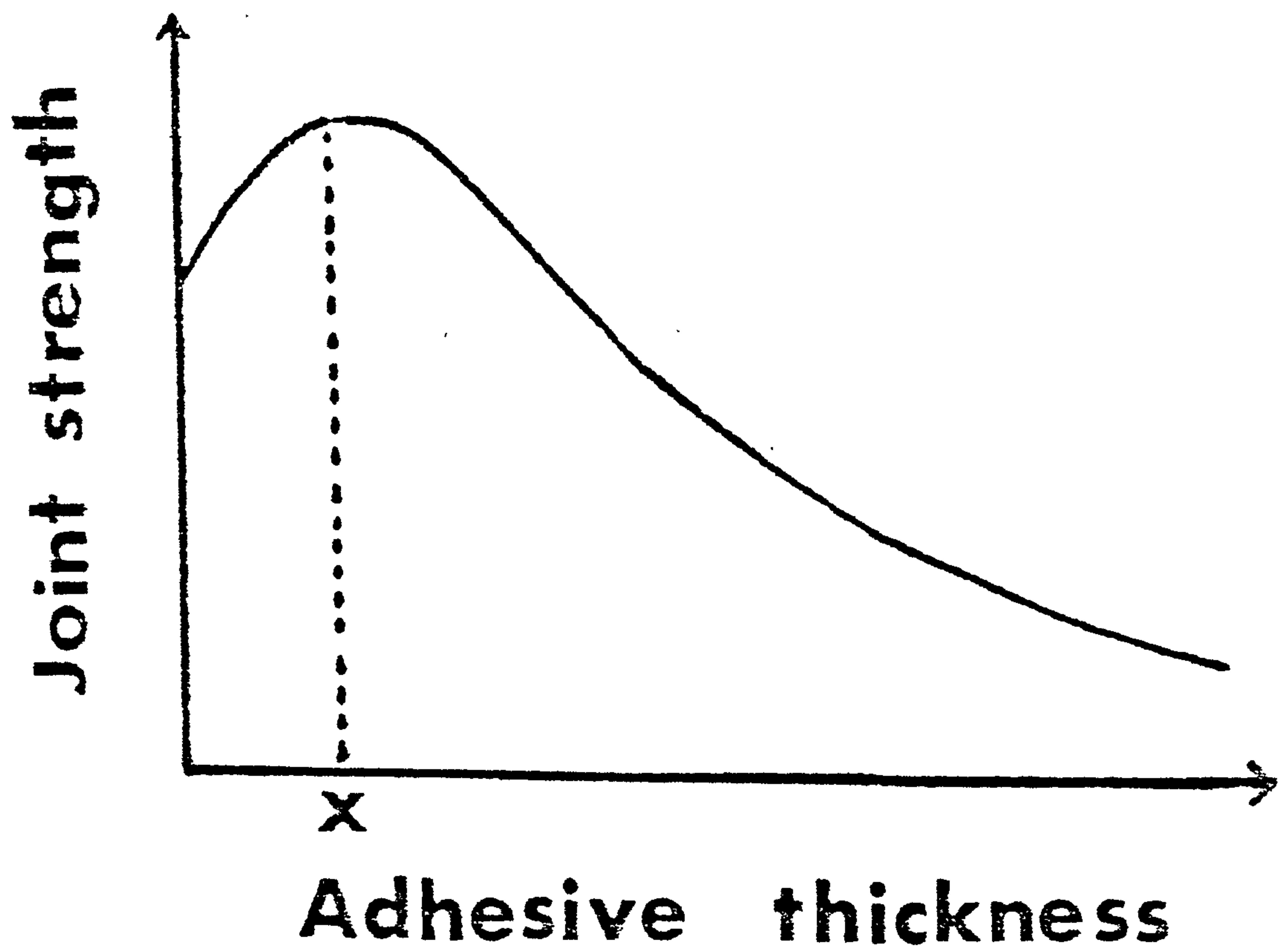


Figure 5 The effect of adhesive thickness on the joint strength (Retief 1970).

Rough surfaces also require a thicker adhesive layer between them to form a continuous film than smoother surfaces (Buonocore 1963).

3.14. ADHESIVE THICKNESS (see Figure 5)

Buonocore notes (1963) that it is generally agreed that thick adhesive layers give weaker joins than thin ones. There are a number of reasons for this. One is the probability of a greater number of imperfections, such as voids and cracks, in thicker layers. These may cause stress concentrations under load, with the likelihood of early failure related to the number and size of these imperfections (Buonocore 1975). Another reason is that they are more likely to become deformed than thin ones and thus will fracture sooner (Retief 1970). Most adhesives undergo shrinkage on hardening or polymerization, which may induce internal stresses acting tangentially to the adhesive-adherend interface. If a thick layer may be considered as being made up of several thin layers, the sum of the stresses caused by shrinkage will increase with the thickness of the adhesive layer. These shrinkage forces tend to pull the adhesive from the adherend and consequently, to decrease adhesion. If adhesion is not actually disrupted during shrinkage it may become so weakened that only a small additional external force will break it (Buonocore 1970, 1975 ; Retief 1970).

Buonocore (1975) does emphasize however, that whilst an adhesive layer ideally should be thin, it should not be so thin as to be lacking in continuity and thus produce a weak join in this manner.

3.15. PROPERTIES OF AN ADHESIVE

An ideal adhesive should therefore conform to the following conditions:

- when liquid, exhibit a zero or near zero contact angle,
- at some time during the bonding operation have a viscosity that should be relatively low (Kinloch 1980),
- it must polymerize at or near body temperature with minimal shrinkage,
- it must be sufficiently cross-linked to minimise expansion or water sorption,
- it must have the same co-efficient of thermal expansion as the adherend,
- it must form a lasting bond (Retief 1970),
- it can either completely displace, react with, or absorb water (Baier 1970),
- it must be resistant to degradation in the oral environment,
- it must be non-toxic (Buonocore 1963)

3.16. EFFECT OF WATER

Adhesion can be weakened or destroyed by water penetrating along the interface between adhering surfaces (Buonocore 1963; Beech 1982).

Many adhesive materials will absorb water (Lee & Swartz 1970) leading to swelling and dimensional changes in their bulk. This will lead to stress concentrations at the interface which will have an adverse effect on the bond strength (Retief 1973).

Adsorbed water may also decrease the surface energy of many high energy solids. At room temperature one condensed

monolayer of adsorbed water will convert these high energy solid surfaces into low energy surfaces (Baier 1970). This is due to the fact that water itself is a low energy surface (Halpern 1981). As little as 0.6% humidity is all that is required for this change to occur (Brauer & Huget 1972).

Water molecules are also strongly attracted to the charged components of ionic bonds, forming a shell about them and effectively reducing their charge intensity (Buonocore 1975).

If an adhesive is not able to react with, dissolve, or displace all of the adsorbed water from the surface of the adhesive joint the resulting bond will be weak (Brauer & Huget 1972).

3.17. CONTAMINANTS

A very thin adsorbed film of oxide or as little as one condensed monolayer of organic contaminant can greatly decrease the adhesion of dry solids (Baier, Shafrin & Zisman 1968; Beech 1978). If multilayer contamination is not displaced by the adhesive it will act as a "weak boundary layer" and low joint strength will result (Kinloch 1980). Buonocore (1981a) notes that saliva is the most common intra-oral contaminant which can disrupt bonding. Dogon (1981) concludes that that the chief reason for failure of a bonded assembly is contamination.

3.18. CONCLUSION

It can be said that a bonded assembly is only as strong as its weakest link. Once good adhesion is achieved, the adhesive bond is not likely to break; instead the adhesive or adherend will

rupture. The resistance of the adhesive or adherend is the limiting factor in bond strength (Buonocore 1975).

4. COUPLING AGENTS

For a glossary of terms used in this chapter refer to Appendix A.

4.1. INTRODUCTION

The need for a chemical binding agent was initially recognized in the mid-1940's when glass fibers were first used as reinforcements in organic resins (Sterman & Marsden 1966c). It was found that priming glass fibres with a vinyl silane increased the flexural strength of glass resins from 50,000 psi to 70,000 psi (Sterman & Toogood 1965). These same silane coupling agents that are used on glass are also effective as primers on metal or ceramic surfaces for adhesion of sealants, paints, adhesives (Sterman & Toogood 1965), and in fibreglass-reinforced epoxy composites. A silane coupling agent is the prime component of commercially available gold bonding materials.

4.2. DEFINITION

Coupling agents may be defined as materials that improve the chemical resistance, especially to water, of the bond across an interface (Sterman & Marsden 1966a; Plueddemann 1982 p.2; Culler 1986). Smith (1982) defines coupling agents as chemical treatments at a molecular level which produce a receptive surface. Lee (1968) considers a coupling agents to be any adhesive which is used to join two dissimilar surfaces.

Vanderbilt and Simko (1960) and Culler (1986), point out that coupling agents are bifunctional; that is, each end of the molecule can react with the surfaces (inorganic and organic) that are being bonded.

