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ABSTRACT

Title of Thesis: Preparation and Testing of Blocked Isocyanate Dental Adhesives

George Sweitzer, Master of Science, 1985

Thesis directed by: Dr. D.S. Kristol

Three monomers were used in this study. Two were prepared from 2,4-toluene diisocyanate (TDI),2-hydroxyethyl methacrylate (HEMA), and either o-methoxyphenol, or o-chlorophenol. The third monomer was prepared from pentaerythritol, TDI, HEMA, and p-cresol.

These monomers were bonded to dentin slices, and then combined with an adhesive copolymer consisting of methyl methacrylate and poly(methyl methacrylate). This mixture was polymerized at room temperature by addition of N,N-dimethyl-p-toluidine, and benzoyl peroxide. This adhesive copolymer was applied to monomer coated slices of dentin, and to aluminum coupons already fixed in a jig. The monomer-coated dentin slices (treated with the adhesive copolymer) were then placed between two coupons secured in the upper and lower portions of the jig. The jig was then closed and a 2 Kg weight was placed on top. The sample specimens were allowed to cure for a specific length of time, then usually stored in water. After storage, the samples were pulled on a Scott CRE/500 tension tester.

Breaking strengths of up to 1889 psi were found when using o-methoxyphenol treated slices, after 96 hours wet.

Breaking strengths of up to 2175 psi were found when using o-chlorophenol treated slices, after 168 hours wet.

Breaking strengths of up to 2270 psi were found when using pentaerythritol and p-cresol treated slices, after 48 hours wet.

PREPARATION AND TESTING OF BLOCKED ISOCYANATE DENTAL ADHESIVES

by
George W. Sweitzer

Thesis submitted to the Faculty of the Graduate School of the New Jersey Institute of Technology in partial fulfillment of the requirements for the degree of Master of Science in Biomedical Engineering
1985

APPROVAL SHEET

Title of Thesis: Preparation and Testing of Blocked Isocyanate Dental Adhesives

Name of Canidate: George W. Sweitzer

Master of Science, 1985

Thesis and Abstract Approved:

---------- 5/13/85

(Dr. David Kristol) (Date)

---------- 5/13/85

(Dr. Richard Parker) (Date)

---------- 5/14/15

(Dr. Howard Perlmutter) (Date)

VITA

Name: George William Sweitzer.

Permanent Address:

Degree and date to be conferred: M.S. Biomedical Eng., 1985.

Date of Birth:

Place of Birth:

Secondary Education: Cranford High School 1977.

Collegiate institutions attended	Dates	Degree	Degree Date
Union College, Cranford, N.J	1977-79	A.A	1979
Purdue University, Lafayette, In.	1980-82	B.S	1982
N.J.I.T., Newark, N.J	1983-85	M.S	1985

Major: Biomedical Engineering

DEDICATION

This thesis is dedicated to Dr. David Kristol, and Dr. James Stackhouse Jr., whose invaluable help was greatly appreciated on many very tough occasions.

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I. INTRODUCTION

The purpose of this research is to develop novel, durable adhesive agents which can bind to dentin.

A. Dentin Bonding

An understanding of how dentin bonding occurs requires a discussion of the fundementals of wetting and adhesion.

1. Wetting and Adhesion

In general, adhesion is described as interfacial bonding that results from attraction between two or more distinctly different types of molecules. Adhesion is different from cohesion in this manner, as cohesion is bonding between the same type(s) of molecules.[1]

An adhesive may be defined as a material which when applied to substrate surfaces can join them together and resist separation. The basic requirement that needs to be met to have good adhesive performance is good interfacial contact (intimate molecular contact at the interface) between th adhesive and its adherend.[2]

When the number of interfacial contacts between the adhesive and the adherend reaches the maximum possible number, the adhesive is said to have completely wetted the adherend.

The phenomenon known as "wetting" is described as the establishment of interfacial contact between the adhesive and the adherend, or in other words, wetting is the ability of the adhesive to flow over the adherend. The extent of the wetting, or the efficiency of the adhesive, depends upon how viscous the adhesive is, the shape of the adherend surface, and most importantly the contact angle at which the adhesive meets the adherend.[1,3]

In regard to the contact angle, a few things can be mentioned. The smaller the contact angle is, the better the wetting will be, and a zero contact angle seems to ensure complete wetting, although Schonhern and Huntzburger have found that good adhesives are not necessarily those which exhibit low contact angles with the adherends.[2] The major factor that further influences the contact angle is surface contamination. The more surface contamination there is, the higher the contact angle will be. If the contact angles are high, then incomplete wetting occurs, and the performance of systems which exhibit incomplete wetting is much worse than a

system in which the wetting is complete.[2,3,4] One reason for this is that non-wetted areas introduce high stress concentrations at the edge of the interfacial microvoids. Another reason is if a multilayer contamination is not displaced by the adhesive, then it may act as a weak boundry layer and low joint strengths will result.[2]

Another factor which may affect wetting is the formation of air pockets which may be created when the adhesive is spread (see Fig. 1).[4] The creation of these air pockets will prevent complete wetting of the surface even if the contact angle is low. This in turn will produce high stress concentrations around the interfacial microvoids, and the stress may become so great a break may occur in the adhesive bond adjacent to the joint.[2]

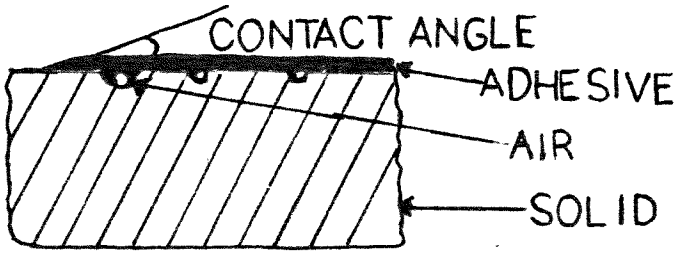


Figure 1: Formation of Air Pockets in Adhesive Surface.

Water present in the oral environment may also have an effect on adhesion, because water can compete for bonding sites with the adhesive, as water is strongly attracted to

most substances due to its polarity, and its tendancy to form H-bonds.[1]

2. The Structure of Dentin

Dentin is a hard, yellowish, and elastic material. It forms the main bulk of the tooth, and also gives the main strength to it. In a morphological sense it resembles bone, as it is made up of collagenous fibers which are in a calcified ground substance. However, it differs from bone in the fact that it contains no cells, but only processes of cells called odontoblasts. The odontoblasts lie adjacent to the dentin in the pulp cavity, and they form the dentin tubules in the dentin matrix. In the formation of the dentin in vivo, the odontoblasts retreat downward as the new layers of dentin are deposited, and as they retreat they leave a single branching process embedded in the dentin matrix. These processes become longer as the odontoblasts keep receding, and eventually form dental tubules, which lead to the odontoblasts.[5]

The function of dental tubules is to transport nutrients and other materials into and out of the dentinal pulp, thus nourishing the pulp, and promoting its life. The tubules are filled with fluid, which consists mainly of water, salts, and

a minor amount of proteins and carbohydrates. These fluids may provide easier transport of substances to the pulp.[8]

The dentin could actually be called a protective cap produced and maintained by the pulp which underlies it, as dentin that is removed from the oral cavity is incapable of growth or reaction. This obviously shows the pulp is very important in the formation of dentin, and in fact the cells which form the dentin and are responsible for its growth (odontoblasts) are located in the pulp.[6]

Dentin, unlike enamel, forms all throughout life. The dentin that forms before the completion of root development is known as primary dentin. All dentin formed after this point is known as secondary dentin. There is also a third type of dentin which arises after injury, and this is known as reparative dentin.[5]

As a person gets older, there is a change in the dentin. It becomes more brittle, and also more translucent at the apex of the root. These changes are caused by the blocking of dental tubules with calcified material. This process is known as sclerosis.[6]

The dentin of teeth removed from the oral cavity

(non-vital dentin) is also more brittle than that of dentin which remains in the mouth (vital dentin). Non-vital dentin is dentin in teeth that have been removed from the pulp.[7] Causton and Johnson[7] found that this aspect can also affect bonding to dentin, as the abilty of dentin to form bonds depends of the freshness of the teeth.

3. Past work on Dentin Bonding

Zinc Phosphate Cements

Zinc phosphate cements are made up of a zinc-oxide powder portion and a liquid portion consisting of a 50% aqueous solution of ortho-phosphoric acid. This liquid portion also contains very small amounts of zinc and aluminum in it. The tensile strengths when using this powder-liquid adhesive have been found to be fairly high in a range of 500-800 PSI (or 3 to 5 MPa).[9] However in other tests by Oilo,[10] the tensile strength of the zinc phosphate cement (and EBA cements) to untreated dentin were found to be quite low (0.6 MPa). These results may be different because of the different test conditions which were employed.

The disadvantages of the zinc-phosphate cements are that they are very soluble in oral fluids, and they are very irritating to the pulp. Depending on the amount of acid present in the liquid portion, mild and reversible injury may occur, or chronic inflammation and necrosis may occur to the pulpal tissue. For these reasons, zinc-phosphate cements are not the most ideal to be used as a dental filling. Variations of these adhesives have also been used in dentistry, such as

zinc-eugenol cements which have been used as temporary fillings. They haven't been used as permanent fillings, because this cement is fairly weak, and it disintegrates in the mouth. However it is less injurious to the pulp than the zinc-phosphates.[9]

EBA cement is also a modification, but in this cement the eugenol is replaced by ethoxy benzoic acid, and much of the zinc oxide is replaced by alumina particles. It has been found that this material has good strength, hardness, and resistance to disintegration. All of the mentioned materials actually show no chemical bonding to the tooth, but rely on mechanical interlocking to retain the restoration.[9] (For structure of EBA cement consult figure 2).

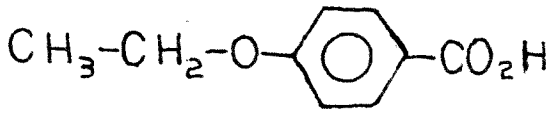


Figure 2: Structure of EBA cement

Polycarboxylate and Glass Ionomer Cements

Polycarboxylate cements were developed by D.C. Smith.[9] They are composed of a powder and a liquid portion, similar to the zinc-phosphate type cements. The powder is a modified zinc oxide and the liquid is a 40% solution of polyacrylic

acid in water. A chemical reaction occurs between these components, and the zinc ions cross-link with the polyacrylic acid molecules. These acid groups can also complex with calcium and other metal ions in the tooth which can react with this acid. The polyacrylic acid will also bond to protein; however, this bond could be benificial to the bonding, or diminish it depending upon conditions of bonding. The tensile strengths of these cements are at least as good as the tensile strengths of zinc phosphate cements. Strengths of over 1000 PSI (7 MPa) have been reported. Unlike zinc-phosphate however, these cements are not very irritating to the pulp. Water solubility has also been found to be low.[9,11]

Wilson and Kent[12] developed the Glass Ionomer cements which have similar adhesive properties as do polycarboxylate cements, with respect to the tooth structure. These cements consist of an acrylic acid liquid, and a calcium alumino-silicate glass powder. Adhesion seems to occur because of ionic and/or polar interactions. Powis et al.[13] and other groups of researchers have stated the mechanism of bonding. The mechanism depends on the ability of -COOH groups present in the acrylic acid to form H-bonds with the apatite structure of the dentin. This ability of the -COOH groups to form H-bonds, ensures very good wetting properties.[9,14] As the cement sets, the H-bonds appear to be replaced by ionic

bridges.[13,14] Adhesion with this cement appears to be physico-chemical rather than mechanical,[12] and seems dynamic in nature with much bond-interchange.[13] In reference to tooth structure, according to Wilson and Prosser,[14] it seems that the bonding of this cement to collagen would be via hydrogen bridges, and the bond to apatite by metal-ion bridges. Studies by Beech[14] have shown adhesion of these Glass Ionomer cements seems to occur solely to the apatite portion of the dentin. This may be because there are many more calcium ions in the apatite then in the collagen. Levine et al[15] supports this theory because the polycarboxylate and Glass Ionomer cements seem to bond more strongly to enamel then to dentin.

A study by Prodger and Symonds[16] found that after storage for 3 months in water at 37 degrees C there was no significant change in adhesion with Alumino-silicate polyacrylate (ASPA) Glass Ionomer cements. Oilo[11] on the other hand using ASPA filling cements found that the value of the material dropped significantly from 1.1 MPa after the first day in water to 0.2 MPa on the second day. Brandau et al[17] have found strong evidence for utility of these cements in a clinical setting. They reported that after 54 months 75% of the restorations had complete retention, 15% were partially missing, and only 10% were completely lost.

It has been found in most cases that the Glass Ionomer cements bond better if no etching is done on the tooth surface. Shalabi et al[18] conjectured that the etching does not improve the bond because this treatment removes not only the smear layer, but also a large amount of calcium ions in the surface of the underlying dentin. This effect would then decrease the ionic interaction between the cement to dentin and they reported lower bond strengths were obtained with etching. Powis et al,[13] Levine et al,[15] and Causton and Johnson[15] seemed to support this view. Hotz et al[12] on the contrary found that the use of a citric acid conditioner improved his results. They suggested that the citric acid solution was effective because it cleaned and wetted the substrate. However, Hotz et al[12] seem to be in a definite minority with that view.

