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Review

The quest for stable biomimetic repair of teeth: Technology of resin-bonded composites

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The rationale leading to the present generation of resin composites is surveyed. There are many sub-classes such as flowable materials with specialized clinical indications. But a simplistic categorization of resin-composite materials is inappropriate. It is better to appreciate the factors that have driven recent developments. These include the search for low shrinkage composites and for greater depth of cure. Other necessary features are good handling behavior and sufficient strength for load-bearing situations. The esthetic challenge is for materials with superior and life-like optical properties and it is important to identify products that are good in every critical property. Nanotechnology has led to certain improvements, but the possibilities and limitations of nanoparticles must be appreciated. In all these developments, the structure and properties of the host tissues are a challenge and inspiration. Thus materials that can emulate the features of enamel and dentin are the goal of biomimetic design.

Keywords: Resin composite, Biomimetic, Photopolymerization, Shrinkage

INTRODUCTION

For more than a century dental scientists and clinicians have sought for ways to repair damaged hard tooth tissues. There is a potential alternative strategy: regeneration. But, despite the remarkable potential of stem cells, this strategy is likely to be restricted to niche areas, such as the dental pulp, gingival tissues and alveolar bone, for the medium term future of clinical dentistry.

The principal requirement for hard tissue repairs is that they must be stable and gradually the wisdom has developed that such repair materials should be biomimetic —that is, imitating the structure and properties of the host tissues. With the decline in use of dental amalgam, resin-composite materials have been developed and refined as the superior restorative material. Here we shall use the acronym RBC —resin-bonded composite. The term "composite", in materials science, denotes: "… a multiphase material that exhibits properties of the constituent materials so as to produce a material with better properties than could be achieved by each constituent material alone". The hard dental tissues, enamel and dentin are excellent examples of composite structure. For dental applications, RBCs are a combination of particles, coated by a coupling agent, dispersed in an organic resinous matrix, as originally developed by Bowen 50 years ago[1]. However we now need to think a little 'outside the box' with the technology of newer RBCs. We should consider further the way that they have a biomimetic character, the possibilities of new matrix monomers or fillers and even the possibility of using reactive fillers, as in resin-modified glass-ionomers, where the filler/matrix boundary may become blurred or indistinct. Also self-repairing or stimulus-response materials may be developed[2].

The number of available formulations is now so large that it is necessary for the dentist to make an informed choice on the basis of clear principles including an understanding of how structural changes affect properties and performance. Almost all of these materials require the application of system adhesives to bond to enamel and dentin. This is a huge and important area of research and development that lies mainly outside the scope of the present review[3]. Though many advances have been made in the development of dental adhesives, two major factors can still affect the stability of the bonding layer: (a) disruption created by the resin composite stress due to polymerization[4] and (b) biochemical deterioration over a long period of clinical service time[5].

RBCs are already used for a variety of applications in dentistry. Even the International Standard (ISO 4049) concerned with these materials has gradually been broadened in scope to include flowable composites, resin cements and pit and fissure sealants.

FUNCTIONAL REQUIREMENTS OF COMPOSITE ORAL BIOMATERIALS

Design priorities for RBCs relate to their key functions especially for the major application as coronal restorative materials. In sequential order of application, we require:

1. User-friendly handling properties.
2. Rapid property development: 'kinetic functionality' as the material hardens by light-cure.
3. Customized space filling: dimensionally stable materials.
4. Distribution of stress/load transmission: strong and retentive/adhesive materials.
5. X-ray contrast: radiopacity.
6. Esthetic appearance: appropriate optical properties: translucency, gloss, opalescence.

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The requirement for dimensional stability embraces several aspects. Polymerization shrinkage should be as low as possible. But also the material should be stable against temperature changes (low coefficient of thermal expansion) and occlusal loading —so that the material does not distort plastically or by progressive creep. Esthetic appearance is of increasing importance and being tooth-colored involves fulfilling even more demanding requirements. Yet the optical properties of natural teeth are very complex due to scattering of light at internal interfaces and by the absorption of wavelengths in pigmented regions of the tooth. There are also metameric effects where the appearance depends on the surrounding intra-oral environment.

ADDITIONAL BIO-FUNCTIONALITY AND THE ROLE OF BIOMIMETICS

Today, biocompatibility is considered a positive attribute of a biomaterial. It is more than the absence of harm (irritancy, carcinogenicity, *etc*). A biocompatible material generates an appropriate response in a given host tissue environment. So such responses can be of biological benefit. This can come about, in the case of implants, by promoting osseointegration. With RBCs there is the possibility of bioactivity either by inherent properties of resin-composite surfaces or by gradual release of substances from within the interior bulk of the material. This connects with the science and technology of controlled drug delivery.

