Fissure Sealants

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Synopsis

The adhesive bonding of a fast-setting system consisting of three different monomers to etched human enamel surfaces was investigated. Combinations of MMA, methacrylic acid, and adducts of glycidyl methacrylate and p-substituted phenols have been employed. Best results were obtained with hydrogen or t-butyl-substituted phenols. It is shown that a well-chosen three-component system has the advantage of a very low initial viscosity and fast setup times over two-component systems. Various com-. positions of three-component systems were studied. The maximum bond strength between enamel surfaces and the polymer was 80 kg/cm². Setup times as well as in vivo setup times are reported.

INTRODUCTION

The purpose of this study is to develop and evaluate a resin system that would serve as a sealant of pits and fissures for caries prevention. The aim of an occlusal sealant is to provide a physical barrier against carious invasion by isolating the underlying pits and fissures from the oral environment. The characteristics of a material satisfactory for clinical application are manifold. Briefly stated, the main requirements are a satisfactory adhesion to enamel, a setting time of a few minutes practical for operating room conditions and patient comfort, a very low initial viscosity to ensure penetration in the hard tissue, a small polymerization shrinkage, lack of toxicity, and resistance to mouth fluids.

Presently, there is no known material capable of forming a permanent bond with untreated enamel surfaces. Several authors,[1-5] however have showed that satisfactory bonding can be achieved after etching. It is therefore essential to understand the relationship between the various adhesives and the etched enamel surfaces.

The objectives of this investigation were directed toward two points: (1) the screening of a three-component system based on MMA, methacrylic acid, and the adduct of glycidyl methacrylate and a p-substituted phenol; (2) to obtain an improved adhesion to enamel by using a very low initial viscosity combined with a short setting time.

DISCUSSION

The molecular forces involved in the adhesion of polymers to enamel may be divided into two classes, physical and chemical. Of special interest, of

course, is a real chemical bond between polymers and the main component
of enamel, the hydroxyapatite. On the other hand the results of many
authors[4,6−8] suggest that mechanical retention still plays a role in the bond-
ing of adhesives to enamel surfaces. The penetration of adhesive material
into the enamel pores appears to be very important to the ultimate reten-
tion.

Briefly stated, the main requirements for an adhesive satisfactory for a
clinical application are: sufficient adhesiveness to the enamel, resistance
to mouth fluids, a setting time practical for the operating room conditions
and patient comfort, lack of toxicity, small coefficient of expansion, and a
limited water sorption.

From the requirements stated above, two parameters seem to be the
most important: e.g., a short setting time to make the adhesive clinical
applicable and a very low initial viscosity. The last point is essential
both for chemical and physical bonding.

In recent years, a large number of adhesives based on acrylics for dental
applications have been developed.[9−11] These sealants are based on a bis-
GMA resin, the reaction product of bisphenol A and glycidyl methacrylate.
The disadvantage of this system is a relative high viscosity combined with
a considerable setting time. A short setting time can be achieved when
UV light is used to initiate the reaction.

In this investigation, an adhesive system consisting of three components
was employed to obtain both a very low initial viscosity and a short (practi-
cal) setting time.

COMPOSITION AND PROPERTIES OF THE ADHESIVES

As stated above, a sealant must have an initial viscosity as low as pos-
sible, while the polymerization should take place within a short time. This
can be achieved by combining three different types of monomers: (a)
MMA or another ester of methacrylic or acrylic acid, e.g.,
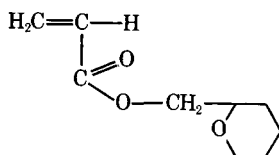
(b) methacrylic or acrylic acid, and (c) the adduct of glycidylmethacrylate
and phenol or a p-substituted phenol,
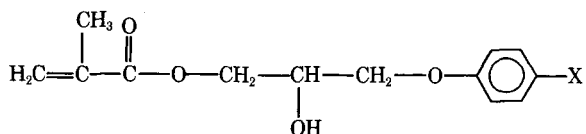
where X should be H or a t-butyl group. The type of monomer mentioned
in (c) resembles the bifunctional monomer used by Bowen et al.,[12] pre-

pared by condensation of bisphenol A and glycidyl methacrylate. It is well known that the monomer used by Bowen et al. is very difficult to prepare in a pure state and can be isolated only as a viscous liquid with some degree of polymerization.[13]

The advantage of the monomers described under (c) is that they can be prepared without unwanted polymerization taking place, leading to a well-defined product. The use of the three pure components enables us to prepare sealants with a considerable lower initial viscosity than with the Bowen system. Compositions and properties of the adhesives prepared by using the monomers mentioned above are listed in Table I. As shown in the table, a really fast-setting adhesive can be obtained only when at least one representative of (a), (b), or (c) is present in the monomer mixture. The composition of the mixture dose not only influence the polymerization time but influences the bond strength to the enamel surface as well. Best results have been obtained using the adduct of glycidyl methacrylate and p-t-butylphenol.

