

Polymer composites for dental fillings

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13.1 Introduction

Human teeth are not just aesthetic; they also play an important role in health and nutrition. Teeth prepare food for swallowing and digestion. Teeth and bones are the hardest part of the human body, and they consist of both organic and inorganic materials. The outer layer of teeth is enamel, and it is the hardest part of the human body; it is mainly made up of hydroxyapatite. Dentine present beneath the enamel is composed of composite material that includes hydroxyapatite, collagen, water, and salt. Fig. 13.1 represents the structural composition of the tooth. Teeth are the only part of the human body that function under different temperature variations (exposure to ice at 0°C and hot coffee and tea), pH variations, and under mechanical stress during chewing. If proper care is not taken, plaque, cavities, and unhealthy gums can cause tooth decay. Decaying of the tooth is mainly due to the activity of bacteria. Different types of bacteria are found in the mouth; some of these are helpful, while some are harmful, which causes tooth decay. With sweet foods, these bacteria react and produce acids, and these acids remove mineral from enamel. Decay begins with enamel and goes deeper to dentine, and finally reaches to the pulp (nerve) of teeth, which creates cavities in the tooth over time. A decaying tooth causes pain, difficulty in eating, tooth loss, and inflammation around the tooth and gum.

The human body has amazing properties for rebuilding injured parts; that is, if a bone fracture occurs, the human body heals the bone by developing new cells and joining them together. But this is not true in the case of teeth. Once a cavity is formed in a tooth, the human body cannot repair it. To repair a tooth cavity, a filling has to be done. With the help of a filling, dentists restore the damaged teeth back to their normal shape and function.

Fillings have been used for a long time. Researchers have found around 7500–9500 years old molars with fillings in Pakistan [1]. Recently, in Italy, scientists found a 6500-year-old tooth in which the filling was made up of bee's wax [2]. It confirmed that fillings have been used for thousands of years. In the beginning of the 19th century, metal (gold, tin, silver, etc.) fillings were used. At the end of the 19th century, amalgam fillings were introduced. Amalgam fillings were made up of silver, mercury, tin, and copper. Amalgam fillings have been used for around 160 years for dental fillings [3]. The presence of mercury in amalgam fillings raises controversy as the amount of mercury used is harmful and can cause several health problems.

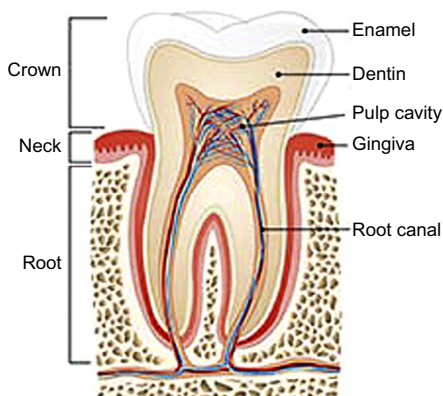


Fig. 13.1 Structural composition of the tooth.

To overcome this problem, white fillings were developed. Composite fillings and glass ionomer cement are two classes of white fillings. Recently, composite fillings have grown in demand. Composite filling used in dental fillings are generally made up of silica or glass bonded with polymer resin.

13.2 Why not amalgam fillings?

Amalgam fillings have been used for more than a century in dental fillings. An amalgam filling is cost effective as well as strong and durable, with at least 15 years' average lifetime [3]. In spite of these characteristics, amalgam fillings have some drawbacks. For example, these do not stick to the tooth, and hence, the dentist has to make a large cut cavity in order to keep the filling in the right place. Silver present in amalgams is considered unattractive by some people (Fig. 13.2). After an amalgam filling, people



Fig. 13.2 Representation of amalgam filling.

may feel pain when they eat or drink hot or cold food, as amalgam fillings conduct heat. Amalgam fillings contain mercury, which is poisonous, and creates an environmental hazard during its disposal process.

