# Filling Materials for the Caries

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## 1. Introduction

Caries is a dynamic process in which mineral is removed during times of high acid production by bacterial plaque (demineralization) and replaced during periods of neutral pH (remineralization). Remineralization is the process by which mineral is deposited into tooth structure from salivary calcium and phosphate during periods of neutral pH. The remineralization process is facilitated by fluoride and can arrest carious demineralization by the formation of a hard outer surface [16].

Dentinal caries is similar to enamel caries, except that dentin demineralization begins at a higher pH (6.4 compared to 5.5) and proceeds about twice as rapidly since dentin has only half the mineral content. Low fluoride levels are insufficient to initiate dentin remineralization but are adequate to facilitate enamel remineralization. In enamel, at fluoride levels around 3 parts per million (ppm), the balance of mineral uptake and loss is shifted from net demineralization to net remineralization. Because dentin composes most root structure and because root surface caries lesions require significantly greater amounts of fluoride than enamel caries lesions to promote remineralization, restorative materials that release fluoride are often recommended for root surfaces [1]. Root caries appears as a softening and/or cavitation in the root surface with no initial involvement of the adjacent enamel. These lesions generally begin at or slightly occlusal to the free gingival margin but can extend into the gingival sulcus and/or undermine the coronal enamel as the caries progresses. Lesions also begin at the margins of restorations that have their cervical interfaces on root structure [19].

Traditional caries management has consisted of the detection of carious lesions followed by immediate restoration. In other words, caries was managed primarily by restorative dentistry. However, when the dentist takes the bur in hand, an irreversible process begins. Placing a restoration does not guarantee a sound future for the tooth; on the contrary, it may be the start of a restorative cycle in which the restoration will be replaced several times. The decision to initiate invasive treatment should be preceded by a number of questions: Is caries present and if so, how far does it extend? I a restoration required, or could the process be arrested by preventive treatment? Sometimes the decision to restore may be based on questionable diagnostic criteria.

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A different treatment strategy is recommended, based on a proper diagnosis of caries, taking into account the dynamics of the caries process. The activity of caries should be determined, and causative factors should be evaluated. Caries risk should be assessed before treatment is considered, and treatment should include preventive regimens to arrest the caries process by redressing the imbalance between demineralization and remineralization.

The treatment goal in caries management should be to prevent new lesions from forming and to detect lesions sufficiently early in the process so that they can be treated and arrested by nonoperative means. Such management requires skill and is time-consuming and worthy of appropriate payment. If these attempts have failed, high-quality restorative dentistry will be required to restore the integrity of the tooth surface [81].

The first popular fluoride-releasing tooth-colored restorative material was silicate cement. Although this material had no bonding properties and did not survive well in the oral environment, recurrent caries lesions associated with silicate cement restorations were rare. This anticaries effect was eventually associated with fluoride-releasing materials have the goal of inhibiting recurrent caries, especially in patients at high risk for developing new lesions.

Fluoride-releasing materials may be classified into four categories (1. Resin composites, 2. Compomers, 3. Resin-modified glass ionomers, and 4. Conventional glass ionomers based on similarities in physical, mechanical, and setting properties. Fluoride-releasing resin composites are on one end of the continuum and conventional glass ionomers on the other. Compomers appear near the resin composite end, and resin-modified glass ionomers are positioned nearer to the conventional glass ionomers [16].

The introduction of adhesive restorative materials has allowed dentists to make smaller preparations, which has led to preservation of hard dental tissues and, along with declining disease prevalence, has allowed elimination of G.V. Black's principle of "extension for prevention." Maximum tooth structure is preserved. However, this approach, sometimes described as a "dynamic treatment concept," cannot prevent repeated treatment procedures and the occurrence of iatrogenic damage [3]. Resin composites have better mechanical properties, no inherent adhesive properties, greater thermal expansion coefficients, and better wear resistance compared with other materials in the continuum, but they have the least fluoride release. Glass ionomers have inherent adhesive properties, release comparatively high amounts of fluoride, and have thermal expansion coefficients similar to tooth structure, but their mechanical properties and wear resistance are poor. Resin-modified glass ionomers contain elements of glass ionomers and light-cured resins. These materials have properties similar to glass ionomers and, like glass ionomers, should not be used for restorations in occlusal load-bearing areas. Although compomers are blends of resin composite and glass ionomer, they incorporate more resin than resin modified glass ionomers, and their physical and mechanical properties are more closely related to fluoride-releasing resin composites. Compomers require a bonding system and acid etching of tooth structure to achieve a clinically usable bond. They release more fluoride than resin composites but less than glass ionomers and are more abrasion resistant than conventional or resin-modified glass ionomers.

The early glass-ionomer restorative materials, called glass-ionomer cements, were rough, had less than optimum esthetic qualities, and had to be protected from hydration and

dehydration with a varnish or light-cured resin, applied to the surface immediately after placement. Finishing was delayed for 24 hours with the earlier materials; this delay was later shortened, through modification of the material, to 7 minutes. The unmodified glass-ionomer materials are rarely used today [16].

Several mechanisms have been suggested for the anticaries effects of fluoride. These include the formation of fluorapatite, which is more acid resistant than hytdroxyapatite, the enhancement of remineralization, interference of ionic bonding during pellicle and plaque formation, and the inhibition of microbial growth and metabolism. Fluoride relased from restorative materials can inhibit caries through all these mechanisms, although it seems likely that enhancement of remineralization is the most important mechanism in the adult. Although the recurrent caries inhibition effects of fluoride-releasing materials are evident, their clinical effectiveness has been questioned based on the durability of the material. Even in primary teeth, these materials should be used selectively, and the time that the material will be expected to survive (how long the tooth will remain in the oral cavity) should be evaluated against its wear effectiveness [52].

For treating carious lesions, especially in the patient with high caries risk, resin-modified glass ionomers and fluoride-releasing resin composites have the greatest potential for success. Resin-modified glass ionomers are recommended as the esthetic restorative materials of choice in the Class 5 situation for patients with high caries risk, especially those with diminished salivary flow, due to their high fluoride release and fluoride recharge capability [16].

As materials continue to proliferate, it becomes increasingly difficult to choose the appropriate material for a particular clinical situation. Fluoride-releasing materials are no exception, and clinicians need guidelines to select and use these materials. There is modest but growing evidence from clinical trials that fluoride-releasing materials, especially glass ionomers, reduce the occurrence of recurrent caries. There is also evidence of a dose-response relationship between fluoride release and decreasing caries. While higher fluoride-releasing materials have greater caries protecting effects, these materials are not panaceas. The physical limitations of glass ionomers and compomers and their poor wear resistance contribute markedly to restoration failure. Evidence suggests that resin-modified glass-ionomer materials may provide an improved combination of physical integrity and caries inhibition [16].

The surfaces are important because all restorative dental materials meet and interact with tooth structure at a surface. Also, all dental surfaces interact with intraoral constituents such as saliva and bacteria. Changing a material's surface properties can mitigate the extent of that interaction. The type of interaction between two materials at an interface is defined as the energy of interaction, and this is conveniently measured for a liquid interacting with a solid under a standard set of conditions as the contact angle ($\theta$). The contact angle is the angle a drop of liquid makes with the surface on which it rests (Fig. 1A). This angle is the result of an equilibrium between the surface tensions of the liquid-gas interface ($\Upsilon_{LG}$), solid-gas interface ($\Upsilon_{SG}$), and solid liquid interface ($\Upsilon_{SL}$). These relationships can be expressed as an equation, as shown in fig. 1A. If the energy difference of the two materials in contact is large, then they will have a large contact angle. If the energy difference is very small, then the contact angle will be low and the liquid will