Adhesives containing the adduct of glycidyl methacrylate and p-nitrophenol polymerize very slowly and therefore do not meet the requirements mentioned. The adduct of glycidyl methacrylate and p-aminophenol was difficult to prepare in a pure state. We have not been able to separate this monomer from the red-colored side products. It was cancelled, therefore.

The behavior of glycol monomethacrylate is very peculiar. Adhesives with this compound present polymerize very fast in polyethylene test tubes; on the other hand, they do not polymerize at all on the enamel surfaces. The polymerization properties of adhesives containing glycol monomethacrylate in the presence of hydroxyapatite will be investigated in more detail.

Little information is available about the desired dynamic-mechanical properties of sealants from a clinical point of view. We believe that a polymer used for sealing pits and fissures should have a slightly rubbery character. The rubbery character favors the possibility of absorbing energy by the polymer. The character of the bond strength between enamel surfaces and the polymers might be due to chemical bonding, mechanical retention, or a combination of both. For both, the penetration of the polymerizing mixture in the enamel surface is essential. We therefore believe that not only the chemical nature of the monomers but also the polymerization speed and the viscosity change during polymerization are important factors to investigate. A kinetic study on this subject is in progress.

EXPERIMENTAL

Preparation of Monomers

The adducts of the phenol derivatives with glycidyl methacrylate were prepared in xylene with NaOH as catalyst in a nitrogen atmosphere.[14] Best results were obtained when glycidyl methacrylate was added to the

TABLE I
Monomer Composition and Properties of Adhesives[a]

Adduct of glycidyl methacrylate and phenol derivative		MMA, wt-%	Methacrylic acid, wt-%	Tetrahydropyran-2-methanol-acrylate, wt-%	Setup time in test tube, min	Setup time in fissure, min	Tensile strength, kg/cm²	Linear polymerization shrinkage, %
Structure	wt-%							
$CH_2{=}C(CH_3){-}CO{-}O{-}CH_2{-}CH(OH){-}CH_2{-}O{-}C_6H_4{-}C(CH_3)_2{-}CH_3$	0	90	10	0	>10			
$CH_2{=}C(CH_3){-}CO{-}O{-}CH_2{-}CH(OH){-}CH_2{-}O{-}C_6H_4{-}C(CH_3)_2{-}CH_3$	40	60	0	0	5.5			
$CH_2{=}C(CH_3){-}CO{-}O{-}CH_2{-}CH(OH){-}CH_2{-}O{-}C_6H_4{-}C(CH_3)_2{-}CH_3$	60	40	0	0	3[b]	>15	27	
$CH_2{=}C(CH_3){-}CO{-}O{-}CH_2{-}CH(OH){-}CH_2{-}O{-}C_6H_4{-}C(CH_3)_2{-}CH_3$	50	45	5	0	1.3	10	56	1.5

Structure							
$CH_2=C(CH_3)-C(=O)-O-CH_2-CH(OH)-CH_2-O-C_6H_4-C(CH_3)_2-CH_3$	50	40	10	0	0.9	4	71	1.3
$CH_2=C(CH_3)-C(=O)-O-CH_2-CH(OH)-CH_2-O-C_6H_4-C(CH_3)_2-CH_3$	50	20	10	20	0.2	1.5	80
$CH_2=C(CH_3)-C(=O)-O-CH_2-CH(OH)-CH_2-O-C_6H_4-C(CH_3)_2-CH_3$	50	30	10	10	0.5	3	50
$CH_2=C(CH_3)-C(=O)-O-CH_2-CH(OH)-CH_2-O-C_6H_5$	50	40	10	0	2.5	>10	50
$CH_2=C(CH_3)-C(=O)-O-CH_2-CH(OH)-CH_2-O-C_6H_4-NO_2$	50	40	10	0	>24 hrs		
$CH_2=C(CH_3)-C(=O)-O-CH_2-CH_2-OH$	50	45	5	0	0.2	does not polymerize	

a All adhesives were polymerized with benzoylperoxide (1% by weight) and N,N-dimethyl-p-toluidine (3% by weight).

b Setup adhesive had a rubbery character.