13.3 Why composite fillings?

Composite fillings are made up of silica, or glass bounded with polymer resins; polymer resins are commonly filled with glass fillers (35%–85%), and methacrylic acid is the main monomer unit. Today, composite fillings are widely used for dental fillings because they can mimic the original color (Fig. 13.3) and texture of the patient's tooth by the addition of different fillers. They can be used to change the shape, size, and color of the tooth. It easily sticks to the tooth; hence, less tooth is removed. Composite fillings have no environmental hazards, as these do not contain toxic metal, like mercury.

13.4 Filling material properties

The basic features of dental filling materials are:

- Physical properties of the filling material must be the same as that of dental tissues.
- Wear resistance properties must be similar to enamel.
- Filling materials must have good optical properties.
- They should be easily distinguishable from the original dental tissue on X-ray.
- They should easily and sufficiently bond with dental tissues.
- They should be easy to handle as well as to polish.
- Filling materials must be biocompatible and tasteless.



Fig. 13.3 Representation of composite fillings.

13.5 Composition of polymer composites for dental filling

Composites were developed in 1962 with dimethacrylates, combined with powdered silanized quartz [4]. Composites have replaced the amalgam due to their unique properties (aesthetic and adhesive properties). Today, composites are used globally as tooth-colored restorative materials. Composites are generally made up of three components: organic materials (resin matrix), inorganic materials (fillers), and coupling agents. Fig. 13.4 represents the classification of dental filling composite materials. Properties of composite materials depend on the volume of each fraction, and the characteristics of adhesion of each part. Composites behave poorly, if internal adhesion of the components is weak.

The organic (resin matrix) part is mainly made up of bisphenol-A-glycidyl dimethacrylate (Bis-GMA). Because Bis-GMA is highly viscous, short chain monomers such as triethylenglycol-dimethacrylate (TEGDMA) are mixed in a different ratio. The higher the ratio of TEGDMA as compared with Bis-GMA, the better the tensile strength; and the higher the polymerization shrinkage is [5], the weaker the flexural strength of the composite is [6]. Table 13.1 lists the composite materials with different resin matrices.

The inorganic (fillers) part mainly consists of silica, quartz, or ceramic. By increasing the content of the filler in composite material, the tensile and compressive strengths, as well as the wear resistance, can be increased [7]. By increasing the filler content, hardness and flexural strength of the composite material can be increased. Nanofillers provide long-term stability and better polishing properties

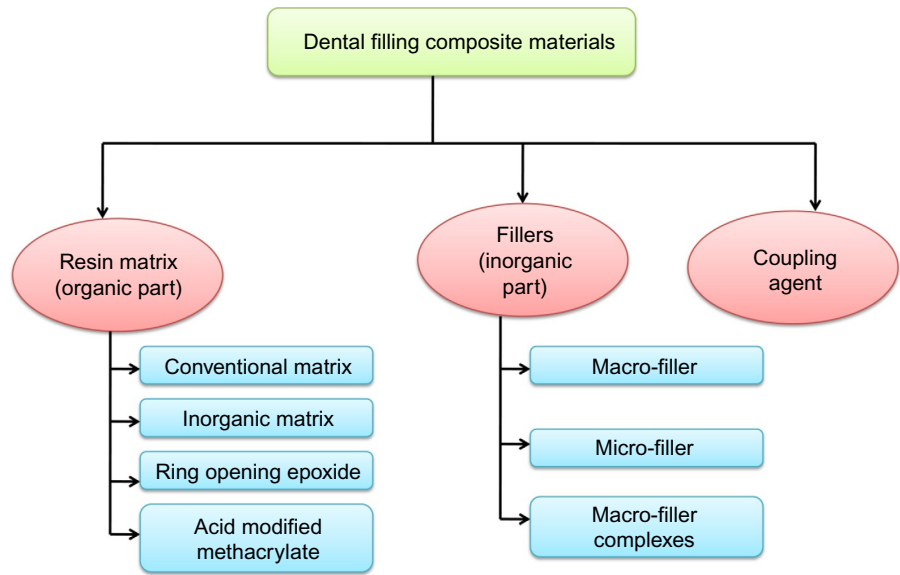


Fig. 13.4 Classification of dental filling composite materials.

