

# Composition of Dental Resin-Based Composites for Direct Restorations

# 2

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Ever since the introduction of light-curable resin-based composites in the 1970s, these mixtures of organic and inorganic phases have continuously evolved to meet the increasing requirements of material design and dental practitioners. However, fundamentally, the chemistry of composite phases has not significantly changed, with material design that commonly involves particle dispersion within a resin matrix. Such matrix is typically based on (di)methacrylate chemistry and a camphorquinone system to initiate polymerization upon light activation. The lack of any substantial shift in the use of conventional manufacturing approaches is, in part, testament to the relative success of resin composites as restorative dental filling materials. Current research focuses on strategies that would allow bulk-curing or bio-active and adhesive properties, which may lead to an improved longevity.

Among the current key requirements for modern resin-based composites (Fig. 2.1), shorter curing times and maximized depth of cure with user-friendly shading systems and handling properties have increased in popularity. To meet these requirements, minor alterations to the composition are made, changing the bulk properties of resin-based composites. Hence, an understanding of the fundamental compositional changes is required in order to grasp the trade-offs and limitations that may arise. As one property is usually pushed forward by manufacturers, practitioners must be provided the opportunity to understand any compromise in other key characteristics. For example, depth of cure may be greatly improved at the cost of increased translucency and reduced cosmetic results and/or mechanical properties.

This Chapter aims to provide a comprehension of modern dental resin composite composition in

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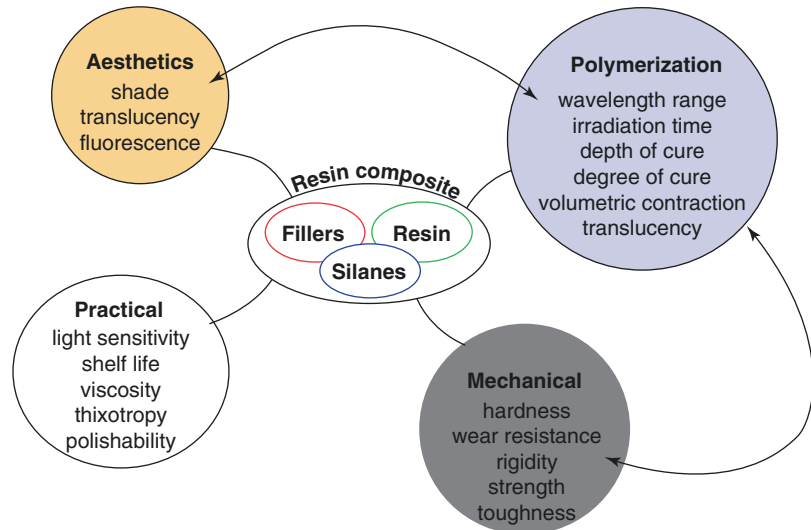
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**Fig. 2.1** Technical and practical requirements for resin-based composites used in dentistry



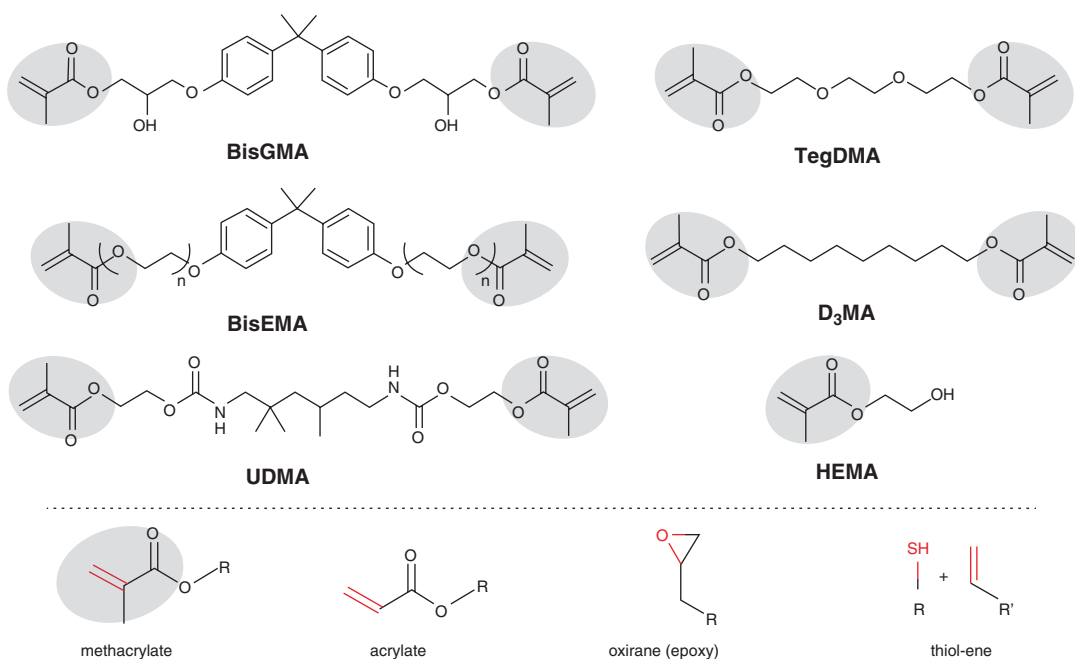
relation to brief historical perspectives and recent innovations, in terms of (a) resin chemistry, (b) chemical and photoinitiator chemistry, (c) inorganic particulate or fibrous filler phase, and (d) silane functionalization.

