quick study

Shining a light on dental composite restoratives

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Dental fillings made from light-activated, polymer-based composites obviate some of the safety concerns associated with the metal amalgams they are replacing. They look better too.

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Despite dramatic oral-health advances linked to better home-care practices and products, improved preventative interventions, expanded insurance, and fluoridated water supplies, people continue to need restorative dental treatment. In the US alone, nearly 100 million dental restorations are placed each year, which makes the dental filling the most commonly encountered biomaterials application in the country and one of the largest as measured by dollar value or material volume.

The roots of restorative dentistry can be traced back more than 2000 years to various materials, including stone chips, natural resins, and metals. Those were used to restore the function, if not the form, of damaged or diseased tooth structure and to provide culture-specific aesthetic modifications. Beginning in seventh-century China, artisans developed restorative materials that were amalgams of mercury—a metal that allowed alloying with little or no heating—and silver; the technology was reinvented in Europe in the early 1800s. Amalgams that also contained varying amounts of tin, copper, and zinc gradually emerged as dental restorative materials of choice due to their strength, durability, and cost. In a clear but disconcerting indication of the widespread need for treatment, restorative dentistry advanced considerably ahead of dental anesthetics, which did not become generally available until well into the 20th century.

Chewing on glass

Now, in the 21st century, polymer-based composite restoratives have overtaken amalgams in the dental materials market due, in part, to their aesthetic appeal and ability to bond with tooth structure. In addition, patients and practitioners have registered an aversion to mercury based on perceived health risks and real environmental concerns. Composite materials, by definition, have two or more compositionally distinct phases. For dental applications, the composite consists of a polymer matrix largely filled with fine glass particles.

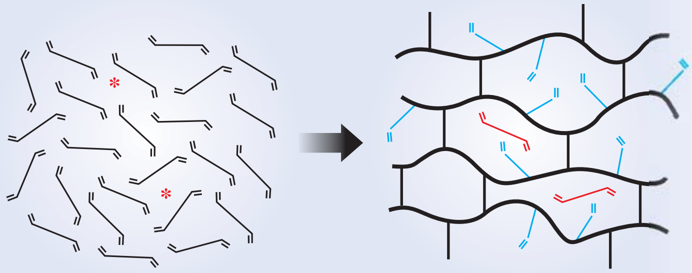
Synthetic polymers were first created in the early 1900s. Widespread polymer use later took off, literally, with the technological leaps made in connection with demands imposed by World War II. To give just one example: Poly(methyl methacrylate), commonly called PMMA, replaced glass in aircraft windscreens and turrets because of its combination of excellent optical properties, low mass, and high strength. Polymer use in nearly every conceivable aspect of everyday life, including dentistry, rapidly followed. By the late 1940s, dentists started using acrylic restorations based on PMMA; they had good aesthetic properties but limited clinical lifetimes. In the late 1950s and early 1960s, acid-etching techniques that remain standard today allowed for the effective bonding of acrylics to dental enamel. During the same period, PMMA was replaced by highly cross-linked polymers obtained from dimethacrylate monomer units. Those new materials had excellent stability, strength, and resistance to chemicals.

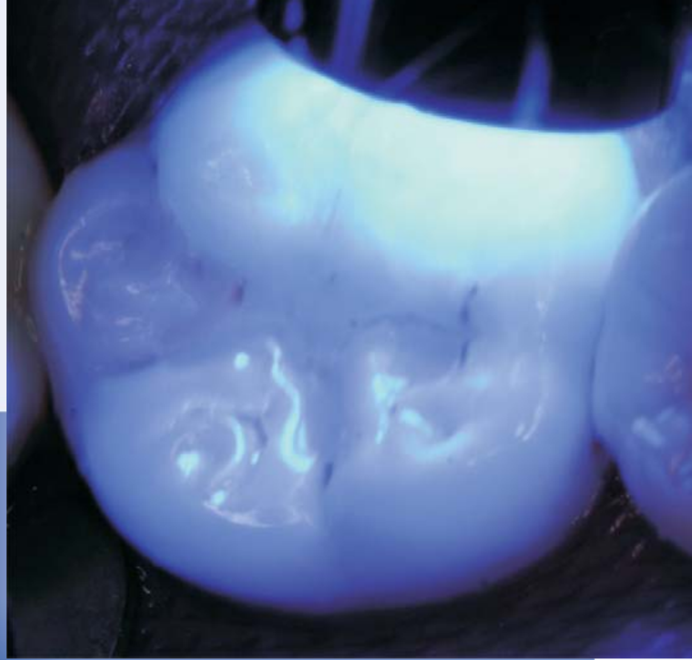
Concomitant with the above advances was the addition of powdered glass fillers to the liquid monomers. The added glass improved physical, mechanical, and clinical handling properties and also provided an artful means to mimic the appearance of a natural tooth. The filler content in composites is generally high, with approximately half the volume being inert glass. As a result, strength and hardness are increased, and thermal expansion, wear, water uptake, and shrinkage associated with polymerization are reduced. Further increases in the filler content have been achieved with the introduction of glass particles in a variety of sizes. Considering the high masticatory stresses generated in the mouth and thereby on dental restorations, it is critical to effectively transfer stress from the polymer to the stronger ceramic filler—a task that requires covalent attachment between the two phases, accomplished by incorporating a polymerizable layer on the surface of the glass filler.

