



Monomer Systems for Dental Composites and Their Future: A Review

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ABSTRACT This review discusses the history of monomers used in resin composites, highlights recent and ongoing research reported in the field of dental monomer systems, and future development. The main deficiencies of current resin composites are polymerization shrinkage and insufficient wear resistance under high masticatory forces. The problem has been approached with the synthesis of potentially low-shrinking/nonshrinking resin composites. Monomer systems have been formulated that improve the degree of conversion and mechanical properties.

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Dental resin composites comprise a blend of hard, inorganic particles bound together by a soft, resin matrix, and generally encompass three main components: the resin matrix comprising: (1) a monomer system, (a) an initiator system for free radical polymerization, and (b) stabilizers for maximizing the storage stability of the uncured resin composite and the chemical stability of the cured resin composite; (2) the inorganic filler consisting of particulates such as glass, quartz, and/or fused silica; and (3) the coupling agent, usually an organo-silane that chemically bonds the reinforcing filler to the resin matrix.

Obviously, the properties, and hence the performance of resin composites, are dependent upon the three basic components of the material. Some of the proper-

ties are mainly related to the filler and the coupling agent, whereas other properties mainly stem from the resin matrix. The first group of properties includes strength, stiffness, abrasion resistance, and coefficient of thermal expansion while color stability and softening tendency can be found in the second group. A third group of properties may be identified that to a higher degree, depends on both filler and matrix. Such properties are polymerization shrinkage and water sorption.

Mechanical properties are, as stated, highly influenced by the filler and the coupling agent, but also the organic matrix plays a significant role for strength, stiffness, and abrasion resistance.

Judging from the formulation changes that have been reflected in commercial resin composites over the years, the development of these materials has

mainly focused on mechanisms of initiation and filler technology, whereas the resin monomer component has remained essentially unchanged. Thus, to this day, the majority of commercial resin composites contain a monomer system based on BisGMA or variations thereof. This fact may indicate that for several years following the development of BisGMA, other components of resin composites than the monomer system were more in need of optimization. However, recent research in the field of dental monomers has produced several results that may be expected to appear in commercial resin composites in the future.

Organic Resin Matrix

The organic resin matrix is a high molecular weight monomer such as bisphenol A glycidyl methacrylate (bis-GMA) or urethane dimethacrylate. Bis-GMA, which stands for 2,2-bis[4(2-hydroxy-3-methacryloxypropoxy) phenyl]-propane, is an aromatic methacrylate developed by Rafael Bowen of the National Bureau of Standards in the early 1960s. Terminal methacrylate groups provide sites for free radical polymerization; it sets to a relatively rigid polymer because it has two benzene rings near its center.¹

Two disadvantages of bis-GMA are its questionable color stability and high viscosity. High viscosity is the result of its -OH groups, which hydrogen bond. To lower the viscosity, manufacturers add low molecular weight (low viscosity) monomers like triethyleneglycol dimethacrylate (TEGDMA) and ethyleneglycol dimethacrylate (EGDMA). These reduce the bis-GMA's viscosity, increase cross-linking, and increase hardness.²

Another monomer frequently used as the matrix for resin composites is urethane dimethacrylate. This monomer was introduced in 1974 and is a brittle

material with low viscosity. No study has shown bis-GMA-based resins to be superior to UDMA-based ones.²

The resin component of a cured dental resin composite is a polymeric matrix. A polymer is a large molecule built up by the repetitive bonding together of many smaller units called monomers. The process by which monomers are joined together and converted into polymers is called polymerization. Monomers used in dentistry are generally liquids, and during the process of polymerization they become converted to solids. The extent to which monomer is changed into polymer is termed the degree of conversion.³

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Various monomer systems used

1. Methyl methacrylate resins
2. Epoxy resins
3. BIS-GMA resins
4. Eutectic monomer system
5. Urethane dimethacrylate resin

Methyl Methacrylate Resins

The story of the current resin monomers extends back to 1843 when J. Redtenbacher, a German chemist, discovered a new acid, to which he gave the name of acrylic acid. By 1900, methacrylic acid, as well as several of its esters including methyl methacrylate, had been synthesized and polymerized. Methyl methacrylate polymerizes by an addition

mechanism through the carbon-carbon double bonds to form poly (methyl methacrylate). In the late 1930s, poly was introduced for denture base resin, and a few years later for indirect filling resin. The discovery of the benzoyl peroxide-tertiary amine redox initiator-accelerator system, allowing methyl methacrylate to polymerize at ambient temperature, laid the basis for direct filling resins, which were developed in Germany during World War II.⁴

The methyl methacrylate resins turned out to be associated with significant defects, including large polymerization shrinkage, high coefficient of thermal expansion, serious discoloration, severe pulp damage, and a high incidence of secondary caries.

Epoxy Resins

Motivated by the inherent limitations of methyl methacrylate resins, American dentist R.L. Bowen, working at the National Bureau of Standards in Washington, D.C., developed other synthetic resins for use as dental filling material. Epoxy resins appeared to be worth investigating as they harden at room temperature with little shrinkage to produce an insoluble polymer.²

Polymerization occurs through the epoxide groups in which the ring is in a somewhat unstable condition and prone to open and combine with nucleophilic compounds. Work on the coefficient of thermal expansion, adhesion to tooth structure, and color stability gave promising results with the first dental resin composite: an epoxy resin with aggregates of fused quartz or porcelain particles. The addition of mineral fillers to direct filling resins had been proposed already in 1951 as a method of reinforcement.

