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## Dental Nanomaterials

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### 1. Introduction

Humankind has always been plagued by the problem of restoring parts of the body lost due to an accident or disease. The replacement of lost teeth is desired for two primary reasons: esthetics and restoration of function (partial or complete).

Restorative dental materials include items such as noble and base metals, amalgam alloys, cements, composites, glass ionomers, ceramics, denture base resins, and other materials used in restorative dental operations. To describe these materials, comparisons are usually made on the basis of physical and chemical characteristics.

Most restorative materials are measured by a set of physical, chemical, or mechanical tests that lend themselves to duplicate, and efforts are being made to control the quality of materials by noting the result of these tests. This approach has led to a number of gradual improvements in the materials available to the professions. As improvements in properties have occurred, refinements in the technique of application have become necessary [1].

An examination of the history of dentistry shows that the various materials available in any given period have always been important to contemporary restorative dental operations. Improvements came slowly and steadily over the centuries at about the same rate as related developments in other fields of science. It becomes evident that many accepted techniques, materials, and practices have resulted from systematic evaluation and development, so that the branch of restorative materials has become an accepted part of the science of dentistry.

With the beginning of the twentieth century came many refinements and improvements in the quality of various materials and processes used in restorative dentistry. Physical and mechanical tests and the fundamentals of engineering practice were applied to structural designs and restorative materials [2].

The development of resin composite, glass ionomer and compomer restorative materials, new and modified polymers for restorations and impressions, new phenolic and resin cements, improved base metal alloys and amalgams have contributed to the service and function of restorative materials.

Many of the advances in biomaterials during the twentieth century occurred after 1950. These advances include chemical and light-cured composites, acid etching of enamel, glass ionomers, high copper amalgams, and cements, to list only a few of the 100 or more major advances.

A variety of cements have been used in dentistry through the years for two primary purposes: as restorative filling materials, either alone or with other materials, and to retain

restorations or appliances in a fixed position within the mouth. In addition, certain cements are used for specialized purposes in the restorative, endodontic, orthodontic, periodontic, and surgical fields of dentistry.

Zinc phosphate, glass ionomer, and zinc oxide-eugenol (ZOE) cements can be applied as a base in deep cavities to insulate the pulp from possible chemical and thermal trauma. A metallic, ceramic, or composite filling material may then be placed over the cement base in sufficient bulk and in proper adaptation to the cavity walls to form the final restoration. The sedative effect of ZOE mixtures has made them valuable for a variety of applications. The ability of the glass and hybrid ionomer and compomer cements to release fluoride and to bond chemically to tooth structure has resulted in their uses as bases and for cementation. Resin cements are used for retention of orthodontic brackets, all-ceramic veneers, crowns and inlays, and resin-bonded bridges because of their strength and ability to bond to acid-etched enamel and dentin treated with a dentin bonding agent [1].

This chapter addresses the ten major classes of dental cements used today based on their chief chemical ingredients and application: Glass and Hybrid Ionomers, Zinc Polyacrylate, Zinc Phosphate, Zinc Oxide-Eugenol, Non-Eugenol-Zinc Oxide, Calcium Hydroxide, Compomers, Composites and Adhesive Resin.

## 2. Glass ionomer cements

As with other dental materials, the chemistry of dental cements has undergone continual evolution. The glass ionomer cements combine the technologies and chemistries from silicate and zinc polycarboxylate cements in order to incorporate the desirable characteristics of both. Thus they contain the ion-leachable fluoroaluminosilicate (FAS) glass of silicate cements but avoid their susceptibility to dissolution by substituting the phosphoric acid and its salts with the polymeric carboxylic acids of the zinc polycarboxylate cements [2]. Like their predecessors, the zinc polycarboxylates, these materials are primarily acid-base cements.

### 2.1 Composition

Glass ionomer cements are supplied as a powder and a liquid or as a powder that is mixed with water. Several products are encapsulated. The liquid typically is a 47.5% solution of 2:1 polyacrylic acid/itaconic acid copolymer (average molecular weight 10,000) in water. The itaconic acid reduces the viscosity of the liquid and inhibits gelation caused by intermolecular hydrogen bonding; D(+) tartaric acid (5%, the optically active isomer) in the liquid serves as an accelerator by facilitating the extraction of ions from the glass powder. The powder of glass ionomer cement is a calcium fluoroaluminosilicate glass with a formula of  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaF}_2\text{-Na}_3\text{AlF}_6\text{-AlPO}_4$

The powder is described as an ion-leachable glass that is susceptible to acid attack when the Si/Al atomic ratio is less than 2:1. Barium glass or zinc oxide may be added to some powders to provide radiopacity. In some products the polyacrylic acid is coated on the powder. The liquids of these products may be water or a dilute solution of tartaric acid in water [3].

### 2.2 Setting reaction

The setting reaction is an acid-base reaction between the acidic polyelectrolyte and the aluminosilicate glass. The polyacid attacks the glass to release cations and fluoride ions. These ions, probably metal fluoride complexes, react with the polyanions to form a salt gel matrix. The  $\text{Al}^{3+}$  ions appear to be site bound, resulting in a matrix resistant to flow, unlike

the zinc polyacrylate matrix. During the initial setting reaction in the first 3 hours, calcium ions react with the polycarboxylate chains. Subsequently, the trivalent aluminum ions react for at least 48 hours. Between 20% and 30% of the glass is decomposed by the proton attack. The fluoride and phosphate ions form insoluble salts and complexes. The sodium ions form a silica gel. The structure of the fully set cement is a composite of glass particles surrounded by silica gel in a matrix of polyanions cross-linked by ionic bridges. Within the matrix are small particles of silica gel containing fluorite crystallites.

Glass ionomer cements bond chemically to enamel and dentin during the setting process. The mechanism of bonding appears to involve an ionic interaction with calcium and/or phosphate ions from the surface of the enamel or dentin. Bonding is more effective with a cleaned surface provided the cleansing process does not remove an excessive amount of calcium ions. Treating dentin with an acidic conditioner followed by a dilute solution of ferric chloride improves the bonding. The cleansing agent removes the smear layer of dentin while the  $\text{Fe}^{3+}$  ions are deposited and increase the ionic interaction between the cement and dentin [2, 3].

### **2.3 Role of tartaric acid**

Tartaric acid is added to prolong the working time of the cement mix, improve the manipulative characteristics and narrow the range of the setting time. In the absence of this component, the mix becomes rubbery within a few seconds and is rather difficult to work with. The mechanism by which tartaric acid operates is believed to be a temporary suppression of the ionization of the polyacid as well as a preferential extraction of the cations from the glass so that polyacrylate complexes cannot form immediately, thus leading to an increased working time. Later, it sharpens the set and accelerates the hardening of the glass ionomer mix [1].

## **2.4 Properties**

### **2.4.1 Setting time**

Glass ionomer cements set within 6 to 8 minutes from the start of mixing. The setting can be slowed when the cement is mixed on a cold slab, but this technique has an adverse effect on the strength [3].

### **2.4.2 Physical properties**

The glass ionomers are rather brittle materials with high modulus of elasticity, low diametral tensile strength and low fracture toughness. They are susceptible to desiccation and hence must be protected with a varnish or a resin bonding agent during the setting process. Compressive strengths are similar to zinc phosphate cements [1, 2].

### **2.4.3 Solubility and erosion**

The glass ionomers are susceptible to erosion in the oral environment, particularly under acidic conditions. The maximum acid erosion allowable by the lactic acid jet method is  $0.05\mu\text{m}$  per hour. The solubility of this class of cements is higher than most other types of permanent luting cements [2].

### **2.4.4 Fluoride release**

Glass ionomer materials exhibit a sustained release of fluoride over a long period of time. The uptake of the released fluoride ion in human saliva [4] and its incorporation into human

enamel have been reported [5]. Although considerable debate exists about the 'clinical proof' of the benefits of fluoride, occurrence of recurrent caries in the teeth where these cements have been used is reported to be rare. Studies have shown that glass ionomers inhibit demineralization of the surrounding tooth structures in vitro [3] and in situ [1] and provide protection against recurrent caries under clinical conditions for patients with high caries risk. This can be attributed to the ability of glass ionomer cements to inhibit demineralization and enhance remineralization through release of fluoride to the adjacent tissue and surrounding fluid. The rate of fluoride release depends on a particular product brand. However, as a general class, glass ionomers release more fluoride than other types of fluoride-releasing materials [6].

#### **2.4.5 Adhesion**

Like the polycarboxylate cements, the glass ionomers can bond to the calcium of hydroxyapatite of tooth tissue [6].

#### **2.4.6 Post-operative sensitivity**

In the past, one of the common complaints against conventional glassionomer luting cements has been the high incidence of post-operative sensitivity [7] with greater incidence reported for the 'anhydrous' type [8]. The most frequent reasons cited for post-operative dentinal hypersensitivity are as given below.

- Desiccation of the tooth. The glass ionomers require water for their setting and may absorb water from the dentinal tubules during this process. This phenomenon is thought to be more prevalent in the anhydrous cements where the dried polycarboxylic acid also needs water for rehydration.
- Initial low pH of the material (although it increases rapidly during the setting process) may irritate the pulp.
- Moisture contamination leading to poor sealing of the tooth and improper margins, hence leakage to bacteria and their by-products.
- Too low a viscosity of the mix causing fluid to be forced down the dentinal tubules during seating of the prosthesis. The lower values of pH (higher acidity) encountered for prolonged periods during setting of conventional glass ionomers compared with other types of cements was cited as a possible reason for pulp sensitivity [9]. The diffusion of acid was observed through 0.25mm dentine disks [10]. However, it has been demonstrated that by following proper clinical procedures during cementation the operator can minimize or eliminate the occurrence of post-operative sensitivity [11, 12].

#### **2.5 Applications**

Glass ionomer cements are used primarily for permanent cement, as a base, and as a Class 5 filling material. The cement has been evaluated as a pit and fissure sealant and as an endodontic sealer. The sensitivity of the cement to moisture and desiccation may minimize its use in these latter applications. Glass ionomer cements are being used clinically for cementation of orthodontic bands because of their ability to minimize decalcification of enamel by means of fluoride release during orthodontic treatment [9].

### **3. Resin-modified glass ionomer cements**

RMGIs, developed in the late 1980s [13], are more recent entrants into the dental cement arena, having been first introduced commercially as a luting cement in 1994. This class of

cements is less technique-sensitive than the conventional glass ionomer materials and possesses some very favorable physicochemical properties compared with conventional GI materials yet releases similar levels of fluoride. Since the RMGI luting cements also allow easy removal of excess cement, show minimal post-operative sensitivity and, so far, have exhibited good clinical performance and durability, this class of material has rapidly become one of the most popular materials for routine crown and bridge applications. Improvements in delivery format have now consolidated their use [14, 15].