As one of the key requirements of resin-composite restoratives is to act, not only as a substitute dentin material, but also as a substitute enamel tissue, these materials must rapidly become hard and strong and remain so. This is not obviously a suitable medium or matrix for surface grafting or controlled release of bioactive species.

The acid demineralization procedure in dentin exposes the collagen fibers that are the scaffold or matrix responsible for the cohesion of the native tissue. The ultrastructure of collagen is well known to be hierarchical in character like many other biological materials. Minimally the collagen provides a network structure and this feature must be duplicated in any biomimetic restorative material. The fibrous nature of collagen might suggest the need for a fibrous composite matrix, but there are practical reasons associated with customized clinical placement that make this approach difficult. Nevertheless, imaging the mineral phase in native collagen shows a very fine-scale distribution of nano-particles.

FILLER PARTICLE SIZE DEVELOPMENTS AND NANO-TECHNOLOGY

Why incorporate particles in a composite? The biological dentin structure suggests this approach by way of mimicry. However particulate inorganic fillers in RBCs provide material strengthening and reinforcement[6]. They are manufactured *via* three main routes: burning silicon compounds in oxygen (pyrolysis); precipitation from solution, the sol-gel route, or by grinding large particles to progressive fineness.

In recent decades, many types, shapes, sizes, volume fractions and distributions of filler particles have been used to provide products for diverse clinical applications. A RBC used for esthetic restorations might exhibit higher polishability, whereas for posterior restorations it might possess high strength to resist occlusal forces. Thus, the filler content plays an essential role in composite properties and many investigations have established the relationship between the filler content and the resultant properties, such as: abrasion resistance and hardness[7,8]; thermal stability[9,10]; radio-opacity[11]; gloss retention and roughness[12]; water sorption; material shrinkage[13]; visco-elastic creep and recovery[14]; elastic moduli[15]; fracture toughness[16]; and fracture behavior[17,18].

Initially, ground quartz fillers, with a mean particle size of 10–20 µm, were incorporated into the methacrylate-based RBCs. Unfortunately, these were very difficult to polish and the end result was an unacceptable appearance.

Consequently, the filler phase was changed to extremely small particles of colloidal silica with a mean size of 0.02 µm. However, the large total surface area of all these small particles made their incorporation in the resinous matrix difficult.

To provide a material with both acceptable esthetics and strength, hybrid materials with a mean particle size of 1 µm were commercialized and variations have been used up to the present time[19].

"Nanofillers" have also been applied in RBC formulations with the expectation that these materials could provide strength and esthetic properties suitable that for both anterior and posterior restorations[20]. However, while this claim may be true, there is much misunderstanding about the possibilities and limitations of true nano-fillers. The special features of nanofillers arise from their fabrication normally as precipitates in solution with particle sizes in the range 5–70 nm. For a given mass they have a huge total surface area. They are spherical particles based on silica (SiO_2) or zirconia (ZrO_2). If they are created in a liquid they are non-agglomerated and do not settle out in low-viscosity liquids, such as monomers, due to thermal agitation (Brownian motion) from the surrounding molecules. They have a low influence on monomer viscosity such that the monomers remain pourable. One of the great benefits of nano-particles is that, being smaller than the wavelength of light, they can form highly translucent materials. However, they are only effective when dispersed to a maximum concentration of 50% in liquid monomer-which may constitute perhaps only 20% of the composite volume. Hence the whole composite contains only about 10% true nanofiller. Thus the remaining percentage (say 70%) of the composite volume has to be supplied by ground glass microfiller, with possible additions of agglomerated sub-micron or so-called 'nano' filler. In some materials special clusters of nano-particles —rather like bunches of grapes— have been added as the main filler[21]. They are formed *via* partial sintering of nanoparticles. They are easier to incorporate into resin monomers and the resultant composites are highly polishable, as the clusters can be cut readily by finishing instruments.

