

THE INTRA-ORAL FACTORS AFFECTING ADHESION

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INTRODUCTION

ONE of the most acute problems associated with restorative dentistry is that most of the available materials lack adhesion, and as a result there is seepage of deleterious agents between the restoration and the tooth. This microleakage has been demonstrated by various techniques: for example radio-active tracers, dye penetration and penetration of bacteria. It is one of the causes of the breakdown at the margins of the filling and the development of secondary caries at the restoration/tooth interface; and it is possible that post-operative phenomena such as tooth sensitivity and pulp pathology are related to it.

These shortcomings have led to extensive research aimed at the development of a material that will bond adequately to tooth structures and thus eliminate the harmful effects of marginal leakage. One with this property could have wide applications. Apart from its use for restorations, it could be employed to bond orthodontic attachments directly to enamel surfaces or to cover the entire surfaces of teeth and thus act as a barrier to the caries process.

Several investigators have undertaken tests in the relevant field. Rose *et al* (1955), who screened a large number of materials, found that none of those then available consistently maintained adhesion to tooth structure. Gwinnett and Matsui (1967) studied the physical relationship between various adhesive materials and enamel surfaces, and concluded that there was no known material capable of forming a permanent adhesive bond with untreated enamel surfaces under oral conditions. Even with the advent of the composite resin systems, in which the matrix is formed by the reaction of an

epoxy resin molecule with methacrylic acid, the position has not changed. Most research workers agree that these resins do not adhere to tooth structure (Swartz, 1969).

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). According to him the polyacrylic acid appears to chelate calcium ions in the mineral phase of the tooth structure thus resulting in an adhesive bond. The polyacrylate cements show considerable adhesion to enamel and the values obtained revealed an approximate 10 per cent reduction after immersion in water at 37°C for two months. Smith found that the much lower initial values obtained with other cements fell off to virtually zero under the same experimental conditions.

A truly adhesive material remains the objective. The reason for its being so elusive for so long is the complexity of problems presented by the oral cavity; because of its destructive nature many of the principles of adhesion, discussed in a previous article (Retief, 1970) are violated. As remarked by Phillips (1966), the advent of a genuinely adhesive material or film will initiate a new era in dental practice.

In this article only the major obstacles to adhesion in the mouth will be discussed.

THE PHYSICAL AND CHEMICAL PROPERTIES OF ENAMEL AND DENTINE

A satisfactory restorative 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 qualities of the tooth surfaces. One of the major problems lies in the

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difference in tooth structure, not only from one tooth to the other but even in adjacent areas of the same tooth. Both the inorganic and organic contents of enamel and dentine may play a part in the adhesive process.

Although enamel is essentially inorganic, the relatively small organic component may be important in securing adhesion. The inorganic component consists of hydroxyapatite. According to Posner (1961) the formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ represents the fundamental chemical repeat unit in the three-dimensional symmetry pattern of the crystal. The hydroxyapatite crystallites are the primary structural units of enamel, and the enamel prisms or rods are the largest structural units. Study of mature enamel has led to a keyhole cross-section being considered the usual structure of enamel prisms (Meckel *et al.*, 1965). While these authors found no evidence of interprismatic substance, they described a sudden change in the orientation of the crystallites in the boundaries between prisms which serve to define the cross-sectional shape of the individual prisms. They believe the sudden change in crystal direction at the junction of adjacent prisms to be responsible for an optical effect which produces the appearance of the prism sheath as seen with the optical microscope. This has been confirmed by Orams (1968). As described by Jenkins (1966), the hydroxyapatite crystal consists of a central core of hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, with some of the ions replaced by F^- and CO_3^{2-} , a more superficial layer of absorbed ions and the superficial hydration layer around it.

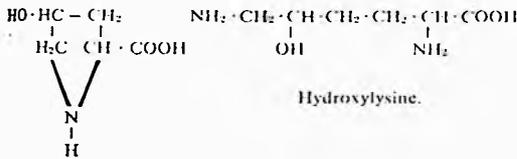
The organic portion of enamel, which comprises approximately 1.0 per cent of the tissue, is mainly protein and lipids. Fearnhead (1963), who showed that the organic matrix has a low crystallinity, discarded the concept that it consists of a highly ordered system of orientated fibres; and Eastoe (1966) expressed the opinion that it is probably either a continuous gel or a viscous sol.

