Chemical Modification of the Dentin Smeared Layer

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CHEMICAL MODIFICATION OF THE DENTIN SMEARED LAYER

by

FRANK A. CINCIONE

A Thesis Submitted to the Faculty of the Graduate School of Loyola University of Chicago in Partial Fulfillment of the Requirements for the Degree of Master of Science in Oral Biology

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VITA

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CHAPTER I
INTRODUCTION

When dentin has been manipulated by dental rotary or hand instruments an amorphous layer of organic material is created and left on the surface. This amorphous mass has been termed the smeared layer. The smeared layer is composed of organic and inorganic debris, saliva, blood and microorganisms. The smeared layer may jeopardize pulpal health due to its large amounts of microorganisms and metabolites for their proliferation. The smeared layer may also mitigate adhesive bonding and minimize close adaptation of restorative materials to the dentin surface. Therefore, it is thought to be desirable to modify or remove the smeared layer for improved adhesion and reduction of potential for bacterial infiltration and growth. Mechanical removal of the smeared layer is difficult, but chemical removal is fairly simple. Knowledge of effective chemical agents for smeared layer removal is limited. This investigation examines chemical agents for smeared layer removal.
CHAPTER II
REVIEW OF LITERATURE

Enamel Structure

Enamel forms a protective covering of variable thickness over the entire surface of the tooth crown. On the cusps of human molars and premolars, the enamel attains a maximum thickness of approximately 2.5 mm, thinning to almost a knife edge at the neck of the tooth. The shape and contour of the cusps receive their final modeling in enamel.\(^1\) Consisting mainly of inorganic material (96\%) and only a small amount of organic substance and water (4\%), enamel is structurally composed of rods or prisms, rod sheaths and a cementing interprismatic substance.\(^2\)

The morphologic appearance of the inorganic apatite crystals has been well characterized over the years, consisting of a cross-sectional pattern resembling keyhole or paddle-shaped prisms.\(^1\) Descriptions of the prism on transverse section have included such terms as hexagons, fish scales, horseshoes and arcades.\(^3,4\) In reality, these terms designate the shape of the prism sheath, while the prism itself resemble a keyhole in cross-section.
These keyhole-shaped prisms are long, rod-like structures with one or two fins extending from and continuous with the main prism. The prisms are oriented with the convex aspects occlusally and the fins cervically and measure about 5 microns in diameter across the head and 9 microns in height in the head to tail dimension. The individual prisms change shape on their course through the enamel. The changes also involve the fins which at any given point seem to adapt to and occupy any available space between adjacent prisms, thus allowing close packing of the prisms and interlocking of adjacent prisms. This arrangement requires little interprismatic substance, but is marked by abrupt changes in crystalline direction. The prisms disappear as they reach the enamel surface where all the crystallites are oriented parallel to each other and are perpendicular to the enamel surface.

The outermost few microns of the enamel are prismless in many areas and have been studied by several investigators. Gwinnett, using polarized light microscopy, x-ray diffraction analysis and electron microscopy, examined the surface of prismless enamel of primary teeth. He reported that the outer layer of the primary tooth enamel possessed a different crystallite arrangement from subsurface enamel and suggested that it may correlate to the break in enamel prism extension.
from the dentino-enamel junction to the surface. Bozalis, et al. reported that the enamel of primary teeth was acid-resistant and tended to interfere with the development of organized prism-end-patterns required for optimal resin attachment.

The arrangement of rods in permanent teeth is similar in the occlusal two-thirds of the crown to the rods in primary teeth with the respect to directionality. Orban states that the rods are generally oriented at right angles to the dentinal surface. In the cervical and central parts of the crown of a primary tooth they are approximately horizontal. Near the incisal edge or tip of the cusps they change gradually to an increasingly oblique direction until they are almost vertical in the region of the edge or tip of the cusps. The arrangement of the rods in permanent teeth is similar in the occlusal two-thirds of the crown. In the cervical region, however, the rods deviate from the horizontal in an apical direction. The course of the enamel rods is of clinical importance in cavity margins because they may break and produce spaces into which leakage of bacteria might occur, inducing secondary dental caries.
Dentin Structure

The dentin constitutes the bulk of the tooth and extends almost the entire length of the tooth. It is covered by enamel on the crown and by cementum on the root. The internal surface of the dentin forms the walls of the pulp cavity which is occupied by the pulpal tissue. Dentin is a living tissue which consists of specialized cells, the odontoblasts, and an intercellular substance. The odontoblast is the cell of the dentin biologically and morphologically. During dentinogenesis protoplasmic extensions of the odontoblasts become entrapped in the ground substance of the dentin while the cell bodies become arranged along the pulp cavity surface of the dentin outside the dentin matrix. These protoplasmic extensions are known as the odontoblastic processes and extended to the outer periphery of the dentin on a perpendicular course to the pulpal cavity terminating at the dentin enamel junction. Although similar in physical and chemical properties to bone, dentin differs in that the tissue-forming cells of bone may be encased in intercellular substance as osteocytes while dentin contains only cytoplasmic processes of the odontoblasts. Dentin is considered a living tissue because of the existence of the odontoblast process which traverses the dentin matrix. These processes also
provide the capacity to react to physiological and pathological stimuli. Stimuli produce changes within dentin such as sclerotic dentin, secondary dentin and dead tracts.

The color of dentin is yellowish white and may differ in primary and permanent dentitions. Dentin undergoes slight deformation and is highly elastic. The hardness of dentin is less than that of enamel but greater than either bone or cementum. The Knoop method is most frequently used for measuring the microhardness of dentin. With this method an indenting tool made of diamond cuts into the dentin producing an indentation which are then measured and calculated with a mathematical formula resulting in the Knoop hardness number (KHN). The hardness number of dentin varies with different layers. The highest microhardness values occur in an area approximately 450 Å from the dentinoenamel junction with a KHN of 70 while the lowest values of 20 KNH is found at the innermost layer of dentin at a distance of 100 Å from the pulp. Dentin is more radiolucent than enamel due to its reduced mineral content.

Dentin consists of 70% inorganic material, 25% organic matter and 5% water. Calcium and phosphorus in the hydroxyapatite arrangement are the major inorganic constituents while carbonate, magnesium, sodium and chloride are present in less amounts. The calcium to phosphorous ratio in dentin is lower than that of enamel. Dentin has a lower
mineral content than enamel but higher than cementum or bone. Likewise, calcium and phosphorous are in a higher concentration in dentin than in either cementum or bone but lower than in enamel. Fluoride is a trace element in dentin but an important element in that its presence renders dentin less soluble. This reduced solubility, and therefore fluoride, plays an important role in dental caries reduction. The fluoride concentration is greatest in dentin around the pulp and decreases toward the dentinoenamel junction. Fluoride is mainly incorporated in dentin during the process of calcification. However, the fluoride concentration in dentin continues to increase during life due to its presence in food and drinking water and topical application. The mineral content of dentin increases with age.

The organic portion of dentin is mainly collagenous fibrils and a ground substance of mucopolysaccharides. The collagen is characterized by the significant pressure of four amino acids, glycine, alanine, proline, and hydroxyproline. Dentin collagen has an increased content of hydroxylysine in comparison to collagen in general. This increase hydroxylysine content is thought to play a role in mineralization of the dentin matrix. Dentin collagen is believed to perform as a nidus in the formation of apatite crystals. Cholesterol, esterified cholesterol, and phospholipids are also present and thought to be related to
the calcification. It is also believed that carbohydrates play a role in calcification.