Alkyl 2-Cyanoacrylates

The alkyl 2-cyanoacrylates, (methyl-,ethyl-, and isobutyl-2 cyanoacrylates), are easily polymerized by an anionic reaction with hydroxyl or amino groups which are predominant in proteins. These cyanoacrylates can also be polymerized by weak bases, such as water or alcohol.(See Figure 3)

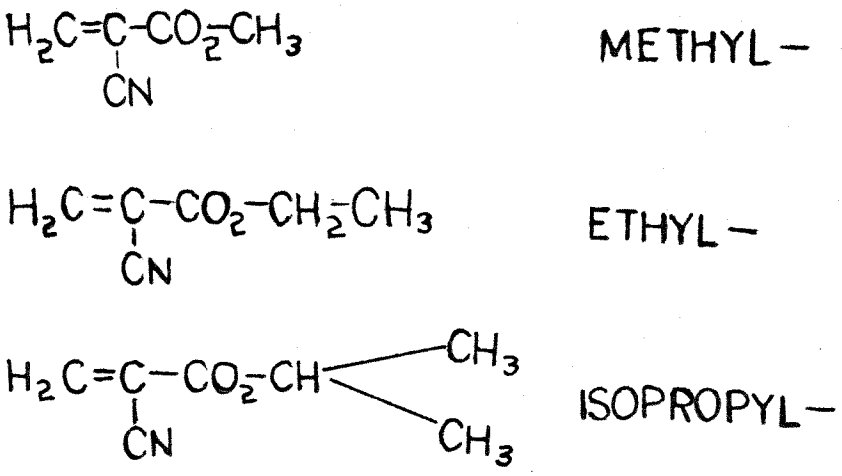


Figure 3: Structure of alkyl-2-cyanoacrylates

Fukushi and Fusayama[20] have found that cyanoacrylates showed a strong adhesion to the dry tooth structure of dentin, and this adhesion to dentin was even stronger than the adhesion to dry enamel. Since cyanoacrylates react with water and organic substances, and these components account for 31% of the dentin, and only 3% of the enamel, this fact should be true. This has great potential, but they also found that the bond strength decreased rapidly after storage in water. Studies by Brauer et al[21] have also supported this fact. Beech[19] on the other hand reported that the bond between dentin and ethyl-2-cyanoacrylate was very stable after one week in water. Brauer et al[21] also found that they had obtained improved adhesiveness in water when they lengthened the ester group and they reported after six months storage in water their samples retained from 70%-73% of their one day bond

strength. They also found that treatment with NN-DMPT sometimes lowered the bond strength, and that phosphoric acid conditioning increased adhesion.

The authors seemed to differ on which alkyl-2-cyanoacrylate gives the best result. Beech[19] and Fukushi and Fusayama[20] had found ethyl-2-cyanoacrylate to give the best bond (about 10 MPa),while Brauer et al[21] have found isobutyl-2-cyanoacrylate to give the best bond (about 5.5 MPa).

Urethane Cements

In 1955 Buonocore[9,22] started to experiment with the use of urethanes as dental adhesives. He observed a great increase in the bond strength of acrylic resins to enamel and dentin when he etched the surfaces with phosphoric acid (85% solution). Bond strengths of about 300 PSI (2 MPa) were obtained by Buonocore after storage for three months in water. In 1969 Buonocore and Casciani[23] reported on the reaction of isocyanates with acrylate or methacrylate compounds containing one or more hydroxyl radicals. They found that isocyanates have the ability to react rapidly with hydroxy (-OH), amine (-NH), and carboxyl (-COOH) groups in protein to form urethane linkages. It is thought that these

linkages should be strong enough to bond the cement to the collagen portion of the dentin. The authors also found that when properly cured, these polyurethane prepolymers had the desired properties of toughness, abrasion resistance, and high impact and tensile strength. However, as is the case of most dental adhesives, they also found that storage in water resulted in softening of the polymers with loss of toughness and reduction of bonding strength.

Lee et al[24] in tests using polyurethanes found that when using various isocyanates and 50% citric acid as an etching agent to facilitate better bonding, adhesion to bovine dentin was between 300-700 PSI, it was their opinion that acid etching was needed to achieve an optimum bond.

Antonucci et al[25] confirmed Buonocore and Cascianiʻs results reporting that the urethane resins were easily polymerized by the use of NN-DMPT in a clinically acceptable time of 2-8 minutes. Lee et al[24] had found similar results, finding 10 minutes to be an optimum time for polymerization with use of NN-DMPT. Antonucci et al[25] also confirmed the fact that there was a decrease in bonding when the samples were put in water for long periods of time. They believe that the competetive action of water with the isocyanate group helps lower the bonding strength. (These reactions are shown in the discussion section of this paper).

Various Other Types of Adhesives

Important work in the area of dental adhesives done with various other types of adhesive materials that do not belong under the catagories mentioned before.

Significant advances in the understanding of dental adhesives have been a result of the work of Dr. R.L. Bowen. Dr. Bowen has written many articles on this subject, and his writings have been so voluminous that they all cannot be mentioned in this paper. He has done much work in the composite resin field, and some of his accomplishments are described below.

Bowen's major work has centered on finding a special coupling agent, which he calls a "surface-active comonomer", which would be be able to bond between the "composite polymeric binder and the enamel or dentin surface", and also be able to maintain adhesiveness in an aqueous environment.[26] At first Bowen found his best results came from using N-phenyl glycine and glycidyl methacrylate (NPG-GMA) as his co-monomer. He found that the NPG-GMA co-monomer promoted bonding greatly when it was used as an intermediate between the methylmethacrylate and the dentin, and after storage in water for 20 hours, the bond strength was 150-320 PSI.[26] On

subsequent tests of this monomer the bonding strengths after 20 hours in water increased. After using a 5% solution of NPG-GMA, the bond was found to be 390-780 PSI. After exposure for 19 days in water Bowen[27] reported that significant adhesion was retained. In later studies Bowen[28] found the use of ferric chloride as a mordant increased the adhesive strength when combined with the surface-active co-monomers devised for the experiment.

Bowen, Cobb, and Rapson[29] confirmed these results in a later study, and found that the strongest bonds were formed when using ferric oxalate as a mordant, and N-(p-tolyl) glycine and glycidyl methacrylate (NTG-GMA) as the surface active co-monomer (along with a cleanser known as PMDM). They reported that with this combination, 4 of the 11 samples treated exhibited over 2000 PSI in tension testing experiments.

Buonocore and Quigley[30] using 80% methylmethacrylate monomer, 10% glycerophosphoric acid dimethacrylate and 10% methacrylic acid for their bonding agent, and paratoluene sulfinic acid as a catalyzing agent, found results of 398 +/- 99 PSI dry and 213 +/- 56 PSI after water immersion for three months. They also found treating the surface with acid resulted in greater bonding.

Munksgaard and Asmussen[31,32] have tried some novel techniques to improve the bond to the dentin. One of these experiments includes the mixtures of 2-hydroxyethyl methacrylate (HEMA) and different aldehydes to use as bonding agents. They had found through previous experiments that acrylic monomers containing acid chloride or isocyanate groups gave relatively low bonding strengths. They suggested that this was probably caused by either a lack of strength of the dentinal collagen, or by the affect of water on the monomers.

Munksgaard and Asmussen's[31] first attempt at using HEMA as a bonding agent was to mix it with formaldehyde. They tested this and found a mean bond strength of 0.6 kg/mm. They found the optimal HEMA concentration to use was 35% to get the best bond, and if they increased the HEMA beyond 35% it caused a decrease in bonding.

The same authors had formed another adhesive monomer[32] to bond to dentin by using a methacryloylchloride and methacryloyl-R-isocyanate mixture, but did not give any results. The purpose of mixing these two constituents together was to try to find a monomer that had the potential to bond to both the organic and inorganic parts of the dentin surface.

Nagata et al[33] used 4-methacryloxyethyl trimellitate anhydride (4-META) as a bonding agent to the enamel and dentin. They reported bonding strengths of up to 18 MPa, in a dry sample test, when this substance was included in the monomer. The dentin was pre-treated with aqueous citric acid and ferric chloride, and polymerization was initiated using tri-n-butyl borane. In other work done by Nagata et al, they found bond strengths up to 6 MPA between the composite resin and the dentin interface, again in a dry sample test, when a peroxide /amine system was used as an initiator and promoter. The researchers found adhesive strengths of up to 12 MPA when using various other additives with 4-META, in dry test samples. They also found a stronger adhesive bond occurred when using dried dentin. The dry sample tests probably tend to yield higher results than would wet sample tests, but this research looks very promising.

4. The Use of Etching the Tooth Surface

In 1955 Buonocore[4,22,44] found evidence that the use of an 85% aqueous solution of phosphoric acid seemed to increase the retention of acrylic resins. This finding started an explosion of research concentrating on the effects of acid etching on retention of restorative adhesives, that is still in effect at present. There are many different and opposing views on this subject, and this thesis will present a few of them.

The major argument against the use of acid pre-treatment conditioning of the dentin surface is that it is injurious to the pulp which lies beneath it,[45] producing an inflammatory response which can effect pulpal response to the adhesive resin cements that are used.

It has been noted by Gwinnett,[45] Johnson and Brannstrom,[7,46] and McInnes-Ledoux and Cleaton-Jones,[47] that when using a conditioner on the dentin surface, the dentin tubule openings (apertures) are greatly opened and widened. Johnson and Brannstrom[7] have found that "mechanical pain-inducing stimuli" are transmitted easier when the exposed dentin tubule openings are wide open. Pashley et al,[47] demonstrated that applying a concentration of 6% citric acid for sixty seconds

on the dentin surface greatly enlarged tubule openings, and "increased the permiability of the dentin". Brannstrom and Johnson[46] have the opinion that opening of these tubules is deleterious to the dentin, as the conditioning agents removed plugs from the dentin tubules which afford protection to the underlying pulp. Since the tubules were open and widened, the liquid surface area of the dentin increased 10% to 25%, and this caused an increased wetness of the dentinal surface. This increased wetness occurs because dentinal fluid is always present "at the openings of the dentinal tubules due to capillary forces", and a greater amount of fluid flows outward because of a continuous flow in the dentinal tubules caused by pressure which is "higher in the pulp than at the outer tubule aperture." Brannstrom and Johnson believe this increased wetness would "impair rather than improve adhesion of many materials to dentin."

Erickson[22] notes that acid etching seems to make the dentin more permiable to the delaterious agent of the composite resin. Lee et al,[44] reported on this and found that the irritating effects of silicate and zinc phosphate cements were thought to be caused by the phosphoric acid content in these liquid cements. Zander,[22] and Brannstrom and Nyborg[22] in related studies took the opinion that these resins were not irritating to the pulp themselves, but that the irritation

was caused by marginal leakage which resulted in pulpal irritation due to a bacterial infiltration. Heys et al[22] found bacteria present in all teeth, but massive amounts were present in acid treated teeth. On the other hand, Vojinovic et al,[22] using citric acid as a conditioner found that it improved the adhesion of resin to the cavity walls, and this reduced bacterial growth between the wall and the filling material.

Lee et al,[44] using discs of dentin found when applying a 50% solution of citric acid (or phosphoric acid), neither was able to penetrate the dentin discs to effect the acid sensitive paper placed below the discs. Even in 1mm samples exposed to a 50% solution of phosphoric acid for five minutes, no acid penetrated the dentin. They also found, after examination under an SEM, that citric acid treatment had a much milder effect on the dentin then did the phosphoric acid treatment, for similar exposure times. They noted that longer etching times for the 50% phosphoric acid did not improve surface roughening, and no effect could be seen inside the tubules when the dentin was etched, even though the outer tubule openings were etched considerably. Johnson et al[44] have found that a relatively thin layer of freshly cut dentin is sufficient to protect the pulp from acid etchants, and Coffey et al[7] found the contents of the

tubules were extremely adhesive and coagulated readily upon exposure to air. Whether this may enhance or inhibit adhesion is not known. Brauer et al,[50] showed pretreatment of dentin to be beneficial for adhesion when using cyanoacrylate adhesives. Their highest values were achieved by using dilute citric acid as a conditioning agent.

Eick et al,[47] and Brannstrom and Johnson,[46] mentioned there was a "smear layer" (also known as grinding debris), on tooth surfaces cut with a diamond saw. Tooth particles from the size of 0.5μ to 15μ were observed to form this layer, and microorganisms were also present. Eick et al,[47] were of the opinion that the smear layer could change the dentin surface morphology and alter the bonding properties which of course would effect retention of the adhesion. Most researchers prefer to remove this layer by using the acid pre-treatment technique, because the adhesive material may actually bond to the smear layer (called by Bowen[48] a "weak boundry layer), instead of on the dentin surface in some places on the dentin. This reduces or prevents durable adhesive bonding to occur, and therefore creates a weaker bond. However, it must be said that this point has been disputed recently, and various researchers believe the smear layer should not be removed. It is not known at this time which side is correct.

The investigators of this thesis have advocated the use of pre-treatment because the pretreatment of the dentin slice, together with the etching of the coupons gives a much rougher surface. The rough surface seems to increase the adhesion due to wetting, and greater wetting ensures greater adhesion. It is to be noted however that no clinical effects have been recorded by the present investigators and in fact the pre-treatment agent may have an effect on the dental pulp.

B. Uses of Isocyanates

Most of the uses of isocyanates in industry have been in the field of polymers, and modification of polymers by isocyanate treatment has been a subject of much interest. Other uses for isocyanates have been found in such varied fields as varnish treatment, tanning of leather, paper treatment, and they are even used sometimes in the production of electrical insulators. [43]

The present experiment attempts to use a diisocyante (tolylene-diisocyanate or TDI) to bond to the collagen portion of dentinal tooth structure, and also to bond with the methylmethacrylate copolymer being used. This process is explained elsewhere in this paper.