## 2.1 Monomers

The resin phase of dental resin composites is composed of reactive monomers, some providing rigidity or reduced shrinkage, while others, less viscous, are used as diluents to accommodate high filler particle loads and appropriate handling properties. Monomers that can be used in resin composites must display an activity of functional groups allowing for fast curing in the ambient, oxygen-rich environment. Further, the polymerization reaction proceeds in a filled paste system that necessarily displays a high viscosity and, hence, limited molecular mobility.

Historically, the monomers used have relied on the methacrylate group for functionality and a core of varying flexibility and hydrophilicity to match that of surface functionalized fillers (Fig. 2.2). The methacrylate-functional monomers satisfy the requirements for fast, in situ free-radical polymerization. The “Bowen” monomer bisphenol A glycidyl methacrylate (BisGMA) synthesized from bisphenol A and glycidyl meth-

acrylate was patented in 1961 (patent US3179623 A). Due to its highly rigid core and relative hydrophobicity, it remains widely used in resin-based composites. BisGMA is however highly viscous ( $\eta = 1200$  Pa.s [1]) which prevents the addition of large amounts of fillers. A comonomer blend based on BisGMA and triethylene glycol dimethacrylate (or TEGDMA,  $\eta = 0.006$  Pa.s [2]) is hence often used. Such blend displays an improved conversion and cross-linking compared to BisGMA alone [3]. As detailed in Chap. 5, much effort has been directed at improving the degree of polymer conversion, which averages 60% in paste-like composites [4]. The classical BisGMA/TEGDMA blend has progressively been replaced or complemented with other molecules in an attempt to overcome the associated drawbacks. Most notably, molecules leading to a reduced “polymerization stress” have been proposed: silorane and thiol-ene systems are two examples of alternative functional chemistries to methacrylates (Fig. 2.2). Few materials based on silorane or thiol-ene systems have been marketed however. One material, the Filtek Silorane (3 M ESPE), was introduced in recent years but removed due the need of a specific bonding agent. This, by some accounts, posed too much confusion. Most validated strategies selected methacrylate monomers of greater flexibility: for example, ethoxylated bisphenol-A dimethacrylate



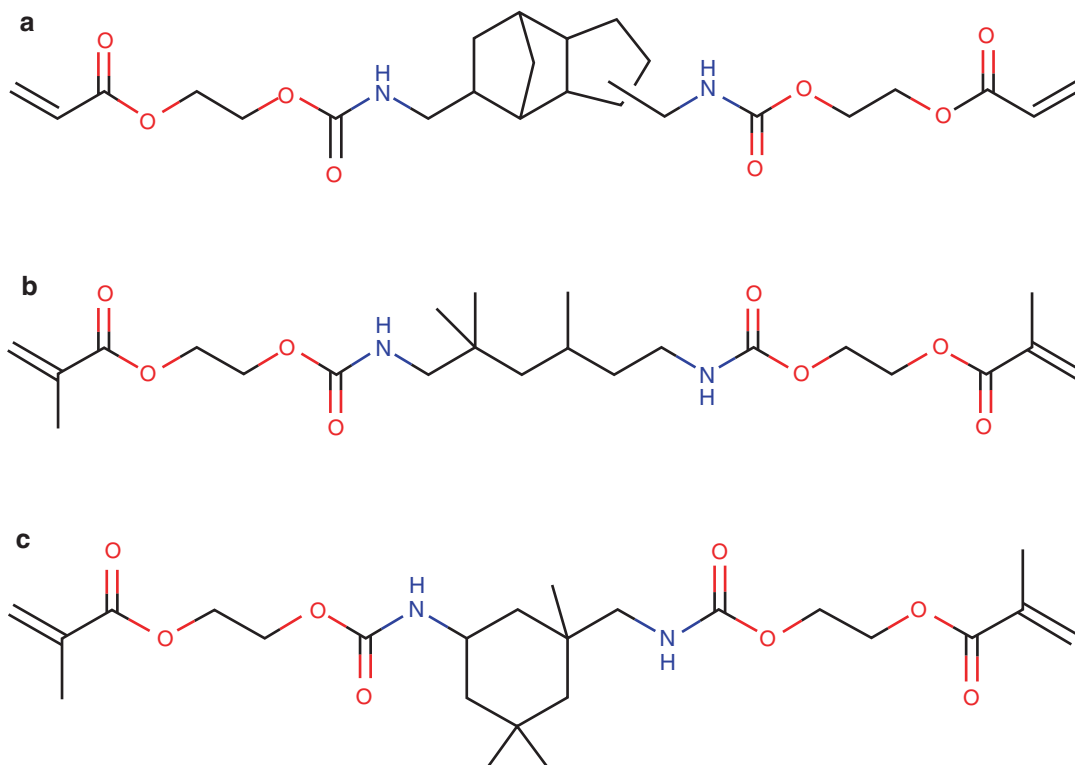
**Fig. 2.2** Molecular structure of typical dimethacrylate monomers used in resin-based dental composites. The methacrylate group is highlighted in *gray* and compared to acrylate, silorane (epoxy), and thiol-ene functionalities

(BisEMA) is a type of monomer with BisGMA core moieties but displaying flexible ethylene glycol spacers. The addition of BisEMA can reduce the viscosity of a blend, improve conversion [5], and decrease polymerization stress, at the cost of a general decrease in mechanical properties [6].

