



Resin-Based Composites: A Comprehensive Review of Material and its Properties

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Abstract

A common trend emerging amongst the population is the demand for esthetic restorations. Resin based composites have revolutionized restorative dentistry not only because of the esthetic appeal but also due to the minimally invasive application and satisfactory clinical performance. They have been a component in restorative dentistry that have been constantly and rapidly developing. Various new chemistries of dental resins are being researched about, advanced filler technologies are being used and novel polymerization techniques are emerging. This review explores the composition, polymerization mechanisms and the associated properties which affect the clinical performance. Further, this review aims to provide a deep insight of resin-based composites and provide clinicians the understanding of the material's role in advancing restorative dentistry.

Keywords: Resin Based Composites; Light Cure; Polymerization

Introduction

Dental caries is a widely prevalent non communicable, multifactorial oral disease, resulting in loss of tooth structure through demineralization and further impairment in masticatory ability [1]. To restore the normal form and physiological function, various restorative materials have been used over the due course of time. Of these, Dental Amalgams have set a standard with its exceptional physical and mechanical properties. However, with the concerns of it being a hazard in terms of health and waste disposal, and the lack of it being aesthetic, tooth-colored materials have come into being.

The history of tooth-colored materials dates back to 1870, with the development of silicate cements. Although it

reported fewer incidences of secondary caries, the poor physical properties and lack of color stability have limited its use. The 1940s saw the development of unfilled polymethyl methacrylate resins, however, the poor color stability and poor mechanical properties still remained a concern. In 1955, Dr. Richard Bowen was the key individual in the development of BisGMA, a bifunctional molecule and this development had revolutionized aesthetic restorations in dentistry due to its natural appearance. The world of composites has been developing ever since, in all the aspects ranging from the chemistry of adhesion to tooth to the physics of light curing.

The term 'composite' is used to denote any material having more than two to three phases. The enamel, dentin and cementum amongst other tissues are the composites of nature. Dental composites are restorative materials having

an inorganic and an organic phase bound together by a coupling agent.

The composites available currently have more evolved chemistries, better handling properties and various types of filler systems. This literature review aims to provide a comprehensive analysis of this material, its compositional chemistry, properties and its impact of the clinical performance along with the recent and future prospects.

Discussion

Composition

In alignment with the term composite, resin based composites (RBCs) too have two distinct phases—a continuous phase and a dispersion phase, held together by a coupling agent.

The **resin matrix** constitutes of the **continuous phase**, holding the particle of the dispersed phase together and providing the set resin the structural integrity. The classically used resin monomers includes BigGMA, a large molecule (800,000 centipoise), UDMA and the smaller molecule monomer, TEGDMA (3-50 centipoise). While BisGMA contributes to the strength and lower polymerization shrinkage, it forms a highly viscous resin. Thus, TEGDMA, amongst other monomers including MMA and EGDMA are used as diluent monomers.

Newer monomers include AUDMA, an aromatic methacrylate, AFM (addition fragment monomers) improve the cross linking of the resin and polycrylate all used in composites manufactured by 3M. These monomers impart better physical and mechanical properties, resulting in a better clinical performance. BisEMA has also been additionally utilized to enhance the flexibility and reduce water sorption in the RBCs [2].

The **dispersion phase** that reinforces the resin matrix is formed by **the fillers**. What began with hard, pure quartz (highly abrasive) has now evolved to boro-alumino-silicate 'soft glasses'. Fillers can be categorized into two basic types –

Inorganic

- Fused silica and colloidal silica obtained by pyrolytic processing (A process to obtain pure silica where, natural salts of silica like silica tetrachloride is heated to 1000-1500 °C in the absence of oxygen to obtain SiO₂)
- Glass based fillers containing barium glass (Eg- Tetric EvoCeram, Ivoclar),
- Alumino-silicate or strontium glass particles
- Ceramic based fillers with zirconia-based reinforcers (Filtek Z-250 XT, 3M)
- Ytterbium Fluoride

Organic

- Pre-polymerized fillers (Tetric PowerFill, Ivoclar)
- Organically modified fillers (ORMOCER's) (Beautifil II, Shofu)
- Bioactive fillers releasing calcium phosphate or Glass Ionomer particles

The filler characteristics directly affect its clinical performance. Smaller fillers allow a higher filler loading by weight in contrast to a larger filler particle size, allowing a higher degree of reinforcement and a combination of smaller filler particle sizes allows multimodal distribution of the fillers, thus, improving the characteristics of the resin. Various filler particles have evolved over time ranging from Macrofilled, Midfilled, Minifilled, Microfill, Microhybrid and Nanohybrid fillers, each having its own advantages and disadvantages and most commercially available resins are in the hybrid filler size ranges (Table 2).

The shape of the filler can either be spherical or irregular (fibers or whiskers). Irregularly shaped fillers intertwine and can help reduce polymerization shrinkage. At this stage it is important to add a note on the Polymeric rigid inorganic matrix material (PRIMM). The fillers intermesh and form the primary phase rather than a dispersed one, with the resin intervening, having a tougher structure, showing less polymerization shrinkage [3].