Subsequently, a few indirectly placed restorations of heat-cured epoxy resin

composite showed good esthetics in the oral cavity. However, epoxy resins were given up due to slow hardening, preventing their use as a direct filling material.^{1,2}

Bis-GMA Resins

In response to the impracticability of epoxy resins, Bowen, in 1956, synthesized a new monomer, initiating the era of dental resin composites. The monomer, 2,2-bis [4-(2-hydroxy-3-methacrylyl-oxypropoxy) phenyl]. Propane, resembles an epoxy resin, except that the epoxy groups are replaced by methacrylate groups. It was prepared from bisphenol A and glycidyl methacrylate, and later also from the diglycidyl ether of bisphenol A and methacrylic acid. Polymerization of the monomer, which was given the acronym BisGMA, occurs through the carbon-carbon double bonds of the two methacrylate groups.^{2,5}

This bulky, difunctional monomer is superior to methyl methacrylate because of its large molecular size and chemical structure, providing lower volatility, lower polymerization shrinkage, more rapid hardening, and production of stronger and stiffer resins. The high viscosity of BisGMA is lowered by admixture with dimethacrylate monomers of a lower molecular weight to achieve a viscosity suitable for incorporating fillers. The monomers most often used as diluents for BisGMA are ethyleneglycol dimethacrylate (EGDMA) and triethyleneglycol dimethacrylate (TEGDMA).⁵

The lower the viscosity of the monomer mixture, the more filler may be incorporated into the mixture. All other things being equal, increased filler content will improve several properties of the polymerized material, e.g., strength, stiffness, and coefficient of thermal expansion. However, a dilution of BisGMA also has negative effects such

as increased polymerization shrinkage, as discussed in the following.⁶

As a consequence of polymerization, resin systems shrink mainly because the formation of a macromolecular chain network from discrete monomer species involves conversion of intermolecular distances of 0.3-0.4 nm into primary, covalent bonds with lengths of about 0.15 nm. The extent of polymerization shrinkage depends, among other things, on the molecular weight and functionality of the monomers. Thus, comparing monomers of the same molecular weight, polymerization shrinkage increases when functionality increases.

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Comparing monomers of the same functionality, polymerization shrinkage increases when molecular weight decreases. Consequently, dilution of BisGMA increases polymerization shrinkage.^{6,7}

Studies on the formation of homopolymers from dimethacrylates of mono-di-tri-, and tetraethyleneglycol have shown that the reactivity of the monomers increases with increasing distance between the methacrylate groups. It follows that TEGDMA is more reactive than EGDMA. Due to favorable stereochemistry, long-chain, flexible dimethacrylates of oligoethyleneglycols have been found to exhibit relatively high degrees of conversion.⁵

Compared with the dimethacrylates

EGDMA and TEGDMA, the aromatic monomer BisGMA is much more rigid. As a consequence, the degree of conversion in BisGMA and TEGDMA copolymers has been found to decrease with an increasing content of BisGMA. Despite the resultant decrease in degree of conversion, an increasing content of BisGMA does not result in reduction in strength or in hardness. This lack of correlation between conversion and hardness, or strength may be explained by the fact that the flexible TEGDMA is substituted by the much stiffer BisGMA in the polymer network.¹

The flexibility of TEGDMA is related to the ether linkages of the molecule, giving rise to only slight barriers to freely rotate about the bonds.

The relative stiffness of BisGMA is related to the bulky, aromatic groups of the central part of the molecule, causing much larger barriers to rotate about the bond. Thus, strength, hardness and certain other mechanical properties are influenced not only by the degree of conversion but also by the nature of the monomeric subunits in the polymer. On the other hand, other properties are determined mainly by the degree of conversion.^{4,7}

As polymerization proceeds, diffusion rates of propagating free radicals and unreacted dimethacrylate molecules are drastically reduced, hampering the complete conversion of methacrylate double bonds. Thus, as much as 25 percent to 50 percent of the methacrylate groups remain unreacted. Of these 25 percent to 50 percent unreacted methacrylate groups, approximately one-tenth is present as residual monomer.^{4,5}

The presence of unreacted monomer or unreacted carbon-carbon double bonds has a plasticizing effect on the polymer. Thus, in contrast to resin composites of differing monomer systems, the physical properties of a given system are cor-

related with the degree of conversion. Furthermore, residual carbon-carbon unsaturation can make the polymeric matrix more susceptible to degradative reactions. These reactions can, according to some authors, result in reduced color stability and wear resistance, and in the formation and release of byproducts such as formaldehyde and methacrylic acid.^{4,6}

Eutectic Monomer Systems

As mentioned previously, BisGMA finds widespread use in current commercial dental resin composites. However, this monomer is not completely color stable, is too viscous for use without being thinned, and cannot be purified by distillation or by crystallization because it is a mixture of high molecular weight optical isomers. In an effort to solve the problems associated with the use of BisGMA, Bowen devised a unique monomer system based on the premise that certain isomeric crystalline dimethacrylates are capable of forming a eutectic that is liquid at room temperature.¹

