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Review Article

A Review on Evolution of Select Dental Materials of the Past and Present

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Abstract

Dental practitioner's attempt to restore function and aesthetics of decayed and deformed teeth has a long history of association with dental materials. The list of materials starts with dental amalgam which at present is branded as an invention of the past. Technological advancements that happened after amalgam has opened up the availability of a big range of materials offering better aesthetics, ease of use, durability and biocompatibility. Composite resins have become the primary choice in tooth restorations, replacement of missing tissue and prevention of further decay or damage. Another field of high-tech advancement happened in the fabrication of dentures. Conventional technology involved in the making of dentures required considerable time and complex procedures. Dentures fabricated exclusively with human skill had limitations with precision and the extended time factor. Patients had to comply with these limitations until CAD/CAM was adapted to dentistry. Evolution of select materials used in dentistry are included in this review viz. dental amalgam, composite resins, materials used for milled and printed dentures.

Keywords: CAD/CAM; Printed Dentures; Milled Dentures; Composite Resins; Dental Amalgam; Digital Light Processing (DLP); Stereolithography (SLA)

Introduction

Restoration and replacement of teeth has necessitated an intensive search for different materials. Gold was the first choice to be used in the mouth for restorative purposes. It was found out in different parts of the world and hence it is difficult to pinpoint an exact date of its discovery. Gold artifacts were discovered from the graves of Bulgaria (4700-4200BC) and Egyptians have started gold mining around 3100 BC. It is interesting to note that written language was developed much later. Gold wires were used to stabilize teeth by ancient Egyptians (2500BC). Gold bands and animal bones were used by Etruscans to replace teeth (500BC). Phoenicians carved ivory teeth and fixed them to the remaining natural teeth with gold wires (300BC). During the past two millennia, animal and human teeth were used for the replacement of human teeth (Figure 1). The earliest dental implants were made of carved shells during the period of Mayans(600AD). Porcelain dentures and teeth were made by a French dentist – Nicolas Dubois de Chemant (1774) and a Pharmacist, Alexis Duchateau. Duchateau was wearing a denture and it was producing a bad odor and he suggested the use of porcelain. However, Chemant received a patent for the porcelain teeth and in 1778 Chemant published his thesis – A dissertation on artificial teeth [1].

Figure 1: Ancient denture.
https://www.facebook.com/groups/archeologyandcivilizations/posts/8894707417289370/

Amalgam, the earliest restorative material

Particles of silver, copper and tin were mixed with liquid mercury and a mouldable material was developed and it was used to restore decayed teeth after preparing a cavity which had a geometric design. After a short period of waiting, the material becomes hard. During the mouldable phase, amalgam was carved to match the tooth morphology. History of dental amalgam is traced back to ancient China (659AD). It was first documented in a Tang dynasty medical text by Su Gong. In the 1800s amalgam was introduced to Europe and America. The toxicity concerns of mercury generated a controversy amongst dentists which is very often termed as 'amalgam war'. Scientific observations of G V Black, made in the late 1800s improved the acceptability of amalgam and he in fact has optimized its composition [2].

In the earlier stages, amalgam contained 65% silver and 25% tin. Later in 1963 high copper dispersion alloy was introduced and which had high strength and corrosion resistance. In spite of the low cost, use of dental amalgam progressively declined because of the limitations in aesthetics and the health concerns regarding mercury exposure (Figure 2). In 1994, Drasch and his colleagues published the results of an investigation in European Journal of Paediatrics and that established a correlation between mercury levels of fetal and infant tissues (brain and kidney) of babies and amalgam fillings present in the mothers' teeth. There after the German government has restricted the use of amalgam [3].