Table 13.1 Composite materials with different resin matrices

Matrix	Main chemical system	Category
Conventional matrix	Methacrylate	Hybrid/nanocomposite
Inorganic matrix	Inorganic polycondensate	Ormocers
Ring-opening epoxide	Acid polymerization	Siloranes
Acid modified methacrylate	Polar groups	Compomers

to composite materials [8]. Nowadays, antimicrobial and caries-inhibiting filler materials are used.

13.6 Nanofiller composites

The classification of fillers according to size was proposed by Lutz and Philip in 1983 [8], and is still very popular. The most useful fillers used in composites for restorative purposes are hybrid and microfillers. Microfiller composites offer better aesthetic properties as compared with hybrid filler composites, but provide poor mechanical properties. To overcome this problem, nanocomposites providing good mechanical strength have been developed [9,10]. Nanocomposites exhibit better polishing properties as compared with microfillers [11]. Other important properties of nanocomposites are: reduced polymerization shrinkage [9,12], enhanced wear resistance [13–15], and better optical properties [10]. Nanocomposites are available in two forms: (i) a nanohybrid type that consists of milled glass fillers and discrete nanoparticles, and (ii) a nanofill type that consists of nanosized filler particles called nanomers. The agglomerations of these nanoparticles are known as nanoclusters. Nanoclusters provide enhanced strength and reliability as compared with microfill or nanohybrids because of their reinforcing mechanism [16].

13.7 Unique features of nanocomposite materials in dental restoration

In nanocomposites, physical, chemical, and biological properties are enhanced because of the fusion of nanosized particles into the resin matrix in large volumes [17]. Some of these properties include:

- The distance between nanofiller particles decreases; hence, the rate of crack formation and propagation also decreases [18].
- Nanocomposites show enhanced hardness, wear resistance, and fracture toughness as compared with composites [19].
- Nanocomposites also possess a high modulus of elasticity, and compressive and tensile strength [19].
- Spheroidal shaped nanoparticles equally distribute the stress throughout the composite resin because of the smooth and rounded edges [20].

- Due to strong interfacial interaction between the resin matrix and filler particle in nanocomposites, polymerization shrinkage decreases [21,22].
- Nanofiller composites decrease solubility and water sorption, but lower the coefficient of thermal expansion [23].
- Nanosized filler particles in nanocomposites are far below the wavelength of light, and hence, not measured by a refractive index, resulting in enhanced translucency as light directly passes through the composite [24,23].
- Nanocomposites also show better polishability, color stability, and an excellent finish with superior gloss retention [23].

Because of these unique properties, nanocomposites are widely used as aesthetic dental restorative materials.

Amalgams used in the past as dental restorative materials are much stronger, but poor aesthetics are main drawback, due to the metallic color, in addition to the drawback of mercury toxicity. Further, a growing demand for aesthetics, mainly in anterior region, forced researchers to develop new dental composites similar to tooth-colored material. In this way, dental composites have been introduced in dentistry. These dental composite materials have been successfully used for tooth restoration in both anterior and posterior regions. Recent advances in dental science have led to the development of composite materials at the nanoscale. These nanocomposites are modified composite resins in which nanofillers are reinforced with an organic matrix. Properties of nanocomposites have been discussed herein. In comparison with previously used dental restorative materials, nanocomposites have a high tensile strength, greater abrasion resistance, higher elastic modulus, greater hardness, increased fracture resistance, reduced shrinkage property, and evenly distributed stress because of the strong interfacial interaction between the resin matrix and nanofiller particles in nanocomposites [20]. The smooth surface provides high translucency and long polish retention properties. A smooth surface also reduces the plaque accumulation, which helps in the prevention of dental disease [25].

