

Composite and sealant resins — past, present, and future

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Abstract

Composite dental filling materials were developed in response to the shortcomings of silicate cements and unfilled resins (based on methyl methacrylate monomer and its polymer). A hybrid monomer, which came to be known as "BIS-GMA" in the dental literature, was synthesized; this molecule resembles an epoxy resin except that the epoxy groups are replaced by methacrylate groups. BIS-GMA formulations can polymerize rapidly under oral conditions, and they have polymerization shrinkage less than that of methyl methacrylate. BIS-GMA resins are used as binders for glass, porcelain, or quartz particles to form relatively durable direct esthetic filling materials. In combination with the acid-etch technique, developed elsewhere, BIS-GMA formulations are used in the repair of fractured incisor teeth. The combination is also useful to bind orthodontic brackets directly to teeth and for surgical procedures in which teeth are not properly placed or aligned for eruption. This resin without filler is also used to prevent decay by the filling of developmental pits and fissures in teeth which would otherwise have a high susceptibility to caries. Improvements in the glass filler for composite resins may lead to greater durability in their clinical uses. Recent developments in adhesive bonding to teeth will also widen the utility of composites.

This is an informal essay that will give a broad perspective and set the stage for more specific discussions in articles following.

Past History

Composite dental filling materials were developed in response to the severe shortcomings of silicate cements.¹ Silicate cement restorations were subject to acidic decay² and were useful for only four to five years on the average.³

Epoxy resins were being used in industrial applications, and their intriguing properties suggested that they might have useful dental applications.⁴ The liquid epoxy resins could be mixed with a liquid hardener whereupon they would solidify at ordinary temperature with very little hardening shrinkage;

they were very adhesive to most solid substances, and became physically strong and chemically inert polymers. At the time, it seemed reasonable that these resins could be used as adhesive binders for particles of porcelain, fused quartz, or other appropriate inorganic filler materials. It was thought that such a mixture might be placed into a dental cavity preparation where the maximally filled epoxy resin would harden and adhesively bond the particles together and the "silica-resin" material to the cavity walls, thereby forming an esthetic, durable restorative material. The major flaw in this scheme was that such materials did not harden quickly enough for use as direct filling materials in dentistry.

This limitation called for the synthesis of a new monomer which would resemble the epoxy resin so as to have relatively low hardening shrinkage, yet exhibit a rapid polymerization and hardening reaction. Methyl methacrylate polymerized rapidly and was used, together with particles of its polymer as a filler, for direct dental fillings. The methyl methacrylate direct filling resins were flawed primarily because of their large polymerization shrinkage, low stiffness, high coefficient of thermal expansion, and other lesser faults.^{5,6}

A hybrid monomer, "BIS-GMA," was then synthesized.⁷ It was a large molecule that resembled an epoxy resin except that the epoxy groups were replaced with methacrylate groups.⁸ Therefore, it could polymerize rapidly under oral conditions, and yet its polymerization shrinkage was only about one-third as great as that of methyl methacrylate. This viscous liquid resin (BIS-GMA) could be used as a binder for glass, porcelain, or quartz particles to form a stiff, strong and relatively durable direct esthetic filling material. This resin came to be known as "BIS-GMA", an acronym that is more convenient than the long chemical name of this molecule.

Dr. Michael Buonocore, Eastman Dental Center, at the University of Rochester School of Medicine and Dentistry, had discovered that acid etching of dental enamel made its surface slightly rough and

porous — thereby receptive to a micromechanical bonding of polymerizable monomers.⁹ In his attempts to prevent decay from forming in developmental pits and fissures, he experimented with various resins as sealants. When BIS-GMA became available, he found it to work best.

Somewhat later, the acid-etching of enamel in and around cavity preparations was found to be beneficial.

Soon after Buonocore published his early findings,^{9,10} Regenos and other research-oriented clinicians¹¹⁻¹³ began using etching of enamel with phosphoric acid solutions as a means of attachment and retention of direct filling resins. They discovered that fractured incisors could be repaired and restored promptly and esthetically without cutting the dentin. Methods were also developed to use acid etching and resins to bond orthodontic brackets directly to teeth, a procedure with advantages in many cases over the cementing of bands. Because the bonding to acid-etched enamel was effective with both the unfilled resins and composite materials containing inorganic reinforcing fillers, there was a gradual transition toward the use of composites with most of these therapeutic procedures.