### 3.1 Composition

The first-generation materials were supplied as powder-liquid configurations and are available in hand-mix or encapsulated versions. Vast differences do exist between products from different manufacturers; hence care has to be taken in choosing a particular commercial product for clinical use. The essential components of a true RMGI are [16]:

- polycarboxylic acid copolymer often modified with pendant methacrylate groups
- FAS glass
- Water
- Water-compatible methacrylate monomers
- Free-radical initiators

#### 3.1.1 Polymeric component

The RMGIs contain some methacrylate components common in resin composites. There are two ways in which the methacrylate component can be introduced. In the first RMGIs introduced to the market, the polycarboxylic acid copolymer chain is modified to contain a pendant methacrylate group. This was achieved by treating some of the carboxylic acid groups of the polycarboxylic acid with isocyanatoethyl methacrylate to provide pendant methacrylate groups connected through the hydrolytically stable amide linkages. The first commercial glass ionomer material (Vitrebond™ RMGI liner, 3M ESPE) was introduced in 1988 using this type of chemistry. The RMGI luting cements from this manufacturer also use the same chemistry. In addition to the methacrylate-modified carboxylic acid, the liquid portion contains a water-miscible methacrylate monomer, e.g. hydroxyethyl methacrylate (HEMA), glycerol dimethacrylate (GDMA), etc. In the second type of RMGI system, the polymer is unmodified polycarboxylic acid. In this case, the liquid is formulated with a mixture of hydrophilic methacrylate monomers and water. Generally, the water content of these materials is lower and the monomer content higher than for the first type. As a result, the coefficient of thermal expansion of these glass ionomers is high. Free radical initiators are added to trigger the curing of the methacrylate groups. Visible light initiators and/or self-cure redox initiators are employed to effect this curing and covalent cross-linking reaction [17, 18].

#### 3.1.2 Nature of the glass

The FAS glass of the RMGI systems is similar in composition to the glasses described for conventional glass ionomers, although some variations are made in order to match the refractive index of the glass with that of the matrix. It is also common to treat the surface of the glass with an organic modifier, such as a methacryloyl functional alkoxysilane, to allow better binding with the methacrylate matrix [19, 20].



### 3.2 Setting reactions

Two distinct types of curing reactions take place in a true light-cured glass ionomer, the traditional acid-base glass ionomer cure and the free radical methacrylate polymerization [14]. In the laboratory, the former can be followed by infrared spectroscopy through the appearance of carboxylate ion peaks. The methacrylate reaction, being a chain polymerization, proceeds at a rate that is several orders of magnitude higher than the acid-base reaction. In practice, the extent to which each of these two reactions occurs is very dependent on a particular system. If the system is low in water and high in the methacrylate components, the ionization of the polycarboxylic acid will be severely suppressed resulting in little acid-base reaction. In one system, the redox initiators are microencapsulated in inert components and mixed with the powder [16]. When spatulated with the liquid, the initiators are triggered and free radical polymerization of the methacrylate groups initiates. In some commercial RMGI luting cements an additional light-curing initiation is provided. However, light will polymerize only the cement exposed at the margins leading to a false sense of security since the bulk of the cement under the crown typically would take longer to undergo a clinical set.

### 3.3 Role of water and tartaric acid

As with conventional systems, water is an integral part of all true RMGIs, being essential for the acid-base glass ionomer reaction to proceed to any appreciable extent and for the release of fluoride from the FAS glass by this mechanism. Tartaric acid may be optionally added to modulate the working time and acid-base glass ionomer setting reaction [1].

### 3.4 Properties

As with conventional glass ionomers, the properties of RMGI luting cements are regulated under the ISO 9917-1:2003 standard for dental water-based cements and self-curing resin-modified cements [3].

#### 3.4.1 Setting and working time

The working time is typically greater than 2.5min from the start of mix at ambient temperature of 23°C. Higher temperatures and vigorous spatulation shorten the working time while lower temperatures prolong it. Excess material can be removed when the cement reaches a waxy stage after placement in the mouth (2–3min at 37°C) using a suitable instrument. The restoration should be finished and the occlusion checked when the material has completely set (about 5min from placement, depending on brand) [6].

#### 3.4.2 Solubility and erosion

RMGI luting cements have greatly improved resistance to dissolution when compared with zinc phosphate, polycarboxylate or conventional glass ionomer luting cements [21]. The ISO 9917-1 erosion test for lactic acid shows the solubility to be virtually zero. This is one of the key advantages of this type of cement [22].

#### 3.4.3 Fluoride release

Although differences exist between manufacturers' brands, in general, the fluoride release and rechargability of RMGI luting cements was found to be similar to that of the conventional glass ionomer cements [23]. The beneficial effect of fluoride from RMGIs has

been shown *in vitro* [17, 18] and *in vivo*. The dentinal caries inhibition of these materials due to sustained fluoride release was also reported to be similar to the conventional glass ionomers [24-26].

#### 3.4.4 Physical and mechanical properties

Both the early mechanical properties, as well as the 'matured' properties, of the RMGIs are much improved over the conventional glass ionomer luting systems. The additional covalent cross-linking in the matrix due to the polymerization of the methacrylate groups contributes towards this effect. Thus, these materials are considerably less brittle and have significantly higher tensile strengths, flexural strengths and fracture toughness values than the corresponding conventional systems [27]. The properties of one paste-paste system were found to be similar to those of the corresponding powder-liquid type [28]. The modulus values are in general lower for the RMGIs [29] and fracture toughness is higher, contributing to the favorable clinical outcomes in high stress-bearing areas [30]. The combinations of these unique characteristics make the RMGIs particularly attractive when used as luting cements under crowns, since they can provide relief of stress created by masticatory forces. All the ultimate properties build up rapidly during the first 24h and then increase slightly during the next 7 days. As with conventional systems, most resin-modified systems do not undergo significant decrease in mechanical properties over time due to fluoride release [31].

#### 3.4.5 Adhesion

Several RMGI systems (e.g. RelyX™ Luting Cement and RelyX™ Luting Plus Cement, 3M ESPE) do not require any etching, priming or conditioning of the tooth and thus can be considered as self-adhesive cements. Others, such as Advance™ (Caulk/Dentsply) and Fuji™ CEM or Fuji™ Plus (GC Dental), suggest the use of additional conditioning agents. Thus Fuji plus luting cement is used with a 10:2 citric acid-ferric chloride etchant due to the more resinous characteristic of the cement [32]. Clinical retention of crowns with the RMGI luting cements has also been found to be excellent in long-term clinical studies. The measured *in vitro* bond strengths of RMGIs are considerably higher than their conventional counterparts, although still not as high as resin adhesive-composite combinations. The failure is usually cohesive in the glass ionomer; hence, as with other glass ionomer cements, the bond strength measurements are not true reflections of interfacial adhesion. The mechanism of adhesion is a combination of two factors:

- The modification of the dentinal smear layer and interpenetration of the dentinal tubules by the fluid cement followed by polymerization and entanglement with collagen fibers
- Ionic reaction of the polycarboxylate with the calcium ions of hydroxyapatite. The first mechanism has been observed by confocal microscopy studies. The second reaction has been verified by fourier transformed infrared spectroscopic studies. The additional feature of increased stress relief afforded by these materials contributes to the long-term durability of the prosthesis. A restoration adhesively cemented with an RMGI luting agent is more resistant to microleakage when compared with a non-adherent cement like zinc phosphate [33]. The RMGIs appear to exhibit minimal microleakage similar to the performance of adhesive resin cements although the latter yield higher *in vitro* bond strength values [34].



### 3.5 Applications

RMGI luting cements are indicated for routine cementation of: PFM crowns and bridges to tooth structure, amalgam, composite or glass ionomer core buildups; metal inlays, onlays or crowns; prefabricated and cast posts. They are also indicated for cementation of copings made with all-alumina or all zirconia cores and provide retention similar to adhesive luting cements. Retention of the all-ceramic crowns with RMGI cement was reported to be excellent and similar to that achieved with adhesive resin luting cements in vitro and with zinc phosphate cements in a split-mouth randomized clinical trial [35].

## 4. Hybrid ionomer cement

Self-cured and light-cured hybrid ionomers (or resin-modified glass ionomers) are available for cementation. Hybrid ionomers are used for restorations in low stress bearing areas and are recommended for patients with high caries risk. These restorations are more esthetic than glass ionomers because of their resin content [36].

### 4.1 Composition

The powder of hybrid ionomers is similar to that of glass ionomers. The liquid contains monomers, polyacids and water. Hybrid ionomers set by a combined acid-base ionomer reaction and light-cured resin polymerization of 2-hydroxyethyl methacrylate. Placing a dentin bonding agent before inserting a hybrid ionomer is contraindicated, because it decreases fluoride release.

One self-cured hybrid ionomer cement powder contains a radiopaque, fluoroaluminosilicate glass and a micro-encapsulated potassium persulfate and ascorbic acid catalyst system. The liquid is an aqueous solution of polycarboxylic acid modified with pendant methacrylate groups. It also contains 2-hydroxyethylmethacrylate (HEMA) and tartaric acid. Another self-cured cement contains a mixture of fluoroaluminosilicate and borosilicate glasses in the powder. Its liquid is a complex monomer containing carboxylic acid groups that can undergo an acid-base reaction with glass and vinyl groups that can polymerize when chemically activated. A light-cured hybrid ionomer cement contains fluoroaluminosilicate glass in the powder and a copolymer of acrylic and maleic acids, HEMA, water, camphorquinone, and an activator in the liquid [37].

### 4.2 Setting reaction

Setting of hybrid ionomer cements generally results from an acid-base glass ionomer reaction and self-cured or light-cured polymerization of the pendant methacrylate groups. Some cements, however, are light-cured only [37].

### 4.3 Properties

Hybrid ionomers bond to tooth structure without the use of a dentin bonding agent. Typically, the tooth is conditioned (etched) with polyacrylic acid or a primer before placing the hybrid ionomer. The transverse strength of a hybrid ionomer is almost double that of a standard glass ionomer. Hybrid ionomers release more fluoride than compomers and composites but almost the same as glass ionomers. Glass ionomers and hybrid ionomers recharge when exposed to fluoride treatments or fluoride dentifrices.

Requirements for light-activated cements, which are water-based and set by multiple reactions, including an acid-base reaction and polymerization (Type I), and by cements that

set only after light-activation (Type III, are described by ANSI/ADA Specification No. 96 (ISO 9917, Part 2). The compressive and tensile strengths of hybrid ionomer cements are similar to those of glass ionomer cements. The fracture toughness is higher than that of other water based cements but lower than composite cements. The bond strength to moist dentin ranges from 10 to 14 MPa and is much higher than that of most water-based cements. Hybrid ionomer cements have very low solubility when tested by lactic acid erosion. Water sorption is higher than for resin cements. Delayed fracture of ceramic restorations cemented with hybrid ionomer cements has been reported. Recently, some hybrid ionomer cements have been modified to have less water sorption. Fluoride release and rechargeability are similar to glass ionomer cements. The early pH is about 3.5 and gradually rises. Clinical experience indicates minimal postoperative sensitivity [36].

