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Adhesion in Dentistry

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None of the materials available to the dental profession at present consistently maintain adhesion to tooth structure in the oral environment (Swartz, 1969). Extensive research efforts are aimed at the development of a genuinely adhesive dental material because the advent of such a material will initiate a new era in dental practice (Phillips, 1967). An understanding of some of the principles involved in adhesion will make this subject less sticky.

THE PRINCIPLES OF ADHESION

Adhesion is defined as the molecular attraction between the surfaces of bodies in contact or the attraction between molecules at an interface. This force is called adhesion when unlike molecules are attracted and cohesion when molecules of the same kind are attracted. The material added to produce the adhesion is known as the adhesive and that to which it is applied the adherend. The interface is the zone between the interacting substances.

The molecular forces involved in adhesion are divided into chemical and physical attractive forces. The chemical or primary attractive forces are intramolecular forces and include those arising from electrovalent, polar and non-polar covalent and metallic bonds. The physical or secondary attractive forces are intermolecular forces and arise from the Van der Waals forces which include the Keesom forces (orientation effect), the Debye forces (induction effect) and the London forces (dispersion effect) and hydrogen bonding.

The physical forces of attraction result in the adsorption of the adhesive on the adherend, in other words 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. The London forces are universal as they are not dependent on the existence of permanent dipoles in adjacent molecules. Although weaker than the chemical attractive forces, the physical forces of attraction are sufficiently strong to produce good adhesive performance no matter what the chemical nature of the two phases in contact, provided that adequate intermolecular contact is achieved at the interface.

Chemisorption is preceded by physical adsorption. The rate of this reaction, however, is 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. Chemisorption gives rise to very strong attractive

forces and once established is not easily reversed.

Adhesion is dependent on intimate interfacial contact as the molecular forces of attraction do not operate beyond 2 or 3 Angstrom units. If solid surfaces are naturally smooth on an atomic scale they will adhere spontaneously when brought together. The molecular forces of attraction will operate all along the interface and a strong bond will result. An example of the adhesive force uniting atomically smooth surfaces is the bond between mica sheets. The strength of this adhesion is in the order of 14,000 lbs/sq. inch, as strong as the mica itself (Buonocore, 1963).

In practice it is impossible to obtain such atomically smooth surfaces; those to be bonded are very rough at an atomic level. If such rough surfaces are brought into contact the molecular forces of attraction will operate only where the tips of the asperities on the surfaces meet. These are so widely spaced that the attractive forces are small and poor adhesion will result. The actual area of contact between rough surfaces is generally a small fraction of the apparent one.

To obtain adhesion between rough surfaces, a liquid adhesive is introduced between the surfaces. The function of the adhesive is to adapt itself to the irregularities of the surfaces to be bonded 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 adherend at the interfaces. For practical reasons it is not only necessary to obtain molecular closeness but also to maintain it. For this reason a liquid adhesive that solidifies is used. This is achieved by the evaporation of a volatile component or by polymerization or cross-linking of the adhesive molecules by means of heat, catalysts or reactive hardeners.

To produce adequate adhesion the liquid adhesive must flow easily over the entire surface, thereby ensuring the wetting of the adherend surface. The fundamental requirement for good adhesive performance is intimate interfacial contact between the adhesive and its substrate or adherend. 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. The extent to which an adhesive will wet a surface depends on the viscosity of the adhesive, the shape of the irregularities on the surface of the adherend (De Bruyne, 1962) and the contact angle at which the adhesive meets the surface of the adherend (Zisman, 1963).

The contact angle, Θ, is the one formed between the surface of the adhesive drop and the surface of the adherend upon which it is resting and it is measured at equilibrium. If the contact angle is small, the adhesive will wet the adherend surfaces and the molecular forces of attraction will operate all along the entire interface and strong adhesion will result. Wetting is therefore a manifestation of the attractive forces between the molecules of the adhesive and the adherend. If, on the other hand, the contact angle is large, incomplete wetting will occur and a weak adhesive bond obtained. The relationship between contact angle, wetting and adhesion is diagrammatically presented in Fig. 1.

The contact angle is therefore a useful inverse measure of the wettability of a surface and hence of the strength of the adhesive bond.

The surface tensions of the adhesive and the adherend play an important role in adhesion. A molecule in the bulk of a liquid or a solid is surrounded by neighbouring molecules and is attracted equally from all sides. A molecule on the surface, on the other hand, is attracted from below and from the sides but not from above. As a result molecules on the surface are in a one-sided field force pulling them downward into the bulk of the liquid or solid. This force is responsible for the surface tensions of liquids and solids.

In 1805 Thomas Young enunciated that the three surface tensions, γ_{SV}, γ_{SL} and γ_{LV} existing at the phase boundaries of a drop of liquid at rest on a solid surface must form a system in static equilibrium.

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

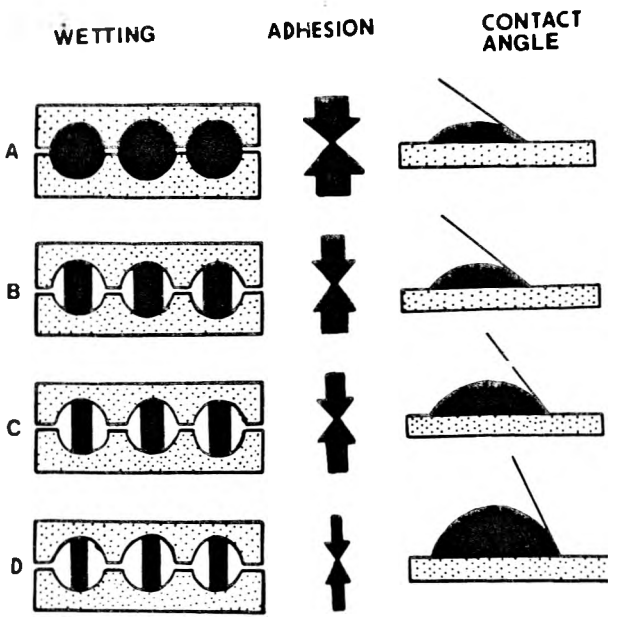


Fig. 1. Diagrammatic representation of the relationship between contact angle, wetting and adhesion.

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

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

The surface tensions γ_{LV}, γ_{SV} and γ_{SL} may be considered as forces. These three forces act at the edge of the spreading liquid. The vectors representing the energies γ_{SV} and γ_{SL} act along the solid surface and γ_{LV}, the surface tension of the liquid, acts at an angle Θ with the solid surface (Fig. 2a).

If the forces are resolved at the point where the three phases meet (Fig. 2b), the following equation is obtained:

$$\gamma_{SL} + x = \gamma_{SV} \quad \ldots\ldots (1)$$

But $$\frac{x}{\gamma_{LV}} = \cos\Theta$$

$$\therefore \quad x = \gamma_{LV} \cos\Theta$$

Substitute the value for x in (1).

$$\gamma_{SL} + \gamma_{LV} \cos\Theta = \gamma_{SV} \quad \ldots\ldots \text{The Young equation.}$$

$$\text{or} \quad \cos\Theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

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 solid in contact with the saturated vapour.

Early man utilized the phenomenon of adhesion without appreciating its significance or knowing the principles of adhesion. The matting of hair with blood, the sticking of wet leaves to bare skin and the trapping of insects with soft pitch are examples of the application of adhesives by primitive man.