In experiments done by other researchers trying to use isocyantes to bond to dentin, Buonocore and Casciani found that polymerization of the HEMA-polyurethane prepolymer reaction products produced clear, hard, and tough materials. However, after storage for long periods of time in water, the materials seemed to lose their toughness, and the bonding strength seemed to have weakend. Antonucci et al [25] in a related study also found evidence of weakening in an oral environment. One main objective of the present study was to

find if these conclusions were in fact true, and if they were true what could be done to retard this effect.

C. Free Radical Initiation by use of Benzoyl Peroxide

1. Vinyl Polymerization - Chain growth, transfer, and termination.

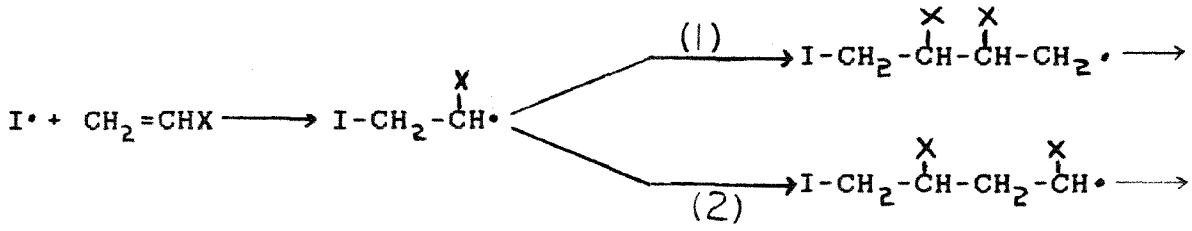
Monomers for addition polymerization usually are of the general formula: ($R_1R_2C = CR_3R_4$). The double bond is capable of being attacked by either free radical or ionic initiators to form an "active center".[35] Studies have suggested that this active center is retained by a "single polymer molecule throughout the course of its growth",[34] and this active center is eventually terminated by a termination reaction.

An active center is formed as follows (using free radicals as examples):

$$I\cdot + CH_2 = CHX \qquad I\text{-}CH_2\text{-}\overset{X}{\underset{|}{C}}H\cdot + CH_2 = CHX \qquad I\text{-}CH_2\text{-}\overset{X}{\underset{|}{C}}H\text{-}CH_2\text{-}\overset{X}{\underset{|}{C}}H\cdot \quad (\text{ETC.})$$

where x may be C_6H_5, Cl, Br, $OCOCH_3$, $COOCH_3$, or H. Disubstituted monomers such as methyl methacrylate can also be included. (I· is the free radical initiator).

There may actually be two possible addition reactions that can occur from the $I\cdot + CH_2 = CHX$ polymerization. They are:



In the chain referred to as (1), the addition reaction is known as "head to head" addition, and the chain referred to as (2), the addition reaction is called "head to tail". The activation energy is higher for (1) than for (2) because the x-group is usually large and hinders the approach of the R radical. Because of this (2) is usually found in greater amounts. Also, (2) is more prevalent because the unpaired electron can participate in resonance with x.(see Figure 5)

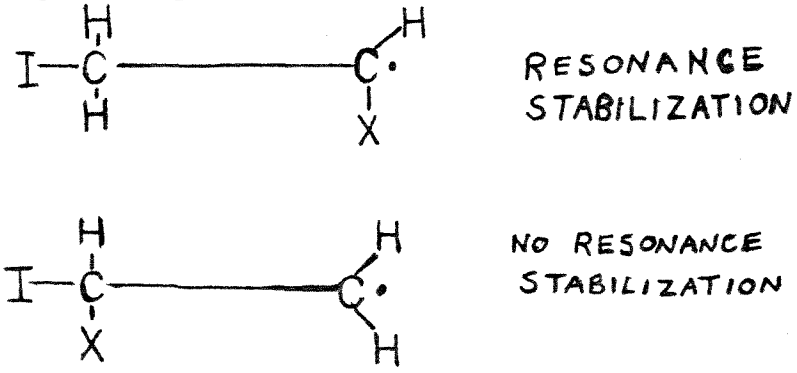


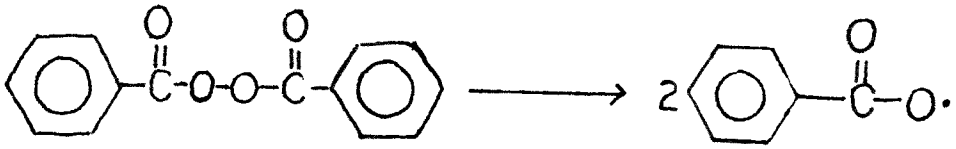
Figure 4: Resonance Stabilization of BP (Addition Reaction)

In the book "Principles of Polymer Chemistry", Paul Flory [36]

explains the theory of the chain propagation step. The chain propagation step generally consists of a free radical attack on one of the double bonded carbon atoms of the monomer. One electron of this double bond pairs with the odd electron on the free radical and the carbon atom. The remaining electron of the double bond shifts to the other carbon atom, which then becomes a free radical.[37]

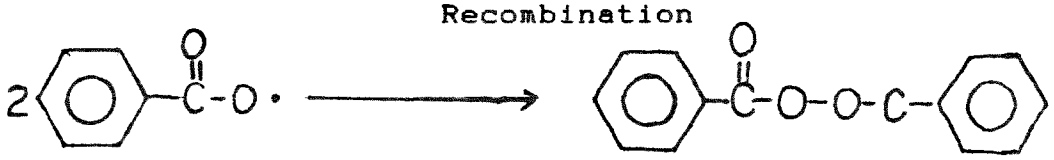
2. Initiation Reactions

The initiators most widely used to form the free radical component are the peroxides, and the most commonly used peroxide is benzoyl peroxide (BP). The peroxides are thermally unstable, and decompose into radicals slowly at temperatures of 50 to 100 degrees C. BP undergoes thermal homolysis to form benzoyloxy radicals:[37]

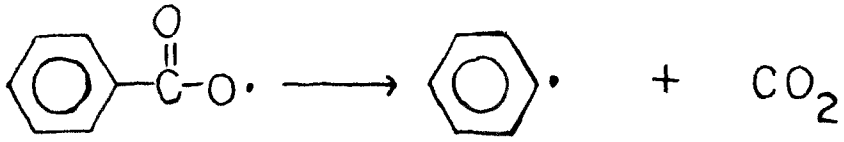


These benzoyloxy radicals are free to undergo many different types of reactions, besides adding to the monomer. These primary reactions include:

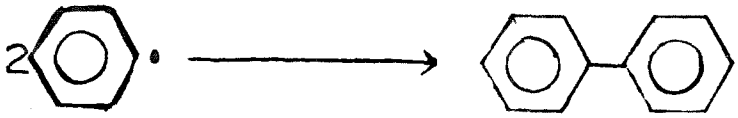
Recombination



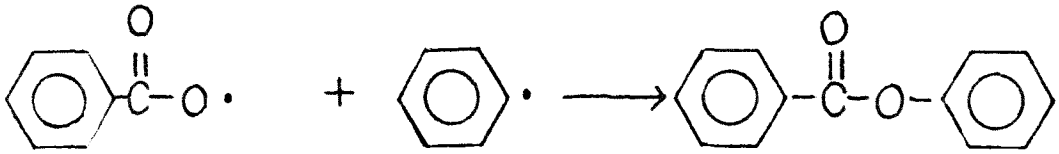
and Decomposition to Phenyl radicals and CO.



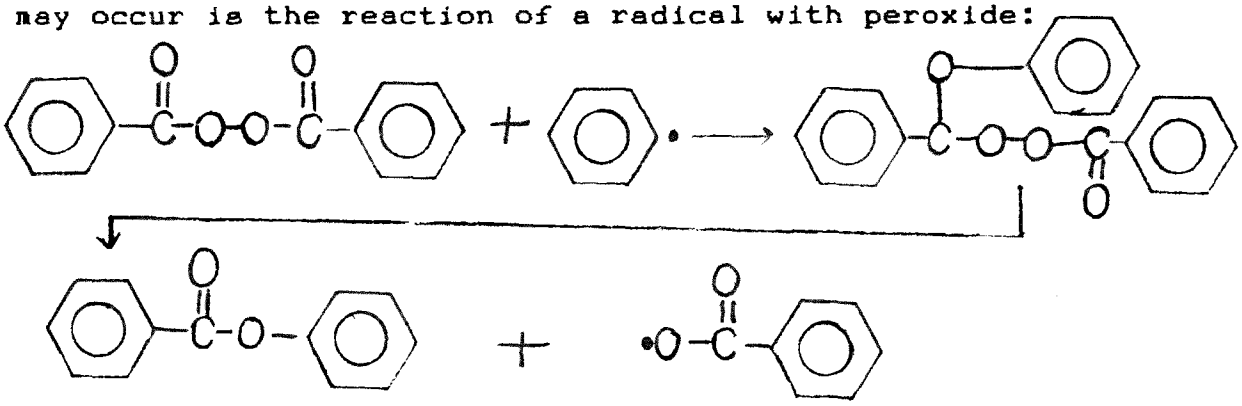
The Phenyl radicals, produced by decomposition, then are able to form biphenyl as a secondary reaction:



or the Phenyl and benzoyloxy radicals can form phenyl benzoate another secondary reaction:



These secondary reactions occur because of the "confining" effect of the solvent molecules. Because of this, the concentration of inhibitor radicals is depleated. In essence these secondary reactions tend to reduce the efficiency of the initiator. A final secondary reaction that may occur is the reaction of a radical with peroxide:



Of course the extent of these secondary reactions depends upon the structure of the peroxide, the stability of the initially formed radicals, and the reactivity of the monomer.[37]

Benzoyl peroxide is commonly used because it is very stable at room temperature (half life of 30 minutes at 100 degrees C.), and the benzoyloxy radicals are stable enough so that they tend to react faster with the reactive monomer molecules than they do in eliminating CO_2.[38] Decomposition of BP can be accomplishe at room temperature by addition of substances known as accelerators or promotors. This point will be mentioned in section D.

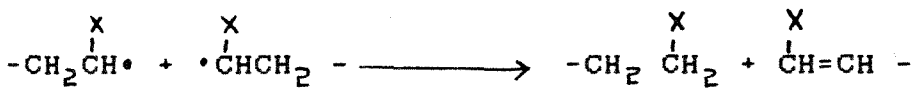
3. Termination

A bimolecular reaction between a pair of chain radicals forming paired-electron covalent bonds with loss of radical activity causes termination of the active centers. There are two processes in which this reaction may occur.

a. Chain Coupling or Combination

or

b. Disproportionation

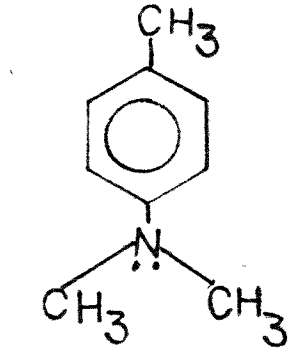


Through careful analysis it has been shown for most vinyl polymers, coupling is the dominant chain-terminating process. However, poly(methyl methacrylate) terminates almost exclusively by disproportionation at high temperatures (above 60 degrees C.), and equally by both methods at lower temperatures.[35,37]

Termination has also been found to be able to take place when a growing chain reacts with a radical that has not reacted with any monomer. This tends to occur only when a high concentration of initiator is used, or when the concentration of monomer is depleted.[35,37]

D. The Purpose of Using an Accelerator (e.g. NN-DMPT)

Tertiary amines have been used for many years as accelerators for methylmethacrylate-peroxide polymerization systems. These accelerators are used to enable rapid polymerization of a monomer or a monomer-polymer mixture, at room temperature.[40] The increase in polymerization rate is affected because peroxides tend to decompose rapidly in the presence of amines. NN-Dimethyl para toluidine (NN-DMPT), is one such amine accelerator that is used in dental applications.