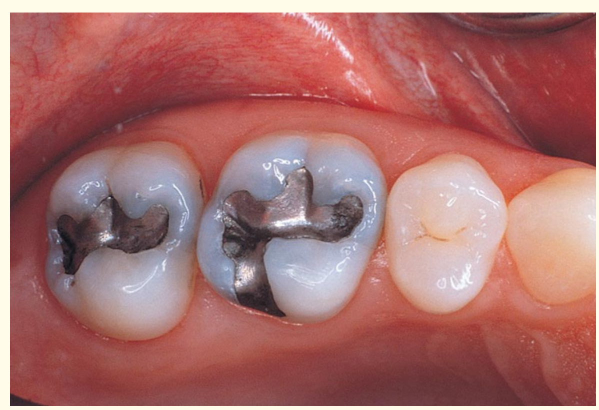

Figure 2: Amalgam filling.
https://turnerdentalcare.com/amalgam-dental-fillings/

Composite resins – a paradigm shift

Tooth coloured resins with matching aesthetics started appearing in the clinical practice with Silicate cements and methacrylate resins. These materials had limitations like discoloration, shrinkage, poor bonding to the tooth and pulpal reactions. Rafael Bowen made a combination of epoxy resin and quartz particles and which resulted in the production of Bis-GMA (bisphenol A glycidyl methacrylate). This resin was known after him -Bowen's resin and he received a patent in 1962 [4]. Modern resin based composites were developed as a sequel and which were stronger, with less shrinkage, having coefficient of thermal expansion similar to tooth and better aesthetic quality. Michael Buonocore introduced acid etching with phosphoric acid to improve the adhesion of acrylic based resin to tooth but later acid etching was adapted to composite resins [5]. Acid etching improved adhesion of composite resins to teeth and provided good sealing with enamel. Introduction of composite resins and acid etch technique have fundamentally changed dental practice and acquired the status of a disruptive technique. In the initial phases, composite resins were used only for anterior restorations and amalgam continued with its usefulness for the posterior restorations. The basic composition of composite resins consists of resin monomers, polymerization initiators, fillers (silane treated glass particles) and pigments (Figure 3).

Figure 3: Composite restorations.
https://www.thehealthsite.com/oral-health/composite-resin-the-white-dental-filling-material-57348/

Initiators of composite resins

Initially developed composite resins consisted of a two-paste system- one contained a peroxide initiator and the other an amine activator. Once the pastes were mixed, that caused polymerisation. This belonged to the class of chemically cured composites and which had poor strength and inferior wear resistance. The amine activator gets oxidised after a time and yellowish discolouration happened which was quite unacceptable for an aesthetic restoration. After mixing, clinician gets very limited working time while handling complex restorations. Self curing materials had high levels of unreacted monomers and which could leach out and caused toxic effects on the pulp. These materials are not chemically stable at room temperature. The chemically cured composite resin has become unpopular for the above mentioned reasons [6].

In 1970, light curing technology was introduced. Ultraviolet light was used to cure composite resins that contained UV sensitive compounds like Benzoin methyl ether or similar compounds. It also had tertiary amine activator. UV light had limitations in obtaining adequate depth of penetration because it had a wavelength below 400 nm. Visible light curing was introduced subsequently by incorporating camphorquinone which is sensitive to visible light of wave length 468 nm (blue). The tertiary amine further reacts and splits the carbon-carbon double bond of the monomer and the polymerisation process gets propagated. The yellow colour of camphorquinone was not aesthetically acceptable and other photo initiators like bisacylphosphine oxides (BAPO) and triacylphosphine oxide (PPD) were used which had acceptable colour and sensitivity to visible light range (400-410 nm) [7].

The light source was produced by quartz tungsten halogen bulbs. Filters were used to limit the wavelength between 400-500 nm and to control the UV output and heat generation. Quartz halogen bulbs generally produce more heat and the light production was comparatively limited. LED lights were introduced in this context. Currently used LED lights consume less power and have irradiance value of 800-2000 mW/cm^2. Battery powered instruments are currently used (Figure 4). In the earlier stages of light curing, operators were using single increment of the composite resin and cured it for 40 seconds. Lights were made with more power and the curing time got shortened to 10-20 seconds. With high powered lights (3000-4000 mW/cm^2) the duration can be reduced to 1-3 seconds. The development of lights has presently reached a stage of lasers and plasma arc technology. Lights with multi wave technology are also used.

Dentists require lights with short curing time and high intensity but at the same time pulp should be protected from the heat generated which can cause thermal injury. Short duration is always

Figure 4: Light curing unit.
https://www.dentalkart.com/light-cure-unit-led-d.html?srsltid

favourable because it saves precious clinical time. At the same time, adequate curing should be ensured to obtain optimum properties like hardness, strength and bonding with the tooth. Mostly used LED curing lights have a wave length of 430-480 nm. This blue light can be hazardous to the retina and hence patients, dentists and assistants should be well protected with orange blue blocking eye wears. The tip of the light should be kept over the resin and close to it [8,9].

Monomers used in resin composites

Dental composite resins have three major components: 1. organic resin matrix, 2. inorganic filler and 3. Coupling agent. A system of initiators/accelerators is also included so that the material gets polymerised or cured. The commonly used monomers are Bis-GMA (Bisphenol A glycidyl methacrylate), Bis-EMA (Ethoxylated Bisphenol A glycidyl methacrylate), UDMA (Urethane di methacrylate) and TEGDMA (Triethylene glycol dimethacrylate). The resin provides a matrix and which gets strengthened by fillers like silica, glass or zirconia particles. The bonding between the organic matrix and inorganic filler is ensured by silane coupling agents. Initiator- accelerator system triggers the polymerisation process. As mentioned above, in light cured composites, a photo initiator like camphorquinone and a co-initiator like tertiary amine are incorporated in the resin. There are some other components like pigments which are added to get colour matching. UV absorbers and inhibitors are also added to provide adequate working time for the clinician.

