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Recent Advances in Dental Composites: A Review

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Abstract—Composite resins are widely used aesthetic materials in restorative dentistry. These materials were introduced to overcome the inherent shortcomings of amalgam restorative materials. Dental amalgams are unesthetic and toxic. Earlier composites lack in mechanical properties to withstand the masticatory forces. Various filler particles have been added to composite resins to improve their physical and mechanical properties. Filled composite resins exhibit high compressive strength, abrasion resistance, ease of application and high translucency. Depending on the filler size and shapes, various composites have been developed until now. This article is a review of numerous types of composites that are technologically advanced to modify their properties.

Keywords---composites, condensable composites, fibre reinforced composites, fillers, flowable composites, nanocomposites, self-adhering composites.

Introduction

"Beauty is power and smile is its sword"-Charles Reade. It has been a matter of great interest to restorative dentist to preserve the tooth structure and restore the surface defects by using materials which gives back the lost form and function and also the aesthetics as close to natural as possible. With their invention

almost 60 years, these aesthetic materials have come a long way and witnessed lot of changes both in their development and also in acceptance in minds of general dentists.¹

The acrylic resin was introduced to the dental profession in the mid-1950's, and it replaced the silicate cement soon from the dentistry as a direct aesthetic restorative material. Since their introduction, acrylic-based materials have continued to play a significant role in restorative and prosthetic dentistry.² The advantages of these acrylic resins include tooth-like appearance, ease of manipulation insolubility in oral fluids, and low cost. However, these materials could not accomplish the requirements of restorative materials as they undergo considerable shrinkage during the polymerization process leading to marginal leakage. In addition, they were having poor wear resistance, high water sorption, and a high coefficient of thermal expansion. Quartz powder was incorporated as a filler to address the inherent drawbacks of the resins. These fillers occupy the spaces between the polymer chains and improve the physical and mechanical properties, which are primarily influenced by the volume fraction of inert fillers³. However, the early composites were lack of proper bonding between the polymeric resin and the filler particles. In 1962, Dr L. Bowen invented a new dimethacrylate resin, such as Bisphenol. A Glycidyl methacrylate (Bis-GMA) and an organosilane coupling agent, which provides a bond between filler particles and the resin matrix³. This invention led to the evolution in resin-based direct aesthetic restorative materials. Composite resins are complex, tooth-colored filling materials that offer excellent esthetic potential and acceptable longevity without the need for extensive tooth preparation, allowing minimally invasive preparation or sometimes no preparation at all. They represent one of many success of modern biomaterial research. However, the early formulations of these resin composite materials had numerous drawbacks such as poor handling characteristics and polymerization shrinkage. To address this, various types of filler particles with different volume fractions have experimented with the resins. This led to the development of macro-filled, small-filled, micro-filled and hybrid composites⁴. Although, these materials showed better improvements compared to earlier versions but not up to the standard. The quest of researchers on improving its properties led to the development of newer versions of composite resins. Therefore, this review focused on discussing various composite resin materials developed in recent years.

Contents History

1955-Buonocre reported acid etching of enamel⁵
Early 1970s-acid etching and enamel bonding were introduced⁶
Late 1970s-UV-cure composites -visible light cure composite (QTH,PAC,Laser,LED)⁷

• Bis GMA-other monomers⁸

1980-Dentin bonding composites were introduced ⁹

1998-Ariston pHc (Stimuli responsive material/Smart material) was introduced. 10 late 2002-Seventh generation bonding agents were introduced. 11

2010-Self- adhesive flowable composites/restoratives were introduced ¹²

Evolution of dental composites

Acrylic resin was introduced to the dental profession in mid 1950s. Since their introduction, acrylic based materials have continued to play a major role in restorative and prosthetic dentistry. ¹³In Mid-20th century, acrylic resin replaced silicate cements as the only esthetic material. the potential for greater application of resins came about with the introduction of bisphenol-A-glycidyl methacrylate, or BIS-GMA, by Bowen in the early 1960s. It was the final attempt to improve the physical properties of acrylics . ¹⁴