The basic structural components of dentin are the odontoblasts and their processes and the dentinal matrix. The odontoblastic processes are cytoplasmic extensions of the odontoblasts which traverse the dentinal matrix in a space called the dentinal tubule. The cell bodies of the odontoblasts are aligned in a monolayer along the pulpal surface of the dentin. Only the cytoplasmic processes occupy the tubules and traverse the matrix. The odontoblastic processes are larger near their junction with the cell body than in peripheral areas of the dentinal matrix. Each odontoblastic process is limited by a cell membrane. The contents of the processes are minimal, however, with microtubules and filaments being the predominant structures while mitochondria, lysosomes and vacuolar structures appearing infrequently.

The odontoblastic processes split and divide near their peripheral ends into terminal branches and extend to the dentinoenamel junction. While traversing the dentin the process produce thin radiating secondary processes enclosed in fine tubules called lateral branches which anastomose with lateral branches of other odontoblastic processes.

The dental matrix consists of calcified collagen fibrils penetrated by the odontoblastic processes. The processes
occupy the dentinal tubules. The dentinal matrix presents differences in gradations in calcification and mineralization. The differences appear to be associated with the dentinal tubules. This circumstance has lead to the (sub)classifications of peritubular matrix and intertubular matrix.

When undermineralized ground cross sections of dentin are examined in transmitted light a ring-shaped transparent or translucent zone surrounding the dentinal tubules is identified from the remaining darker dentin matrix. This zone is actually the wall of the dentinal tubule and has been referred to as the peritubular dentin, the translucent area, calcified canalicular sheath, peritubular translucent zone and the periprocess solid area. The matrix beyond this zone is termed intertubular dentin. Peritubular dentin is more highly mineralized than intertubular dentin and is an annular, hypercalcified zone around the odontoblast process. It is composed of inorganic material in the form of apatite crystals with a small amount of organic substance. The organic portion is a very delicate organic matrix which is destroyed and lost in demineralized sections giving rise to the appearance that the odontoblastic process is surrounded by an empty space. The organic matrix contains fibrils which intermix and are in continuity with the collagenous fibers of the intertubular matrix.
The intertubular matrix of intercanalicular dentin or intertubular dentin comprises the majority of the dentinal substance. It is the main structural component of dentin and surrounds the peritubular dentin or the odontoblastic processes in areas where no peritubular dentin is present. The matrix is comprised of large numbers of fine collagen fibrils with an amorphous organic ground substance and smaller amounts of apatite crystals. The collagen fibers resemble collagen found in tendons and other types of typical collagen of the body with crossbanding of 640 Å intervals and diameters of 600-700 Å. The fibers are densely packed, form interlacing bundles running in crisscross fashion between dentinal tubules generally parallel to the surface of the dentin and at right or oblique angles to the dentinal tubules. However, the matrix immediately beneath the enamel and cementum contain fibril bundles which are generally oriented at right angles to the dentin surface. It is hypothesized that some of these fine fibrils may project into the interprismatic substance of the enamel and may provide a mechanism for anchoring the enamel to the dentin. The course of the fibrils in this region produce a distinctive microscopic appearance which has lead to it being called mantle dentin.

The apatite crystals of dentin are plate-like structures with a maximum length of 100 Å and 20-35 Å in thickness. The
apatite crystals follow the collagen fibers in approximately parallel fashion. The apatite crystals are similar to those found in bone and cementum but very different to those found in enamel. Dentin mineralization is due to crystal deposition around and between the collagen fibers. However, some evidence suggests the fibrils may actually undergo mineralization. The apatite crystals vary in size and distribution with those located closest to the pulpal tissue being smaller and less densely distributed.

Indented incremental lines which indicates growth or periods of deposition are present. These lines are called the imbrication lines or incremental lines of von Ebner, and are oriented perpendicular to the dentinal tubules. The distance between the lines represents the amount of dentin depositions occurring in 24 hours and the average distance between the lines is approximately 4 to 8 microns in the crown and decreases in the root. Disturbances in mineralization causes hypocalcified bands or contour lines to appear in dentin. These are known as the contour lines of Owen. Also present in dentin is the neonatal line. The neonatal line demarks dentin deposited prior to birth from dentin deposited subsequent to birth. The neonatal line is apparent only in the deciduous dentition and the maxillary and mandibular permanent first molars. Mineralization of dentin originates in nidus' which coalesce to form a homogeneous, incremental layer of dentin.
If the globules of mineralization fail to unite or fuse irregular boundaries of uncalcified matrix remain and are known as interglobular dentin. It is found most often in the crown portion of the tooth along the incremental lines of calcification.

Dentin is a vital tissue and responds to aging and pathological influences by the deposition of new layers of dentin and through alteration of the original dentin. This dentin is deposited on the pulpal surface of the dentin during life and is irregular in configuration.

When insult or injury occurs to dentin it undergoes a defense response. The defense response of dentin is the deposition of hard tissue to seal off the injury. The newly deposited dentin is called reparative dentin. The tubules of reparative dentin are severely twisted, reduced in number or are often absent altogether. Reparative dentin is a common response to dental procedures.

Changes in structural composition of dentin can also occur as a result of noxious stimuli. Sclerotic or translucent dentin is produced when the dentinal tubules are obliterated and the tubular content is replaced by calcified material. Calcium salts are deposited in or around degenerating odontoblastic processes obliterating the tubules.

Dentin is a living permeable tissue composed of fluid-filled microscopic tubules that penetrate the mineralized
dentin matrix from the pulp to the periphery of the tooth.\textsuperscript{14} Dentin permeability has been defined as the movement of fluids or chemicals such as microbial products through dentin.\textsuperscript{15} This movement may be in the nature of bulk fluid flow (filtration) or the diffusion of substances in the solution along a concentration gradient.\textsuperscript{16,17} Permeability is dependent upon the surface area of the exposed or cut dentin, the thickness of the remaining dentin and degree of dentin tubule occlusion.\textsuperscript{18} Superficial dentin has fewer tubules per mm\textsuperscript{2} than deeper dentin and as the pulpal tissue is approached the tubules are not only more numerous per unit area, but wider in diameter.\textsuperscript{15} The dentinal tubules are the major channels for solute diffusion across dentin. Therefore if dentin permeability is proportional to the product of the tubule number and diameter, and if both the number and diameter of tubules increase as they converge on the pulp chamber\textsuperscript{19} then dentin permeability should increase in proximity to the pulp. It has been demonstrated that dentin permeability does increase exponentially as the pulp chamber is approached\textsuperscript{20} and that deep dentin is far more permeable than superficial dentin. Permeation of materials across dentin is painless. Fluid flow across dentin is the basis for the hydrodynamic theory of dentin sensitivity espoused by Brännstrom.

The pulp possesses two major types of sensory nerves. Large, myelinated A-fibers are considered responsible for the
sharp, brief, well-localized pain of dentinal sensitivity. Unmyelinated C-fibers are responsive for the dull, prolonged, poorly localized pain of pulpitis. Hydrodynamic stimuli such as osmotic, thermal and tactile stimuli, produce rapid shifts in the fluid contents of dentinal tubules and activate fibers.\textsuperscript{21,22} Tissue destruction is necessary before C-fibers are activated.

**Adhesion**

Adhesion is the attraction exerted between body surfaces in contact or the attraction between molecules at an interface.\textsuperscript{23} Greener, Harcourt, and Lautenschlager\textsuperscript{24} define adhesion as the force which causes two substances to attach when they are brought into intimate contact with one another. Depending essentially on the forces of molecular attraction between surfaces, adhesion exists only at short distances of separation; these are of the order of no more than $1 \times 10^{-4}$ of a micron (Angstrom units).\textsuperscript{25} This implies that surfaces which are flat at an atomic level, if brought into contact, will adhere spontaneously to each other with a strong bond without the need of an intermediate adhesive layer.

