

The oldest and most used composite in orthodontics can, and must be replaced !

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Abstract

Bis GMA, a resin launched about half a century ago, is still widely used in sealants, adhesives and restoratives in spite of being reported to be toxic, cytotoxic, mutagenic, carcinogenic and oestrogenic¹. The examination of its properties shows that except one, mechanical strength, all the others are barely acceptable.

Its mechanical strength has been recently identified as being due to a pre-liquid crystal structure. Its backbone acts like a molecular rod, a property shared with many natural products and with the strongest polymers. One of these, Kevlar™, is the strongest polymer known, being five times stronger than steel, weight per weight.

Building upon this finding, the inoffensive molecular rod containing compounds found in nature and today's chemistry can lead to monomers exceeding the strength of bis GMA.

Introduction

While there are over sixty monomers currently used in dentistry, only two "resins" are currently used in sealants, adhesives and restoratives. Some formulations also include polyurethane dimethacrylates 1,6-bis (urethane-ethyleneglycol-methacrylate), 2,4,4-trimethylhexane, short UDMA, but bis phenol A di (glycidyl methacrylate), widely known as bis GMA or "Bowen's resin," still reigns supreme after almost half a century. As shown below, an analysis of properties of this monomer shows that while most of its properties are barely acceptable, the only exception is its strength.

Bis GMA's properties

Monomer	Shrinkage, %
Methyl methacrylate	21
TEGDMA	14
UDMA	4.4
Bis GMA	4.4

1. Shrinkage. As long as the cyclic monomers currently used expand, instead of shrinking (phenomenon that leads to poor marginal adaptation in fillings and in premature attachment debonding), bis GMA can be rated barely acceptable, being at the level of other monomers.

2. Color. While the monomer is almost colorless, its polymer discolors when subjected to light or bleaching agents. Composites become colored due to the remaining (unpolymerized) double bonds as well as to the tertiary aromatic amines used as polymerization kickers. Hydroquinone, otherwise a powerful polymerization inhibitor, can not be used for similar reasons.

UV stabilizers often have to be added: opaque containers are a must. Despite these problems, bis GMA behaves acceptably from this point of view.

3. Setting vs. shelf life. After initiation (chemical or photochemical), bis GMA should react fast in the presence of appropriately selected comonomers to become solid within 3 min and strong enough to be worked out within two hours. In contrast, the system should be stable enough at room temperature to allow proper use after years. This is realized with the help of polymerization inhibitors, compounds that may impede with the resin's desired setting. As there are no other systems that behave remarkably better, bis GMA may be considered as acceptable.

4. Fluidity. The ideal monomer should allow a good bonding to substrates by penetrating in their fissures (mechanical interlocking), accept a high load of filler in composites and have a low freezing point. While bis GMA doesn't freeze at the normal room temperatures (its T_g is -60°C), it is too viscous to be used as such and has to be amply diluted with aliphatic monomers such as triethylene-glycol dimethacrylate (TEGDMA). Based upon the above considerations, it is obvious that bis GMA has too high a viscosity for the purposes intended.

5. Water affinity. Since the resulting composites have to withstand exposures of decades in a (wet) oral environment, the monomer used as matrix has to be water-hating, even if this results in a lack of affinity toward the enamel (water loving). The polymer has been found to absorb almost one molecule of water for each bis GMA/TEGDMA molecule.² As the composites based upon bis GMA are undoubtedly a net advance from this point of view versus both silicate cements and poly methyl methacrylate matrices, bis GMA's resistance to water is deemed better than that of the others, but still too low...

6. Leaching. The matrix of an ideal restorative/adhesive should both be deprived of monomers and oligomers that may be released and capable of entangling leachable components. While the bis GMA polymer per se is too bulky to leach, bis GMA/TEGDMA-based composites release twice as much TEGDMA than these made of UDMA/TEGDMA.³ While large, bis GMA's molecule has insufficient functional sites and not enough cross-linking to generate a network that may retain leachable compounds. As it was shown above with the help of an acidulated gel of KMnO_4/K , a number of commercial composites based upon the classic system bis GMA-TEGDMA leach enough to generate problems.⁴

7. Adequate molecular weight & structure. An adequate polymer matrix should exhibit a low dispersion and be deprived of monomers and oligomers. An abundance of short

almost the same, longer dimension. As the present bis GMA/TEGDMA system starts from relatively small molecule monomers, it leads to copolymers that comprise undesirable short, water-soluble chains.