Even lower animals have used the phenomenon of adhesion for hundreds of thousands of years, for example, the lowly barnacle adhering tenaciously to rock. The barnacle has the ability to attach itself to a variety of substrates under the most adverse conditions. Scientists are attempting to extract this information from the barnacle. The secretory mechanism has been identified but the exact chemical composition of this bioadhesive has eluded them (Hillman and Nace, 1970; Cook, 1970).

Isaac Newton in his "Opticks" stated more than 250 years ago that "there are agents in nature able to make the particles of bodies stick together by very strong attractions and it is the business of experimental philosophy to find them out" (Cited by De Bruyne, 1962). The extensive use of adhesives at the present time has amply confirmed Newton's prevision.

Adhesives are widely used in industry. Epoxy-glass laminates have found application in practically all stages of the fabrication of aircraft. The Boeing 727, for example, contains more than 1½ tons of reinforced plastics. The use of other types of plastics in aircraft has become fashionable these days but for purposes other than adhesion. Adhesives are also extensively used in the building industry to bond structural materials, in the electrical industry as an insulating medium and as general purpose casting and moulding compounds (Lee and Neville, 1967). Furthermore adhesives are commonly used for domestic purposes and most of us have used these adhesives on numerous occasions. I am referring to the adhesive tapes, glues, pastes and putties which are commercially available.

The widespread use and application of adhesives in industry are due to several factors. The Industrialist is in the fortunate position that he can very often select conditions required for optimal adhesion. He can work under dry conditions, apply the adhesive at high temperatures and pressures, is usually not pressed for time and the toxicity of the adhesive system is not of prime importance.

To obtain adhesion in the mouth is a much more difficult task. The development of a truly adhesive dental material remains the objective of many

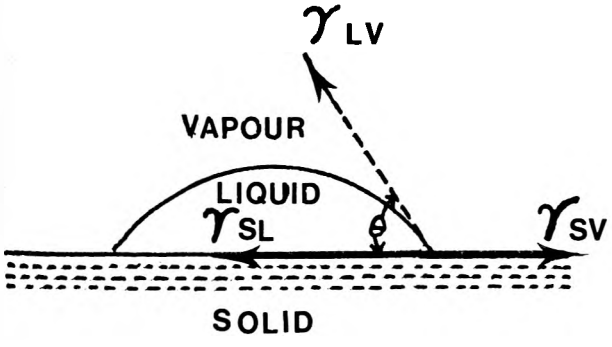


Fig. 2a. The surface tensions at the phase boundaries of a liquid at rest on a solid surface.

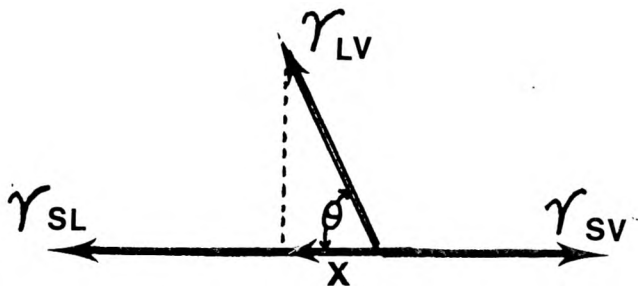


Fig. 2b. Resolution of forces at the point where the phases meet.

research workers. The problems encountered in the oral environment are numerous and complex and not conducive to obtaining and maintaining adhesion.

THE INTRA-ORAL FACTORS AFFECTING ADHESION

1. The physical and chemical properties of enamel and dentine.

A satisfactory adhesive dental material must take into account the physical and chemical properties of the dental hard tissues to which it must adhere. These properties of enamel and dentine will determine the adhesive potential of the tooth surfaces. Both the inorganic and organic content of enamel and dentine may play a part in the adhesive process.

Enamel, the outer covering of the crowns of teeth, is the hardest tissue in the human body. It is composed of 95% inorganic material which mainly consists of hydroxyapatite, 4% water and approximately 1% organic material. The relatively small organic component plays a very important part in determining adhesion to tooth structure. Eastoe (1966) expressed the opinion that the organic component is present either as a continuous gel or a viscous sol.

Glantz (1969) studied the wettability of enamel, dentine and synthetic hydroxyapatite. He found that the critical surface tension of wetting of enamel and dentine were 46,1 dynes/cm and 44,8 dynes/cm respectively, whereas the synthetic hydroxyapatite surface had a high energy surface (> 72 dynes/cm). These results suggest that the enamel and dentine surfaces are covered with a low energy organic film. He confirmed this by determining the wettability of E.D.T.A. decalcified and non-decalcified dentine and obtaining practically the same results for these surfaces. He concluded that the high energy inorganic hydroxyapatite does not participate in forming the low energy surface of dentine. He explained the mechanism of the formation of the low energy surfaces of enamel and dentine by presuming that at least some part of the organic phase is mobile and exists in the form of a gel. If the high energy hydroxyapatite crystals are exposed during treatment of the surfaces, the gel part of the low energy organic phase will cover the high energy inorganic phase as a result of the energy differences between the two phases. For proper wetting of the adherend surface to occur, the surface tension of the unpolymerized adhesive must be lower than the critical surface tension of wetting of tooth structure. It is therefore extremely difficult to obtain adhesion to low energy tooth surfaces.

Dentine is composed of about 80% inorganic hydroxyapatite which is embedded in or surrounded by a protein matrix. The dentine matrix is traversed by numerous tubules and it is estimated that the tubules constitute approximately 10% of the dentine cross-section (Fig. 3). The dentinal tubules contain

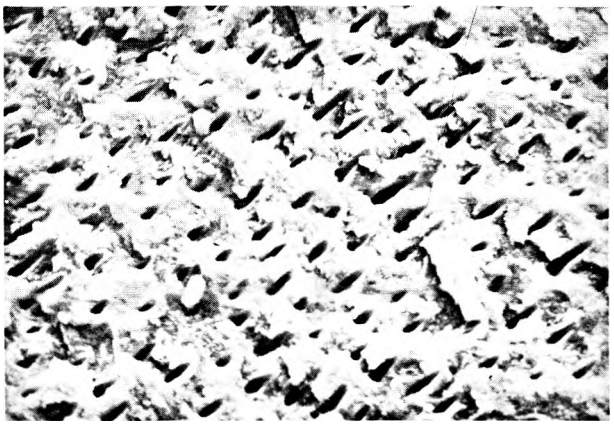


Fig. 3. Dentinal tubules traversing dentine matrix. S.E.M. x 500

the wet protoplasmic processes of the odontoblasts, the dentine-forming cells which lie in the pulp adjacent to the dentine. Adhesion to the wet protoplasmic processes does not occur but a truly adhesive material will interact with the surface of the calcified matrix while mechanical interlocking may be achieved by the penetration of the adhesive into the tubular portion (Massler, 1961).

Collagen constitutes approximately 90% of the organic component of dentine and consists mainly in the form of tropocollagenous macromolecules. The collagen of the matrix may play an important part in adhesion and it is interesting to postulate on its role in this regard.

The amino acids of collagen can be grouped as follows:

The amino acids of collagen
- Non-polar amino acids (63%).
- Polar amino acids
  - Hydroxy and sulphur containing amino acids (17%).
  - Acidic and basic amino acids (20%).