#### **4.4 Applications**

Self-cured hybrid ionomer cements are indicated for permanent cementation of porcelain-fused-to-metal crowns; bridges; metal inlays, onlays, and crowns; post cementation; and luting of orthodontic appliances. Additional uses include adhesive liners for amalgam, bases, provisional restorations, and cementation of specific ceramic restorations. Light-cured hybrid ionomer cements are used primarily for liners and bases. One light-cured product is recommended for direct bonding of orthodontic brackets and bands [35].

### **5. Zinc phosphate cement**

Zinc phosphate cement has been a mainstay in dentistry for crown and bridge applications for well over a century and has undergone many refinements in formulation and compounding. However, with the advent of newer chemical technologies its use has gradually declined over the last decade. This type of cement is supplied as a powder-liquid formulation [38].

#### **5.1 Composition**

The powder consists of mainly amorphous zinc oxide as the major ingredient with small amounts of oxides of magnesium and bismuth added mainly to facilitate the calcining process for manufacture of the powder. Small quantities of silica (typically fumed) are often added to aid in providing the right viscosity and yield stress. Minor amounts of barium and calcium compounds may be added by various manufacturers to provide a smooth, creamy mix, which is desirable for easy flow during cementation of the restoration. Some products also contain tannin fluoride although it is doubtful if the amount of fluoride released is of clinical significance.

The liquid consists of an aqueous mixture of orthophosphoric acid with small amounts of aluminum and zinc phosphates which act as buffers in reducing the reactivity of the free acid. The amount of water used in the formulation is quite critical since it dictates the setting time – too little prolongs the setting time whereas too much shortens it [39].

#### **5.2 Setting reaction**

When the alkaline zinc oxide powder is incorporated in the acidic liquid an exothermic acid-base reaction ensues. Initially, the mix becomes fluid and creamy which aids in the placement of the prosthodontic device. Within a few minutes the mass hardens to a set

cement which may contain varying amounts of crystalline phosphates of zinc including the formation of hopeite,  $Zn_3(PO_4)_2 \cdot 4H_2O$ , in the presence of excess moisture [22, 39].

### 5.3 Properties

The clinically significant properties of zinc phosphate cements include setting time, solubility and film thickness. The mechanical properties of importance are strength, modulus of elasticity and hardness. Most commercial materials meet the American National Standards Institute/American Dental Association (ANSI/ADA) Specification 96 (ISO 9917-1: 2003). In comparison with the more recent types of cements, the modulus of elasticity is quite high, which causes them to be rather brittle materials that are prone to fracture. The solubility of the set cement is relatively high at about 0.2% in 24h compared with some other classes of cements. Furthermore, these materials have virtually no adhesion to the dentinal core of the tooth preparation [38].

### 5.4 Applications

Zinc phosphate cements have had a long history of clinical usage for routine luting of metal-supported crowns and bridges [22]. Other uses include cementation of orthodontic bands, as a basing material and as temporary restorations. Occasional post-operative sensitivity has been reported by patients with the use of this type of cement [38]. The exact cause of this is not known and has been linked to acidity of the un-neutralized orthophosphoric acid residues in the cement and/or the movement of dentinal fluid across the tubules in excessively desiccated dentine due to an improper seal. The use of resin desensitizing agents has been advocated to counter post-operative sensitivity without compromising crown retention [39, 40].

## 6. Zinc polyacrylate cements

Zinc polycarboxylate cements, sometimes referred to simply as 'polycarboxylate' or 'polyacrylate' cements, are based on the reaction of zinc oxide with polycarboxylic (same as polyalkenoic) acid in water [41]. Like the zinc phosphate cements these are also supplied as powder-liquid compositions.

### 6.1 Composition

Zinc polyacrylate cements are supplied as a powder and a liquid or as a powder that is mixed with water. The powder is quite similar to that of zinc phosphate cements and consists mainly of sintered zinc oxide ground to a fine particle size. The sintering process reduces the reactivity of the amorphous zinc oxide and helps in the manipulation of the cement. Small amounts of magnesium oxide (1-5%) are added to aid the sintering process while the incorporation of fumed silica helps in the mixing and flow of the cement. Fluoride salts, e.g. stannous fluoride, may also be incorporated in small amounts to improve mechanical strength and to serve as a source of leachable fluoride. In some commercial embodiments the powder is coated with 5-20% of anhydrous polyacrylic acid to make it less technique-sensitive during the mixing process.

The liquid consists of an aqueous solution of a polycarboxylic acid, generally a homopolymer of polyacrylic acid or a copolymer of acrylic acid with itaconic or maleic acids. The average molecular weight (weight average) is usually in the range 20000-50000.

The viscosity of the solution may be controlled by the addition of small amounts of tartaric acid. For products where the powder is coated with polycarboxylic acid, the liquid is either a dilute solution of the polyacid or simply water [42].

## 6.2 Setting reaction

The polycarboxylic acid reacts with the basic zinc oxide in a neutralization reaction forming a zinc polycarboxylate complex salt [42]. This results in the formation of a cross-linked polycarboxylate hydrogel reinforced by the oxide particles. The cross-linked gel is bound to the polyanion chains by electrostatic interaction. The setting reaction has been studied by infrared spectroscopy which shows that the carboxylic acid groups (COOH) are progressively converted to carboxylate (COO<sup>-</sup>) groups as the cement hardens. Water plays several important roles in controlling the chemistry and properties of all acid-base cements. These are outlined below.

1. As a diffusion medium. Water is needed for the acids to ionize so that the protons can be dissociated and solvated and the acidic property can be manifested. It is also needed for the diffusion of the metallic ions of the bases (e.g. zinc oxide) so that these can enter the liquid phases and thus react with the acid. In addition, it is essential for the diffusion of fluoride ions, where present, out of the set cement.
2. As a stabilizer of the carboxylate complexes. A portion of the water coordinates with the zinc carboxylate complexes by electron donation to stabilize them. This is known as bound water and cannot be easily removed from the stabilized matrix.
3. As a plasticizer. The residual water helps to plasticize the set cement and makes it more resilient and less prone to failure by fracture.

## 6.3 Properties

### 6.3.1 Setting and working time

Setting and working time are two important clinically relevant parameters for any cement. The working time is the time available for the manipulation of the unset cement while the setting time is the time required by the material to set or harden from a fluid or plastic state to a rigid one. While at the end of the setting time the hardening reaction may not be complete it generally progresses far enough for the dentist to proceed to successive steps in the procedure without fear of premature dislodgement of the prosthesis. There is no standard value for the working time, but it should be reasonably long so that adequate time is available for mixing and placing the cement. Since both the working time and setting time are dependent on the same chemical reaction the former should not be too long to ensure the setting of the cement within a reasonable time. The rate of setting is affected by the following parameters:

- Reactivity of the zinc oxide
- Particle size of the zinc oxide
- Presence of additives
- Molecular weight and concentration of the polyacrylic acid
- Powder/liquid ratio

The first four parameters are controlled by the manufacturer. The last one is dependent on the operator. Hence, accurate dispensing of the powder and liquid are essential if consistent setting is to be obtained. For commercial cements the working times are 2-4min and set times are between 5 and 8 min [41, 42].

### 6.3.2 Strength

In general, zinc polycarboxylate cements are lower in compressive strength than zinc phosphates but, due to the presence of a polymeric matrix, are tougher and less brittle. Plastic deformation is exhibited at higher load values, which contributes to the increased toughness of these cements. Compressive and diametral tensile strengths of the cement develop rapidly within the first hour to about 60–80% of its strength at maturity, while it takes about 24h for maximum strength to be attained [41].

### 6.3.3 Solubility and erosion

The solubility of the cements when tested in water alone is low (0.1–0.5%) compared with the zinc phosphate cements, although solubility in distilled water does not always correlate to solubility in oral conditions. These cements are rather susceptible to erosion in an acidic environment, however. A quantitative measure of this property is defined in the ISO 9917-1 specification using the impinging lactic acid jet method devised by Beech and Bandyopadhyay [43].

### 6.4 Applications

Zinc polycarboxylate cements have a fairly long record of clinical success when used for specified indications. The most frequent use is for cementation of cast alloy- and metal-supported inlays, onlays and single-unit crowns. Because of the lower values of compressive modulus these materials should not be used for permanent cementation of long-span bridges. Less frequently they are also used as cavity liners and orthodontic band cementation but in such cases a higher powder/liquid ratio is recommended by manufacturers. The comparatively high long-term solubility and low hardness limit the utility of this class of materials for permanent cementation, resulting in a decline in their use in recent times [42].

## 7. Zinc oxide-eugenol and non-eugenol cements

When certain types of zinc oxide are mixed with eugenol, the mix sets to a hard cement that is compatible with both the hard and soft tissues of the mouth. Cements of this type have been used extensively since the 1890s. Simple mixtures of these two materials do not have great strength when compared with zinc phosphate cements, and their use has been limited to situations in which strength is not important. Quite early it was found that they had a sedative effect on exposed dentin. For many years, ZOE cements have been used as provisional restorations, soft tissue packs in oral surgery and periodontics, and root canal sealers. Because eugenol acts as an inhibitor for free-radical polymerized materials, select other materials for provisional restorations when bonding of the permanent restoration is anticipated. Non-eugenol-zinc oxide cements are also available for temporary cementation. These cements are suitable for patients sensitive to eugenol [26, 29, 36].

### 7.1 Composition

The powder is mainly zinc oxide, with added white rosin to reduce the brittleness of the set cement, zinc stearate as a plasticizer, and zinc acetate to improve the strength of the cement. The liquid is eugenol with olive oil as a plasticizer. Two compositional changes have been used to increase the strength of the cement for luting purposes. In one, methyl methacrylate polymer is added to the powder, and in the other, alumina ( $Al_2O_3$ ) is added to the powder



and ethoxybenzoic acid (EBA) to the liquid. A typical polymer-reinforced cement has 80% zinc oxide and 20% poly(methyl methacrylate) in the powder and eugenol in the liquid [14]. These cements are sufficiently strong for final cementation of fixed prostheses and are used also as cement bases and provisional restorations. A typical EBA-alumina-reinforced ZOE cement contains 70% zinc oxide and 30% alumina by weight in the powder. In some cases, rosin and copolymers may be added to reduce the brittleness and film thickness and improve the mixing qualities. The liquid of the EBA-alumina reinforced cements contains 62.5% ortho-EBA by weight and 37.5% eugenol by weight. The non-eugenol-zinc oxide cements typically contain an aromatic oil and zinc oxide. Other ingredients may include olive oil, petroleum jelly, oleic acid, and beeswax [17, 31].