Continued progress in adhesive bonding between restoratives and hard tooth tissues—enamel and dentin—has also led to notable improvements in the clinical performance of dental composites. The bonding process, though, is very sensitive to the specific techniques employed.

Radical-induced polymerization

Free radicals, or unpaired electrons, are the basis for the chain reaction that links individual monomer molecules to form the polymer. Since a single initiating radical can rapidly propagate through hundreds or even thousands of monomeric carbon–carbon double bonds to generate extended polymer backbone structures, one needs to regulate radical production in order to have a controlled polymerization reaction. Dimethacrylate monomers are the starting material for nearly all dental resins. As shown in the figure, the part of





Visible-light photoinduced decomposition of an initiator (red asterisk) forms free radicals that add to monomer double bonds. Resulting new radicals continue the polymerization process, which yields polymer chains (bold) that are interconnected, or "cross-linked," to give a three-dimensional, giant macromolecule. The sketch also shows pendant sites (blue), wherein reactive sites are attached to the polymer chain, and unreacted monomers (red). The photo shows a clinical application of photoinitiated polymerization. The curing light enters the tooth from above the frame of the photo. Also visible are reflections of that light. (Photo courtesy of Thomas Berry.)

the monomer between its two double-bond reactive groups becomes a cross-link that interconnects the polymer chains to give a rigid, stable, three-dimensional network.

Early versions of dental composites relied on systems that required mixing immediately prior to use. A small quantity of radical inhibitor provided a short working time before polymerization transformed the composite paste to a hard solid. During that brief interval, the dentist had to mix the composite and place it in the cavity. After UV photopolymerization was introduced in the late 1960s as an effective means to produce industrial coatings, the technology was quickly adapted for dental sealant and composite restorative materials. That advance eliminated the composite mixing process that unavoidably introduced porosity. It also decoupled working time from setting time and gave the dentist the freedom to properly place and bond the material.

At first, UV dental curing lights were not powerful. That limitation and the high absorptivity of the photoinitiators effectively restricted the composite depth of cure to very thin, incrementally placed layers. In addition, exposure to direct or reflected UV radiation posed safety concerns for both patients and dentists. Despite those issues, dental practitioners rapidly accepted photopolymerization due to its ease of implementation. By the 1980s photopolymerization of dental composite restoratives was being conducted with visible-light irradiation at wavelengths of 400–500 nm, still the industry standard. Thanks to a combination of increased output intensities of curing lights, naturally deeper penetration of longer-wavelength light, and visible-light initiators with relatively low absorptivities, composite layers that are approximately 2 mm thick can be reliably photopolymerized with a total exposure time of less than a minute.

Initiators activated with UV radiation are typically single components, but the lower energy of the longer-wavelength visible light generally requires use of two-component photoinitiator systems whose components coexist stably in the dark but rapidly form free radicals throughout the irradiation period. A free-radical inhibitor extends the shelf life of the material and prevents premature polymerization due to low-level ambient-light exposure before and during composite placement.

That composites are polymerized in a patient's mouth imposes significant processing constraints. The reaction process must be rapid, but not so rapid as to cause an excessive temperature rise that would harm dental pulp tissue. And once the restoratives are in place, patients unknowingly make extreme demands on their performance.

The conversion of monomer to polymer typically incorporates only about 50–65% of the available methacrylate functionality into the final, vitrified polymer. As illustrated in the figure, a majority of the residual reactive sites are covalently tethered to the polymer network at pendant sites. Approximately 5–10% of the original monomer remains completely unreacted and eventually can leach from the composite filling. The free monomer also poses concerns about local and systemic biocompatibility. Thus one wants to maximize conversion during placement of the restoration. Moreover, higher conversion ensures enhanced mechanical properties for the polymerized composite.

On the other hand, a higher degree of conversion produces more polymerization shrinkage. In adhesively bonded dental restorations, the additional shrinkage leads to increased stress at the interface between restoration and tooth. Too great a stress results in a gap that allows marginal staining and, in the worst case, secondary cavities that result from bacterial access.

The above difficulties notwithstanding, dental composites are widely used, highly successful restorative materials with longevity results comparable to dental amalgam. Even so, ample opportunities exist for further improvement. The dimethacrylate monomers used in dental materials have changed little over the past 50 years. Some of the new work with composites concerns novel fillers and the internal interfacial region between polymer and filler. However, a considerable effort, both in academic and industrial labs, is focused on updating and even custom designing the polymers employed in restorative materials. It is a safe assumption that dental composites will continue to evolve and that their use will continue to increase. In the longer term, suitable regenerative materials should eventually emerge as viable alternatives to permanent restorative treatments.

Additional resource

▶ E. P. Allen et al., *J. Prosthet. Dent.* **92**, 39 (2004). ■