appear to wet the solid by spreading. Wetting is a qualitative description of the contact angle. Good wetting, or spreading, represents a low contact angle. Partial (poor) wetting describes a contact angle approaching 90 degrees. Non wetting is a contact angle approaching 180 degrees (see fig. 1B).
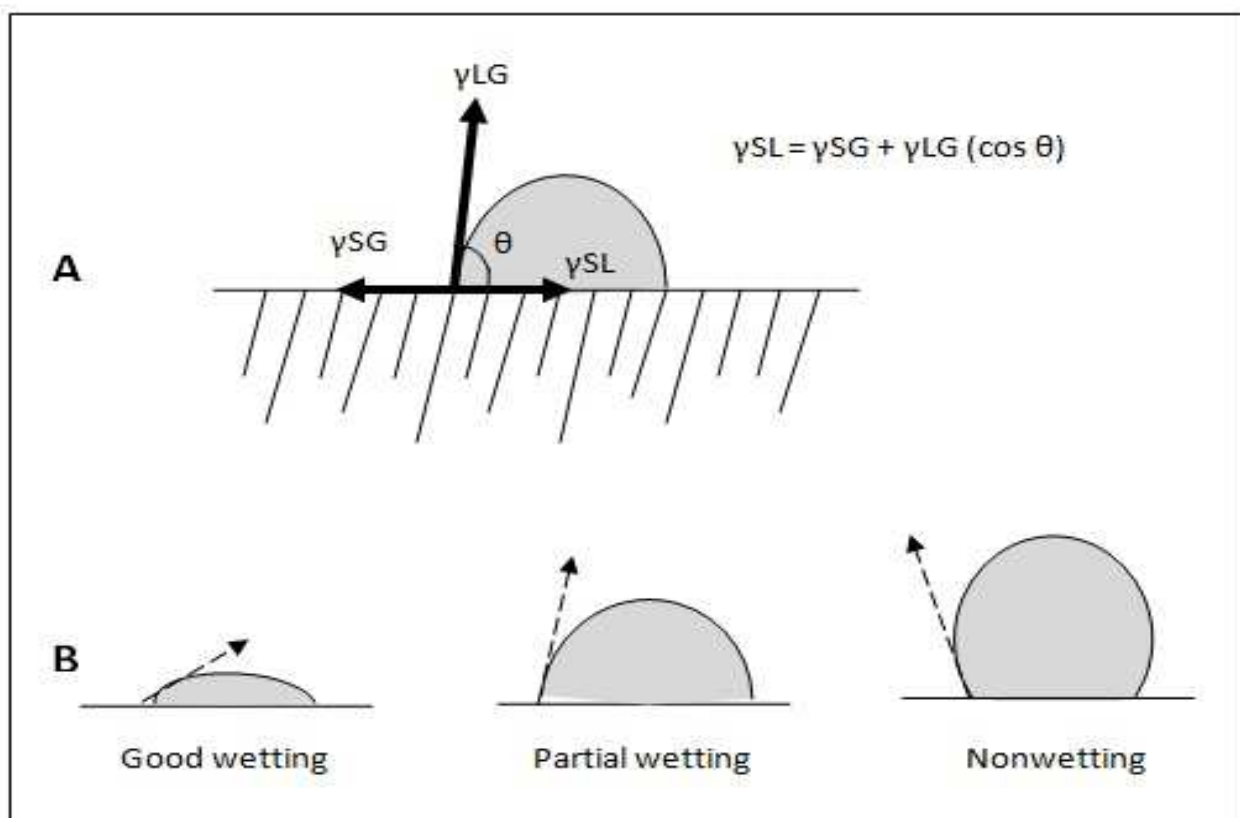


Fig. 1. Interfacial interactions of materials. A) Interaction quantified as contact angle (see formula). B) Interaction described in terms of good wetting (spreading), partial (poor) wetting, or nonwetting.

It is very important that film formers such as varnishes, liners, cements, and bonding agents have good wetting on tooth preparation surfaces on which these materials may be placed, so that they adapt to the microscopic interstices of the surfaces. However, in other instances, poor wetting may be an advantage. For example, experimental posterior composites have been formulated to have high contact angles to retard water and/or bacterial interactions. In most cases, wetting can be anticipated on the basis of the hydrophilicity (water-loving) or hydrophobicity (water-hating) of materials. Hydrophilic surfaces are not wet well by hydrophobic liquids [7].

Teeth also can be restored using indirect restorations are fabricated outside of the mouth. Most indirect restorations are made on a replica of the prepared tooth in a dental laboratory by a trained technician. Tooth-colored indirect systems include laboratory-processed composites or ceramics such as porcelain fired on refractory dies or hot pressed glasses. In addition, at least one chairside computer-aided design/computer-assisted manufacturing (CAD/CAM) system is currently available and is used to fabricate ceramic restorations [73].

This chapter reviews the glass-ionomer cements, compomers, and direct composite restorative materials (also dentin bonding agents) and their composition, classification, and clinical application and performance after removing caries.

## 2. Glass-ionomer cements

The original glass-ionomer cements (GICs), which are governed ISO 9917.1-2007 are water-based materials which set by an acid-base reaction between a polyalkenoic acid and a fluroaluminosilicate glass [86] and have been one of the most widely researched dental materials since their introduction in the 1970s. Since these were brittle materials, attempts were made to enhance the physical properties by the addition of either metal particles (silver or gold), by a fusion process resulting in a 'cermet' (ceramic-metal), or amalgam alloy particles by a simple addition ('admix'). An important characteristic of glass-ionomer is its ability to bond to tooth structure, one mechanism being that of a hydrogen bond between the carboxyl group of the polyacid and the camcium in the tooth structure. It has also been shown that there is a micromechanical penetration of the GI into the tooth. They have a coefficient of thermal expansion similar to the tooth, which may help reduce microleakage and therefore postoperative sensitivity and can be bulk-filled and finished faster than a composite. The newer generations of glass ionomer materials are faster setting and no longer sensitive to hydration or desiccation during setting. One main advantage of glass ionomer materials is their chemical bonding ability to tooth structure, making them more resistant to leaks. Compared with resin system bonding, glass ionomer bonding is more degeneration-resistant and does not breakup, unlike the hydrolytic degradation of the hybrid layer of the resin system. Further modification of water-based ('conventional') GICs took place in the early 1990s by the addition of water-soluble resin, to produce the 'resin-modified' GICs. The purpose of adding resin was to enhance the physical properties and to reduce the sensivity to water balance of the conventional GICs. The first of the 'resin-modified' GICs (RM-GICs) was Virtabond (3M Dental Products, St Paul, Minnesota, USA), now called Vitrebond (3M/Espe Dental). Other names for RM-GIC which have been used include 'resin-ionomers', 'resinomers', 'hybrid ionomers' and 'light-cured glass ionomers' [17, 79, 80, 84].

### 2.1 Setting reactions

After mixing powder and liquid, the acid etches the gllas which reslts in a release of calcium, aluminium, sodium and fluoride ions into solution. This is an acid-base reaction where the water serves as the medium for the reaction. The metal ions react with the carboxyl (COO) groups to form a polyacid salt, which becomes the cement matrix, and the surface of the glass becomes a silica hydrogel. The unreacted cores of the glass particles remain as a filler [79, 84].

Although the clinical set is completed within a few minutes, a continuing 'maturation' phase occurs over subsequent months. This is predominantly due to the slow reaction of the aluminium ions [45] and is the cause of the set material's sensitivity to water balance. The set material needs to be protected from salivary contamination for several hours, otherwise the surface becomes weak and opaque, and from water loss for several months, otherwise the material shrinks and cracks and may debond [45, 79].

The RM-GICs also undergo an acid:base reaction (which is a pre-requisite for any material to be described as a glass-ionomer cement). However, there is an additional resin polymerization phase. Depending on the product, the resin polymerization may be self-cure, light-cure or both. On mixing powder and liquid, the acid:base reaction, and if present, the self-cure resin polymerization reaction, begin and setting commences. Restorative RM-GICs (in contrast to luting RM-GICs) undergo photopolymerization on exposure to light, resulting in clinical set. However, the acid:base reaction continues, albeit much more slowly. Although the set material can be contoured and polished under water spray immediately following polymerization, delayed polishing has been recommended [88]. However, dehydration remains a potential problem. All GICs show an increase in translucency at seven days compared to that at placement, resulting in an aesthetic improvement [45, 79].

## 2.2 Classification

The most practical classification of the GICs is on their clinical usage [45, 87]. Type I GICs are the luting cements, characterized by low film thickness and rapid set; when available as an RM-GIC, the photopolymerization reaction will be absent. Type II GICs are restorative cements, with sub-types 1 and 2. Type II-1 GICs are aesthetic cements (available in both conventional and resin-modified presentations) and Type II-2 GICs are 'reinforced' (however, despite their description, are not necessarily stronger than Type II-1 products). However, they are more wear-resistant. Type III GICs are the lining cements and fissure sealants, characterized by low viscosity and rapid set.