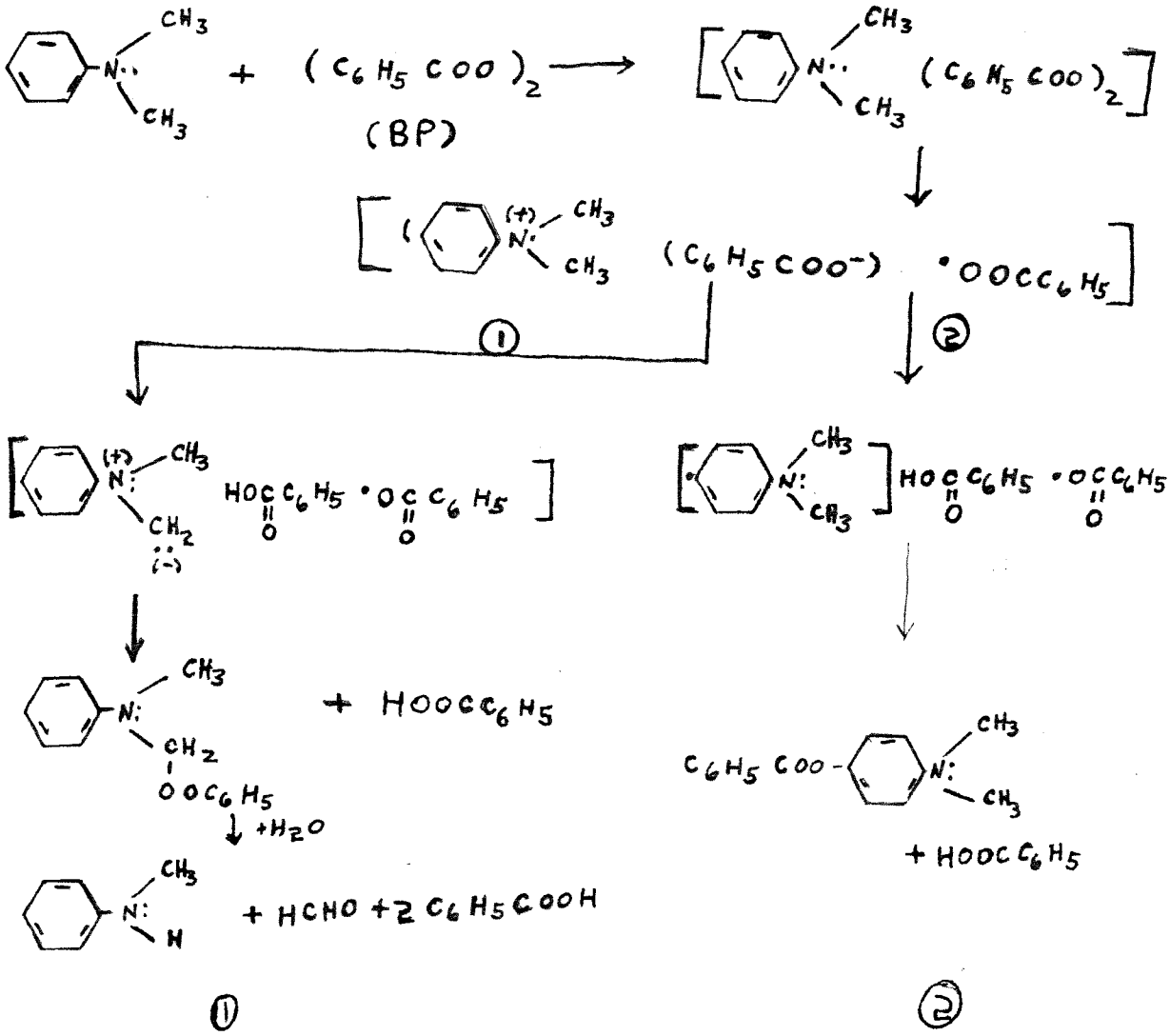
(N,N—DMPT)

The amine accelerator is able to exert a significant influence on the properties of the polymerized material. It can affect such things as the esthetics of the tooth, mechanical strength, and how well the monomer-polymer mixture polymerizes. As an example, the amines are usually unstable and produce colored oxidation products. NN-DMPT has a yellowish color so the color instability in this case is not

great as it can still match the tooth color. On the other hand there are some amines that have a great color instability which can lead to an undesirable color in the final product.

Tertiary amines such as NN-DMPT, accelerate the radical decomposition of peroxides such as BP, to initiating products by a complex process that involves electron transfer to the peroxide from the unshared electron pair on the nitrogen atom. The rate at which this occurs supposedly determines the rate of decomposition of BP.[41] The kinetics of this reaction have been studied by Bartlett and Wozaki,[40] and Meltzer and Tobolsky,[40] using BP and dimethylaniline. Dimethylaniline is similar to NN-DMPT, but instead of CH in the para-position of the molecule, it has a hydrogen atom. Meltzer and Tobolsky[40] found that dimethylaniline in a BP-dimethylaniline initiated polymerization system doesn't seem to effect the propogation or termination steps of the chain reaction, but it seems to affect the initiation step.

Horner et al[40] proposed the mechanism shown below to describe activated decomposition of BP when effected by dimethylaniline. Two major products occur:



Supposedly during the reaction between the NN-DMPT and BP, a transition state occurs in which transfer of electrons from the nitrogen to the peroxide occurs. The benzoate anion removes a proton from the aminium cation, either from the position of the side chain, or from the aromatic nucleus.[40] The para position seems most preferred, as the highly reactive

tertiary aromatic amine accelerators are usually ones which have para aryl substituents that are electron donating, such as CH_3[41]. When an electron transfers from the carbon to the nitrogen, free radicals are formed. After this, these free radicals can then undergo oxidative dealkylation, substitution, reaction with solvent or oxygen, or they may act as polymerization initiators in the presence of vinyl monomers.[40]

When this reaction occurs in the presence of air (i.e. oxygen), the oxygen is absorbed and secondary peroxides can be formed. These peroxides then decompose, and hydrogen peroxide and N-methyl-aniline are formed.[40] Goode and Gratsch[40] have established that one mole of amine is needed to decompose one mole of peroxide when in benzene.

The use of these fast acting tertiary amine accelerators, gives us the advantage of being able to attain clinically acceptable hardening times (2-10 minutes), thus reducing patient chair time. Also good mechanical strengths have been obtained using these accelerating systems.

II. THEORY

A. The Mechanics of Bonding to Dentin in This Experiment.

Dentin is made up of two types of material, an inorganic portion consisting of hydroxyapatite (which is the same substance that makes up enamel), and an organic portion made up of collagen. The primary interest of the investigators of this thesis was to try and utilize the organic portion of the dentin as a bonding site for an adhesive monomer. The monomer consists of a diisocyanate, tolylene-2,4-diisocyanate (TDI). Isocyanates are functional groups which contain a carbon atom with a nitrogen and an oxygen double bonded to it (R-N=C=O). The isocyanates are very reactive toward the oxygens of water (H O), alcohols (R'OH), and the nitrogens of amines (RNH). The reactions of most interest in regard to bonding to dentin are the reactions of the alcohols, which form carbamates ($R-\underset{H}{N}-\underset{OR'}{C}=O$), and the reaction with the amines which form ureas ($R-\underset{H}{N}-\underset{NH\,R'}{C}=O$).[42]

1. Reactions of Isocyanates

The most characteristic reaction of isocyanates involve reactions with compounds with active hydrogens. [42, 43]

$$R\text{-}N{=}C{=}O + HX \longrightarrow RNH\text{-}CX{=}O$$

The reaction of isocyanates and water involves two steps:

$$R\text{-}N{=}C{=}O + H_2O \longrightarrow R\text{-}NH\text{-}COOH \longrightarrow RNH_2 + CO_2$$

$$RNH_2 + RNCO \longrightarrow RNH\text{-}\overset{\overset{O}{\|}}{C}\text{-}NHR$$

All types of alcohols react to give carbamates:

$$R\text{-}N{=}C{=}O + R'OH \longrightarrow R\text{-}NH\text{-}\underset{\underset{R'}{|}}{C}{=}O$$

Amines react to form ureas:

$$R\text{-}N{=}C{=}O + R_2'NH \longrightarrow R\text{-}NH\text{-}C{=}O$$

2. Blocked Isocyanates

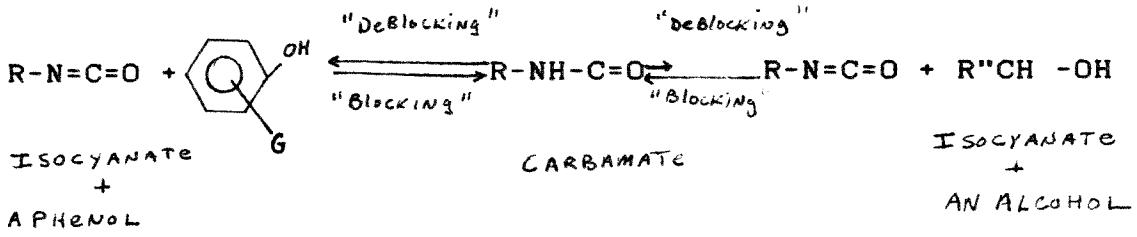
For purposes of bonding to dentin the present investigators were interested in forming isocyanates that would not react with water until they were bound to the dentin surface. Using isocyanates is very difficult because of their sensitivity, before bonding, to moisture from solvents, from resins, from the air in conditions of high humidity,and mostly from water present in the teeth themselves. To combat this moisture sensitivity "blocked" isocyanates were used. A blocked isocyanate is one that will not react with any compound containing an active hydrogen group, such as water or alcohol, at room temperature, and they contain no free isocyanate groups.[43]

Isocyanates may be blocked and deblocked [42,43]

$$R\text{-}NH\text{-}C(=O)\text{-}O \underset{\text{"Blocking"}}{\overset{\text{"DeBlocking"}}{\rightleftharpoons}} R\text{-}N=C=O + HOR'$$

The extent of deblocking or dissociation that occurs depends upon the structure of R and R'. If R and R' are aromatic (contain a benzene ring) the deblocking reaction occurs to a much greater degree. However, even if R and R' are both phenols, the deblocking at room temperature will only be 0-5%.

Carbamates have the ability to form an equilibrium mixture with a corresponding free isocyanate and phenol, or a corresponding free isocyanate and alcohol):

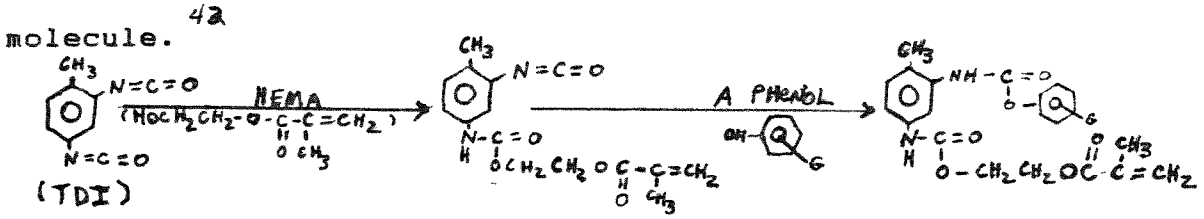


Where R' is an aliphatic group, R'OH is an alcohol, and where a phenol is used, R' is an aromatic group where G may be any substituent. Alcohol derived carbamates are less likely to deblock than are phenol derived carbamates.[42]

The reactions between amines and isocyanates producing ureas are not readily reversible and are less likely to deblock than are carbamates.[42,43]

3. Reaction Chemistry

By using TDI, the present investigators found that they could create a molecule that could chemically bond to the dentin and also to the filling material. To do this they reacted each isocyanate separately, first with HEMA, and then with a phenol which was able to readily dissociate from the molecule.[42]



By Treating TDI first with HEMA, the predominant reaction occurs at the para position which is much more reactive than is the ortho position. HEMA being an alcohol rather than a phenol, also has little or no tendency to deblock. When the TDI-HEMA compound is treated with a phenol, the reaction takes place at the ortho-position (this reaction takes quite a long time, and excess phenol must be used), producing a "blocked monomer".[42]

The blocked monomer is insoluble in very non-polar solvents such as petroleum ether. However, it is soluble in the more polar solvent tetrahydrofuran (THF) and 1,2 - dimethoxyethane (DME).[42]

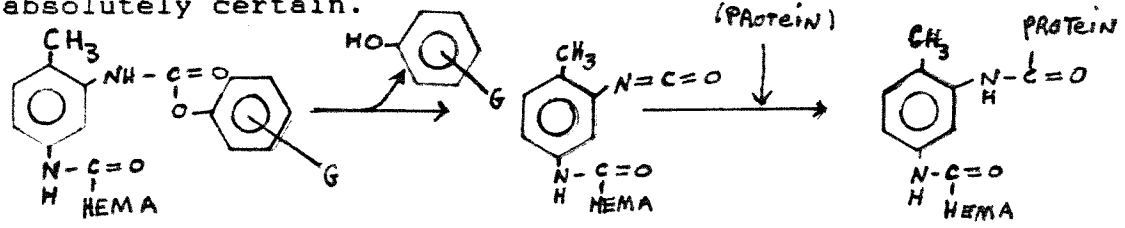
When the blocked monomer is dissolved in DME, and a dentin slice is soaked in this solution, reaction between the dentin slice, and the blocked monomer can occur. Since dentin contains collagen, there are a large number of amino acids which have many side chains, which contain alcohol and amino groups.[42]

Thus, there are many possible sites in collagen for bonding to the blocked monomer. (see Fig. 5)

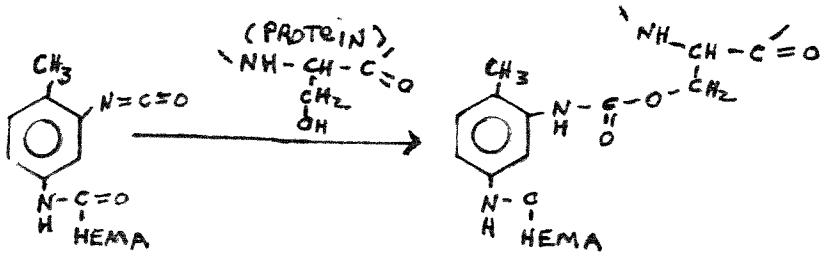
FUNCTIONAL GROUP	Amino Acid
AMINE	LYSINE, ARGENINE, HYDROXYLYSINE
ALCOHOL	SERINE, THREONINE, HYDROXYPROLINE, HYDROXYLYSINE

Figure 5: Bonding Sites in Collagen for Blocked Monomers

The blocked monomer may then deblock and produce a free isocyanate which then can react with an amino group to form a urea (shown below). The rate and extent of deblocking are dependent upon many variables, such as effects of solvent, structure of the molecule, structure of the side chain, and temperature. However, the mechanism of deblocking is not absolutely certain:[42]



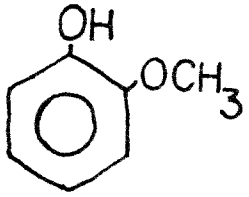
If the deblocked monomer reacts with an alcohol, an alcohol-derived carbamate is formed:[42]



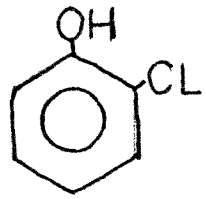
The adhesive is now bonded to the dentin. The next and final step of this process is bonding the adhesive monomer to the filling material (co-polymer). The 75% MMA and 25% PMMA mixture is polymerized by the addition of NN-DMPT (accelerator), and BP (initiator), so that polymerization is possible at room temperature. By adding this mixture onto the monomer coated dentin slice, a co-polymerization between the monomer and the MMA-PMMA occurs. [42]

III. RESULTS AND DISCUSSION

Three monomers were used to bond to the dentin slice. Two were prepared using TDI, HEMA, and either o-methoxyphenol or o-chlorophenol (Fig. 6). The third was prepared using pentaerythritol, TDI, HEMA, and p-cresol. (Fig. 6).