There are two forms of adhesion that occur in dentistry; mechanical and chemical. During mechanical adhesion, the phases of one material lock into the phases of another material. Chemical adhesion results from, formation of a chemical molecule or bond.\textsuperscript{25} Molecular forces of different
substances held together are called adhesive, while molecular forces of the same substance held together are called cohesive. Physical forces include Van der Waals forces, dipole forces, induced dipoles and non-polar dispersion effects which result when the electrons of one molecule interact with those of another molecule. Hydrogen bonding may also be considered a physical force involved in adhesion. Chemical bonds are those resulting from the interaction of ionic, covalent and metallic molecules and are termed primary bonds. These chemical bonds are considerably stronger than those secondary bonds created by physical forces.

The material used to produce the adhesion is known as the adhesive and that to which it is applied, the adherend. The objective to lasting adhesion lies not only in molecular closeness, but also in maintaining this proximity. In order to achieve the molecular closeness required for adhesion, fluid adhesives are used. A liquid with low surface tension is more apt to flow over the entire surface of the adherend and come in contact with all the small roughness present. Such a characteristic is referred to as wetting. The better the adhesive wets the surface of the adherend, the greater the likelihood that adhesion will occur between the two.

The wetting characteristics of an adhesive are generally determined by measuring the angle formed by a drop of the adhesive placed on the surface of the adherend. This measurement is called the contact angle.
defines the contact angle (theta) as the angle between the solid surface and the tangent to the liquid surface at the contact point. The contact angle may vary from 0 to 180 degrees. Wetting is thus interpreted according to the following rules:

1) non-wetting = theta greater than 90 degrees
2) wetting = theta less than 90 degrees

If the molecules of the adhesive are not attracted to the surface of the adherend, the adhesive tends to form a ball and a very large contact angle results (non-wetting). On the contrary, if there is a strong attraction between the adhesive-adherend molecules, the adhesive readily flows over the surface and a very low contact angle is formed (wetting). The ideal adhesive would spread out in such a thin film that the contact angle would be zero.\(^{(27)}\) (Illustration 1.)

\[ \text{Illustration 1. Schematic of a drop profile for conditions of non-wetting, wetting and spreading (Greener, E. H., Harcourt, J.K., Lautenslager, E. 1972).}^{(23)} \]
It should be noted that the contact angle is an equilibrium angle defined for smooth, flat surfaces. Because tooth surfaces are rough and curved, the contact angle, when applied to dentistry is only indicative of true equilibrium.\textsuperscript{29} Air pockets may be created during the spreading of the adhesive which will prevent complete wetting of the entire surface, even when the liquid has a low contact angle. (Illustration 2.)

Illustration 2. Air pockets created in a surface irregularity. Such areas may contribute to the propagation of adhesive failure by concentration of stresses at these points (Phillips, 1973).\textsuperscript{31}

Areas of discontinuity between adhesive and solid may contribute to the rupture of the adhesive joint. The adhesive joint is subjected to thermal changes and mechanical stresses. Such conditions produce stress concentrations around these voids. These stress concentrations can be much higher than
the mean applied stress and will initiate a fracture in the adhesive bond adjacent to the void. The crack may propagate from one air pocket to the next and the total joint may fracture as if it had a built-in zipper.\cite{31}

The thickness of the adhesive layer is another important factor in obtaining and maintaining adhesion.\cite{8,32-34} It is generally recognized that thick adhesive layers produce weaker joints than thin ones. The reason for this has been the subject of much discussion:\cite{32,34,36}

1. more voids and cracks are likely to occur in thicker layers, 2. thicker layers become deformed more easily and 3. a thin layer will produce less shrinkage during polymerization. The curing process for most dental polymers sets up sheer forces which can fracture the molecular and mechanical bonds at the adhesive surface.\cite{25}

When one attempts to apply the various principles of adhesion to dental structure, it is obvious that the problems are indeed complex.\cite{7,35,37} The tooth composition is inhomogeneous. Both organic and inorganic components are present in different amounts in dentin as opposed to in enamel. A restoration that would adhere to the organic portion would not likely adhere to the inorganic components and an adhesive bond to enamel would probably not similarly adhere to dentin.\cite{31}
Possibly, the problem of greatest significance is adhesion in an aqueous environment. The inorganic phase of tooth structure has a strong affinity for water. Beebe\textsuperscript{38} reported that a patient’s tooth cannot be thoroughly dried at room temperature. In order to completely remove moisture, the enamel and dentin would have to be heated to a temperature unrealistic for the oral cavity. Zisman,\textsuperscript{39} through the use of butanol as a vehicle for the displacement of moisture, was able to remove all but a mono-layer. Phillips\textsuperscript{31} states that, "the presence of at least a mono-layer of water on the surface of the prepared cavity must be accepted." This moisture layer reduces the surface energy and thus deters the wetting of the adhesive material. As long as the tooth is dry, resins adhere firmly; however, in order to function in vivo, the adhesive must be modified so that it can withstand an aqueous environment continually subjected to thermal, chemical and mechanical stresses.\textsuperscript{34}

\textbf{Dental Adhesives And Composite Resins}

Williams\textsuperscript{25} suggested that the ideal dental adhesive (composite) should: 1) provide a lasting bond with both enamel and dentin; 2) polymerize rapidly at or near body temperature; 3) have little or no volume shrinkage; 4) be sufficiently cross-linked to minimize expansion or water sorption; 5) have
sufficient strength to resist mastication forces; 6) have the same coefficient of thermal expansion as tooth structure; 7) be non-injurious to the pulp and oral tissues; 8) bond in a humid environment; 9) have a modulus of elasticity less than that of the surfaces joined; 10) be low in initial viscosity and 11) have good wettability. In addition to these considerations, the adhesive should either displace moisture or make use of it. Fluid exchange continually takes place through the tooth structure, and it is not possible to completely desiccate the enamel surface. At our current level of technology, an ideal adhesive material has yet to be developed.

Various adhesives, however, have been developed over the years which attempt to fulfill many of Williams' criteria. Of the adhesives currently in use today, the most important group advocated for posterior restorative purposes are based on polymer research undertaken by Bowen. In 1955-1956, Bowen published the initial reports detailing his attempts to develop filled epoxy resins as adhesive restoration materials. Further progress led to his 1963 description of the resin that formed the basis of the first commercial composite - Addent 35 (1965). 'Bowen's Resin" is the addition reaction product of Bis(4-hydroxyphenyl) dimethyl-methane and glycidylmethacrylate, also called BIS-GMA.
Restorative resin technology, as described by Phillips,\textsuperscript{41} has gone through the following stages:

First was the introduction of the autopolymerizing, unfilled acrylic resins. The composite system was then introduced in order to enhance certain properties and overcome some of the problems that had become evident in the clinical performance of unfilled resins. The composite resins themselves underwent many changes in formulation (for example, composition and geometry of the filler), while the advent of acid etching techniques added still another dimension by markedly improving the mechanical bonding of these nonadhesive systems to enamel. In an attempt to further enhance adhesion, enamel bonding agents were then introduced. Lastly, the development of the composite system was designed to provide a smoother finished surface to the restoration.

The composite resin system was a natural outgrowth from the era of unfilled acrylic resin materials. Low hardness and strength, inferior resistance to abrasion and high coefficient of thermal expansion of acrylic resins imposed obvious limitations to their clinical usefulness, especially as a posterior restorative.\textsuperscript{42}

Composite resin filling materials are room temperature-polymerizing resins that contain about 75-80 percent by weight (50 percent by volume) of viterous filler. Various types of fillers are employed. Glass beads and rods were used with the first system, whereas quartz, strontium and borosilicate glass are found in many of the current products. The composition, particle size and geometry influence the properties of the final structure. Filler particles are coated with a coupling agent such as vinyl silane to promote adhesion between filler
and resin in order to prevent water penetration at their interface or dislodgement of the filler during function. Inclusion of a high percentage of inert filler reduces the coefficient of polymerization shrinkage and water sorption to levels less than those found in pure resin systems.