Three aromatic diesters, the bis (2-methacryloyloxyethyl) esters of phthalic (MEP), isophthalic (MEI), and terephthalic acids (MET), were synthesized and purified by recrystallization. The ternary eutectic was found to have a viscosity suitable for use in resin composites. Numerous physical properties of three experimental resin composites based on this ternary eutectic dimethacrylate were determined. It was concluded that the mechanical properties were comparable with those of BisGMA-based resin composites, and that further improvements in polymerization shrinkage and color stability were needed.^{1,5}

In a clinical trial, one of the experimental resin composites was found to compare favorably with Addent 35 (3M), which was based on BisGMA. The

problem of color instability stemmed from the tendency of the isomeric dimethacrylates to form yellow-tinted charge-transfer complexes with the tertiary aromatic amines commonly used as polymerization accelerators in the initiator system. It has been stated that by the use of alternative accelerators, e.g., ascorbyl palmitate, the problem of color instability is avoided allowing the formulation of excellent resin materials.^{1,3}

Urethane Dimethacrylate Resins

A group of monomers that have found commercial use are the urethane dimethacrylates. The first type of urethane

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dimethacrylate to appear was synthesized from hydroxyalkyl methacrylates and diisocyanates. These monomers have molecular weights nearly equal to that of BisGMA, but are less viscous. The most commonly used monomer of this type, 1,6-bis (methacryloyloxy-2-ethoxy-carbonylamino)-2,4,4-trimethylhexan (UEDMA = UDMA), is the reaction product of 2-hydroxyethyl methacrylate and 2,4,4-trimethyl-hexamethylenediisocyanate.³ This monomer has been used alone (e.g., Isocap, Vivadent; Isopast, Vivadent) or in combination with other monomers such as BisGMA and TEGDMA (e.g., Heliomolar,

Vivadent; Estic Microfill Composite, Kulzer; Estilux Microfill Kulzer; Durafill Light-curing Composite, Kulzer).^{5,8}

As mentioned previously, urethanes have also been synthesized by the reaction of the secondary hydroxyl groups of BisGMA with isocyanates to create less hydrophilic monomer systems. Thus, Nuva-Fil (L.D. Caulk) as well as ful-fil and Prisma-Fil (L.D. Caulk) were based on oligomers synthesized from BisGMA and hexamethylene diisocyanate. Another urethane dimethacrylate system was used in Fotofil (Johnson & Johnson ICI), the very first proprietary resin composite to be visible light activated.⁸

The results of in vitro studies, in which all other components than the monomer system were kept constant, indicate that resin composites based on UEDMA will have improved mechanical properties compared with resin composites based on BisGMA. Also, there are indications that higher degrees of conversion are obtainable with urethane dimethacrylates as compared with BisGMA:TEGDMA mixtures. All other things being equal, this would result in improved biocompatibility of the resin composite.⁸

Dimethacrylates with aromatic groups have been reported to produce rigid polymers, while dimethacrylates with aliphatic groups produce flexible polymers. It has been theorized that dimethacrylates with "hard" segments (aromatic groups) and "soft" segments (aliphatic groups) in the same molecule will result in polymers with increased toughness. For the purpose of designing such a polymer, a dimethacrylate with a polyurethane chain was synthesized from HEMA and a polyurethane diisocyanate, imprecisely described as a "polyurethane diisocyanate, imprecisely described as a polyester urethane with propylene glycol and hexanediol."⁸

The dimethacrylate, (PUDMA),

incorporated two phenylmethyl groups as hard segments and propylene glycol or polymethylene as a soft segment. When heat-cured, this homopolymer exhibited less water sorption, lower volume shrinkage, and greater deflection than did polymers of BisGMA or of TEGDMA, while maintaining acceptable flexural strength and modulus of elasticity.^{7,8}

Advances in Monomer Systems

1. Nonshrinking monomer system
2. Hydrophobic monomer system
3. Anti-cariogenic and anti-microbial monomer system
4. High-strength, high-conversion monomer system

Nonshrinking Monomers

Resin systems shrink during polymerization mainly because the monomer molecules are located at van der Waals distances from one another, while in the corresponding polymer; the monomeric units are within covalent bond distance of each other. Thus, in the polymer, atoms are closer to one another than they were in the original monomer. How well monomer and polymer molecules pack, if crystals are present in either phase, can also have a large effect on shrinkage.^{9,10}

Shrinkage that occurs in a cavity before the gel point while the monomer-polymer is still fluid can be partially compensated for by flow of resin composite from the free surface of the filling. This mode of compensation is not possible after gelation and, consequently, large stresses are built up in the filling. In many cases, these stresses result in adhesive failure, in which the resin composite pulls away from the cavity wall, or in cohesive failure, voids or micro cracks are produced within the resin phase.^{10,11}

Providing the tooth restoration interface remains intact, polymeriza-

tion shrinkage has been reported to pull the cusps of MOD cavities inward, resulting in cuspal flexure. This movement has been suggested to be responsible for postoperative sensitivity and oblique cuspal fracture. Conclusively, polymerization shrinkage is one of the main factors that determine the longevity of resin composite restorations.¹⁰