O-METHOXYPHENOL



O-CHLOROPHENOL

PENTAERYTHRITOL

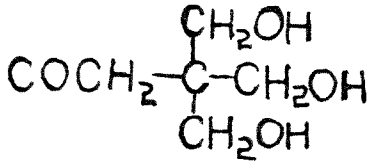


Figure 6: Structures of Monomers Used in Experiment

Various conditioning (pre-treatment) agents were used on the dentin slices before applying the monomer solution. The conditioning agent most frequently used was citric acid (5% aqueous solution), but also used, (only in tests with o-methoxyphenol as the monomer), were tannic acid (25% aqueous), and ferric oxalate (6.8% aqueous).

Samples were dried at room temperature from 0 to 168

hours, and they were immersed in distilled water at room temperature for a period of 0 to 672 hours.

1. O-Methoxyphenol Samples

The first samples prepared, using o-methoxyphenol, (Table 1, Group #1) did not meet our expectations. Tannic acid was used as the conditioning agent. The filling material (copolymer) was composed of 70% MMA and 30% PMMA, and this was polymerized with 8 drops of NN-DMPT, and 0.02g of BP. The average psi and standard deviation was 521 ± 321 in 7 samples that were dried for two weeks, and then stored in distilled water for one week. The results were by no means poor; however, as the experiment proceeded, better results were obtained with different monomers under different conditions. We have found that more experience in the preparation of samples leads to greater bond strengths. This is due to the fact that as the experimenter becomes more aquainted with the testing procedure he can work faster,and he can treat the slices of teeth with various reagents more efficiently.

Time is important because the filling material begins to polymerize within two minutes and this will affect the bond between the monomer and the filling material.

Furthermore, with more experience the experimenter learns to treat the slices of teeth more uniformly with the pretreatment solution, solvents, and the copolymerization mixture

Previous workers had reported poorer results with o-methoxyphenol derived monomer when using tannic acid as the conditioning agent. One reason the tannic acid may not have been a favorable conditioner is that the tannic acid may bind to the $-NH_2$ groups of the collagen portion of the dentin. Since these groups are important in reacting with the TDI, a lessening of bonding may have occurred.

In the next set of experiments, ferric oxalate, recommended by Bowen to increase the bond strength was next used as the conditioning agent with o-methoxyphenol as the monomer, and the same proportions of copolymer were used. The ferric oxalate treated samples were not encouraging. The first samples (group # 2 - ferric oxalate), pulled dry after 48 hours, yielded encouraging results of 1070 $\pm$ 421 psi, were obtained with 3 samples. However, with samples tested 24 hours dry, and one week wet (group # 3) the strength fell to 264 $\pm$ 192 psi. These results were unfortunately quite low.

At this point in time, we began using a 75%-25% MMA-PMMA

solution instead of a 70%-30% MMA-PMMA solution. The advantages of the 75%-25% solution were that it was faster to make, and it also kept longer in storage, (after a time the MMA-PMMA solution polymerizes spontaneously even if stored in a refrigirator under nitrogen. With less PMMA, the mixture tends to not polymerize as fast. For the next group of tests (Group # 4) the same conditioning agent and the same monomer were used on 20 samples. Ten drops of NN-DMPT were used instead of eight drops. The purpose of adding more promoter was to determine whether it would speed-up the setting time. In samples 6 to 11 of this group and for most subsequent samples, degreasing the aluminum coupons was performed by using petroleum ether instead of chloroform. From sample # 12 on, we began rinsing slices in DME before coating them with the monomer, so that slice surface would be free of any water which might affect the bond strength. Coupons were also neither etched nor degreased, in order to determine their effect on the bonding strength. It was observed that on a few occasions when etching and degreasing were not performed, adhesive seperations were noticed at the coupon interface. With etching and degreasing this is a rare event. Freshly distilled DME was used in all samples beginning with # 20. These variations yielded results which were not impressive (281 $\pm$ 237 psi).

Group # 5 was a 3 sample group, identical to group # 4, except that 12 drops (instead of 10) of NN-DMPT were used. The results obtained under the conditions of 24 hours dry and 192 hours wet were 680 $\pm$ 497 psi. These results were encouraging. More investigation is needed to evaluate the effect of ferric oxalate as a conditioner.

The next groups of samples were made using citric acid as the conditioning agent (group #'s 6-9). The only variable which we altered in this part of the experiment was the amount of NN-DMPT used (from 10 to 16 drops). Furthermore, all of the coupons (after sample # 3 in group # 7) were degreased with petroleum ether, in the ultrasound cleaner. All other variables that were utilized in Group # 5 still apply.

The results of the first group tested with citric acid (group # 6), were 779 $\pm$ 198 psi. These results were for a group of three samples, using 16 drops NN-DMPT. They were kept dry for 168 hrs., and for zero hours wet. In group # 7, six samples were tested, with the conditions of 48 hours dry and zero hours wet. The samples 1-3 in this group were treated with 10 drops of NN-DMPT, and samples 4-6 were treated with 14 drops of NN-DMPT. The results of group # 7 were quite impressive, 1705 $\pm$ 578 psi, but it must be

mentioned these samples were tested dry. In group # 8, six samples were treated with the conditions of 48 hours dry and 96 hours wet; 14 drops of NN-DMPT were used, and the result was 804 $\pm$ 630 psi.

In Group # 9, 16 drops of NN-DMPT were used, and the samples were kept dry for 24 hours, and wet for 168 hours. The results from this batch were 906 $\pm$ 344 psi. It was unexpected that this result would be greater than the result in group # 8, because the bond strength should deteriorate with longer storage in water. The differences in the groups were that in group # 8, the slices were soaked in citric acid for five minutes rather than the usual two minutes, and 12 drops of NN-DMPT were used in group #8. It is not known which factor, if any, may have caused the difference. Group # 9 polymerized very quickly using the 16 drops of NN-DMPT, and this could be a major factor, but one must keep in mind the large variabilty between tooth samples also.

This concluded the tests with the o-methoxyphenol-TDI monomer, which seems to have some potential as a dentin bonding agent.

2. O-Chlorophenol Samples

With the variables essentially standardized attention was turned to the o-chlorophenol monomer. The NN-DMPT concentration was set at 12 drops for all samples, and citric acid was set at 5%.

Group # 1 (table 2) consisted of six samples which were kept dry for 72 hours and wet for zero hours. The results, 1608 $\pm$ 421 psi, were good, but they did not approach the best dry results found when using o-methoxyphenol and citric acid. However, the results of the next 32 samples (group # 2) which were kept 48 hours dry and zero hours wet, yielded a value of 1910 $\pm$ 1184 which exceeded the o-methoxy-, citric acid results by over 100 psi. The variance in these samples was high and caused great concern. After group # 2 more care was taken to make certain that the coupons were aligned properly in the jig in order to ensure even distribution of the 2 Kg load placed on the jig. It is believed that this course of action did help, because the variance was never that high again. The variance seems inherent in this type of testing, as is noted in most of the research conducted in this area.

In group # 3, Table 2 displays the results for the first samples that were immersed in water. The seven samples were

kept dry for 48 hours and wet for 24 hours. The results (1027 $\pm$ 249 psi), were the best results for a wet sample that had been obtained up to this point. From the fourth sample on, a new monomer drying stand was used. Prior to this time the monomer-coated slices were dried in a watchglass. However, it was noted that the samples did not dry evenly this way, possibly due to the presence of excess monomer on the bottom of the watchglass that remained after decanting the monomer solution. This resulted in an uneven spreading of the monomer on the tooth slice. Therefore, a better monomer drying stand was implemented, consisting of a large cork with six slits in it, which enabled the cork to hold six slices. The monomer-coated teeth could then be removed from the watchglass, set in these slits, and allowed to dry more evenly.

In the next grouping of samples (# 4), the setting time for the dry condition was the same as in group # 3 (48 hrs.), but the six samples tested were left immersed in water for 96 hours. The results (700 $\pm$ 293 psi) were not as good as the o-methoxyphenol results (804 $\pm$ 630 psi) using citric acid under comparable conditions. The decreased variance found in the o-chlorophenol sample however, was an indication that aligning the coupons properly may have helped standardize the procedure.

For the next group of samples (# 5), a longer drying time of 96 hours and an immersion time of 24 hours in water was employed for the 11 samples tested. These longer drying times are not clinically feasible, but are used in the experiment to determine the effect of longer drying times on bonding strengths. Analysis of the results indicates that these longer drying times increase the bonding strengths (vida infra).

For group # 5 the average results, 1871 $\pm$ 847 psi, were the highest obtained up to this point. One sample with a breaking strength of 3401 psi, was the highest value yet obtained. Because these results were so encouraging, the next group (# 6) was left to dry for the same amount of time (96 hrs.), but after being dried the samples were immersed in water for 168 hours. The results, 375 $\pm$ 173 psi with the high being 669 psi and using the same conditions, definitely showed the samples bond strengths deteriorate after longer periods of time in water. A dramatic example of this effect was shown by group #'s 7 and 8. In group # 7, six samples were set to dry for 192 hours, and were not immersed in water for any length of time. This long drying time was used again to determine whether doubling the drying time would significantly improve bond strength. The results, 3690 $\pm$ 748

psi, were almost twice that of the 96 hour dry samples of group # 5, with a high of 5064 psi. Group # 8 had a sample size of five, and the same drying conditions. However, when these samples were immersed in water for 24 hours, the results were not even half of the dried sample results shown in group # 7 (1608 $\pm$ 429 psi). This dramatically established that placement in water produces degradation.

Efforts were then turned to determining bond strengths from samples that were prepared in a procedure utilizing more clinically acceptable time frames.

In group # 9, ten samples were prepared in an effort to keep the drying times and the immersion in water times equal, e.g.-24 hours dry and 24 hours wet. The results obtained, 1332 $\pm$ 756 psi, were very good compared with other samples that were done with 24 hours of water immersion. These results even surpassed the total average of group # 3 in which the conditions were 48 hours dry and 24 hours wet. It was felt that improved techniques accounted, in part, for the increase. It was decided for the next group of samples to allow them to cure in the jig for one hour and then immerse them in water for 48 hours. These time intervals were used to determine the effect that applying simulated clinical conditions would have on the bond strengths. The result of

group #10, (ten samples) was 1647 $\pm$ 721 psi. These results were somewhat surprising, as it was believed that this result would have been less than that of group # 9, as the samples in group # 9, were only in water half the time, and also were dried 24 hours before immersion in water. The only difference that could be seen between these sample groups, except for conditions of storage, was that in making group # 10, a fresher batch of chemicals was used (newly distilled DME, new bottle of MMA-PMMA solution, and new BP were used). So it seems tha freshness of the materials used in assembling a sample has a great effect on bonding.

The next factor to study was what effect storage in water for periods longer than 48 hours would have on the samples. Three samples in group # 11 were kept wet for 336 hours after a 48 hour dry period, and the results, 1254 $\pm$ 582 psi were good. Group # 12 consisted of 22 samples transferred directly from the jig, after a one hour cure, and immersed in water for one week (168 hrs.) All of the conditions were the same as Group # 11 except etching of the coupon faces was restored from this sample group onward,for the o-chlorophenol monomer. The average results were found to be 825 $\pm$ 532 psi. The high sample had a psi of 2175, and the low had a psi of 269. This test group and the following test groups gave an indication of just how much the samples did degrade. Group #

10 (0 hours dry, 48 hours wet) had a average bond strength of 1647 $\pm$ 721 psi. Comparing this to group # 12 (0 hours dry, and 168 hours wet), the average results of group # 10 were twice as great as those of group # 12. Group # 13 was tested under the same drying conditions, but the water immersion time was increased to 336 hours. The results, 320 $\pm$ 265 psi, were found to be less than half of the group # 12 results. However, this water degradation seems to level off after a while, as group # 14 (0 hrs. dry , 1 month (672 hrs.) wet, 4 samples), showed average results of 326+/-266 psi, which are remarkably close to group # 13 samples. These were the last samples done with the o-chlorophenol monomer, and up to now these have been the best results obtained in this experiment.

3. Pentaerythritol and p-cresol Monomer Samples

This monomer (Fig. 7) was synthsized by Y.Y. Su, for the purpose of increasing the number of side chains that could bond to dentin to two, instead of the normal one bonding side chain as in the TDI monomers. It was hoped that this molecule would create a better bond to the collagen portion of the dentin, therefore making for greater bond strengths.