Causton (1982) notes that several types of coupling agent have been used in dentistry, including, n-Phenyl Glycine derivatives, phosphonate derivatives, silane derivatives, polyurethanes and grafted proteins.

Although any polar functional group in a polymer may contribute to improved adhesion, only a methacrylate-chrome complex and the various organofunctional silanes have shown promise as true coupling agents (Plueddeman 1982 p.2, 141). Sterman and Toogood (1965) define an organofunctional silane as a class of silicone having reactive groups attached to the silicon. Among the more common reactive organic groups reported by them are vinyl, alkyl amines, methacryloxypropyl, alkyl mercapto, and alkyloxy epoxy radicals.

4.3. USES

Organofunctional silanes may be used as adhesion promoters between organic polymers and mineral substances under a variety of circumstances to provide improved mechanical strength and chemical resistance to the system (Plueddemann 1982 p.167). The silane adhesion promoter, or "coupling agent", may function as either ;

- 1) a finish, or surface modifier,
- 2) a primer, or size,
- 3) as an adhesive, depending on the thickness of the bonding material at the interface (Plueddeman 1982 p.4).

Almost every type of organic polymer is compatible with silane coupling agents, ranging from thermoset resins through elastomers to thermoplastic resins. The silane may be applied to the substrate as a pretreatment, such as when it is when used to

prime gold alloy surfaces prior to bonding; or, in many systems, the silane may be added to the resin. In this case it migrates to the substrate during normal mixing and application procedures, as it does in dental composite resins (Stermann & Marsden 1966b).

Vinylfunctional silanes have generally been displaced by methacrylate-functional silanes as commercial coupling agents of choice (Stermann & Marsden 1963b). These are known industrially as A-174, produced by Union Carbide (Union Carbide Product Information 1965), and Z-6030 produced by Dow-Corning (Glenn 1979).

4.4. PRIMER REQUIREMENTS

Silane modified primers have been developed to promote adhesion of virtually any organic thermoplastic or thermosetting polymer to metals, glass, and other mineral surfaces. Certain generalisations can be made about the requirements for a silane to function as a primer;

1. The primer must form a strong boundary layer.
2. The final boundary layer must be either tacky or rigid with sufficient toughness and strength to carry the mechanical load imposed on the composite.
3. The boundary layer must have polar functional groups for bonding to the mineral.
4. The primer must have partial compatibility with the matrix polymer.
5. The primer film must be able to contribute to a boundary layer at the interface.
6. The primer boundary layer must survive any environment (Pleuddemann 1982 p.157).

4.5. THEORIES OF BONDING WITH COUPLING AGENTS

Consideration of the various theories of adhesion may be of assistance in understanding the mechanism of bonding through silane coupling agents. Unfortunately even at this stage, the actual method of adhesion is still uncertain (Chen & Brauer 1982).

4.5.1. THE CHEMICAL BONDING THEORY.

According to Plueddemann (1982 p.17) this is the oldest and best known of the theories. It can be used to describe the bonding of the filler particles to the resin matrix of dental composite materials by the vehicle of a coupling agent.

Coupling agents contain chemical functional groups that can react with the silanol groups in filler particles. Attachment to the filler particles can thus be made by covalent bonds. These bonds contribute to overall strength by their resistance to water (Stermann & Marsden 1966c).

As well, coupling agents contain at least one other, different functional group which can co-react with the resin matrix. If this occurs, the coupling agent may act as a bridge to bond the glass filler particles to the resin matrix with a chain of primary bonds (Stermann & Marsden 1966b).

Covalent bonding between coupling agent and a mineral surface, such as gold, is more difficult to verify. Silanols of a hydrolyzed silane coupling agent will first form hydrogen bonds with hydroxyl groups of a mineral surface or possibly with a layer of water on the mineral surface. Clark and Pleuddeman (1963) suggest that these hydrogen bonds can "exchange"

positions with equivalent neighbouring groups conferring mobility on the coupling agent.

It appears uncertain at this stage whether these silanol groups ever condense to form oxane bonds with the surface, or whether such bonds are necessary at all for the coupling mechanism to operate (Plueddemann 1982 p.18).

What does appear certain at this stage (Plueddemann 1982 p.20) is that the chemical bonding mechanism can be demonstrated empirically, between silanes and thermosetting resins such as dental composite, and the bonding of silane to glass or silica.

4.5.2. THE WETTING THEORY.

In order to obtain complete wetting of a surface the adhesive must initially be of low viscosity and have a surface tension lower than the critical surface tension (γ_c) of the adherend surface.

It was initially thought that silanes acted to effect the γ_c of the treated surface, in order to provide a surface with a γ_c higher than the surface tension of liquid resins (Glenn 1979). This empirically was found not to be the case as acceptable silane coupling agents commonly used in the reinforced plastics industry exhibited relatively low γ_c when compared with unacceptable silane coupling agents (Stermann & Marsden 1966c).

From this evidence Pleuddemann (1982 p.21) concluded that the reactivity of the silane during polymerization is of obviously greater significance than the polarity or wettability of the treated surface.

4.5.3. MORPHOLOGICAL MODIFICATION THEORY

It has been proposed by Plueddemann (1982 p. 22) that silane treatments on reinforcements and fillers, in some way modified the morphology of the adjacent polymer to improve adhesion. This hypothesis has provided two areas of speculation, the deformable layer and the restrained layer theories.

4.5.3.1. The Deformable Layer Theory

This theory suggests that a flexible, deformable phase seems desirable to accommodate stresses set up at the interface due to differential thermal shrinkage between resin and filler when the adhesive is setting (Clark & Plueddemann 1963).

4.5.3.2. The Restrained Layer Theory

At the opposite extreme, this theory proposes that the silane coupling agents function by "tightening-up" the polymer structure in the interface region (Plueddemann 1982 p.24). Plueddemann considers that a restrained layer would give optimum desirable qualities.

4.5.4. ACID-BASE REACTIONS

It is known that modification by addition of suitable acid or base solvents may be important in aligning silane coupling agents on a mineral surface. Plueddemann (1982 p.26) states, however, that there is little evidence of improved water resistance through acid-base reactions across the interface.

4.6. CHEMISTRY OF SILANE COUPLING AGENTS

The "coupling" mechanism of organofunctional silanes depends on a stable link between the organofunctional group (R) and hydrolyzable groups (X) in compounds of the structure $RSiX_3$. The organofunctional groups (R) are chosen for their ability to

react with the polymer resin (Stermann & Marsden 1965, Retief 1975), while the hydrolyzable groups (X) are short chain ethers (alkoxy groups) which can be hydrolyzed in slightly acidic water.

This hydrolysis produces silanol groups which are very reactive with themselves (condensation/polymerisation) and the inorganic (mineral) surface (Culler 1986; Plueddemann 1982 p.29). These hydrolyzable groups are chosen on the basis of handling ease and the nature of the hydrolysis by-products (such as HCl, HOAc or ROH), as they have little effect on the performance of the coupling agent in the resulting composite (Stermann & Marsden 1966b, 1966c). Common examples of these groups are -OH, -Cl, -OAc or -NR₂ (Stermann & Marsden 1966c).

4.6.1. HYDROLYSIS AND CONDENSATION

Trialkoxysilanes, RSi(X)₃, hydrolyze stepwise in water to give the corresponding silanols, which initially are soluble and fusible but ultimately condense to siloxanes (rigid, cross-linked polymers of silica joined by oxane bonds). Contact of a treated surface with polymer matrix is made while the siloxanols still have some degree of solubility (Plueddemann 1982 p.128). Stermann and Toogood (1965) point out that it is the siloxane linkage which gives these polymers their exceptional stability.

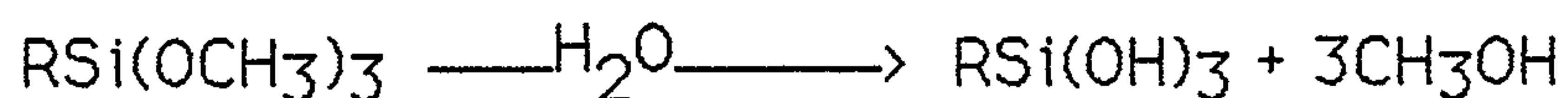
All commercially available coupling agents have three hydrolyzable groups per silicon atom. Primers having one or two hydrolyzable groups per silicon atom result in the formation of di- or polysiloxanes, which have little or no ability to bond to mineral surfaces under normal conditions (Stermann & Marsden 1966b). This is due to the fact that only one of the three silanol groups can hydrogen-bond to the mineral surface within a given radius because of the size of the silane molecule. The other two

silanols must first form hydrogen bonds with neighbouring silane units to bring them into close enough contact for polymerisation and condensation (Lee 1968; Pleuddeman 1982 p.121).