Thus motivated, a search was started for a nonshrinking resin system. The first approach used bicyclic compounds in ring opening polymerization. In such monomers, for every van der Waals distance converted to a covalent distance, at least two rings are opened during

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polymerization. Bailey reported that a variety of bicyclic monomers, including spiro orthoesters, spiro orthocarbonates, bicyclo ketal lactones, trioxabicyclooctanes and unsaturated diketals of benzoquinone, would undergo a double-ring opening with either no change in volume or an actual expansion.⁹

The use of spiro orthocarbonates as a component in dental resin composites resulted in a nearly volume neutral polymerization and in a doubling of the adhesive strength of the resin to etched enamel compared with a control. These advantages were obtained despite the presence of a large proportion of un-

reacted crystalline spiro orthocarbonate in the polymerized resin. Although these formulations showed some reductions in polymerization shrinkage when compared with the control resins, their shrinkage was still substantial.¹⁰

In alicyclic spiro orthocarbonates, a structure with an additional aliphatic ring is fused to the cyclic orthocarbonate rings. This spiro orthocarbonate monomer consists of four rings, two on each side of the spiro carbon. The expansion of the spiro orthocarbonate on polymerization is, as mentioned previously, attributed to a double spiro ring opening of the spiro orthocarbonate molecule, which involves the breaking of two covalent bonds to form one new bond.⁹

The expansion on homopolymerization was found to be 3.5 percent and experimental spiro orthocarbonate epoxy resins showed expansions between 0.1 percent and 0.8 percent compared with the 0.3 percent shrinkage of the epoxy resin control. Epoxy resins are suspect from a biocompatibility point of view.^{10,11} A study of the mutagenicity of the experimental spiro orthocarbonate epoxy resins indicated a mutagenicity of the epoxy formulation per se, whereas the spiro orthocarbonate proved non-mutagenic. In abandoning the epoxy resins in favor of BisGMA:TEGDMA resins, the shrinkage reducing or the eliminating effect of the spiro orthocarbonate was found to be minimal.¹²

A new class of difunctional monomers, termed oxybismethacrylates, was synthesized. Oxybismethacrylates exhibit cyclopolymerization, which is a polymerization process in which nonconjugated diene monomers undergo alternating intermolecular addition and intramolecular cyclo addition. This type of reaction generally involves 1,6-dienes, which

cyclize to introduce five- and/or six-membered rings into the polymer backbone.¹³

When preliminarily evaluating these cyclopolymerizing monomers for use in dentistry, Stansbury in 1990 found a potential for developing high-conversion, low-shrinking monomers.⁹ A 30 percent to 40 percent reduction in shrinkage was observed upon homopolymerization of oxybismethacrylate monomers and oligomers compared to dimethacrylates commonly used in dentistry.¹⁴

Depending on polymerization conditions, oxybismethacrylate monomers can produce either cyclopolymer exclusively or a mixture of cross-linked and cyclized polymer arising from competing 1,2- and 1,6-addition pathways. For polymerization shrinkage to be minimized, a resin must be prepared in which the monomer components can efficiently engage in the cyclopolymerization while still maintaining an adequate cross-link density in the resulting polymer. It seems that such resins with reduced, but not eliminated, polymerization shrinkage are now available in a form, which is compatible with the conventional dimethacrylate monomers used in dentistry.¹⁵

An *in vitro* biocompatibility test of oxirane/polyol dental composites and physical properties was done. It was observed that suitable oxirane/polyol formulations can be designed and optimized for development of dental composites with acceptable mechanical properties and biocompatibility. However, a leachable analysis of extracts obtained from longer incubation periods is needed before final conclusions could be drawn about the leachability of oxirane components.¹⁶ ESPE developed other epoxy-based systems for use in dental resins.

These siloxane-based oxirane molecules are capable of cationic polymer-

ization and produce composite materials with adequate properties for dental composites. They showed shrinkage after 60 minutes and 1.6 percent after 24 hours, which is half that of other posterior composites.¹⁷ Farracain et al. reported that synthesis of methacrylated derivative of styrene-allyl alcohol, MSAA comonomer replaced 20 percent or more bis-GMA in a bis-GMA/TEGDMA resin composite formulation containing 62 volume percent filler and showed reduced polymerization contraction by 20 percent, presumably by facilitation molecular rearrangements to relieve stresses.³

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Anti-cariogenic Monomer Systems

Yet another idea that could alleviate the detrimental effects of polymerization shrinkage has been a resin composite with anti-cariogenic effect. One approach has been to prevent plaque accumulation on and around resin composite fillings by the incorporation of an anti-bacterial agent into the resin matrix.¹⁸ Different chlorhexidine compounds have been added to experimental materials, and these were found to exhibit anti-bacterial activity by the release of the chlorhexidine. However, the idea has not been used commercially, probably due to the reduction of activity with time and the deterioration of

mechanical properties, which accompany the release of anti-bacterial agents.¹⁹

Light curable anti-bacterial, dental composite restoration materials, consisting of 80 weight percent of a strontium fluoroaluminosilicate glass dispersed in methacrylate monomers have been produced. The monomers contained 40 weight percent to 100 weight percent of a 10 weight percent chlorhexidine diacetate (CHXA) in hydroxyethylmethacrylate (HEMA) solution and 60-0 weight percent of a 50/50 mix of urethane dimethacrylate (UDMA) and triethyl-ene glycol dimethacrylate (TEGDMA). Both polymer and bacterial microleakage were prevented with a 90 weight percent HEMA/CHXA restoration in the bovine dentine due to swelling compensation for polymerization shrinkage in combination with anti-bacterial release.¹⁸