13.8 Antibacterial dental filling composites

Several scientific methods, such as minimum inhibitory concentration, direct contact, and the agar diffusion test, have been done for the measurement of antibacterial properties of composite materials [26–34]. The agar diffusion test is simple, cost effective, and a widely used method. In this method, a cured specimen is placed on an agar plate inoculated with oral bacteria (streptococci or lactobacilli), and an inhibition zone is formed around the material if water soluble compounds are released from the cured specimen. From agar diffusion test, it has been determined that cured material does not release any antibacterial components. In the direct contact test, inhibitory bacterial growth on the surface of cured material has been observed. But no useful results have been obtained. The actual composite materials have little or no antibacterial properties themselves. Silica- and zirconium-based filler-loaded composites have no antibacterial properties [35]. Methyl methacrylate-based composites show few antibacterial properties, while triethyleneglycol dimethacrylate (TEGDMA),

Table 13.2 Minimum inhibitory concentrations (mg/mL) of resin composite components against *S. mutans* [30]

Monomers	Inhibitory effect	Catalyst	Inhibitory effect
2,2-Bis[4-(3-methacryloyloxy-2-hydroxypropoxy)phenyl]propane (Bis-GMA)	No inhibitory effect	Camphorquinone (CQ)	1.0
Triethyleneglycol dimethacrylate (TEGDMA)	No inhibitory effect	Benzoyl peroxide (BPO)	No inhibitory effect
Methyl methacrylate (MMA)	18.0	<i>N,N</i> -Diethanol- <i>p</i> -toluidine (DEPT)	1.0
Urethanedimethacrylate (UDMA)	No inhibitory effect	2-(Dimethylamino)ethyl methacrylate(DMAEMA)	16.0



Fig. 13.5 Plaque formation on the surface of tooth.

2,2-bis[4-(3-methacryloyloxy-2-hydroxypropoxy)phenyl]propane (Bis-GMA) and urethanedimethacrylate (UDMA) used in restorative composites has no antibacterial activity against *Streptococcus mutans* [30]. Amine compounds show antibacterial activities at higher concentrations as compared with the antimicrobial agent chlorhexidine (Table 13.2).

Absence of antibacterial properties of composite restorative dental materials results in no inhibitory effect against bacterial growth (mutans streptococci), and plaque formation on the surface of the tooth (Fig. 13.5).

On the basis of this feature, composites are different from amalgam or glass-ionomer cements, which show some antibacterial properties, as they release metal ions or fluoride. Several studies have been reported that showed more plaque accumulation or bacterial adherence on composites material as compared with other restoratives materials [36–40]. The Constant Depth Film Fermentor (CDFF) has been developed,

in which microbial biofilm is grown in the laboratory, under controlled conditions. This method is suitable for the study of antibacterial properties of restorative materials, as it develops microbial biofilms similar to those in the oral cavity [41]. In order to obtain dental composites with antibacterial properties, various modifications have been endeavored, described as follows:

- Direct addition of antibacterial agents
- Immobilized antibacterial monomers
- Fluoride releasing composite
- Silver containing composite
- Polyethylenimine nanoparticles
- Antibacterial prepolymerized filler materials

13.9 Direct addition of antibacterial agent

In this method, chlorhexidine, benzalkonium chloride, 2,4,4-trichloro-2-hydroxidiphenylether (triclosan), and several other antibacterial agents have been assimilated in dental composite materials. Chlorhexidine diacetate reduces the formation of microbial biofilm on the cured surface for almost one week in CDF [42]. A quaternary ammonium compound (benzalkonium compound) having antibacterial properties is widely used in dental composites [43,44]. Benzalkonium chloride is positively charged, and hence initiates the antibacterial activity through the deformation of the negatively charged bacterial membrane [45]. Benzalkonium chloride (0.25–2.5 wt%) containing dental composite materials shows antibacterial activity against *S. mutans* and *S. sobrinus* [44]. Triclosan exhibits antibacterial property, as it interferes with bacterial growth with its enzymatic activity [46].

13.10 Immobilized antibacterial monomer

The quaternary amine derivative, 12-methacryloyloxydodecylpyridinium bromide (MDPB), is a positively charged antibacterial monomer that is attracted to, and causes damage to, the cell wall of negatively charged bacteria [47]. Dental restorative composite material consisting of 0.2–0.5 wt% MDPB monomers shows an effective antibacterial effect. These monomers also have no adverse effect on mechanical, chemical, and biological properties of the composite [48–50].