In the mid- to late-1990s, high powder:liquid ratio conventional GICs were introduced, alternatively termed 'packable' or 'high viscosity' GICs [62]. These products (e.g., Ketac Molar, 3M/Espe, Seefeld, Bavaria, Germany; Chemflex, Dentsply, York, Pennsylvania, USA; Fuji IX and Fuji IX GP, GC International) are promoted principally for small cavities in deciduous teeth, temporary restorations, liner/base applications, and in the 'Atraumatic Restorative Treatment' (ART) technique [26, 79]. The most recently accepted uses of GICs have been as a liner and base under deep composite restorations, which was described in 1984 [38] and has been referred to as the *sandwich technique*, Deep cervical lesions and proximal boxes of class II cavities whose gingival floor is on root surfaces are areas where there is increased diameter of dentinal tubules that will affect the bond strength because of increased chances of hydrolytic degradation (The 'open sandwich' technique, also known as the 'cervical lining'). Because of their chemical bonding capabilities, glass ionomer adhere to these surface better then dental adhesive-bonding agents. Based on evidence-based dentistry protocols, the recommendation is to treat the surfaces with a polyacrylic acid conditioner, which is rinsed before glass ionomers are applied. This weak acid modifies the smear layer by leaving the smear plugs behind, improving the seal and eliminating postoperative sensitivity. A new self-conditioner for resin-modified glass ionomers, recently developed by Fuji (GC America, IL, USA), does not require rinsing before applying the glass ionomer material [9]. Both Fuji II and Fuji IX (GC America, IL, USA) have unique automix dispensing capsules, simplifying placement of these materials. Resin-modified ionomers, such as Fuji II LC, are routinely used as liners at 1 mm or less, and a material such as Fuji IX or Riva (SDI, Bensenville, IL, USA) is preferred for larger areas of dentin replacement.

Based on abundant evidence, conventional and metal-modified glass ionomers are not recommended in class 2 restorations in both primary and permanent molars. To compensate

for this, RM-GICs were developed to produce better mechanical properties than the conventional ones. The resin hydroxyethyl methacrylate (HEMA) or bis-glycerol methacrylate was added to the liquid. The resin modification of these cements allowed the base curing reaction to be supplemented by a light or chemical curing process, allowing for a command set. The obvious advantages were better fracture toughness, increased tensile strength, and a decrease in desiccation and hydration problems [20]. The limiting factors were the setting shrinkage, which was found to be greater than with conventional cements, and the limited depth of cure with more opaque lining cements [5]. The mean age of these failed glass ionomer restorations at replacement in permanent teeth in general practice was found to be 5.5 years for patients older than 30 years [43]. Secondary caries, bulk fracture (1.4%–14%), and marginal fracture (from poor anatomic form) constituted the main reasons for failure. In developing countries, highly viscous glass ionomer materials have became popular in atraumatic restorative treatment techniques for class 1 restorations in posterior teeth. In class 2 restorations, these high viscous glass ionomers are still considered satisfactory after 3 years of clinical service, despite large percentages of failed restorations. However, a recently concluded retrospective study showed that the failure of class 2 restorations with these materials rose to 60% at 72 months. It was hypothesized that caries-like loss of material was seen on radiographs and that the presence of proximal contacts promoted disintegration of these materials [66, 80].

## 2.3 Bonding mechanism

The bonding mechanism of the GICs to dental hard tissues is very complex, and may be different for RM-GICs compared to conventional GICs. Simplistically, an ionic bond occurs between the carboxyl ($COO^-$) ions in the cement acid and the calcium ($Ca^{++}$) ions in enamel and dentine.

When freshly mixed conventional GIC is placed on enamel or dentine, dissolution of any smear layer occurs but demineralization is minimal since the tooth hydroxyapatite buffers the acid, and polyalkenoic is quite weak [83]. Phosphate ions (negatively charged) and calcium ions (positively charged) are displaced from the hydroxyapatite, and are absorbed into the unset cement. This results in an intermediate layer between the 'pure' GIC and the 'pure' hydroxyapatite; the so called 'ion-exchange' layer [45]. Problems of specimen preparation of a water-based material have hindered investigation of this layer, although better techniques are now becoming available [49].

The ion-exchange layer appears to consist of calcium and phosphate ions from the GIC, and aluminium, silicic, fluoride and calcium and/or strontium ions (depending on glass composition) from the GIC [67]. The thickness of the ion-exchange layer appears to be in the order of a few micrometres, and merges into the GIC on one side and into the enamel/dentine on the other. Unfortunately there is some confusion in the literature [24, 31, 49, 76] regarding the ion-exchange layer. Other terms have been proposed such as 'zone of interaction', 'interdiffusion zone', 'hybrid layer', 'interphase', and 'intermediate layer'. In particular, the notation 'hybrid layer' causes confusion with the 'hybrid layer' formed between resin composite and dentine (see below). The term 'ion-exchange layer' should be used, since it accurately describes its nature. It has been shown that this layer is resistant to acid and base treatment, and has thus also been referred to as the 'acid-base resistant layer' [79].

Measurement of the bond strength of GIC to enamel and dentine is complicated by the brittle nature of the GIC. Laboratory bond strength tests invariably result in cohesive failure of the GIC, rather than failure within the ion exchange layer. Consequently, the true strength of the ion-exchange layer is not known; values in the range 3-10 MPa are commonly reported, i.e., approximately the cohesive strength of GIC [76, 79].

## 2.4 Fluoride release

The release of fluoride ions is one of the notable characteristics of GICs. It is present originally as a flux in the manufacture of the glass, and is released from the glass particles on mixing with the polyalkenoic acid. The presence of fluoride also has benefits in increasing translucency and strength and improving handling properties [29]. The mechanism of release is complex and not fully understood. However, it is maximum in the first few days and decreases rapidly to a lower level over weeks, and maintains a low level over months. It has also been shown that GIC can be 'recharged' with fluoride, resulting in a subsequent short-term boost in release. Most of the fluoride is released as sodium fluoride, which is not critical to the cement matrix, and thus does not result in weakening or disintegration of the set cement. Resin-modified GICs show similar dynamics of fluoride release, although for both types of material the dynamics of release and the amounts released depend on the particular material and the experimental design [79, 89].

## 2.5 Biological properties

Several metallic ions are released from GIC, as well as fluoride. The highest release occurs from the unset material, and as described above, most research has been done on fluoride. Hydroxethylmethacrylate (HEMA) is released from RM-GICs and can diffuse through dentine in laboratory studies. Since HEMA can induce allergic and toxic responses, the clinical relevance of its release requires more investigation [70]. Nevertheless, to date there is no evidence that HEMA in dental materials is responsible for any local or systematic adverse effects.

Glass-ionomer cement has been shown to have an antimicrobial effect in several studies, and greater than that shown by other materials such as amalgam and resin composite. However, again it is difficult to do more than generalize, as the results depend on the experimental method, the bacteria used and the product tested [70]. There are several theories regarding the antibacterial activity. Most workers propose that fluoride is responsible, possibly acting synergistically with pH. However, other released agents have been cited as possible antibacterials, including zinc [77] and polyalkenoic acid [68], acting alone or synergistically with pH and fluoride [79].

## 2.6 Clinical performance

One of the principal benefits of GICs is their adhesion to the dental hard tissues, and this has been confirmed in non-undercut non-carious cervical lesions (NCCLs) where dentine is the main substrate. However, because of the low fracture toughness of GICs (including RM-GICs), they are recommended principally for non-stress-bearing areas, e.g., carious and non-carious cervical lesions and approximal anterior lesions. Nevertheless, the high powder:liquid ratio materials may be useful in the restoration of small cavities in deciduous

teeth. Clinical studies on RM-GICs are less extensive because of their more recent introduction [6, 13]. However, the results are mixed with respect to both brand comparisons and comparisons with polyacid-modified resin composites. One presentation of an RM-GIC is in a low powder:liquid ratio form (Fuji Bond LC; GC International), and is used in a similar way to a dentine bonding agent. Excellent five-year results have been obtained for the retention by this material of resin composite in non-carious cervical lesions [78].

Evidence is accumulating that GIC may have an important role in minimum intervention dentistry. Modern concepts of operative dentistry propose that only the 'infected' dentine should be removed, leaving the 'affected' dentine which has the potential to remineralize. Recent evidence suggests that such remineralization may be potentiated by GIC [3], and this has special relevance in the ART technique [79].

## 3. Compomers (Polyacid-modified resin composites)

Polyacid-modified composite resins, known trivially as compomers, are a group of aesthetic materials for the restoration of teeth damaged by dental caries. They were introduced to the profession in the early 1990s [40], and were presented as a new class of dental material designed to combine the aesthetics of traditional composite resins with the fluoride release and adhesion of glass-ionomer cements. The trivial name was devised from the names of these two "parent" materials, the "comp" coming from composite, and "omer" from ionomer [60]. The term *polyacid-modified composite resin* was originally proposed for these materials in 1994 [39] and has been widely adopted both by manufacturers and researchers since that time. However, it has been criticised on the grounds that it ". . .may over-emphasize a structural characteristic of no or little consequence" [60]. This is a somewhat strange criticism, since to formulate these materials, manufacturers have modified them specifically by the introduction of acid functional macro-monomers. They are, therefore, without question "polyacid modified". Whether this modification confers clinical benefits, or indeed whether these materials can usefully be considered to be distinctive materials is more debateable. The conclusion of Ruse is that ". . . They are, after all, just another dental composite", but this seems to the present author to be somewhat extreme, and there is considerable evidence that compomers possess characteristic properties, and are therefore distinct from conventional composite resins [50, 55, 60, 85].