Glantz (1969) studied the wettability of enamel and dentine. He determined the

contact angles of six liquids on their ground but otherwise untreated surfaces, and on a synthetic hydroxyapatite surface. He found that the means of the critical surface tensions, γ_c , 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 (> 72.6 dynes/cm); these results suggest that the enamel and dentine surfaces are covered with a low energy organic film. He demonstrated that the low energy surfaces of both enamel and dentine are probably formed from the organic phases of these tissues. He investigated the wettability of E.D.T.A. decalcified and non-decalcified dentine and obtained practically the same contact angles on these two surfaces. His studies also showed that the hydrophilic hydroxyapatite does not participate in the forming of 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 phase as a result of the energetic difference. Further, Zisman (1965) found that a high energy surface such as a *clean* tooth surface is a powerful absorber of contaminants, hence it will be extremely difficult to keep a tooth surface so prepared free from contamination.

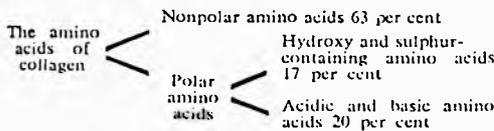
Dentine is composed of about 80 per cent inorganic material which is embedded in or surrounded by a protein matrix. Collagen constitutes approximately 90 per cent of the organic portion and exists mainly in the form of tropo-collagenous macromolecules. The remaining 10 per cent of the organic fraction consists of citrates, lactates, residual proteins and lipids. The collagen of the matrix may play an important part in adhesion and it is interesting to postulate on its role in this regard.

There are 18 amino acids in collagen, some abundant, others sparse (Mellon, 1961); and two of them, hydroxyproline and hydroxylysine, are exclusive to it.



Hydroxyproline.

The one that most frequently occurs is glycine; it accounts for one third of the units in the collagen molecule. The following is how these acids can be grouped :



In the nonpolar amino acids both the polar groups are utilized in the formation of the polypeptide chain; they do not contribute reactive groups to the collagen unless they occupy a terminal position. In the polar amino acids the predominant groups available for possible reactions with adhesives are the hydroxyl, carboxyl and amino. The hydroxyl group can react with acetyl chloride, the carboxyl with alcohols, the amino with aldehydes, and all three with epoxy compounds, to mention but a few of the possible reactions. According to Glenn (1961) stereo restriction due to the helical arrangement of the polypeptide chains in the collagen macromolecule must be considered. These helices are tightly bound together by hydrogen bonding and van der Waal's forces. It is believed, however, that the nature of the helix is such that all these polar chains are situated on its outside, which should make the polar groups accessible for reactions.

The calcified portion of the dentine which consists of hydroxyapatite crystals, is divided into the intertubular and peritubular matrices (Takuma, 1960). The dentine matrix is traversed by a large number of protoplasmic processes from the odontoblasts and it is believed that the living protoplasmic contents occupy approximately 10 per cent of the dentine cross-section. Any adhesive material placed on freshly cut dentine lies in direct contact with the protoplasmic contents within the dentinal tubules. Adhesion to the wet protoplasmic contents of the

tubules probably 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).

In addition to the physical and chemical properties of enamel and dentine, the study of intra-oral adhesives must take into account the organic film that covers all erupted teeth. Nasmyth's membrane, also known as the primary cuticle, and which is commonly thought to be lost soon after eruption of the tooth. Meckel (1965), who classified four types of organic film acquired after eruption, believes it most likely that they are of salivary origin. His investigations revealed that there is no distinguishable borderline between the deepest layer of this film, the subsurface cuticle and the organic framework of the enamel.

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 measurements, that liquids which wet hydroxyapatite might also form hydrogen bonds with the mineral. Glantz (1969) proved that, in addition to van der Waal's dispersion forces, polar forces and hydrogen bonds play a part in the bonding to enamel and dentine surfaces. His experimental results enabled him to calculate the minimal values of these forces. It is generally accepted, however, that although the polar Keesom forces and hydrogen bonding will enhance adhesion and covalent bonding between the adhesive and the tooth surface will markedly increase it, provided the adhesive wets the tooth surface completely the physical van der Waal's dispersion forces (London forces) will be strong enough to provide adequate adhesion.