Recent modification to composite resins have improved their physical and mechanical properties. With a variety of shades, translucencies, effects, opacities and innovative placement techniques, today's composite allows simple reproduction of polychromatic and optical properties of natural dentition. Advances in curing technology have yielded light-cured systems that make it possible to harden resins on demand as well as to improve working time and ease of manipulation. Nowadays, a number of sources for photoinitiating composite resins are available : halogen lamps, plasma arc lamps, laser and light emitting diode (LED) lights. LEDs are promising alternative for photo curing dental materials. Their use in dentistry has been discussed ever since blue diodes were developed in 1990s. 17

Classification According to Sturdavent ¹⁸

- Based on filler particles type:
 - Homogeneous composites
 - Macrofill-macrofillers are in the range of 10-100 µm
 - Midfill-midfillers from 1-10 µm
 - Minifill-minifillers from 0.1-1 µm
 - Microfill-microfillers from 0.01-0.1 µm
 - Nanofill-nanofillers from 0.001-0.01 µm
 - Megafill-very large individual filler particles ,called megafillers
 - Heterogeneous Composites
 - Hetero-Midfill
 - Hetero-minifill
 - Hetero-Microfill
 - Hybrid composites
 - Midi-Micro hybrid
 - Mini-Micro hybrid
 - Mini -Nano hybrid
- Based on matrix composition:
 - BIS-GMA based composites
 - UDMA based composites

- Based on polymerization method:
 - Light cured composites
 - chemical cured composites
 - dual cure composites
- Based on viscosity:
 - Packable composites
 - flowable composites

Common descriptive parameters

Traditional Composite Resins-These composites are also referred to as conventional or macrofilled composites .Because these materials are no longer widely uswd,the term traditional is more meaningful than is conventional $^{19}\cdot\text{Traditional}$ composite resins are described as containing conventional macrofiller particles which are mechanically ground or crushed from larger pieces of purely inorganic materials such as quartz ,glass,borosilicate or a ceramic this process results in particle taking on the splinter or irregular shape ,producing sizes ranging from 0.1 to 100 $\mu\text{m}.$ 19

Intermediate Composite Resins-the intermediate composite resins have filler particles ranging in size from 1-5 μm . The size distribution permits maximum filler loading ,as compared to microfilled composites, which generally are considerably less filled . the midfills have an average particle size of 4 μm with a range of 1-10 μm .

Hybrid Composite Resins-A composite resin classified as hybrid or blend contains colloidal silica particles in addition to larger filler particles.colloidal silica particles are produced by burning silicon tetrachloride in a mixture of hydrogen and oxygen gas ,which produces colloidal silicon dioxide ,alaso called as pyrogenic particles.such particles can be made by allowing colloidal particles of sodium silicate to react with hydrochloric acid to form silicon dioxide and sodium chloride.²¹

Microfill Composite Resins-Microfiller particles are finely dispersed radiolucent glass spheres created chemically by hydrolysis and precipitation .Originally ,the average size of these particles was 0.04µm or 0.05µm^{.21}and even more recently 0.04-0.06.Examples-Filtek A110(3M ESPE,St.Paul,Minnesota) Renamel microfill

Homogenous Microfilled Composite Resins-are combination of an organic matrix and directly admixed microfiller particles .However the inorganic loading with such small particles (0.04-0.2µm)is still limited because of their large surface area.²²

Heterogenous Microfilled Composite Resins-Hetrogenous or inhomogenous microfilled composite resins are combination of an organic matrix, directly admixed microfilled particles and microfiller based complexes. the 3 different types are-

• splintered pre-polymerized microfilled complexes

- spherical polymer based microfilled complexes
- Agglomerated microfilled complexes ²²