8. Risk. A chapter 1 and a fully dedicated web site⁵ show that bis GMA and its hydrolysis product, bisphenol A, are far from being safe. Bis GMA has been found to be allergenic, toxic, cytotoxic, mutagenic and oestrogenic, while its parent, bisphenol A, has been described as toxic, teratogenic, oestrogenic, antiandrogen, aneuploidic and resistant to biodegradation¹. These problems are due to the aromatic character which renders phenols acid, and to the biomimeticism of the structures involved. The body confuses these compounds for estrogens, leading to undesirable consequences and possibly to death.

9. Resistance to wear & erosion. The main reason why bis GMA composites are still preferred resides in the exceptional strength of their matrix. As it can be seen below, such composites have mechanical properties similar to the enamel. Sealants that better withstand erosion, restoratives that last and adhesives that bond for years render bis GMA a winner despite of the many attempts to replace it. Out of the nine properties previously examined, only one is outstanding, remaining unequalled after almost half a century. After decades of attempting to find a substitute for bis GMA, the researchers of the most focused institution on the matter, at NIST/Gaithersburg, have arrived to the conclusion that "except for improvements in water-resistance, monomers with better mechanical properties than Bis GMA and UDMA could not be synthesized".⁶

	Tensile strength psi	Compressive strength psi	Modulus of elasticity psi x 10 ⁶
Bis GMA/TEGDMA composite	6000-7700	23600-31200	0.7- 2. 6
Silicate cement	440-1010	24600-31000	3.1
Unreinforced resin	3800-5100	12100	0.26
Enamel	1500	40-50	1.8- 8. 2

Attempts to replace bis GMA

After decades of trials and errors, the scientific community seems to have reached the consensus that the ideal resin should be a polyfunctional methacrylate. Polyfunctional, to provide cross linking, i.e. generate three-dimensional, strong copolymers: methacrylate, to provide a moiety that polymerizes fast and better withstands water. Once the double bond needed for polymerization has to be provided by an acid which cannot be used as such (methacrylic acid is both toxic and corrosive), the search was, and still is, for its most suitable counterpart (moiety) which would check these properties while possibly adding desirable ones. To minimize the shrinking generated during polymerization, the volume of the -OH bearing moiety has to be as large as feasible, or even to expand during the polymerization process. This has led to the study of cyclic ethers, lactones, lactams, spiro-carbonates, etc., compounds that incur in such conditions the opening of a ring, i.e. an expansion in volume. If these attempts would prove to be successful, the resulting monomers would be less toxic than the diglycidyl ether of bisphenol A (DGEBA) used today.

Monomers comprising aromatic (benzene) cycles continue to be proposed,⁶ as such or as large monomers.⁷ Such polymers limit the amount of smaller, unreacted molecules that may weaken the structure and leach, but may also hydrolyze and release phenols and other noxious compounds. Polyurethane dimethacrylates (UDMA) were found to be less toxic than those containing benzenic cycles,⁸ but they do not exhibit the superior mechanical properties shown by bis GMA. Monomers that contain acid groups such as phosphoric, phosphonic, phosphinic, sulfuric, sulfonic or sulfonic: their functionality may enhance adhesion to teeth tissues, but their resistance to water remains doubtful.⁹

The key for future lies already here !

Till recently,¹⁰ what renders bis GMA polymers strong was an enigma. The far reaching answer is its rigid backbone derived from bis phenol A. This pre-molecular rod structure is encountered also in the polycarbonate resin used for CDs, Invisalign® retainers as well as for "bullet-proof" glass in military aviation, riot shields, vandal proof glazing and safety helmets. Such structures do not bend due to a phenomenon known as "steric hindrance": in bis GMA, the two methyl (-CH₃) groups force the bis GMA molecule to be straight and planar, as the rotation/bending of the two cycles is restricted by the size of these central, neighboring groups.