While few filling materials or modified commercial adhesives exhibit lasting adhesion to untreated tooth surfaces, several workers have reported that a significant improvement can be effected by conditioning the enamel and dentine surfaces. Buonocore (1955) explored a number of

avenues in an attempt to obtain bonding between acrylic fillings and tooth structure. He found that adhesion can be considerably increased by treating the enamel surface with 85 per cent phosphoric acid for 30 seconds. He deduced that a simple decalcification to remove the superficial tooth structure is all that is necessary to produce a surface more receptive to adhesion. It is not unlikely, however, that the acid enlarged the surface area appreciably and that the increased adhesion was therefore a purely physical phenomenon. Buonocore *et al* (1968) studied the penetration of resin filling materials and two experimental adhesives into enamel surfaces to learn whether mechanical factors due to resin penetration are involved in the bonding of these materials to acid-conditioned enamel surfaces. They found that enhanced bonding to such surfaces appeared to be associated with the presence of "prism-like" tags presumably formed by the penetration of the resin into enamel spaces created by the acid treatment. These authors used a milder conditioning agent: a 50 per cent phosphoric acid solution containing 7.0 per cent dissolved zinc oxide by weight.

Newman *et al* (1968) and Newman (1969) showed that the hydrophobic tooth structure can be made hydrophilic by treating the surface with 85 per cent phosphoric acid; and they reported that the contact angles of water and epoxy resins were greatly reduced on conditioned enamel surfaces compared with those recorded on untreated surfaces. The relationship between contact angle, wetting and adhesion was described in a previous article (Retief, 1970).

THE AQUEOUS ENVIRONMENT

As bonding is best obtained and maintained under dry conditions, water in the oral cavity presents a problem. An adhesive must be capable of bonding to tooth surfaces which cannot tolerate adequate drying, and continuous contact with water must not affect this property adversely.

Rose *et al* (1961) found that very few materials constantly maintained adhesion after immersion in water for five minutes; and that after immersion for 16 hours, none of them exhibited any adhesion

whatsoever. They stressed that the behaviour of adhesives when tested on dry teeth has no bearing on their adhesion when tested in the presence of water. Cornell's experiments (1961) disclosed that although a number of materials gave excellent adhesion initially, they all failed to continue to do so when tested under physiological conditions over a long period.

As the hydroxyapatite surface has a strong affinity for water, hence to remove it completely the hydroxyapatite must be heated to a high temperature. Investigations by Beebe (1961) revealed that the "bare" surface of bone mineral can be obtained only after heating to 450°C *in vacuo*; and 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. The presence of at least a monolayer of water on the hydroxyapatite surface must be accepted.

Even if it were possible to dry a tooth surface completely the dryness could not be maintained because of the fluid flow from the pulp to the enamel surface. Gunnar Bergman (1963), who developed a technique to demonstrate this flow, found 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 has to compete with it; and Zettlemyer (1961) found that compounds containing nitro groups can do so. The ideal filling material, however, must be successfully competitive with water over long periods because of the exchange processes that take place in the tooth. The problem therefore is to obtain and maintain adhesion. The presence of water in the oral environment can be the precursor of chemical activity at the adhesive/adherent 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.

Zisman (1965) investigated the displacement of water from a tooth surface by surface-chemical methods. He managed to remove all of it, except the strongly adsorbed monolayer, by means of butanol. He showed that a drop of this liquid of only 0.01 cm³ will displace a layer of water 2.0 mm thick from a surface 5.0 cm². Hydrogen bonds are formed between the hydroxyl groups of the butanol molecules and the adjacent water molecules respectively. This inter-molecular bonding leads to a cloud of water molecules accompanying each butanol molecule as it advances over the moist tooth surface. Unfortunately the butanol will evaporate and the water film will return.