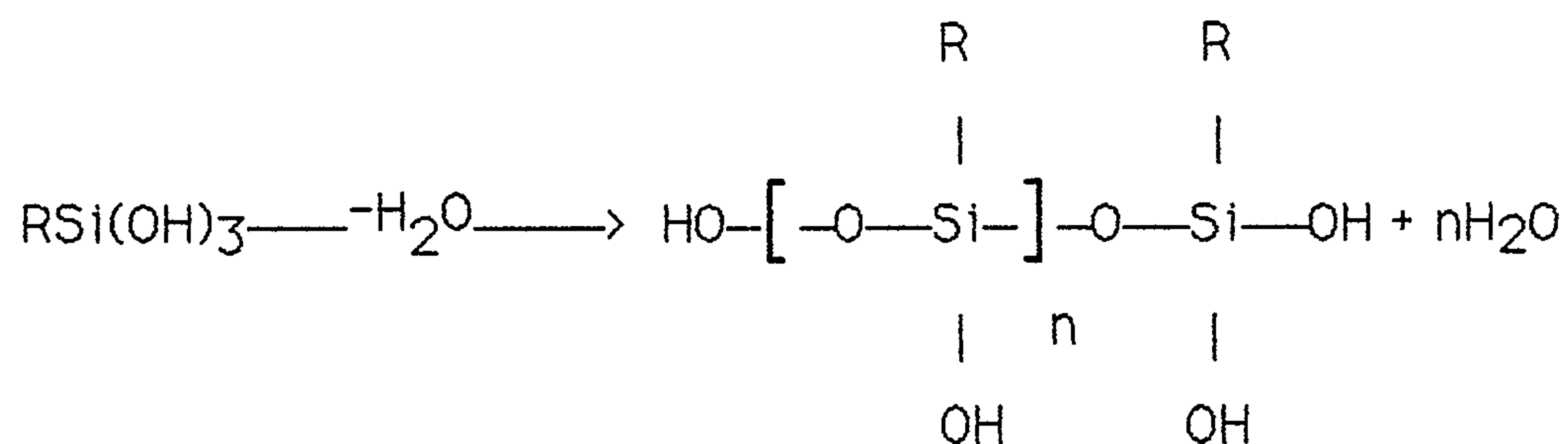
Both hydrolysis and condensation are strongly dependent on pH, as under optimum conditions hydrolysis is relatively fast (minutes), while the condensation reaction is much slower (several hours). Both acids and bases are known to be powerful catalysts for hydrolysis (and reformation) of siloxane bonds (Pleuddemann 1982 p.119).

Under mildly acidic conditions, neutral alkoxysilanes, such as γ -methacryloxypropyltrimethoxysilane, the silane coupling agent in Scotchprime (3M Co.) and Fusion (George Taub Products), hydrolyze rapidly to form monomeric silanetriols and then condense slowly to polymeric organic siloxanols. The overall reaction may be described by the following formulae;

Hydrolysis:



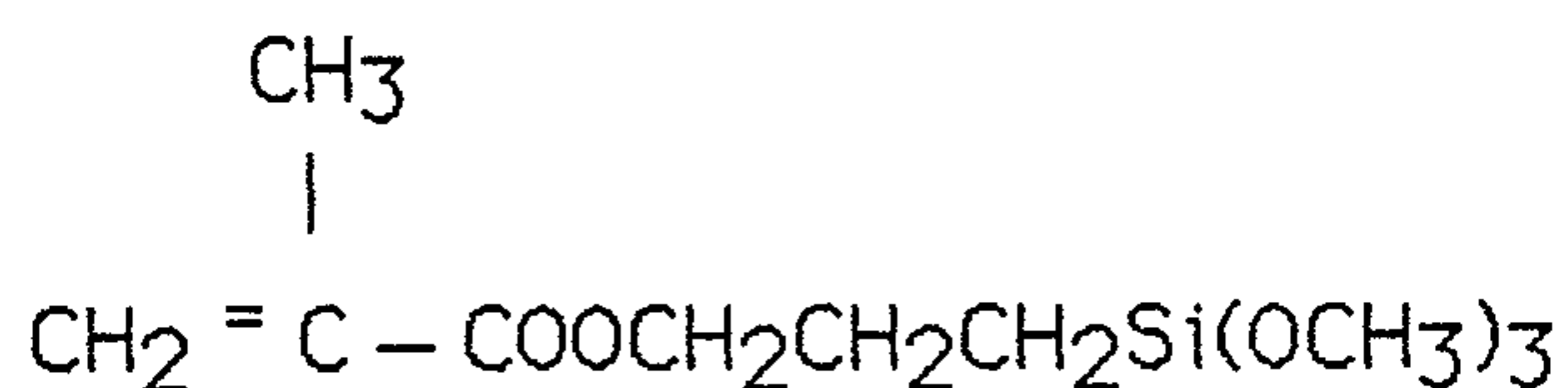
Condensation:



4.7. RESIN REACTIVITY

The great variety of organofunctional groups currently available provides coupling agents that are highly reactive with all of the present thermoset resin systems. Choice of a silane coupling agent for a particular resin system, however, is limited to those silanes that have a functional group readily capable of forming covalent bonds with the resin (Clark & Plueddemann 1963). Unlike the hydrolyzable groups discussed previously, these groups must be bonded to silicon in a hydrolytically and thermally stable manner (Stermann & Marsden 1966c).

γ -methacryloxypropyltrimethoxysilane, the silane component of Scotchprime and Fusion, is an example of a methacrylate-functional silane. It has the formula;



Methacrylate-functional silanes copolymerize readily with acrylic monomers (Plueddemann 1982 p.39) as well as epoxy resins. In their studies, Stermann and Marsden (1963a) rated methacryloxypropyltrimethoxysilane as the best silane for overall bonding performance. This is probably due to the presence of the unsaturated carbon bond (see Figure 6).

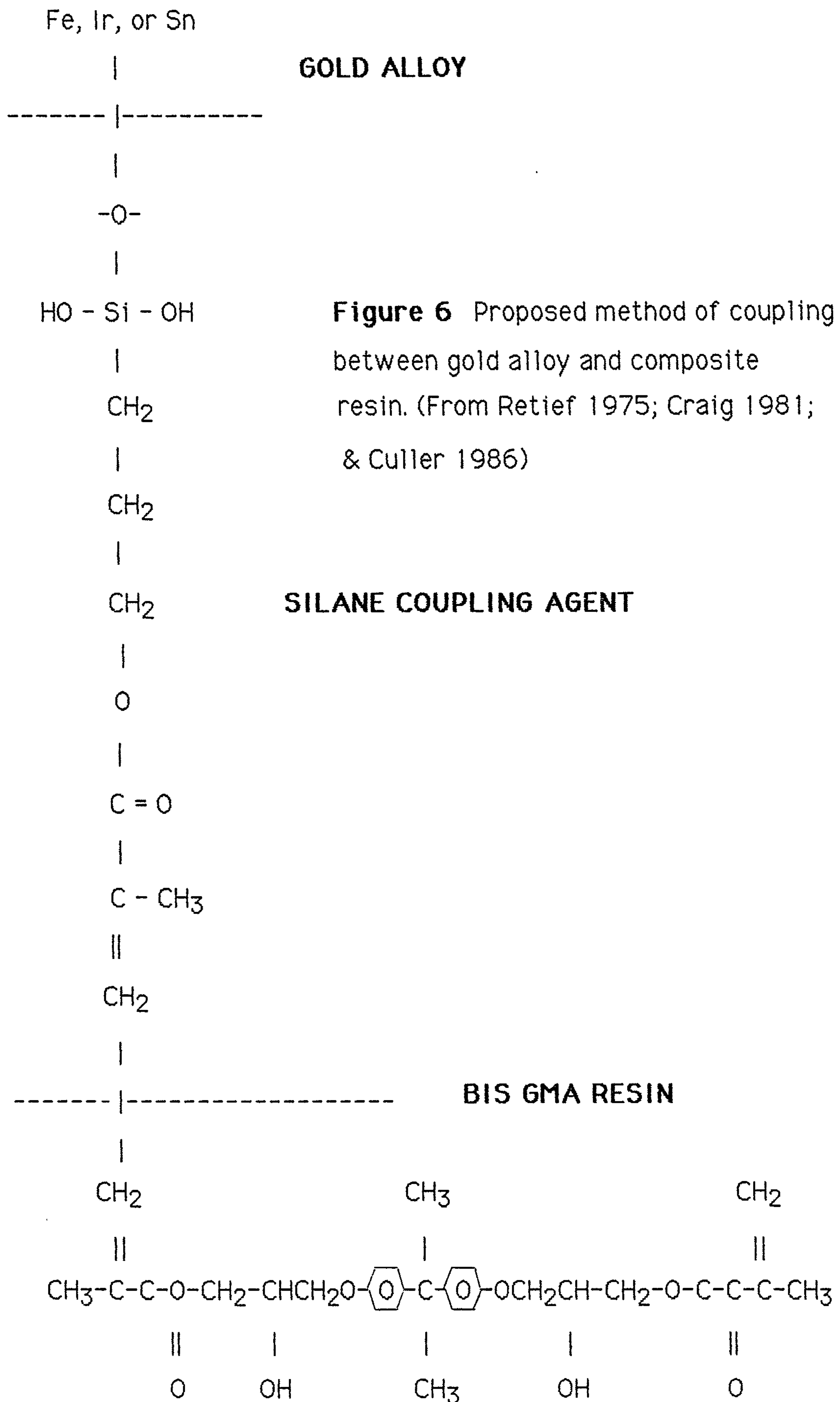


Figure 6 Proposed method of coupling between gold alloy and composite resin. (From Retief 1975; Craig 1981; & Culler 1986)

4.7.1. THERMOSETTING RESINS

Silane coupling agents were originally developed for use with thermosetting resins (Stermann & Marsden 1965). The two thermoset resins that command the greatest attention in the field of glass reinforcement are polyester and epoxy resins (Stermann & Marsden 1966c). Lee (1968) states that it is considered factual that thermosetting resins can form chemical bonds with silane coupling agents.