One of the major variables in RBC formulation is the volume-fraction (v_f) —the fraction of the RBC paste occupied by filler particles. If these were all one size, and approximately spherical in shape, the maximum v_f would be about 64%. However, there is an unavoidable size variation. If one or more smaller ranges of particles are added to larger particles, these may occupy spaces in between. There are practical limits as to how far this size-optimization can be taken, because of the consequences for system viscosity. Nevertheless, RBCs have been made with a volume-fraction as high as 85%, leaving just 15% of the total volume to be made up by the organic matrix. The resultant pastes will be very stiff, and possibly a volume-fraction of 75% may be sufficient and optimal. However, very stiff RBC pastes may be handled clinically either *via* (a) ultrasonic application or (b) pre-heating. With high volume-fractions (say above 64%) there is a very high incidence of particle-particle contact. This makes the pastes stiffer but also ensures higher modulus and stress (load) transfer when the materials are cured. By contrast, some flowable RBCs have lower v_f, although reduced v_f is not the only way to formulate a flowable material, as this may be achieved by more fluid monomers.

DIMETHACRYLATE-MATRIX COMPOSITES AS THE PRESENT NORM

The current benchmark RBC is represented by modern nano-hybrid composites suitable for many different clinical situations. These ‘universal composites’ are commonly based on a Bis-GMA matrix in combination with a high filler content of mostly dental glass particles with a mean particle size <1 µm and nano-particles, as explained above.

A typical range for flexural strength is 100–120 MPa and the new generation of composites has a typical volumetric shrinkage mostly in the range of 1.4–2.5%. Modern products claim natural shade adaptation, easy polishability and convenient handling properties.

The resin matrix is formulated with organic monomers, in the fluid state, that are converted into a rigid polymer network. Bis-GMA has been a widely used since the introduction of RBCs and is extremely viscous due to hydrogen bonding between adjacent molecules via the hydroxyl groups. This hinders the addition of fillers. Consequently, diluent monomers, such as triethyleneglycol dimethacrylate (TEGDMA), have to be used. Some other monomers can also be used as the resinous matrix, for example, urethane dimethacrylate (UDMA), Bis-EMA, EGDMA and others. Structurally, all these molecules consist of two methacrylate functional groups separated by ‘spacer groups’ that are either totally or only partially flexible. Bis-GMA and other dimethacrylates based around the modified bis-phenol-A structure are relatively inflexible. They are able to react together through the radical addition polymerization process, activated by light irradiation.

An initiator/co-initiator system is required to start the polymerization process. Also, an inhibitor to allow long-term storage, and pigments that provide a wide range of tooth-matching color-shades[22] are necessary.

A coupling agent is used to bond the inorganic phase (filler particles) with the organic phase (resinous matrix)[23]. The most common agent is γ-methacryloxypropyl-triethoxysilane (γ-MPTS); and its use increases the mechanical properties. The silane agent enables stress transfer between the resin and the particulate phase, during loading, and reducing the number of crack initiation sites. Furthermore, this coupling agent reduces the water sorption/solubility phenomena and increases the material’s wear resistance[19].

Until recently, all dental RBC matrices were polymerized by free-radical addition (FRA) polymerization mechanisms, activated by light irradiation or *via* chemical mixing. The general FRA polymerization mechanism for light-activated dental composites has discrete stages: activation/initiation, propagation and termination. Many RBCs use camphoroquinone (CQ) as the photo-initiator[24-26]. Consequently, visible light is required, centered in the blue region of the spectrum (400–550 nm), nowadays emitted from a light-emitting diode (LED) sources. Light activates CQ and converts it to an excited triplet state. The excited CQ then reacts with a co-initiator to form free radicals, which are molecules with unpaired electrons, starting the polymerization process (activation and initiation stages)[27].

When a free radical reacts with a monomer molecule, an active center is created. Thus, propagation involves growth of each polymer chain by rapid sequential addition of monomer to the active centers *via* covalent bonds until the maximum degree of conversion (DC) of C=C double bonds, to C–C bonds, is reached. This is normally much less than 100%, typically 60–65 %. Individual polymer chains, with free radical chain-ends, may become de-activated by several possible mechanisms so that they cannot grow anymore (termination). Moreover, active radical-ended chain units become trapped in the increasingly viscous matrix and thus are sterically and thermally hindered from further reaction at the ambient temperature, especially after the vitrification point (glassy condition) is reached.

The rate of monomer disappearance (conversion into polymers) as a function of time is known as the rate of polymerization (Rp). For dimethacrylates, there is sharp increase in (Rp) (auto-acceleration) as the conversion of monomer increases. Thus, Rp achieves a maximum value (R_p^{max}) and then suddenly decreases (auto-deceleration). This happens because, as indicated above, while the polymer chains grow, the viscosity of the medium also increases, restricting the propagation and diffusion of the polymer chains. The reaction kinetics are described in detail elsewhere[28,29].