In the non-polar amino acids both the polar groups are utilized in the formation of the polypeptide chain and do not contribute reactive groups to the collagen unless they occupy a terminal position. The predominant groups in the polar amino acids available for possible reactions with adhesives are the hydroxyl, carboxyl and amino groups (Mellon, 1961).

It is difficult to describe the mechanism of adhesion to the heterogeneous surfaces of enamel and dentine. Posner (1961) stated that hydrogen bonding can contribute to the adhesion between enamel

apatite surfaces and filling materials. Schwartz and Galligan (1965) showed, by means of infra-red analysis, that liquids which wet hydroxyapatite might also form hydrogen bonds with the mineral. Glantz (1969) proved that, in addition to the Van der Waals dispersion forces, polar forces and hydrogen bonding play a part in the bonding to enamel and dentine surfaces. His experimental results enabled him to calculate the minimal values of these forces.

2. The aqueous environment

Adhesion is best obtained and maintained under dry conditions and water in the oral cavity presents serious problems. Cornell's experiments (1961) disclosed that although a number of materials gave excellent adhesion to tooth structure initially, they all failed to continue to do so when tested under physiological conditions over an extended period of time.

The hydroxyapatite crystal consists of a central core of hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, an intermediate layer of adsorbed ions and a superficial hydration layer around it (Jenkins, 1966). The hydration layer is strongly bound to the hydroxyapatite. Investigations by Beebe (1961) showed that the adsorption energy of one monolayer of water on the hydroxyapatite surface is from 18 - 21 kilo calories/mole. These figures, when applied to a tooth surface, mean that a patient's tooth cannot be thoroughly dried at room temperature even if a vacuum pump is applied to his mouth. Beebe (1961) found that the "bare" surface of bone mineral can be obtained only after heating to 450° C **in vacuo.** Some patients may tolerate the first treatment but none will survive the latter exposure.

Even if it were possible to dry a tooth surface completely, the dryness could not be maintained because of the fluid flow which occurs from the pulp of a tooth to the enamel surface. Bergman (1963) developed a technique to demonstrate this flow and showed that the enamel fluid appears spontaneously and that no increased intrapulpal pressure is required. Linden (1968) used physical principles to explain the process and proved that the rate of flow decreases in older permanent teeth.

As water is ever present on the tooth surface and as it actually functions as a liquid adhesive, a dental adhesive must compete with it for the binding sites on the tooth surface.

The presence of water in the oral environment may be the precursor of chemical activity at the adhesive/adherend interface which will eventually dislodge the bond. In addition many adhesive materials will absorb water 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.

3. Surface Roughness

Adhesion is best obtained between smooth surfaces. Scott and O'Neil (1961) and Boyde and Knight (1969) studied the effect of cutting instruments generally used in dentistry for cavity preparation and found that they produced marked irregularities in the tooth surfaces (Fig. 4). A rough surface is desirable if the restorative material depends on mechanical interlocking for its retention. A rough surface, however, does not lend itself to good adhesive performance. Adhesives usually are applied in the viscous state and voids are readily formed on rough surfaces. As most of the adhesives shrink during curing, embedded surface projections from the adherend surface may be sheared from the cavity wall (Fig. 5). The contact area between the adhesive and the adherend will be greatly reduced thus lessening the effective area over which the molecular forces of attraction can operate.

If ever an adhesive restorative material is developed the present cutting procedures will have to be modified to reduce the surface roughness.

4.Debris in the cavity

Provenza and Sardana (1965) proved that even after careful cleaning a considerable amount of debris remains on the floor and walls of a cavity. The presence of debris particles will almost certainly interfere with adhesion. Huntsberger (1965) showed that when an adhesive completely wets a particle it will be pulled into the liquid adhesive and when this

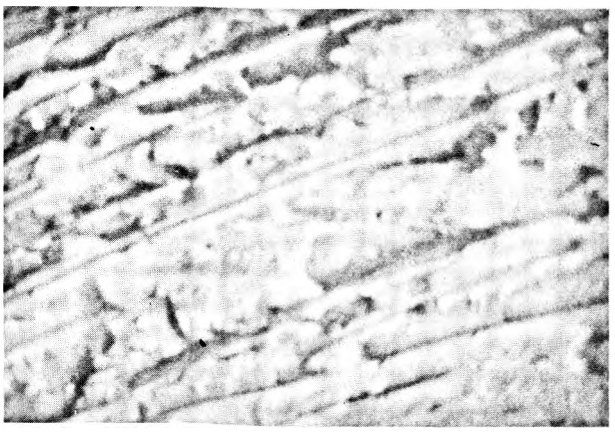


Fig. 4. Marked irregularities produced by dental cutting instruments on tooth surfaces. S.E.M. x 500.

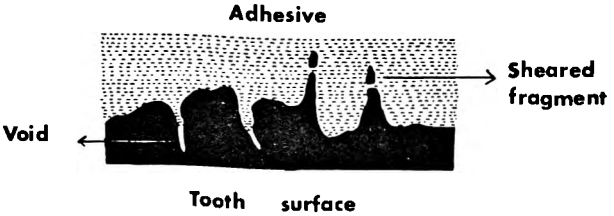


Fig. 5. Adhesion to a rough tooth surface.

obtains the particle influences the adhesive performance only through its mechanical behaviour. A particle will not be completely wetted if the liquid adhesive exhibits even a small contact angle with it. As a result an air bubble will form at the adhesive/particle interface. Even if the solid particle is subsequently wetted and pulled into the adhesive the air bubble will persist at the interface (Fig. 6). Stress concentrations could originate around these entrapped air bubbles and adversely affect the adhesive performance.

5. **Conditions to which the adhesive are exposed in the mouth**

Biting stresses on restorations may amount to thousands of pounds per square inch. The average biting force recorded is 170 pounds and if it is assumed that this force is applied to the apex of a cusp over an area of 0,006 square inch, the compressive force exerted will be 28,000 pounds per square inch. A force of this magnitude will either break the restoration or destroy the adhesive bond.

Instantaneous temperature changes in the mouth may be as great as 50° C. This is of real significance if there is a pronounced difference in the coefficient of thermal expansion of the filling material and the tooth components. The coefficient of thermal expansion of adhesive materials can be approximated to that of enamel or dentine by the addition of inert fillers.

The pH in the mouth fluctuates rapidly between acidity and alkalinity and the warm humid environment is conducive to corrosion.

6. **Factors involving the intra-oral use of adhesives**

The toxicity of the adhesive to the pulp, the oral tissues and the organism as a whole must be considered. Most of the catalysts and reactive hardeners used to polymerize resins are toxic but fortunately few remain so after polymerization has been completed. Chemical, biological and clinical tests are essential both for the initial screening and final evaluation of the acceptability of a potential adhesive dental restorative material.

Many excellent commercial adhesives must be excluded for intra-oral use because they are solids at mouth temperature and are applied to the adherend surfaces at high pressures and cured at temperatures which cannot be tolerated in the mouth.

The numerous factors which have to be considered in the development of a truly adhesive dental material make it obvious that this objective will not easily be attained. If ever these obstacles are overcome, an adhesive dental material will have wide applications in several branches of dentistry.