### 3.1 Composition and setting

As has already been stated, compomers resemble traditional composite resins in that their setting reaction is an addition polymerization. It is usually light-initiated, and the initiator is camphorquinone with amine accelerator, and as such is sensitive to blue light at 470 nm [40]. There is, however, at least one brand, designed for use as luting cement, Dyract Cem, that is a two-paste system. Cure is brought about as a result of mixing the two pastes, each of which contains a component of the free radical initiator system. The set material, though, does not differ in any fundamental way from those compomers that cure photochemically.

A key feature of compomers is that they contain no water and the majority of components are the same as for composite resins. Typically these are bulky macro-monomers, such as bisglycidyl ether dimethacrylate (bisGMA) or its derivatives and/or urethane dimethacrylate, which are blended with viscosity-reducing diluents, such as triethylene

glycol dimethacrylate (TEGDMA). These polymer systems are filled with non-reactive inorganic powders, such as quartz or a silicate glass, for example $SrAlFSiO_4$. These powders are coated with a silane to promote bonding between the filler and the matrix in the set material. In addition, compomers contain additional monomers that differ from those in conventional composites, which contain acidic functional groups. The most widely used monomer of this type is so-called TCB, which is a di-ester of 2-hydroxyethyl methacrylate with butane tetracarboxylic acid [23]. This acid-functional monomer is very much a minor component and compomers also contain some reactive glass powder of the type used in glass-ionomer cements [25, 50].

Despite the presence of these additional components, compomers are similar to composite resins in that they are fundamentally hydrophobic, though less so than conventional composite resins. They set by a polymerization reaction, and only once set do the minority hydrophilic constituents draw in a limited amount of water to promote a secondary neutralization reaction [23]. They lack the ability to bond to tooth tissues, so require bespoke bonding agents of the type used with conventional composite resins, and their fluoride release levels are significantly lower than those of glass-ionomer cements. Such low levels of fluoride release have been shown to compromise the degree of protection afforded by these materials in *in vitro* experiments using an artificial caries medium [41].

### 3.2 Effect of water uptake

A distinctive feature of compomers is that, following the initial polymerization reaction, they take up small amounts of moisture *in situ*, and this triggers an acid–base reaction between the reactive glass filler and the acid groups of the functional monomer [51, 60]. Among other features, this process causes fluoride to be released from the glass filler to the matrix, from where it can readily be released into the mouth, and act as an anticariogenic agent [41]. Polymerization is associated with contraction and the development of measurable stresses, and it may be that the sorption of water plays some part in reducing these stresses *in vivo* [25, 50].

The role of the reactive glass in the water uptake process has been considered in one report [1]. A conventional composite resin formulation was used as the matrix phase, with filler being either an unreactive glass, Raysorb T-4000, or the ionomer glass G338, whose composition and properties have been described extensively in the literature. In each case, the glass was used both with and without a coating of silane coupling agent (Υ-methacryloxy propyl trimethoxysilane). The results show that silanation reduced the water uptakefor both of the glasses and also improved the strength. However, incorporating G338 rather than Raysorb T-4000 gave an inferior material since it took up more water and was of lower strength. Previous studies of water sorption by composite resins have shown that the water accumulates around the filler particles [69], so that one conclusion of the study is that G338 is more hydrophilic than Raysorb T-4000. This suggests that it provides part of the driving force for water uptake by compomers, and also that it is responsible for a decline in their overall mechanical properties relative to conventional composite resins.

Compomers are designed to absorb water, and are able to up of the order of 2–3.5% by mass of water on soaking. This water uptake has been shown to be accompanied by neutralization of the carboxylic acid groups, as shown by changes in bands at 1705 and 1555 cm−1. The

former band arises from the presence of carboxylic acid groups within the material, and gradually reduces in intensity on exposure to water. By contrast the latter band arises from the presence of carboxylate salts, and shows a corresponding increase in intensity with time. Neutralization has been shown to be controlled by rate of water diffusion and is therefore fairly slow. Although compomers are designed to take up water in order to promote a later neutralization, these processes have been shown to have an adverse effect on many of their mechanical properties [50].

### 3.3 Fluoride release

Compomers are designed to release fluoride in clinically beneficial amounts. Fluoride is present in the reactive glass filler, and becomes available for release following reaction of this glass with the acid functional groups, triggered by moisture uptake. In addition, commercial compomers contain fluoride compounds such as strontium fluoride or ytterbium fluoride, which are capable of releasing free fluoride ion under clinical conditions, and augment the relatively low level of release that occurs from the polysalt species that develops. Fluoride release occurs to enhanced extents in acidic conditions, and in lactate buffer has been shown to be diffusion-based [64].

The conventional way of determining fluoride release is to employ an ion-selective electrode, and to treat the sample solution with an equal volume of the decomplexing TISAB (total ionic strength adjustment buffer). This liberates fluoride from any potential complexes, and enables to full amount of fluoride to be determined [50].

The authors speculated that the complexation was caused by the elevated levels of aluminium released under acidic conditions. As an example, for Compoglass F, aluminium concentration rose from 4.68 ppm in water to 104ppm in lactic acid solution. Aluminium is known to form complexes of the type $AlF_2^+$ and $AlF^{2+}$ [2] and these have been widely assumed to occur, for example in glass-ionomer cements. However, an alternative suggestion has been made by Billington et al. [8], who have suggested that complexation as monofluorophosphate is also a possibility, and they note that phosphorus levels released by glass-ionomer cements are also typically elevated under acidic conditions. This is also possible for compomers, as their glass filler components are similar to those used in glass-ionomers, and they, too, show elevated phosphorus release under acidic conditions [25, 50].

### 3.4 Clinical performance

Right from the time they were first launched, compomers have shown acceptable clinical performance in a variety of clinical applications. However, wear characteristics of early materials were poor and there were concerns about their durability. Despite this, the early results were promising, and more recently, results with newer formulations have also been good.

Compomers are designed for the same sort of clinical applications as conventional composites. These include Class II and Class V cavities, as fissure sealants, and as bonding agents for the retention of orthodontic bands. Their fluoride release, however, is seen as a useful feature for use in paedodontics, and certain brands have been produced that are specifically aimed at children [25, 50].

Compomers have been widely used in Class V restorations. For example, the compomers Dyract AP, Compoglass F and F2000 were evaluated for use in this application over a 2-year period [37]. This study concluded that, after this time, all three materials showed an acceptable level of clinical performance.

Colour stability has been found to be somewhat of a problem with compomers in a few studies. This is not entirely surprising, given that they are designed to take up water, which is likely to alter appearance through a change in refractive index, and also to carry with it coloured chemical species (stains) from certain foodstuffs such as coffee and red wine. In a 3-year study of Class V restorations of Dyract, Demirci et al. [21] found that all Ryge criteria were good, except those relating to colour change, *i.e.* colour stability and marginal discoloration. In both of these there were significant changes [21].

Compomers have been used as fissure sealants [28], and a clinical study examined the teeth of children aged between 7 and 10 years sealed by the compomer Dyract Seal. Sealed teeth were examined post-operatively at 3, 6, 12 and 24 months, and were also evaluated by the Ryge criteria. In general Dyract Seal behaved as well as a conventional composite resin sealant, except on the criterion of marginal integrity, showing that this material was acceptable for its clinical application, at least of the 24 months period of the study [28].

Compomers have also been used for Class I [56] and Class II restorations. In the Class I study, they were used in composite laminate restorations, and were shown to perform as well as conventional composite resins [56]. In the Class II study, they were studied over 7 years in children aged between 3.6 and 14.9 years. Again performance was indistinguishable from that of conventional composite resins.

Lastly, compomers have been employed as cements for orthodontic bands and there have been a number of full studies of compomers in this application [34]. Results have been generally extremely good for compomers, except in the realms of taste, as determined by the patient, and in which compomers scored less well than glass-ionomers. Thus, compomers have been shown to have acceptable performance as materials for use in orthodontic band retention, though the final choice of cementing agent could be left to patients. If they found the taste of the compomer particularly objectionable, a resin-modified glass-ionomer could be used equally effectively instead [50].

Overall, the major conclusion from these clinical results is that compomers perform well, and are suited to their suggested uses in dental restoration. The reduction in strength due to water uptake does not seem to be important clinically and these materials are suited to use in vivo.

