A review of adhesion science

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ABSTRACT

Objective. Adhesion or cohesion includes an adherend, adhesive, and intervening interface. Adhesive joints may include one or more interfaces. Adhesion science focuses on understanding the materials properties associated with formation of the interfaces, changes in the interfaces with time, and events associated with failure of the interfaces.

Methods. The key principles for good interface formation are creation of a clean surface, generation of a rough surface for interfacial interlocking, good wetting of the substratum by the adhesive/cohesive materials, adequate flow and adaptation for intimate interaction, and acceptable curing when phase changes are required for final joint formation.

Results. Much more effort is needed in the future to carefully assess each of these using available testing methods that attempt to characterize the energetics of the interfaces. Bonding involves potential contributions from physical, chemical, and mechanical sources but primarily relies on micro-mechanical interaction for success. Characterization of the interface before adhesion, during service, and after failure would be much more useful for future investigations and remains as a great challenge.

Significance. Scientists should more rigorously apply techniques such as comprehensive contact angle analysis (rather than simple water wettability) for surface energy determination, and AFM in addition to SEM for surface texture analysis.

1. Introduction to adhesion science in dentistry

Everyone has an image of adhesion that includes glue, tape, barnacles sticking to boats, insects walking on ceilings, children's stickers, and a host of dental materials examples. Adhesion involves the tendency of atoms or molecules to stick to each other. Strictly speaking, cohesion involves like materials sticking together, and adhesion involves dissimilar atoms or molecules sticking together. Both events are relevant to dental materials. This paper deals with both but will focus mostly on adhesive events.

Early records of cohesion techniques such as cold welding of gold and silver from the 1st and 2nd centuries BC [1] are applicable to the fabrication of direct gold foil restorations, which were used in restorative dentistry. Cold welding is an example of cohesion, not adhesion, but the dental example involves both cohesion of the gold and adhesion (mechanical interlocking) into the prepared cavity. Another early example

of adhesion which is used in dentistry today came from the 4th–7th centuries AD, enamelling for artwork and jewelry. This type of adhesion is used for ceramo-metal restorations. A non-dental example is when Sir Isaac Newton observed in the 17th Century that if he placed two transparent optical elements of the same refractive index together, there was no reflection at the point of contact. This principle formed the basis for building interferometers. The consequences of different types of interfaces will be discussed in the following sections.

2. Science of adhesion

It is important at this point to acknowledge that the science for creating adhesion or cohesion involves quite different energetic considerations than that science of interpreting their associated failures. The topic of adhesion includes (1) formation of adhesion-or-cohesion, (2) characterization of the adhesive-or-cohesive interfaces, (3) destruction of the interfaces (bond strength testing), and (4) failure analysis of interfaces. Our focus will be primarily on the first two topics, since it is clear that separation of a bonded joint is not simply the reverse of making that joint in the first place. Data on joint breaking strengths teach little about the surface properties initially supporting good bond formation.

2.1. Definitions for adhesion and cohesion

Adhesion involves molecular interactions at the interface between materials. Any event described as adhesion is really an assembly involving an "adherend" (or substratum) with an applied "adhesive" that creates an intervening "interface." The combination is defined as an "adhesive joint." Quite often a joint is more complex and includes two or more interfaces. In dentistry adherends can be quite varied (e.g., enamel, dentin, amalgam, composite, ceramic, cast metal, glass ionomer, etc.) and adhesives can involve single interfaces (e.g., sealants, ceramic bonded to metal) or multiple ones (composite bonded to dentin, ceramic restorations bonded to tooth structure). Any interface may include adhesion and/or cohesion [2–5].

2.2. Cohesion versus adhesion

Cohesion involves intermolecular attractions between like-molecules/atoms and is often reported as the cohesive strength of a material or tissue. For example, when measuring bond strength between dentin and an adhesive, we often examine the fracture surfaces to determine which of the materials actually failed and thus, determine whether the strength value measured is truly a measure of the bond strength, or is a measure of the cohesive strength of the adhesive, the adherend or some combination of the two.