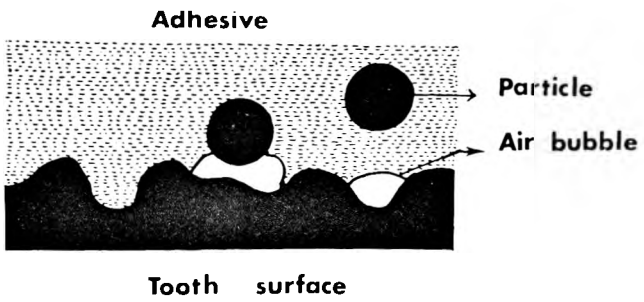


Fig. 6. Air bubbles formed at the adhesive/tooth interface as a result of incomplete wetting of the debris particles.

ADHESION IN RESTORATIVE DENTISTRY

A major part of dental practice is restorative dentistry which includes the treatment of localized lesions in teeth and the replacement of lost tissue with restorative materials. The lack of adhesion of the available filling materials to tooth structure presents a serious problem as it leads to seepage of harmful agents along the interface between the restoration and the tooth (Fig. 7). The marginal leakage leads to breakdown of the marginal areas of the filling and results in the development of secondary decay along the interface between the restoration and the tooth structure. It is likely that certain post-operative phenomena such as tooth sensitivity and pulp pathology are associated with the leakage pattern (Phillips, 1967).

The microleakage can be demonstrated by various techniques:

1. Radioactive isotopes.
2. Fluorescent dyes.
3. Scanning electron microscopy.
4. Penetration of bacteria.

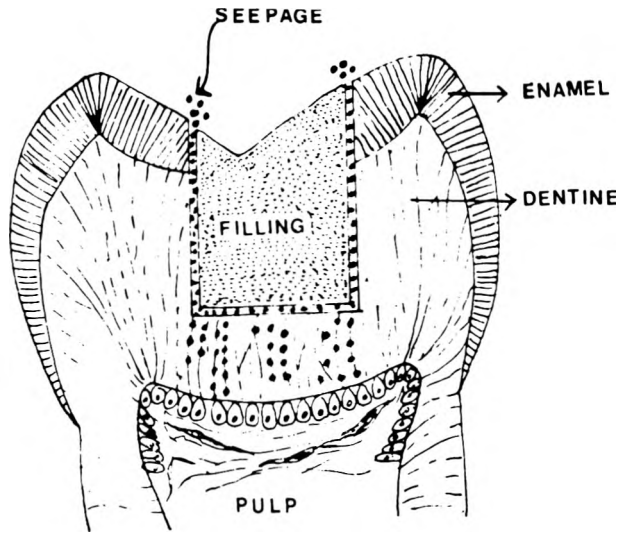


Fig. 7. Marginal leakage at the restoration/tooth interface.

The first three techniques are often used in the Dental Research Unit. A surface view of a restorative material obtained with a scanning electron microscope clearly shows the space between the restoration and the enamel surface (Fig. 8).

The marginal leakage could be eliminated by a restorative material or film capable of forming strong adhesive bonds with enamel and dentine which would survive in the mouth. The availability of such a material will most certainly change the method of cavity preparation. At the present time the classical cavity preparation is box-shaped with the walls flaring somewhat at the base of the cavity to provide mechanical retention for the restorative material. With an adhesive restorative material a simple, bowl-shaped cavity will suffice thus preserving healthy tooth structure and resulting in a considerable saving in time for the operator (Fig. 9).

As recently as 1967 Gwinnett and Matsui, with perhaps a note of despair, reported that "presently there is no known material capable of forming a permanent adhesive bond with untreated enamel surfaces under oral conditions". Progress, however, can be reported. A new dental cement, composed of a polyacrylic acid liquid and a modified zinc oxide powder, recently has been developed by Smith (1968). Setting of the cement is due to a chemical reaction in which zinc ions link adjacent polyacrylic acid molecules producing a large cross-linked structure. The acid groups in the long chain molecule also have the ability to chelate to calcium and thus bond to tooth structure (Smith, 1971).

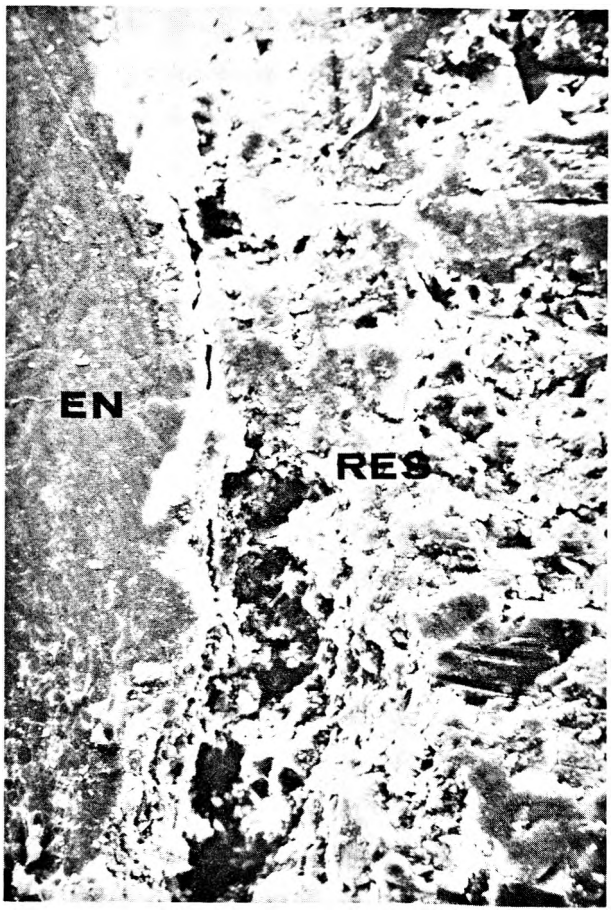


Fig. 8. Space between the restorative material and enamel surface. S.E.M. x 200. EN — Enamel, RES — Restoration.

Another exciting development in the field of restorative dentistry is the advent of the composite restorative materials. The base resin consists of the reaction product of bis phenol A and glycidyl methacrylate, a molecule originally synthesized by Bowen (1962). The term composite indicates the presence of a large percentage of reinforcing filler in the form of glass, quartz or pure silica. The physical properties of the resin matrix are significantly improved by the incorporation of the inorganic filler (Phillips, 1970). By the incorporation of an organo-functional silane coupling agent effective adhesive bonding of the filler particles to the polymerizing resin phase is obtained (Bowen 1962, 1963).

The composite restorative materials may be regarded as contact adhesives which unfortunately lose their adhesive qualities in the mouth soon after exposure to the oral moisture (Buonocore, 1968). Adhesion can be considerably improved by utilizing yet another phase in the formulation. Bowen (1965a) synthesized a surface-active comonomer, the reaction product of N-phenyl glycine and glycidyl methacrylate, which functions as a coupling agent between the organic phase of the restorative material and tooth structure. He demonstrated that significant improvement in the water-resistant bonding of the composite resins and various substrates are obtained by the introduction of the surface-active comonomer (Bowen, 1965b, c). This system is diagrammatically presented in Fig. 10 and indicates to what length research workers have gone to obtain adhesion to tooth structure.