In surgical orthodontics, bonding to acid-etched enamel allowed the more convenient and effective attachment of orthodontic buttons or pads with eyelets to unerupted teeth that are not properly placed or aligned for normal eruption, or that have failed to erupt.

Present Practices

Although there is not uniform agreement about the best agent for etching enamel for adhesive resin applications, there are both experimental¹⁵ and theoretical¹⁶ reasons for using phosphoric acid at a concentration of about 30% as an etching agent. The dentin surfaces should be protected from the application of an acid like this, because there is increased pulp irritation — not only from the acid treatment itself, but also from subsequent response to composite restorations if a calcium hydroxide type of liner is not used.

There is experimental evidence on both sides of the controversy regarding the use of an unfilled resin layer applied to acid-etched enamel before the application of a composite material. For most photo-initiated systems, there is adequate free monomer available from the composite mixture to penetrate the small volume of the pores in the acid-etched enamel surface. At the other extreme, with a very dry mix of chemically activated composite (especially if the mixing and placement is not quick) it is quite possible that the prior application of an unfilled resin, used sparingly, might give more reliable bonding.

There has been a trend, unfortunately, in many of the commercial composite formulations toward the use of lower viscosity liquids and lower volume percentages of reinforcing filler materials. This may facilitate mixing and placement by the use of syringes; however, the physical properties and values of the resulting restorations suffer from increased hardening shrinkage, reduced stiffness, decreased color stability, and other factors. Thick mixes (that is, a minimum amount of slightly viscous monomers with a maximum amount of inorganic reinforcing filler) mixed thoroughly and placed immediately will give the best results. The material hardens best if protected from air, which inhibits surface hardening. The maximum feasible time should be allowed for polymerization before it is trimmed or finished.

After a composite restoration is finished to contour, it should be “etched” so as to remove debris from surface air bubbles and to provide “extension for prevention” of the resin glaze that is subsequently applied. Currently it is difficult for the practitioner to apply a thin glaze or veneer of transparent and invisible resin to etched enamel surfaces because of air inhibition of surface polymerization. If the inhibited layer is comparable in thickness to the desired glaze (polymerized layer), currently available materials are difficult to use for this purpose; the glaze must be applied as two layers, applied extra thickly, or covered with something that will exclude atmospheric oxygen during polymerization.

Composite materials were designed as a replacement for silicate cements, and not much thought was given during their development as to their use in posterior restorations. The poor durability of composite materials on the occlusal surfaces of posterior teeth contraindicates their use on the occlusal surfaces of permanent dentition, unless esthetics is an overriding consideration. In many cases occlusal composite restorations will remain in fairly good condition for a couple of years, thereafter showing increasing loss of surface material. In the case of deciduous teeth, the question of the suitability of composite materials for occlusal restorations involves a number of variable factors including the estimated length of time until the tooth is shed and replaced, the durability of the particular composite material under these conditions, esthetics, ease of placement, cost of the materials, and other factors. Present practices and associated rationale are more fully described elsewhere in this journal.

Future Possibilities

It is justifiable to speak of future dental practice because it takes many years for nascent technology emerging from scientific research laboratories to be developed and made commercially available for den-

tists' use. Therefore, some of the current research successes represent future improvements in patient care.

The durability, repairability, and quality of the surface texture of composites are matters that are receiving considerable research. The weakest link in the physical integrity of composite materials is probably the bonding between the organic resin and the surfaces of the inorganic filler particles. Anything which improves the strength and durability of this interaction could lead to restorations that are stronger and more durable.