While claims for adhesion are sometimes made or implied by manufacturers, none of the restorative commercial composites are actual adhesives in the classic sense of the term. All rely upon mechanical bonding of the resin to tooth structure.

Composite Resins For Posterior Teeth

In recent years, there has been increasing concern about exposure of dental health personnel to the mercury in dental amalgam alloy restorations. Concerns have also been expressed about the future cost and availability of the metals in dental amalgam. This has led to efforts to improve the characteristics of composite resin materials and evaluate their clinical performance in vivo.

The results of a one-year study comparing the clinical performance of a composite and an amalgam seemed to verify claims that composite resins can serve as a substitute for amalgam. In the study, no substantial difference in the rate of wear could be detected between the composite resin
restorations and the amalgam controls; however, as the investigation continued, substantial changes were shown to have occurred during the second twelve months of service.\textsuperscript{50} These findings prompted many investigators to discourage the use of composites in areas of high stress concentrations.\textsuperscript{51-55}

When subjected to occlusal loading, the wear patterns of composite resins and silver amalgam are appreciably different. Amalgam restorations undergo a degradation at the tooth-restoration interface. This type of defect, referred to as marginal or ditching, is the result of electrochemical corrosion in conjunction with mechanical stressing.\textsuperscript{45} The composite resin restoration does not undergo marginal failure or ditching, regardless of the extent of wear. Instead, the entire surface of the restoration undergoes a generalized loss of material.\textsuperscript{52} Lienfelder\textsuperscript{45} suggests that the wear pattern is analogous to the reduction of the surface level of a liquid in a container after the walls of the vessel have been perforated. Corrosion is the process by which amalgam restorations primarily deteriorate, whereas resins primarily deteriorate from mechanical wear.

Another problem associated with the use of conventional composite resin in posterior teeth is the possible loss of material in the interproximal contact area, with subsequent mesial migration of teeth distal to those undergoing loss of interproximal contact.\textsuperscript{45} When subjected to normal masticatory
loading, one tooth may move more to the facial or lingual
direction than one immediately adjacent to it and a slow but
gradual loss of material may result. Leinfelder stated that
conventional composite resins should not be recommended for
the restoration of Class II cavity preparations in permanent
teeth.

Little has been reported on the performance of composite
resins in primary molars. Nelson compared two composites
with an amalgam in 50 pairs of Class II preparations in
primary teeth. Dental composite preparations were etched for
60 seconds with 38% phosphoric acid and a low viscosity
bonding agent was applied. Results were reported after three
years; no significant differences were observed in color
matching, cavosurface staining, or marginal adaptation.
Anatomic form was similar for two years, but the three-year
evaluation showed amalgam to be slightly superior in anatomic
form. He concluded that composite resins were a suitable
restorative material for primary molars when the tooth can be
expected to be functional for three years or less. In 1981,
Tonn, et al. performed a similar clinical trial in primary
teeth utilizing a different brand of resin and alloy. After
two years of clinical performance there was no significant
difference in marginal integrity, but anatomic form was
superior in amalgam restorations.
Enamel Treatment And Acid Conditioning

Since the presence of surface debris was the major factor preventing wetting by adhesives, a pre-bonding treatment of the enamel was recommended. Investigators suggested that a surface treatment would not only remove most of the debris, but would also alter the surface tension of the tooth. Early attempts of pre-bonding treatments involved protocols such as scrubbing with detergent; washing with hydrogen peroxide; and etching with dilute hydrochloric acid, EDTA or phosphoric acid. Of the methods investigated, etching proved to be the most efficient surface cleanser and the best method to increase adhesion. In 1955, Buonocore was the first to use 85 percent phosphoric acid to etch or "condition" enamel prior to the use of acrylic restorative materials to improve marginal adaptation. Following Buonocore's initial investigation, other researchers have attempted to more precisely determine how acid conditions the enamel for resin bonding.

Gwinnett and Matsui suggested that mechanical retention played a role in the bonding of adhesives to enamel. Slight etching created a tremendous increase in the surface area and opened up pores and spaces in enamel into which the adhesive could flow and ultimately polymerize. Assuming the adhesive material had good "wetting" properties and good strength, the strength of the bond should be enhanced with increased
penetration into the enamel. The extent of penetration was dependent on the number of spaces available in the enamel and the depth of the tag was dependent on the speed of polymerization of the material. This study also reported that newly erupted teeth etched more readily than those that had been in the mouth one or two years.

In 1968, Newman, et al.\(^64\) found that a 40 percent phosphoric acid etch lowered the contact angles quite drastically. They suggested that acid treatment raised the critical surface tension of wetting to a point where it closely matched the surface tension of the adhesive.

Poole and Johnson\(^65\) studied the effects of formic, lactic and hydrochloric acids as well as EDTA (ethylene diaminotetraacetic acid) under the scanning electron microscope. They attempted to determine the influence of prism direction and crystallite orientation on the pattern of etching and reported that all of the acids preferentially dissolved the axial portions of the prism heads so that the etched surfaces transverse to the prism heads had a honeycomb appearance. Etched surfaces parallel with the prism direction showed troughs and ridges. In contrast, EDTA preferentially dissolved peripheral regions of prisms, leaving axial portions relatively unaffected.

Lee, et al.\(^37\) investigated the effect of citric and phosphoric acids as etchants on teeth that had been exposed to
natural fluoridated water. Fifty percent acid solutions were used. Scanning electron micrographs revealed that primary teeth from an area of high natural fluoride are highly resistant to acid etching with citric acid and almost equally resistant to etching with phosphoric acid, although the later was more effective. Their work suggested that in areas of high fluoridation, phosphoric acid might be preferable to citric acid as an etchant. Silverstone showed that an unbuffered solution of 30 percent (w/w) phosphoric acid produced the most consistent and evenly distributed etch over a single enamel surface and an increase in the resultant tensile bond strength of more than 50 percent.66

Gwinnett67 investigated the effect that the prismless layer of enamel, common in primary teeth, had on the incidence of sealant retention. This was also reported by Buonocore68 and Robb, et al. 69 No resin tags were observed in scanning electron microscope photomicrographs where prismless enamel existed, but were present where such enamel had been removed. The length of the resin projections in association with the prismless enamel were significantly shorter than those related to prismatic enamel. Bozalis, et al.70 reported that it was necessary to etch the primary tooth enamel surface for 120 seconds in order to produce etching patterns comparable to that observed in permanent enamel.

Primary enamel has a lower mineral content than permanent
enamel - 86 percent by volume versus 92 percent by volume of mineral salts. In addition, a significant increase in the internal pore volume has been found for primary enamel when compared with permanent enamel. As a result of its lower mineral content and higher internal pore volume, erupted primary tooth enamel is likely to contain larger amounts of exogenous organic material than surface enamel from permanent teeth. This factor may be a major consideration in the etching characteristics of primary tooth enamel and could in part explain the necessity for longer etching times.