Nanocomposites-Nanotechnology is the production of functional materials and structures in the range of functional materials and structures in the range of 1-100 nanometers(nm)-the nanoscale-by various physical and chemical methods. At present there are two distinct types of dental composite available that contains nanoparticles:

- NANOFILLS-these contain nanometer sized particles (1-100nm) throughout the resin matrix.²²
- NANOHYBRIDS-these consist of large particle(0.4-0.5microns)with added nanometer sized particles. Thus they are hybrid materials ,noit true nanofill composites. ²³

Recent advances in composites Direct composite resin Condensable/Packable or Polymeric rigid inorganic matrix material (PRIMM)

This new concept was developed by Dr. Lars Ehrnford of Sweden in 1995.²⁴This system is composed of a resin matrix, and an inorganic ceramic component. Rather than incorporating the filler particles into the composite resin matrix, he devised a unique system by which the resin is incorporated into the fibrous ceramic filler network. The filler mainly consists of aluminium oxide and silicate or strontium glasses. The glass particles are liquefied to form molten glass which is forced through a die to form thin strands of glass fibers. The diameter of these fibers being approximately 2-3 µm. 23 These glass fibers are crushed into small fragments and then reheated to a sufficient temperature to cause superficial fusion of glass fibers at selected sites (silanation). This forms a continuous network of small chambers or cavities(dimensional interfacial chambers = 2 um). The manufacturers then infiltrate these spaces within the fibrous network with an optimized resin depending upon the final application use of the restorative material (BISGMA/UDMA resin). This concept provides a basis for fabricating packable or condensable posterior composite resin. Colloidal silica ultrafine particles are also incorporated to control the handling characteristics such as viscosity, resistance to flow, condensability and reduced stickiness. ²³ Greater the condensation pressure used, greater is the expression of residualresin, and greater is the density of the inorganic phase. Hence this new concept resulted in advantages like better marginal adaptation, lower potential for incorporation of microscopic porosities, lesser polymerization shrinkage (as any polymerization shrinkage that takes place will be localized within the small ceramic chambers/spaces), optimal mechanical characteristics like flexural strength, modulus of elasticity and coefficient of thermal expansion andgreater wear resistance. 23

Flowable composites²⁴

Flowable composites were developed mainly inresponse to requests for special handling properties for composite resins rather than any clinical performance criteria. Hence their physical properties had limitations. They were created by

reducing the filler content of traditional hybrid composites and retaining the same filler size and adding increased resin to reduce viscosity of the mixture. Since the filler content was reduced in these composites they lack sufficient strength to withstand high stresses and because of the increased resin content these composites show more polymerization shrinkage and have lower elastic moduli and high fracture toughness. They cannot be used in high stress bearing areas and also difficult to manipulate because of stickyness.

Indirect composite resins

Because of the major clinical problems clinicians have experienced with direct posterior composite resins, the indirect inlay or onlay systems were introduced. Since the restoration is made on a die rather than directly on the tooth the restoration has superior adaptation, contour and proximal contact. On the whole there is a dramatic improvement in the general clinical performance. A number of highly improved indirect resin restorative systems have been introduced with unusually good properties like wear resistance, esthetics, marginal adaptation, control over polymerization shrinkage.²⁴

Artglass²⁴

Artglass is a non conventional dental polymer marketed since 1995. It is most commonly used in inlays, onlays and crowns. The resin matrix is composed of BISGMA/UDMA. This configuration provides a higher level of cross linking and better control over the positions along the carbon chain where cross linking occurs. This aids in improving the wear resistance and other physical and mechanical properties of the resin matrix. Filler is radiopaque barium glass (mean particle size $0.7\mu\text{m}$). A moderate amount of colloidal silica is also incorporated for the purpose of enhancing certain handling characteristics. Artglass is photocured using a special xenon stroboscopic light. The emission ranges from 320 –500nm. This range is significant because excitation of the initiator, camphoroquinone, is optimized at about 470 nm. Artglass has the advantages of having considerably more wear resistant than conventional light cured composites, good marginal adaptation, esthetics and superior proximal contact.²⁴

