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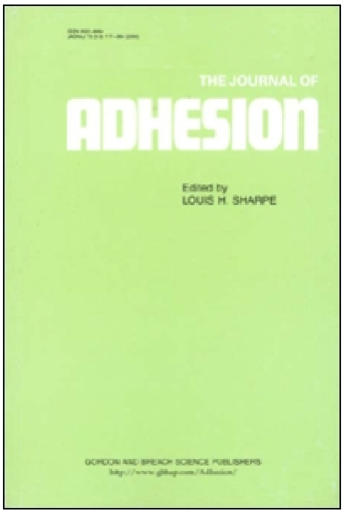

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The Evolution of a Polyurethane Dental Adhesive System

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The Evolution of a Polyurethane Dental Adhesive System

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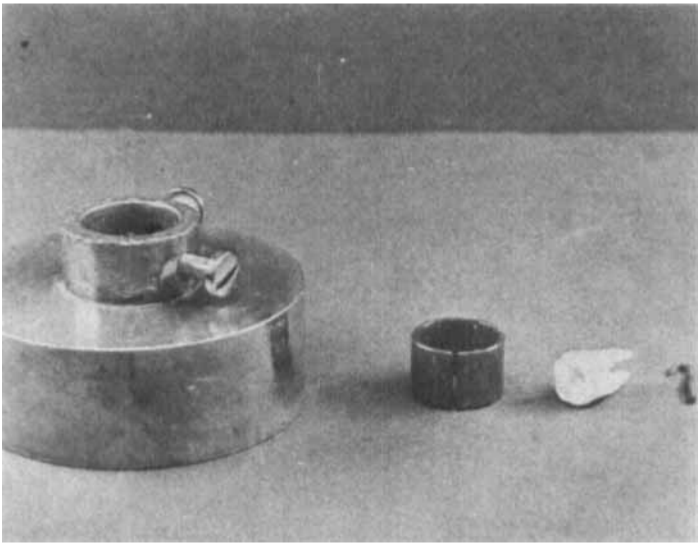
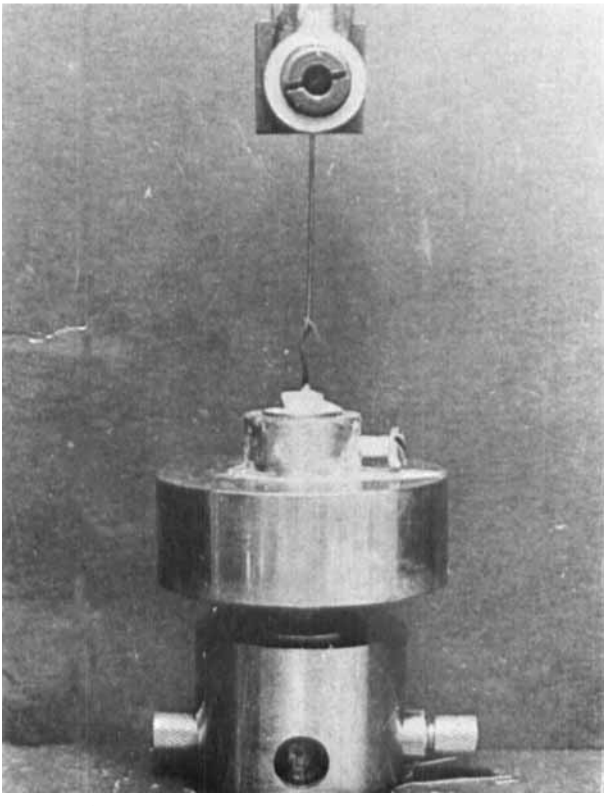
Screening of common adhesives showed that polyurethanes, as a class, to be most suitable for adhering to wet tooth tissue. The isocyanate groups in the adhesive may react with the tooth mineral; this view is supported by a number of approaches, including measuring γ_c at several humidities, which may be interpreted as showing tooth tissue surfaces to be rich in hydroxyl groups. The bonding of polyurethanes to enamel could be improved by pretreatments (including acid etching and acetone drying) and by proper choice of polyol, fillers, and coupling agents. From scanning electron micrographs the etching is interpreted to debride a weak boundary layer. The preferred formulation was a TiO_2-filled polyurethane formed from equal weights of castor oil and polymethylene polyphenyl isocyanate catalyzed by from $1\frac{1}{2}$ to 10% of tin octoate. Joints of teeth bonded with polyurethanes withstood long-term exposures to water and synthetic saliva and dental restorations in rabbits appeared to adapt well.

INTRODUCTION

Properly inserted, the dental restorative materials used today stay in place by mechanical interlocking in an undercut, rather than adhering "chemically"[1]. A truly adhesive dental restorative material has been sought for some years[2] as leading to reduced leakage around the joint margins and requiring less loss of healthy tooth tissue during preparation and insertion of the restoration. Many synthetic organic polymeric systems have been used and tested in dental research. In a recent review of this past work[3] it was pointed out why, at the present time, selected polyurethanes are the materials of choice for adhesives and are close to clinical trials. It is the purpose of this paper to present a conspectus of their development and a description of the tooth-adherend system.