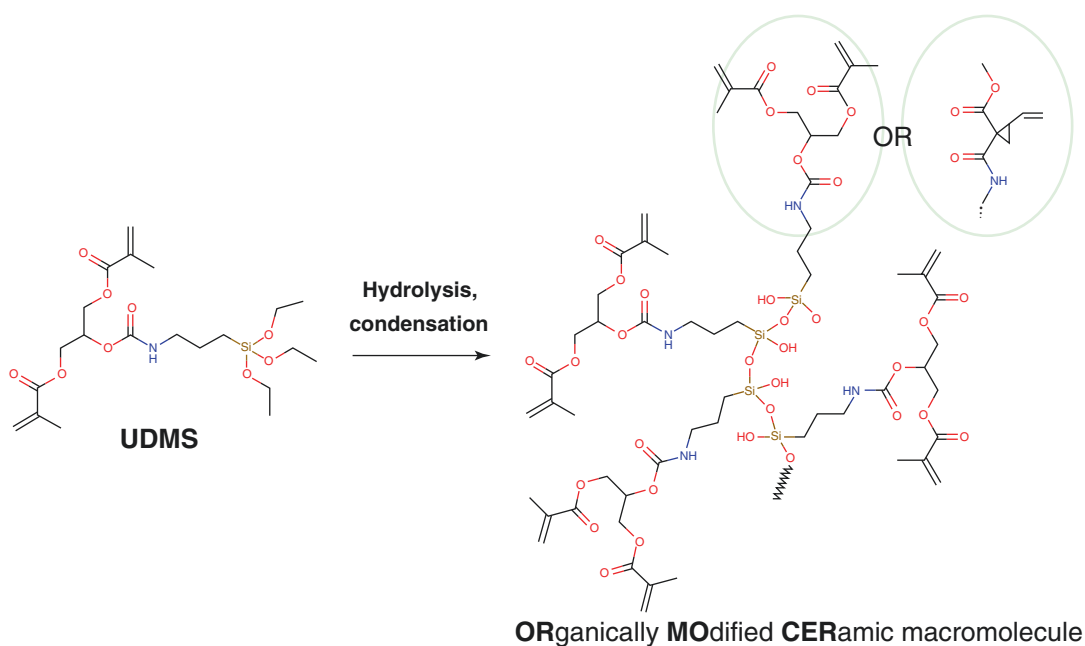
Due to doubts about the stability of BisGMA and release of bisphenol A (the biological risk of which remains controversial, though very unlikely considering the concentrations observed [7, 8]), monomers such as urethane dimethacrylate (UDMA) have been introduced. The molecule, as shown in Fig. 2.2, has a lower molecular weight ( $M = 470$  g/mol) and is more flexible than BisGMA. Resin blends composed of UDMA as replacement of BisGMA typically are less viscous, hence reducing the need for a diluent [3]. Further, the monomer to polymer conversion and mechanical strength are generally greater when replacing BisGMA with UDMA ([3, 9], respectively). However, the molecule presented in Fig. 2.2 (CAS registry number CAS 72869-86-4) is not the only one referred to as UDMA: the denomination is misleading as a variety of mole-

cules are labeled with the “urethane” short name [10]. In fact, while urethane groups ( $-\text{NH}-\text{C}(\text{O})-\text{O}-$ ) can be observed in “UDMA” molecules, entirely different structures exist (Fig. 2.3). Hence, modern dental composites that contain “urethane” monomers may display advantageous properties, although it remains difficult to associate these to specific molecules.

Some years ago, organic/inorganic oligomer-based materials were introduced to the market, termed “Ormocers” (ORganically MODified CERamics). Generally, Ormocers can still be considered as glass-filled composites. The main departure from conventional chemistries lies in the nature of the resin phase. Oligomers within Ormocer materials consist of condensed (silane) molecules similar to those used to functionalize the surface of fillers in conventional resin composites. By hydrolyzing and condensing silanes, oligomers of specific composition and structure may be obtained (Fig. 2.4). The main goal of Ormocer molecules is to increase the amount of silicon in resin composites, a change marketed as an increase in filler content. Furthermore, the oligomers can replace BisGMA, TegDMA, and



**Fig. 2.3** “Urethane” di(meth)acrylate monomers used in dental composites, as described in patent US 20100076115 A1 (a) and manufacturer information (b and c)



**Fig. 2.4** Scheme exemplifying silane condensation to prepare an organic-inorganic macromolecule, where the functionality available for polymerization can be methacrylate, vinylcyclopropane, etc. UDMS stands for Urethane DiMethacrylate Silane

other conventional dimethacrylates so long as their viscosity and hydrophilicity allow for appropriate handling properties and filler loading [11]. The organic/inorganic oligomers may maintain the methacrylate functionality or switch to ring-opening chemistries [12]. In the latter case, a lower volumetric shrinkage could be expected due to an inherently lower molar shrinkage coefficient [13]. The oligomers may constitute the whole resin phase so long as the viscosity and hydrophilicity allow for appropriate handling properties and filler loading. However, little is known about the actual design of the organic/inorganic molecules in commercial materials, and further characterization is required in order to correlate compositional changes to clinical results. A commercial Ormocer material was shown to perform as well as other clinically validated resin composites after 3 years [14]. Additional studies will determine the long-term performance of current Ormocers.