ADHESION IN PREVENTIVE DENTISTRY

Dental caries is the most common disease afflicting mankind. The average child in the United States of America has an 80% chance that by the time he is 18 years of age all of his molars will be decayed,

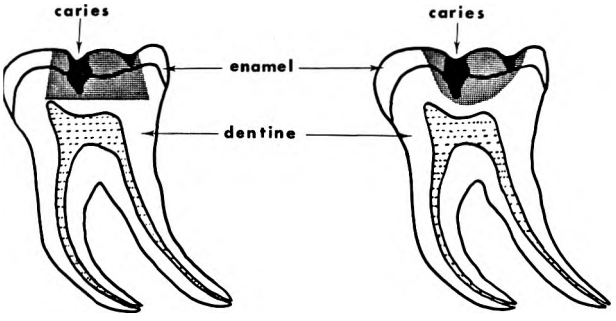


Fig. 9. Classical and modified cavity preparation.

missing or have fillings in them. In South Africa the position is no better. Ockerse (1947) showed that of 78,000 white school children examined, 85% suffered from dental caries.

For too long dentistry has concerned itself primarily with the restoration of tissues eroded by caries. Prevention of dental caries must surely be our ultimate goal and dental adhesives may play a very important part in preventive dentistry.

Caries is an infectious disease resulting from the mutual interaction of three major factors of which diet, microflora and host factors are fundamental (Keyes, 1969). Dietary habits associated with modern civilization undoubtedly contribute to the caries problem. Public education programmes may help to change the dietary habits of certain population groups and restriction of consumption of various cariogenic materials can reduce the incidence of caries (Weaver, 1950). It is doubtful whether any programme designed to substantially alter the dietary habits will meet with any success. An anti-microbial approach is presently being investigated by many research workers (Scherp, 1971). Measures directed at the host factors have been more successful.

The regulation of the fluoride content of the public water supplies to 1,0 ppm of fluoride is the most safe, practical and effective means of preventing dental decay (Doherty, 1968). In the absence of water fluoridation in South Africa, topical fluoride therapy, i.e. the local application of fluoride containing medicaments to the surfaces of teeth, plays a very important part in the prevention of dental decay. Local fluoride therapy decreases the incidence of dental caries by as much as 60% (Horowitz and Heifetz, 1970) but unfortunately the beneficial effect is mainly confined to the smooth surfaces of the teeth. The reduction in the incidence of dental caries on the occlusal surfaces of teeth is much less (Sumnicht, 1969).

The concept of sealing the pits and fissures on the occlusal surfaces of teeth, which themselves constitute a predisposing host factor, offers a new dimension in caries prevention (Gwinnett, 1972). The posterior teeth, both in the primary and permanent dentition, have fine developmental pits and fissures on their occlusal or biting surfaces. The pit and fissure site consists of a blind, narrow crevice in which food debris and micro-organisms accumulate (Fig. 11). The carious lesion is consequently very often initiated in the pits and fissures of posterior teeth. Sealing of these pits and fissures will prevent not only the accumulation of micro-organisms but also the availability of fermentable substrates in these sites.

Several pit and fissure sealants are now commercially available. One of these has been developed by Buonocore (1970). This particular sealant contains an ultraviolet light sensitive catalyst and an ultraviolet gun with which the sealant is polymerized. The occlusal surfaces of teeth are etched with an attenuated phosphoric acid solution prior to the application of the adhesive and the composition hardened within 30 seconds by exposure to long-wave ultraviolet light from the gun. Effective sealing of the crevice is obtained with this technique (Fig. 12). In clinical studies extending over two years, marked protection against occlusal caries has been reported (Buonocore, 1971). Recently Handelman, Buonocore and Heseck (1972) evaluated the effect of the ultraviolet light polymerized adhesive when applied to pits and fissures of posterior teeth that had demonstrable caries. These authors reported that there was an approximate fiftyfold decrease in the numbers of

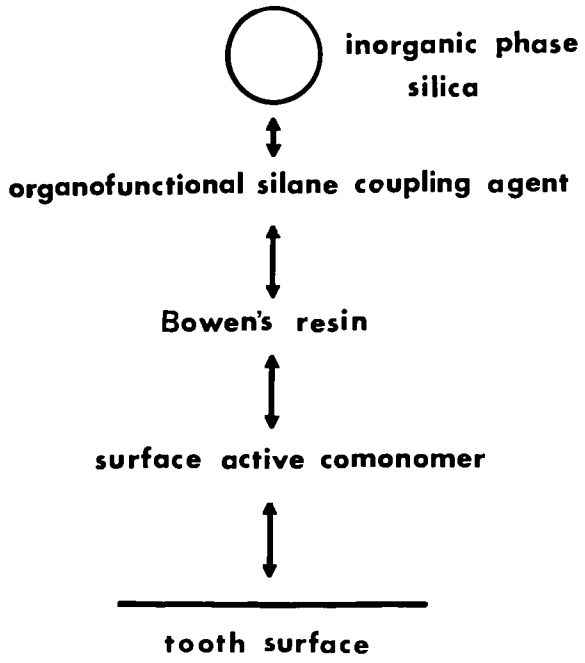


Fig. 10. Composite restorative system with surface-active comonomer.

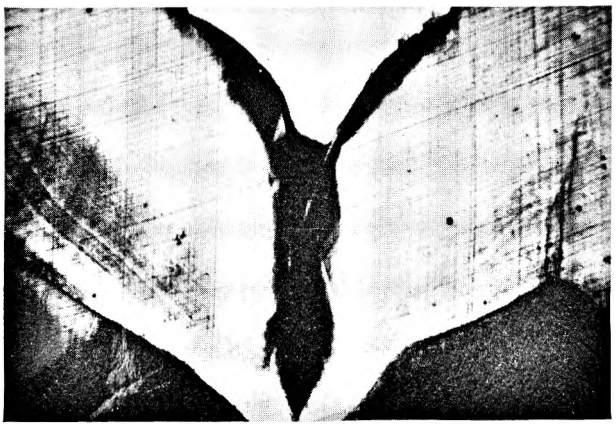


Fig. 11. Fissure extending into the enamel surface. Ground section x 40.

cultivable micro-organisms from the infected dentine from sealed teeth compared with those in unsealed control teeth.

The Council of Dental Materials and Devices of the American Dental Association believes, however, that additional studies are necessary with the available pit and fissure sealants in order to determine the true place of these materials in preventive dentistry (1971). The Council has recently (1972) granted provisional certification of one of the commercially available sealants.

ADHESION IN ORTHODONTICS

Orthodontics is that branch of dentistry which is concerned with the realignment of irregular teeth. Orthodontic appliances are used to direct mechanical forces to the teeth thus producing a gradual repositioning of teeth. Appliances may be either removable or fixed. The conventional fixed appliance demands the placement of metal bands around individual teeth. Each band carries an attachment or bracket through which an archwire is threaded. The forces are applied to each tooth by the archwire and by careful manipulation full three dimensional control over tooth movement may be achieved. The placement of fixed appliances would be simplified and many of the disadvantages of the techniques used at present reduced if the orthodontic bands could be eliminated and the attachments bonded directly to the tooth surface.

I wish to discuss some of our efforts in bonding orthodontic attachments directly to enamel surfaces (Retief and Dreyer, 1967; Retief, Dreyer and Gavron, 1970; Dijkman and Retief, 1972).

Only a limited number of the wide range of adhesives used commercially are usable in medicine and dentistry and even fewer are potentially adhesive to hard tissues. The demands for aesthetics rule out a great proportion, the toxicity of the adhesive or curing agent many and the physical and chemical properties even more.

The choice of adhesives for intra-oral use is limited to three types of resins (Lee and Swartz, 1970).

1. Acrylics.
2. Polyurethanes.
3. Epoxy resins.

We selected the epoxy resins for further investigation because of their properties.