Cohesion involves primary bonding and may include strong secondary bonding such as hydrogen bonding. It is a relatively strong force among polar molecules such as water, in which hydrogen bonding forms extensively. The propensity for water droplet formation on low energy surfaces is, in part, a result of cohesive forces in water. Higher energy surfaces better compete with water's cohesive forces and thus the water droplets are flatter or spread completely. An example of cohesion inside of a restorative dental material is gold foil. The "sea of electrons" forms a strong bond from its overlapping metallic bonds among gold atoms. At the same time, the restoration is held in place within tooth structure by gross mechanical interlocking.

2.3. Types of adhesion

Adhesion or cohesion may be categorized by the type of physical, chemical, and/or mechanical bonding processes that contribute to the interfacial strength of the assembly. Remember that bonding occurs within the adherend, within the adhesive, and between the two at the interface. We are most often focusing on the bonding at the interface. Physical bonding forces are generally very weak. Chemical bonding is strong but also very difficult to produce in a dense manner across an interface. Mechanical bonding is the most effective means of creating strong joints. Each includes different subtypes as well. Each will be considered in more detail as follows.

Physical adhesion or bonding is always present even though it is weak. Thus, while van der Waals forces occur at every interface, they are often supplemented by significant contributions from stronger bonds that may be present, such as those from permanent dipoles in addition to the van der Waals induced dipoles. For example when water is present, such as water between two glass slides, the permanent dipoles allow for hydrogen bonding at the interface, but such bonding does not occur to polyethylene or other polymers which lack H-bonding partner sites [3].

Chemical bonding includes possibilities for covalent, ionic, metallic, and, in some cases, chelation bonding. There are numerous possibilities for creating chemical bonding. As previously noted, cohesion of gold to itself will create an interface that essentially disappears as the surface atoms become bonded. However, for other systems, trying to create bonds between unlike surfaces such as metal–ceramic and polymer–polymer interfaces, the situation is much more complicated and may result in very limited chemical bonding and much lower interfacial strengths.

There are many examples of creative ways to promote some chemical adhesion by using organo-silane coupling agents. Despite opportunities for chemical reactions or for chelation reactions, most of the moieties involved do not produce much chemical bonding at all. Rather they function to dramatically improve the wetting of phases and act by increasing the adaptation of materials along interfaces.

Chemical adhesion has been sought for decades in numerous dental materials applications. The results have largely been disappointing. Contaminants are hard to eliminate completely and interfere with the intimate adaptation needed to form bonds. At the same time, the theoretical bond densities that could form are quite small and therefore are normally overshadowed by mechanical bonding.

Mechanical interlocking is a common type of adhesion. This is certainly true for dental materials as well [2,4,6]. There are several different variations on the theme, but all involve the adhesive penetrating into the adherend and becoming mechanically interlocked at some level. A classic non-dental example is a Velcro closure. A simple dental example is an amalgam restoration placed into cavities with

undercuts to provide retention. Other examples cover the spectrum of interlocking, from dental cements that fill the roughness in castings and help retain them, to the penetration of monomers into etched enamel, which are then polymerized to form tags of several micrometers in size for retention. There is also permeation of monomers throughout the collagen fibril matrix in etched dentin to form the hybrid layer. Heterogeneity of the adherend microstructure contributes a variety of options for mechanical interlocking.

3. Requirements for creating good adhesion

There are several sequential events that are required to form an effective adhesive/cohesive joint. These are discussed in detail as follows.

3.1. Clean surfaces

A principal requirement for strong adhesive bonds is that the surface be clean and therefore in a high energy state. Films of water, organic debris, and/or biofilms are always present in the clinical situation, and interfere with wetting and spreading. These cannot be removed by tooth brushing with dentifrices alone. Teeth that are prepared for dental restorative procedures have low energy surfaces because of contaminants and smear layer that remain on the surface. Acid etching removes most of the contaminants, produces surface roughness for micro-mechanical interlocking, and forms facets on the mineral crystals [3]. Etched enamel is wet readily by monomers, allowing good penetration, and forms micromechanical bonds easily [4,6]. Hydrophilic monomers can penetrate into surface cracks among or within the enamel crystals and thus help resist crack propagation after polymerization. The process also may displace any water layer on the prepared surface. Organic groups that enhance wetting include –OH, –SH, –COOH, and –NH$_2$. Unfortunately the presence of F discourages wetting [3].