Chlorhexidine salts are available in various formulations for dental applications. Anusavice et al. tested the hypothesis that the release of chlorhexidine from a urethane dimethacrylate and triethylene glycol dimethacrylate resin system can be effectively controlled by the chlorhexidine diacetate content and pH. It was seen that the rates of release were significantly higher in pH 4 buffer, which was attributed to the increase of chlorhexidine diacetate solubility at lower pH. The higher level of filler loading reduced the degree of polymerization, leading to a greater loss of organic components and higher chlorhexidine release rates.¹⁹

Methacrylate copolymer systems with release of anti-microbial and anti-viral drugs have been formulated. Tallury et al. studied the release of anti-viral drug acyclovir (ACY) and anti-bacterial drug chlorhexidine diacetate (CDA) from synthesized copolymers of ethyl methacrylate and hexyl methacrylate of different molecular weights. They found

that varying the copolymer molecular weight, as well as the drug concentration, alters the drug release rates, and thus it is possible to control the drug release rates to a desired value.²⁰

With the purpose of developing a nonreleasing anti-bacterial resin composite, new monomers with anti-bacterial properties have been synthesized. The most promising monomer, 12-methacryloyloxydodecylpyridinium bromide i.e., MDPB, is a compound of the anti-bacterial agent dodecylpyridinium bromide and a methacrylyl group. Since MDPB can copolymerize with conventional dental monomers, the anti-bacterial portion of this molecule is chemically bound to the resin matrix after curing. BisGMA-based resin composite incorporating MDPB has been shown to have inhibitory effect on surface growth of *Streptococcus mutans* without releasing the anti-bacterial component.^{21,22}

Furthermore, MDPB has been found to have no adverse effect on curing or mechanical properties. However, a subsequent study has proven MDPB to have little bactericidal effect. The anti-bacterial effect of MDPB-containing resin composites is thought to be attributable mainly to an anti-adhesive activity of immobilized MDPB. As also Imazato et al. saw it, the essential question now is whether sufficient effect will be maintained once the surface is covered with acquired pellicle.²¹

MDPB, 12-methacryloyloxydodecylpyridinium bromide, was tested for its ability to inhibit the growth of organisms associated with active root caries lesions and to modify the growth characteristics of these organisms. It exhibited the potential to inhibit the growth of microbiota associated with active root caries lesions i.e., *S. mutans*, *S. oralis*, *S. salivarius*, *Actinomyces naeslundii*, *A. israelii*, *A. gerenscerviae*.²²

The anti-bacterial activity of an adhesive resin incorporating the anti-bacterial monomer 12-methacryloyloxydodecylpyridinium bromide (MDPB), as well as its bonding characteristics in terms of bond strength into dentin and curing ability, was investigated. The results indicated that an adhesive resin with anti-bacterial activity after curing could be produced by incorporation of MDPB without influencing bond strength or curing performance, suggesting the comprehensive bonding system including MDPB-containing primer and adhesive should be highly effective in its anti-bacterial effect before and after curing.²³

ONE OF THE MATERIALS associated with fluoride release, fluoride uptake by adjacent enamel, and low prevalence of secondary caries was silicate cement.

Fluoride is well-documented as an anti-cariogenic agent and the beneficial effect of fluoride on the human dentition has motivated the incorporation of fluoride into a host of dental materials. One of the materials associated with fluoride release, fluoride uptake by adjacent enamel, and low prevalence of secondary caries was silicate cement.²⁴ In an effort to duplicate the fluoride-release behavior of silicate cement, other fluoride-containing dental materials have been developed and investigated, including cavity varnish, silver amalgam, polycarboxylate cement, glass ionomer cement, and resin composite.

Different methods have been investigated to combine fluoride with resin composite. One method incorporates fluoride as part of the filler system in the form of the nearly insoluble salt, YbF₃, (Heliomclar Radiopaque, Vivadent).²⁵ By other methods, fluoride is added to the resin system. Resin composite with a content of NaF has been found to release fluoride that is taken up by adjacent enamel. When NaF is added as a soluble salt, physical properties seem to be maintained, and although the amount of fluoride released is smaller than that of glass ionomer cements, the resin composite is expected to have an anti-cariogenic effect in vivo. For NaF (and YbF₃) to be released, water must diffuse through the matrix, dissolve the fluoride, and the fluoride must then diffuse out.^{1,24}

According to another method, fluoride is bound to the resin matrix. For the fluoride to be released, water must diffuse into the matrix, cause a chemical change that liberates the fluoride, and then carry the fluoride out. In polymers, this fluoride-releasing principle allows the matrix to reorganize at the molecular level and thus to maintain structural integrity. One such material that has been developed is an acrylic-amine BF₃ Lewis salt that can copolymerize with BisGMA resins.²⁵

Fluoride release has been reported to occur as a consequence of BF₃ separating from the amine complex and being hydrolyzed to form F⁻. This fluoride-containing monomer has been incorporated in a light-curing sealant for use in orthodontics (Flurobond, Ormco) and as a composite surface sealant (Optiguard, Kerr).