These include:

1. Their reactivity is borderline but can readily be increased by the use of suitable curing agents and catalysts.
2. Before polymerization, the liquid mixture has a low viscosity and is a good wetting agent.
3. No gas, which can weaken the solidifying adhesive or affect the interface, is evolved during curing.
4. They set with minimal shrinkage and therefore a minimum of locked-in stress.
5. When cured under contact or atmospheric pressure, they develop powerful adhesive bonds with many materials.
6. The cured resin is hard, abrasive resistant and dimensionally stable.

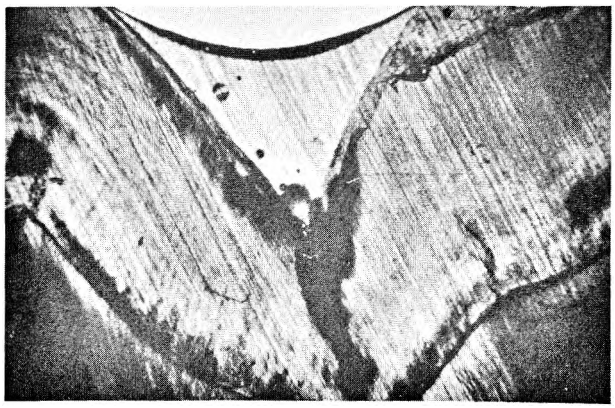


Fig. 12. Effective sealing of fissure. Ground section x 40.

The epoxy resin formulation developed in the Dental Research Unit for the direct bonding of orthodontic attachments consists of the following components:

Epoxy resin	— Epikote 828
Curing Agent	— Epikure U
Catlayst	— Phenol
Thixotropic agent	— Aerosil

The curing agent, Epikure U, is a modified polyamine which is less irritating than the pure primary/secondary aliphatic amines and, in addition, has a low sensitivity to moisture during the curing process (Shell Tech. Bull. SC: 61-83). Phenol was found to be a suitable catalyst in increasing the rate of cure after the attachment plus the adhesive had been placed on the tooth surface. The thixotropic agent was added to reduce the flow of the curing resin and thus the displacement of the orthodontic attachments when they were positioned on inclined tooth surfaces. The epoxy resin, Epikote 828, consists mainly of the diglycidyl ether of diphenylol propane (Shell Tech. Bull. TB/RES/157/3). The two terminal epoxide groups are the reactive groups in the molecule.

Two types of linkages are responsible for the conversion of the liquid resin to the cured, solid end product (Skeist, 1964).

1. A linkage to a **reactive hardener** which combines with one or more additional molecules of resin.

2. A linkage to other epoxy intermediate molecules with the aid of a **catalyst.**

The curing rate of the epoxy formulation was too slow for clinical application. The effect of temperature on the reactivity of epoxy resins follows the Arrhenius equation in which a 10°C temperature rise is said to double the rate of reaction (Cupples, Lee and Stoffey, 1970). A preheat schedule was determined for the adhesive formulation and it was found that by preheating the mixed resin for six minutes at 50°C prior to its application, optimal bond strength was obtained.

The tensile disruptive force required to break a prepared bond was used as a measure of bond strength because this technique is probably the simplest reproducable method for determining the strength of an experimental bond. Two techniques are used to determine adhesion to tooth structure. The first technique was developed by Hanke (1966) and modified by Phillips, Swartz and Rhodes (1970). The prepared specimens are mounted in a test jig consisting of a series of joints to produce an universal joint. The second technique was developed by Lee, Swartz and Culp (1969) and employs a pneumatic grip system to hold the assembled test specimens. Both techniques were designed to eliminate as nearly as possible all forces other than tensile during the testing procedure. An Instron Table Model 1026 tensile testing machine was used to determine the bond strength. A loading speed of 0,05 cm/minute was employed and the force required to break an experimental bond automatically recorded.

The bonding of the epoxy resin formulation to untreated enamel surfaces is poor. This is not surprising because in the industrial application of adhesives, surfaces to be bonded are carefully conditioned prior to the application of the adhesive (Lee and Neville, 1967). Buonocore (1955) was the first to describe that bonding to tooth structure could be substantially increased by conditioning the enamel surface with phosphoric acid. The adhesion of the epoxy formulation is markedly increased by etching the enamel surface with 50% phosphoric acid prior to the application of the adhesive.

Additional effects of phosphoric acid etching have been studied and the results submitted for publication (Retief, 1973). The glistening appearance of the enamel surface is dulled by the application of phosphoric acid. When viewed in a scanning electron microscope, an unconditioned enamel surface has a relatively smooth, featureless appearance. Surface treatment with phosphoric acid exposes the enamel prisms and produces the characteristic "prism end" structure. At higher magnifications a typical honeycomb appearance is observed which clearly demonstrates the preferential etching action of the acid. Contact between the adhesive and untreated enamel surfaces is poor while intimate interfacial contact is obtained between the resin formulation and conditioned enamel surfaces. Thin sections were prepared through the adhesive/enamel interface and the enamel slowly dissolved with a weak hydrochloric acid solution. This technique enabled us to show resin tags up to 50 micrometres in length projecting from the adhesive surface into the etched enamel surface. Phosphoric acid etching produces a marked increase in surface area available for bonding and creates spaces and pores in the enamel surface into which the polymerizing resin penetrates. Mechanical retention therefore plays a major part in the bonding of the adhesive formulation to etched enamel surfaces.

The contact angles of the uncured epoxy resin, Epikote 828, used in the adhesive formulation were recorded on etched and unetched enamel surfaces. An instrument, similar to that designed by Glantz (1969) was used in this investigation. The mean contact angle was reduced from 28.3° on unconditioned surfaces to 14.3° on etched enamel surfaces. These results indicate that phosphoric acid etching produces an increase in the wettability of the enamel surface.

The adhesive formulation adheres poorly to stainless steel. The adhesion to stainless steel was supplemented by mechanical retention. This was achieved by welding 60 mesh stainless steel gauze to the band material which formed the bases of the orthodontic attachments. Special orthodontic attachments were manufactured by Unitek Corporation for this study. Undercut grooves in the bases of these brackets provided the additional retention (Fig. 13).

The epoxy resin formulation was subjected to clinical trials and the following procedure adopted. The four components of the adhesive formulation are thoroughly mixed. The fact that the adhesive formulation is a four component system is a distinct disadvantage of this technique. The mixed adhesive is spread evenly on the mixing slab and the attachments, with the bracket portion protected with an elastic band, embedded in the resin. The mixed resin is preheated for six minutes at 50°C. During this interval the teeth are polished, etched with phosphoric acid, washed and dried with compressed air. The orthodontic attachments, with a thin layer of attached resin, are placed on the tooth surfaces in the desired position and the patient allowed to rinse after 20 minutes. A the next visit the excess material is removed and the archwires placed in position.

In a preliminary study 22 of the 102 bonded attachments became detached. The majority of the

detached brackets were dislodged within 24 hours and before the arches were placed. In subsequent clinical trials full mouth bonding was carried out. Poor results were obtained in the younger patients but much more encouraging results obtained in older patients. Two of the patients in the latter group are the only cases reported in the literature in which full mouth direct bonding has been successfully applied and the treatment completed (Figs. 14 and 15).

I wish to make it quite clear that this type of treatment has not progressed beyond the experimental stage. This study at best shows that teeth can be moved by forces exerted on bandless attachments over a prolonged period of time.