(A) Components unassembled



(B) Components assembled on Instron tester

FIGURE 1 Tensile testing equipment

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The requirements for the application and performance of dental adhesives impose greater constraints than for other more familiar adhesive applications. Certainly, in no other technology is the designer of an adhesive joint similarly restricted to a medically acceptable, low temperature and fast setting, high strength adhesive, which at the time of application and over the long term must be resistant to water, oral enzymes, and the mechanical stresses of mastication. Dental adhesives are discussed here in the broad sense of means for making a bond between dentin or enamel and another member (which may be the adhesive itself), in a wet environment, no matter if the material is to be applied clinically as a total restoration, adhesive, or cavity liner.

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TEST METHODS

Two methods were used to test the joint strength of the dental adhesives. One is the butt joint test on flat bovine teeth sections described by Lee *et al.*[4], wherein the joint is formed between the tooth and an acrylic or steel rod. Results from this method are expressed here as stress (psi) to failure.

The second method was developed at our laboratory[5] and is a combination of features of several previously reported methods. The crown on a sound human bicuspid or molar is removed by grinding under water with successively finer silicon carbide papers. Then, a conical cavity is ground into the flat exposed dentin (with a 10S diamond dental bur) to an approximate size of 5 mm diameter by 2½ mm deep, without penetrating the pulp cavity. The cavity is filled with the formulation under test and a brass pin is inserted in the restoration to provide an attachment to the Instron crosshead.

The prepared tooth is mounted in a brass cylinder (as shown in Figure 1a) before inserting the restoration, and is held in place by filling the cylinder with dental stone (a form of gypsum, similar to plaster of Paris). Several notches are first ground in the root portion of the tooth with an abrasive disc to provide reentrant regions. These, along with the normal curvature of the root, provide a mechanical interlock to keep the tooth from pulling out of the non-adhesive dental stone. Figure 1b shows the mounted tooth on the Instron tester. The results from this test are expressed as force (lb) to failure.

Test results from both methods are reported for the average of 5 or more specimens after storing the joints for from 1 to 3 days under distilled water.

THE ADHEREND SURFACE

The exposed portion of most mammalian teeth consists of an outer layer of enamel, the hardest tissue in the body, composed almost entirely (ca. 97%)

of mineral, principally hydroxyapatite. At modest magnifications, enamel has a rod-like morphology[6], as shown in the scanning electron micrograph of a bovine tooth section in Figure 2.

Below the enamel layer of the tooth is the less hard dentin tissue which is composed of about 70% hydroxyapatite and about 30% organic material—a collagenous protein. The dentin portion contains minute tubules (ca. 3 μm diameter at the pulpal end in adult human teeth), inter-connected along their length, and extending down to the interior of the pulp portion of the tooth. It is through these tubules that the dentin is kept "alive" by fluid infusion from the pulp[7]. The morphology of the dentin is illustrated by the SEM photo of a bovine tooth section in Figure 3. It is only these two principal portions—the enamel and dentin—of the tooth which need concern us here.

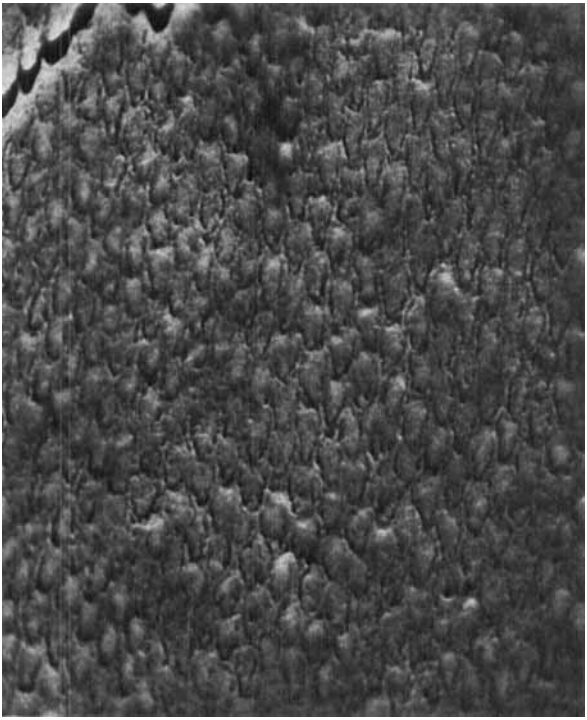

FIGURE 2 Bovine enamel, following acid etch
SEM magnification 2700×

The surfaces of dentin and enamel have received only minor attention in the literature. Uy and Chang[7] reported the critical surface tension (γ_c) of

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human and bovine teeth to range from 24 to 39.5 dyn/cm at 37°C, 100% rh and from 38 to 49 dyn/cm at 23°C, 50% rh. These surprisingly low values for a mineral substance are suggestive[3] of the effect of an adsorbed layer of water, similar to what has been observed on glass[8], quartz[9], and a protein[10]. This possibility was investigated by measuring γ_c of various tooth surfaces, as a function of relative humidity, in the following way.