Further efforts have focused on the development of self-adhesive composites, whose composition should provide adhesion to dental tissues without the use of a separate bonding layer. While the strength of such self-adhesion remains quite low [15], the resin composite utilizes monomers presenting acid groups capable of reacting with calcium groups in hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ). Several different monomers were produced based on carboxylic or phosphoric acid groups as with chemistries used for self-etching or so-called ‘universal’ dental adhesives. Self-adhesive composites must display a pH low enough ( $\approx 2-3$ ) to etch the smear layer and bind to exposed mineralized collagen fibers [16]. At such pH, the hydrolytic stability of conventional dimethacrylates is severely compromised, and designing self-adhesive resin composites with a suitable shelf life is complex [17]. Further, self-adhesive composites must display a low viscosity and be amphiphilic in order to wet dentin but also prevent phase separation in the material. Unfortunately, as with Ormocers, information regarding developments and the composition of the commercial self-adhesive resin compos-

ites is scarce. One study did investigate the nanostructuring of the interface between an experimental two-part self-adhesive resin composite containing a phosphoric acid ester molecule and mineralized tissues [18]. Results showed the formation of a hybrid layer typical of relatively high-pH self-etch adhesives ( $\text{pH} > 2$ ). The interaction was limited, and authors indicated acceptable bond strength to dentin but not to enamel. In vitro, the bonding effectiveness of current self-adhesive resin composites to enamel and dentin remains suboptimal, with adhesion values lower than that of one-step (and most simple) adhesives [15, 19]. The technology is still evolving and improving and, in many ways, following closely to the development of self-adhesive resin cements and resin composite bonding systems.

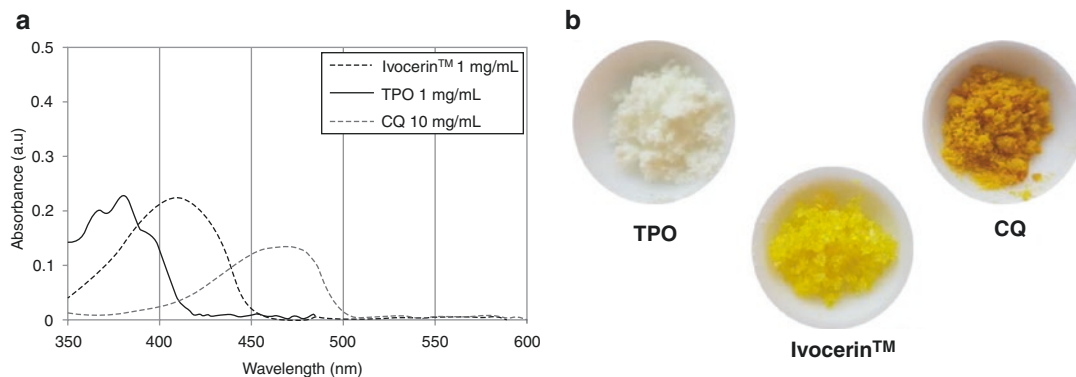
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## 2.2 Initiators in Conventional Photopolymerization

The in situ photopolymerization of dental resin composites requires the use of a molecule or system capable of inducing optimal polymerization throughout a significant depth (several millimeters) of pigmented material, with clinically compatible irradiation times ( $\approx 20$  s). Historically, and typical of most commercialized materials today, the type II photoinitiator camphorquinone, combined with a co-initiator, usually a tertiary amine, is used. On absorbing of corresponding photons, the photoinitiator system starts a free-radical polymerization (FRP) process. Camphorquinone absorbs over the 400–500 nm range with a peak of absorption located at 470 nm (Fig. 2.5). Alternative and simpler type I photoinitiator molecules have been suggested, such as phosphine oxides or germanium-based molecules. Such systems absorb at lower wavelength, with an absorption maximum located around 400 nm. While manufacturers provide little information on composition, the introduction of LED light-curing units provides two discrete outputs usually located at approximately 410 nm and 470 nm, which confirms the use of different photoinitiators [20, 21].

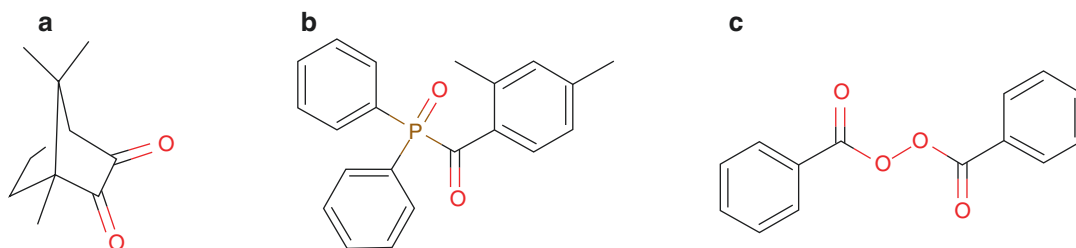
As the different absorption profiles suggest (Fig. 2.5a), CQ imparts a yellowish color to resin composite bulk, while the molecule phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide (TPO) appears as a white powder (Fig. 2.5b), and Ivocerin™, a germanium-based photoinitiator, is standing in between. This is of importance as resin composites for anterior applications, for example, “enamel” shades, can require high translucency with minimal pigmentation. Besides the absorption spectra, the chemistry of initiators also affects color. Experimentally, nonpigmented resin composites based on phosphine oxides show better color stability than those using CQ [22, 23], associated to differences in polymer networks. Phosphine oxide-containing resin composites may present a more cross-linked polymer network [24, 25], making it less susceptible to pigment diffusion (such as tannins) and color variations.