STRATEGIES TO REDUCE POLYMERIZATION SHRINKAGE

Volumetric shrinkage occurs during the overall process of methacrylate polymerization because the distance between groups of atoms in neighboring monomer molecules, resulting from van der Waals interactions, is reduced to establish the linking covalent C–C bonds in the new polymer backbone. The magnitude of *composite* volumetric shrinkage is dictated by the filler volume fraction, monomer composition and the final DC of the resin matrix(30). RBCs now used in restorative dentistry exhibit volumetric shrinkage ranging from less than 1% up to 6%, depending on the formulation and curing conditions(31-33).

Shrinkage by itself is not inherently the problem, but shrinkage-stress. This arises from the coupling of the shrinkage effect with both the increasing stiffness (elastic modulus) of the setting composite and the location of the setting composite in a cavity where it is normally bonded to the containing cavity walls.

Thus all methacrylate monomers shrink intrinsically to a greater or lesser extent according to the number of polymerizable C=C units that react. For unfilled monomers the shrinkage can range between 2 and 14%. The actual shrinkage occurring depends upon the DC of the matrix monomers. Thus one strategy to reduce shrinkage and its consequences can be to deliberately limit the DC or possibly the rate of conversion (polymerisation). But there is another possible strategy to reduce intrinsic monomer polymerization shrinkage: that is, to use different types of monomer!

Different resin-monomers may achieve the goal in three possible ways: by having either (1) increased molecular mass per reactive group, that is by creating larger 'spacer groups' between C=C functionality or (2) different functional group chemistry, with a lower unit volume-change on polymerization, or (3) spacer groups that pack compactly alongside adjacent molecules and are indirectly disrupted to occupy greater volume during functional group reaction. In case 1, the number of reactive sites per unit monomer volume would be reduced. For composite shrinkage, increasing the filler volume fraction also reduces the density of reactive sites per unit composite volume. One example of case 3 is the concept of using monomers with liquid-crystalline spacer units. Some monomers with liquid crystalline spacer groups were found to shrink less, due to the transition of their closely-packed nematic phase to a less dense isotropic amorphous state when photocured. This was promising with unfilled monomers, but less feasible with composite formulations(34).

There are some limitations in several of these approaches. The use of high-molecular-mass monomers is limited by their viscosity, increased stickiness, and difficult flow behavior, which compromise the handling characteristics of the resulting composites. Increasing the filler volume fraction has some limits, because a given amount of resin can incorporate only a finite amount of filler particles without adversely affecting the wetting of the increased filler surface.

RECENT CHANGES IN MATRIX CHEMISTRY: ORMOCER AND SILORANE

The changes in monomer chemistry were at first directed to improve the already clinical successful methacrylate-based systems, by modifying the Bowen monomer (Bis-GMA) to create monomers with lower viscosity rather than lower shrinkage(22,35-36). These include the hydroxyl-free Bis-EMA(37), aliphatic urethane dimethacrylates (UEDMA)(38), partially aromatic urethane dimethacrylate(39) or highly branched multi-methacrylates(40).

Investigators have made several attempts to reduce shrinkage by changing the nature of the resin. ORMOCERs —a group of 'organically modified ceramics' — were developed by the Fraunhofer Institute for Silicate Research in Würzburg, Germany. They have many industrial and biomedical applications including polymerizable matrix systems for dental composites(41,42). Their dental application has been licensed to a number of major dental manufacturing companies and they are being used in some clinically successful dental composites. They are formulated as novel three-dimensionally cross-linked inorganic-organic polymers, synthesized from sol-gel precursors forming an inorganic Si-O-Si network by hydrolysis and polycondensation reactions. In dental applications the ORMOCER molecular core structure is modified by the addition of covalently bonded multi-methacrylate functionality. This means that these matrix structures are polymerizable by light curing with conventional photo-initiators. They also have filler particle additions to create a composite structure. ORMOCERs have a very similar coefficient of thermal expansion to tooth structure and have low wear rates. Their shrinkage is comparable with hybrid composites, despite having lower filler content. However one of the ORMOCER dental composites also has additional dimethacylate monomer (TEGDMA) added to the formulation, to improve the flow characteristics. This is less than ideal and experimental ORMOCER matrices free of added TEGDMA are preferable.