## 7.2 Setting reaction

The setting of ZOE cements is a chelation reaction in which an amorphous, zinc eugenolate is formed. The setting reaction is shown below, where two molecules of eugenol react with ZnO in the presence of water to form the chelate, zinc eugenolate. Excess zinc oxide is always used, so the set material consists of a matrix of amorphous zinc eugenolate that binds the unreacted zinc oxide particles together. The setting reaction is accelerated by increases in temperature or humidity. EBA also forms a chelate with zinc oxide, and its presence allows some crystalline zinc eugenolate to form, which provides additional strength. The reaction is not measurably exothermic, and the presence of moisture is essential for setting to occur [32].

## 7.3 Properties

The variety of compositions of the ZOE cements and the many uses to which they are applied make it difficult to write a specification for these cements. ANSVADA Specification No. 30 (ISO 3107) for dental zinc oxide-eugenol cements and zinc oxide non-eugenol cements gives standards for temporary cements, permanent cements, filling materials and bases, and cavity liners. It sets requirements for the general characteristics of the powders, liquids, and pastes used in these cements and for the important physical properties of setting time, compressive strength, disintegration, film thickness, and acid-soluble arsenic content, where these are applicable [38].

## 7.4 Applications

A range of ZOE and modified ZOE cements are suitable for many uses in restorative dentistry, and the practitioner should become familiar with each type and its application. Base Materials having a compressive strength of 5.5 to 39 MPa are used as a cement base, and the strength reaches a maximum in about 12 to 15 minutes. They are normally used under zinc phosphate cement, which acquires about three times the strength in the same time. The ZOE cements have the advantage that the thermal insulating properties of the cements are excellent and are approximately the same as those for human dentin [33].

# 8. Calcium hydroxide

## 8.1 Composition

The base paste of a typical product contains calcium tungstate, tribasic calcium phosphate, and zinc oxide in glycol salicylate. The catalyst paste contains calcium hydroxide, zinc

oxide, and zinc stearate in ethylene toluene sulfonamide. The ingredients responsible for setting are calcium hydroxide and a salicylate, which react to form an amorphous calcium disalicylate. Fillers such as calcium tungstate or barium sulfate provide radiopacity. A light-cured calcium hydroxide base consists of calcium hydroxide and barium sulfate dispersed in a urethane dimethacrylate resin [11].

## 8.2 Properties

Calcium hydroxide cements are used for lining deep cavities or for direct pulp capping. The antibacterial action of calcium hydroxide makes these cements useful in indirect pulp-capping procedures involving carious dentin. ZOE cements are used in deep cavities to retard penetration of acids and reduce possible discomfort to the pulp. Both calcium hydroxide and ZOE low strength bases are often used with a high strength base in restoring a tooth. Root canal sealers containing calcium hydroxide have been developed.

The important properties of these bases are mechanical and thermal properties, solubility, and pH. Calcium hydroxide (self-cured bases have low values of tensile strength and compressive strength, or elastic modulus, compared with high-strength bases. Although setting times vary between 2.5 and 5.5 minutes, compressive strengths of these cements continue to increase over a 24-hour period. For a group of five commercial products, compressive strengths ranged from 6.5 to 14.3 MPa at 10 minutes to from 9.8 to 26.8 MPa at 24 hours. The low elastic modulus of calcium hydroxide bases restricts their usage to areas not critical to the support of restorations [40].

Mechanical support should be provided by sound dentin or by a high-strength base. Calcium hydroxide bases are, however, considered strong enough to support the forces of condensation of amalgam [10].

### 8.2.1 Thermal properties

Calcium hydroxide bases may provide some thermal insulation to the pulp if used in sufficiently thick layers. A thickness greater than 0.5 mm is not suggested. Practically, thermal protection should be provided by the overlying high-strength base [38].

### 8.2.2 Solubility

The solubility of calcium hydroxide bases has been measured in several solvents for various periods of immersion. For a group of five commercial products, values ranged from 0.4% to 7.8% in distilled water at 37°C for 24 hours, from 0.1% to 6.2% in 35% phosphoric acid for 60 seconds, and from 0.3% to 1% in ether for 10 seconds [18]. One product that was resistant to dissolution in water and in acid disintegrated when exposed to ether. Some solubility of the calcium hydroxide is necessary to achieve its therapeutic properties, although an optimum value is not known. Clearly the use of acid-etching procedures and varnish in the presence of calcium hydroxide bases must be done with care. Over a long term, some calcium hydroxide products seem to "disappear" from the cavity. The cause of this dissolution is unclear, but some products have been reformulated in an attempt to minimize the problem [25].

### 8.2.3 pH

The pH of commercial products has been measured at between 9.2 and 11.7. Free calcium hydroxide in excess of that necessary to form the calcium disalicylate stimulates secondary dentin in proximity to the pulp and shows antibacterial activity [31].

## 9. Compomers

Compomer cement is the newest resin-based cement indicated for cementation of cast alloy crowns and bridges, porcelain-fused-to-metal crowns and bridges, and gold cast inlays and onlays. Cementation of all-ceramic crowns, inlays, onlays, and veneers, with some exceptions, is contraindicated. The cement should not be used as a core or filling material. Compomers are also known as *poly acid-modified composites*. A compomer cement was recently introduced for orthodontic bonding [41].

### 9.1 Composition

The cement powder contains strontium aluminum fluorosilicate glass, sodium fluoride, and self and light-cured initiators. The liquid contains polymerizable methacrylate/carboxylic acid monomer, multifunctional acrylate/phosphate monomer, diacrylate monomer, and water [40].

### 9.2 Setting reaction

Setting is the result of self- and light-cured polymerization. Once the cement comes into contact with oral fluids, an acid-base reaction may occur. The carboxylic acid groups contribute to the adhesive capability of the cement [42].

### 9.3 Properties

Compomer cement has high values of retention, bond strength, compressive strength, flexural strength, and fracture toughness. The cement has low solubility and sustained fluoride release [22].

## 10. Composites and adhesive resins

Cements based on resin composites have been used for cementation of crowns, conventional bridges, and resin-bonded bridges; for bonding of esthetic ceramic and laboratory-processed composite restorations to teeth; and for direct bonding of orthodontic brackets to acid-etched enamel. Recently, composite cements have been developed for cementation of provisional restorations. ISO 4049 for polymer-based filling, restorative, and luting materials (ANSI/ADA No. 27) describes the following three classes of composite cements [33, 29]:

Class 1-self-cured materials

Class 2-light-cured materials

Class 3-dual-cured materials

Property requirements based on ISO 4049 can be summarized as follows:

Class 1, 2, 3: film thickness, max. – 50  $\mu\text{m}$

Class 1, 3: working time, min. – 60 seconds

Class 1, 3: setting time, max. – 10 minutes

Class 2: depth of cure, min. – 0.5 mm

(Opaque), 1.5 mm (others)

Class 1, 2, 3: water sorption, max. – 40  $\mu\text{g}/\text{mm}^3$

Class 1, 2, 3: solubility, max. – 7.5  $\mu\text{g}/\text{mm}^3$

### **10.1 Cementation of alloy crowns and bridges, resin-bonded bridges, and provisional restorations**

Synthetic resin cements based on methyl methacrylate have been available since 1952 for use in cementation of inlays, crowns, and appliances. In the early 1970s, a resin composite was introduced as a crown and bridge cement [1].

### **10.2 Composition**

Self-cured composite cements are typically two paste systems. One major component is a diacrylate oligomer diluted with lower-molecular weight dimethacrylate monomers. The other major component is silanated silica or glass. The initiator-accelerator system is peroxide-amine [27].

### **10.3 Setting reaction**

One adhesive resin cement is a self-cured, powder-liquid system formulated with methacryloxyethylphenyl phosphate or 4-methacryloxyethyl-trimellitic anhydride (4-META). The 4-META cement is formulated with methyl methacrylate monomer and acrylic resin filler and is catalyzed by tri-butyl-borane. Another adhesive resin cement is a phosphonate cement supplied as a two-paste system, containing Bis-GMA resin and silanated quartz filler. The phosphonate molecule is very sensitive to oxygen, so a gel is provided to coat the margins of a restoration until setting has occurred. The phosphate end of the phosphonate reacts with calcium of the tooth or with a metal oxide. The double-bonded ends of both 4-META and phosphonate cements react with other double bonds when available. Setting of resin cements results from self or light-cured polymerization of carbon-carbon double bonds [39].

### **10.4 Properties**

Composite cements used for cementation of provisional restorations (25 to 70 MPa) have a substantially lower compressive strength than composite cements used for permanent cementation (180 to 265 MPa) [22].

### **10.5 Applications**

Adhesive resin cements and composite cements in conjunction with bonding agents are being used as cements for posts and cores. Bond strengths of 14 MPa have been reported for silica-treated posts cemented with 4-META resin cement in extracted teeth. The use of resin-bonded bridges declined dramatically in the late 1980s [37].

## **11. Nanocomposites**

Resin composites are used to replace missing tooth structure and modify tooth color and contour, thus enhancing facial esthetics. The development of composites about 1960 has resulted in higher mechanical properties, lower thermal coefficient of expansion, lower dimensional change on setting, and higher resistance to wear, thereby improving clinical performance. Later development of bonding agents for bonding composites to tooth structure has also improved the quality of composite restorations [44].

Composites were initially developed for anterior Class 3 to Class 5 restorations, in which esthetics was crucial, and for Class 1 restorations, in which moderate occlusal stresses occur.

In the 1990s, modifications of materials and techniques extended their application to Class 2 and Class 6 posterior restorations. Laboratory- processed composites are used for crowns and even bridges, when reinforced with fibers, and can be bonded to an alloy substructure. A resin composite is composed of four major components: organic polymer matrix, inorganic filler particles, coupling agent, and the initiator-accelerator system [45].

### 11.1 Polymer matrix

The organic polymer matrix in most composites is either an aromatic or urethane diacrylate oligomer. Oligomers are viscous liquids, the viscosity of which is reduced to a useful clinical level by the addition of a diluent monomer [45].

The two most common oligomers that have been used in dental composites are dimethacrylates (Bis-GMA) 2,2-bis[4(2-hydroxy-3-methacryloyloxy-propyloxy)-phenyl]propane and urethane dimethacrylate (UDMA). Both contain reactive carbon double bonds at each end that can undergo addition polymerization. A few products use both Bis-GMA and UDMA oligomers. The viscosity of the oligomers, especially Bis-GMA, is so high that diluents must be added, so a clinical consistency can be reached when they are compounded with the filler. The most widely used resin in dental composites is based on the copolymer prepared from a combination of Bis-GMA and triethylene glycol dimethacrylate (TEGDMA) (Fig. 1). TEGDMA is usually added to Bis-GMA in order to achieve workable viscosity limits since the latter monomer possesses very high viscosity ( $>10^6$ cP) due to the intermolecular hydrogen bonding. In Bis-GMA/TEGDMA dental resin systems, Bis-GMA functions to limit the polymerization induced volumetric shrinkage and to enhance resin reactivity, while TEGDMA provides for increased vinyl double bond conversion [46].