The efficiency of initiators depends on several characteristics, including the absorption yield efficiency ( $\epsilon$ , in L/mol.cm) [26], which describes how many photons can be absorbed per initiator molecule at a given wavelength. When comparing TPO and CQ in terms of absorption, the data shown in Fig. 2.5 highlights the greater efficiency of TPO at lower concentration (10x lower). The greater absorption maxima of TPO are related to the aromatic rings, or chromophores, present in TPO (Fig. 2.6). In addition, the TPO molecule upon excitation yields two active radicals [27], while a type II photoinitiator system such as CQ/amine yields one [28]. The overlap between the absorption spectra and the light-curing unit (LCU) emission spectrum also greatly influences polymerization efficiency. Modern LED LCUs display narrow outputs (approx. 40 nm wide) located around the absorption maxima of initiator molecules, which ensures that emitted photons



**Fig. 2.5** Absorption spectra (a) of diphenyl(2,4,6-trimethylbenzoyl) phosphine oxide (TPO), camphorquinone (CQ), or benzoyl germanium (Ivocerin™) photoinitiators in the range 350–600 nm. Note the differ-

ences in absorption range, absorption maxima, and absorption taking into account the concentrations. Visual aspect of initiators in powder form (b)



**Fig. 2.6** Initiators used in dental composites for photo or “self” polymerization. (a) Camphorquinone, (b) TPO, and (c) benzoyl peroxide (BPO)

can be absorbed and utilized to initiate polymerization rather than contributing to the exotherm of polymerizing material and heating the surrounding tissues, such as the dental pulp.

Finally, in some resin composites, the polymerization is not light initiated but rather starts upon mixing two pastes. This may be needed for resin composite materials used for cementation of indirect restorations or root filling in the placement of posts or other applications where light transmission might be problematic. Such “auto” polymerization typically results from the reaction of benzoyl peroxide (BPO, Fig. 2.6) with a tertiary amine contained within separate pastes. In order to accommodate an appropriate working time, inhibitor molecules are added to the composite to prevent premature hardening following mixing. These, such as butylated hydroxytoluene (BHT) or 4-methoxyphenol (MEHQ), are antioxidants and consume active radicals, and the polymerization reaction only starts once they have been depleted.

## 2.3 Fillers

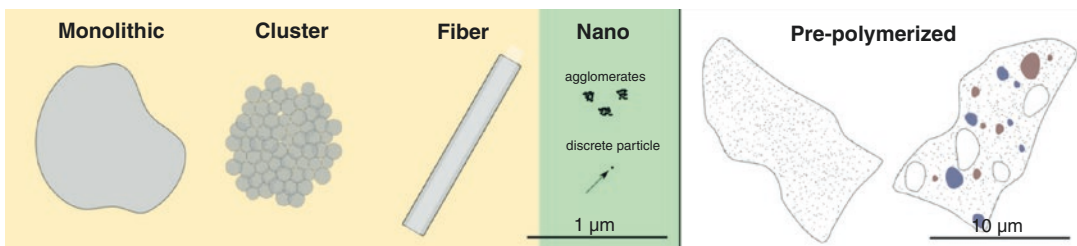
### 2.3.1 General Description

In order to increase mechanical properties of resin-based dental restorative materials, fillers must be optimally loaded and dispersed in the resin matrix. The inorganic filler particles act as reinforcing phase, increasing the elastic modulus of the resin composite, providing resistance to wear, and improving fracture toughness, and, prior to curing, influence handling properties that must be adapted for shaping and sculpting by the

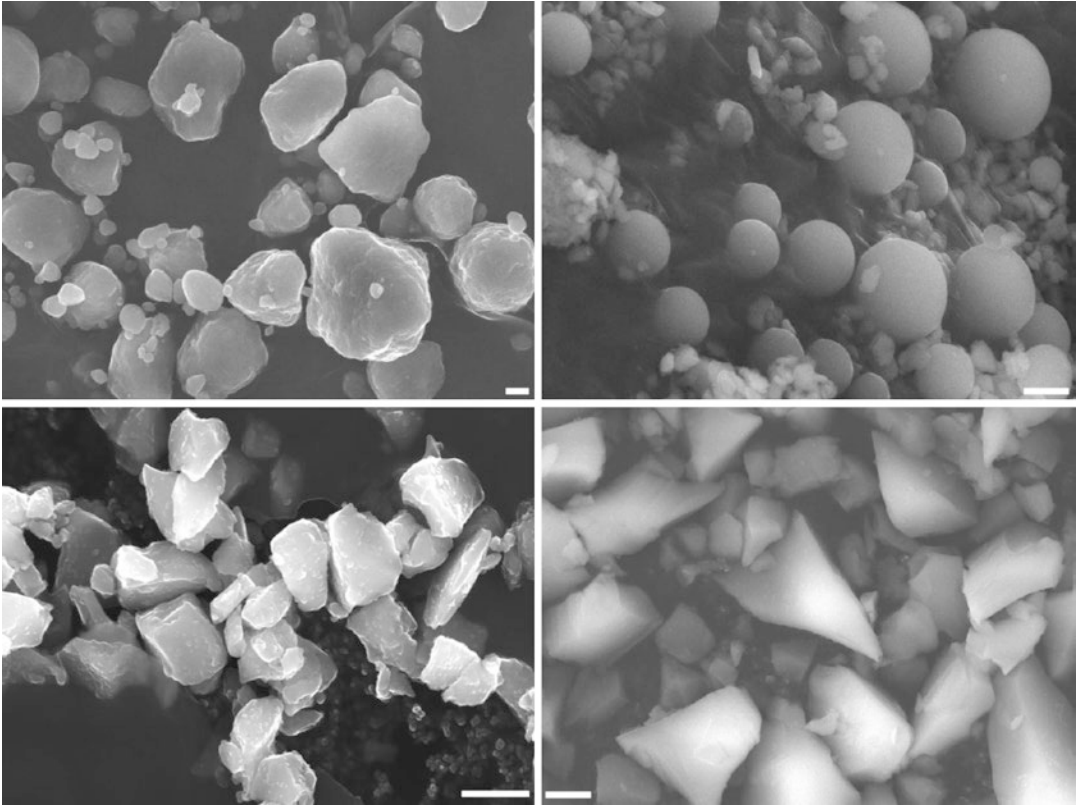
practitioner. Fillers, composed of inorganic oxides and glasses, can be described by their type (glass composition), morphology (size distribution and shape), density, radiopacity, refractive index, and surface porosity [29–33]. These characteristics, used as basis for classification and categorization of dental resin composites, along with their evolution are reviewed in Chap. 6.