Marshall, et al. found a high degree of variability in etching patterns from tooth to tooth, and in different parts of the same tooth when using the same clinical etching procedures. Silverstone also confirmed that sound, distinct etching patterns occur and classified them into three basic types. In Type 1, the most commonly produced, there appeared to be preferential removal of prism centers. When the reverse pattern is observed in which prism peripheries were removed leaving the cores intact, it was classified as Type 2 etching. The least common etching pattern, Type 3, produced an etched surface that bore no resemblance to prism morphology. These findings differ from studies by Michols, et al. and Poole, et al. in which acid, irrespective of direction of attack,
removed rod centers and EDTA removed rod peripheries, but agreed with results of Marshall, et al.\textsuperscript{73} and Bozalis, et al.\textsuperscript{70}

**Acid-Etch Bonding Mechanism**

Acid-etching by phosphoric acid solutions in the range of 35-50 percent involves dissolution of the outermost enamel and the production of a rough porous surface. Penetration of a polymerizable monomer composition into the etched surface results in a mainly mechanical bond after setting to a solid resin. The acid-etch technique has been used extensively for permanently bonding resins to the enamel surface in preventative and restorative dentistry, and for temporary attachment of orthodontic brackets. Emphasis has been given recently to debonding procedures and to the effects these procedures have on the enamel surface after bracket and adhesive removal.\textsuperscript{76-79} To date, most of the attention in this area has been focused upon the morphologic description of the remaining enamel surface after various removal and polishing procedures using the scanning electron microscope.\textsuperscript{80}

One disadvantage of the acid-etch procedure is the loss of surface enamel which contains most of the enamel fluoride.\textsuperscript{75} Only a few investigators have quantified the depth of enamel loss associated with debonding. Some, using indirect measuring techniques based on measurements from fixed steel
reference markers, quote enamel loss in the 50-60 micron range. Others, however, suggest the total loss is less than 5 micron. To substantiate their claim, the presence of perikymata ridges over a large part of the enamel surface after complete bonding/debonding procedure is offered as evidence. These reports suggest a difference of opinion regarding the amount of enamel lost and raised questions about the validity of the various measuring techniques used.

It is known, however, that each step in bonding, cleaning, acid-etch, and removal of attachments and residual resin contributes to the loss of enamel structure. Debonding with subsequent cleanup procedures at the end of treatment may be rather time consuming. Care must be taken not to induce iatrogenic effects, including cracks, scratches and removal of pieces of enamel. All adhesive remnants should be removed at the time of debonding, as abrasive wear of most orthodontic adhesives apparently is minimal.

The benefits of developing a system to create a strong, impermeable bond between dental restoratives and tooth structure are obvious to the dental profession. However, the weak link in the system is in the ability to bond to dentin. The goal of any dental restorative procedure is to obtain as close an adaptation as possible between the restorative material and the remaining tooth structure in order to restore the odontogenic defect and return the tooth to its pretreatment
strength and function. It is toward this end that dentin bonding is intended. Effective dentin bonding would also allow for more conservative treatment of odontogenic lesions and defects.

In the early 1980's, the first generation of dentin bonding agents were developed and widely used. The mechanism of dentin bonding was, and is to the present, a combination of physical adhesion through dentin resin tags and a possible chemical bonding with collagen and hydroxyapatite. A weak physical bond is formed when the dentin adhesive penetrates the dentin tubules and polymerizes to form dentin tags. Chemical bonding occurs at the amide, hydroxy, carboxylic, or amino side groups of the long collagen chains and at the calcium or hydroxy sites of the hydroxyapatite molecule. However, dentin bonding requires intimate and thorough contact with dentin.

Charbengau et al. demonstrated that when surfaces are cut or abraded, a layer of the resultant debris is deposited on the surface. This amorphous layer of cutting debris was also described by Provenza and Sardana in 1965. In 1970, Eick et al. used the scanning electron microscope to examine the cut tooth surface and identity the debris present. In the study he made mention that the cut surface "seemed to have a smeared layer". Others have identified the existence of this layer of debris and the term "smeared layer" has
become widely accepted to describe this entity. The smeared layer is produced by both rotary and hand instruments. It is believed to result from high heat concentrations and plastic deformation of the tooth structure during cutting procedures. The smeared layer is an amorphous mass consisting of organic and inorganic material that includes tooth particles from 0.5 mm to 15mm, saliva, blood, microorganisms and large amounts of organic compounds containing nitrogen, sulfur and carbon.

The smeared layer may jeopardize adhesive bonding and minimize close adaptation of restorative materials to tooth structure. It has also been demonstrated\textsuperscript{92} that microorganisms can survive in the smeared layer between a restoration and a tooth. Therefore, it is desirable to remove the smeared layer to improve adhesion and eliminate the potential for bacterial growth. However, the smeared layer is resistant to mechanical removal but can be removed by chemical means. It is desirable to remove the smeared layer but to leave that portion lodged in the dentinal tubules as plugs, the peritubular dentin or otherwise open and widen the cut ends of the dentinal tubules. Ideally one would want to remove the smeared layer, leave the dentin tubule plugs intact, kill or remove any microorganisms but leave the dentin intact and in health.

With this goal in mind many chemical solutions have been investigated in an effort to evaluate their effect on the morphology of prepared dentin and the solubility of the
Bowen investigated eleven acid buffer solutions and distilled H₂O. He concluded that the smeared layer on dentin can be substantially removed by a 30 second exposure to a 0.16 molar solution of ascorbic acid or buffered solutions of some acids. In some cases there was minimal opening of dentinal tubules. Duke et al. demonstrated that a commercially available polyacrylic acid (Durelon liquid) was effective in removing the smeared layer but also opened the cut dentinal tubules. They also found flour of pumice, prophylaxis paste, 3% hydrogen peroxide and a commercially available cavity cleaner (Cavilax) to have minimal effect on the smeared layer. Hinoura et al. had similar findings with hydrogen peroxide, pumice and polyacrylic acid. They also found that treatment with 50% citric acid removed the smeared layer but opened the dentinal tubules to a great degree. Ebb, Von Der Lehr and Herrin investigated the use of abrasive particles (pumice and Prekleene), 0.5% sodium hypochlorite, 3% hydrogen peroxide, Oral 5 solution and 40% polyacrylic acid for smeared layer removal. They found a very minimal application of 40% polyacrylic acid to be the only effective solution of the group. However, the method of application is impractical. Brännstrom and Johnson investigated the effects of 3% hydrogen peroxide, 30% hydrogen peroxide, ether-acetone solution, 50% citric acid, 50% phosphoric acid, 20% lactic acid and two commercially available cavity cleaners as dentin
cleaning agents. They found the peroxide solutions, ether-acetate solutions and the cavity cleaners to be ineffective. However, the acid solutions produced a clean dentinal surface but also opened and widened the apertures of dentinal tubules.

McInnes-Ledoux et al.\textsuperscript{98} found 0.1\% citric acid in 30\% ethanol to be ineffective in cleansing the smeared layer while a 1\% aqueous citric acid solution and 1\% citric acid in 30\% ethanol solution proved to remove the smeared layer, dentinal plugs and opened and enlarged the dentinal tubules creating a bell shaped aperture. Pashley et al.\textsuperscript{99} demonstrated almost total removal of the smeared layer from dentin etched with 6\% citric acid for 60 seconds. However this and shorter treatment time produced greatly enlarge tubule openings and increased the permeability of the dentin. Brännstrom, Nordenvall and Glantz\textsuperscript{100,101} found solutions of EDTA and a surface-active cavity cleanser to have the ability to remove most of the smeared layer without excessive removal of dentinal tubule plugs or removing peritubular dentin.