Although Bis-GMA has widely been used as the main monomer in most resin composite systems due to its superior aesthetic quality, simple operation technique, enhanced mechanical strength, less shrinkage, higher modulus, and reduced toxicity because of its lower volatility and diffusivity into the tissue, and the composites have undergone significant development since their advent, they still have shortcomings limiting their application. Lack of good adhesion to the tooth structure and polymerization shrinkage are the most important problems. Considerable interest has been devoted to synthesizing new monomers to provide alternative monomers to overcome the problems [47].

BTDMA as a dimethacrylate monomer containing carboxylic acid groups in its structure has been shown that can interact with the  $\text{Ca}^{2+}$  ions of the tooth structure so it has the potential to provide better adhesion properties in dental composites (Fig. 1) [48].

### 11.2 Fillers

As dental composites cannot withstand heavy occlusal forces, many ways have been introduced to reinforce them, such as using fibers and whiskers as reinforcing agents. Some of dental resins are reinforced with inorganic fillers [49]. A wide variety of fillers have been employed in composites to improve the properties and developments in filler technology are responsible for many improvements in composites which are used today [45]. Despite many improvements in this field, dental composites do not have enough toughness, strength and durability in order to be used in stress bearing areas. There are numerous types of inorganic fillers. Fillers such as  $\text{SiO}_2$ ,  $\text{ZrO}_2$  and  $\text{Al}_2\text{O}_3$  of micron or nano particle size are usually used. Most of the fillers which are used to reinforce dental composites are silicate glasses [50].



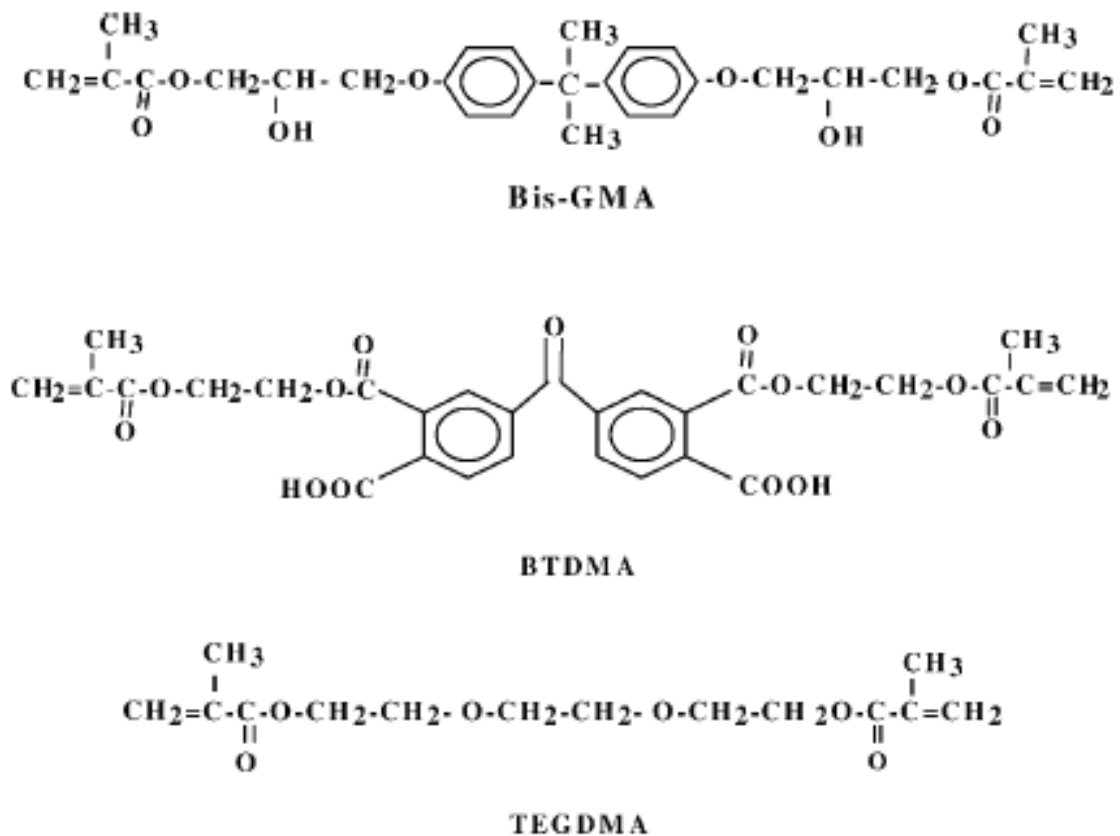


Fig. 1. Chemical structures of Bis-GMA, BTDMA and TEGDMA

The relatively low strength and durability of the composites, however, have limited their uses. The strength of the inorganic filler reinforced dental composites is usually in the range from 80 to 120 MPa, and the average life time is 5 years or less. By comparison, dental amalgams have strength over 400 MPa and have a life time of more than 15 years. Investigations of the reasons for failure revealed that, among other things, inorganic filler was a major contributor. Ironically, the inorganic fillers which are added for the purpose of fortifying the dental composites are actually responsible, at least in part, for the demise. Stresses are transmitted onto the filler particles projecting from the occlusal surfaces through the boluses of foods during chewing [51].

Glass-ceramics are polycrystalline materials which consist of a glass matrix and one or more crystalline phases. The glass fillers are not strong enough and exhibit cracks that either cut through the glass fillers or propagate around the filler particles. To overcome the problem, much effort has been made into the use of glass fibers, nanoporous fillers, branched fibers or even ceramic whiskers [45].

Since the inorganic filler particles are considerably harder than the dental resin matrices, the stresses are transmitted through the filler to the resin. Wherever the submerged portions of the filler particles are angulated or irregular in shape, the stress concentration may become excessively high. Such a condition tends to generate small cracks around the filler particles, thereby weakening the matrices locally. Reinforcement with nanofibers was shown substantial improvements on mechanical properties of dental composites, such as flexural strength, elastic modulus and the work-of-fracture. The small diameter of nanofibers also provides for a large ratio of surface area to volume, which can enhance the intermolecular hydrogen bonding between nanofiber filler and the resin matrix. Furthermore, nanofibers

are continuous. If a micro-crack is initiated in a matrix under contact wear and/or other stresses, the nanofibers remain intact across the crack planes and support the applied load. Therefore, crack opening is resisted by the nanofibers and the matrix is reinforced [52].

The uniform distribution of nanofibers improved the strength and modulus of the resulting nanocomposite nanofiber. The silanized single crystals on the surface of nanofibers also enhance the intermolecular interaction/bonding between the nanofiber filler and the resin matrix [49].

Apart from fillers, a good bond between fillers and the resin matrix is essential in dental composites. Silane coupling agents provide the bond between two components in dental composites, but this bond can be degraded by water absorbed by the composites. The idea of increasing the micro-mechanical retention between fillers and resin in order to reinforce the coupling agent was first described by Bowen et al. in 1976. Their strategy was to use multi-phase glasses which can be etched and produce porous fillers [53].

Recently, nanosized particles dispersed in the organic matrix to give high strength, hardness and toughness.

A helpful method of classifying dental composites is by the particle size, shape, and distribution of filler. Early composites contained large (20 to 30 $\mu\text{m}$ ) spherical particles, followed by products containing large irregularly shaped particles, microfine particles (0.04 to 0.2 $\mu\text{m}$ ), fine particles (0.4 to 3 $\mu\text{m}$ ), and finally blends (microhybrids) containing mostly fine particles with some microfine particles. Based on the type of filler particles, composites are currently classified as *microhybrid* and *microfilled* products. Microhybrid composites contain irregularly shaped glass (borosilicate glass; lithium or barium aluminum silicate; strontium or zinc glass) or quartz particles of fairly uniform diameter. Typically, composites have a distribution of two or more sizes of fine particles plus microfine filler (5% to 15%). This distribution permits more efficient packing, whereby the smaller particles fill the spaces between the larger particles. Microhybrid composites may contain 60% to 70% filler by volume, which, depending on the density of the filler, translates into 77% to 84% by weight in the composite. Most manufacturers report filler concentration in weight percent (wt %) [50].

Microfilled composites contain silica with a very high surface area (100 to 300  $\text{m}^2/\text{g}$ ) having particle diameters of 0.04 to 0.2  $\mu\text{m}$ . Because of the high surface area, only 25% by volume or 38% by weight can be added to the oligomer to keep the consistency of the paste sufficiently low for clinical applications. Fillers consisting of microfine silica in polymerized oligomers are prepared and ground into particles 10 to 20  $\mu\text{m}$  in diameter. These reinforced fillers may be added to the oligomer in concentrations, so the inorganic content can be increased to 32% to 50% by volume or about 50% to 60% by weight. A variation of this modification is used in which most of the filler is reinforced filler, with smaller amounts of silica added to the oligomer. Another modification (homogeneous microfill) has no reinforced filler, but rather microfine silica dispersed in the oligomer [48].

### 11.3 Coupling agents

The coupling agent, an organosilane (silane), is applied to the inorganic particles by the manufacturer before being mixed with the unreacted oligomer. Silanes are called *coupling agents*, because they form a bond between the inorganic and organic phases of the composite. The silane contains functional groups (such as methoxy), which hydrolyze and react with the inorganic filler, as well as unsaturated organic groups that react with the oligomer during polymerization. During the deposition of the silane on the filler, the methoxy groups hydrolyze to hydroxyl groups that react with adsorbed moisture or -OH

groups on the filler. They can also condense with  $-OH$  groups on an adjacent hydrolyzed silane to form a homopolymer film on the surface of the filler. During the setting reaction of the oligomer, the carbon double bonds of the silane react with the oligomer, thus forming a bond from the filler through the coupling agent to the polymer matrix. This coupling reaction binds the filler and the oligomer, so when a stress is applied to a composite, the stress can be transferred from one string filler particle to another through the rather low-strength polymer. As a result, the strength of the composite is microfine in polymer filler, intermediate to that of the filler and the polymer separately. This bond can be degraded by water absorbed by the composite during clinical use [51, 53].

#### 11.4 Initiators and accelerators

Composites are light cured or self-cured, with the former being more common. Light activation is accomplished with blue light with a peak wavelength of about 470 nm, which is absorbed usually by a photo-activator, such as camphoroquinone (Fig. 2), added by the manufacturer in amounts varying from 0.2% to 1.0%. The reaction is accelerated by the presence of an organic amine containing a carbon double bond. The amine and the camphoroquinone are stable in the presence of the oligomer at room temperature, as long as the composite is not exposed to light [54].