Two “classes” of particles used in modern dental resin composites may be distinguished based on manufacturing processes and size, i.e., micro- and nanoscale particles (Fig. 2.7, orange and green boxes, respectively). While the latter, with, by definition, an average particle size smaller than 100 nm, are produced using a bottom-up approach, the micro-sized particles are usually milled, ground, and sieved from larger sizes. Historically, the first fillers to be introduced were large ( $> 10 \mu\text{m}$ ) micron-sized particles. The need for improved cosmetic results, polishability, and higher filler loading to improve mechanical properties led to a decrease in average particle size (1–10  $\mu\text{m}$ ) and more refined particle size distribution. In recent years, resin composites with submicron average particle sizes have been marketed (0.2–1  $\mu\text{m}$ ). The nanoparticles, typically fumed silica, act in part as viscosity modifiers and display sizes in the range of 10–40 nm but are rarely observed as discrete, non-agglomerated particles. Weak physical interactions at the nanometer scale promote agglomeration, and nanoparticles often appear as agglomerates. In order to aid dispersion, particles must be properly silanated (Sect. 2.4).

The morphology of microparticles may be controlled through the grinding process and greatly influences packing and hence maximal



**Fig. 2.7** Filler classes and possible geometries and composition. The pre-polymerized fillers can be composed of ground composite using nanoparticles and/or glass particles, which may vary in composition



**Fig. 2.8** Morphology of fillers—microparticles—separated from the resin phase in four different commercial resin composites. The scale bar indicates 1  $\mu\text{m}$  in all SEM pictures

filler loading. Filler morphology varies greatly (Fig. 2.8) but is difficult to relate to packing and the bulk properties of a material. Resin composites often contain more than one size distribution (bimodal) to allow for more efficient packing where smaller particles can occupy interstices between larger fillers [29, 33].

Filler content is negatively correlated with the volumetric shrinkage and polymerization stress [34]. While several strategies have been investigated to limit stress development during curing, increasing the filler content appears as an efficient solution. In modern resin composites, this content is invariably higher than 35 vol%, even in “flowables.”

The composition of fillers varies among commercial composites and is optimized to match the refractive index of the resin but also to provide radiopacity (Sect. 2.3.2). Conventional monolithic microparticles (Fig. 2.7) are composed of

silica-rich glasses, with doping oxides such as alumina and barium oxide ( $\text{Al}_2\text{O}_3$  and  $\text{BaO}$ ), which are commonly used for radiopacity [35]. Less common elements such as Sr, Yb, or Zr can also be found. Few changes in terms of composition were observed over the last two decades, but efforts rather went to generating particular structures and microstructures (Chapter 2c.iii, Specific Fillers).

### 2.3.2 Optical Properties of Fillers (Visible Light and X-Rays)

Photopolymerization of dental resin composites requires a design enabling polymerization throughout a significant depth (several millimeters), with limited irradiation time. Light penetration depends on the transmission of light or how much light reaches the deeper resin composite layers.



**Table 2.1** Representative refractive indices for several resin blends and fillers. Information extracted from manufacturers' websites and reference [36]

Resin blend		Fillers	
Type, description	Refractive index	Type, description	Refractive index
TegDMA/BisGMA 30/70	1.524 → 1.556 <sup>a</sup>	Barium borosilicate glass, Esstech Inc.	1.553
TegDMA/BisGMA 90/10	1.474 → 1.538 <sup>a</sup>	Aluminosilicate glass ceramic, Esstech Inc.	1.54
TegDMA, Esstech Inc.	1.4595	Barium borosilicate glass "IS 50 1102 dental glass 1,0"; Ferro Corp.	1.52
HEMA, Sigma-Aldrich	1.453	–	

<sup>a</sup>Refractive index variation after polymerization (the value increases)

Ideally, fillers should transmit light in the visible range so that color is mainly controlled through the addition of a selection of pigments. Loss of light with depth is mainly due to refraction: the law of refraction describes the extent light deviates at an interface from its original direction, which is related to the difference in the refractive index of each phase. In resin composites, each filler particle represents an interface with the resin matrix. It is assumed that a similar refractive index of fillers to that of the resin blend will increase light transmission and depth of cure.