Another fluoride monomer that has been synthesized consists of methacrylyl fluoride. The fluoride ion is formed when the acid fluoride is hydrolyzed by water. The monomer has been used in a light-cured sealant and found to release fluo-

ride for over two years while maintaining tensile strength. A third fluoride-exchange material is based on an acrylic-amine HF salt that can copolymerize to impart a fluoride-releasing capacity to light-curing resin composites and sealants.^{1,25}

A fluoride-releasing dimethacrylate monomer containing a ternary zirconium fluoride chelate was synthesized.²⁶ The combined use of the fluoride-releasing dimethacrylate monomer and fluoride-releasing filler can provide sustained high fluoride release and recharge as well as acceptable mechanical and physical properties. Simply adding organic fluoride salt in the monomer yields composites with poor mechanical and physical properties.

Pulp tissue reactions to a fluoride-releasing all-in-one resin bonding system (Reactmer Bond and Reactmer Paste) in nonexposed monkey teeth were histopathologically evaluated.²⁷ The pulpal response of the Reactmer group was minimally different from that of the control group. Consequently, the Reactmer system was determined as being biologically compatible with vital pulps.

Hydrophobic Monomer System

Sankarapandian et al. studied the water sorption, hardness, and glass transition of several bis-GMA analogues that substituted F and phenyl groups on the central carbon.²⁸ Fluorine addition to the central methyl group reduced sorption to less than 10 percent of bis-GMA, and the fluorinated polymers were more stable during water storage, showing less reduction in hardness. It was also reported that the increased flexibility of these resins contributed to a higher DC than occurs in bis-GMA during polymerization.

Fluorinated dimethacrylates based on bis-GMA and UDMA with lower water sorption than bis-GMA resins have been synthesized by Stansbury and Antonucci.²⁴

Mixtures having adequate strength for dental composites are created when these resins are mixed with fillers treated with silane coupling agents, such as 10-methacryloxydecyl-triethoxysilane, that are more hydrophobic than the normal gamma-methacryloxypropyl-trimethoxysilane.

In similar work, TEGDMA has been tried with limited success as a more hydrophobic diluent compomer to be used with bis-GMA base monomer for composites. The water sorption of composites have included the synthesis of UDMA analogues containing either a phenoxyethyl group on the periphery or a bulky aliphatic group

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to replace the core segment of the UDMA. The objective is to reduce the possibility for water to attack the urethane linkages through steric hindrances. These resins showed 10 percent to 30 percent reduction in water sorption compared to conventional UDMA, but also had lower flexure strength. Because of their low viscosity, these monomers are proposed as comonomers rather than base monomers for composites.^{3,29}

High-Conversion, High-Strength Monomer Systems

As mentioned previously, a large number of methacrylate groups of the dimethacrylate monomers in most

resin composites are left unreacted in the cross-linked polymer. As the presence of significant residual unsaturation impairs the physical, mechanical, and chemical properties, new monomer systems with a potential for better conversion have been requested.

High conversion is not a goal in itself, however. For instance, increasing the content of TEGDMA in a BisGMA:TEGDMA comonomer will increase conversion, leave hardness unaffected, but at the same time make the material very brittle and prone to fracture. Also, the degree of conversion of dimethacrylates may be very high if the distance between the methacrylate groups is long, i.e., the molecular weight is high. However, if the monomer is very flexible and not sufficiently bulky, mechanical properties will be poor. The task, therefore, is to develop high-conversion resin systems while not impairing mechanical properties.³⁰

Stansbury and Antonucci theorized that one practical means of addressing the relatively low degrees of conversion of dental resins would be the use of a more reactive diluent monomer.³¹ The monomer in mind was *c*-methylene- γ -butyrolactone (MBL), the cyclic analog of methyl methacrylate, which they evaluated for use as a comonomer in BisGMA-based dental resins. MBL is highly mobile and, apart from other favorable properties as compared with methyl methacrylate, is more reactive.

As anticipated, MBL had a beneficial influence on the degree of conversion of the experimental resins. Increased conversion was obtained and mechanical properties were preserved or even improved, and the authors concluded that methylene lactone polymers might result in new materials with enhanced performance.

To minimize the detrimental effects of polymerization shrinkage and

to maximize the degree of conversion, mechanical properties, and wear resistance, the concept of resin composite inlays was introduced a little more than 15 years ago. It was hoped that extraoral polymerization would increase the longevity of resin composite restorations and bring resin composite closer to being a feasible amalgam substitute.³⁵

Subsequently, the marginal adaptation of resin composite inlays has been reported to surpass that of resin composite fillings. The inlay technique has not, on the other hand, been found to provide significant or long-term improvements in mechanical properties, although it appears to be an effective mechanism for increasing the degree of conversion. Judging from the relatively limited use of resin composite inlays, direct as well as indirect, the advantages of resin composite inlays have not been sufficiently pronounced to convince the dental profession of their justification.⁷

The addition of cross-linking agents has also been investigated in resin composite filling materials. Aldehyde and diketone were hypothesized to be able to increase the degree of cross-linking by reacting with methacrylate double bonds and other pendant and backbone functional groups from different polymer chains in either nucleophilic or free radical reactions.³² The significant improvements in mechanical properties found as a consequence of aldehyde or diketone addition were seen as indications of an enhanced degree of cross-linking. Subsequent determinations were made of the effect of propanal (propionaldehyde) and diacetyl (2,3-butanedione) on the degree of conversion of methacrylate double bonds.