4.7.1.1. Polyester Resins

Polyester resins are highly reactive with methacryloxypropyltrimethoxysilane producing excellent wet and dry strength values (Clark & Plueddemann 1963; Stermann & Marsden 1966c). The methacrylate-functional silane imparts good handling properties to glass and is commonly used with polyesters cured at room temperature (Plueddemann 1982 p.143).

4.7.1.2. Epoxy Resins

Plueddemann, Clark, Nelson, and Hoffman (1962) note that almost all functional groups are capable of reacting with an epoxy resin. Bowen's Resin (BIS-GMA) used in dental restorative composite is a combination of an epoxy resin and glycidyl methacrylate (Braden, Causton & Clarke 1976). Stermann and Marsden (1963a) note that concentrations of silane as low as 0.5% are sufficient working levels for application to epoxy resins.

4.7.2. THERMOPLASTIC RESINS

Silane coupling agents are also successful when combined with specific thermoplastic resins, such as polystyrene. These will not be discussed further as they are not within the scope of this study.

4.8. SOLUTIONS OF SILANE COUPLING AGENTS

Organofunctional trialkoxysilanes hydrolyze in water and then condense to oligomeric siloxanols, as discussed previously. Stability and reactivity of aqueous solutions of silanes depend on many factors, including the nature of the organofunctional group on silicon.

Organofunctional alkoxysilanes are often hydrolyzed before being applied to surfaces to function as primers (Clark & Plueddemann 1963). Both Scotchprime and Fusion are applied in this manner. Methacrylate-functional silanes are insoluble in water initially, but become soluble when prehydrolyzed (Plueddemann 1982 p.63). Plueddemann (1982 p.158) discusses methods of preparing methacrylate-functional silanes in a pre-hydrolyzed form in an alcohol solvent. This is the manner of presentation of Scotchprime, but not of Fusion. Prehydrolysis in a concentrated solution apparently causes internal cyclization of siloxane structure to give a less highly cross-linked cured film. This is the reason for preparing the solution with an alcohol solvent, since the internal cyclized structures are less effective as primers when they are applied from concentrated solutions as a thicker film. Primer performance in this case would thus be dependent on the mechanical properties of the film. However, when applied from a dilute alcoholic solution film properties are of little significance and the silane functions only as a surface modifier in the form of an oriented monolayer (Plueddemann 1982 p.64, 202).

To this dilute alcohol solution approximately 1% of water and 0.1% acetic acid is added. This produces a stable solution. When this is used as a primer to bond to gold alloy surfaces the

acetic acid volatilizes with the initial solvent loss. Unfortunately organofunctional silanes in neutral or acidic solution tend to hydrolyze into silanols without forming polymers (Lee 1968). Formation of polymers prior to application to the substrate decreases the silane's ability to cross-link.

Pleuddemann (1982 p.120) notes that hydrolysis of an alkyl silicate in an ethanol solution results in equal distribution of the ethanol between polymer and solvent, suggesting a true equilibrium of hydrolysis and re-esterification. Re-esterification of silanols by alcohol must therefore be much more rapid than direct trans-esterification of alkyl silicates.

Bascom (1968) concluded from his studies that the addition of acetic acid to a hydrocarbon solvent would enhance the coupling effectiveness of γ -methacryloxypropyltrimethoxy-silane and yield more stable silane bonds. Chen and Brauer (1982) stated a similar effect with the addition of 2% of a primary amine, η -propylamine.

4.9. THICKNESS OF SILANE LAYERS

Silane coupling agents used as adhesion promoters only require a chemical modification of the surface that can be accomplished by a few monolayers of silane (Causton 1982), whereas primers on massive structures require a sufficiently thick hydrolyzed silane layer to contribute mechanical film properties and possibly solvent effects for the matrix resin (Plueddemann 1982 p.83). Theoretically only a monolayer of organofunctional silane would be required for simple chemical bonding across the interface. Several authors indicate, however, that more than a monolayer of silane is required for optimum

performance as an adhesion promoter (Stermann & Bradley 1961; Stermann & Marsden 1966c; Pleuddemann 1982 p.136).

The thickness of siloxane film adsorbed on a mineral surface, depends on the nature of the organofunctional group on silicon, the availability of water, pH and age of the silane solution, topography of the surface, and presence or absence of specific catalysts. Pleuddemann (1982 p.87) suggests that monolayer coverage is more likely to be obtained when a mineral surface is treated with a dilute solution of an organofunctional silane in an anhydrous organic solvent.

4.10. ACTION OF WATER ON SILANE BONDS

Alkoxysilanes are capable of reacting with surface moisture to generate silanol groups which can form strong hydrogen bonds with a hydroxylated surface. In addition, they are capable of reacting with surface hydroxyl groups to form covalent oxane bonds with the mineral surface (Pleuddemann 1982 p.98).

Since a hydrolysis-resistant bridge of covalent bonds is readily formed between coupling agent and resin, the water resistance of composites is determined largely by equilibrium conditions of bonds between coupling agent (or resin) and hydroxyl groups of the mineral in the presence of water (Pleuddemann 1982 p.116).

Once water molecules cluster at an adhesive interface, they are capable of hydrolyzing any type of bond that can be formed between resin and metal oxide. Even though siloxane bonds are thermally stable, these bonds are hydrolyzable, and the rate of hydrolysis increases dramatically with increasing temperature and pH (Pleuddemann 1982 p.210). Silane coupling agents do not

function to exclude water from the interface, as was once thought (Pleuddeman, Clark, Nelson & Hoffman 1962), but somehow function to retain adhesion in the presence of water (Clark & Pleuddemann 1963).

Water resistance of composites is favoured by:

- 1) Using a resin with low water absorption.
- 2) Using a water-resistant substrate e.g. quartz
- 3) Having an appropriate silane coupling agent at the interface (Pleuddemann 1982 p.124).

Plueddemann (1982 p.114) points out that it is well established that silanes form oxane bonds with mineral surfaces. But it is still uncertain why such bonds should contribute such outstanding water resistance.

4.11. CHARACTERISTICS OF SILANE BONDS WITH MINERAL SURFACES

The bond between silane coupling agents and organic resins may be pictured as a bridge of organic covalent bonds (Schwaber & Rodriguez 1967), while the bonds between silane coupling agents and mineral surfaces are typically inorganic with a high degree of ionic character.

The silicon-carbon bond has 12% ionic character, while the silicon-oxygen bond is 50% ionic in character (Chen & Brauer 1982). Oxane bonds between silicon and most metals are even higher in ionic character.

4.12. EFFECTS OF SILANE COUPLING AGENTS ON PARTICLE-FILLED COMPOSITES

Silane coupling agents have demonstrated significant improvements in, and retention of, general mechanical and electrical properties in glass reinforced composites of all thermosetting resins (Stermann & Marsden 1965; Stermann & Marsden 1966b).

They are used in the manufacture of modern-day composite restorative materials to bind the filler particles to the resin matrix. The service life of dental composites is assumed to be strongly dependent on the bonding between the resin matrix and reinforcing filler (Chen & Brauer 1982).

Coupling agents may also be used to improve the bond between a composite restorative material and a mineral substrate.

The filler surface interacts with the polymer through catalytic activity, orientation of molecular segments, and other modifications of polymer morphology. One important function of silane treatments on fillers is to reduce the inhibitory action of fillers on cure of thermosetting resins and to promote alignment of molecular segments of thermoplastic polymers.

Although a chemical binding mechanism is generally proposed as the mechanism of bonding through silane coupling agents, there is much evidence to suggest that failure in composites is often in a boundary layer of the matrix resin rather than at the true interface (Vanderbilt & Simko 1960). A major function of adhesion promoters must therefore be to strengthen this boundary layer. A silane at the interface may protect a mineral surface against fracture, or may strengthen the boundary

layer of resin to have a positive effect on composite properties even if failure is not at the interface (Pleuddemann 1982 p.167).

As a general rule, it appears that silane treatment of any filler with a Moh hardness number of 3 or less will have limited effectiveness in strengthening rigid thermoset or thermoplastic resins, since cleavage will occur in the filler before failure in the resin or interface (Pleuddemann 1982 p.172).