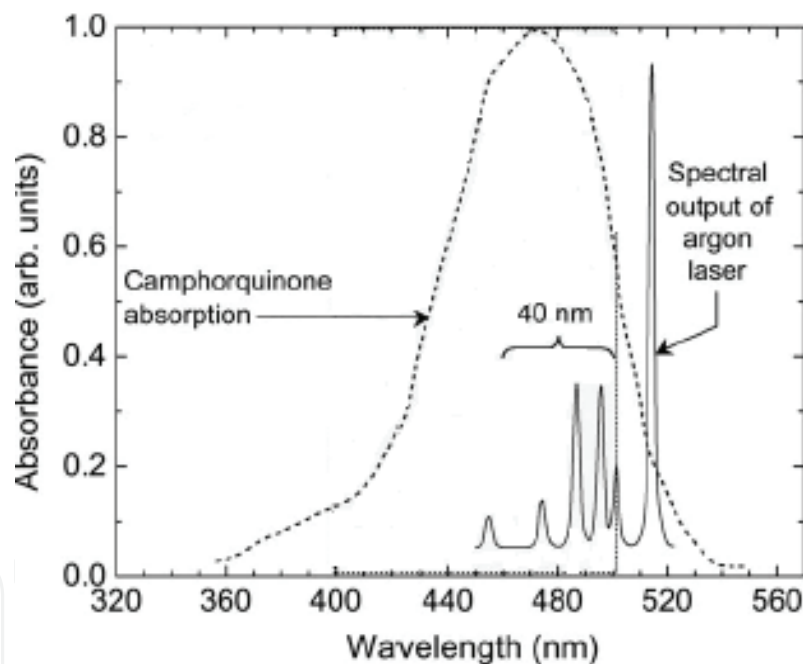


Fig. 2. Absorption spectrum of camphoroquinone [55]

Although camphoroquinone is the most common photo-activator, others are sometimes used to accommodate special curing conditions, such as the use of plasma-arc lights with rapid-cured composites.

Chemical activation is accomplished at room temperature by an organic amine (catalyst paste) reacting with an organic peroxide (universal paste) to produce free radicals, which in turn attack the carbon double bonds, causing polymerization. Once the two pastes are mixed, the polymerization reaction proceeds rapidly.

Some composites are dual cured. These formulations contain initiators and accelerators that allow light activation followed by self-curing or self curing alone [55].

### 11.5 Pigments and other components

Inorganic oxides are usually added in small amounts to provide shades that match the majority of tooth shades. Numerous shades are supplied, ranging from white bleaching shades to yellow to gray. An ultraviolet (W) absorber may be added to minimize color changes caused by oxidation.

Composites are formulated to contain accelerators and initiators that allow self-curing, light curing, and dual curing. ISO 4049 for polymerbased filling, restorative, and luting materials (ANSVADA No. 27) describes two types and three classes of composites, as shown by the following [53]:

Type 1: Polymer-based materials suitable for restorations involving occlusal surfaces

Type 2: Other polymer-based materials

Class 1: Self-cured materials

Class 2: Light-cured materials

Group 1: Energy applied intra-orally

Group 2: Energy applied extra-orally

Class 3: Dual-cured materials

## 12. Types of composites

### 12.1 Light-cured dental nanocomposites

Light-cured composites are discussed in this chapter, because most composites and compomers are light activated. These composites are supplied in various shades in syringes, syringes, and compules. The syringes are made of opaque plastic to protect the material from exposure to light and thus provide adequate shelf life. If packaged as a compule, the compule is placed on the end of a syringe, and the paste is extruded after removal of the protective tip. The advantages of compules are ease of placement of the composite paste, decrease in cross infection, and protection of the paste from exposure to ambient light.

Polymerization of light-cured composites is initiated by visible blue light [53].

The polymerized resin is highly cross-linked because of the presence of the difunctional carbon double bonds. The degree of polymerization varies, depending on whether it is in the bulk or in the air-inhibited layer of the restoration [50].

The polymerization of light-cured composites varies according to the distance from the composite to the light and the duration of light exposure. The percentage of the double bonds that react may vary from 35% to 80%. The degree of polymerization is higher for laboratory composites that are post-cured at elevated temperatures [51, 53].

### 12.2 Self-cured/dual-cured dental nanocomposites

Self- and dual-cured composites are typically packaged in syringes or tubs of paste and catalyst and require mixing. The polymerization reaction of self-cured composites is chemically initiated with a peroxide initiator and an amine accelerator.

Dual-cured products use a combination of chemical and light activation to carry out the polymerization reaction [52].

### 12.3 Polymerization

Exposure times for polymerization vary depending on the type of light-curing unit and the type, depth, and shade of the composite. Times may vary from 20 to 60 seconds for a restoration 2mm thick. Microfilled composites require longer exposure than microhybrid

composites because the small filler particles scatter the light more. Darker shades or more opaque composites require longer exposure times (up to 60 seconds longer) than lighter shades or more translucent composites. In deep restorations, add and polymerize the composite in layers. One layer bonds to another without any loss of strength. The setting time of light-cured composite and the depth of cure within a given mass depend on the intensity and penetration of the light. A material with a low absorption coefficient cures to the greatest depth. The presence of ultraviolet absorbers for color stabilization, fluorescent dyes for esthetics, or excessive initiator concentration has a detrimental effect on completeness of cure [55].

### 13. Properties of dental nanocomposites

The chemical and physico-mechanical properties of composites depend on their resin compositions, filler type, size and content. Important properties of the nanocomposites include degree of conversion, flexural strength, flexural modulus, working and setting times, polymerization shrinkage, thermal properties, water sorption and solubility, color stability and radiopacity. These parameters were studied systematically. For dental nanocomposite, an improvement in physical properties is expected due to the increased interfacial interactions between resin and fillers [56].

Among the other factors such as light intensity, initiator system, light irradiation method and polymerization temperature, varying the relative amounts of the matrix monomers has a significant effect on the mechanical properties of the resin composites [57].

#### 13.1 Degree of conversion

The most important dental composite characteristics are the degree of conversion (DC) and the depth of polymerization. These are great importance for the clinical longevity of the restorations. The DC of resins is a major factor influencing their bulk physical properties. In general, the higher conversion of double bonds, the greater mechanical strength. The DC is the measurement of the percentage of consumed double bonds. Conversion of the monomer to the polymer in light-activated composites is dependant on several factors, such as light source, power density, light wavelength, resin composition, transmission of light through the material and amount of activator-initiator and inhibitor present [58].

Low DC of dental composite may give inadequate wear resistance and a low bonding stability to tooth surface. This clinical problem can result in marginal shrinkage, subsequent loss of anatomic form and fractures in the restorations. Several methods have been used to investigate the effectiveness of irradiation source on the polymerization of dental composite, such as micro hardness, optical microscopy and vibration methods including infrared spectroscopy (FTIR) and Raman spectroscopy (RS) [59].

Vibration methods allow precise assessment of the depth of polymerization and DC (i.e., the percentage of vinyl group converted to aliphatic functions) of methacrylate composite resins.

##### 13.1.1 Method of test

To measure the degree of conversion, the uncured composite is placed between two polyethylene films, pressed to form a very thin film and absorbance peak obtained by transmission mode of FTIR. Then the sample is cured and the absorbance peak recorded for the cured sample. The quantity of the remaining double bonds is determined by a method



described by Ruyter and Gyrosi. The percentage of unreacted carbon-carbon double bonds is determined from the ratio of absorbance intensities of aliphatic C=C (peak at  $1638\text{ cm}^{-1}$ )/aromatic C...C (peak at  $1608\text{ cm}^{-1}$ ), which is used as an internal standard, since it doesn't change during the polymerization reaction, before and after curing of the specimen. The percentage degree of conversion is obtained as follows [60]:

$$DC\% = \left(1 - \frac{\left[\frac{\text{abs}(\text{aliphatic} : \text{C} = \text{C})_{1638\text{cm}^{-1}}}{\text{abs}(\text{aromatic} : \text{C}\dots\text{C})_{1608\text{cm}^{-1}}\right]_{\text{Cured}}}{\left[\frac{\text{abs}(\text{aliphatic} : \text{C} = \text{C})_{1638\text{cm}^{-1}}}{\text{abs}(\text{aromatic} : \text{C}\dots\text{C})_{1608\text{cm}^{-1}}\right]_{\text{Uncured}}}\right) \times 100 \quad (1)$$

Commercial dental restorative materials are usually polymerized in less than 60 s with a degree of conversion from 40 to 75%. Our previous research on preparation of dental nanocomposites based on Bis-GMA, TEGDMA and nano  $\text{SiO}_2$  indicated that higher resin concentration and power density resulted in a higher degree of conversion [61].

## 13.2 Mechanical properties

### 13.2.1 Flexural strength and modulus

The flexural strengths of the various composites are similar. The flexural modulus of microfilled and flowable composites are about 50% lower than values for all-purpose and packable composites, which reflects the lower volume percent filler present in the microfilled and flowable composites.

If the amalgams are to be replaced by composites as restorative materials, they must possess some acceptable mechanical characteristics such as high strength and high wear resistance to stand a normal biting or chewing force [61].

#### 13.2.1.1 Method of test

The flexural strength and flexural modulus of the polymerized composites are measured with three-point bending test according to the ISO4049:2000 (Fig. 3). The samples for measuring both flexural strength and flexural modulus are prepared in a rectangular brass mold (length= 25 mm, width= 2 mm, height= 2 mm) (Fig. 4). Five specimens for each experimental group are required and their mean value is determined.

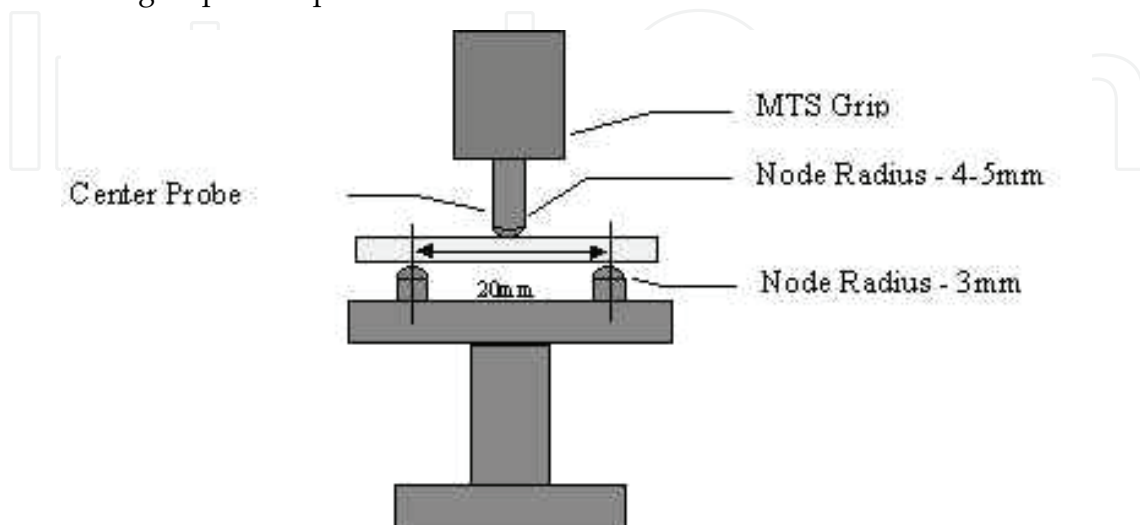


Fig. 3. Method of three-point bending test



Fig. 4. Mold of flexural strength and flexural modulus tests

The flexural strength and flexural modulus were calculated from the following equation [60]:

$$FS = \frac{3fl}{2bh^2} \quad (2)$$

$$FM = \frac{fl^3}{4bh^3d} \quad (3)$$

where  $f$  is the maximum force (N),  $l$  the distance between the supports (mm),  $b$  the specimen width,  $h$  the height of the bar (mm) and  $d$  rate of curvature under load (mm).