Belleglass HP²⁴

Belleglass HP was introduced by Belle de St. Clairein 1996 as an indirect restorative material. Resinmatrix contains BISGMA and fillers. The Belleglassis polymerized under pressure of 29 psi at elevated temperature of 138C and in the presence of nitrogen, an inert gas. The elevated temperature increases the polymerization rate. The increased atmospheric pressure reduces the vaporization potential of the monomers at elevated temperatures. Use of nitrogen gas during polymerization process relates to an increase in thewear resistance i.e. nitrogen provides an oxygen free environment, which in turn results in higher levels of polymerization; more translucency of cured mass. Oxygen if gets entrapped in the composite, it interferes with polymerization and reduces translucency. It is esthetically appealing and highly wear resistant.²⁴

Nanocomposites²⁵

The use of nanoparticles in dental composites is notnew. Colloidal silica particles of a diameter of approximately 40 nm have been in use in dental microfilled and hybrid composites for more than 10 years. Nanoparticle filled composites exhibit outstanding esthetics, are easy to polish and posses an enhanced wear resistance. Nanoparticle fillers may include colloidal silica or Ormocers, such as in Ceram X from Dentsply. Similar particles may be used in resin-based bonding systems. Nanoparticle particle filled dental composites may show an enhanced fracture toughness and adhesion to tooth tissue.

Antimicrobial materials

Antimicrobial properties of composites may be accomplished by introducing agents such as silver or one or more antibiotics into the material. Microbes are subsequently killed on contact with the materials or through leaching of the antimicrobial agents into the body environment. Silver and titanium particles were introduced into dental composites, respectively, to introduce antimicrobial properties and enhance biocompatibility of the composites. ²⁶Dental composites containing 1% (w/w) quaternary ammonium polyethylenimine (PEI) nanoparticles were tested for their antimicrobial activity. The antibacterial properties of these composites were based on contact mechanism rather than on leaching. The mechanical properties were notsignificantly affected by introducing the PEI nanoparticles. The antimicrobial effect lasted for at least 1 month. ²⁷Alkylated ammonium chloride derivatives and ²⁸ chlorhexidine diacetate have also been introduced as antimicrobial agent into dental composites.

Stimuli response materials / Smartmaterials ²⁴

Stimuli response materials possess properties that may be considerably changed in a controlled fashion by external stimuli. Such stimuli may be for example changes of temperature, mechanical stress, pH, moisture, or electric or magnetic fields. Stimuli responsive dental composites may be quite useful for example for "release-on command" of antimicrobial compounds or fluoride to fight microbes or secondary caries, respectively.

Self-repairing materials

One of the first self-repairing synthetic materials reported, interestingly shows some similarities to resin-based dental materials, since it is resin based. This was an epoxy system which contained resin filled microcapsules. If a crack occurs in the epoxy composite material, some of the microcapsules are destroyed near the crack and release the resin. The resin subsequently fills the crack and reacts with a Grubbs catalyst dispersed in the epoxy composite, resulting in a polymerization of the resin and repair of the crack.²⁴

Conclusion

The science and technology of composite dental restorative materials have advanced considerably over past few years. Use of composites in dentistry is an

example of te evolution of technology in the best sense. Nowadays, composites have unquestionably acquired a prominent place among the filling materials employed in direct techniques .their considerable aesthetic possibilities give a rise to variety of therapeutic indications, which continue to grow as a result of great versatility of the presentations offered; also these material conserve the tooth structure better because these are retained by adhesive methods rather than depending on cavity design.

With increase patient demands for esthetic restorations, the use of direct filling composite material will continue to grow .Failaures in dentistry are frequently blamed on the materials.In reality, 'user error' is often the culprit.interpreting the research data and understanding our option based on patients caries risk status are the first step towards success.

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