## 4. Dentine Bonding Agents (DBAs)

The concept of bonding a restorative material to the dentine surface is by no means a new idea. Even at the time of Buonocore using phosphoric acid to bond to enamel, the idea of bonding to dentine was considered. However, due to limitations of materials and knowledge of the structure and nature of dentine the dream remained just that until the late '70s. In fact Buonocore did try to introduce a dentine adhesive but was unsuccessful [15]. The earliest bonding agent which showed some success was introduced by Fusayama [27]. At the same time Bowen [12] in the USA started investigating new formulations of resins

that were more water tolerant as well as methods of treating the dentine with oxalates to gain adhesion. The concern of many clinicians at that time was the potential damage phosphoric acid was going to cause the dental pulp if dentine was etched [79]. The first work to investigate the mechanism of bonding to the dentine was by Nakabayashi [47]. His paper of 1982 has now become one of the classic papers to first identify a layer between the resin and dentine substrate referred to as 'hybrid' dentine, in that it was the organic components of the dentine that had been permeated by resin (Fig. 2). The term 'hybrid layer' has now become synonymous with bonding of resins to etched dentine. There has been a tremendous amount of research done on the hybrid layer, its structure, formation and how it can be improved. Without a hybrid layer a bond will not be formed to the dentine. Therefore, it is essential for some modification to be made to the dentine surface so a mechanical interlocking of resin around dentinal collagen can occur. This layer has also been referred to as the 'resin-dentine interdiffusion zone' [79].
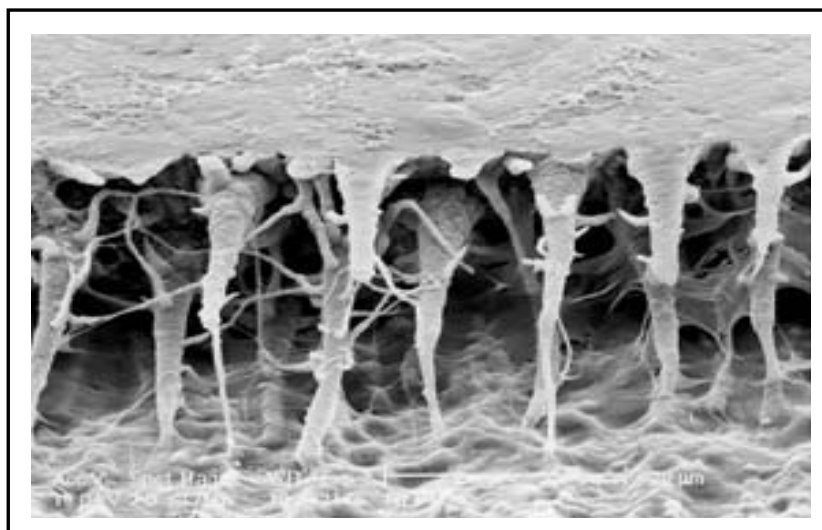


Fig. 2. Bonded specimen in which the dentine (mineral and protein) has been removed. The infiltration of resin into the acid-etched dentine can be seen with an associated permeation of resin throughout the dentine tubular network and its lateral branches.

### 4.1 Classification

Dentine bonding agents have gone through many changes over the last 10 years. This has led some people to refer to the changes as 'generations' of material, implying that there has been some chronological development. This is a falsehood – for example, the first 'self-etching' type material was introduced by Coltène (Altstätatten, Switzerland) as 'ART Bond'. Therefore, it is more logical to classify materials by the number of steps needed to complete the bonding process.

### 4.1.1 'Three-step' or 'Conventional' systems

This group represents those materials that have separate etching, priming and adhesive steps. It just so happens that this group of materials is also the oldest. However, they are still widely used and have been shown to provide reliable bonding. The greatest problem with this group would seem to be that three distinct steps are needed, which gives rise to possible

problems through contamination of the bonded surface prior to placement of the resin composite filling material; in other words, they are more technique sensitive [47, 79].

### 4.1.2 'Two-step' systems

This group has two subgroups; the first includes those systems that have a separate etch and have combined the priming and bonding steps. These systems are often referred to as 'Single-bottle' systems. In general, the problems experienced with the Conventional Systems still exist with the Single-bottle systems. Although one step has been eliminated, the great problem is ensuring good infiltration of the priming-bond into the demineralized dentine. The other subgroups combine the etching and priming steps together and are referred to as 'Self-etching primers'. These systems also have not been without their problems. The major concern has been their ability to etch the enamel to a great enough extent to ensure a good seal. This seems to be overcome now [42]. The problem of technique sensitivity also seems to have been significantly reduced with these systems compared with the Conventional and Single-bottle systems. This is attributed to the fact that the self-etching priming agent does not have to be washed off the dentine, therefore eliminating the need to maintain the dentine in a moist state. The method of demineralization of these materials is by the use of an acidic resin that etches and infiltrates the dentine simultaneously. The dentine is an excellent buffer, so the acidity of the self-etching primer is rapidly reduced and after polymerization is neutralized [32].

### 4.1.3 'One-bottle' or 'All-in-one' systems

This fourth group is the simplest of all the DBAs. They combine all steps into one process. Their mode of demineralization is identical to that of the self-etching priming materials, but the bonding resin is also incorporated. These systems also have the problem of not etching the enamel as effectively as phosphoric acid. In addition these systems are the newest and have no long-term clinical data to demonstrate their effectiveness, although early studies are showing some variability in the success of these materials [14].

### 4.2 Bonding mechanism

As already mentioned, the mechanism of bonding of resin-based DBAs is via a hybrid layer. This is a micromechanical interlocking of resin around dentinal collagen fibrils that have been exposed by demineralization. The interlocking occurs by the diffusion of the resins in the primer and bonding resin. The formation and structure of the hybrid layer has been extensively studied, and has also been referred to as the resin-impregnated layer, the resin-dentine interdiffusion zone. The thickness of the hybrid layer ranges from less than 1μm for the all-in-one systems to up to 5μm for the conventional systems. The strength of the bond is not dependent on the thickness of the hybrid layer, as the self-etching priming materials have shown bond strengths greater than many other systems but exhibit a thin hybrid layer. Sugizaki [72] showed that the etching, washing and drying process caused the dentine to collapse due to the loss of the supporting hydroxyapatite. Further work showed that this collapse of the collagen was an impediment to the successful diffusion of the resin to the base of the region of demineralization. To overcome this problem, Kanca [33] introduced the 'wet bonding technique' which left the demineralized collagen fibres supported by residual

water after washing. This allowed the priming solution to diffuse throughout the collagen fibre network more successfully. However, when it comes to clinical practice, it is very difficult to find the correct balance of residual moisture. Sano *et al*. [65] showed in their work on nanoleakage that most resin-based DBAs allowed the ingress of silver nitrate along the base of the hybrid layer. However, the clinical significance of this is unclear. It may be a pathway for fluid to affect collagen not coated by resin, and the outcome may be degradation of the bond over time. However, the degree of nanoleakage is very much material dependent rather than system dependent, meaning that there are conventional systems and self-etching priming systems that show small amounts of nanoleakage whereas others show more. For the self-etching systems, these are able to solubilize the smear layer and demineralize the underlying dentine, forming a quite thin hybrid layer [25, 35, 36, 79].

## 4.3 Bonding substrate

Dentine is quite a variable tissue. Within the tooth itself the dentine approaching the dentino-enamel junction is more highly mineralized and the area occupied by the tubules is less than that of dentine adjacent to the pulp. In addition to this, dentine should be considered as a dynamic tissue that changes due to ageing, in response to caries and restoration placement. Most changes relate to occlusion of tubules and also an increase in the mineralization of the dentine. The implication of this is that the dentine becomes slightly more difficult to etch and exposure of collagen fibrils can also be reduced, hence there is a potential for the bond to be somewhat tenuous. This is particularly the case for the highly sclerosed dentine of non-carious cervical lesions (NCCLs). Laboratory studies indicate that the hybrid layer of the dentine surface of NCCLs is thinner than that of normal dentine [29, 63]. In addition, it seems that some bonding systems do not adhere as well to this surface and show a slightly decreased bond strength [25, 35, 79].

A considerable amount of work has also been done looking at the variation of the bond to caries-affected dentine. Some of the early studies used artificial caries like lesions. However, this does not reproduce the situation that occurs in the oral cavity since caries is a process of demineralization and remineralization associated with the damage of the supporting collagen matrix [48, 53]. The increased thickness of the hybrid layer is mainly because the dentine is already partially demineralized from the caries and the action of the acid etch is therefore somewhat greater. This provides a clear basis for not etching for longer than that recommended by the manufacturer. In addition, the water content of caries-affected dentine is believed to be greater than normal dentine. This too will also have an effect on the ability of the resins to penetrate to the full depth of the demineralized dentine. In the case of caries-affected dentine treated with chemo-mechanical caries removal solutions, there appear to be no adverse effects on the bond with a DBA [79].