The two distinct phases can exist together by being bonded to each other via the coupling agent. Organosilanes like γ -methacryloxypropyltrimethoxysilane are commonly employed agents. These compounds through the two binding sites bond to the resin phase on one end and to the fillers on the other. Titanates, zirconates, 3-glycidoxypropyltrimethoxysilane (used with organosilanes) are some other coupling agents.

Minor constituents include activators, initiators, optical modifiers and inhibitors. Tertiary amines like Dimethyl p-toluidine and Dihydroxy ethyl p-toluidine activates initiators like benzoyl peroxide in case of self-cure or campheroquinone (CQ) in case of light cure RBCs to release a free radical. To limit inadvertent polymerization in order to increase the shelf life of the resins, inhibitors like butylated hydroxytoluene or Hydroquinone or Monomethyl ether of hydroquinone are used.

Polymerization

With the constantly developing chemistries of monomers, various polymerization modes have come into being. The classical polymerization pathway was the **free radical addition polymerization** enclosing three major steps-

- **Initiation:** Free radical generated by activation of initiators by tertiary amine or light

- **Propagation:** The free radicals open the carbon-to-carbon double bond, give rise to a new free radical specie that furthers the reaction
- **Termination:** Finally, the polymerization propagates until all the monomers have reacted to form a polymer and terminates.

Methacrylate polymerize in this way, forming a highly crosslinked matrix, however, a heterogenous one, resulting in higher shrinkage stresses and strain Vinyl monomers like triethyleneglycol-divinylbenzyl ether and allyl 3,5-bis(((allyloxy) carbonyl) oxy) benzoate (35DACBzA) are allyl based and undergo a **radical polymerization**. These monomers resulted in improved mechanical properties, lower volumetric shrinkage and shrinkage stresses, and higher degree of conversion. Admira Fusion (Voco) is an example of this [4,5].

Thiol-ene based and spiro orthoester based monomers are some of the latest developments, that undergo click-chemistry polymerization where the monomers fit with each other in a 'snap'.

Silorane based composites like the Filtek silorane (3M) and vinyl cyclopropanes and epoxy monomers undergo ring opening polymerization. The characteristic ring opening reduces the volumetric shrinkage otherwise seen in polymerization.

Classification

Based on the polymerisation mechanism, RBCs can be categorised as self-cure, light cure and dual cure resins.

Self-cure resins are supplied as 2 pastes, a base and catalyst each containing an initiator and activator. Although they were simple to use, they displayed bulk discoloration and had a limited working time of 90 seconds only.

The light cure resins are currently widely used resin composites. This type has a photosensitive initiator that gets activated by light of appropriate wavelength (400-500nm). The currently available RBCs are activated by light in the visible light range (380-480nm). It is now essential to understand some key relations proposed in electromagnetic radiation physics.

The Grothus- Draper law tells us that for a photochemical reaction to take place, a photon must be absorbed by the atom.

The Stark- Einstein law states that one atom can only absorb one photon. This makes it clear that for any photochemical reaction, the initiator can be activated only with a light of appropriate wavelength. Based on this, 2 types of initiators are used in dentistry, namely, the Type I or high quantum yield initiators that show α -cleavage and do not require additional co-initiators and required lesser wavelength of light for its activation as they have low energy bonds. They also offer improved tissue colour matching as they contain lesser pigment.

Type II initiators or the low quantum yield type that show H-abstraction type initiation and require greater amounts of energy and a co-initiator for complete activation. Germanium based initiators like Ivocerin by Ivoclar is a type I initiator, while CQ and 1-phenyl-1,2 propanodione (PPD) [6].

Sl. No.	Type of curing light	Mechanism of action	Wavelength emitted
1	QTH	Tungsten becomes incandescent on applying energy due to vaporization of atoms, producing photons. On cooling, atoms settle back.	400-500 nm
2	PAC	Electrodes ionize Xe gas when high voltage is applied. This created a plasma that emits light.	390-510 nm
3	Argon laser	Electrons move from higher to lower energy and emit energy in the form of light.	488 nm
4	LED	I Generation – GaN based in LED casing II Generation – LED chip III Generation - Polywave	Low radiance 420 – 500 nm 390-430 + 440- 500 nm

Table 1: Dual cure resins are a hybrid of the self-cure and light cure resins.

They display both types of polymerizations due to which they are used to lute ceramic inlays or in core build up.

Based on Filler Particle Size

Sl. No.	Type of filler	Size	Weight	Advantages	Disadvantages
1	Macrofilled	4-40 μ	75%	High strength	Poor polishability Poor wear resistance
2	Microfilled	0.04 μ	45-55%	High polishability	Low modulus of elasticity
3	Hybrid Microhybrid Nanohybrid	1-2 μ 1-100 nm	75-80%	Strength Wear resistance Polishability Aesthetics	Surface becomes dull eventually
4	Nanofilled	5-75 nm	50%	Good mechanical properties Long term polish maintenance Optical properties	Aggregation issue High cost

Table 2: Based on viscosity, resins can be in packable or flowable forms.