Consequently, it was concluded that the enhancements in mechanical properties probably reflected an increased conversion of double bonds rather than a

cross-linking of other functional groups.³³ Also, propanal and diacetyl were suggested to exert their effect mainly via chain transfer reactions. A recent study confirmed that these agents become bound in the polymer structure, and a theory of the chain transfer reaction mechanisms was presented; how propanal and diacetyl have been proposed to act as chain transfer agents and offer explanations as to the effects on strength, hardness, and degree of conversion of varying content of a chain transfer agent.³³

In an attempt to develop a mechanically stronger and hopefully more wear

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and fracture resistant resin composite, Peutzfeldt and Asmussen proposed that the degree of cross-linking in the polymer matrix could be increased by the addition of carboxylic anhydride to conventional monomer mixtures. Most pronounced effects of anhydride addition were measured for resin composites based on UEDMA and HEMA, as compared with materials based on BisGMA and TEGDMA and for materials also containing methacrylamide. Such materials resulted in a 20 percent increase in strength and stiffness. Experiments directed to optimize the postcuring conditions of resin composites containing carboxylic anhydrides

indicated that a one-hour heat treatment at 150 degrees Celsius was preferable.

Furthermore, in the early stages of polymerization, characterized by substantial unsaturation, a cross-link will be formed to an adjacent unreacted double bond. In a late stage of polymerization, some remaining unreacted double bonds may be expected to be situated singly rather than in pairs or groups as they do in resins with a lower degree of conversion, i.e., in the early stages of polymerization.^{32,34} At this late stage, the chain transfer agent will cause an increase in degree of conversion but not in additional cross-linking.

Consequently, it seems that the use of additives with the effect of diacetyl and propanal, causing some 15 percent increase in degree of conversion of methacrylate double bonds and some 25 percent increase in mechanical properties, could be one viable means of developing resin composites for use in stress-bearing areas.³⁴

Prakki et al. evaluated the effect of two additives, aldehyde or diketone, on the wear, roughness, and hardness of bis-GMA-based composites/copolymers containing TEGDMA, propoxylated bis-GMA or propoxylated fluorinated bis-GMA combined with aldehyde (24 mol percent and 32 mol percent) or diketone (24 mol percent and 32 mol percent).³⁵ It was seen that Bis-GMA/TEGDMA and bis-GMA/CH(3)bis-GMA copolymers with additives became smoother after abrasion test and improved the degree of conversion of some composites/copolymers thereby enhancing mechanical properties.

Conclusion

Since the beginning of the 21st century, dental composites have made their presence felt and have become the leading dental restorative material. There have been many improvements in the proper-

ties of this material by change mostly in the filler particles. The real problem could not be fixed unless the matrix system was improved. Recently, there has been a remarkable invention of expanding monomers that have shown promising results by reducing or eliminating the polymerization shrinkage. The incorporation of acyclic spiro ortho carbonates and oxybis-methacrylate with combinations have been able to achieve that goal and soon it will be seen composites marketed with negligible shrinkage. Research on fluoride and chlorhexidine-releasing monomers has been going on for more than a decade. Composite materials with fluoride release are in the market but with limited mechanical properties.

The use of MDPB, chlorhexidine and copolymers of various fluoride-releasing systems have been combined with the matrix systems with increased mechanical properties, and, in a few years, one should see dental composites with potent anti-microbial effect with high strength.

The degree of conversion for dental composites is also being increased by adding propanal- and diacetyl-based agents to increase the cross-linking, whereby increasing the wear resistance and strength of the composite. Composites, the restorative material of present and the future, have undergone many changes their composition and will surely and constantly improve to be the ideal restorative material for the future. ■■■■