Fig. 1. Enamel surface after etch of 30 sec with a solution of 50 wt-% H_3PO_4 and 8 wt-% ZnO.   Magnification 800×.

phenol solution at 80°C, keeping the reaction mixture at this temperature for 15 min followed by heating the mixture to 120°C for 1 hr.

The acrylates of tetrahydropyran-2-methanol and 3-phenylpropanol-1 were prepared by heating a solution of the alcohol of 30% by weight to 80°C in a nitrogen atmosphere followed by adding an equimolar quantity of acrylic acid chloride over a period of 30 min.   After heating the reaction mixture to 90°C for another period of 30 min, the mixture was distilled. The other monomer types, the initiator, the accelerator were obtained commercially (Merck Ltd., Darmstadt).   Vinyl compounds were purified by extraction and/or distillation.

Preparation of Adhesives

Adhesives were prepared by mixing the given amounts of monomers. For an easy recognition of the adhesives in the fissures, pigment can be added.   (For instance, Echt Rot, Hoechst Ltd.)   Polyethylene test tubes fitting in an amalgam mixer were used for small-scale testing.   Before the test, $1/2$ g adhesive and 5 mg benzoylperoxide were mixed in the mixer mentioned for 30 sec in order to dissolve the benzoylperoxide.   Sub-
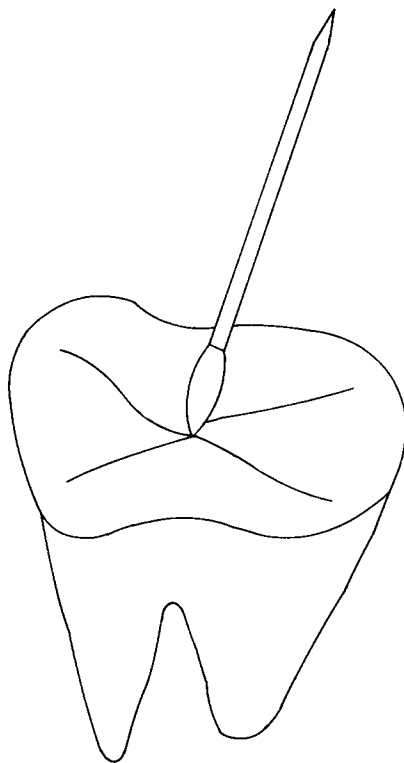
Fig. 2. Application procedure. Due to the low viscosity, a gentle touch of the fissures is sufficient.

sequently, 15 mg N,N-dimethyl-p-toluidine was added to accelerate the polymerization. After the addition of the accelerator, the adhesive should be used as soon as possible.

Estimation of Setup Times

In order to estimate the setup time of an adhesive in a test tube, a bent stainless-steel wire was put in the polymerizing mixture. The setup time was taken as the time when the hardened adhesive could be removed from the test tube by means of the wire. For estimation of the in vivo setup time in the fissures, the adhesive was applicated on etched, third molars free of tooth decay. By using an explorer, the in vivo setup time was estimated. The last-mentioned parameter is very important when the adhesive is to be used in practice; a patient can be released when the last-mentioned setup time is reached.

Pretreatment and Sealing of Fissures

All teeth employed were freshly extracted, third molar free of tooth decay, which had been stored in distilled water. Firstly, the fissures were cleaned
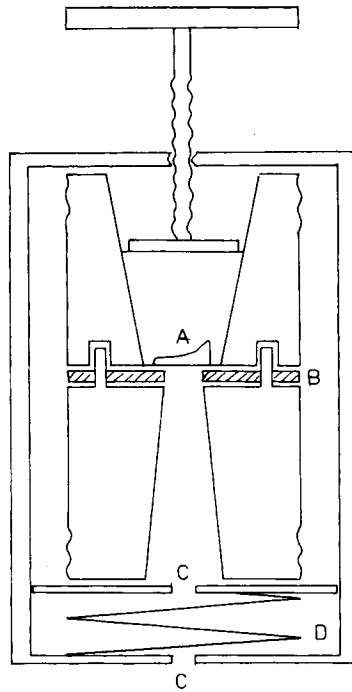
A   EMBEDDED INCISOR