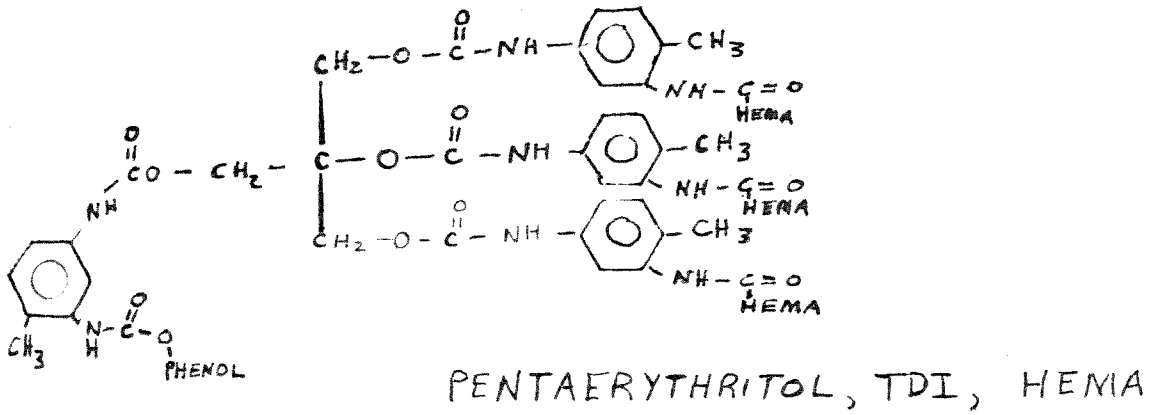


Figure 7: Structure of Pentaerythritol-TDI + HEMA + p-cresol

In testing this monomer, 5% citric acid was again used as the conditioning agent, and all the standardized conditions mentioned in the previous samples apply. The first tests (Group # 1 -Table 3), were for dry samples (48 hours dry) without water immersion. The eleven samples in this group had an average of 1324 $\pm$ 588 psi, which is comparable to the other monomers tested under the same conditions.

Group # 2, was tested under the same drying condition (48 hours) but the eight samples were put in water for one week. The average results, 307 $\pm$ 103 psi, did not compare with the results obtained for the other monomers. Four samples (Group # 3) prepared the same day as Group # 2 were kept dry for 48 hours and in water for 240 hours. Their bond strengths were only 224 $\pm$ 77 psi. These results were very

disapointing, so lengthening the drying time was attempted to determine whether the results would improve. Group # 4 consisted of six samples which sat dry for 96 hours, and then were put in water for one week. The results, 448 $\pm$ 221 psi, were found to be better than were the results obtained under the same condition with the o-chlorophenol TDI monomer (375 $\pm$ 173 psi). Since the result of Group # 4 turned out so well, it was decided to test the next samples without any time dry, and 48 hours immersion in water. The results of the seven samples in this group # 5 averaged 1408 399 psi. The result was not as good as, but was reasonably close to the o-chlorophenol TDI results under comparable conditions (1647 $\pm$ 721).

In the last test done with pentaerythritol (group # 6), three samples were placed in water for 336 hours, after sitting dry for 48 hours. The results, 1266 $\pm$ 569 psi, were even better than the three o-chlorophenol TDI samples pulled under the same conditions.

The pentaerythritol monomer looks very promising, and more testing should be done with it. Why the results were not as good at the beginning is puzzling, and it may be attributed to the technique of handling the very low density pentaerythritol monomer.

In the future it may be beneficial to reduce the DME volume in order to obtain a more concentrated monomer solution which may react faster with the dentin.

Many other tests not touched upon in this thesis may be performed in this area. To obtain data that better describes the stability of the adhesives the investigators could include many variations in these experiments such as thermocycling the specimens while stored in water, and perhaps even storing samples in water for much longer periods of time, i.e.- six months to a year. One caveat, however, is that the introduction of too many variables leads to a complex situation where it becomes very difficult to determine the contribution that any single variable makes to the overall results. It is only by addition of a few variables at a time that any logical conclusion can be drawn.

4. Measuring Bond Strength

To measure the bond strength a suitable tension testing apparatus must be employed. In our research a Scott CRE/500 tension testing machine was used to determine the results. The test involves the determination of a shear force necessary to separate an aluminum coupon, which is adhered to

a monomer coating on the dentin slice mixture by a MMA-PMMA mixture, from the dentin slice. The shear tests are fairly simple and offer a high degree of reliability.[44] Tensile strengths of the adhesive bonds were determined on the testing machine at a crosshead speed of 1 mm/min. The only factor that cannot be controlled by the testing apparatus is the thickness of the adhesive resin, and Bowen et al,[29] have shown this may effect bonding strength to a degree. One thing must be known while using a tension testing machine, and that is the tensile strengths are not a measure of the retentive property of the cement. What they do measure is the tensile strength of the adhesive film in the joint. The cohesive strength of the adhesive film is the factor limiting the strength of the joint. Studies by Koehn[29] have found that the strength of an adhesive joint may be determined by the environment of the joint, rather than by the forces of specific adhesion. This means that bond strength of an adhesive is not an inherent property of an adhesive, but it depends on the test specimens used and the conditions of the test. Another interesting fact is that a chemically adhesive joint, like we are using, is stronger in tension than a mechanically adhesive joint.[44, 50]

IV. CONCLUSION

The monomer that gave the best results was the one derived from o-chlorophenol, TDI and HEMA, with an average of 1647 721 psi with 48 hours in water and no drying time. The pentaerythritol-TDI-HEMA-p-cresol monomer results were promising, with a 1408 399 psi result under the same conditions. Further testing should be done with this monomer. The o-methoxyphenol-TDI-HEMA monomer showed the least promise of the three. However, this was the first monomer used in this experiment, and much of the development of the experimental technique was done on this monomer (i.e changing variables). Because the same conditions were not imposed upon it as were imposed on the other two monomers it is difficult to make comparisons with this latter monomer. Water immersion times for two weeks or greater were performed on the o-chlorophenol and pentaerythritol monomers were encouraging, but much water deterioration was noticed.

The major factors that influenced bond strength in this experiment were duration of the experiment, and freshness of the materials used. Time is important for two reasons: one occurs in the process of applying the filling material (co-polymer). If the filling material is put on the coupons and the monomer coated dentin slices too slowly,

self-polymerization may occur without significant attachment to the monomer, thus reducing adhesive strength. The other instance where time plays a different but still important role is in the time of storage of the bonded dentin slices, because the samples degrade if left in water for long periods of time.

Freshness of the materials that are used is the most important parameter aside from good laboratory technique. If the materials are not fresh, they tend not to react as well with each other. For example, as the batch of MMA-PMMA gets older, it tends to start polymerizing by itself even without addition of NN-DMPT, and BP. Therefore, for the best results, fresh materials are always needed.

V. EXPERIMENTAL

A. Aluminum Coupon Treatment

[1] Coupons were faced (see Fig. 8) on drill press, using a special attachment (see Fig. 9) to hold four coupons at a time. The coupons were faced on 320 grit sandpaper, in order to remove all debris from the coupon faces; this results in a mirror-like finish (See Fig. 10).

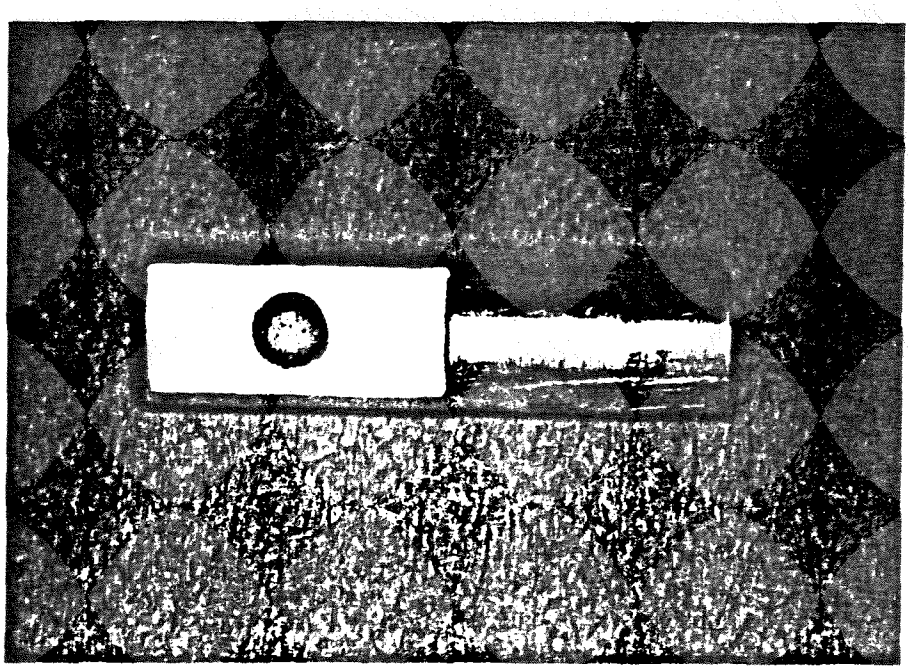


Figure 8: Aluminum Coupon

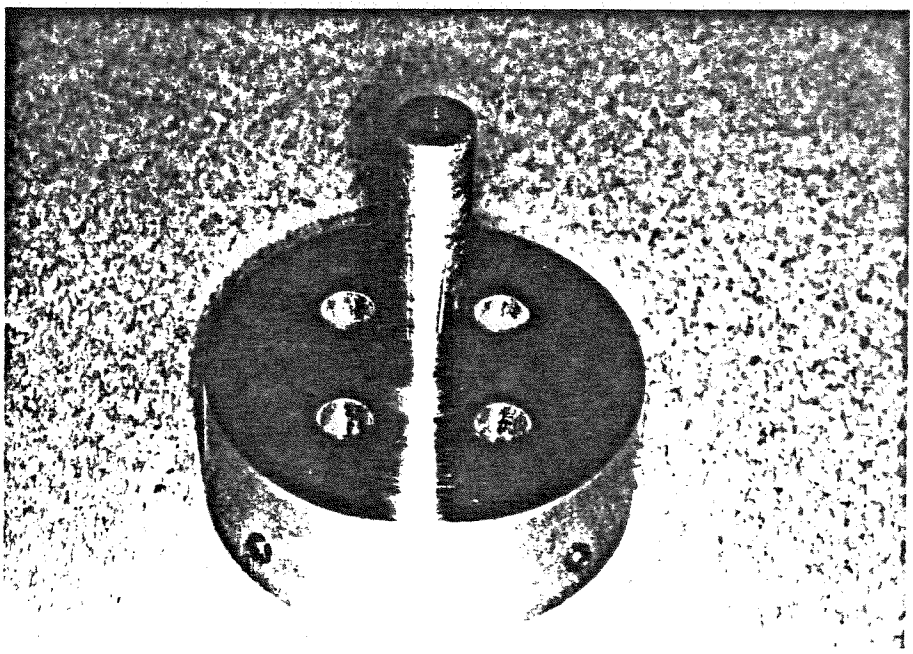


Figure 9: Coupon Facing Attachment

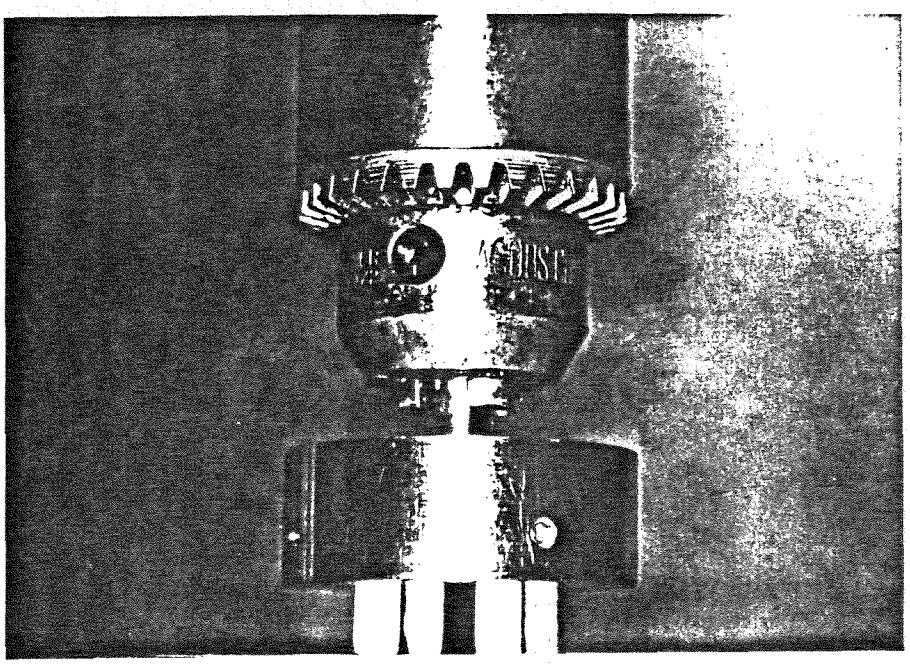


Figure 10: Coupons in Facing Attachment on Drill Press

[2] Coupons were sandblasted in order to roughen faces to ensure a surface for better wetting with the adhesive.

[3] After sandblasting, coupons were degreased (to remove all oil film) in petroleum ether for five minutes in an ultrasound machine. Then coupons were set on absorbent paper to dry.