Refractive index of the polymer increases with increasing cross-linking density of the resin, i.e., most manufacturers design resin composites with a filler refractive index close to that of the cured copolymer blend (Table 2.1). It follows that most current commercial resin composites increase in translucency as polymerization proceeds. However, some modern so-called "bulk-fill" materials exhibit a reduction in light transmission, and increased opacity, as the resin cures in order to better mimic the aesthetic properties of enamel. There is no current consensus on how light transmission changes throughout polymerization affect degree of conversion with depth.

The light emitted from a resin composite, perceived by the eye, is a mixture of light reflecting off its surface and emitted from the bulk after scattering and absorption. In order for a resin composite to blend with surrounding mineralized tissues, optical properties should be optimized to match that of dentin and enamel. Particle size and filler content, for example, influence optical characteristics. A decrease in particle size is associ-

ated with an increase in transmittance, related to a decrease in scattering [37]. Further, the higher the filler content, the higher the scattering coefficient [38] and hence the lower the transmission [37]. It follows that more translucent resin composites, for example, "enamel" shades, generally have a lower filler content. Modern resin composites still fail to match the optical properties of enamel, including the absorption and scattering over the visible range of light [39]. Further research in composition, including that of fillers, is required to reach optimal material blending with tissues.

Opacity to X-rays (high-energy photons) or radiopacity is a crucial requirement for resin composites. In order to properly diagnose secondary carries, a dental practitioner must be able to clearly distinguish a restorative material from degraded tissues. The main tool for diagnosis is X-ray imaging, where carious tissues appear more radio-transparent as they are demineralized. This is explained by X-ray absorption being directly related to the atomic number of atoms encountered. ISO 4049 specifies the minimal radiopacity for resin composites, with the standard chosen as the absorption of a 1 mm-thick layer of pure aluminum (atomic number,  $Z = 13$ ) [40]. The resin phase of resin composites contributes very little to X-ray absorption. Consequently, resin composites must incorporate a high fraction of radiopaque fillers composed of heavy elements such as strontium ( $Z = 38$ ), zirconium ( $Z = 40$ ), barium ( $Z = 56$ ), lanthanum ( $Z = 57$ ), Ytterbium ( $Z = 70$ ), or bismuth ( $Z = 83$ ), the most common being barium [32, 35]. Modern resin composites meet the ISO requirement for radiopacity [41, 42].

### 2.3.3 Specific Fillers

The geometry and microstructure of fillers can be engineered to provide specific properties and improvements with regard to bulk and surface properties. To date, the modifications and specificities can be grouped as follows: fibers or fiber-like particles, clusters, and pre-polymerized fillers.

#### 2.3.3.1 Fibers

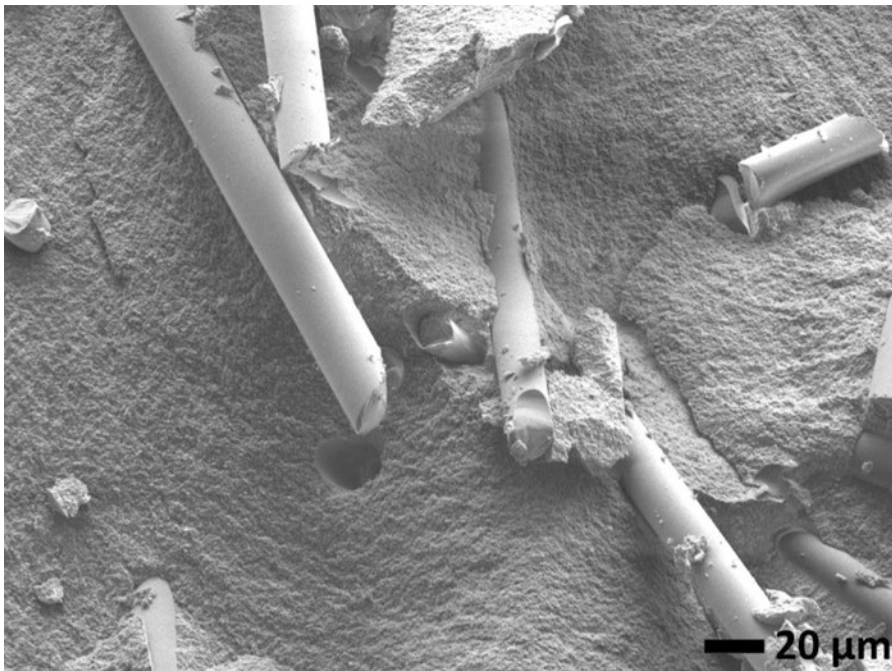
To improve the fracture toughness of resin composites, particles with a high length to diameter ratio have been used, both experimentally [43] and in commercial materials [44]. When silanized, fibers may increase the strength of a composite due to the additional “pullout” that must occur for a crack to progress around them. The fibers in dental composite are typically silica-based ( $\text{SiO}_2$ ). The glass fibers were adapted or directly taken from industrial applications and are denoted E (E for “electrical”) or S type depending on their origin: the former was originally developed for insulation in electronics and

contains a mixture of  $\text{SiO}_2$ , alumina ( $\text{Al}_2\text{O}_3$ ), calcium, magnesium, and boron oxides ( $\text{CaO}$ ,  $\text{MgO}$ , and  $\text{B}_2\text{O}_3$ ). The S-glass (S for “stiff”) fibers are composed of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{MgO}$ . Both types of glasses are amorphous and resistant to deformation compared to the polymer matrix: their elastic moduli are greater than 60 GPa [45].