However, the bond to radicular and pulp chamber dentine does seem to vary quite a lot depending on the DBA used. This perhaps provides a strong case for being careful with the selection of a DBA for these regions of the tooth. It is believed that it may be necessary to use different DBAs for different regions of the tooth, or a system needs to be selected where it has been shown to provide a reliable bond to all parts of the tooth. Another alternative is the use of GIC restorative materials when then is a deep cavity on the radicular surface of a tooth, as it is known that a reliable bond can be achieved and moisture control is not such a problem [25, 35, 79].

**4.4 Clinical studies**

There has been a considerable amount of work done to evaluate the success or otherwise of DBAs in clinical studies. However, one of the great problems has been that many of the DBAs have been considerably changed or a new material introduced by the time these studies are completed or published. Many of the studies have also been performed on NCCL, which means the outcomes cannot really be applied to restorations in other parts of the mouth because NCCL dentine is usually sclerosed and therefore different from that of an intracoronal cavity. However, these outcomes will provide some indication as to whether the DBA is able to achieve a durable bond under very harsh conditions. Since the early materials were introduced, the retention rates of the DBAs to sclerosed cervical dentine have steadily improved to extent that retention rates are little different from GICs [79].

With regard to clinical studies on posterior teeth restored with a DBA, there is still little evidence available. It would seem though, that clinical studies of resin composite restorations are showing evidence that when placed in the correct manner and the patient has a low caries rate, restoration survival is approaching that of amalgam [30].

When it comes to the use of DBAs, it is important to follow the manufacturers' directions carefully. Overetching can create a situation where there will potentially be a region of poorly or uninfiltrated dentine. This zone may be susceptible to acid or enzyme attack from oral bacteria, hence leading to bond failure [82].

In the case of the self-etching priming materials, this is not believed to be a problem. However, the converse problem may occur: as mentioned, the dentine or smear layer may neutralize the etching primer if the primer has a relatively high pH. The anecdotal evidence would seem to indicate that gentle agitation of these solutions may assist with the etching. However, there are no research data to support this [35, 79].

# 5. Direct composite restorative materials

A generalized definition of a composite is a multiphase material that exhibits the properties of both phases where the phases are complimentary, resulting in a material with enhanced properties. The first tooth-colored composite was silicate cement, which was introduced in 1870s. This composite formulation was based on alumino-fluro-silicate glasses and phosphoric acid. The dispersed phase was residual glass particles, and the matrix phase was the aluminum phosphate salt formed from the partial acid dissolution of the glass particles; however, these were brittle, required mechanical retention, and had an average longevity of only a few years. of only a few years. The first polymeric tooth-colored composite used in dentistry was based on poly (methylmethacrylate). This material was developed in the 1940s, and consisted of a poly (methylmethacrylate) powder, methyl methacrylate monomer, benzoyl peroxide, and n,n-dimethlyparatoluidine. These materials could be classified as composites, because upon mixing, the polymer powder formed a dispersed phase and the monomer polymerized to form the continuous phase. The polymerization was initiated at room temperature, using the redox initiator combination of benzoyl peroxide and n,ndimethlyparatoluidine. Although these materials were initially esthetic, they were plagued with a variety of problems, including poor color stability, high polymerization shrinkage, a lack of bonding to tooth structure, and a large coefficient of thermal expansion (CTE). The first polymer matrix composite incorporating silica fillers was

introduced in the 1950s. These composites had improved mechanical properties and good esthetics; they did not bond to tooth structure, and still exhibited significant polymerization shrinkage [10, 46, 55, 58].

One way to address the polymerization shrinkage problem is to use high molecular weight monomers. In 1962 Bowen [11], while at the National Bureau of Standards, synthesized an acrylated epoxy using glycidylmethacrylate and Bisphenol A epoxy for use as a matrix for dental composite. The resulting monomer, called Bis-GMA or Bowen's resin, possessed the viscosity of honey, and therefore limited the amount of filler particles that could be incorporated. Subsequent experiments incorporated triethylene glycol dimethacrylate (TEGDMA) as a diluent to reduce the viscosity. This monomer combination worked well, and has become one of the most widely used matrix monomer combinations for dental composites to date. The structures of Bis-GMA and TEGDMA are shown in Figs. 3 and 4, respectively.
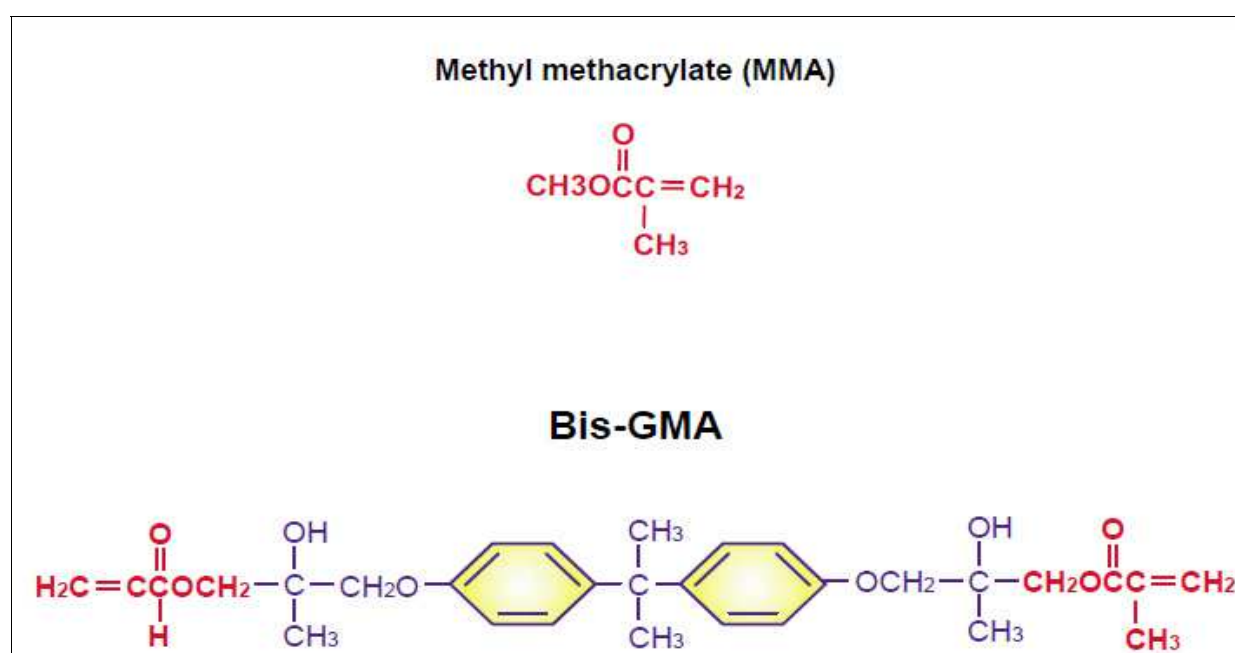


Fig. 3. The chemical structure of Bis-GMA, a resin invented by Ray Bowen. It also is referred to as Bowen's resin.
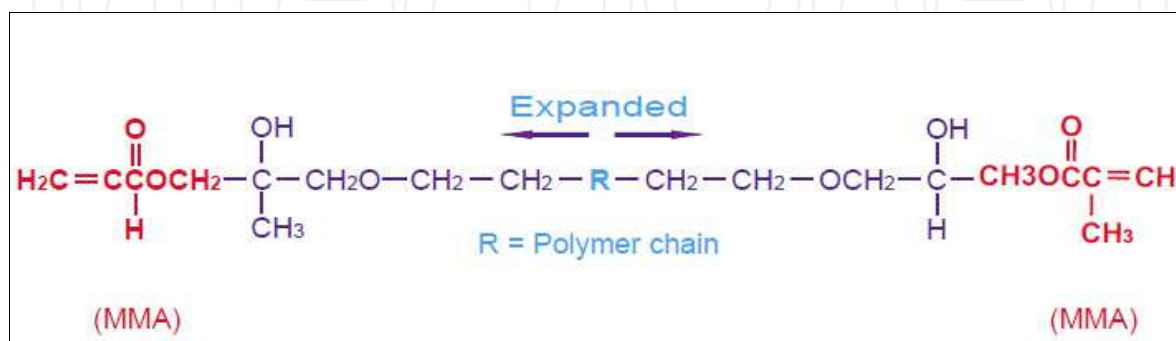


Fig. 4. TEGDMA. The chemical structure of triethyleneglycol dimethacrylate (TEGDMA, which is also abbreviated TEDMA and TEGMA). The structure of methyl methacrylate (MMA) is shown for comparison.