Ring-opening monomer systems have been synthesized and investigated as possible dental resin monomers for many decades. Some, such as spiro-orthocarbonates were tried as additives to dimethacrylates(43). However, the most notable innovation of this type was the development of the Silorane™ composite by 3M ESPE (Seefeld, Germany)(32,44). Silorane™ is an epoxy functionalized cyclic siloxane whose name is derived from the combination of its chemical building blocks siloxanes and oxiranes. The material is a cationic ring-opening monomer system. The network of Silorane is generated by the cationic ring-opening polymerization of the cycloaliphatic oxirane groups. The cationic cure starts with the initiation process of an acidic cation. This opens the oxirane ring and generates a new acidic center, a carbocation. After the addition to an oxirane monomer, the epoxy ring is opened to form a chain or, in the case of two- or multifunctional monomers, a network. Nanocomposites containing Silorane and fillers exhibit low shrinkage and acceptable mechanical properties. Satisfactory clinical investigations have been published45). However, the material has not been a commercial success, for several reasons, and it has now been withdrawn from the market.

METHACRYLATE-MATRIX COMPOSITES FIGHT BACK!

Despite the intense interest shown in novel non-methacrylate resin-composites and significant financial investment in their development, there are still good reasons why di- or multi-methacrylate systems remain popular and viable for further development and refinement. These reasons include readily compatible adhesive systems and the ability to mix and match materials, especially when undertaking composite repairs. Several newer types of methacrylate composite system have been introduced.

However, it is not sufficient to produce a resin-composite with low shrinkage. It is clear from clinical trials and reviews that materials intended for universal applications must have sufficient mechanical strength, especially as it is now routine to place composites in larger multi-surface class II cavities. In a 2005 review it was concluded that that clinical data indicate both secondary caries and restoration fracture are the most common clinical problems in posterior composite restorations46). In a survey of prospective studies on the clinical performance of posterior resin composites published between 1996 and 2002 it was concluded that the most frequent failure mode up to 5 years was restoration fracture, followed by secondary caries47). With composite restorations placed in larger cavities, the main reason for failure of was found to be fracture48,49), also for periods longer than 11 years. The compromises necessarily to create universal composites, by decreasing the filler size to improve esthetics, could have led to decreased mechanical properties. Hence to address these two modes of failure, it is important to have an equal emphasis on low shrinkage and high strength50).

The material Kalore (GC Dental, Tokyo, Japan) is an interesting material that incorporates a very large dimethacrylate monomer produced by the DuPont Company. This large size reduces the functional-group density, facilitating low shrinkage.

A novel monomer system was developed by the Dentsply company. This is termed a stress-decreasing resin (SDR technology). This is marketed as a flowable composite, (SureFil, Dentsply Sirona, Konstanz, Germany) which has some excellent handling properties and on setting generates a low shrinkage-stress. This is intended for application in the base of a cavity, with very good adaptation. It is not intended for restoration of the outer coronal third. Here a stronger composite is indicated. The exact setting mechanism of this monomer is not completely clear. Nevertheless it is noteworthy among current materials as the first technology that allowed 4 mm bulk placement in flowable consistency.

Vertise Flow (Kerr Dental, Orange, CA, USA) is another interesting flowable material, which also claims to be self-adhering to both dentin and enamel. So it is designed to function without a system adhesive. Inevitably this involves the incorporation of some hydrophilic monomers, which makes the product prone to hygroscopic expansion. This may limit the approach to the flowable category.

Venus Diamond (Kulzer Dental, Wehrheim, Germany), is a material that has been re-designed both as respects the filler system and the matrix monomer system. The latter incorporates a new urethane acrylate monomer that will co-polymerize with methacrylate monomers. The filler system is optimized with multi-modal particle size ranges. This delivers a resin-composite of high strength, good esthetics and low shrinkage.

There are a number of possible future strategies for development. These include: (1) self-adhesive composites; (2) fiber-reinforced composites; (3) self-healing composites (4) remineralizing composites; and (5) antibacterial composites. The question remains, however, as to whether all these strategies can co-exist in a single biomaterial51)?

CONCLUSION

A variety of technologies have been deployed to reduce polymerization shrinkage and stress of resin-composites. Reduced shrinkage stress is a key indicator for a long lasting marginal integrity. But improved mechanical performance is important to prevent fracture of fillings, which is another typical mode of restoration failure. Some products appear to fulfill a complete set of requirements, especially low shrinkage stress and high mechanical performance. However the full range of new products and monomer systems should be evaluated critically.

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