13.11 Fluoride-releasing dental composites

Fluoride exhibits antibacterial properties as tooth remineralization. The increased resistance to bacteria is induced by fluoride [51]. Fluoride also interferes with the metabolic activity of bacteria and helps remove dental plaque [52]. Fluoride is incorporated as an inorganic water soluble salt, added to glass fillers, bonded to inorganic

resin, and is also used as an organic fluoride salt [53–57]. In these forms, fluoride is released from the dental composite.

13.12 Silver-containing dental composites

Silver containing dental composites destroy the bacteria by their enzymatic activity [58]. The silver-containing dental composites, such as silver-glass fillers, silver-apatite, silver-zeolite, silver-zirconium phosphate, and silver-silica gel show effective antibacterial properties [59–66]. Silver-zirconium phosphate or silver-silica gel containing dental composites have no adverse effect on mechanical properties. At 10–20 wt% concentration, silver-apatite and silver-zeolite containing composites show antibacterial properties.

13.13 Polyethylenimine nanoparticles

The quaternary ammonium group of polyethylenimine (PEI) exhibits antibacterial activity by the deformation of the bacterial cell membrane [67]. Polyethylenimine nanoparticles containing dental composites (1 or 2 wt%) exhibit strong antibacterial properties [68,69].

13.14 Antibacterial prepolymerized resin fillers

Filler system consisting of prepolymerized resin methacrylate and antibacterial MDPB(PPRF) monomers with glass silica have been developed [70]. Dental composites containing PPRF (17.9 wt%) reduce the accumulation of *S. mutans* in vitro [71].

Some of the antibacterial nanocomposites applicable in dentistry are listed in Table 13.3.

13.15 Improvement and development of dental filling composite materials

Monomers used in dental filling composites are strongly related to reactivity, stability, viscosity, polymerization shrinkage of the composite, mechanical properties of the composite such as water uptake and swelling of cured dental composite material. Polymerization shrinkage of the composite depends upon the molecular mass of the monomers. Polymerization shrinkage is more pronounced in the case of low-molecular weight-monomers, as compared with high-molecular-weight monomers; but high-molecular-mass monomers show high viscosity. Hence, high-molecular-mass monomers, reactive diluents, and suitable fillers have been used in dental

Table 13.3 List of antibacterial nanocomposites used in dentistry

Application	Method of use	Remarks	References
Silver nanoparticles (AgNPs)			
Root canal irrigation	Used in an aqueous composition comprising of ethylenediamine tetraacetic acid, chlorhexidine, and <i>N</i> -cetyl- <i>N,N,N</i> -trimethylammonium bromide	Effective against <i>Enterococcus faecalis</i> A 197A	[72]
Adhesive	Conjugated with polyvinylpyrrolidone, polyacrylic acid, glycerol, antiseptic cetrimide, sodium alginate, and fir balsam	AgNPs sizes ranging from 1 to 5 nm provided considerable reduction of the length of adaptation to blade denture, caused no toxic action on tissues of denture-supporting area, and showed optimal adhesive properties	[73]
Adhesive	Conjugated with calcium phosphate (hydroxyapatite)	Hydroxyapatite with particle size smaller than 150 nm and AgNPs smaller than 50 nm	[74]
Antibacterial medicine formulations	Applied as layer with particle sizes of 9.3, 21.3, and 98 nm on enamel surfaces	Led to a substantial antiadherence activity against [4TD\$DIF] <i>Streptococcus mutans</i>	[75]
Implants	Applied as a coating agent on titanium	AgNPs 6 nm diameter prevented bacterial proliferation both in vitro and in vivo against specific species such as <i>Escherichia coli</i> and <i>Staphylococcus aureus</i>	[76]
Antibacterial medicine formulations	Applied as colloidal suspensions	Presented a synergistic effect with other antimicrobials and antibiotics such as chitosan, ampicillin, kanamycin, erythromycin, and chloramphenicol	[77–79]
Mouthwash	Stabilized by chitosan in a fluoride solution and applied once per year as a colloidal suspension on decayed primary teeth	AgNPs colloidal suspension was able to arrest caries in 66.7% of the patients. Conversely, only 34.7% of the patients in control group demonstrated arrested caries in the decayed teeth that were treated with water as the placebo	[80]