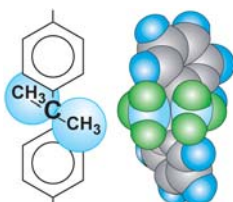


Fig. 1. Bis phenol A's rigid, elongated structure

In any composite, a fibrillar structure reinforces the material. Fibers measuring 25 μm x 2 μm are currently used to reinforce high-strength composites: at a smaller scale, reinforcing fibers are called whiskers and measure around 10 x 1 microns. At an even smaller scale, nano-whiskers such as those of cellulose are measured in billionth of a meter, or nanometer.

The phenomenon of composite reinforcement goes as far as the atomic scale. In the bis GMA's case, the length of these molecular rods is of about four times their width.

Nano tube fillers are already used in dental composites. Thus, Pentron Clinical and its subsidiary Jeneric claim to have created the first nano-hybrid composite¹¹: their Nano-Bond System contains silica-containing "cage-like" nano-particles. ESPE/3M's Filtek Supreme has a filler¹² (20-75 nm in size) which forms "clusters" having a total size of 0.6-1.4 μm . Dentsply Caulk's TPH³ Micro Matrix Restorative and Esthet-X's resin matrices are filled to 60% by volume (77% by weight) with both a barium-alumino-fluoroboro-silicate glass (0.6 to 0.8 μm) and silicon dioxide particles (10 to 20 nanometers)¹³. A similar composite is sold by Kerr¹⁴ under the name PureNano™.

A giant step forward will soon be the use of "liquid crystal" (LC) monomers, as these can transform the matrix itself in an assembly of reinforcers. "Liquid crystal" is a fourth "state", in which certain kinds of matter can enter into under the right conditions. If a LC substance becomes too cold, it reverts to an ordinary solid. If it becomes too hot, it reverts to an ordinary liquid. LCs are essentially more like liquids than they are like solids.



Fig. 2. Liquid crystals' rigid, elongated structure

All the molecules that can generate a LC phase are long and have a rigid central region (backbone). Their part-crystal and part-liquid nature results in innumerable applications, such as in display technology (LCD), detergents, emulsifiers and in high technologically "smart" materials. Far from being "exotics", LCs can also be found in lecithin, DNA, cholesterol esters, lipids, cellulose, sugars, chitin, xylans and gangliosids. A well known related LC material is the "silk" extruded by spiders.

The interest in LC monomers lies also in the fact that their rod-shaped molecules tend to orient themselves along definite directions, behavior that has received the name nematic (from Greek, νημα = thread). In some cases, rigidity and elongation are given by resonance, an extended electron transfer over several (condensed or bridged) polynuclear aromatic cycles (resonance). As a result, several such monomers, derivatives of LCs, have already been suggested as replacements for bis GMA...

Another phenomenon favoring to the formation of rod-shaped molecules is steric hindrance, presented above. As a difference from the already examined case of bis GMA, where it renders almost planar and rigid aromatic cycles, steric hindrance can act also on selected natural products such as some carbohydrates. With the help of modern chemistry, these can be modified to become non-toxic monomers.

Conclusion

Nano fillers are already used to reinforce dental composites, and white nanotubes (BN) may soon join them. Along with these, LC monomers will lead to incredibly strong composites. What is to be watched, however, is the use of the LC derivatives of polycyclic aromatic compounds. Indeed, as early as in 1915, Yamagiwa has succeeded in inducing skin cancers on rabbit ears by repeatedly painting these with coal-tar, a material known to be rich in polynuclear aromatic compounds. If successful, would we then return to another, mechanically superior but even riskier bis GMA?

In contrast, steric hindrance and hydrogen bonding, the most important LC generators in nature, can be used to transform inoffensive products in suitable monomers.

After almost half a century, of intensive use, bis GMA composites can, and must be replaced with safer products.

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For details, see *The Orthodontic Materials Insider*,
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