FIGURE 3 Bovine dentin, following acid etch
SEM magnification 2700×

Bovine tooth chips were polished flat and mounted in a Plexiglass chamber on a contact angle goniometer. Dry tank air (dew point −62°C) was passed at a low and controlled flow rate through bubble columns containing saturated salt solutions, through a glass wool trap, then into the chamber, as a dynamic means to maintain constant rh. To approach 0% rh, the teeth were first dessicated over P_2O_5 (in vacuum) for 48 hours and P_2O_5 was included in the test chamber. (Under these conditions, the teeth crack and may have undergone irreversible changes.) The test liquids used for contact angle measurements are listed in Table I; they were chosen to cover the

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TABLE I

Liquids used for contact angle measurements

Liquid	γ_L[a]
octyl ether	27.3 dyn/cm
hexadecane	27.5
bicyclohexyl	30.0
isopropyl bicyclohexyl	30.9
1-methyl naphthalene	38.7
methylene iodide	49.7

[a] du Nouy method, 24°C, corr.

necessary range of surface tension while trying to avoid using hydrogen-bonding or pi-bonding liquids. (The liquids were percolated through silica gel and adsorption alumina and their surface tensions checked against literature values judged to be reliable, before use.) Values of γ_c were determined in the usual way[11] from a plot of the cosine of the contact angle against surface tension. (The plots for dentin showed more scatter than those for enamel, possibly due to capillary intrusion of the test liquid in the dentin tubules). The results are listed in Table II for tooth surfaces prepared by polishing to a high finish (visibly scratch free) and by polishing followed by acid etching. It has been reported that, at least under some circumstances, acid etching makes the tooth surfaces more wettable by water[7,12].

TABLE II

Critical surface tension of bovine tooth tissue at different relative humidities at 25°C

	γ_c, dyn/cm			
rh, %	Polished[a]		Etched[b]	
	dentin	enamel	dentin	enamel
0	—	—	25	25
12.0	26	26	27	27
33.2	33	32	—	—
53.4	—	—	27	29
97	30	27	27.5	27.5

[a] γ-alumina to a visibly high polish
[b] 50% aq. formic acid, 1 min.

At high rh γ_c is low, 27 to 30 dyn/cm. in general agreement with Uy and Chang[7] and consistent with the findings for other surfaces[8,9,10], which have

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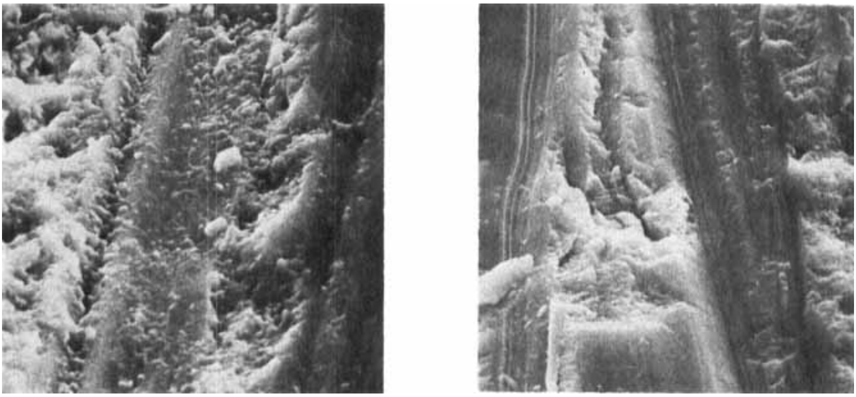
been interpreted as due to an adsorbed water layer. Surprisingly, also at low rh γ_c is low, not the expected high value for clean mineral surfaces. Extending the interpretation, we may speculate that even at low rh the surface of tooth tissue is rich in hydroxyl groups and/or firmly adsorbed water. Certainly, there are alternative interpretations of these γ_c measurements. One is that the dentin surface is mixed mineral and organic matter because of the high protein portion of dentin. Yet, enamel which has a low content of organic matter, shows essentially the same low γ_c value. Another is that the tooth surface has become contaminated with organic matter in the course of performing the measurements. This seems unlikely in that when the teeth were removed from the chamber they could be wet by water. The low values of γ_c reported here, measured in a particular way with carefully selected liquids, does not imply the surfaces are not wettable by hydrogen bonding liquids; this point has been discussed[8,9]. Earlier work has also shown that the contact angle of a polyethylene glycol (Carbowax 350, $\gamma_L = 44$ dyn/cm) is very near zero on a single crystal of hydroxyapatite[13].

Earlier work[14] showed the difficulty in displacing water from tooth surfaces by organic liquids. The possibility that such displacement may be through hydrogen bonding had been tested by measuring the shift in the ir hydroxyl stretch (3421 cm^{-1}) of hydroxyapatite when test liquids were mixed with the powdered mineral. Shifts of up to 38 cm^{-1} were recorded but no direct correlation with water displacement could be established. The few organic acids which displaced water from dentin and enamel surfaces and showed a large ir shift also have a high initial spreading coefficient against water[15], but the data are too incomplete to draw broad conclusions.

Another aspect of the adherend surface which must be considered is the possibility of formation of a weak boundary layer; when tooth substance is ground with dental burs the familiar surface anatomy is obscured by considerable debris when viewed with electron microscopes[16]. This can also be seen in Figure 4, showing scanning electron microscope (SEM) photos of bovine enamel, polished underwater with successively finer silicon carbide papers, and finally with γ-alumina, a fine particle size polishing agent. In no instance can the enamel anatomy be seen. If the surface is etched with weak acid (e.g. 25% aq. citric), the surface debris is removed; that is how the specimens shown in Figures 2 and 3 were prepared.