Gajewski et al. have compared the properties of the resins and observed the following: the highest rate of polymerisation was exhibited by UDMA followed by TEGDMA, BisEMA and BisGMA. UDMA and TEGDMA showed similar flexural modulus and BisEMA and BisGMA showed significantly inferior values. Flexural strength was highest for UDMA when compared to other three resins. Water sorption was highest for BisGMA followed by TEGDMA, BisEMA and UDMA. Solubility was in the following descending order TEGDMA, UDMA, BisGMA and BisEMA. In order to get desirable properties for the composite restorative resin, appropriate co-polymers can be combined [10].

Control of shrinkage in composite resins

Curing shrinkage of resins is a widely recognised phenomenon. In the initial phases of development, composite resin was placed in small increments and cured. Another method used was soft start light curing technique. Initially a low intensity light is used and in this phase the material flows and the stress is reduced. This is followed by a high intensity light when the material solidifies and complete curing happens. This method effectively reduces shrinkage, ensures superior marginal adaptation and physical and mechanical properties. Controlling the filler content and filler particle size can have an influence on shrinkage. Nano sized filler particles (1-100 nanometres) not only controls shrinkage but produce smooth finish and superior polish. In hybrid composites, both nano and micro sized particles are included and that improves strength and hence used for both anterior and posterior teeth. Nano particles optimise the particle packing and reduce the volume of resin component and thereby the shrinkage gets reduced [11-13].

Another method adopted to control shrinkage is to use different monomer systems having higher molecular weights like Ormocers which reduces the carbon double bond (C=C) formation per unit volume and hence the shrinkage. Another example is silorane based monomer which is a combination of siloxane and oxirane (epoxy) and can cause localised expansion capable of offsetting the shrinkage. Thiolene based monomers and addition fragmentation chain transfer monomers are also capable of controlling shrinkage [14,15].

Futuristic innovations in composite resins

The striking feature noticed in composite resins is the colour compatibility with natural teeth. Subsequent research has made the resin strong and it has bonded to the natural teeth with enhanced adhesive quality. Present focus is on bioactive composites which can interact with the microbial environment [16]. With bioactive composites, recurrence of caries process is controlled and tooth structure is reconstituted through remineralisation. The antibacterial activity against caries-causing microbes is achieved through either direct elimination of the bacteria or by preventing biofilm formation. Incorporation of quaternary ammonium compounds and 12-Methacryloyloxydodecyl bromide (MDPB)into the resin structure eliminates caries causing bacteria. Evaluation of the effectiveness of these composites on dental caries is ongoing and it may take a few more years to get a definitive proof [17-19].

Self-healing composite is another interesting area of development. These materials are capable of stopping cracks from propagating and healing it by incorporated intrinsic agents or by extrinsic energy sources. Presently this is in the theoretical stage but soon it may be made available [20,21].

Another research area is materials that can stimulate stem cells present in the pulp so that dentine and pulp can be regenerated. Conventional restorative materials do a synthetic replacement whereas stem cells make it a biologic restoration. Such materials contain composite hydrogels with lithium calcium silicate, calcium phosphate and silicate based materials. In this context we have to remember MTA (mineral trioxide aggregate) which was very popular in pulp capping and formation of reparative dentine [22].

Resin for 3D printing

Polymethyl methacrylate (PMMA) has been in popular use as a denture base material (DBR) for more than eight decades. The sustained acceptance of PMMA has been due to low toxicity, reasonably good strength to withstand masticatory load, ease of fabrication and superior aesthetic quality. PMMA has an inherent property of brittleness which may lead to fracture against application of accidental impact force. Fabrication of dentures is not patient friendly process because of the multiple visits it takes. Denture fabrication involves complex laboratory steps and requires assistance of a specialised technician. Technological advancement like three dimensional printing (3D) is fast emerging as an alternative to conventional denture fabrication. Digital light processing (DLP) and stereolithography (SLA) are the two popular processing techniques which cures resin layer by layer. Different dental and related prostheses get acceptable precision and fit by employing the printing technology. Lack of bonding between the layers of print resin do happen at times causing limitations in the physical and mechanical properties. The colour stability also gets occasionally challenged with printed CD prostheses. A remarkable achievement is the ease with which a copy denture is made because the design of the denture is stored in the files and any number of duplicates can be fabricated [23] (Figure 5).