<i>Zirconium oxide nanoparticles (ZrONPs)</i>			
Adhesives cements	Applied with Ca/PO ₄ -based structures	Favored the remineralization of mineral-depleted dentin, providing substantial gains in hardness and modulus of elasticity within the hybrid layer. Interfered with matrix metalloproteinase-mediated collagen degradation	[81]
Resin composite adhesives	Incorporated into dental resins	ZnONPs effects were compared with those of AgNPs. A more potent antibacterial effect was observed for ZnONP-doped resins compared with resins doped with AgNPs (20 nm) against <i>S. mutans</i> and <i>Lactobacillus</i> . The effect was attributed to the larger particle size of ZnONPs (50 nm)	[82]
Implants	Applied as a coating material along with nano-hydroxyapatite	ZnONPs 10–120 nm diameter prevented infection on dental implants and promoted osteoblast growth. Produced a significant antimicrobial effect against <i>S. aureus</i>	[83]
Antibacterial medicine formulations	Applied as antibacterial agents (suspensions) for peri-implantitis	ZnONPs effects were compared to those of AgNPs particle size ranging from 10 to 50 nm. AgNPs were more efficient than ZnONPs	[84]
Implants	Grown as nanotubes on titanium surfaces and incorporated with ZnONPs	Zinc oxide nanoparticles of 20–50 nm were bonded to the walls of TiO ₂ nanotubes which provided antibacterial activity against <i>S. mutans</i> and <i>Porphyromonas gingivalis</i> through a constant and slow release of zinc ions	[85]
<i>Titanium oxide nanoparticles (TiO₂NPs)</i>			
Bleaching agents	Applied in a gel to increase the bleaching efficacy of hydrogen peroxide	In the presence of TiO ₂ NPs the H ₂ O ₂ concentration could be decreased to 6% with no clinical difference in the bleaching effect compared with H ₂ O ₂ (35%)	[86]

Continued

Table 13.3 Continued

Application	Method of use	Remarks	References
<i>Chitosan nanoparticles</i>			
Implants	Employed in nano-hydroxyapatite-coated titanium implants as a chelating agent for calcium ions	When human bone-marrow mesenchymal stem cells came into contact with chitosan-pretreated surfaces, they were able to differentiate into bone-forming cells	[87]
Resin composite adhesives	Conjugated with silver nanoparticles	Silver nanoparticles 5 nm diameter displayed high antibacterial activity against <i>S. mutans</i>	[88]
<i>Cu₂ONps (cuprous oxide) and CuONPs (cupric oxide)</i>			
Resin composite adhesives	The antimicrobial effects of these compounds were compared with those of silver, ZnO, TiO ₂ , and tungsten oxide (WO ₃) nanoparticles, as well as to Ag + CuO and Ag + ZnO composites	Antimicrobial activities of the nanoparticles were in descending order, Ag > Ag + CuO > Cu ₂ O > CuO > Ag + ZnO > ZnO > TiO ₂ > WO ₃	[84]

composites to set a correlation between polymerization shrinkage, viscosity, and a filler load of composites. The basic requirements of monomers in dental filling composite materials are illustrated in Table 13.4.

Several investigations have been performed in order to enhance the performance of dental composite materials in the following ways:

- To reduce the polymerization shrinkage
- To upgrade the mechanical properties
- To enhance the biocompatibility
- To reduce the recurrent carries
- To enhance the average life

Today, researchers are motivated to develop new monomers for dental fillings to overcome the demerits of resin composites. These new monomers are assumed to perform better functions such as antiplaque formation and release of fluoride ions. Mechanical and other processing properties of dental filling composites have been improved by the development of crosslinking monomers. Developments of some monomers with respect to low shrinkage, crosslinking properties are described as follows.