Investigations show that maximum flexural strength and flexural modulus of the nanocomposites can be achieved by increasing the intensity and percentage of filler [61].

### 13.2.2 Compressive strength and modulus

The compressive strengths of the various composites are similar. The flexural modulus of microfilled and flowable composites are typically lower than values for all-purpose and packable composites, which reflects the lower volume percent filler present in the microfilled and flowable composites. For comparison, the modulus of elasticity in compression is 62 GPa for amalgam, 19 GPa for dentin, and 83 GPa for enamel [22].

### 13.2.3 Knoop hardness

Values of Knoop hardness for composites (22 to 80 kg/mm<sup>2</sup>) are low compared with values of 343 kg/mm<sup>2</sup> for human enamel and 110 kg/mm<sup>2</sup> for dental amalgam. The Knoop hardness of composites with fine particles is somewhat greater than values for composites with microfine particles because of the hardness and volume fraction of the filler particles. These values indicate a moderate resistance to indentation under functional stresses for the more highly filled composites, but this difference does not appear to be a major factor in resisting functional wear [59].

A microhardness measurement such as Knoop can be misleading on composites with large filler particles (>10 μm in diameter), in which the small indentation could be made solely on

the organic or the inorganic phase. However, with most current products, filler particle sizes have become much smaller ( $<1 \mu\text{m}$ ), and the microhardness values appear more reliable [62].

#### 13.2.4 Bond strength to dental substrates

The bond strength of composites to etched enamel and dentin is typically between 20 and 30 MPa. Bonding is principally a result of micromechanical retention of the bonding agent into the etched surfaces of enamel and dentin. In dentin, a hybrid layer of bonding resin and collagen is often formed, and the bonding adhesive penetrates the dentinal tubules [48].

Composite can be bonded to existing composite restorations, ceramics, and alloys when the substrate is roughened and primed appropriately. In general, the surface to be bonded is sandblasted (microetched) with  $50 \mu\text{m}$  alumina and then treated with a resin-silane primer for composite, a silane primer for ceramic, or a special alloy primer. Bond strengths to treated surfaces are typically greater than 20 MPa [51].

#### 13.2.5 Depth of cure (light-cured composites)

Maximum intensity of the light radiation beam is concentrated near the surface of a light-cured composite. As the light penetrates the material, it is scattered and reflected and loses intensity [49].

A number of factors influence the degree of polymerization at given depths from the surface after light curing. The concentration of photoinitiator or light absorber in the composite must be such that it will react at the proper wavelength and be present in sufficient concentration. Both filler content and particle size are critical to dispersion of the light beam. For this reason, microfilled composites with smaller and more numerous particles scatter more light than microhybrid composites with larger and fewer glass particles. Longer exposure times are needed to obtain adequate depth of cure of microfilled composites [55].

The light intensity at the resin surface is a critical factor in completeness of cure at the surface and within the material. The tip of the light source must be held within 1 mm of the surface to gain optimum penetration. More-opaque shades reduce light transmission and cure only to minimal depths (1 mm). A standard exposure time using most visible lights is 20 seconds. In general, this is sufficient to cure a light shade of resin to a depth of 2 or 2.5 mm. A 40-second exposure improves the degree of cure at all depths, but it is required to obtain sufficient cure with the darker shades. Application of the light beam through 1 mm or less thickness of tooth structure produces a sufficient cure at shallower depths, but the hardness values obtained are not consistent. Because the light beam does not spread sufficiently beyond the diameter of the tip at the emitting surface, it is necessary to "step" the light across the surface of large restorations so the entire surface receives a complete exposure [53, 56].

Larger tips have been manufactured for placement on most light-curing units. However, as the light beam is distributed over a larger surface area, the intensity at a given point is reduced. Use a longer exposure time of up to 60 seconds when larger emitting tips are used. To evaluate the effective depth of cure of a specific light-curing unit, cut a small section of 5 to 10 mm from a clear straw and place it on a glass slide. Pack the section with composite. Apply the light directly to the top surface for 20 to 40 seconds according to the recommended technique. Cut off the straw, and scrape uncured composite from the bottom of the specimen with a sharp knife. Measure the length of the apparently cured specimen and divide in half to estimate the effective depth of cure [47, 50].

### 13.3 Physical properties

#### 13.3.1 Working and setting times

For light-cured composites, initiation of polymerization is related specifically to the application of the light beam to the material; about 75% of the polymerization takes place during the first 10 minutes. The curing reaction continues for a period of 24 hours. Not all of the available unsaturated carbon double bonds react; studies report that about 25% remain unreacted in the bulk of the restoration. If the surface of the restoration is not protected from air by a transparent matrix, polymerization is inhibited; the number of unreacted carbon double bonds may be as high as 75% in the tacky surface layer. Although the restoration can be finished with abrasives and is functional after 10 minutes, the optimum physical properties are not reached until about 24 hours after the reaction is initiated [29, 32].

For most composites that are initiated by visible light, there is a critical time period after dispensing of the paste onto a paper pad during which fresh composite flows against tooth structure at an optimum level. Within 60 to 90 seconds after exposure to ambient light, the surface of the composite may lose its capability to flow readily against tooth structure, and further work with the material becomes difficult. Fluorescent lights labeled "gold" can be substituted to provide unlimited working time for light-cured composites. The setting times for chemically activated composites range from 3 to 5 minutes. These short setting times have been accomplished by controlling the concentration of initiator and accelerator [33].

A controlled setting time allows for the individual polymerization of small increments of composite, thus permitting the use of multiple shades of composite within a single restoration and accommodating polymerization shrinkage within each increment as opposed to the total shrinkage in a bulk-cure method [46].

#### 13.3.2 Polymerization shrinkage

Free volumetric polymerization shrinkage is a direct function of the amount of oligomer and diluent, and thus microhybrid composites shrink only 0.6% to 1.4%, compared with shrinkage of microfilled composites of 2% to 3%. This shrinkage creates polymerization stresses as high as 13 MPa between the composite and tooth structure. These stresses severely strain the interfacial bond between the composite and the tooth, leading to a very small gap that can allow marginal leakage of saliva. This stress can exceed the tensile strength of enamel and result in stress cracking and enamel fractures along the interfaces. The potential for this type of failure is even greater with microfilled composites, in which there is a much higher volume percent of polymer present, and polymerization shrinkage is greater. The net effect of polymerization shrinkage can be reduced by incrementally adding a light-cured composite and polymerizing each increment independently, which allows for some contraction within each increment before successive additions [56, 57, 63, 64].

Composites with epoxy resin and nanosilica fillers provide materials with high mechanical properties and low polymerization shrinkage.

#### 13.3.3 Thermal properties

The thermal expansion coefficient of composites ranges from 25 to 38  $\times 10^{-6}/^{\circ}\text{C}$  for composites with fine particles to 55 to 68  $\times 10^{-6}/^{\circ}\text{C}$  for composites with microfine particles. The values for composites are considerably less than the average of the values for the polymer matrix and the inorganic phase, however, the values are higher than those for dentin (8.3  $\times 10^{-6}/^{\circ}\text{C}$ ) and enamel (11.4  $\times 10^{-6}/^{\circ}\text{C}$ ). The higher values for the microfilled composites are related mostly to the greater amount of polymer present. Certain glasses



may be more effective in reducing the effect of thermal change than are others, and some resins have more than one type of filler to compensate for differential rates [58].

Thermal stresses place an additional strain on the bond to tooth structure, which further compounds the detrimental effect of the polymerization shrinkage. Thermal changes are also cyclic in nature, and although the entire restoration may never reach thermal equilibrium during the application of either hot or cold stimuli, the cyclic effect can lead to material fatigue and early bond failure. If a gap were formed, the difference between the thermal coefficient of expansion of composites and teeth could allow for the percolation of oral fluids [62].

The thermal conductivity of composites with fine particles ( $25$  to  $30 \times 10^{-4}$  cal/sec/cm<sup>2</sup> [°C/cm]) is greater than that of composites with microfine particles ( $12$  to  $15 \times 10^{-4}$  cal/sec/cm<sup>2</sup> [°C/cm]) because of the higher conductivity of the inorganic fillers compared with the polymer matrix. However, for highly transient temperatures the composites do not change temperature as fast as tooth structure and this difference does not present a clinical problem [61].

#### **13.3.4 Water sorption**

The water sorption of composites with fine particles ( $0.3$  to  $0.6$  mg/cm<sup>2</sup>) is greater than that of composites with microfine particles ( $1.2$  to  $2.2$  mg/cm<sup>2</sup>), because of the lower volume fraction of polymer in the composites with fine particles. The quality and stability of the silane coupling agent are important in minimizing the deterioration of the bond between the filler and polymer and the amount of water sorption. It has been postulated that the corresponding expansion associated with the uptake of water from oral fluids could relieve polymerization stresses. In the measurement of hygroscopic expansion starting 15 minutes after the initial polymerization, most resins required 7 days to reach equilibrium and about 4 days to show the majority of expansion. Because composites with fine particles have lower values of water sorption than composites with microfine particles, they exhibit less expansion when exposed to water [58, 60].

#### **13.3.5 Solubility**

The water solubility of composites varies from  $0.01$  to  $0.06$  mg/cm<sup>2</sup>. Adequate exposure to the light source is critical in light-cured composites. Inadequate polymerization can readily occur at a depth from the surface if insufficient light penetrates. Inadequately polymerized resin has greater water sorption and solubility, possibly manifested clinically with early color instability [61].

During the storage of microhybrid composites in water, the leaching of inorganic ions can be detected; such ions are associated with a breakdown in interfacial bonding. Silicon leaches into the water bath in the greatest quantity ( $15$  to  $17\mu\text{g/ml}$ ) during the first 30 days of storage and decreases with time of exposure. Microfilled composites leach silicon more slowly and show a 100% increase in amount during the second 30-day period ( $14.2\text{pg/ml}$ ). Boron, barium, strontium, and lead, which are present in glass fillers, are leached to various degrees ( $6$  to  $17\mu\text{g/ml}$ ) from the various resin-filler systems. Breakdown and leakage can be a contributing factor to the reduced resistance to wear and abrasion of composites [59, 63].

##### **13.3.5.1 Method of test**

Solubility and water sorption are measured according to ISO 4049. Composite is inserted into stainless steel mold, with 6mm diameter and 1mm thickness, between two glass slides.



The composite then cured on each side to form disk shape specimen. Five specimens are required for each test. After curing, the weight of the specimen ( $m_1$ ) was measured. Then, the disc is immersed in distilled water for a week at room temperature so that unreacted monomers would be eliminated.