B   FILLING GAP
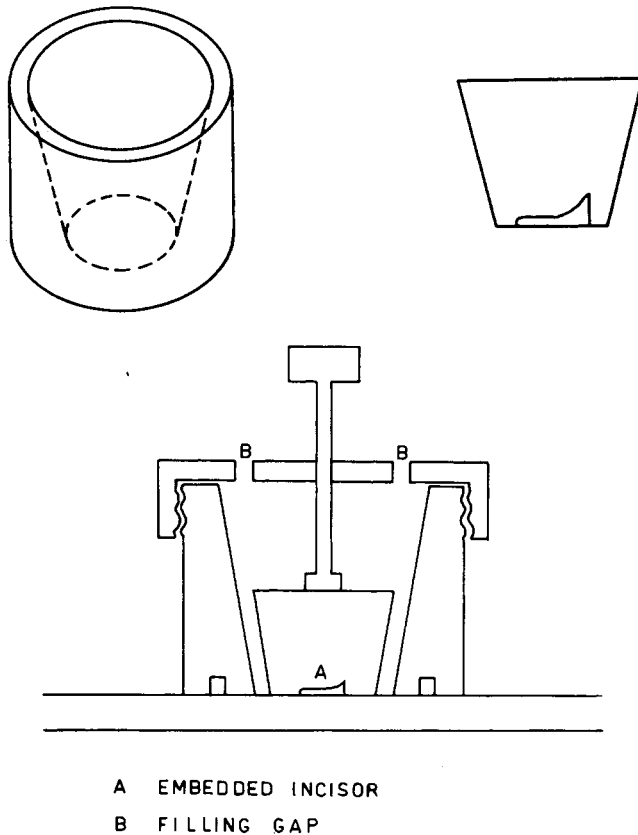
Figs. 3 and 4.   Detailed view of embedding procedure.

with dental pumice, rinsed with water, and dried with compressed air. Prior to sealing, the fissures were etched with an etching solution containing 50% orthophosphoric acid and 8% ZnO by weight.   Only one drop of the etching solution was applicated on the molars.   When necessary, the acid was spread out by means of an explorer.   After 30 sec of application of the acid, the fissures were rinsed with distilled water and dried with compressed air.   The cleaned, etched fissures (see Fig. 1.) were sealed with freshly pre-pared adhesive by using a small hair brush.

The application of the excellent flowing adhesive is very easy and simple. A gentle touch with the top of the brush is sufficient of fill the whole fissure pattern spontaneously (Fig. 2).

Estimation of Tensile Strengths

The teeth employed for this type of experiments were recently extracted incisors with relatively flat surfaces.   The crowns of the incisors were em-bedded in fast-setting PMMA (de Trey's Rapid Repair) in a conical brass ring.   The setup is shown in Figure 3.   The embedded incisors were

A EMBEDDED INCISOR
B RUBBER FOIL
C FILLING GAP
D SPRING

Fig. 5.   Preparation of adhesive joint between adhesive and enamel for tensile testing.

ground and polished until a flat, smooth enamel surface was obtained. Subsequently, the embedded elements were put in a conical ring of stainless steel with a screw thread.   This ring has a larger diameter than the first one.   Embedded element and ring were placed on a flat glass plate, while the element was loaded with a weight of 10 g. (see Fig. 4).   The space between the stainless-steel ring and the polymer used for embedding was filled up with the same material mentioned.

The prepared enamel surfaces were pretreated and etched as described above.   The adhesive was applicated on the etched surface in a stainless-steel apparatus as shown in Figure 5.   One hour after application of the adhesive, the two conical rings were placed in a Zwick tensile testing machine, Type 1461 (5000 kf), by means of the screw threads followed by the measurement of the bond strength between enamel and adhesive.   The surface area of the enamel in contact with the adhesive was always 20 mm².

Polymerization Shrinkage

Shrinkage caused by polymerization was estimated in a mold with precisely known dimensions.   The conical mold had a removable bottom and

was made of stainless steel.   The mold was filled with pretreated adhesive. One hour after filling, the dimensions of the setup adhesive were measured with a microcator and the shrinkage calculated.

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