Recently, researchers have investigated the addition of hydroxyethylmethacrylate (HEMA) to augment the removal of dentin smeared layer. HEMA forms covalent bonds with amino and hydroxyl side groups of collagen and is hydrophilic. These properties allow HEMA to wet dentin very thoroughly and the methacrylate portion to react well with the resin portion composites. HEMA has been added to prospective smeared layer
removers in an effort to increase the bond strength of dentin bonding resins. The 3M company has introduced a dentin bonding agent based on this principle which consists of a primer and a dentin adhesive. The primer is a solution of HEMA and an organic acid (maleic acid). It has been demonstrated that this solution removes some of the smeared layer but does not open the dentinal tubules.
CHAPTER III

STATEMENT OF THE PROBLEM

The purpose of this investigation is to study the influence of acidic solutions upon the morphology of prepared dentin surfaces. Specifically it is desired to observe the ability of the solutions to modify or remove the smeared layer. Hydroxyethylmethacrylate (HEMA) will be present or absent in the acidic solutions to study its influence. Various solutions of organic and inorganic acids alone and grafted to HEMA will be employed. The influence of pH of acidic solutions and dentin smeared layer modification will be examined. The evaluation of the effects of the solutions upon prepared dentin will be made through examination with the scanning electron microscope.
CHAPTER IV
MATERIALS AND METHODS

Selection And Preparation

Extracted, erupted and unerupted, noncarious human third molars were used to obtain samples of dentin. The teeth and subsequent samples were stored in isotonic saline with 0.2% sodium azide as a preservative. The teeth were mounted and sectioned across their long axis with a low speed diamond saw (Isomet, Buehler Ltd. Lake Bluff, IL) with irrigation into slices 1-2mm thick. Only those sections composed of dentin and a periphery of enamel were used. A fresh smeared layer was produced with 320-grit silicon carbide sandpaper. Each dentin slice or section was mounted on an aluminum stubb for scanning electron microscopy with either silver metallic paint or a contact adhesive. Each sample was treated with a different test solution with the exclusion of one sample to establish a base line appearance of the dentin smeared layer. Only sufficient amounts of each solution to wet the surface of each sample was used. The solution was brushed on the surface of the dentin for 30 seconds and allowed to air dry unless a commercial product was employed in which case the manufacturer’s instructions were followed. The treated
samples were then allowed to dry in ambient air for two to three days. After air drying the samples were then placed in a desiccator of calcium chloride for two to three days and finally placed in a desiccator of $P_2O_5$ for two to three days for complete drying.

The solutions which were used in this investigation were as follows:

- 37% phosphoric acid
- Scotchbond dentin primer
- Mirage bond dentin conditioner
- 10% maleic acid
- 10% sulfobenzoic acid
- 30% sulfobenzoic acid + 50% Vinol
- 30% sulfobenzoic acid + glycerol
- 10% glutaric acid with HEMA grafted (reaction product) + 50% free HEMA
- 30% sulfobenzoic acid with HEMA grafted (reaction product) + 20% free HEMA + 50% VINOL
- 30% sulfobenzoic acid with HEMA grafted (reaction product) + 30% free HEMA + 40% Vinol
- 30% sulfobenzoic acid with HEMA grafted (reaction product)
- 30% sulfobenzoic acid with HEMA grafted (reaction product) + 24% glycerol 6% silicon dioxide
30% sulfobenzoic acid with HEMA grafted (reaction product) + Vinol
10% citraconic acid with HEMA grafted (reaction product)
7% succinic acid with HEMA grafted (reaction product) +
   5% sulfobenzoic acid with HEMA grafted (reaction product)
7% succinic acid with HEMA grafted (reaction product) +
   3% sulfobenzoic acid with HEMA grafted (reaction product)
7% maleic acid with hydroxypropylmethacrylate
   (reaction product) +3% sulfobenzoic acid with HEMA
   grafted (reaction product)
2.5% maleic acid, + 50% free HEMA
10% maleic acid with HEMA grafted (reaction product) +
   50% free HEMA

Subsequent to desiccation each sample was sputter-coated for 30 seconds to produce a thin covering of gold of approximately 200 Å thick. The thin layer of gold is required to prevent charge build-up. Charge build-up will deflect the incident electron beam and destroy or distort the transmitted image.

All solutions were proprietary agents obtained from Bisco Inc., Itasca, Illinois.
Scanning Electron Microscopy Analysis

The scanning electron microscope used in this study was an SX-30E manufactured by International Scientific Instruments, Inc., Milpitas, California. The scanning electron microscope functions by collecting and displaying secondary emitted and back scattered electrons from the surface of a specimen. For this investigation the operation mode of the scanning electron microscope was 15 kilovolts acceleration voltage with a working distance of approximately 10mm. Magnification ranged from x 500 to x 10,000. Excellent reproduction and detail were obtained from this instrument.

Photographing the image (or the photomicrograph) was accomplished by a Polaroid Land Camera, 50 series using type 55 ASA 50 film with an aperture of f8.
CHAPTER V
RESULTS

Subsequent to preparation, treatment, and mounting the specimens were individually placed on the stage of the scanning electron microscope and viewed on the rapid scanning monitor screen of cathode ray tube (CRT). The structures were viewed at magnifications of X1000 to X3000 however for most specimens the interests of this investigation were best served by a magnification of X2000. Reproductions of the magnified samples were made with the polaroid land camera producing black and white prints or photomicrographs. Samples were evaluated as to the appearance of the dentin in the photomicrographs. Evaluations were made as to the 1) Presence or absence of the smeared layer, 2) If present the appearance of the smeared layer in comparison to an unmodified smeared layer, 3) Presence or absence of dentinal plugs, 4) The degree of widening of dentinal tubuli orifices if the plugs are absent.

Thorough understanding of the dental structures which were examined required initial observation of etched enamel and cut dentin. Figure 1, 2 and 3 represent three basic appearances of enamel which has been etched with 37%
phosphoric acid as described by Gwinnett. Figure 1 is a scanning electron micrograph showing the preferential loss of calcified material from the core of the enamel rods while Figure 2 is a micrograph showing the preferential loss of calcified material from the periphery of the enamel rods. Figure 3 represents a lack of a significant pattern to the etched surface resulting in an amorphous appearance to the surface. However, all the etched surfaces display a high degree of irregularity which provides for the micromechanical locking or adhesion of composite resins.

Figure 4 is a photomicrograph of the smeared layer of cut dentin and is similar to that described by Charbengau and Provenza and Sardana and quantified by Eick. The smeared layer in this figure is similar to that produced by dental rotary instruments. The smeared layer is present on dentin which has been manipulated by dental rotary or hand instruments. However, to some degree a smeared layer may be present on dentin which is exposed to the oral cavity and mechanically manipulated by tooth brushing or other similar activities.

This investigation began with treatment of dentin samples with acidic solutions without the addition of hydroxyethylmetacrylate. Because of its impact upon the dental profession the first solution evaluated was the original Scotchbond dentin primer by the 3M corporation.
Figure 5 is a photograph of a dentin sample treated with Scotchbond primer for 60 seconds. The sample was then dried without washing the solution from the surface as directed by the manufacturer. Scotchbond dentin primer was an acidic solution with an approximate pH of 2.0 which consisted of a resin component containing chlorophosphorous esters of BIS-GMA, TEGMA, and benzoil peroxide in an alcoholic solution of a tertiary amine and sodium benzene sulfonate. The smeared layer appears to have been dissolved and redeposited on the surface of the dentin. A minority of the dentinal tubules appear to have intact smeared plugs. The dentinal morphology is present intact, however significant modification has occurred.

Figure 6 is a photograph of the dentin appearance after being treated with a 10% maleic acid solution for 60 seconds and allowed to dry without washing. The smeared layer appears to be removed and the dentinal plugs eliminated to a large extent. The dentinal tubule apertures do not appear widened to any significant degree and remnants of organic tissue appeared to be present in the tubules.

Figure 7 is a photomicrograph of a dentin sample treated with a 10% maleic acid solution with the addition of .04 micron silicodioxide particles as a thickening agent. Where the dentin substrate is visible the smeared layer appears to be removed. The dentinal plugs are also eliminated
and the tubule apertures do not appear widened. However a
fine granular debris to be present on the dentin surface.