13.16 Spiro orthocarbonate monomers

Spiro orthocarbonates are ring opening monomers showing almost zero shrinkage or expansion during polymerization. First, spiro orthocarbonate used in dental resin formulations is crystalline 3,9-dimethylene-1,5,11-tetraoxaspiro[5.5] undecane [89]. This monomer is used as a slurry with dimethacrylates, but crystalline spiro orthocarbonate remains partially undissolved and unreacted. To overcome this problem, free-radical polymerizable spiro orthocarbonates are synthesized for dental fillings. Depending on the substituents and ring size of the spiro orthocarbonates, the melting points of these monomers are below room temperature [90–92]. Spiro orthocarbonates have some disadvantages, including low reactivity and sensitivity for water and acidic compounds.

Table 13.4 Basic requirements of monomers in dental filling composite materials

Basic requirement	Usefulness
Crosslinking properties	Sufficient mechanical properties of filling material
Low volume shrinkage or expansion during polymerization	No marginal gap
Resistance to oral condition	Low failure rate of composite filling material
High photopolymerization rate	Short curing time is required
Low water uptake	Longer durability
Low oral toxicity	Minimum toxicological risk for patient
High light and coloration stability	Long-term aesthetics

13.17 Cyclic ethers

Cyclic aliphatic epoxy compounds significantly show the lower shrinkage as compared with methacrylate resin. Today, cyclic ether monomer compounds have grown in demand, based on patent applications [93–97]. Epoxy resins are more reactive, and can be cured in a short time period by cationic photopolymerization using a visible light source. Several cyclic ether monomers, such as cycloaliphatic epoxide 3,4-epoxycyclohexyl-methyl-3,4-epoxycyclohexane-carboxylate, diglycidyl ether of bisphenol A, polytetrahydrofuran as polyol and diphenyliodonium hexafluoroantimonate, and so forth have been used in dental filling composites. These monomers are more reactive, and have enhanced mechanical and physical properties. Besides epoxy resins, oxetanes have also been used in dental fillings [97,98]. These are more reactive, and their reactivity is controlled by ring stress and basicity of ring oxygen.

13.18 Cyclic acetals and allyl sulfides

Cyclic acetals and allyl sulfide monomers undergo cationic ring-opening and free radical polymerization [99].

Cyclic ethers and allyl sulfide monomers are stable in the presence of water. These monomers have no volume change upon polymerization, and hence, are in growing demand. Ring-opening polymerization of cyclic ethers has several advantages, such as:

- Low polymerization shrinkage
- Good chemical resistance
- Low oxygen sensitivity
- Good adhesion properties
- Possibility of a hybrid system with methacrylate

One drawback of these monomers is their lower reactivity, as compared with methacrylates, and high flexibility of the amorphous structure.

13.19 Vinylcyclopropanes

Vinylcyclopropane monomers undergo free-radical polymerization with low shrinkage properties [100]. Crosslinking polymerization of vinylcyclopropanes is slower as compared with methacrylates [101]. Vinylcyclopropane and methacrylate-containing hybrid monomers have been used to enhance the network formation of crosslinking of these hybrid monomers [102,103]. Some advantages of vinylcyclopropanes are:

- Low oral toxicity ($LD_{50} > 2000$ mg/kg)
- Stability in the presence of humidity
- Stability in the presence of acidic and basic impurities
- No mutagenicity and low cytotoxicity
- Low volume shrinkage

13.20 Liquid crystalline monomers

Liquid crystalline monomers show lower polymerization shrinkage, and low viscosity with a tailor-made molecular structure. Photoinitiated polymerization of liquid crystalline diacrylates occurs at a very high rate in a liquid-crystalline state, as compared with a crystalline state. These monomer-based composites have a low rate of shrinkage, but a high melting point, which creates complications in curing conditions. This problem is solved by modifying the spacer length, and with the addition of suitable mesogenic groups, and by varying the mesogenic groups [104–106]. Liquid crystalline monomers are very promising in dental fillings because of:

- Low polymerization shrinkage
- Low viscosity
- High monomer conversion
- A more flexible polymer network
- Enhanced mechanical properties

13.21 Branched and dentritic monomers

Various noncrystalline branched monomers have been prepared and used in dental filling composites [107–109]. These monomers have exhibited low viscosity, as well as polymerization shrinkage at the same time. Branched and dentritic monomers are very useful in dental formulations because with these monomers, composites with low viscosity, low shrinkage, and improved mechanical properties can be obtained.