4.12.1. WETTABILITY

The wettability of silane-treated fillers will depend on the nature of the organofunctional group on silicon and on the orientation of the silane on the filler surface (Pleuddemann 1982 p.182).

4.12.2. VISCOSITY

Silane-treated fillers often provide lower viscosities in filled resins than do untreated fillers. Neutral silanes, such as methacrylate functional silanes, modified with catalytic amounts of an amine or a titanate, are generally more effective as additives than the pure silane in modifying viscosity. Performance as a coupling agent also is improved by such modification (Pleuddemann 1982 p.187).

4.12.3. COUPLING AND ADHESION

Adhesion across the interface in filled polymer composites is essential for improved shear strength and chemical resistance. Improved impact strength is not a good measure of coupling activity, since treatment of fillers with release agents can impart very high strength to composites (Pleuddemann 1982 p.188).

Orientation of the silane on the filler is controlled by the pH of the solution (Pleuddemann 1982 p.189).

4.13. CONCLUSION

Organofunctional silanes have an advantage over other organic compounds in that the silanes have the potential for bonding to hydroxylated surfaces through several mechanisms. At closer range, Van der Waal's forces, hydrogen bonding, and covalent bonding are possible through silanol groups. By combining all of these possibilities in a single molecule, the silanes are uniquely capable of competing with water for hydroxylated surfaces (Pleuddemann 1982 p.208).

Understanding of the basic function of adhesion promoters is becoming clearer and ultimately the use of coupling agents will result in major improvements in bond durability.

According to De Lollis (1980), the use of adhesion promoters in dentistry is here to stay .

5. BONDING TO METAL SURFACES

5.1. INTRODUCTION

The first structural-metal adhesives, developed around 1909, were composite polymers containing phenol formaldehyde. These were improved upon in 1942 with the advent of the neoprene phenolic adhesives making possible metal to metal bonds which were stronger than riveted joints. Around the same time the vinyl phenolics were first developed and are still used in modern aircraft. About 1955 the first epoxies were produced. These have become the most popular type of adhesive and are available in many forms (De Lollis 1980).

A little later the acrylic adhesives were developed and have been available since about 1960. The second generation of acrylics are elastomer modified methacrylic resins. They can bond to metals, ceramics, and plastics (De Lollis 1980).

5.2. PROPERTIES OF METAL SURFACES

5.2.1. SURFACE CHEMISTRY

Surfaces of metals, metal oxides and silicates, in equilibrium with atmospheric moisture, are made up of hydrated hydroxyl groups. De Lollis (1980) notes that it takes about five hours for a metal surface, exposed to the atmosphere, to attain this equilibrium.

5.2.2. OXIDES

Oxidation is the process whereby a substance combines with oxygen, and more broadly speaking, simply refers to the increase in valence state of the element concerned (West 1985).

Zisman (1963) points out that if it were not for the oxide and/or water adsorbed on almost all metals at ordinary temperatures it would be impossible to avoid serious adhesion and cold-welding on rubbing metals together. Buonocore (1975) claims that a layer of oxide found on a freshly cut metal surface represents a firmly bonded contaminant layer. However, he notes that some contaminants may aid in bonding, in which case it may be inadvisable to attempt to remove them. This notion of oxides as both contaminants and adhesion promoters is prevalent in the literature.

Studies have shown (Wade & Hackerman 1964) that the surfaces of oxides exposed to atmospheric conditions differ chemically from those oxides that are in the bulk phase. OH groups modify the surface of an inorganic metal oxide chemically and promote phenomena such as hydrogen bonding.

5.2.3. CONTACT ANGLE

Contact angle of water and most organic solvents for a polar metal is zero if the metal surface is clean. De Lollis (1980) defines a polar metal surface as one which normally forms an oxide under ambient conditions. De Lollis (1980) also points out that true cleanliness is a rare commodity and states that at a practical level a clean surface is one which, after being degreased, etched, and rinsed in distilled or deionized water, is dried with clean air.

5.2.4. EFFECT OF WATER

Baier, Shafrin and Zisman (1968) note that high-energy solids such as metals, readily adsorb water, which at room temperature may convert them to low-energy surfaces. Ideally then, an adhesive to metal should contain accessible hydrophilic

groups which will tend to spread more readily on moist surfaces. If an adhesive is not able to compete with water on the metal surface the bond resulting will be weak. It appears very unlikely that all water could ever be displaced and that a monolayer of water will always remain.

5.3. BONDING AGENTS

5.3.1. PRIMERS

De Lollis (1980) states that primers in common use as metal surface conditioners perform four different functions:

- 1) as protection against corrosion,
- 2) as intermediate layers to modify the properties of the bond,
- 3) to aid processing by positioning bonded parts,
- 4) for bond improvement.

Primers are used to condition the metal surface to ensure that water is no longer preferentially adsorbed at the adherend surface.

5.3.2. SILANES

These have been discussed extensively in chapter 4 and the reader is referred to that chapter for a more detailed discussion.

Silicates and metal oxides have a high affinity for silanes (Stermann & Marsden 1963b). Stermann and Toogood (1965) point out that substrates such as copper, aluminium, and steel are being successfully bonded to silicone rubber using a silicone primer.

Pleuddemann (1982 p.151) notes that a simple primer on metal may give performance comparable to more expensive etching and chemical modification that provides a porous surface on the metal for mechanical interlocking of epoxy adhesives. The

primer can overcome the presence of a potentially weak boundary layer by producing chemically durable bonds (De Lollis 1980). The water required for the hydrolysis/polymerization of a silane coupling agent is available from the metal surface (Bascom 1968).

Plueddemann (1982 p.91) questions the role of silanes in metal bonding and notes that simple electrostatic attraction of coupling agent silanols for hydrated oxide surfaces cannot be a major factor in bonding across the interface, since such silanols are more effective on acidic oxide surfaces than on basic oxide surfaces.

Gettings and Kinloch (1977) studied the type of bonding between silane-based primers and mild-steel substrates using X-ray photoelectron spectroscopy and static secondary ion mass spectroscopy. They found direct evidence of a chemical bond, which they felt was probably -Fe-O-Si= , between the metal oxide and the polysiloxane primer. They determined this fact by establishing the presence of FeSiO^+ radicals.

5.4. EFFECT OF ACID-ETCHING ON METAL SURFACES

Phosphoric acid is used industrially on metal surfaces to remove contaminants and promote the adsorption of phosphate groups onto the surface to improve adhesion (Buonocore 1955). The removal of contaminants will convert a low energy surface into a high energy surface, more amenable to bonding.

5.5. OTHER METAL BONDING AGENTS

5.5.1. POLYCARBOXYLATE CEMENTS

These cements were developed by Smith (1968) in his search for a dental cement that would offer good adhesion under moist conditions. A hydrophilic liquid, such as a concentrated aqueous solution of polyacrylic acid, when reacted with a modified zinc oxide forms a cement that bonds to tooth surfaces (Brauer & Huget 1972). This material also adheres well to many metals including stainless steel (Buonocore 1970), sterling silver and amalgam (Moser, Brown & Greener 1974) but according to Phillips, Swartz and Rhodes (1970) and Brauer and Huget (1972), does not bond to gold. Moser, Brown and Greener (1974) explained that this is due to the fact that pure gold is inert and offers no potential reactive sites for the cement to combine with.

5.5.2. GLASS IONOMER CEMENT

This cement forms effective adhesive bonds to platinum and gold surfaces which have been plated with tin. It does not adhere to surfaces of pure gold and platinum (Hotz, McLean, Sced & Wilson 1977).

5.6. BONDING TO GOLD

De Lollis (1980) notes that an oxidized polar metal surface is more adsorptive and develops greater adhesion than a low-energy, dispersive noble metal (non-oxidizing) surface (Barquins & Cognard 1986). This is surprising since, by the nature of metals, the surface energy of gold should be high. Cognard (1984) has attempted to explain this phenomenon by venturing that a "clean" gold surface has a high energy but that it is very easily

contaminated by adsorbed hydrocarbons which produce a low energy surface layer.

Bascom (1968) feels that the ionic metallosiloxane bonds are susceptible to hydrolysis and because of this, chemical bonding to gold is doubtful. He also states that it is doubtful that a gold surface contains enough water, despite an earlier statement, to form more than a monolayer of polysiloxane. According to Bascom the presence of at least ten monolayers is required to form an adequate bond.

5.7. BONDING BETWEEN GOLD ALLOY AND PORCELAIN

Bonding of ceramic to metal alloy depends on the wetting of the alloy surface by the fused porcelain (Anderson 1976) and an interaction between selected atoms in the metal with the porcelain (Craig 1985c). The mechanism of the bond between gold and porcelain may be broken down into its component parts as: mechanical, chemical, dendritical, transition phase, and van der Waal's.