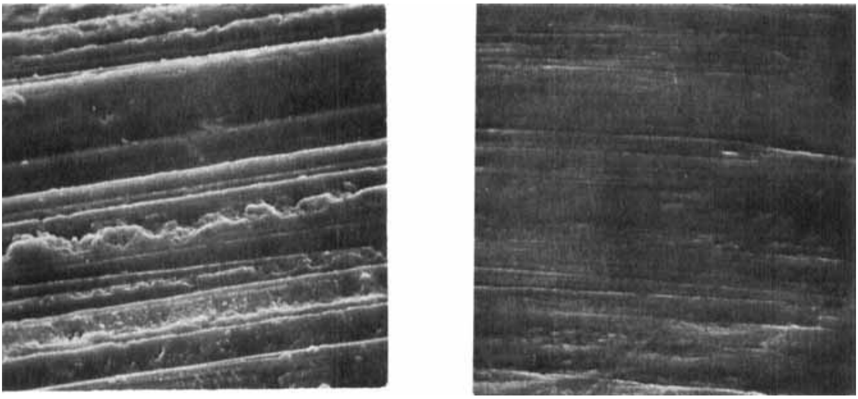
The use of acid etching to improve adhesion was reported in 1955[17]. Since the advent of the scanning electron microscope this effect may be interpreted as debridement of weak boundary layers. In a later section of this paper the large effect etching can have on the bond strength of polyurethane adhesives is discussed and illustrated. Also, at least in the case of dentin, it is possible to etch too far, as shown in Figure 5. Here, a good deal of the surface dentin tissue was removed, exposing the delicate tubular

FIGURE 4 Bovine enamel polished with various grades of abrasive



(A) 220 grit paper

(B) 400 grit paper



(C) 600 grit paper

(D) γ-Alumina

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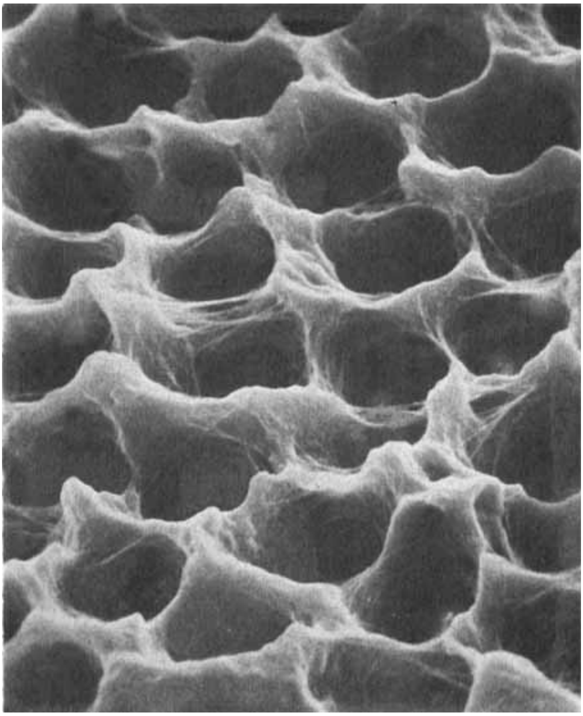

FIGURE 5 Etched bovine dentin showing extensive tissue destruction

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labyrinth structure. This surface, as an adherend, could have a weak boundary layer (there is insufficient mineral to support the load and it may be impossible to form the joint without included defects, such as air bubbles) and the joint shows low strength.

THE ADHESIVE

Polyurethanes evolved as materials of choice for dental adhesives in 1966[13]. Prior to that time, there had been a wide screening of many polymers on teeth[14] which showed that few types were satisfactory for achieving any sort of reasonable bond strength. As a class, the epoxies can be formulated to give reasonable bond strengths with tooth tissue, and be resistant to the wet oral environment, but not in a manner that is clinically acceptable[18].

The urethane polymers of interest are the condensation products between an aromatic isocyanate and an aliphatic polyol. With the current understanding of tooth surface chemistry it is not surprising that these materials evolved. Presumably, free isocyanate groups react with surface hydroxyls and/or trace water and in this way "dry" and/or "bond" to the surface. Thus, if the isocyanate is applied as a pretreatment, it should react with the adsorbed surface moisture (or moisture in the organic portion of the dentin) to form an integral polyurea and subsequent application of polyurethane mixtures could bond to this layer.

This concept of an isocyanate pretreatment, or reaction with the surface, was tested experimentally along with the refinement of rinsing the tooth surface with acetone immediately prior to such pretreatment to remove superficial water[5]. In one experimental series, a drilled cavity was rinsed twice with acetone, blown dry with a 30 second air blast, then filled with Nacconate 80 (a mixture of 80% 2,4-tolylene diisocyanate and 20% 2,6-tolylene diisocyanate) and let stand one hour. Following this, the excess isocyanate was blown out with air blasts, leaving a thin film; the polyurethane mix was then added. The effectiveness of this treatment in increasing the bond strength is shown in Table III. The pretreatment with acetone, followed by Nacconate 80, was superior to either acetone or Nacconate alone, or to no pretreatment at all.