Figure 8 is a photomicrograph of a sample treated with a
10% solution of sulfobenzoic acid with the .04 micron
silicon dioxide thickening agent present. The sample was
treated for 60 seconds and allowed to dry without washing.
The dentin surface appears irregular with a deposit present.
The dentin tubule apertures do not appear widened however
there is an absence of dentinal plugs. The smeared layer
appears to have been removed or significantly modified with a
granular texture on the dentin surface.

Figure 9, 10, and 11 are photomicrographs of dentin
samples treated with a 37% phosphoric acid gel solution with
a .04 micron silicon dioxide thickening agent. These samples
were treated for 10, 20 and 30 seconds respectively. rinsed
and dried. Each figure presents some interesting
characteristics. All these samples display the same granular
texture of the dentin surface present in the other samples
treated with solutions using silicon dioxide as a gelling
agent. The sample treated for 10 seconds [Figure 9] displays
smeared layer removal with dentinal plug elimination. The
tubule openings do not appear widened. There is a small
portion of smeared dentin in the center portion of the
photomicrograph. It is conjectured that this area of smeared
dentin is present due to incomplete contact and wetting of the
smeared layer by the gel etchant in the 10 seconds of exposure.

The sample treated for 20 seconds [Figure 10] displayed dentinal tubules with the same smear plugs removed and the apertures of many tubules widened beyond their limits. The sample treated for 30 seconds [Figure 11] displays dentinal tubules with the smear plugs removed and significant widening of the dentinal tubule openings. Degradation or destruction of the peritubular dentin is evident.

These three figures display the progressive demineralization of dentin by phosphoric acid. Demineralization of dentin and enamel is concentration and time dependent. Increased acid concentration and time of exposure will produce increased demineralization. Decreased acid concentration and duration of exposure produces reduced demineralization. A striking affect of increased acid concentration and/or duration of exposure on the treatment of dentin is the removal of peritubular dentin with resultant widening of the dentin tubule orifices.

Figure 12 is a photomicrograph of a dentin sample treated with the commercial product Mirage Bond. The dentin conditioner of this system is a 2% solution of nitric acid with the addition of N-phenyl glycine. This conditioner was applied for 30 seconds to the dentin sample and then dried.
The smeared layer appears to be minimally affected. The striations characteristically present in the smeared layer were present in this sample. The craze lines in the areas of the dentin tubules are probably artifacts of drying and desiccation for the scanning electron microscope.

Investigations then moved to samples treated with acidic solutions which included the addition of hydroxyethyl methacrylate. A difference in the character of the smeared layer of cleansed dentin was hoped to be visualized.

The first sample was treated with the reaction product of glutaric anhydride and HEMA as a 10% aqueous solution. Additional free HEMA was added to a 50% concentration and the pH of the solutions was adjusted to 1.5 with the addition of 10% nitric acid solution. The dentin was treated for 30 seconds and then dried. As is evident by Figure 13 the smeared layer appears to be unaffected. There appears to be no difference in the appearance of the smeared layer when compared to samples which were not treated. In this sample it appears the dentin was protected from the acidity of the solution.

Figure 14 and 15 represent samples treated with the reaction product of sulfobenzoic acid and HEMA. The solution in these samples was a 30% reaction product with the addition of free HEMA and Vinol as a thickening agent. The sample in Figure 14 had a free HEMA concentration of 20% and a Vinol
concentration of 50% with a pH of 1.1. The sample was treated for 20 seconds, rinsed and allowed to dry. The smeared layer was thoroughly removed, the dentinal tubule plugs eliminated and the tubule orifices opened. The smeared layer removal was quite aggressive.

The sample in Figure 15 had a free HEMA concentration of 30% and a Vinol concentration of 40% with a pH of 8. The sample was treated for 20 seconds and allowed to dry. This sample also displayed aggressive smeared layer removal. It appeared that there was more peritubular dentin loss causing increased widening of the dentinal tubules.

Figure 16 is a photomicrograph of a dentin sample treated with a 30% aqueous solution of sulfobenzoic acid with 50% Vinol present as a thickening agent. There was no HEMA present in this solution. The smeared layer was aggressively removed and the dentinal tubule plugs removed. There also appeared to be increased demineralization of the peritubular dentin with increased widening of the dentinal tubules. This sample did appear to reveal slightly more aggressive dentin demineralization than the sample treated with a HEMA containing solution.

Figure 17 is a photomicrograph of a sample treated with a 30% sulfobenzoic acid and HEMA solution (reaction product) with 40% water and 30% glycerol added as a thickening agent. In this sample the smeared layer was partially removed and the
dentinal tubule plugs were partially removed. There was much less aggressive demineralization of the dentin substrate. Grafting HEMA to sulfobenzoic acid reduces its activity and modification of the smeared layer.

The photomicrograph in Figure 18 is of a dentin sample treated with a 30% sulfobenzoic acid and HEMA (reaction product) solution with 40% water, 24% glycerol and the addition of 6% silicodioxide as a thickening agent. The smeared layer and dentin tubule plugs were removed. Once again a fine granular texture was present on the dentin surface.

The reaction product of succinic acid and HEMA and the reaction product of sulfobenzoic acid and HEMA were also combined to produce test solutions. Figure 19 is a photomicrograph a sample treated with an aqueous solution containing 7% of the first reaction product and 5% of the latter reaction product. The resultant solution had a pH of 1.8. The sample was treated for 20 seconds and dried. The smeared layer was affected minimally. The dentinal tubule plugs remained intact and minimally disturbed. An additional dentin sample was then treated with the same contributing acidic solutions with a reduction of the SBA-HEMA content to 3%. The solution pH then increase to 2.0. The sample was treated for 20 seconds and then dried. In this sample [Figure 20] the smeared layer appeared intact.
Figure 21 represents a dentin sample treated with a solution of the reaction product of citraconic anhydride and HEMA. A 10% aqueous solution was produced with a pH of 2.3. The sample was treated for 20 seconds and allowed to dry. The smeared layer appeared intact and the dentinal tubule plugs intact and undisturbed. However, the smeared layer appeared to possess a very smooth texture in comparison to the usual appearance of the smeared layer.

An acidic solution was made with the reaction products of maleic acid and hydroxypropylmethacrylate and the previously used SBA-HEMA solution. This was mixed in a final concentration of 7% and 3% respectively with a resultant pH of 1.1. The dentin sample was again treated for 20 seconds and allowed to dry. Figure 22 reveals a relatively intact smeared layer. Approximately half of the dentinal tubules appear opened to some degree. However, the smeared layer is minimally affected.

Figure 23 is a photomicrograph of a dentin sample treated with a solution of 2.5% maleic acid, 50% HEMA, and 47.5% water with a pH of 1.5. The smeared layer was aggressively affected. The dentin tubule smeared plugs were removed in a significant number of tubules. However, the peritubular dentin appeared intact and unaffected.

Figure 24 is a photomicrograph of a dentin sample treated with a solution made of the reaction product of maleic
anhydride and HEMA at 10%, 50% HEMA and 48% water. The solution pH increased over time to 1.5. The dentin sample was treated for 20 seconds and dried. The smeared layer appeared to be moderately affected and the tubule smeared plugs relatively intact. The peritubular dentin appeared to be unaffected.
CHAPTER VI
DISCUSSION

Treatment of dentin with acidic solutions appears to be an extremely effective procedure for modification and/or removal of the dentin smeared layer. Most of the solutions investigated, whether organic or inorganic acids, affected the smeared layer. It appears that the real question should be to what degree did particular acidic solutions or families of acidic solutions affect cut dentin. A second question to guide further investigation would be what degree of dentin modification is desirable.