After that, the specimen is removed, dried and stored in an oven at 37°C until a constant mass ( $m_2$ ) had been achieved. The solubility is determined from the following equation [61]:

$$SL\% = ((m_1 - m_2) / m_2) \times 100 \quad (4)$$

The specimen is dipped again in distilled water at room temperature so that the water sorption could be measured and after different time periods, it is removed and blotted dry according to the ISO 4049 standard to remove excess water and is then weighed. Its weight is recorded until there is no significant change in weight.

The value of water sorption is calculated for each specimen from the following equation [61]:

$$WS_t\% = ((m_t - m_2) / m_2) \times 100 \quad (5)$$

Where,  $WS_t$  denotes water sorption at time  $t$ ,  $m_t$  weight at time  $t$  and  $m_2$  initial weight.

Meanwhile, there is another method for calculation of SL and WS. The diameter and the thickness of the specimen is measured at five points and the volume ( $V$ ) is calculated in cubic millimeters. The values of solubility and water sorption are obtained for each disc using the following formulae [61]:

$$SL = (m_1 - m_2) / V \quad (6)$$

$$WS_t = (m_t - m_2) / V \quad (7)$$

### 13.3.6 Color and color stability

The color and blending of shades for the clinical match of esthetic restorations are important. Universal shades vary in color among currently marketed products.

Change of color and loss of shade-match with surrounding tooth structure are reasons for replacing restorations. Stress cracks within the polymer matrix and partial debonding of the filler to the resin as a result of hydrolysis tend to increase opacity and alter appearance. Discoloration can also occur by oxidation and result from water exchange within the polymer matrix and its interaction with unreacted polymer sites and unused initiator or accelerator [55].

Color stability of current composites has been studied by artificial aging in a weathering chamber (exposure to UV light and elevated temperatures of 70 °C) and by immersion in various stains (coffee/tea, cranberry/grape juice, red wine, sesame oil). Composites are resistant to color changes caused by oxidation but are susceptible to staining [59].

### 13.3.7 Radiopacity

Modern composites include glasses having atoms with high atomic numbers, such as barium, strontium, and zirconium. Some fillers, such as quartz, lithium-aluminum glasses, and silica, are not radiopaque and must be blended with other fillers to produce a radiopaque composite. Even at their highest volume fraction of filler, the amount of

radiopacity seen in composites is noticeably less than that exhibited by a metallic restorative like amalgam. The microhybrid composites achieve some radiopacity by incorporating very finely divided heavy metal glass particles [63].

Aluminum is used as a standard reference for radiopacity. A 2-mm thickness of dentin is equivalent in radiopacity to 2.5 mm of aluminum, and enamel is equivalent to 4 mm of aluminum. To be effective, a composite should exceed the radiopacity of enamel, but international standards accept radiopacity equivalent to 2 mm of aluminum.

Amalgam has a radiopacity greater than 10 mm of aluminum, which exceeds all the composite materials available [61].

### 13.3.8 Wear rates

Clinical studies have shown that composites are superior materials for anterior restorations in which esthetics is essential and occlusal forces are low. One problem with composites is the loss of surface contour of composite restorations in the mouth, which results from a combination of abrasive wear from chewing and toothbrushing and erosive wear from degradation of the composite in the oral environment [39, 57].

Wear of posterior composite restorations is observed at the contact area where stresses are the highest. Interproximal wear has also been observed. Ditching at the margins within the composite is observed for posterior composites, probably resulting from inadequate bonding and polymerization stresses. Currently accepted composites for posterior applications require clinical studies that demonstrate, over a 5-year period, a loss of surface contour less than 250 pm or an average of 50 pm per year of clinical service. Products developed as packable or laboratory composites usually have better wear resistance than microfilled or flowable composites [28, 34].

### 13.3.9 Biocompatibility

Nearly all of the major components of composites (Bis-GMA, TEGDMA, and UDMA, among others) have been found cytotoxic *in vitro* if used in pure form, but the biological liability of a cured composite depends on the release of these components from the composite. Although composites release some levels of components for weeks after curing, there is considerable controversy about the biological effects of these components. The amount of release depends on the type of composite and the method and efficiency of the cure of the composite. A dentin barrier markedly reduces the ability of components to reach pulpal tissues, but these components can traverse dentin barriers, albeit at reduced concentrations. The effects of low-dose, long-term exposures of cells to resin components are not generally known. On the other hand, the use of composite materials as direct pulp-capping agents poses a higher risk for adverse biological responses, because no dentin barrier exists to limit exposure of the pulp to the released components. The effects of released components from composites on oral or other tissues is not known with certainty, although no studies have documented any adverse biological effects. The tissue at highest risk from this type of release would appear to be gingiva in close, long-term contact with composites [1, 8, 43].

Components of composites are known allergens, and there has been some documentation of contact allergy to composites. Most of these reactions occur with dentists or dental personnel who regularly handle uncured composite and, therefore, have the greatest exposure. There are no good studies documenting the frequency of allergy to composites in the general population [61].

Finally, there has been some controversy about the ability of components of composites to act as xenoestrogens. Studies have proven that Bis-phenol A and its dimethacrylate are estrogenic in vitro tests that measure this effect using breast cancer cell growth. Trace levels of these components have been identified in some commercial composites; however, estrogenicity from cured commercial composites has not been demonstrated. Furthermore, there is considerable controversy about the accuracy and utility of in vitro tests using breast cancer cells to measure a true estrogenic effect. An early study in this area, which claimed that dental sealants and composites were estrogenic in children, has since been largely discredited [53, 58].

## **14. Composites for special applications**

### **14.1 Microfilled composites**

These composites are recommended for use in Class 3 and Class 5 restorations, where a high polish and esthetics are most important. One product has been used successfully in posterior restorations. They are composed of light-activated, dimethacrylate resins with 0.04- $\mu\text{m}$  colloidal silica fillers with a filler loading of 32-50% by volume. Because they are less highly filled, microfilled composites have higher values of polymerization shrinkage, water sorption and thermal expansion as compared with microhybrid composites [56].

### **14.2 Packable composites**

These composites are recommended for use in Classes 1, 2, and 6 (MOD) cavity preparations. They are composed of light-activated, dimethacrylate resins with fillers (fibers or porous or irregular particles) that have filler loading of 66% to 70% by volume. The interaction of the filler particles and modifications of the resin cause these composites to be packable [63].

Important properties of packable composites include high depth of cure, low polymerization shrinkage, radiopacity, and low wear rate (3.5 pm/year), which is similar to that of amalgam. Several packable composites are packaged in unit-dose compules. A bulk-fill technique is recommended by manufacturers but has not yet been demonstrated effective in clinical studies. Use singlebottle bonding agents with these composites [28].

### **14.3 Flowable composites**

These light-cured, low-viscosity composites are recommended for cervical lesions, pediatric restorations, and other small, low stress-bearing restorations. They contain dimethacrylate resin and inorganic fillers with a particle size of 0.7 to 3.0  $\mu\text{m}$  and filler loading of 42% to 53% by volume. Flowable composites have a low modulus of elasticity, which may make them useful in cervical abfraction areas. Because of their lower filler content, they exhibit higher polymerization shrinkage and lower wear resistance than microhybrid composites. The viscosity of these composites allows them to be dispensed by a syringe for easy handling [44, 51, 61].

### **14.4 Laboratory composites**

Crowns, inlays, veneers bonded to metal substructures, and metal-free bridges are prepared indirectly on dies from composites processed in the laboratory using various combinations of light, heat, pressure, and vacuum to increase the degree of polymerization and the wear resistance.

For increased strength and rigidity, laboratory composites can be combined with fiber reinforcement. Restorations are usually bonded with composite cements. Cavity preparations for indirect composites must be nonretentive rather than retentive, as typically prepared for direct placement [61].

#### **14.5 Core composites**

At times, so much tooth structure is lost from caries that the crown of the tooth must be built up to receive a crown. Amalgam is the most common core material, but composite is becoming popular. Composite core materials are typically two-paste, self-cured composites, although light-cured and dual-cured products are available. Core composites are usually tinted (blue, white, or opaque) to provide a contrasting color with the tooth structure. Some products release fluoride [63].

Composite cores have the following advantages as compared with amalgam: can be bonded to dentin, can be finished immediately, are easy to contour, have high rigidity, and have good color under ceramic restorations. Composite cores are bonded to remaining enamel and dentin using bonding agents. Be careful to use a bonding agent recommended by the manufacturer of the core material, because some self-cured composite core materials are incompatible with some light-cured bonding agents [64].

### **15. Summary**

It is fortunate that many types of dental nanomaterials are available as restorative materials. The requirements may vary for different patients, and the processing facilities can dictate which material to use.

There are also significant differences between dental materials. Amalgam is a highly successful material clinically and is very cost effective, but alternatives such as esthetic restorative materials are now very competitive in terms of frequency of use. The ultimate goal of advanced dental nanomaterials research is to produce a material that can be used in all circumstances as an amalgam replacement material.

As a result, contemporary dentists have many options available for consideration when choosing a dental material. The choice of the composite or cement, whether old or new, should depend on the particular clinical situation and specific criteria. While improved physical properties or in vitro adhesion strengths may be considered advantageous, they have not automatically resulted in improved clinical performance. Ease of manipulation and handling, the materials clean-up and minimal technique sensitivity are important factors in ensuring clinical success. These factors -coupled with results of favorable long-term clinical studies including absence of post-operative sensitivity, long-term retention of the prosthodontic device and marginal integrity- should be the deciding factors that clinicians take into consideration while selecting the materials for a particular procedure.

Dental materials such as composites and cements are used to replace missing tooth structure and modify the color and contour of the teeth in order to enhance esthetics and nano particles are used in the dental materials to give excellent physical and mechanical properties due to high strength, hardness and toughness of this component.

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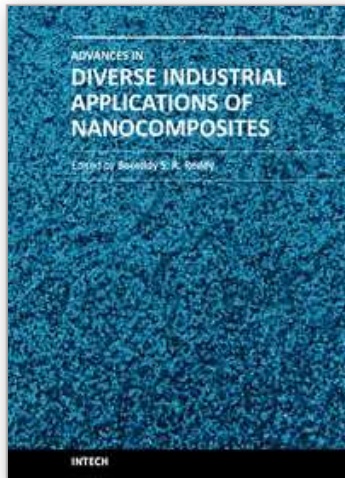
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## **Advances in Diverse Industrial Applications of Nanocomposites**

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Nanocomposites are attractive to researchers both from practical and theoretical point of view because of combination of special properties. Many efforts have been made in the last two decades using novel nanotechnology and nanoscience knowledge in order to get nanomaterials with determined functionality. This book focuses on polymer nanocomposites and their possible divergent applications. There has been enormous interest in the commercialization of nanocomposites for a variety of applications, and a number of these applications can already be found in industry. This book comprehensively deals with the divergent applications of nanocomposites comprising of 22 chapters.

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