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TABLE III

The effect of cavity pretreatments on the adhesion of polyurethane restorations[a]

Pretreatment	Avg. tensile force to failure
Acetone, then dried	8.0 lb
Acetone, then Nac. 80	13.4
Nacconate 80	8.0
None	5.9

[a] Nacconate 80/Pluracol P2010, 1/1, w/w, soaked in water 1 day before testing

Perhaps related to this effect, it has been observed that excess isocyanate is needed to achieve high bond strengths. For example, in the system tolylene diisocyanate—polypropylene glycol (Pluracol P 1800), maximum adhesion was found on polished dentin and enamel at an NCO/OH molar ratio of 10/1[13]. An optimum NCO/OH ratio of about 8/1 was found for the system Nacconate 80—castor oil, as shown in Table IV[5]. A similar result was recently reported for a urethane adhesive system with an optimum ratio of 4/1 for enamel and possibly higher for dentin, but it is not clear from the report which materials were used[19]. There is no apparent reason why each system seems to have a different optimum NCO/OH ratio.

TABLE IV

Joint strength of Nacconate 80–castor oil polyurethane restoratives at different NCO/OH ratios

Mole ratio NCO/OH	Qualitative nature on dentin flats	Joint strength lb
4/1	Tough	9.4
8/1	More brittle	12.7
20/1	Yet more brittle	2.9
40/1	Very brittle	4.7

The choice of isocyanate and polyol are important, as expected[13,19]. As an example, Table V lists the strengths of joints made using the polyurethane as a liner to cement a conventional dental acrylic restorative (essentially poly[methylmethacrylate]) to dentin[20]. Here, the isocyanate used was PAPI, polymethylene polyphenyl isocyanate (Upjohn).

TABLE V[22]

Joint strength of urethane lined acrylic restorations[a] (urethane liner[b])

Polyglycol	Joint strength, lb.
Polypropylene glycol[c] 1010	4.3
Polypropylene glycol[d] 2010	13.4
poly(ethylene-co-propylene) glycol[e]	6.6
Trimethylolpropane based polypropylene glycol[f]	8.9

[a] After testing, the joints were examined under the microscope. The failure was judged to be adhesive.

[b] Cross-linked with PAPI plus 0.01% tripropylamine; NCO/OH = 10/1

[c] Pluracol P-1010

[d] Pluracol 2010

[e] Pluronic L-101

[f] Pluracol TP-1540

After a screening of several polyols, generally the highest joint strengths were obtained with a polyurethane from castor oil (90% triglyceride of ricinoleic acid, 10% triglyceride of oleic acid) and PAPI, catalyzed with tin octoate. However, as discussed in the next section, the joint strength can be increased more by adjuvants, such as fillers, coupling agents, and etching, than by making small changes in the choice of reactants in the adhesive.

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JOINT STRENGTH ADJUVANTS

Several means have been proposed over the years for improving dental adhesives by bonding the adhesive chemically to the mineral or protein portion of teeth[3]. Some other suggestions, such as coupling agents, choice of filler, and acid and enzyme debridement, have been investigated along with polyurethanes.

The general improvement in adhesion due to coupling agents is well documented, including dental adhesion, with probably the first such use reported in 1961[21]. Urethanes offer the opportunity for several courses of reaction with the functional groups of a coupling agent. For example, some bifunctional compounds, which can be termed coupling agents in the broad sense of the words, have been used between a urethane adhesive and acrylic restorative[22]; some selected results are given in Table VI. The polyurethane was based on castor oil and PAPI and filled with TiO_2.

TABLE VI

Effect of coupling agents on adhesion of PMMA to formic acid treated bovine enamel

Amount coupling agent, phr[a]	Joint strength with coupling agents, psi			
	A[b]	B[b]	C[b]	D[b]
0	695	695	695	695
2	1270	1070	1160	1190
5	1125	1380	1000	1340

[a] Parts per 100 parts of resin, by weight

[b] A = 2-Hydroxyethyl methacrylate
B = 2-Hydroxypropyl methacrylate
C = 2-t-Butylaminoethyl methacrylate
D = 1,3-Di(allyloxy)-2-hydroxymethylpropane

The PMMA (poly[methylmethacrylate]) was applied as a preformed rod wetted with monomer, to simulate an acrylic restorative. The coupling agents were chosen to contain moieties reactive with both the acrylic and urethane polymers on polymerization. The coupling agents were mixed in the polyurethane before applying and curing and their effect was to nearly double the joint strength of the cured system. Silane coupling agents have also been used with polyurethane dental adhesives[19].

The PAPI–castor oil polyurethane adhesives may be further improved by incorporation of particulate fillers[22,23]; Table VII shows some representative data for TDI and PAPI cured castor oil adhesives. There does not appear to be a chemical rationale behind the effects of the various fillers and many of the same materials do not increase the joint strength if the castor oil is cross-linked with tolylene diisocyanate.