[4] Once dried, coupons were put (using surgical gloves) into top (removable) portion of a stainless steel jig which had a six coupon capacity, and then sat them in a petrie dish half

full of an etching solution consisting of deionized water, sulfuric acid, and sodium dichromate. The coupons were put into this solution (face down) for eight minutes at a temperature of 35 degrees C. After eight minutes the coupons were taken out of the etching solution, and the faces were rinsed with distilled water, and the coupons were set to dry, or put in oven to dry.

[5] Once the coupons were dried and cooled, using surgical gloves and tweezers, rubber rings were slipped on from the bottom of the coupon upwards, until the rings were even with the coupon surface (face) (see Fig. 11). Coupons were placed with faces up into the jig (which created a rigid environment which enabled the forces of a 2 Kg weight to be evenly distributed) by numbers (coupons labelled # 1-6), on both the bottom half of the jig, and the upper (removable) portion. Both jig portions were kept seperated until the treated dentin slices were placed upon the coupons (procedure explained below). The upper part was closed upon the bottom part, a 2 Kg weight was placed on top, and samples sat for 30 minutes to one hour in the press.

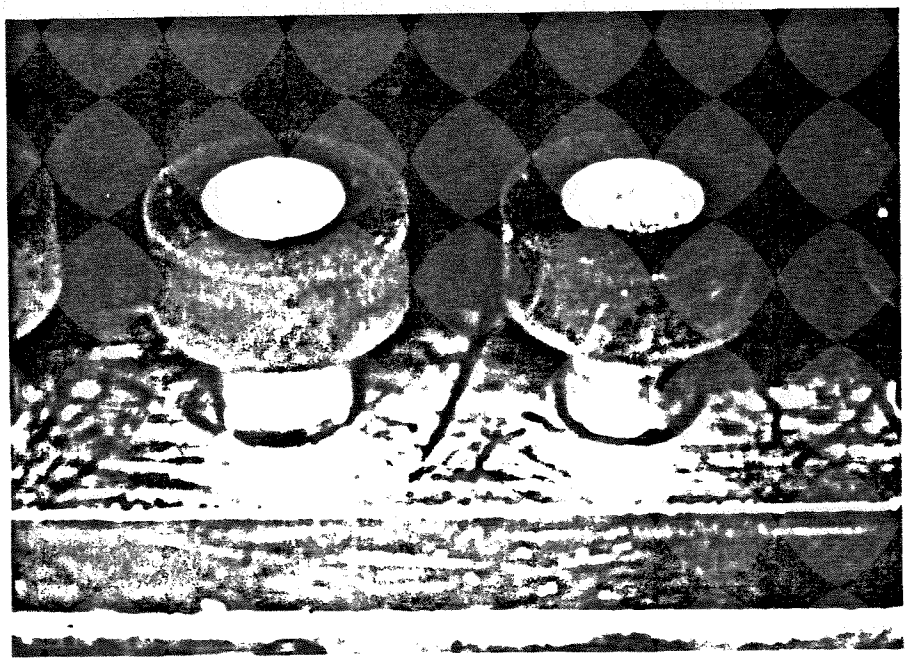


Figure 11: Coupons with Rubber Rings Attached

B. Dentin Slice Treatment

[1] Dentin slices were cut from intact, non-carious, third molars, using an Isomet diamond saw (see Figs. 12, 13). Slices were optimally around 400 . Slices were stored in distilled water until needed.

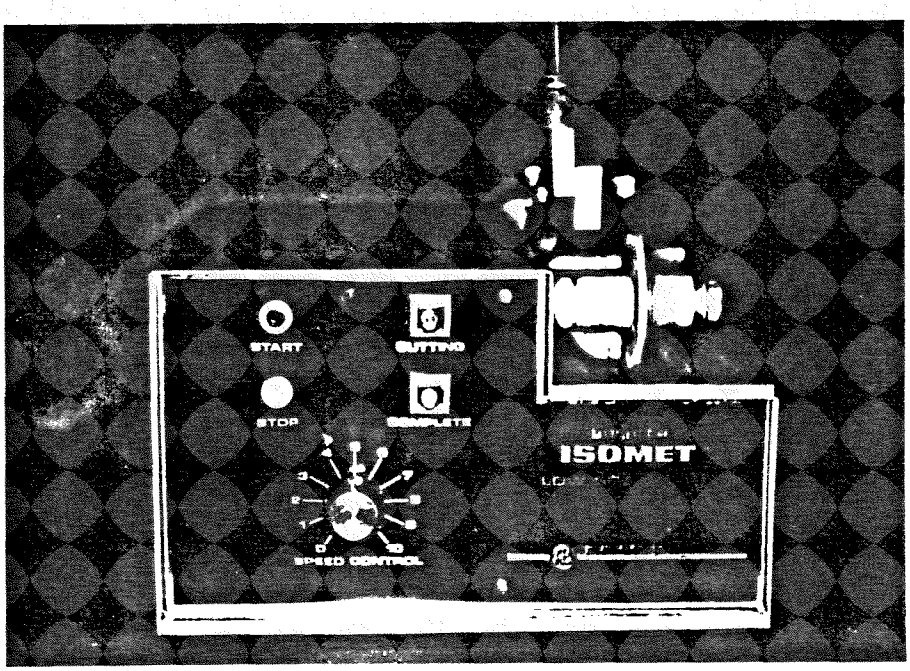


Figure 12: Isomet Diamond Saw

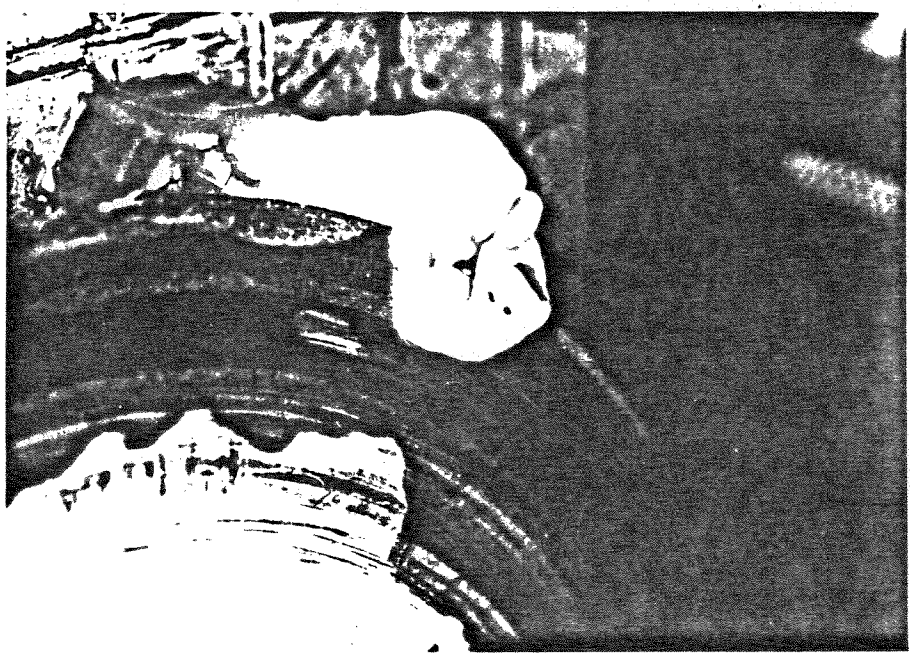


Figure 13: Tooth Being Sliced on Saw

[2] 1.5 grams of powdered monomer was measured and then mixed with 5 mL dimethoxyethane (DME) to create the monomer solution.

[3] Six slices were taken out of storage, and blotted dry on absorbent paper. They were then placed in a clean watchglass, and aqueous pre-treatment solution, (different from coupon etching solution, usually 5% citric acid was used) was poured on, and the slices were allowed to soak for two minutes. The

etchant was then decanted, and the slices were rinsed thoroughly with distilled water for thirty seconds.

[4] After the slices were rinsed, they were transported to another clean watchglass. DME was poured on and the slices soaked in it for two minutes. The DME was then decanted into a waste jar.

[5] While the slices were still wet with DME, the monomer solution was poured on them and they were allowed to soak for five minutes in it. The monomer solutionwas then decanted into a waste jar.

[6] Slices were then put in monomer drying stand to dry. The MMA-PMMA mixture was then made up in another watchglass (Explained in [7]), or if preferred, it could be made during the last 2 minutes that the slices are in the monomer solution and the copolymer could be put directly on the still "wet" slices. Generally the experimenters let the monomer dry, but this is an alternate method. It has not been established which technique is better.

[7] To make the MMA-PMMA mixture (copolymer), two grams of the 75% MMA - 25% PMMA solution were used, and to this 0.02 grams of BP and 10-12 drops of NN-DMPT were added. This

mixture is mechanically stirred until well mixed, (with each element stirred in separately), and placed onto the bottom coupons in the jig. This mixture was also placed on the teeth slices. If one is pressed for time (MMA-PMMA mixture starts thickening, just put this mixture on the slices alone.(The mixture usually polymerizes within two to eight minutes). Slices were then placed on bottom part of jig.

[8] The upper part of jig was closed upon the bottom part of jig, and then the two Kg weight was placed on top. Samples sat thirty minutes to one hour, depending upon how the samples polymerized and hardened (see Fig. 14).

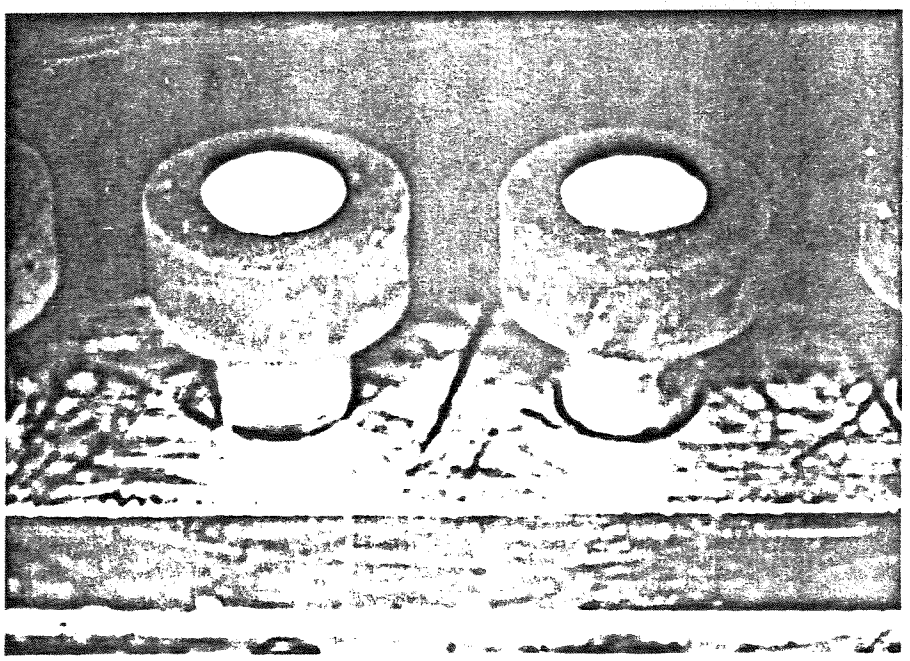


Figure 14: Finished Samples

APPENDIX I

Sample Calculations

In the course of the experiment, two different sets of calculations were used. The first set shown were used from the beginning of the experiment until 9/21/84 when the tension testing machine was recalibrated. After recalibration, a different set of calculations were used.

Calculations: First Set - Using Scott CRE/500 Tension Tester.

Full Load Scale = 250 Kg

50% Load Scale = 125 Kg

Full Load Volts = 0.700 mv

Area of Coupon = $\pi/4 \times (0.25)^2 = 0.049087$

Example:

$$\frac{125\ Kg}{0.700\ mV} = \frac{X\ Kg}{R\ mV}$$ WHERE R = DIGITAL READOUT

$$(125\ Kg)(R\ mv) = (X\ Kg)(0.700\ mV)$$

$$\frac{(125\ Kg)(R\ mV)}{0.700\ mV} = X\ Kg$$ TO CONVERT INTO POUNDS

$$(2.2) X\ Kg = Q\ LBS$$

$$\frac{Q\ LBS}{0.049087\ (AREA)} = \text{POUNDS/SQUARE INCH (Psi)}$$

Revised Calculations - Using Scott CRE/500

Full Load Scale = 500 lbs

50% Load Scale = 250 lbs

Full Load Volts = 0.700 mv

Area of Coupon = $\pi/4 \times (0.25)^2 = 0.049087$

Example:

$$\frac{250 \text{ LBS}}{0.700 \text{ MV}} = \frac{X \text{ LBS}}{R \text{ m.v}}$$ WHERE R = DIGITAL READOUT

$$(250 \text{ LBS})\, R \text{mv} = (0.700 \text{ mv})(X \text{ lbs})$$

$$\frac{(250 \text{ LBS})(R \text{mv})}{0.700 \text{ mv}} = X \text{ lbs.}$$

$$\frac{X \text{ Lbs}}{0.049087} = \text{PSI}$$

TABLE 1

o-methoxyphenol-TDI and HEMA

Group # 1 - Tannic Acid

70-30% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
336	168	930
"	"	407
"	"	704
"	"	272
"	"	898
"	"	128
"	"	309

AVG + S.D = 521 $\pm$ 321

TABLE 1

o-methoxyphenol-TDI and HEMA

Group # 2 - Ferric Oxalate

70-30% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
48	0	688
"	"	1001
"	"	1521

AVG + S.D = 1070 $\pm$ 421

TABLE 1

o-methoxyphenol-TDI and HEMA

Group # 3 - Ferric Oxalate

70-30% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
24	168	440
"	"	624
"	"	464
"	"	136
"	"	257
"	"	257
"	"	67
"	"	24
"	"	240
"	"	344
"	"	48

AVG + S.D = 264 $\pm$ 192

TABLE 1

o-methoxyphenol-TDI and HEMA

Group # 4 - Ferric Oxalate

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
24	168	96
"	"	128
"	"	200
"	"	176
"	"	88
"	"	120
"	"	432
"	"	24
"	"	368
"	"	1057
"	"	280
"	"	472
"	"	56

TABLE 1 - Group # 4, (cont.)