Both of these monomers contain two reactive double bonds, and when polymerized, form covalent bonds between the polymer chains known as cross-links. Cross-linking improved the properties of the matrix phase, and the composite produced had improved mechanical and physical properties. Additional composite formulations have been prepared using various diluent monomers such as methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA), and an additional high molecular weight monomer based on a urethane dimethacrylate (UDMA). The chemical structure for UDMA is illustrated in Fig. 5 [10, 25, 46, 55, 58, 75].
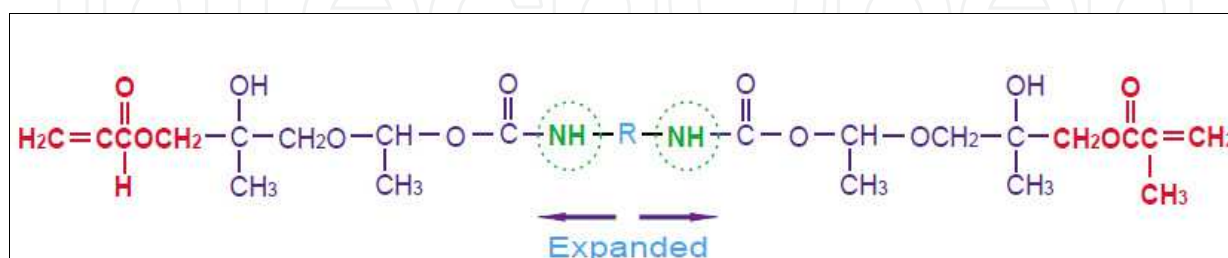


Fig. 5. Urethane dimethacrylate. The chemical structure of popular difunctional urethane resins. R = a number of carbon compounds that can be used to lengthen or alter the properties of the monomer. Nitrogen in the form of NH–R–NH is the urethane component.

## 5.1 Composite resin chemistry

To reduce polymerization shrinkage and increase mechanical and physical properties requires the use of high molecular weight monomers that have the ability to cross-link. The high molecular weight reduces the volume change during polymerization. Cross-linking forms covalent bonds between the polymer chains, resulting in a dramatic increase in modulus and reduction in solubility [57]. Bowen's resin is the reaction product between Bisphenol A and glycidyl dimethacrylate. A lower molecular weight monomer such triethylene glycol dimethacrylate (TEGDMA) or EDMA is added to reduce the viscosity and allow increased filler loadings to be used. These monomers are also multifunctional and increase the number of cross-linking reactions during setting of resin matrix. These lower viscosity monomers may comprise 10% to 50% of a composite's composition.

One of the most significant problems with current monomers used for direct composite restorative materials is the shrinkage that occurs during polymerization. Currently, all commercial dental composites are based on vinyl monomers polymerized using free radical initiators. Conversion of these monomers results in a decrease in distance between the molecules, from a Van der Waals gap to the distance of a covalent bond. Although this distance is very small for a single monomer, the distance change over a long polymer chain is significant. Inclusion of filler reduces the volume of resin and its volume change, but the amount of filler incorporation is approaching the maximum theoretical packing fraction of 74 volume % for close-packed structures. The amount of shrinkage is controlled by the volume of resin, its composition, and the degree of conversion. Current commercial dental composites have a volumetric shrinkage ranging from 1.6 to 8 volume%. The contraction stress developed at the margin of the restoration can be sufficient to overcome the bond strength of the bonding system, resulting in a contraction gap. The contraction gap can lead to microleakage and all its associated problems (eg, secondary caries and pain) [55, 57].

One approach to reduce polymerization shrinkage and contraction stress is through the development of low-shrinkage or expanding monomer systems. These resin systems are based on ring-opening polymerization reactions that do not shrink to the extent of conventional vinyl polymerization resins. Monomers based on spiro-ortho carbonate have been prepared and evaluated in composite formulations. Although the composites formulated using these monomers did show less polymerization shrinkage, the property improvements were only incremental, and probably not significant enough to be realized clinically [10, 25, 55, 57].

One problem that has not been addressed is the large difference between the Coefficient of Thermal Expansion (CTE) of resin composites and tooth structure. The CTE of tooth structure ranges from 9 to 11 ppm/_C, compared with 28 to 50 ppm/_C for dental composite restoratives [4]. The differential expansion and contraction of composites cause additional stress at the margin of the restoration that contributes to fatigue failure of the bond between the composite and tooth structure. Currently the only way to lower the CTE of composites is to increase the filler loading.

## 5.2 Composite fillers

The reinforcing phase in direct dental restoratives is based on glass or ceramic particles. Incorporation of these inorganic particles imparts improved strength and wear properties, decreased CTE, and reduced polymerization shrinkage. In addition, incorporation of heavy metals into the filler provides radiopacity. The initial composite fillers were limited in size because of the limited ability to grind and sieve quartz, glass, borosilicate, or ceramic particles. The particle size range was from 0.1 to 100 mm. Smaller particles have been prepared through hydrolysis or precipitation to produce what is termed fumed or pyrolitic silica. The particle sizes obtained from this process range from 0.06 to 0.1 mm 6.

The most recent process to form particles is through sol-gel chemistry, which uses silicate precursors that are polymerized to form particles ranging from nm to mm dimensions. This sol-gel process can be used to form almost mono dispersed particle sizes, which can be a significant advantage because different particle sizes can be produced and blended to optimize the packing efficiency and filler loading of the composite. In addition, the ability to produce submicron size particles allows the production of nanocomposites in which the particles approach the size of the polymer matrix molecules. Theoretically, nanocomposites have the potential to exhibit excellent mechanical and physical properties at higher filler loadings [25, 55, 80].

## 5.3 Curing of dental composites

The majority of current dental composites are cured using visible light ranging from 450 to 475 nm. Light sources include quartz halogen, laser, plasma arc, and most recently, light emitting diodes (LED). The minimum energy required for adequate curing is 300 mW/cm². Newer lights have incorporated curing modes that step or ramp up the light intensity with time. These modes were added in an attempt to control the polymerization shrinkage and reduce the polymerization contraction stress. Although these lights have shown some promise, the clinical effectiveness of these controlled polymerization techniques is unknown. All of the lights used for curing composite increase the temperature of the

composite to varying extents, which can actually increase the degree of conversion; however, high-intensity light sources may cause sufficient temperature increases to result in damage to the pulp [7, 25, 55].

## 5.4 Composite classification: properties and applications

Composites generally are classified with respect to the components, amounts, properties of their filler or matrix phases, or by their handling properties. The most common classification method is based on filler content (weight or volume percent), filler particle size, and method of filler addition. Composites also could be defined on the basis of the matrix composition (BIS-GMA or UDMA) or polymerization method (self-curing, ultraviolet light-curing, visible light-curing, dual curing, or staged curing), but these do not communicate as much information about the properties. One of the most often used classification systems is based upon filler particle sizes. That system is extended here to include the particle size by order of magnitude, acknowledging mixed ranges of particle sizes, and distinguishing procured composite pieces as special filler. Composite filler particles are called *macrofillers* in the range of 10 to 100 μm, *midifillers* from 1 to 10 μm, *minifillers* from 0.1 to 1 μm, and *microfillers* 0.01 to 0.1 μm. Very large individual filler particles, called *megafillers*, also have been used in special circumstances. New ultrasmall fillers are being used that are from 0.005 to 0.01 μm in diameter and are called *nanofillers*. Accordingly, composites are classified by particle size as *megafill, macrofill, midifill, minifill, microfill,* and *nanofill*. Composites with mixed ranges of particle sizes are called hybrids, and the largest particle size range is used to define the hybrid type (e.g., minifill hybrid) because microfillers are normally the second part of the mixture. If the composite simply consists of filler and uncured matrix material, it is classified as homogeneous. If it includes procured composite or other unusual filler, it is called heterogeneous. If it includes novel filler modifications in addition to conventional fillers, then it is called modified, such as fiber-modified homogeneous. Another consequence of advances in the control of filler particle size, particle size distribution, particle morphology, and monomer technology has been the introduction of composites with specific handling characteristics. These include *flowable composites* and *packable composites*. *Flowable composites* are a class of low-viscosity materials that possess particle sizes and particles size distrubutions similar to those of hybrid composites, but with reduced filler content, which allows the increased amount of resin to decrease the viscosity of the mixture. *Packable composites*, also referred to as *condensable composites*, were developed in a direct effort to produce a composite with handling characteristics similar to amalgam, thus the moniker of "packable" or "condensable". These "amalgam alternatives" are intended primarily for Class I and Class II restorations. For posterior composite restorations, it is also possible to place one or two large glass inserts (0.5-to 2-mm particles) into composites at points of occlusal contact or high wear. These pieces of glass are referred to as *inserts* (or *megafillers*). Although they have demonstrated improved wear resistance to contact area wear, the techniques are more complicated and do not totally eliminate contact frea area wear. Furthermore, the bonding of the composite to the insert is questionable [7, 16, 55].