De Bruyne (1938) enunciated the following rule for adhesives: "Provided we use pure or simple substances as adhesives then there is a good deal of evidence that strong joints can never be made by polar-adherends with nonpolar adhesives or to nonpolar adherends with polar adhesives". A nonpolar adhesive liquid usually will have a lower surface tension (γ_{LV}°) than the critical surface tension of wetting (γ_c) of the polar adherend, and good wetting and spreading should result. Nonpolar adhesives, however, are very hydrophobic materials and polar

adherends are hydrophilic and can absorb water. A polar surface such as a *clean* tooth surface always has at least a monolayer of water, which leads to poor wetting by the nonpolar adhesive. A liquid polar adhesive has a higher surface tension (γ_{LV}°) than the critical surface tension of wetting (γ_c) of a nonpolar adherend, hence poor wetting will be encountered. As many polar liquid adhesives can, however, absorb water or displace adsorbed water from an adherend surface, their adequate wetting and spreading may ensue.

SURFACE ROUGHNESS

Although surfaces may appear smooth they are rough at an atomic level, and the real area of contact is merely a fraction of the apparent one. It is agreed that adhesion is improved when the adherend surfaces are smooth. A rough surface is desirable if the restorative material depends on mechanical locking for its retention: for example amalgam or zinc-phosphate cement. The extent to which the shape of the depressions on the adherend surface affects the adhesion was described in a previous article (Retief 1970). A rough surface may result in air being trapped in the depth of the depressions, reducing the contact between the adhesive and the adherend and thus lessening the effective area over which the molecular forces of attraction can operate (Fig. 1). Adhesives usually are applied in the viscous state and voids are readily

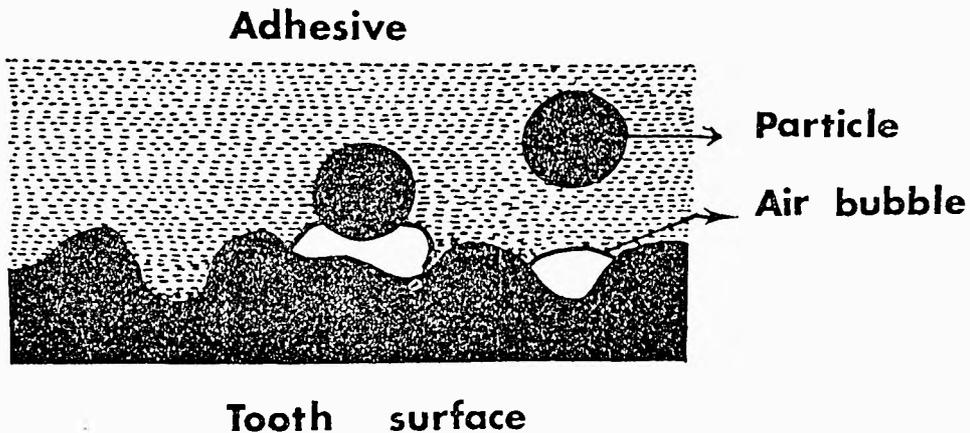


FIG. 1. Adhesion to a rough tooth surface.

formed on a rough surface. Stress concentrations could originate about these voids. As most of the adhesives shrink during curing or after hardening, embedded surface projections from the adherend surface may be sheared from the cavity wall or pieces of restorative material may be broken, depending on which of them is the weaker. With a difference in the thermal expansion of the filling material and the tooth structure, expansion of the former because of water absorption or occlusal forces may contribute to this feature (Buonocore, 1963).

Scott and O'Neil (1961) studied the effect of cutting instruments generally used on enamel and dentine. The surfaces were characterised by patterns of tool marks which undoubtedly reflected both the type of instrument used and the manner in which it was applied. Boyde and Knight (1969) examined instruments commonly employed in cavity preparations and the fitting of restorations, and found that they produced marked irregularities in the tooth surfaces. If an adhesive restorative material eventually is developed, the present cutting procedures will have to be modified to reduce the surface roughness.