5.7.1. MECHANICAL BOND

This occurs as a result of roughening of the gold surface, either by; sandblasting (Anderson 1976), oxidation of the surface, electrochemical erosion of the metal surface by molten glass, selective oxidation of grain boundaries, etching by acid in pretreatment for fusing, or by precipitation of dendritic crystals by reduction of metal oxides contained in glass (Yamamoto 1985).

5.7.2. CHEMICAL BOND

This results from electrons shared at the interface on fusion of the metal and porcelain. Precious metal alloys in dentistry contain minute amounts of tin, indium, and iron which

form oxides on the alloy surface on heating. These metal oxides are capable of cross-linking with silica (the major component of dental porcelain) in the molten state to form strong chemical bonds (Yamamoto 1985).

5.7.3. BOND DUE TO TRANSITION PHASE

This is a type of chemical bond (Yamamoto 1985) formed indirectly through an intermediary layer of undissolved oxide on the metal surface. With a precious metal alloy this forms a strong bond.

5.7.4. BOND DUE TO MOLECULAR ATTRACTION (van der Waal's forces)

This is a significant part of the joint formed by the electrostatic reaction between two atoms as they approach each other within a range in which chemical bonding does not occur (Yamamoto 1985). The metal oxides have uneven electrical charge distribution and this produces a permanent dipole (Anderson 1976).

5.8. FACTORS INFLUENCING BOND STRENGTH BETWEEN METAL AND CERAMIC

Bond strength varies according to the properties of the additive elements (i.e. tin, iron, and indium). The addition of tin greatly increases the bond strength. The addition of 0.25% of iron increases the bond strength but amounts of iron above this concentration decrease the bond strength.

The amount of base metal oxide, especially tin oxide, which is produced on the alloy surface by heating, influences the bond strength even more significantly than the amount of tin added to the alloy (Yamamoto 1985). Similarly, increasing the oxide

content on the alloy surface improves the degree of surface wettability.

Eden, Craig and Peyton (1970) claim that highly reproducible metal surfaces allow an evaluation of bond test results without the variation inherent in dental substrates.

6. METHODS OF ORTHODONTIC **BOND STRENGTH TESTING**

6.1. INTRODUCTION

The measurement of adhesion is a complex problem. Destructive "end-use" tests in which an attempt is made to assess the performance of an adhesive are commonly used to measure quantitatively the adhesive strength (Brauer & Huget 1972; Brauer 1975). Values observed in debonding experiments are strongly dependent on the mode of failure.

Test methods usually involve loading specimens dynamically to failure after exposing the specimens to conditions simulating the oral environment such as water and other fluids (Lee, Swartz & Culp 1969). The testing of adhesive bonds evaluates not only the adhesive material, but also the bonding technique, including the preparation of surfaces, the application of the adhesive, and the curing process (Parker & Taylor 1966).

Numerous tests have been devised to measure the stress-transfer capability between adhesives and substrates (Pleuddemann 1982).

6.2. DEFINITIONS

De Lollis (1980) defines "bond strength" as the unit load applied in tension, compression, flexure, peel, impact, cleavage, or shear, required to break an adhesive assembly, with failure occurring in or near the plane of the bond. Alexandre, Young, Sandrik and Bowman (1981) define "bond strength" as the load, applied parallel to the bracket-adhesive-substrate interfaces, necessary to cause failure, divided by the area of the adhesive

under the bracket. Bond strength should not be confused with the shear strength of the adhesive, which would imply cohesive failure. Failure inevitably occurs as a mixed phenomenon at the interface. Failure never occurs purely adhesively or purely cohesively.

6.3. MECHANISMS OF BOND FAILURE

De Lollis (1980) notes that on a short time basis and in the absence of environmental exposure, a good bond usually first fails cohesively. He points out that there is a field of thought that feels that a well prepared bond can only fail cohesively.

Factors which may contribute to bond failure can be listed as :-

1) Desorption by water: This may occur either by the adhesive directly absorbing the water with subsequent permeation to the interface, or the water may diffuse along the adhesive-adherend interface (De Lollis 1980).

2) Phase discontinuity: The difference between the adhesive and the adherend (De Lollis 1980).

3) Differences in the co-efficient of thermal expansion: This can lead to stresses at the interface (De Lollis 1980).

4) Swelling of the adhesive due to water absorption: This can lead to stresses at the interface (De Lollis 1980).

5) Corrosion of the adherend by the adhesive. (De Lollis 1980)

6) Disturbance of the bonding system during setting (Gorelick, Masunga, Thomas & Zachrisson 1978).

7) Failure to remove contaminants prior to bonding (Gorelick, Masunga, Thomas & Zachrisson 1978).

8) Use of an incorrect adhesive (Gorelick, Masunga, Thomas & Zachrisson 1978).

9) Extremes of salivary pH (Newman 1973).

10) Forces of mastication and excessive archwire forces (Newman 1973).

11) Failure to follow the manufacturer's instructions (Gorelick, Masunga, Thomas & Zachrisson 1978).

6.4. STRESS TESTS

6.4.1. STRUCTURAL BONDS

A structural bond is one which stresses the adherend to the yield point, thereby taking full advantage of the strength of the adherend. The stronger the adherend the greater the demands on the adhesive. Thus, few adhesives qualify as "structural" for metals (De Lollis 1980).

However, it is not essential that all metal-to-metal bonds be structural. The primary consideration for nonstructural bonds is that the adhesive bond be good enough to withstand the intended service condition with a reasonable factor of safety, without necessarily having the ability to stress the metal to its yield point (De Lollis 1980).

6.4.2. VALIDITY OF STRESS TESTS

Årtun and Bergland (1984) feel that laboratory bond-strength tests have significant weaknesses. The forces can only be standardized in two directions (shear and tensile) and many factors, such as curved surfaces, are not taken into account. Beech and Jalaly (1981) previously, however, did not feel that this was a weakness since all forces acting clinically on a bonded

bracket may be resolved into these components acting at right angles.

6.4.3. JOINT DESIGN

A lingual orthodontic button bonded to a flat gold surface represents, on a macroscopic scale, a butt joint. According to De Lollis (1980) the butt joint is a most unfavourable design. It represents a great discontinuity in the strength of the assembly and is very sensitive to side loading i.e. shear loading.

6.5. TYPES OF STRESS

De Lollis (1980) states that the types of stresses placed on bonded assemblies can be resolved into three basic types: shear, tensile and peel. He further goes on to state that test methods and specimens in industry have been standardized, making it possible for different laboratories to evaluate adhesives and obtain comparable results. Unfortunately this does not appear to be the case with dental adhesives testing (Bishara, Khowassah & Oesterle 1975).

6.5.1. SHEAR TESTS

Pure shear stresses are those which are imposed parallel to, and in the plane of the bond (De Lollis 1980). They are difficult to determine for bonded specimens (Parker & Taylor 1966) and may not be applicable to curved surfaces (Khowassah, Bishara, Francis & Henderson 1975).

Craig (1985c) defines shear strength, as the maximum stress that a material can withstand before failure in a shear mode of loading. He calculates this strength by dividing the force by the area.

6.5.2. TENSILE TESTS

Pure tensile tests are those in which the load is applied normal to the plane of the bond and in line with the centre of the bonded area (De Lollis 1980).

6.5.3. PEEL TESTS

Peel tests are designed to measure the resistance of adhesive bonds to highly localized stresses. Peel forces are therefore considered as being applied to linear fronts (De Lollis 1980).

6.5.4. OTHER TESTS

These include cleavage, creep, fatigue and impact tests (Parker & Taylor 1966; De Lollis 1980).

6.6. FAILURE SITES

Jassem, Retief and Jamison (1981) and Årtun & Bergland (1984), from their experiments, note that during application of tensile and shear forces, test specimens failed predominantly at the bracket-resin interface. Failure at this site is not a true reflection of the bond strength of the resin system. Beech (1982) notes that many simple tests are designed to measure the strength of the joint rather than the interfacial bond strength. If true adhesion exists, interfacial failure will be rare (Falconer, MacDonald & Walker 1964).

6.7. METHODS OF SHEAR TESTING

Most authors have used a rectangular stainless steel orthodontic wire bent into a square shape, and engaged under the tie-wings of an edgewise bracket bonded to the test substrate.

The testing machine, usually an Instron model, is used in the tension mode (Moin & Dogon 1978; Mascia & Chen 1982).

It is the opinion of this author that this method must incorporate the additional variable of the elastic deformation of the the wire used, as well as more closely resembling a shear-peel rather than a true shear test. Several authors, including Moin and Dogon (1978) and Mascia and Chen (1982), also report that the bracket wings of the edgewise bracket often fracture during testing, further complicating the test, and adding suspicion of additional elastic deformation occurring in the bracket itself.

It would seem more accurate to use a rigid shearing edge to test the adhesive and eliminate the variable of elastic deformation.

6.8. REASONS FOR SHEAR TESTING

In shear bond testing the maximum force is exerted along the interface and the fracture path will not deviate unless there is a major flaw in the adhesive or at the substrate interface (Beech & Jalaly 1981). In this way a more reproducible interfacial fracture is observed with less cohesive failure (Eden, Craig & Peyton 1970; Beech & Jalaly 1980). Despite this Thanos, Munholland and Caputo (1979) and Beech and Jalaly (1981) state that there is a much greater spread of values with shear than with tensile tests.