3.2. Surface roughness

Wettability is enhanced for most practical dental situations by the presence of microsurface roughness. Wettability is related to roughness by the Wenzel equation [7] that states that:

$$r = \frac{\cos \theta_1}{\cos \theta_2},$$

where r is the ratio of the contact angles of the smooth and rough surfaces, respectively. This equation predicts that for contact angles less than 90°, wetting is increased by surface roughness, but decreased for non-wetting materials with contact angles greater than 90°. The Wenzel effect has been confirmed for a number of dental materials investigations including polymer surfaces [8], cements [9], and composites [10].

3.3. Proper contact angle and good wetting

Adhesion requires intimate contact of the materials to be joined. Since the surface of a material is different from the

Table 1 – Contact angles (degrees).	
Teflon–Hg	150
Teflon–water	112
PE–water	103
Skin–water	90
Gold–water	66
Pt–water	40
Glass–water	<5

interior, understanding of the surface characteristics of materials is essential to understanding and promoting adhesion. In the interior atoms are in equilibrium and the interatomic forces between adjacent atoms in the crystal structure are in balance. At the surface this is not true because there are no interatomic interactions on the external surface of the atoms. The surface free energy, γ, represents the difference between an atom on the surface and an atom in the interior [2,3,5]. The affected surface layer is likely to be at least 5 atomic layers thick [1]. Surface physics and chemistry are affected in adhesives or tissues [3].

For adhesion to occur the adhesive must wet the substratum. The most common method of observing wetting is measuring the contact angle. The contact angle is the internal angle in a droplet of liquid in contact with a solid. It represents the energetic equilibrium between the solid, liquid, and gas phases involved. In most cases, the gas phase is air, and one simply focuses on the liquid droplet and solid substratum because the gas phase at the operative microscopic solid/liquid/gas interface is always fully saturated with the liquid's vapor.

Wetting is categorized from liquid (usually water, but not necessarily) contact angle as non-wetting (>90°), wetting (<90°), and spreading (∼0°), although all liquids do wet all solids to some extent; degree of wetting = degree of adhesion. The goal is always to select conditions that promote spreading, without going so low in liquid surface tension that the liquid's cohesive strength is adversely diminished. The equation governing the energy balance in an interface is Young's equation [11]:

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} \cos \theta,$$

where "θ" is the contact angle, and "s", "v," and "l" refer to the solid, liquid, and vapor phases, respectively. The "critical surface tension" of a solid is related to its surface free energy and is determined from a graph of liquid surface tension versus contact angle, when various liquids of known surface tension are plotted versus contact angle. The critical surface tension is the value obtained when the graph is extrapolated to a contact angle of 0°.

Contact angles of common liquid/material combinations are in Table 1 [2].

Low contact angles are formed by liquids or monomers on clean high energy surfaces. High energy surfaces include solids that are strong, hard, crystalline, and have high melting points. Etched enamel is a high energy surface. Lower energy surfaces include softer solids with lower melting point materials, such as dentin collagen and ubiquitous oral salivary films [3]. An otherwise high energy enamel or dentin surface can easily become contaminated. While an adhesive may still wet these contaminated surfaces, the strength and integrity of any

adhesive is limited to the strength and integrity of the surface film which it overlays.

This situation may be summarized in terms of energy as the adhesion at an interface occurs if there is a net reduction in energy by forming the interface. The work of adhesion can be determined for an interface of A and B by [11]:

$$W_{AB} = \gamma_A + \gamma_B - \gamma_{AB}.$$

If the materials in contact cannot interact to reduce the total energy of the system, then materials will try to reduce the contact area of interaction, such as water beading on a Teflon surface. The round shape of the droplets is consequence of surface tension [2,3].

Although the liquid/vapor surface tension of water is about 72 dynes/cm, the energy required to expose new water surface area, the critical surface tension for spreading over bulk water is 22 dynes/cm at 20 °C, the lower surface tension required to cover that same area of water. Familiar dental polymers have values of 20–45 dynes/cm [12]. In 1973, Baier determined the critical surface tension of teeth in vivo to be ~32 dynes/cm [3]. Eick quoted values of 42 for smear layer covered dentin, 29 after EDTA demineralization, and 27 after 2.5% nitric acid treatment from Benediktsson's MS thesis at UAB [13]. Phosphoric acid etching increases it to about 44 dynes/cm. Thus, acid etching of enamel and dentin increases wetting and promotes mechanical interlocking. Monomers dissolved in solvents such as water, acetone, or alcohol displace water, promote wetting, and expand the collagen network in dentin, thus enhancing adhesion at several levels [13].