The direct bonding technique has several advantages over the conventional circumferential banding technique used at present.

Advantages of banless orthodontics

1. Because of the ease of application and the reduction in operating time, the stress to both the patient and operator is reduced.
2. Gingivitis is frequently associated with the conventional technique. Minimal gingival irritation is caused by the direct bonding of orthodontic attachments.
3. The elimination of overhanging edges in the interdental area also results in improved oral hygiene.
4. When teeth are crowded it becomes imperative to separate the teeth prior to the fitting and cementing of bands. This procedure is obviously unnecessary with the direct bonding technique.
5. Conventional banding of partially erupted teeth is often difficult and traumatic for the patient. The direct bonding of attachments to the exposed surfaces of these teeth presents no problems.
6. The last stage of treatment has to be devoted to space closure after removal of the bands. No space closure is required with direct bonded attachments.
7. Orthodontic bands may become loose and remain undetected during treatment. As a result marked decalcification can occur under these bands. This problem is not encountered with the direct bonding technique because loosening of the attachments results in complete displacement.

The need for a truly dental adhesive material is obvious. The destructive nature of the oral environment and the numerous factors encountered in the mouth which adversely affect adhesion will make the development of such a material a difficult task. The only solution to this complex problem is a multi-disciplinary approach and this is fully recognized by research workers in this particular field of dentistry. I can foresee that the dental profession will have truly adhesive materials available in the not too distant future. Our colleagues will be better equipped not only to reduce the incidence of dental caries but also to restore teeth with longer lasting fillings.

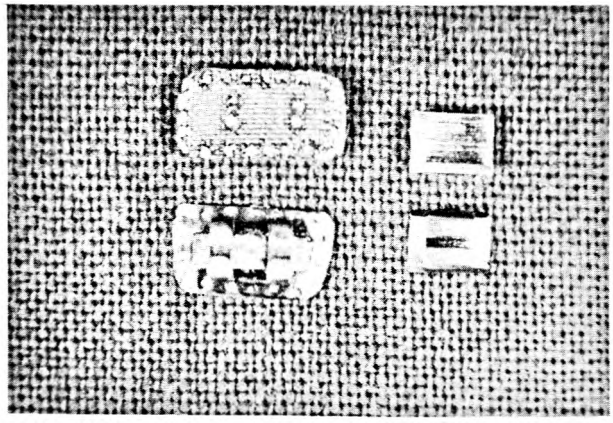


Fig. 13. Specially constructed (left) and Unitek attachments (right) used in the direct bonding technique.

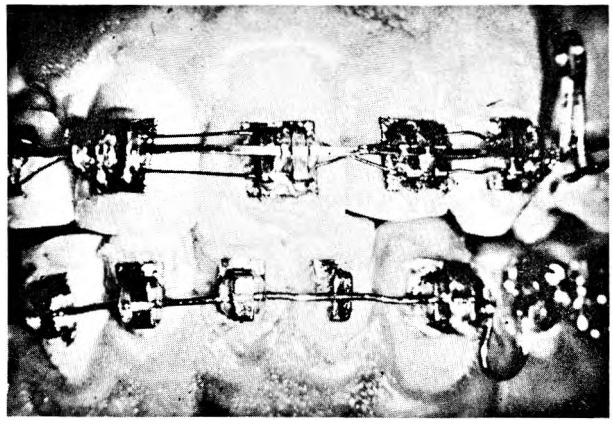


Fig. 14. Full mouth direct bonding of orthodontic attachments.

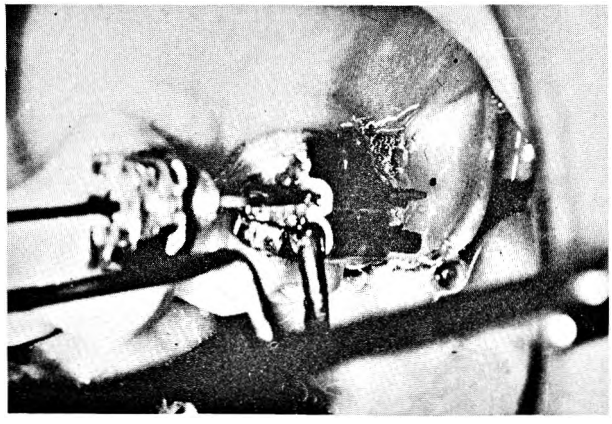


Fig. 15. Directly bonded attachments on posterior teeth. Extra-oral traction was applied.

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REFERENCES

Beebe, R.A. (1961). Gas adsorption studies on bone mineral. *Workshop Proceedings, Adhesive Restorative Dental Materials.* Eds. Phillips, R.W. & Ryge, G. pp. 75-84. Indiana: Owen Litho Service.

Bergman, G. (1963). Techniques for microscopic study of the enamel fluid *in vitro. Odontologisk Revy,* **14,** 1-7.

Bowen, R.L. (1962). Dental filling material comprising vinyl silane treated fused silica and binder consisting of the reaction product of bis phenol and glycidyl acrylate. U.S. Patent No. 3,066, 112, Nov. 1962.

Bowen, R.L. (1963). Properties of silica-reinforced polymer for dental restorations. *Journal of the American Dental Association,* **66,** 57-64.

Bowen, R.L. (1965a). Surface-active comonomer and method of preparation. U.S. Patent No. 3,200,142, Aug. 1965.

Bowen, R.L. (1965b). Adhesive bonding of various materials to hard tooth tissues. III. Bonding to dentin improved by pretreatment and the use of surface-active comonomer. *Journal of Dental Research,* **44,** 903-905.

Bowen, R.L. (1965c). Adhesive bonding of various materials to hard tissues. IV. Bonding to dentin, enamel and fluoroapatite improved by the use of a surface-active comonomer. *Journal of Dental Research,* **44,** 906-911.

Boyde, A. & Knight, P.J. (1969). The use of scanning electron microscopy in clinical dental research. *British Dental Journal,* **127,** 313-322.

Buonocore, M.G. (1955). A simple method of increasing the adhesion of acrylic filling materials to enamel surfaces. *Journal of Dental Research,* **34,** 849-853.

Buonocore, M.G. (1963). Principles of adhesive retention and adhesive restorative materials. *Journal of the American Dental Association,* **67,** 382-391.

Buonocore, M.G. (1968). New anterior restorative materials. *International Dental Journal,* **18,** 406-420.

Buonocore, M.G. (1970). Adhesive sealing of pits and fissures for caries prevention, with use of ultraviolet light. *Journal of the American Dental Association,* **80,** 324-328.

Buonocore, M.G. (1971). Caries prevention in pits and fissures sealed with an adhesive resin polymerized by ultraviolet light. A two-year study of a single adhesive application. *Journal of the American Dental Association,* **82,** 1090-1093.

Cook, M. (1970). Composition of mussel and barnacle deposits at the attachment interface. *Adhesion in Biological Systems.* Ed. Manly, R.S. Ch. 8, 139-150. New York: Academic Press, Inc.

Cornell, J. (1961). Adhesion to natural teeth. *Workshop Proceedings, Adhesive Restorative Dental Materials.* Eds. Philips, R.W. & Ryge, G. p. 159. Indiana: Owen Litho Service.

Council on Dental Materials and Devices. (1971). Pit and fissure sealants. *Journal of the American Dental Association,* **82,** 1101-1103.