The packable versions are modifications of the hybrid composites that have elongated filler particles. These fillers interlock and limit the flow of the resin. Poor wear resistance of the packable versions has been documented.

The flowable resins are the less viscous forms with niche applications due to its poor polymerization shrinkage and low physical properties. They can be employed as cavity liners, gingival third restorative materials and as pit and fissure sealants.

Properties

Physical properties:

Working time: For light-cured composites, curing is considered to be "on demand." Polymerization is initiated when the composite is first exposed to the curing light.

- A thin layer of air-inhibited, unpolymerized material remains on the surface of the polymerized layer, which is advantageous for subsequent incremental placement during layering.
- **Polymerization shrinkage:** As the monomer is converted to polymer, there is a net shrinkage in the volume of the material. This polymerization shrinkage gives rise to contraction gaps that leads to post-operative sensitivity and secondary caries. According to classic literature, although polymerization shrinkage is inevitable, the stresses arising from it can be alleviated to an extent. 5 commonly used strategies for this includes using a thick layer of primer, or a thick liner (RMGIC) or a thin layer (0.5mm) of flowable resin which are more flexible and can absorb these shrinkage stresses. Alternatively, 'soft start' polymerization has also been used, which includes an 'exponential' or 'stepped' increase in the intensity of curing. 'C-factor' also plays an important role in the polymerization shrinkage stresses. As the stresses built in the material can be dissipated through the unbonded surface. Thus, preparations with more bonded surfaces show lesser mitigation of the

shrinkage stresses.

- **Solubility:** In the case of insufficient polymerization of the composite resin, due to insufficient intensity of the curing light, it increases the solubility and water sorption properties of the composite resin.
- **Degree of conversion:** Degree of conversion (DC) is the measure of the extent of polymerization. Higher the DC, better are the associated properties. This factor in turn depends on the depth of cure (as the light intensity reduces as the light travels through the preparation), the type of fillers (smaller the filler size, lesser is the scattering of light, higher the DC) and the amount of initiators and inhibitors.

Mechanical properties:

Strength

- Compressive strength – 250-400 MPa
- Tensile strength - 30-50 MPa
- Flexural strength – 90-140 MPa
- Thus, the current concepts in cavity preparation, including 'scooped out' or 'soccer shape' are associated with RBCs are such that the harness more compressive strength in contrast to tensile stresses, since the material is more resilient towards compressive stresses [7].

Wear resistance

RBCs are subjected to 2 body and 3 body wear and hence the net volume loss by wear must be ensured to be as minimum as achievable. The wearing away of the resins further depend upon the filler particle size, the DC, occlusal loading and finishing and polishing of the restoration.

Matrix constraint

When subjected any form of thermal stresses, composites undergo shrinkage or expansion. The tougher and harder filler particles resist these thermal induced volumetric changes but up to a certain extent, beyond which failure of the material occurs by fracture at the resin-filler interface.

Fracture toughness

The resistance to fracture of any RBC depends on the ability of the coupling agent to transfer the stresses from the weaker matrix to the stronger filler.

Biological properties:

Biocompatibility

This biological property is an essential requirement check in relation to two soft tissues, the pulp and the gingiva. Any pulpal reactions may occur either due to the chemical toxicity of the material itself or due to the marginal leakage. Any chemical toxicity seen is due to leaching out of the uncured components from the material resulting in pulpal reactions. From a toxicological point of view, the newer materials, having a higher DC, does not pose much concern. From an immunological point of view, the reported incidence of allergic reactions in the patient and the operator is rare.

Since RBCs can be finished and polished to obtain a smooth surface, plaque retention is not a concern and hence, the biocompatibility with the gingival tissue is high.

Many composites used previously had Bis-GMA as its major monomer, the precursor of which was the Bis Phenol A, also known as BPA. BPA is a well-known endocrine disruptor. It is known to be a xenoestrogen and androgen agent, thus, a greater concern when used in developing children [8]. The current stand of the ADA about this concern is that BPA in RBCs is not of much concern in most forms except sealers and the patient can be protected by adopting various strategies including proper rubber dam isolation and following manufacturer's instructions amongst others. Most composites currently available too are known to be BPA free, like the Venus Diamond (Kulzer), Tetric N Ceram (Ivoclar), G-aeneal (GC) etc [9-13].

Optical Properties:

- **Color stability:** RBCs in dentistry are known to undergo 3 types of color changes, the surface discoloration, bulk discoloration and marginal discoloration. They are susceptible to any of these types of discoloration due to inadequate or improper handling leading to debonding of the filler to the matrix, causing oxidation and staining.
- **Radio-opacity:** According to the ISO4049 and ADA 27, the RBCs must have a radio opacity similar to dentin in order to detect any failures or secondary caries. Heavy metals added like Sr, Ba, Zr or YtF imparts radio opacity to the resins.

Conclusion

In conclusion, resin-based composites have revolutionized modern restorative dentistry, offering a unique combination of strength, aesthetics, and functionality. Through this

review, we have explored the material science behind these composites, delving into their composition, physical and mechanical properties and seen how these affect the clinical performance.

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