### 5.4.1 Microfilled composites

Microfilled composites were introduced to the market from the late 1970s to the early 1980s. Microfilled composites were developed to provide the dental profession with a material that

possessed outstanding polishability and esthetics. These composites incorporate particles ranging from 0.04 μm to 0.4 μm. The early versions of microfilled resins were limited in the amount of filler that could be incorporated, because of the high surface area-to-volume ratio of the filler that caused large viscosity increases in the formulation. These composites only contained 35 to 67 weight % and 20 to 59 volume % glass fillers. One way to increase the volume of small particles is through the use of prepolymerized particles. In this process, submicron-sized particles are mixed with monomers such a Bis-GMA and TEGDMA at elevated temperatures. The mixture is then cured at elevated temperature and pressure, using benzoyl peroxide as an initiator. After polymerization, the material is chilled and ground to form particles having a size range of 1 to 200 μm. The prepolymerized particles allow higher filler loadings to be obtained with smaller particles; however, the prepolymerized particles cannot be bonded to the matrix phase using silane coupling agents. Interfacial bonding requires diffusion of the matrix monomers into the particles, with subsequent polymerization to provide micromechanical interlocks. Some investigators have suggested that the lack of interfacial bonding in these systems may contribute to failure [55, 57, 59].

Therefore microfilled composites have a lower elastic modulus and lower fracture strength than materials that contain higher concentrations of filler. The prepolymerized particles allow the filler content to be maximized and polymerization shrinkage to be minimized, however, while making these composites highly polishable and possessing the ability to maintain a smooth surface during clinical wear. Because of these properties, microfilled composite resins are indicated for Class V restorations, non–stress-bearing Class III restorations, and small Class I restorations. They are also indicated for direct composite resin veneers if the patient does not demonstrate any parafunctional habits, such as bruxism. Because of their lower fracture strength and potential for marginal breakdown, microfills are generally contraindicated for posterior load bearing restorations such as Class II and large Class I restorations [55, 71].

## 5.4.2 Hybrid composites

The majority of resin composites in clinical use today are categorized in the general term of "hybrid composites." This broad category includes traditional hybrids, micro-, and nanohybrids. The "hybrid" moniker implies a resin composite blend containing submicron inorganic filler particles (.04 μm) and small particles (1 μm–4 μm). The combination of various sizes of filler particles corresponds to an improvement in physical properties as well as acceptable levels of polishability. These improvements in wear resistance and fracture strength, along with good polishability, make hybrids the material of choice for Class III and Class IV restorations. In addition, practitioners have used these traditional hybrids in posterior load-bearing surfaces such as Class I and Class II restorations because of their improved strength and wear resistance.

Recent improvements in filler technology by manufacturers have allowed blends of both submicron particles (0.04 μm) and small particles (0.1 μm–1.0 μm) to be incorporated into a composite formulation. These materials are classified as micro-hybrid composites. The mixture of smaller particles distinguishes microhybrids from traditional hybrids and allows for a finer polish, along with improved handling. The desirable combination of strength and

surface smoothness offers the clinician flexibility for use in posterior stress-bearing areas as well as anterior esthetic areas. Although microhybrids offer superior strength, their polishability is not better than a traditional microfilled composite resin. The trend in the newer microhybrid materials is to maximize filler loading and minimize filler size. The latest version of microfilled hybrids has used nanofiller technology to formulate what have been referred to as nanohybrid composite resins. Nanohybrids contain nanometer-sized filler particles (.005–.0l microns) throughout the resin matrix, in combination with a more conventional type filler technology. Nanohybrids may be classified as the first truly universal composite resin with handling properties and polishability of a microfilled composite, and the strength and wear resistance of a traditional hybrid. These nanohybrids can be used in any situation similar to the microhybrids, with possibly a slight improvement in polishability because of the smaller particle size [55, 74].

### 5.4.3 Packable composites

Packable or condensable composites were developed to provide a composite that handled more like amalgam. This marketing ploy by dental product manufacturers was an attempt to increase the use of composites by older dentists who were not trained in their use in dental school, and younger dentists who were looking for a more user-friendly material. Packable composites have a higher viscosity and are less ''sticky'' than other composite restoratives. The viscosity increase is obtained through changes in the particle size distribution and incorporation of fibers [81]. These composites were introduced to the market as amalgam substitutes, as practitioners searched for the ideal esthetic material with handling properties similar to amalgam. Another desire was to find a material that would establish adequate proximal contacts more easily than traditional hybrid composites. Claims of improved handling properties and better adaptation to the matrix band in Class II restorations have piqued the interest of many clinicians. The dental professions have referred to these materials as ''packable composites'' instead of ''condensable,'' because of their greater viscosity and decreased stickiness compared with conventional hybrid composites. When initially placed, these materials were more viscous than traditional hybrid composites; however, after placement the viscosity decreased as the temperature of the material equilibrated with the temperature of the oral cavity. Although the ''packable composites'' showed improved handling properties for restoring Class I and II preparations, they have not fully solved the problem of achieving adequate interproximal contacts. Because packable composites do not have substantially better mechanical properties than hybrid composites, they would not be expected to perform better clinically [86]. In addition, because of the development of improved placement instruments and matrix systems to achieve better interproximal contacts, the need for packable or condensable materials has decreased, resulting in a decreased market share. In summary, the mechanical properties of the packable composites are not significantly better than other hybrid formulations, and there have not been sufficient long-term clinical studies to determine how these materials will perform long-term in the oral cavity. Their use as a direct dental restorative may be limited [18, 55, 57].

### 5.5 Clinical survive probability of composites

Composites are monitored in clinical studies by using United States Public Health Service (USPHS) categories [61] of interest: color matching, interfacial staining, secondary caries, anatomic form (wear), and marginal integrity [7].

Changes in restorative treatment patterns, the introduction of new and improved restorative materials and techniques, effective preventive programs, enhanced dental care, and growing interest in caries-free teeth have greatly influenced the longevity of dental restorations; however, failure of restorations is a major problem in a practice treating primarily permanent teeth. Studies show that 60% of all operative work done is attributed to the replacement of restorations [44]. Composites have improved since their introduction, and their survival rates are improving. Clinical studies to evaluate the latest composite technologies have not been published; therefore most of the survival data are on older composite compositions.

In the 1970s, degradation or wear was considered the main reason for failure of composite restorations. Improvements in filler technology and formulation of composite materials have resulted in new reasons for replacement. Twenty years later, studies revealed secondary caries to be the new cause of failure. The main factors responsible for the change in reasons for replacement include improved clinical technique based on more adequate teaching of posterior composites at dental schools, and on gained experience through trial and error of clinicians in practice [55]. Advancements in composite properties and adhesive technology also contributed to these changes.

In comparison of survival probability between amalgam and composite, a time period involving 3, 4, 5, and 7 years was considered [54]. In permanent teeth, the following values were measured: 3 year, 97.2% (amalgam) to 90% (composite); 4 year, 96.6% (amalgam) to 85.6% (composite); 5 year, 95.4% (amalgam) to 78.2% (composite); and 7 year, 94.5% (amalgam) to 67.4% (composite).

In summary, longevity of composite restorations depends upon factors involving the materials, the patient, and the dentist. The request for these esthetic, tooth-colored restorations will continue to increase, and patients must be educated about the expected life of these restorations as well as their advantages and disadvantages, so they can make an informed decision on a treatment option.

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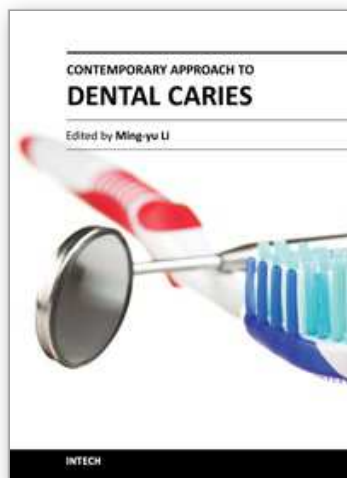
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