One experimental approach toward getting a better interaction between the organic resin and the inorganic reinforcement of a composite restorative material is the use of a three-dimensional glass fiber network.¹⁷ This can be obtained by heating a cotton-like form of superfine glass fibers under pressure. This results in a sintering, or melting together of the glass fibers, where they contact one another, thereby forming a dense network with microscopic pores. This three-dimensional glass network can then be broken into "particles" of suitable size, treated with an appropriate silane coupling agent, and combined with a hardenable liquid resin so as to form a composite restorative material. The hardening of the resin should form an interlocking composite of continuous organic and inorganic phases; it is hoped that this will lead to improvements in properties such as polymerization shrinkage, modulus of elasticity (stiffness), and resistance to wear. It will be of considerable interest to follow the developments in this research.

The development and use of "semiporous" glass filler particles is a somewhat different experimental approach toward the objective of improving physical properties of composites by increasing the bonding between the inorganic and organic phases. In this case, only the surface of glass filler particles is made porous. This is done by acid-etching the glass particles (analogous to the acid etching of enamel) to get superficial porosity into which the liquid resin can flow and polymerize. To obtain a glass that would have the necessary X-ray opacity, the appropriate refractive index, and would be capable of giving a porous surface when acid etched, a new kind of glass was developed.¹⁸⁻²⁰ Experimental quantities of this glass have been prepared by glass manufacturers, and samples have been made available to dental manufacturers for their appraisal research and product development.

The improvements in composite properties made by one of these or other research activities will possibly include improved surface texture of finished composites with significantly greater durability

in the oral environment. An acid-etch treatment of the restoration surface as well as the adjacent enamel surface could give interpenetrative bonding to a resin used as a glaze. This same mechanism may allow for bonding of repair increments.

The X-ray opacity of such restorations is expected to be intermediate between that of dental amalgam, which is almost totally opaque, and quartz-filled composites which are practically radiolucent. With this intermediate radiopacity, voids from trapped air under restorations, air bubbles within the restorations that inevitably occur during the mixing and placement of such materials, and secondary or underlying decay associated with the restorations become visible. Voids have been present in radiolucent and radiopaque restorations but have gone undetected because of the extreme radiolucency of the one and the total radiopacity of the other.

To the extent that new composite material can be bonded to older restorations and to tooth surfaces, it might be unnecessary to remove all of a restoration to fill a void needing a remedy.

If the restorative materials continue to change for the better, it is quite probable that the techniques for their proper use will also change. These changes can be expected to lead to modified cavity preparations. For example, a classical cavity preparation for a gold foil restoration cannot be expected to be ideal for a future durable and adhesive composite resin material.

One feature that will probably change the least is the access form of the cavity. It will continue to be necessary to remove softened or discolored enamel or dentin, and access to do this will doubtless be necessary.

A novel method for discriminating between carious dentin that should be removed and underlying dentin that should be retained under a restoration is that of staining or dyeing the carious dentin with a colored solution. For example, a 1% solution of Acid Red in propylene glycol has been proposed by Fusayama²¹ as an objective way of indicating that part of the carious layer of dentin that needs to be removed.

The ideal retention form and resistance form of prepared cavities will depend upon the degree and reliability of adhesive bonding between the restorative material and the hard tooth tissues, and on the physical properties of the completed restoration.

For instance, it is currently recommended that most composite restorations utilize acid etching of the enamel and that the cavosurface should be a beveled, rounded, or chamfered configuration and not a ninety-degree angle. This extends the enamel sur-

face which, after acid etching, allows additional retention and sealing of the restoration by penetration of the liquid resin into the microscopic pores etched into the ends of the enamel rods cut in making the bevel or chamfer. Since the tensile strength of the composite material is greater than the tensile strength of human enamel,²² the tapering resin at the margin resists the stresses built up during hardening shrinkage and increases subsequent margin integrity if there is good penetration of the resin into the etched enamel.

From an *in vitro* study, there has been a research report that the use of pyruvic acid might have certain advantages over phosphoric acid as an etchant for dental enamel.²³ Although a number of studies have been made comparing the relative merits of different concentrations of phosphoric acid, there have been relatively few studies exploring the merits of other kinds of acids (having various dissociation constants and pKa values) wherein the optimum concentration of each acid is determined. It would not be surprising if phosphoric acid were not only the only acid found suitable for the acid etching of enamel.