3.4.   *Low viscosity adhesives and adequate flow*

Even though the critical surface tension is appropriate for contact, the adhesive generally must be low enough in viscosity and be capable of sufficient flow within the available application time to spread and adapt to the details of the adherend surface.

Viscosity behavior in response to shear stresses for most adhesives for dental materials is pseudoplastic. Dental materials often include a critical shear stress barrier for the onset of flow [14]. Each of these can be measured in a straight-forward manner using commercial rheometers or viscosity methods.

Yet, this is still only part of the story. Most adhesive systems require successful penetration into small surface roughness features. The tendency to flow into holes can be measured in terms of a penetration coefficient [15]. The penetration coefficient, PC, is defined as the term in parentheses in the Washburn equation:

$$d^2 = \frac{\gamma \cos \theta / 2\eta}{rt},$$

where d is the distance moved by the liquid, γ is the surface tension of the liquid, θ is the contact angle, η is the dynamic viscosity of the liquid, r is the radius, and t is the penetration time. Larger PC values correspond to faster penetration. This was first utilized to rate early sealant compositions and their abilities to penetrate pits and fissures. However, there is strong interest in applying the same approach to rate existing adhesives for micro-interdigitation along roughened or porous dental substrates.

3.5.   *Resistance to phase separation*

Dental adhesive compositions are primarily based on volatile diluents that cause adhesive phase separation during the last stages of flow as solvent loss is occurring rapidly. While some of the problems have been described there is very little clear understanding of what the actual interfacial phases might be by the conclusion of the adhesion formation event. This clearly deserves much more attention.

3.6.   *Adhesive solidification*

While many situations in dentistry involve heat to create adhesive interactions, enamel and dentin adhesive systems require polymerization of the liquid components as their final stage. Many of the dental situations requiring the use of adhesives are challenged by poor access for visible light curing. It is obvious that effective adhesion requires adequate degree of conversion. This information needs to be collected on actual bonded dental assemblies and not simply on the adhesive itself. The most popular method of measuring this is to measure the relative conversion of available double bonds during polymerization setting reactions [16]. This approach only examines the material within the adhesive and not the bonding at the interface. This is much more challenging.

4.   **Characterization of adhesive joints**

4.1.   *Phases present in adhesive systems*

Many sophisticated surface analysis methods are available, but none is as easy to use as contact angle measurements. There are major advantages for these techniques in revealing the microstructure and properties of adhesive systems. However, special care must be taken to avoid or at least be aware of surface alterations caused by them [12]. Many also require a high vacuum, which either disqualifies its use on natural tissues or alters the tissues. A brief summary of advantages and disadvantages of several of them follows [12].

ESCA (electron spectroscopy for chemical analysis), also called XPS (X-ray photoelectron spectroscopy) uses an X-ray beam focused on a specimen that causes emission of inner shell electrons. The energy of the electrons is measured to identify the elements present. The equipment is expensive and requires a high vacuum, but there is little specimen damage.

SIMS (secondary ion mass spectroscopy) uses an ion beam (Xe, Ar, Ce, Ga) that sputters the surface and measures the mass of the atoms on the surface. It requires a high vacuum and is expensive. It measures only the outermost 1–2 atoms, which makes it truly a surface measurement. Like ESCA, SIMS requires a very dry specimen so its use on natural tooth tissues is limited.

FTIR (Fourier transform infrared spectroscopy) uses infrared radiation to determine chemical composition at a much lower resolution and is less surface sensitive. An advantage of this technique is that it can be used on wet specimens.

Raman spectroscopy uses inelastic scattering of light, from a laser in the visible or near IR or near UV range, and gives

chemical information. Raman microspectroscopy allows high resolution imaging of compositional variations.

SEM/EDS (scanning electron microscopy/energy dispersive X-ray spectroscopy) is the major topography and chemical analysis technique used in dental materials research. It has the advantage of depth of field, producing topographical images. Chemical analysis is done by analyzing the X-rays ejected by the electrons. Some SEM/EDS equipment needs a high vacuum, while some allows moisture to remain on the specimen (as in environmental SEM, ESEM).