DEBRIS IN THE CAVITY PREPARATION

Scott and O'Neil (1961) and Provenza and Sardana (1965) proved that even after careful cleaning a considerable amount of debris remains on the floor and walls of the cavity. Massler (1961) described three levels of debris formation within the cavity after its preparation: gross debris;

small particles, approximately 10-20 microns; and submicroscopic particles, about 0.1 micron. He expressed doubt as to whether the submicroscopic and microscopic particles are removed during the toilet of the 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 that when this 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 (Fig. 2). Even if the solid particle is subsequently wetted and pulled into the adhesive the air bubble will persist within the adhesive. Stress concentrations could originate around these entrapped air bubbles and adversely affect the adhesive performance.

CONDITIONS TO WHICH THE ADHESIVE IS EXPOSED DURING USE

The oral environment is ideally suited for destruction. Biting stresses on restorations may amount to thousands of pounds per square inch. The average biting force measured is 170 lbs 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. The pH in the mouth fluctuates rapidly between

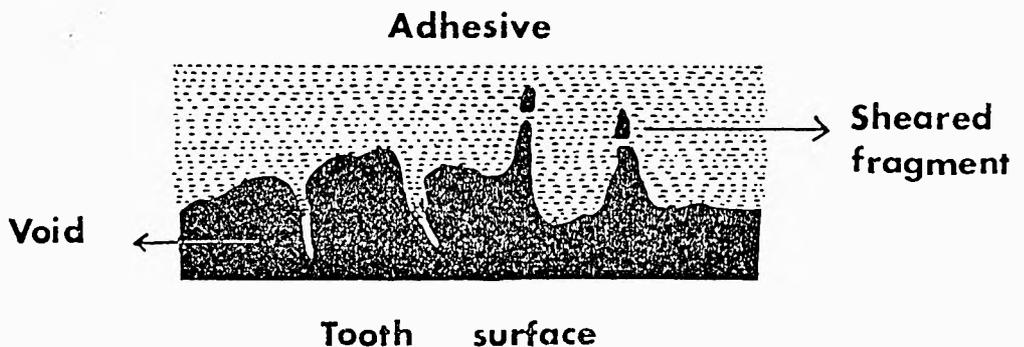


Fig. 2. Air bubbles formed at the particle/adhesive interface as a result of incomplete wetting of the debris particles by the adhesive.

acidity and alkalinity, and the warm humid environment is particularly conducive to corrosion.

Instantaneous temperature changes in the mouth may be as great as 65°C. This is of very 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. If this is not compensated for, stress concentrations will develop in the adhesive material because of the temperature cycling in the mouth.

OTHER FACTORS INVOLVING THE ADHESIVE ITSELF

Several other factors must be considered before the adhesive can be used in the mouth: its toxicity to the pulp, the oral tissues and the organism as a whole. Most of the catalysts or reactive hardeners employed to polymerize resins probably 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 for final evaluation of the toxicity.

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 temperatures, or because they have to be cured at temperatures which cannot be tolerated in the mouth.

This discussion of the numerous factors involved in a truly adhesive dental restorative material renders it obvious that many obstacles have yet to be overcome before the quest is successfully ended.

THE REQUIREMENTS OF AN IDEAL ADHESIVE RESTORATIVE MATERIAL

1. The adhesive must produce a lasting bond with both enamel and dentine.
2. It must polymerize at or near body temperature with minimal shrinkage.
3. It must be sufficiently cross-linked to minimise expansion or water sorption.
4. It must have sufficient strength to resist masticatory forces.
5. It must have the same coefficient of thermal expansion as tooth structure.

6. Neither it nor its constituents must be toxic to the pulp and the gingival tissues.
7. It must be resistant to any type of degradation in the oral cavity.

SUMMARY

Extensive research is aimed to produce a restorative material that will bond adequately to tooth structure and so prevent marginal leakage. It is extremely difficult to obtain adhesion in the mouth because of the destructive nature of the oral environment. The problems to be considered in the development of an adhesive restorative material are discussed. These include the heterogeneity of the enamel and dentine surfaces, the aqueous environment, the roughness of the surfaces of the prepared cavity, the debris in the cavity preparation and the conditions to which the restorative material are exposed in the oral environment. The requirements of an ideal adhesive dental restorative material are listed.

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