With tensile testing the force is transmitted through the body of the adhesive and partial cohesive failure rather than interfacial failure occurs (Short, Hembree & McKnight 1975; Beech & Jalaly 1981). This is because the area placed under the

greatest tension will be the weakest area in the bulk of the adhesive.

Newman (1973), Retief (1974) and Lee, Orlowski, Enabe and Rogers (1974) felt that shear stress was the most representative parameter of the stresses imposed on a bracket in place on a tooth in the mouth. Hormati, Fuller and Denehy (1980) agreed and stated that shear stresses are the predominant force applied to an acid-etched composite restoration in the mouth. Tavas and Watts (1979) felt that shear-peel is a severe test of adhesion which is most likely to correlate with clinical performance.

Numerous authors have conducted shear stress tests including; Miura, Nakagawa and Masuhara (1971), Keizer, ten Cate and Arends (1976), Carlyle, Chamma, Moir and Williams (1978), Alexandre, Young, Sandrik and Bowman (1981), Beech and Jalaly (1981), Maijer and Smith (1981), Buzzitta, Hallgren and Powers (1982), and Knoll, Gwinnett and Wolff (1986).

Eden, Craig and Peyton (1970) state that shear tests require relatively simple equipment for specimen preparation, conditioning, and testing, and offer a relatively high degree of reliability. Similarly, Mascia and Chen (1982) preferred the shearing mode over others, for increasing the consistency of their results. Parker and Taylor (1966) point out that theoretically it should be easier to break a joint by shear forces than by tensile forces. In other words, the shear strength of a bond will be less than the tensile strength. In contrast to this Ghassemi-Tary (1977) commented that shear strengths of bonded brackets were greater than tensile strengths. Beech and Jalay (1981), testing five direct bonding adhesives, found shear strength to be greater in all instances than tensile strength and could find no simple

relationship between the two. Several other authors have found similar results (Reynolds & von Fraunhofer 1976; Aguirre, King & Waldron 1982; and Mascia & Chen 1982).

Beech and Jalaly (1981) felt that the shear bond strength may be partly related to the modulus of elasticity of the adhesive. The higher the modulus the more evenly distributed the stress over the whole bonded area. The American Council on Dental Materials (1982) notes that thin adhesive films give higher shear strengths.

6.9. CLINICAL APPLICABILITY

Beech and Jalaly (1981) state that there is no simple relationship between bond failure in vivo, and bond strength. However, they proposed that bond strength above a certain minimum, at which good clinical performance is obtained, will not produce any improvement in clinical failure rate.

Buonocore (1981b) raises the question of whether it is at all possible to extrapolate to the clinical situation from in vitro experimentation.

7. FORCES ENCOUNTERED DURING ORTHODONTIC TREATMENT

7.1. REQUIREMENTS OF ADHESIVE SYSTEMS

The mechanical strength of an adhesive and the bracket material, as well as the adhesive forces at the interfaces, must be sufficiently great to resist the forces exerted during the entire orthodontic treatment procedure (Keizer, ten Cate & Arends 1976). Practically speaking, a bonding technique yielding bond strengths of a constantly high value is required to prevent premature loss of brackets. It is therefore necessary to define an acceptable bond strength.

7.2. FORCES FROM ORTHODONTIC APPLIANCES

Newman (1963) noted that the ideal orthodontic force should be in the range of 0.3 to 1.1 N and that the maximum force exerted on an orthodontic attachment, by an orthodontic appliance under clinical conditions, is approximately 3MPa. Keizer, ten Cate and Arends (1976) agreed with this statement by Newman.

Newman (1965) reported that shear force on an attachment $0.125''^2$ would be about 1 MPa if a force of 5 N were exerted by activation of an orthodontic loop, but expressed the view that this was an excessive force producing tissue damage, and should be avoided. Jenkins (1966), however, notes that masticatory forces alone or combined with forces from orthopedic-type appliances may exceed these values.

Thurrow (1966) agreed with Newman and defined "light orthodontic force" as from 0.8 to 1.1 N.

Mizrahi and Smith (1971) found that none of their experimental archwires exerted a load greater than 0.8 N.

Reynolds (1975) notes that maximum orthodontic forces are unlikely to exceed 14.7 N.

7.3. METHODS OF MEASURING BITE FORCE

Brudevold (1951) and Yurkstas and Curby (1953) used an apparatus consisting of a variable-inductance strain gauge which was incorporated into an artificial tooth to form a bite element. One to three of these bite elements were inserted into a removable prosthetic appliance and connected to associated electronic equipment.

Linderholm and Wennstrom (1970) employed a bite force dynamometer with strain gauges attached to steel plates covered with gutta percha to measure bite force at separations of 3 to 4 mm.

Garner and Kotwal (1973) used a bite pad of hard rubber attached to two biting surfaces by cold-cure resin. A recorder with a strain stress transducer conditioner, and automatic timer was used to record strain gauge output.

Haraldson, Carlsson and Ingervall (1979) used strain gauge transducers mounted in bite forks on subjects with oral implant bridges and compared this information with normal subjects.

Proffit and Fields (1983) and Proffit, Fields and Nixon (1983) employ two types of occlusal force transducers, a thin (2mm) peizo-foil transducer and a thicker (6mm) quartz crystal transducer. The advantage of the foil is that it is available in sheets which are 30 μm thick which allows measurement of occlusal forces with much less separation than previously. The

force transducer is placed on the disto-buccal cusp of a lower first molar, preferably on a tooth without restorations and in good occlusion. A matrix of restorative resin is used to provide contact between the transducer and the central fossa of the upper molar. Proffit, Fields and Nixon (1983) contended that six mm of molar separation is commonly required for chewing food. Unfortunately their technology does not permit closer approximation of the teeth than two mm for measuring occlusal force during swallowing. Most normal subjects bring their teeth together during swallowing (Cleall 1965).

7.4. FACTORS AFFECTING BITE FORCE

Proffit and Fields (1983) found that long-faced individuals generated less occlusal force overall than normal-faced individuals and divided their results into three categories:

1) Swallowing

Normal subjects generated 25.6 N at 6 mm opening.

Long-faced subjects generated 33.3 N at 6mm opening

2) Chewing

Normal subjects generated 92.2 N at 6mm opening

Long-faced subjects generated 72.9 N at 6mm opening

3) Maximum Biting Force

Normal subjects generated 152.0 N at 6mm opening

Long-faced subjects generated 119.4 N at 6mm opening

This last data was obtained by requesting the subject to bite as hard as they possibly could.

Garner and Kotwal (1973) determined that males bite harder than females, older patients bite harder than younger patients, and the greater the linear contact of incisive edges (as would be

expected), the stronger the bite. They further proposed that patients with deep overbites generated greater biting force than those with a normal amount of overbite. The later work of Proffit, Fields and Nixon (1983) appears to be an extension of this principle.

Exercise also has an effect on bite force as individuals who habitually chew on one side of their mouths show a biting force for that side of more than double the value of the unused side. Jenkins (1966) notes that the masticatory muscles and pain receptors in the periodontal ligament are the limiting factors in increasing maximum bite force.

Proffit, Fields and Nixon (1983) felt that differences in body build and general muscular strength could contribute to occlusal forces differences. They expected larger individuals to produce more force than smaller ones and similarly, muscular individuals to be more powerful than slender individuals.

7.5. BITE FORCE STUDIES

Studies of the forces generated by occlusion date back to the 19th century (Proffit, Fields & Nixon 1983). Jenkins (1966) believes that the earliest recorded masticatory forces date back even further to Borelli's work in 1681. Newman (1969) notes that when bonding to the labial surface of anterior teeth, the direct forces of mastication are not transmitted to the adhesive joints ordinarily. However, this would not be the case with lingual orthodontic appliances.

7.6. CHEWING

Brudevold (1951) and Yurkstas and Curby (1953) using strain gauges in removable prostheses reported chewing forces ranging from 5.9 to 14.7 N and 2.9 to 17.7 N respectively. Yurkstas and Curby (1953) found that difficulty encountered in crushing food did not lead to greater force being used but rather to an increase in the number of chewing strokes. They also noted that it was rare for the teeth to make contact during chewing.

Jenkins (1966) describes chewing forces in young people with a civilised diet to be about 445 N for molar teeth and about 147 N for incisor teeth. The average figure for women being less than that for men for molar teeth only. He does not clarify whether this force value applies to individual teeth or to groups of teeth. Jenkins (1966) also states that posterior teeth exert greater force due to the increased nature of the periodontal support these teeth have.

Mizrahi (1968) reports loads of 118 N being produced during mastication. Buonocore (1970) notes that average biting forces are only around 10 N but that point contacts involving cusps and incisal edges may well generate pressures up to 70 N.