TABLE VII

Effect of fillers on the joint strength of two castor oil polyurethanes

Filler	Conc., phr[a]	Joint streangth, lbs.	
		Nacconate 80[b]	PAPI[c]
None	—	12.7	7.3
ZnO, USP	50	5.9	12.4
	100	4.2	19.1
TiO_2, reagent grade[d]	50	5.5	17.6
	100	15.0	25.2
Super Floss[e]	50	16.1	17.8
Snow Floss[f]	37	14.1	26.7
Adsorption Alumina[g]	50	4.9	31.1
ZrO_2, electronic grade[h]	100	—	10
	150	—	9
Asbestos, crude[i]	12.5	—	14
	25	—	15

[a] Parts of filler per 100 parts resin, by weight.
[b] NCO/OH = 7/1
[c] NCO/OH = 5/1
[d] Fisher Scientific Co.
[e] Dessicated diatomaceous earth, Johns Manville
[f] Hydrated diatomaceous earth, Johns Manville
[g] Fisher Scientific Co.
[h] Harshaw Chemical Co.
[i] Raybestos–Manhattan

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The effect of acid etching the dental tissue to debride the surface was mentioned earlier. Some selected results are given in Table VIII illustrating the general improvement in bond strength. The effect of etching is much

TABLE VIII

Adhesion of filled PAPI–castor oil resin to citric acid treated bovine enamel

Treatment time, min	Joint strength	
	25% aq. acid	50% aq. acid
0	410 psi	410 psi
0.5	940	1420
1	1230	1360
5	970	1410

greater on enamel than on dentin consistent with the general observation that the joint strengths of polyurethanes, and other materials, are always higher to enamel than dentin.

The reasons for generally lower joint strength with dentin, compared to enamel, are obscure but may be related to the substantial protein portion in dentin. Conceivably, if the protein could also be etched away, bonding would be to the hydroxyl-rich mineral surface. This concept was tested by denaturing the protein with concentrated aqueous urea solutions before bonding (which had no effect) and by removing the protein with enzymes.

The collagen in polished or acid-etched dentin surfaces can be detected by staining with van Gieson's reagent, a histological stain of aqueous fuchsin and picric acid[24]. Bovine dentin sections were exposed to solutions of various proteolytic enzymes until some were found which gave a negative stain for collagen within a reasonable time. Some of the surfaces were first acid etched, others polished before enzyme treatment and subsequent bonding with a polyurethane. The effect of the enzyme was generally negative, as shown in Table IX, in that the treatment lowered the joint strengths in spite of protein removal. A possible reason for this is shown in Figure 6, SEM photos of dentin surfaces before and after enzyme treatment. Enzyme treatment by itself, without prior acid etching, leaves a "dirty" surface. Enzyme treatment after acid etching disturbs the dentin morphology. (Compare Figure 6C with 3.) Both these results, and those from a study of acid etching, indicate that any treatment which disturbs the natural morphology of the tooth surface results in a lower joint strength. The reasons for the generally lower joint strengths with dentin are still speculative.

TABLE IX

Effect of enzymes on adhesion to bovine dentin

Treatment	Joint strength psi
10 min. collagenase	250
acid etch; 10 min. collagenase	96
30 min. collagenase	190
acid etch; 30 min. collagenase	120
24 hr. collagenase	140
acid etch; 24 hr. collagenase	130
5 min. papain	450
acid etch; 5 min. papain	190
20 min. papain	200
acid etch; 20 min. papain	380
acid etch only	440

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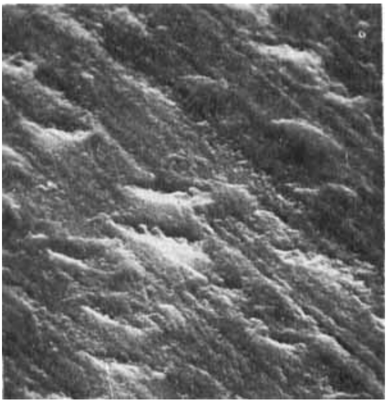
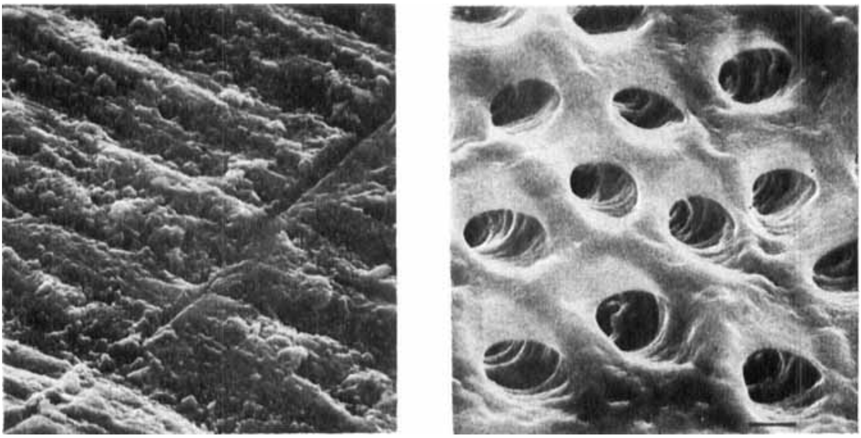
FIGURE 6 Collagenase treatment of bovine dentin



(A) Polished: no enzyme treatment



(B) Polished; enzyme-treated

(C) Polished, etched, enzyme-treated

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PREFERRED ADHESIVE SYSTEM

The preferred adhesive is equal by weight PAPI and castor oil (NCO/OH = 2 5:1) with from 100 to 150 parts by weight TiO_2 filler per 100 parts of this resin mix, catalyzed with from 1:1.5 to 10% of its weight of tin octoate. Over this range of catalyst concentration the cure time (time to dimensional stability) will range from 30 minutes (at the low catalyst concentration) to 5 minutes (at the high). Further cure to a hard, rigid, mass will take place slowly thereafter, but will, for all intents and purposes, be complete after 10–15 minutes with the higher catalyst concentrations. (These times are within current clinical practice.)