Council on Dental Materials and Devices. (1972). Nuva-Seal pit and fissure sealant classified as provisionally acceptable. *Journal of the American Dental Association,* **84,** 1109.

Cupples, A.L., Lee, H. & Stoffey, D.G. (1970). The design and synthesis of epoxy resins for rapid room temperature cures with primary amines in small masses. *Advances in Chemistry Series,* **92,** 173-207.

De Bruyne, N.A. (1962). The action of adhesives. *Scientific American,* **206,** 114-126.

Dijkmen, J.F.P. & Retief, D.H. (1972). Clinical experience with an epoxy resin adhesive for direct bonding of orthodontic attachments. *Journal of the Dental Association of South Africa,* **27,** 37-44.

Doherty, J.M. (1968). Use of dietary fluorides. *Wisconsin Medical Journal,* **67,** 599-602.

Eastoe, J.E. (1966). The changing nature of developing dental enamel. *British Dental Journal,* **121,** 451-454.

Glantz, P. (1969). On wettability and adhesiveness. *Odontologisk Revy,* **20** (Supplement 17), 1-132.

Gwinnett, A.J. (1971). Caries prevention through sealing of pits and fissures. *Journal of the Canadian Dental Association,* **37,** 458-461.

Gwinnett, A.J. & Matsui, A. (1967). A study of enamel adhesives. The physical relationship between enamel and adhesive. *Archives of Oral Biology,* **12,** 1615-1620.

Handelman, S.L., Buonocore, M.G. & Heseck, D.J. (1972). A preliminary report on the effect of fissure sealant on bacteria in dental caries. *Journal of Prosthetic Dentistry,* **27,** 390-392.

Hanke, G. (1968). *Screening test methods and their application in measuring adhesion of selected dental resins.* Thesis, Indiana University School of Dentistry.

Hillman, R.E. & Nace, P.F. (1970). Histochemistry of barnacle cyprid adhesive formation. *Adhesion in Biological Systems.* Ed. Manly, R.S. Ch. 6, pp. 113-121. New York: Academic Press, Inc.

Horowitz, H.S. & Heifetz, S.B. (1970). The current status of topical fluorides in preventive dentistry. *Journal of the American Dental Association,* **81,** 166-197.

Huntsberger, J.R. (1964). Wetting and adhesion. *Chemical and Engineering News,* **42,** 82-87.

Huntsberger, J.R. (1965). Wetting and adhesion. *Adhesive Restorative Dental Materials* - II. Eds. Austin, R.H. *et al.* pp. 7-16. Bethesda: U.S. Department of Health, Education and Welfare. [Public Health Service Publication No. 1494 (1966)].

Jenkins, G.N. (1966). *The Physiology of the mouth.* 3rd ed., p. 65. Oxford: Blackwell.

Keyes, P.H. (1969). Present and future measures for dental caries control. *Journal of the American Dental Association,* **79,** 1395-1404.

Lee, H. & Neville, K. (1967). *Handbook of epoxy resins.* New York: McGraw-Hill.

Lee, H. & Swartz, M.L. (1970). Surface preparation and various adhesive resins. *Adhesion in Biological Systems.,* Ed. Manly, R.S. Ch. 17, pp. 269-289. New York: Academic Press, Inc.

Lee, H., Swartz, M.L. & Culp, G. (1969). Static load testing of dental adhesives. *Journal of Dental Research,* **48,** 211-216.

Linden, L. (1968). Microscopic observation of fluid flow through enamel *in vitro. Odontologisk Revy,* **19,** 349-365.

Massler, M. (1961). *Workshop Proceedings, Adhesive Restorative Dental Materials.* Eds. Phillips, R.W. & Ryge, G. p. 65. Indiana: Owen Litho Service.

Mellon, E.F. (1961). Structure and chemical reactions of collagen. *Workshop Proceedings, Adhesive Restorative Dental Materials.* Eds. Phillips, R.W. & Ryge, G. pp. 48-51. Indiana: Owen Litho Service.

Ockerse, T. (1947). *Dental Caries — Clinical and experimental investigations.* Thesis submitted for the D.Sc., University of Pretoria.

Phillips, R.W. (1967). Advances in adhesive restorative dental materials. *Journal of Dental Research,* **47,** 1662-1667.

Phillips, R.W. (1970). Composite restorative resins. *Journal of the American Dental Association,* **80,** 357-358.

Phillips, R.W., Swartz, M.L. & Rhodes, B. (1970). An evaluation of a carboxylate adhesive cement. *Journal of the American Dental Association,* **81,** 1353-1359.

Posner, A.S. (1961). The structure in the mineral portion of teeth. *Workshop Proceedings, Adhesive Restorative Dental Materials.* Eds. Phillips, R.W. & Ryge, G. pp. 15-25. Indiana: Owen Litho Service.

Provenza, D.V. & Sardana, R.C. (1965). Optical and ultrastructural studies of enamel and dentin surfaces as related to cavity preparation. *Adhesive Restorative Dental Materials.* II. Eds. Austin, R.H. *et al* pp. 68-97. Bethesda: U.S. Department of Health, Education and Welfare. [Public Health Service Publication No. 1494 (1966)].

Retief, D.H. & Dreyer, C.J. (1967). Epoxy resins for bonding orthodontic attachments to teeth. *Journal of the Dental Association of South Africa,* **22,** 338-346.

Retief, D.H., Dreyer, C.J. & Gavron, G. (1970). The direct bonding of orthodontic attachments to teeth by means of an epoxy resin adhesive. *American Journal of Orthodontics,* **58,** 21-40.

Retief, D.H. (1973). The effect of conditioning the enamel surface with phosphoric acid. *Journal of Dental Research, 52,* In press.

Scherp, H.W. (1971). Dental caries: Prospects of prevention. *Science,* **173,** 1199-1205.

Schwartz, A.M. & Galligan, J.D. (1965). Tooth conditioning agents for promoting adhesion of restorative materials. *Adhesive Restorative Dental Materials.* II. Eds. Austin, R.H. *et al.* pp. 132-154. Bethesda: U.S. Department of Health, Education and Welfare. [Public Health Service Publication No. 1494 (1966)].

Scott, D.B. & O'Neill, J.R. (1961). The microstructure of enamel and dentin as related to cavity preparation. *Workshop Proceedings, Adhesive Restorative Dental Materials.* Eds. Phillips, R.W.

& Ryge, G. pp. 27-37. Indiana: Owen Litho Service.

Skeist, I. (1964). *Epoxy resins.* 5th ed., Ch. 3, p. 21. New York: Reinhold Publishing Corporation.

Smith, D.C. (1968). A new dental cement. *British Dental Journal,* **125,** 381-384.

Smith, D.C. (1971). A review of the zinc polycarboxylate cements. *Journal of the Canadian Dental Association,* **37,** 22-29.

Sumnicht, R.W. (1969). Research in preventive dentistry. *Journal of the American Dental Association,* **79,** 1193-1201.

Swartz, M.L. (1969). Research in dental materials. *Journal of the American Dental Association,* **79,** 901-917.

Weaver, R. (1950). Fluorine and wartime diet. *British Dental Journal,* **88,** 231-239.

Young, T. (1805). *Philological Transactions of the Royal Society of London,* **95,** 65. Cited by Zisman (1963).

Zisman, W.A. (1963). Influence of constitution on adhesion. *Industrial and Engineering Chemistry,* **55,** 19-38.