Dry (Hrs)	Wet (Hrs)	Psi
24	168	304
"	"	24
"	"	120
"	"	384
"	"	256
"	"	248
"	"	368
"	"	728
"	"	240
"	"	304

AVG + S.D = 281 ± 237

TABLE # 1

o-methoxyphenol-TDI and HEMA

Group # 5 - Ferric Oxalate

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
24	192	856
"	"	120
"	"	1665

AVG + S.D = 680 $\pm$ 497

TABLE 1

O-methoxyphenol-TDI and HEMA

Group # 6 - Citric Acid

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
168	0	784
"	"	976
"	"	576

AVG + S.D = 779 $\pm$ 198

TABLE 1

o-methoxyphenol-TDI and HEMA

Group # 7 - Citric Acid

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
48	0	2177
"	"	840
"	"	1304
"	"	1689
"	"	2337
"	"	1881

AVG + S.D = 1705 $\pm$ 578

TABLE 1

o-methoxyphenol-TDI and HEMA

Group # 8 - Citric Acid

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
48	96	136
"	"	600
"	"	1168
"	"	624
"	"	1889
"	"	408

AVG + S.D = 804 $\pm$ 630

TABLE 1

o-methoxyphenol-TDI and HEMA

Group # 9 - Citric Acid

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
24	168	960
"	"	1425
"	"	944
"	"	680
"	"	520

AVG + S.D = 906 $\pm$ 344

TABLE 2

o-chlorophenol-TDI and HEMA

Group # 1 - Citric Acid

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
72	0	1489
"	"	1521
"	"	1753
"	"	960
"	"	1697
"	"	2265

AVG + S.D = 1608 $\pm$ 421

TABLE 2

o-chlorophenol-TDI and HEMA

Group # 2 - Citric Acid

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
48	0	1024
"	"	1184
"	"	400
"	"	104
"	"	1497
"	"	784
"	"	1225
"	"	873
"	"	2255
"	"	1433
"	"	1044
"	"	1113
"	"	735

TABLE 2 - Group # 2 (Cont.)

Dry (Hrs)	Wet (Hrs)	Psi
48	0	2110
"	"	2197
"	"	1841
"	"	1164
"	"	1746
"	"	582
"	"	3201
"	"	1892
"	"	3420
"	"	3347
"	"	1906
"	"	713
"	"	1921

TABLE 2 - Group # 2 (Cont.)

Dry (Hrs)	Wet (Hrs)	Psi
48	0	4264
"	"	2098
"	"	3383
"	"	4205
"	"	3056
"	"	4416

AVG + S.D = 1910 $\pm$ 1184

TABLE 2

o-chlorophenol-TDI and HEMA

Group # 3 - Citric Acid

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
48	24	832
"	"	778
"	"	904
"	"	1040
"	"	640
"	"	816
"	"	1120
"	"	864
"	"	960
"	"	1233
"	"	888
"	"	1064
"	"	1192

TABLE 2 - Group # 3 (Cont.)

Dry (Hrs)	Wet (Hrs)	Psi
48	24	1112
"	"	1793
"	"	1433
"	"	840
"	"	1080
"	"	1324
"	"	589
"	"	1033
"	"	1281
"	"	1492
"	"	458
"	"	968

AVG + S.D = 1027 $\pm$ 299

TABLE 2

o-chlorophenol-TDI and HEMA

Group # 4 - Citric Acid

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
48	96	360
"	"	712
"	"	560
"	"	1112
"	"	976
"	"	480

AVG + S.D = 700 $\pm$ 293

TABLE 2

o-chlorophenol-TDI and HEMA

Group # 5 - Citric Acid

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
96	24	2793
"	"	3401
"	"	2401
"	"	928
"	"	2561
"	"	1969
"	"	1585
"	"	1793
"	"	1209
"	"	1257
"	"	680

AVG + S.D = 1871 $\pm$ 847

TABLE 2

o-chlorophenol-TDI and HEMA

Group # 6 - Citric Acid

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
96	168	313
"	"	211
"	"	349
"	"	335
"	"	669

AVG + S.D = 375 $\pm$ 173

TABLE 2

o-chlorophenol-TDI and HEMA

Group # 7 - Citric Acid

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
192	0	3660
"	"	5064
"	"	2998
"	"	3798
"	"	3565
"	"	3056

AVG + S.D = 3690 $\pm$ 748

TABLE 2

o-chlorophenol-TDI and HEMA

Group # 8 - Citric Acid

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
192	24	1564
"	"	2248
"	"	1601
"	"	1585
"	"	1040

AVG + S.D = 1608 $\pm$ 429

TABLE 2

o-chlorophenol-TDI and HEMA

Group # 9 - Citric Acid

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
24	24	1135
"	"	1091
"	"	1492
"	"	1761
"	"	684
"	"	1652
"	"	575
"	"	568
"	"	669
"	"	655
"	"	1019
"	"	764

TABLE 2 - Group # 9 (Cont.)

Dry (Hrs)	Wet (Hrs)	Psi
24	24	1746
"	"	2299
"	"	3049
"	"	2401
"	"	1979
"	"	437

AVG + S.D = 1332 $\pm$ 756

TABLE 2

o-chlorophenol-TDI and HEMA

Group # 10 - Citric Acid

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
0	48	1113
"	"	524
"	"	2117
"	"	2059
"	"	2394
"	"	815
"	"	989
"	"	2299
"	"	2437
"	"	1724

AVG + S.D = 1647 $\pm$ 721

TABLE 2

o-chlorophenol-TDI and HEMA

Group # 11 - Citric Acid

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
48	336	669
"	"	1259
"	"	1833

AVG + S.D = 1254 $\pm$ 582

TABLE 2

o-chlorophenol-TDI and HEMA

Group # 12 - Citric Acid

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
0	168	451
"	"	269
"	"	589
"	"	531
"	"	466
"	"	582
"	"	2175
"	"	706
"	"	677
"	"	2161
"	"	728
"	"	1244

TABLE 2 - Group # 12 (Cont.)

Dry (Hrs)	Wet (Hrs)	Psi
0	168	698
"	"	160
"	"	1528
"	"	1186
"	"	677
"	"	611
"	"	822
"	"	399
"	"	735
"	"	757

AVG + S.D = 825 $\pm$ 532

TABLE 2

o-chlorophenol-TDI and HEMA

Group # 13 - Citric Acid

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
0	336	182
"	"	240
"	"	226
"	"	146
"	"	771
"	"	182
"	"	124
"	"	392
"	"	829
"	"	109

AVG + S.D = 320 $\pm$ 265

TABLE 2

o-chlorophenol-TDI and HEMA

Group # 14 - Citric Acid

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
0	672	211
"	"	233
"	"	720
"	"	138

AVG + S.D = 326 $\pm$ 266

TABLE 3

pentaerythritol-TDI-HEMA and p-cresol

Group # 1 - Citric Acid

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
48	0	633
"	"	691
"	"	2277
"	"	1382
"	"	1193
"	"	575
"	"	975
"	"	1630
"	"	2139
"	"	1288
"	"	1783

AVG + S.D = 1324 $\pm$ 588

TABLE 3

pentaerythritol-TDI-HEMA and p-creaol

Group # 2 - Citric Acid

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
48	168	327
"	"	233
"	"	284
"	"	502
"	"	364
"	"	182
"	"	211
"	"	349

AVG + S.D = 307 $\pm$ 103

TABLE 3

pentaerythritol-TDI-HEMA and p-cresol

Group # 3 - Citric Acid

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
48	240	335
"	"	167
"	"	175
"	"	218

AVG + S.D = 224 $\pm$ 77

TABLE 3

pentaerythritol-TDI-HEMA and p-cresol

Group # 4 - Citric Acid

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
96	168	357
"	"	371
"	"	335
"	"	895
"	"	327
"	"	400

AVG + S.D = 448 $\pm$ 221

TABLE 3

pentaerythritol-TDI-HEMA and p-cresol

Group # 5 - Citric Acid

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
0	48	1783
"	"	1273
"	"	1288
"	"	1281
"	"	2270
"	"	1302
"	"	1426

AVG + S.D = 1408 $\pm$ 399

TABLE 3

pentaerythritol-TDI-HEMA and p-cresol

Group # 6 - Citric Acid

75-25% MMA-PMMA

Dry (Hrs)	Wet (Hrs)	Psi
48	336	982
"	"	1921
"	"	895

AVG + S.D = 1266 $\pm$ 569

TABLE 4

Aluminum Bonded to Aluminum

70-30% MMA-PMMA

Psi
2450
1880
2545
2401
2560
1552
2630
2872
2750
2790
2811

AVG + S.D = 2476 $\pm$ 412

TABLE 4

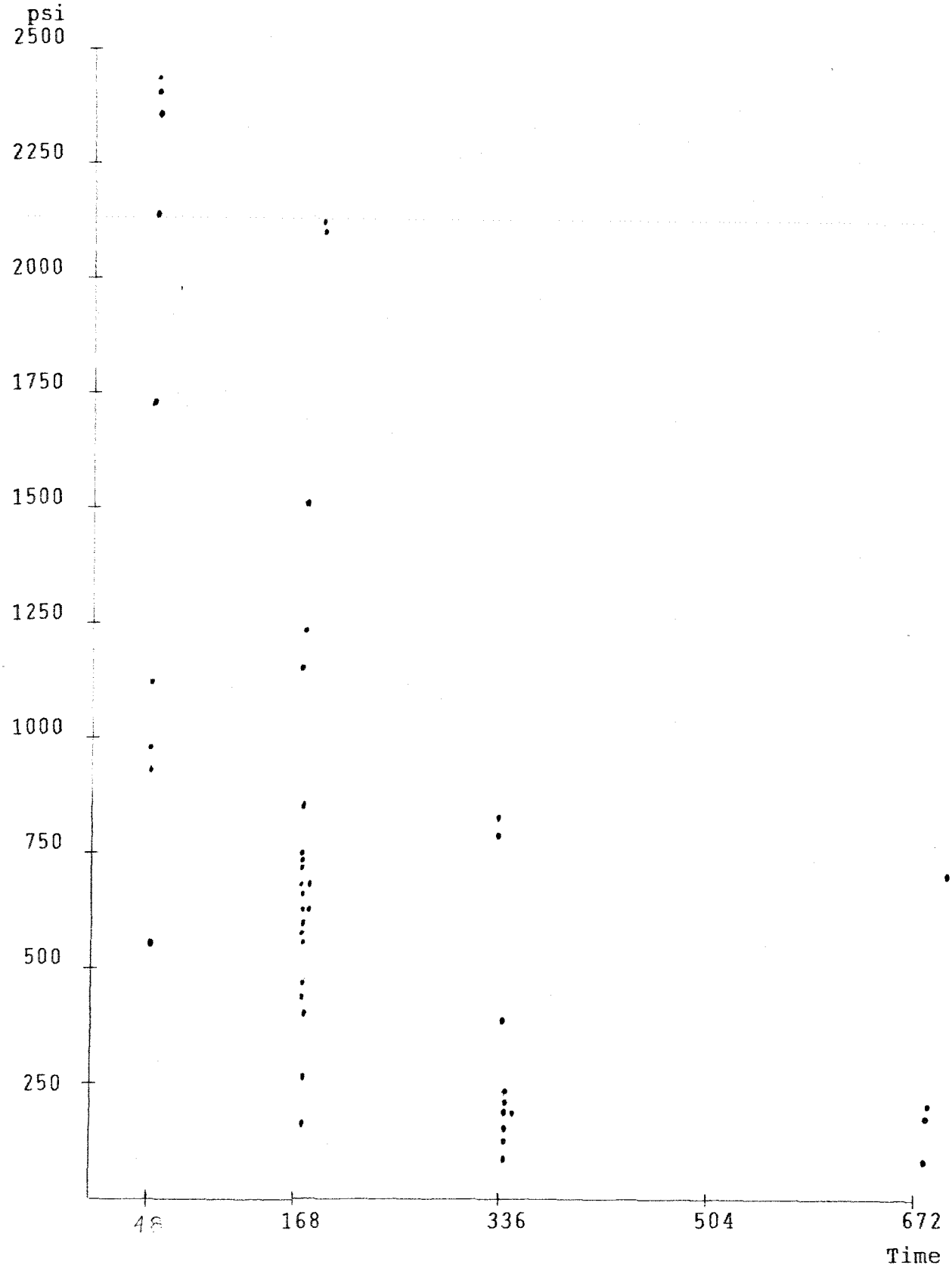
Aluminum Bonded to Aluminum

75-25% MMA-PMMA

Psi
2249
2513

AVG + S.D = 2381 $\pm$ 187

WATER DEGRADATION
o-chlorophenol monomer, 48, 168, 336, and 672 hours wet.
psi vs. time



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