Figure 5: Printed denture.
https://www.themodinstitute.com/dental-ce-courses/master-of-digital-3d-printing/3d-printed-removables/

On conducting a comparison, about the number of visits made, amongst patients who received conventional dentures and digital dentures, it was observed that 50% of the patients who received conventional dentures had to make six or more visits whereas only 5% patients made six or more visits with digital dentures. Conventional denture group had 2-3 post operative visits and the digital group had only 1-2 post operative visits [24]. Printed dentures provide a favourable time frame to fabricate and it is a fact that will get high rate of acceptance amongst the geriatric patients.

Composition of 3D printing resin

A typical composition of 3D printing resin is given below:

- Oligomers – acrylate modified poly lactic acid, epoxy acrylates or poly urethane acrylates
- Active monomers – acrylate esters like 2-hydroxy ethyl methacrylate (HEMA). The monomer reduces the viscosity of the resins, making it printable. After reaction, they become part of the polymer chain.
- Photo initiators – These compounds are activated by UV light and initiates a chain polymerisation. Common example is TPO (diphenyl (2,4,6-trimethyl benzoyl) phosphine oxide)
- Photo polymerisation technique used is either Stereolithography (SLA) or Digital light processing (DLP). After printing, the object needs further treatment. The printed object is treated with isopropyl alcohol to wash off excess uncured resin. Then final curing is done with UV light to enhance the properties like hardness, strength and stability [25].

Acrylic resin for CAD/CAM milled denture

The concept of CAD/CAM dentures was initiated by Maeda et al. in the year 1994. Initially it was a rapid proto typing system and later milled dentures were made by copy milling using CNC machine. Presently milled dentures use a fully digital work flow. Impressions are made either with intra oral scanning or digitized conventional impression. This is followed by designing denture base and tooth arrangement and the final denture is milled from pre polymerised PMMA using CAM. CAD/CAM resins have consistent quality in terms of strength, wear resistance, colour stability, biocompatibility due to low residual monomer and predictable long term performance. Milled CDs provide high flexural strength than conventional and 3D printed CDs. They can provide high yield strength, superior toughness and high flexural modulus. CAD/CAM CDs provide better retention and stability than conventional CDs. The design of CAD dentures can be stored for later use like rapid remakes. Resins used for milled dentures have minimum porosity and are hygienic. Milled dentures provide good surface finish and they need only minimum polishing. Milling is a time consuming process and that can be considered as a limitation. Resins (PMMA/composite resins) used for milling are supplied as prepolymerised discs [26,27] (Figure 6,7).

Figure 6: PMMA disc used for milled dentures. https://instituteofdigitaldentistry.com/cad-cam/the-evolution-of-dentures-from-traditional-to-digital/

Figure 7: Resin disc and milled denture. https://www.pearsondental.com/catalog/product.asp?majcatid=13023

Conclusions

The present review has included, three different classes of materials viz. dental amalgam, restorative composite resins and resins used for CAD/CAM prostheses – both milled and printed ones. These materials represent different evolutionary phases in the history of restorative dentistry. While amalgam has gone into oblivion considering the contemporary usage because of the limitations in aesthetics and environmental concerns, composite resins have acquired a relevant and important position in the present day dental practice. Versatility of the composites due to the high ranking aesthetics, superior bonding and conservative tooth preparation have endorsed and established an unquestionable position for them in the present day.

CAD/CAM dentures, inclusive of both milled and printed ones, have revolutionised prosthodontic rehabilitation through ushering in a new dimension to precision, reproducibility and efficient work flow. Milled resins have higher strength and reduced porosity. Flexural strength of milled resins ranges from 120-146 MPa. Milled dentures have high compressive strength and surface hardness. Printed resins have flexural strength of 65 MPa. Though it is lower than that in milled resins, it is considered as clinically acceptable. Surface hardness of printed resins is lower but impact strength is high. If the printing orientation is vertical, flexural strength and hardness will be superior. It has been observed that post curing and addition of nano particles can improve the properties of printed resins [28]. However long term clinical data, standardisation of printing parameters, material aging concerns and biocompatibility related factors require further investigations.

With the present pace of research and developments, within a few years we may come across self adhesive composites which is a singular product combining restorative resins and adhesives. Self healing composites that repair micro cracks and smart composites that respond to stress, temperature and pH changes are eagerly awaited by dental professionals.

Conflict of Interest

The authors declare that they do not have any conflict of interest.

Author Contributions

Conceptualization-K. Chandrasekharan Nair, Review of articles-Viswanath Gurumurthy, Pradeep Dathan; Mohan kumar, Initial draft preparation: Pradeep Dathan, Bheemalingeswara Rao Review and editing- K. Chandrasekharan Nair, Supervision-K.Chandrasekharan Nair.

All the authors have read and agreed to the published version of the manuscript.

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