A pH of 2-2.5 appears to be a threshold above which minimal affect is produced on the dentin smeared layer. A pH of 1-1.5 appears to be a second threshold for removal of the smeared layer and dentinal tubule smeared plugs. However, time of exposure to the agents plays a significant role. As should be expected as exposure time increases the pH can be increased. Conversely as the time of exposure decreases the pH must be decreased. Accordingly concentration of acid solutions can be varied with time of exposure i.e., the shorter the time of exposure the higher the acid concentration should be. These variables lend quite a large degree of
freedom to titrate the affect on and degree of modification of the dentin smeared layer accomplished.

Content of the solution can have an affect on the dentin surface. In samples treated with solutions containing submicron silica as a thickening agent a granular appearance was revealed in the photomicrographs. This fine granular appearance was not present in samples treated with solutions where Vinol, a polyvinol alcohol, was employed as a thickening agent. The fine granular appearance is due to the submicron silica -SiO₂- loosely attached to the dentin surface and remaining on the surface after rinsing of the sample or allowing the sample to dry. To what degree the submicron silica is attached to the sample is an important question. Can it be removed with copious amounts of rinsing? Is it physically or ionically bound to the dentin? Does the presence of the silica particles impede or impair adhesion? If removal or elimination of the particles from the surface is extremely difficult or impossible the clinical implications may or not be significant. Many commercial gel etching agents available today employ submicron silica as a thickening agent. Findings from further research in this area may have important consequences.

The addition of HEMA to acidic solutions appears to have some affect on dentin at the microscopic level. Furthermore, some affect is noticed whether the HEMA is bound or free in
the solution. Figure 6 is a photomicrograph of a sample treated with maleic acid without bound or free HEMA present. The smeared layer appears to be removed, the smeared plugs eliminated and the peritubular dentin relatively intact. Figure 24 is a photomicrograph of a sample treated with a solution of maleic acid bound to HEMA and free HEMA. The smeared layer appeared to be moderately affected and the tubule smeared plugs relatively intact. The peritubular dentin did not appear to be affected. The addition of HEMA to the maleic acid solution appears to have an attenuating affect on smeared layer removal. There does not appear to be the same aggressiveness of the maleic acid in each of these solutions.

Figure 17 is a photomicrograph of a sample treated with sulfobenzoic acid bound to HEMA. The smeared layer was partially removed and the dentinal tubule plugs were partially removed. There was not aggressive demineralization of the dentin surface. Figure 14 and 15 are photomicrographs of dentin samples treated with sulfobenzoic acid bound to HEMA with free HEMA present. There was very aggressive smeared layer removal and smeared plug elimination. Figure 16 is a photomicrograph of a sample treated with sulfobenzoic acid with no HEMA present. There appears to be only slightly more aggressive action upon the dentin substrate. The addition of HEMA to the sulfobenzoic acid does not appear to have as great
of an affect on smeared layer removal as it does when added to maleic acid. There is a disparity in the samples treated with bound acid versus those treated with bound acid and free HEMA. One would surmise that the free HEMA increased the aggressive activity of this solution. This is a questionable result and initially was quite perplexing. However, glycerol had been used as a thickening agent in this solution instead of vinol. The addition of glycerol could quite possibly explain the diminished activity of this test solution. Figure 25 is a photomicrograph of a sample treated with sulfobenzoic acid bound to HEMA with vinol as a thickening agent. The smeared layer has been removed and the smeared plugs partially removed. The overall appearance of this treated sample is more congruent with the previously discussed samples. With these samples the bound acid was the least performer, the bound acid with free HEMA a more aggressive performer and the free acid alone was the most aggressive performer. The acidity of HEMA, a pH of 4, itself probably mediates a more aggressive removal of the smeared layer and dentin substrate.
CHAPTER VI
SUMMARY AND CONCLUSIONS

Samples of dentin were treated with a number of acidic solutions. Photomicrographs from a scanning electron microscope were taken of the samples to evaluate the affect each solution had on the cut dentin surface. Trends or patterns in dentin modifications were also noted.

Qualitative evaluations were made as to the:
1. Presence or absence of the smeared layer.
2. If present, the appearance of the smeared layer in comparison to an unmodified smeared layer.
3. Presence or absence of dentinal plugs.
4. The degree of widening of dentinal tubule orifices if the plugs are removed.

The following observations and conclusions were generated from this investigation:
1. Treatment of dentin with acidic solutions appears to be an effective procedure for modification and/or removal of the dentin smeared layer.
2. A pH of 2-2.5 appears to be a threshold above which minimal effect is produced on the smeared layer.
A pH of 1-1.5 appears to be a threshold for removal of the smeared layer and dentinal tubule smeared plugs.

3. If smeared layer modification is desired, as the time dentin is exposed to acidic solutions increases the pH of the solution may be increased. Conversely as the pH of the solution decreases the time of exposure must be decreased.

4. As the concentration of an acidic solution increases the time of exposure for dentin can decrease for smeared layer modification. Conversely as the concentration of the acid solution decreases the time of exposure must increase.

5. Rinsing treated dentin surfaces may not have as great an affect on smeared layer modification or removal as would be expected.

6. Addition of thickening agents to acidic solutions can affect their ability to modify the smeared layer and dentin surface or overall activity of acidic agents. Thickening agents can also leave residues on the dentin surface which potentially can affect following dentin interaction.

7. The addition of HEMA to acidic solutions appears to have some affect on dentin at the microscopic level. HEMA is a hydrophilic resin which theoretically penetrates the dentin surface
readily. Once the dentin substrate has HEMA present demineralization by acidic solutions is affected. HEMA competitively occupies the dentin surface reducing the ability of acidic solutions to affect dentin. Although HEMA itself has some affect on the dentin substrate it appears to mitigate the effect of acidic solutions. This investigation did not characterize that interaction.
FIGURE 1. Enamel 37% phosphoric acid pH -.25

FIGURE 2. Enamel 37% phosphoric acid pH -.25
FIGURE 3. Enamel 37% phosphoric acid pH - .25

FIGURE 4. Dentin smeared layer
FIGURE 5. Scotchbond dentin primer

FIGURE 6. 10% Maleic acid pH 1.5
FIGURE 7. 10% Maleic acid with submicron silica  pH 1.5

FIGURE 8. 10% Sulfobenzoic acid with submicron silica  pH 1.7
FIGURE 9. 37% Phosphoric acid with submicron silica pH -.25

FIGURE 10. 37% Phosphoric acid with submicron silica pH -.25
FIGURE 11. 37% Phosphoric acid with submicron silica pH - 25

FIGURE 12. Mirage Bond dentin primer
FIGURE 13. 10% Glutaric acid with HEMA grafted + HEMA pH 1.5

FIGURE 14. 30% Sulfobenzoic acid with HEMA grafted + HEMA + Vinol pH 1.1
FIGURE 15. 30% Sulfobenzoic acid with HEMA grafted + HEMA + Vinol pH .8

FIGURE 16. 30% Sulfobenzoic acid with Vinol pH .8
FIGURE 17. 30% Sulfobenozoic acid with HEMA grafted + Vinol pH 1.1

FIGURE 18. 30% Sulfobenozoic acid with HEMA grafted + glycerol + submicron silica pH 1.1
FIGURE 19. 7% Succinic acid with HEMA grafted + 5% sulfobenzoic acid with HEMA grafted  pH 1.8

FIGURE 20. 7% Succinic acid with HEMA grafted + 3% sulfobenzoic acid with HEMA grafted  pH 2.0
FIGURE 21. 10% Citraconic acid with HEMA grafted pH 2.3

FIGURE 22. 7% Maleic acid with hydroxypropylmethacrylate + 3% sulfobenzoic acid with HEMA grafted pH 1.1
FIGURE 23. 2.5% Maleic acid with 50% HEMA pH 1.5

FIGURE 24. 10% Maleic acid with HEMA grafted + HEMA pH 1.5
FIGURE 25. 30% Sulfobenzoic acid with HEMA grafted + VINOL pH 1.3
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