REFERENCES

1. Peutzfeldt A, Resin composites in dentistry: The monomer systems. *Eur J Oral Sci* 105(2):97-116, April 1997.
2. Soderpolin KJ, Mariotti A, BIS-GMA-based resins in dentistry: Are they safe? *J Am Dent Assoc* 130:201-8, 1999.
3. Ferracane JL, New polymer resins for dental restoratives. *Oper Dent* 6:199-209, 2001.
4. Henriks-Eckerman ML, Suuronen K, et al, Methacrylates in dental restorative materials. *Contact Dermatitis* 50(4):233-7, April 2004.
5. Floyd CJ, Dickens SH, Network structure of Bis-GMA- and UDMA-based resin systems. *Dent Mater* 22(12):1143-9, December 2006.
6. Phillips RW, Skinner's science of dental materials. The ed., Philadelphia, Penn, WB Saunders Co., 1973.
7. Craig RG, Powers JM, Restorative dental materials, 11th ed., C.V. Mosby Co., 329-626, 2002.
8. Khatri CA, Stansbury JW, et al, Synthesis, characterization and evaluation of urethane derivatives of Bis-GMA. *Dent Mater* 19(7):584-8, November 2003.
9. Stansbury JW, Synthesis and evaluation of novel multifunctional oligomers for dentistry. *J Dent Res* H:434-7, 1992.
10. Palin WM, Fleming GJ, Low-shrink monomers for dental restorations. *Dent Update* 30(3):118-22, April 2003. Review.
11. Tanaka J, Hashimoto T, et al, Polymer properties on resins composed of UDMA and methacrylates with the carboxyl group. *Dent Mater J* 20(3):206-15, September 2001.
12. Kostoryz EL, Tong PY, et al, In vitro toxicity of spiro-orthocarbonate monomers designed for nonshrinking dental restoratives. *J Biomater Sci Polym Ed* 11(2):187-96, 2000.
13. Eick JD, Kotha SP, et al, Properties of silorane-based dental resins and composites containing a stress-reducing monomer. *Dent Mater* 23(8):1011-7, August 2007.
14. Stansbury JW, Cyclopolymerizing able monomers for use in dental resin composites. *J Dent Res* 69:844-8, 1990.
15. Fong H, Dickens SH, Flaim GM, Evaluation of dental restorative composites containing polyhedral oligomeric silsesquioxane methacrylate. *Dent Mater* 21(6):520-9, June 2005.
16. Eick JD, Kostoryz EL, et al, In vitro biocompatibility of oxirane/polyol dental composites with promising physical properties. *Dent Mater* 18(5):413-21, July 2002.
17. Byerley TJ, Eick JD, et al, Synthesis and polymerization of new expanding dental monomers. *Dent Mater* 8(6):345-50, November 1992.
18. Leung D, Spratt DA, et al, Chlorhexidine-releasing methacrylate dental composite materials. *Biomaterials* 26(34):7145-53, December 2005.
19. Anusavice KJ, Zhang NZ, Shen C, Controlled release of chlorhexidine from UDMA-TEGDMA resin. *J Dent Res* 85(10):950-4, October 2006.
20. Tallury P, Airrabeelli R, et al, Release of anti-microbial and anti-viral drugs from methacrylate copolymer system: Effect of copolymer molecular weight and drug loading on drug release. *Dent Mater* 24(2):274-80, February 2008.
21. Imazato S, Torii M, Tsuchitani Y, Immobilization of an antibacterial component in composite resin. *Dent Japan* 30:63-8, 1993.
22. Yoshikawa K, Clark DT, et al, The effect of anti-bacterial monomer MDPB on the growth of organisms associated with root caries. *Dent Mater J* 26(3):388-92, May 2007.
23. Imazato S, Kinomoto Y, et al, Anti-bacterial activity and bonding characteristics of an adhesive resin-containing antibacterial monomer MDPB. *Dent Mater* 19(4):313-9, June 2003.
24. Stansbury JW, Antonucci JM, Dimethacrylate monomers with varied fluorine contents and distributions. *Dent Mater* 13(3):166-73, May 1999.
25. Chan WD, Yang L, et al, Fluoride release from dental cements and composites: A mechanistic study. *Dent Mater* 22(4):366-73, April 2006.
26. Xu X, Ling L, et al, Formulation and characterization of a novel fluoride-releasing dental composite. *Dent Mater* 22(11):1014-23, November 2006.
27. Sonoda H, Sasafuchi Y, et al, Pulpal response to a fluoride releasing all in one resin bonding systems. *Oper Dent* 27(3):271-7, 2002.
28. Sankarapandian M, Shobha HK, et al, Characterization of some aromatic dimethacrylates for dental composite applications. *J Mater Sci Mater Med* 8(8):465-8, August 1997.
29. Li T, Craig RG, Synthesis of fluorinated Bis-GMA and its use with other fluorinated monomers to formulate hydrophobic composites. *J Oral Rehabil* 3(3):158-62, March 1996.
30. Shobha HK, Sankarapandian M, et al, Structure property relationship among novel dental composite matrix resins. *J Mater Sci Mater Med* 8(6):385-9, June 1997.
31. Stansbury JW, Antonucci JM, Evaluation of methylene lactone monomers in dental resins. *Dent Mater* 8:270-3, 1992.
32. Peutzfeldt A, Asmussen E, Influence of aldehydes on selected mechanical properties of resin composites. *J Dent Res* 71(8):1522-4, August 1992.
33. Peutzfeldt A, Asmussen E, Ketones in resin composites. Effect of ketone content and monomer composition on selected mechanical properties. *Acta Odontol Scand* 50(4):253-8, August 1992.
34. Peutzfeldt A, Asmussen E, In vitro wear, hardness, and conversion of diacetyl-containing and propanal-containing resin materials. *Dent Mater* 12(2):103-8, March 1996.
35. Prakki A, Cilli R, et al, In vitro wear, surface roughness and hardness of propanal-containing and diacetyl-containing novel composites and copolymers based on bis-GMA analogs. *Dent Mater* 24(3):410-7, March 2008.

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