AFM (atomic force microscopy) has gained much popularity in analyzing surface topography. It operates on the principle of measuring the deflection of a sharp tip. Many other modes, such as piezo force microscopy and measurement of mechanical properties at a fine scale are available. A major advantage is that these instruments can operate in liquid, thus reproducing the clinical situation better than most other analytical techniques.

5.　Geometry of adhesive layer

In the absence of efficient and effective chemical bonding, interfaces depend primarily on intimate atomic contact and mechanical bonding for success. Rough surfaces are generally more advantageous than smooth ones. Mechanical bonding can be viewed at a variety of levels as macro-mechanical retention, micro-mechanical retention, and nano-interdigitation.

Macro-mechanical bonding has been used in dentistry for decades by creating dentin undercuts in the cavity designs of intra-coronal restorations to prevent removal and by relying on surface roughness of both extra-coronal restorations and tooth structure to allow dental cements to prevent restoration withdrawal.

Micro-mechanical bonding is the basis of most of contemporary adhesive dentistry. It depends on microsized relief of enamel and dentin surfaces to allow adhesive penetration that interlocks it into surface spaces. The surface relief is created by acid etching. The interlocking occurs at two levels. The first involves the formation of microtags of resin around enamel prisms or within dentinal tubules. The second involves a much finer penetration of adhesive nanotags among enamel crystals or into the dentin collagen spaces. Nanotags seem to be much more important to overall retention and can be imagined as a nano-interdigitation mechanism.

These adhesive bonds involve the formation of an interphase. Determination of parameters such as permeability coefficient helps to predict the contributions of diffusion bonding [13]. Another interesting result of interphase adhesion is the phenomenon of stringing. During debonding, strings of adhesive are stretched across the original interface, bridging the gap, and preventing complete crack formation. This discourages the propagation of a crack at the interface. This phenomenon is common with general-purpose adhesives or glues.

Nano-interdigitation also occurs when adhesive monomers diffuse into existing polymer phases, polymerize, and become molecularly intertwined with existing molecules. While there are no new chemical bonds formed between the old and new polymer molecules, breaking of one or the other polymer chains is generally required to make the interface fail. This is a mechanism that commonly occurs with methyl methacrylate monomer in acrylic dough systems used for denture bases and teeth or with acrylic bone cements.

A related event occurs when atoms or molecules diffuse across an interface, rearrange the bulk material, and eliminate the original boundaries. With metal and ceramic systems, this type of diffusion requires heating to promote atomic movements [1]. A good example is sintering of ceramic or metal powders.

6.　Adhesion changes in service

The past few years have seen an intense growth in research monitoring changes over time in bond strength as a function of water effects, deleterious intraoral enzymes, thermal cycling, mechanical cycling, and other special intraoral events in the mouth like bleaching. These are left to others at this conference to assess. Clearly, there needs to be a model for testing these in an effective manner. It should include careful microstructural characterization and not just property testing.

The ultimate goal of good adhesion in dental materials is to produce an interface that is strong and durable. A well-formed interface should have minimal imperfections [11]. Understanding the changing microstructure of the interface and its defects over time continues to be a great challenge.

7.　Failures of adhesive/cohesive joint

7.1.　Bond strength evaluation

Historically, it has been much easier to screen the effectiveness of bonding by destructively testing adhesive/cohesive joints. Bond strength testing has "ruled" much of the last four decades of dental materials research. Yet, in the absence of well-understood substrata, adhesive systems, and interfaces, any interpretation of the failure events has been suppositional at best. Others presenting at this meeting will deal with the details of testing results, testing variables, and testing problems.

7.2.　Fractographic analysis

A potentially valuable tool for post-test characterization of failures is fractographic analysis. Effective fractography demands much more than simply a classification of the remaining interfacial phases along the fracture faces as related to the adhesive materials (adhesive), the substratum (cohesive), or both (mixed). Rather, effective analysis considers identification of the fracture origin (crack initiation), the direction and pattern of crack propagation, the energetics of the fracture (single event or fatigue; brittle or ductile), and the phases included along the fracture plane. Very little of this has been done for dental materials in general, much less for bonded systems. This is one of the future challenges for this area of science.

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