In acid etching enamel, the importance of washing with clean water and the prevention of even the slightest contamination before, during, or after drying with compressed air has not been adequately emphasized either in the dental literature or in the instructions supplied by dental manufacturers. The term "rinse," often used, is ambiguous in that it can be interpreted to include the swishing of water around in the mouth by the patient after taking water from a cup. Many sealants and acid-etched enamel applications have failed because the washing of the acid-etched enamel surface was not done adequately and exclusively with clean water. Water-soluble crystals form on the surface while the acid is etching the enamel. These must be completely dissolved and removed during the washing step.

Furthermore, even the slightest trace of saliva, blood, or even tooth debris might negate the bonding. It was once thought that gross contamination with saliva or other material, sufficient to clog the openings of the pores, was at fault. Now, it seems that even invisible traces of saliva or other soluble materials can reduce bonding. This is probably due to a lowering of the surface tension of the water on the enamel when an attempt is made to dry it with compressed air. Most semi-soluble materials, which would certainly include salivary solutes, traces of blood, or other materials that might be found in the mouth, can significantly lower the surface tension of water.

The mechanism by which the water in the pores of etched enamel is removed by an air stream has

just recently been explained by Asmussen and Jørgensen.²⁴ This emptying requires the high surface tension of water, a small capillary (pore) diameter, and a wetting of the capillary walls by the water. The diameters of the pores in acid-etched enamel are small enough and water readily wets their surfaces; the dentist need not be concerned with these two factors. However, the surface tension of water can very easily be lowered by contamination with any of a large number of things, and this is where the dentist's attention needs to be focused. If the water is clean, the compressed air stream over the surface will remove the superficial water and allow the automatic ejection of the water, as vapor, from the depths of the pores. This happens because the surface tension in such small pores lowers the pressure in the water so much that it boils out.²⁴

Resins that are sufficiently liquid to be pourable at room temperature will readily flow into these emptied pores by capillary action, but the resin cannot go into the pores if the water has not come out of them first. Lowering the viscosity of the resin below that of a viscous but pourable liquid will undesirably increase its polymerization shrinkage.

Adhesive bonding to dentin is more difficult. Even so, recent experimental research efforts give good reason to predict that future clinical dentistry will be able to utilize materials and methods for significant adhesive bonding to dentin as well as to enamel.

The scanning electron microscope has been especially valuable to researchers in showing that the surface of dentin that has been cut by rotary or hand instruments is covered by a smeared or disturbed surface layer.²⁵ Some workers removed this with the strong acids used to etch enamel, but there is evidence that such treatment can cause pulp irritation, especially if followed with a composite material in the absence of a protective calcium hydroxide liner.²⁶ Others have found that the smeared layer can be removed without significant enlargement of the dentinal tubular openings,²⁷ or pulp irritation,²⁸ by the brief application of isotonic concentrations of acids of intermediate strength.

In the research laboratory, dentin surfaces can be treated with a mordant²⁹ (a metallic salt solution) which chemically modifies the dentin surface and makes it more receptive to adhesive materials. Other solutions are then applied which lay down coupling agents³⁰ that provide a basis for adhesion with a subsequently applied composite resin.³¹ Figures 1-3 show the fractured surface of an adhesive bond to the dentin of an extracted tooth. After storage in water for two days, breaking the bond required 1,910 pounds per square inch (13.2 MPa) in tension.

It is quite possible that when these adhesive



Figure 1. Scanning electromicrograph of the dentin surface after breaking the adhesive bond. The bond strength was 1,910 psi (13.2 MPa), and the fracture occurred partly at the interface (adhesive failure) and partly through the composite resin (cohesive failure) leaving remnants of the composite material adhering to the dentin surface. Original magnification 47x.