Linderholm and Wennstrom (1970) obtained chewing forces ranging from 294 to 353 N on the molar teeth of male and female subjects. Bishara, Khowassah and Oesterle (1975) feel that masticatory forces generated in the molar region may reach as much as 23 MPa. Warner (1976) cites forces ranging from 0.7 to 1.5 MPa occurring during mastication.

Proffit and Fields (1983) note that the long-faced individual exerts considerably less occlusal force during simulated chewing, and brings the teeth together with

significantly less force during swallowing than does the normal individual.

Haraldson, Carlsson and Ingervall (1979) reported forces during chewing of 33 to 52 N in a normal control group.

Of interest is Jenkin's (1966) statement that individual teeth which are out of alignment, are found to be incapable of transmitting normal biting force.

7.7. MAXIMUM BITING FORCE

Brudevold (1951) recorded a maximum biting force of 88.3 N on a first molar tooth. Yurkstas and Curby (1953) recorded maximum biting forces on a single tooth of 117.7 N and found these forces usually were in the range of 58.8 to 78.5 N. Linderholm, Linqvist, Rinqvist and Wennstrom (1971) measured maximum bite forces in 12 year olds and found an average figure of 431.5 N with no statistical differences between the sexes. They concluded that, compared to previous studies, the maximum bite force of a child was only slightly less than that of an adult and that bite force did have a small correlation with body build and muscle force in children.

Linderholm and Wennstrom (1970) examined 18 to 31 year old males and females for maximum biting force. They found forces of 480.5 N on the molars and 215.8 N on the incisors of males and 421.7 N on the molars and 196.1 N on the incisors of females. It should be noted, however, that their female sample was only one-quarter of their male sample. Garner and Kotwal (1973), in their studies of maximum incisal biting force, obtained a mean figure of 155.7 N.

Reynolds (1975) describes an average maximum biting force of 687 N (i.e. a range of 98 to 981 N), but doesn't specify how he obtains these extremely high values.

Haraldson, Carlsson and Ingervall (1979) reported an average maximum bite force of 169 N in a normal group.

Finn (1978) reports that maximum biting force in the molar region was twice as great for normal subjects as for long-face subjects (570 vs 294 N), while short-face subjects had still higher measurements. Proffit, Fields and Nixon (1983) concur with Finn's assessment. Zachrisson (1977) cites the molar region as producing the greatest masticatory forces. Knoll, Gwinnett and Wolff (1986) found that forces generated in the posterior quadrants ranged above 294 N, compared to incisal biting forces which have been reported in the 127 to 147 N range.

7.8. ACCEPTABLE BOND STRENGTHS

Mizrahi and Smith (1971) concluded from their studies that the majority of bond failures are due to forces exerted during mastication. Knoll, Gwinnett and Wolff (1986) noted that there is a higher failure rate clinically among bonded brackets on posterior teeth than on anterior teeth. This may be due to the non-uniformity of resin thickness beneath the brackets resulting from variations in posterior dental anatomy.

According to Keizer, ten Cate & Arends (1976) the average bond strength minus three times the standard deviation should equal the maximum force exerted on a bracket during orthodontic treatment. The forces exerted on an orthodontic bracket include; those from orthodontic appliances, swallowing, chewing, and voluntary clenching contacts (maximum bite force).

Newman (1973) notes that acceptable bond strength varies with patient co-operation. In a co-operative patient adhesive strength values as low as 89 N may be acceptable.

Reynolds (1975) notes that an acceptable bond strength for a bonded system would be in the range of 5.9 to 7.8 MPa. Mizrahi (1968) notes that the orthodontic force required to move a single-rooted tooth should not exceed 4 N.

Creugers (1986) describes a bond strength of 20 MPa at the resin/metal interface as the minimum acceptable.

For clinical use an orthodontic direct bonding adhesive should develop bond strengths of approximately 39 N in 5 minutes and 58 N in 24 hours as measured by shear testing (Tavas & Watts 1984).

Lopez (1980) appears to embody the confusion over acceptable levels of bond strength when he states that "the mean bond strength required of an adhesive is difficult to determine, since occlusal loads vary considerably, and an assessment of the force transmitted to an individual tooth is difficult to obtain."

NB: All of the force values reproduced in this chapter were derived from their original source by using the conversion factors listed in Appendix B.

8. ORTHODONTIC BONDING MATERIALS

Phillips (1975) defines an orthodontic composite material as a three-dimensional combination of at least two chemically different materials with a distinct interface separating the components. He distinguishes this class of material from either reinforced acrylic resins or unfilled acrylic resins. Craig (1981) defines the two different materials Phillips mentions as a high strength dispersed phase and a lower strength matrix phase. The matrix phase consists of polymers and remnants from monomers, organic compounds used as viscosity controllers, polymerization inhibitors to provide adequate shelf life, chemical initiators and accelerators. The dispersed phase usually contains inorganic micro-, or colloidal-sized, particles and may contain polymer particles. The most common reinforcing materials are quartz, borosilicate glasses, and glass ceramics. The interfacial phase consists of a coupling agent, such as an organosilane, containing functional groups that attach to the dispersed phase and the matrix phase.

The percentage of filler varies from 33 to 80% between products. Silar, a micro-filled composite has only 50% filler particle content by weight. The American Council on Dental Materials (1982) notes that heavily filled composite resins have increased physical properties when compared with unfilled or lightly filled resins. They also point out that composite resins reach their maximum strength values over a period of several hours but that it is usually possible for clinicians to tie orthodontic attachments after about six to ten minutes.

Most orthodontic bonding cements can be classified as either acrylic or diacrylic resins (Reynolds 1975). The acrylic resins are based on self-curing acrylics and consist of methylmethacrylate monomer and ultra-fine powder, whilst most diacrylic resins are based on an acrylic modified epoxy resin i.e. Bis-GMA.

More recently Halpern (1981) notes that virtually all commercial orthodontic adhesives now use Bowen's Bis-GMA [2,2-bis-[-4(2-hydroxy-3 methacryloyloxy-propyloxy) -phenyl-]-propane] resin in their formulations. It combines the setting versatility of acrylic resin with the strength and stability of epoxy resin (Reynolds 1975). Bis-GMA polymerizes by three-dimensional cross-linking which contributes to greater strength, lower water absorption and less polymerization shrinkage. The strength of these resins can be further improved by the addition of large silane-coated silica filler particles (Gorelick, Masunga, Thomas & Zachrisson 1978; Soderholm 1984).

Bowen (1963) claims that the incorporation of vinylsilane-treated silica powder into composite resin improved the physical properties of the material when compared with resin without the vinylsilane surface treatment. Chen and Brauer (1982) noted that the improvement in service life of dental composite is a result of the addition of a silane coupling agent, and especially the improvement in the ability of the composite to retain its strength after long exposure to water.

Studies by Guzman, Faust and Powers (1980) and Buzzitta, Hallgren and Powers (1982) indicate that diacrylate cements are the strongest cements for bonding metal brackets to tooth.

9. RELATED STUDIES

To this author's knowledge there have only been two other studies on bonding orthodontically to dental gold alloys.

Wood, Jordan, Way and Galil (1986) stated in their study that prior to their work none had previously been undertaken in this field. They obtained 24 gold molar crowns to which they bonded 48 edgewise incisor brackets. They do not specify the type of gold alloy from which the crowns were constructed though it seems most likely, from their illustrations, that they were of a yellow type-three alloy. Roughening of the surfaces was performed by use of a carborundum stone in a dental handpiece. Whilst this may be clinically applicable it must detract from the uniformity of the experiment. The brackets were bonded with two commercially available materials, of which only one, Fusion, laid specific claim to achieving a bond with dental gold alloys. The crowns were debonded by shear stressing after 24 hours during which time the specimens were not maintained in a fluid environment to simulate oral conditions, but were stored dry.

Wood, Jordan, Way and Galil concluded from this study that neither of the bonding agents tested was effective in providing a chemical bond to the type of gold used. However, clinically acceptable bond strength could be achieved by roughening the gold alloy surface.

In the second recorded study, by Stokes, Hood and Tidmarsh (1986), published during the experimental stage of this thesis, the authors bonded with Fusion and Scotchprime to discs cast from Degudent U gold alloy. These discs were roughened with 240 grit silicon carbide paper and bonded with lingual buttons using

Silar restorative material. As a comparison, a separate group was roughened with 600 grit paper and bonded with Silar only, without Fusion or Scotchprime. Each group consisted of ten samples. All the specimens were stored in water for 24 hours at an unspecified temperature, after which they were shear stressed to failure. Shear testing was performed in an Instron machine in a manner resembling shear-peel rather than pure shear stress.

From this study Stokes, Hood and Tidmarsh disagreed with Wood, Jordan, Way and Galil and stated that bond strength to gold, with or without silane priming agents, would be insufficient to be clinically viable. They also proposed that the silane priming agents tested did not improve the bond obtained. In conclusion, these authors felt that alternative methods of bonding would be more appropriate, and at the present stage, the practise of orthodontic bonding to gold alloys was impractical.