13.22 Glass ionomer cements

Glass ionomer cements are the mixture of glass and an organic acid. Initially, glass ionomers were used to replace the lost osseous; but now, these are used in dentistry because of their tooth-colored resemblance and translucency. Glass ionomer cement does not require any binding agent when placed in cavities [110]. Glass ionomer cement also does not undergo any shrinkage or micro-leakage; these are chemically set by an acid base reaction. It also releases fluoride, which helps in preventing carious lesions. Glass ionomers have some drawbacks as well, such as: poor strength and toughness, instability in water, and poor cost effectiveness.

13.23 Compomers

The word “compomer” is derived from two words: “composite” and “glass ionomers.” Compomers, or polyacid-modified composite resins [111], are a group of photocurable dental filling composites. A compomer is basically used to describe

a single component, water free, light cured composite consisting of acid-modified dimethacrylate reinforced with silanized calcium-, barium-, strontium-, and aluminum-fluorosilicate glass particles [112]. Structures of compomers generally consist of at least two polymerizable methacrylic residues and acid groups [113]. Compomers improve the physical properties and clinical handling of glass-ionomer cements. Oligomeric polyacid-based compomer monomers are able to react with methacrylate by free-radical polymerization and acid-base neutralization reactions in the presence of water. Besides decreased compressive and flexural strength, compomers have combined properties of composite resin, as well as glass-ionomer cements showing:

- High mechanical properties
- A very low effect of water on stiffness
- Easy clinical handling
- No polymerization shrinkage
- Adhesion to tooth structure
- Fluoride release

13.24Ormocers

Ormocers are a new type of hybrid (organic-inorganic) dental composite material [114,115]. Ormocers are made up of three components: (i) the organic part, (ii) the inorganic part, and (iii) polysiloxanes. The organic part is polymer, and has the advantages of crosslinking, hardness, good optical behavior, polarity, and efficient abrasion resistance [116]. Thermal expansion and chemical stability depend on the inorganic part, which is basically made up of glass and ceramics. Elastic and interface properties depend on the polysiloxane part of the ormocers. The polymer and inorganic parts are joined together by a multifunctional silane group. The properties of ormocers are not as good as those of hybrid composite materials, as they show the highest cytotoxicity as compared with composites, and possess very low wear resistance; hence, uses of ormocers in a pure state for restorative purposes are limited.

13.25Radiopaque monomers

Radiopaque monomers give some usefulness to dentistry, such as the possibility to detect marginal defects, secondary caries, and other imperfections on X-rays. Radiopaque monomers are generally used in the posterior region. Radiopaque properties in filling composites are achieved by a filler that absorbs or reflects X-rays. Composites with low loaded filler, or that are unfilled, do not show this property [117]. Radiopaque polymers can be obtained by two ways: either using heavy metal-containing monomers, or by using iodine/bromine-containing monomers. Mechanical properties of metal-based radiopaque monomers are inferior [118]. Iodine- or bromine-based monomers for radiopaque polymer matrices are widely used.

13.26 Conclusion and future prospects

Due to the toxicity of mercury present in amalgams, and the unpleasant look after filling, composite filling materials were developed, and efforts are continuously being made by researchers to improve the clinical performance and handling of these composite materials. Composites with better filling properties are continuously being developed. Antibacterial composite materials have been developed that inhibit the bacterial growth and plaque formation on the cured surface. In recent years, developments of nanocomposites have grown enormously, which have improved and provided new methods for dentistry. Nanoparticle-based composites offer good aesthetic properties and provide better physical and mechanical properties. In the future, it is hoped that nanocomposites will play an important role in dentistry. The regeneration capacity of teeth is very limited, therefore, a combination of nanoparticles and stem cells may enhance the regeneration capacity of dentin, enamel, and cementum. Developments of nanoparticles with special biological properties and surface topographies, and their incorporation with suitable composite materials, provide a promising way to repair dental tissue. With the help of nanocomposites, optimal responses for dental restoration may be possible with their unique features such as biocompatibility, inert behavior, antimicrobial properties, and enhanced surface-protein interaction.

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