The adhesive is mixed and handled as a two component package. Generally, the TiO_2 (reagent grade) is dispersed in the castor oil—catalyst mix on a 3-roll paint mill. To a weighed portion of this paste is added a weighed portion of PAPI. (Alternatively, some of the TiO_2 could be dispersed in the PAPI.) The two components are easily mixed with a spatula, on a flat surface.

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THE JOINT SYSTEM

The PAPI–castor oil polyurethane, filled with TiO_2, and applied to acid etched teeth, shows a joint strength of about 1400 psi, which is a high value for a dental adhesive using the butt joint test. Conceivably, this value could be increased by approaches such as by the use of coupling agents, isocyanate pretreatment, or further studies of fillers, etc. Yet, before such refinements are investigated, there are three basic questions which should be answered: (1) Can the joints withstand the wet oral environment over the long term? (2) Does the polyurethane adhere to dental tissue *in vivo*? (3) Are the joint strengths high enough for the intended end use application?

The first question, whether the joint can withstand the wet oral environment, is answered partly in that all of the joint pulls reported here were after at least 1 day, and usually after 3 days soaking in distilled water. In addition, from time to time, joints of a particular adhesive were stored for an extended period of time under water and specimens were tested at intervals. Table X lists results from such an experiment for Nacconate 80–Pluracol polyether-based urethanes stored up to one year under distilled water. There is essentially no loss in strength.

As an additional check, joints formed from the preferred castor oil–PAPI–TiO_2 adhesive mixture were stored in synthetic saliva prepared according to Ref. 25. After three weeks at room temperature, joint strength against enamel were essentially unchanged (ca. 90% of their original value)

TABLE X

Effect of water storage on polyurethane restorations

	Joint strength			
	N-80[a] + P1010		N-80 + P2010	
Storage time[b]	Pretreated	Not treated	Pretreated	Not treated
1 wk	9.3 lb	9.2 lb	11.6 lb	10.6 lb
2	9.2	8.7	11.7	10.1
4	9.2	8.6	11.8	9.8
13	9.8	8.1	12.4	11.0
52	—	—	11.6	10.8

[a] N-80 is Nacconate 80 with the designated Pluracol. Pretreatment was rinsing the cavity with acetone, blown-dry, then N-80 for 1 hr before filling.

[b] Stored under water at room temperature.

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but those against dentin fell to 53% of their original value. Because these results may indicate the polyester is degrading (hydrolyzing) during the three week storage, two additional checks were made. In one, small cylinders ($\frac{1}{8}''$ diameter x $\frac{1}{4}''$ high) of this polyurethane were cast and their compressional moduli measured by loading to 550 g in an Instron and permitting the cylinder to recover. (There is full recovery at this load.) Then, samples were stored in air, distilled water, and fresh human saliva (changed twice daily). Over 35 days storage there was a small, but significant *increase* in compressional modulus (e.g. from 20,000 to 26,000 psi for the samples in saliva).

As a more aggressive check on the stability of the preferred castor oil-based polyester formulation, the accelerated storage method of Gehimer and Nieski[26] was used, a method developed to test the stability of urethane potting compounds. Cast discs ($\frac{1}{4}$ x 2 inches diameter) were stored for up to 35 days at 100°C, 95% rh, by placing them in a dessicator over saturated K_2SO_4, placed in an oven. The changes in mechanical properties were followed by measuring the Shore D hardness; the results are shown in Table XI. Although the samples discolored, the changes in hardness were small, unlike the results reported by Gehimer[26] for an unfilled castor oil-based urethane of undisclosed isocyanate and NCO/OH ratio. From all of the stability results, we judge the filled urethane restorative should be stable over the long run and suitable as a dental material.

The question of whether the polyurethane will adhere *in vivo* was examined by inserting the restoratives in suitably prepared rabbits' incisors. New Zealand white rabbits (adults, 2 to $2\frac{1}{2}$ lbs.) were anaesthesized (Nembutal, iv), and a cavity drilled in each of their four front incisors close to the gum line.

TABLE XI

Change in Shore hardness of polyurethanes[a] stored at 100°C, 95% rh

Parts by wt. TiO_2 per 100 parts resin[a]	Shore (*D*) Hardness, day				
	0	3	10	21	35
0	23	89	86	84	85
100	82	98	96	95	90
150	92	98	97	92	92

[a] PAPI–castor oil, NCO/OH = 2.5, catalyzed with tin octoate.