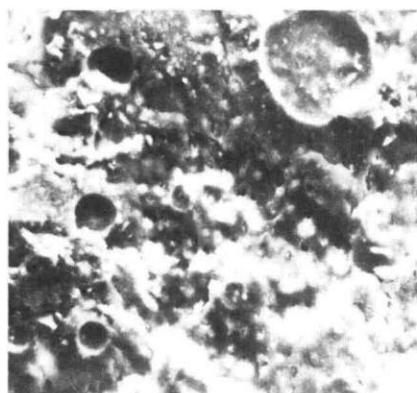


Figure 2. Higher magnification of an area of Figure 1. The circular features are regions in the composite containing air bubbles when the material was mixed and placed on the surface. Air bubbles represent sites of relative weakness, and the fracture tends to leave the interface and involve these voids. Small depressions representing the openings of dentinal tubules where the fracture involves the altered layer of surface dentin can be seen in other areas. Original magnification 470x.

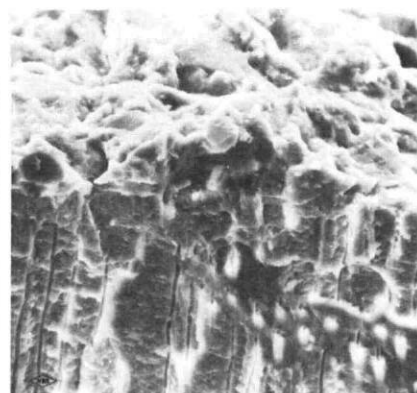


Figure 3. The surface in the upper part of this picture is the same fractured surface shown in Figures 1 and 2. However, in this case the dentin specimen was fractured again to observe the internal aspects of the dentin underlying the adherent composite material. Filler particles and resin overlie an altered dentin region containing enlarged and mostly-filled dentinal tubule openings. With this bonding method, however, the dentinal tubules are neither enlarged nor filled with resin "tags" to any significant depth beneath the adhesive interface. Original magnification 600x.

materials become available to the dentist, the materials, to be successful, will be accompanied by a very detailed description of the steps that must be followed. The future might offer a tradeoff: a reduced amount of cutting of sound enamel and dentin (with the maintenance of greater strength and integrity of the tooth crown due to a reduction, or possibly an elimination, of classical retention form and resistance form); an elimination, of microleakage and marginal staining; and a lessened need for anesthetics to maintain patient comfort. These benefits may well require precise adherence to exacting procedures in the application of the adhesive restorative materials.

With the advent of effective adhesive bonding, it is quite possible that dentists can routinely apply esthetic or invisible protective coatings for entire tooth crowns as a logical extension of sealants and glazes. These can be used as protection against white spots and smooth-surface carious lesions for newly-erupted (or perhaps not-so-newly-erupted) teeth. Such thin veneers will doubtlessly wear away in areas subject to mastication, brushing, interproximal contact, and vigorous flossing; these areas, however, are less prone to the development of lesions. In regions that are not self-cleansing (that is, tooth surfaces least accessible to natural and artificial cleansing), cross-

linked polymeric coatings might remain intact for long periods of time, protecting these areas from low pH of plaque and nutrient stagnation. Preventive measures of this kind may not now be considered cost-effective, at least as a public health measure; nonetheless, fluoridation, antibacterial dentrifices, and mouth rinses, improved levels of oral home care, and lessened busyness in dental practices may raise the feasibility of some of these forms of dental treatment in many practices.

Composite and sealant resins will probably have a future. If research to improve these materials is not adequately supported, if dental manufacturers fail to transfer technology from the laboratory to the marketplace, if dental practitioners hold them in a low esteem (thinking them to be a quick and easy way to provide second class dentistry), then the future of composites and sealants may be dim — if not dismal. The more probable course is that of continued advancements in the scientific laboratories, ready acceptance and promotion by manufacturers, and careful use by conscientious dentists who constitute the majority of our colleagues. The placement of the best possible composite restoration (including the use of materials yet to be developed) might be as demanding and give as much cause for pride, because of the merits of its serviceability, as have been the place-

ment of top-rate gold foil, porcelain inlay, silver amalgam, or other traditional restorations.

Future improvements in the level of oral hygiene, the use of fluorides, antiseptics, sealants, and protective coatings to prevent decay, together with improvements in composites to repair traumatically damaged or malformed teeth, can lead to better general health because of better oral health.

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