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A spherical dental bur was used to prepare a hemispherical cavity to avoid any possibility of undercutting. The cavities were etched with 25% aqueous citric acid for one minute, rinsed, blown dry, and the preferred polyurethane mix was inserted. Within 10 minutes the composition had set sufficiently that it could be carved. Figure 7 shows the restorations on day 1; Figure 8 shows the restorations on day 7. (The animals were kept on a normal diet of laboratory rabbit pellets and water *ad lib.*) The front incisors of a rabbit grow; when the restorations reached near the tooth edge (7–16 days) the animals were sacrificed. In no case were any restoratives lost due to adhesive failure. After sacrifice the teeth were cross-sectioned and the bond line inspected. In every case, adaptation was good with no evidence of leakage at the bond line. Indeed, using an *in vitro* marginal leakage test[27], similar restorations in extracted human teeth withstood 30 cycles of temperature cycling (0° to 50°C, 1 minute at each temperature followed by 1 month under water at room temperature) with no evidence of leakage of a Victoria Blue dye solution around the margins for 5 of 7 specimens tested. The other 2 showed only slight dye infusion.

Figures 7 and 8 show some surface defects in the restorations, possibly due to gas bubbles. These same defects can be seen in the bulk if a restoration is sectioned. The defects can be reduced by keeping all ingredients dry before mixing and use. The bubbles can be further reduced by curing the urethane under confinement, such as from a matrix band.

The limited experiments with rabbits showed that the polyurethane cross-linked and adhered for the duration of the experiment under these *in vivo* conditions. Further, the polyurethane adapted well to the joint margins and the restorations withstood the stresses of mastication for the periods of the experiments. The polyurethane could be inserted under conditions approaching a clinical situation, although, the bubble formation was clearly evident and this is judged a negative. The results of these *in vivo* experiments have no further significance; because they are of limited duration, until the

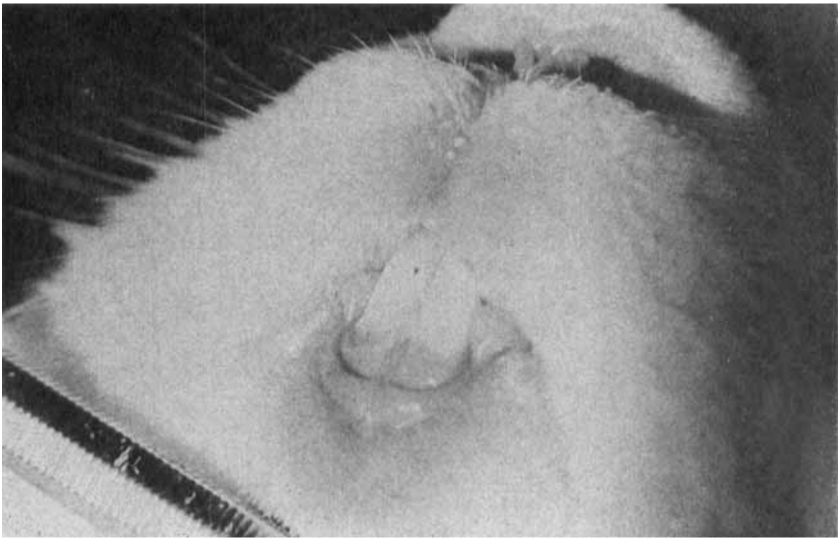

FIGURE 7 Adhesive polyurethane restorations in hemispherical cavities in rabbit incisors—first day

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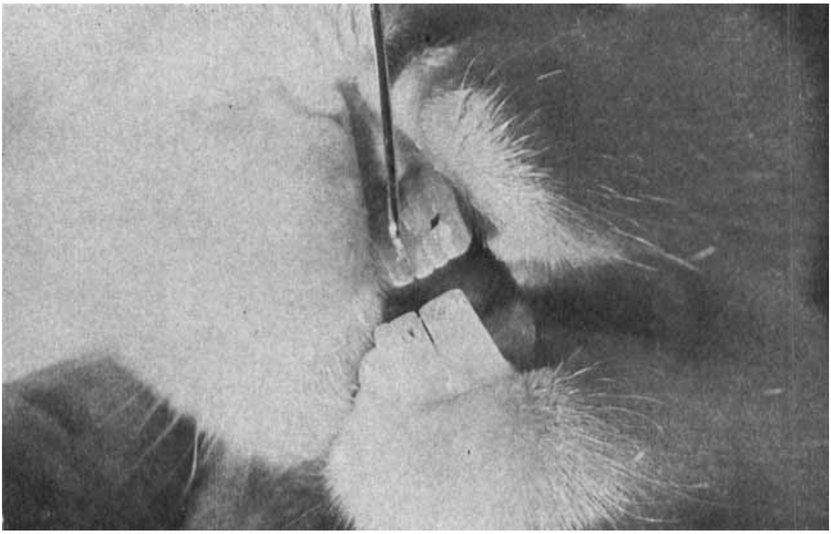

FIGURE 8 Adhesive polyurethane restorations in hemispherical cavities in rabbit incisors—seventh day

rabbits' teeth grow too long, it may be possible that other candidates restorative materials would perform as well under the same conditions. Of course, it would have been beneficial to insert another material as a control. However, commonly used dental filling materials, such as the acrylics, shrink and fall out of hemispherical cavities almost as soon as they are inserted.

The final question concerning the joint system, whether the strengths are high enough for use in the human mouth, is answerable only by suitable clinical trials. The development of a polyurethane adhesive described here has been undertaken by another laboratory[19]; they describe use of a polyurethane cavity liner in dogs' mouths and use of a polybutadiene diol-based polyurethane as a sealant for pits and fissures in otherwise sound teeth. More clinical work is needed, as with any medical or prosthetic device.

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