Given the morphology of glass fibers, their use in resin composites is complicated and often limited to nonaesthetic but functional materials, e.g., composites in prosthodontics (dentures) or orthodontics (retainers). The introduction of fibers is difficult as the length of fibers usually exceeds the millimeter, and their diameter is in the tens of micrometers (Fig. 2.9). The random orientation of fibers prevents packing, resulting in potential voids. In resin composites, the presence of fibers is associated with rough surfaces [46] and poor wear resistance [47].

#### 2.3.3.2 Clusters

So-called (nano)clusters are fillers composed of submicron particles that are agglomerated after sintering or chemical binding. These clusters are



**Fig. 2.9** Fracture interface after 3-point bending testing of a fiber-reinforced dental composite (Xenius, GC)

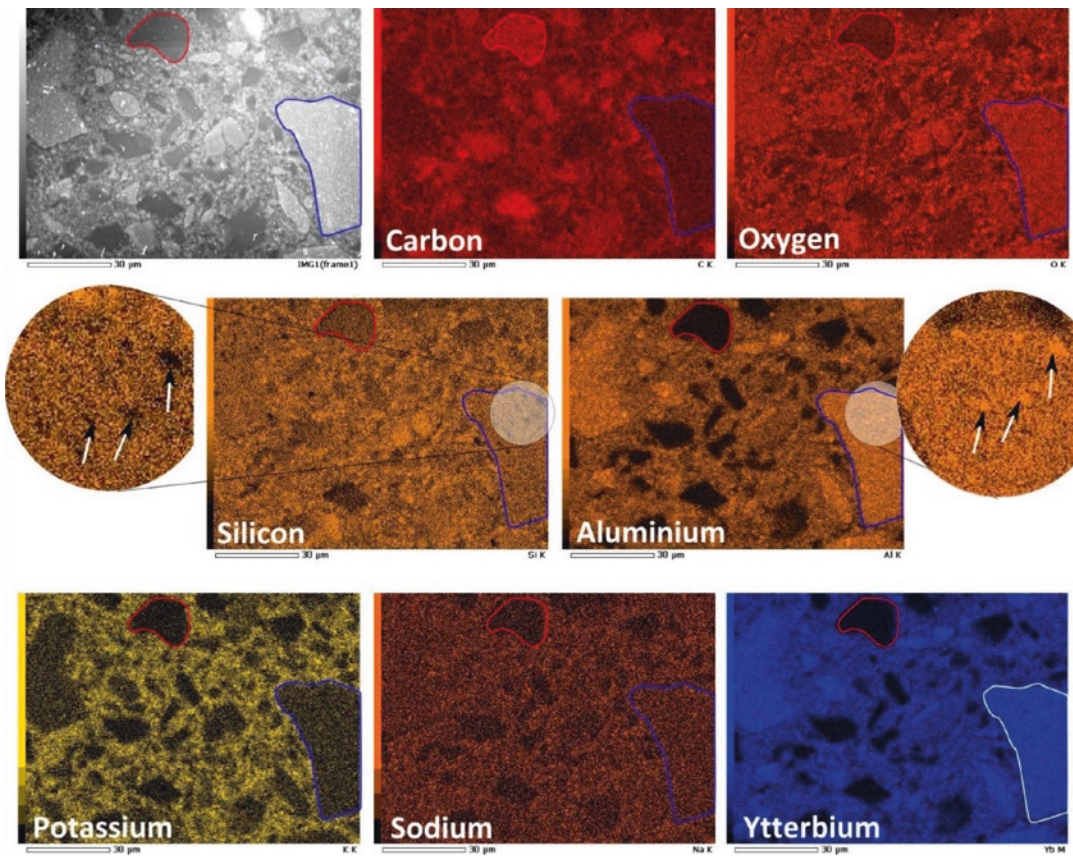
proposed as a solution to improve the strength of composites: upon meeting a cluster, a growing crack would have to physically separate the clusters into aggregates of smaller size to progress, an energy-consuming mechanism. Thermally processed clusters, sintered particles, can be viewed as ceramic fillers. Depending on the glass composition of the particles, some amount of crystallinity could be expected [31].

### 2.3.3.3 “Pre-polymerized” Fillers

The aesthetic quality of a composite relies on several factors, most noted previously and related directly to fillers. Maintaining high filler contents can also prove difficult due to issues with filler dispersion. Manufacturers have introduced

pre-polymerized particles as early as the 1980s to solve these problems.

Pre-polymerized fillers (PPFs) are ground, cured resin composites, which may be originally filled with nano- and/or micron-sized particles (Figs. 2.7 and 2.10). These PPFs are clearly distinguishable from “structural” fillers (see EDX map in Fig. 2.10), which are added in the final resin composite along with PPFs [48]. The size of PPFs usually exceeds 10  $\mu\text{m}$  (Fig. 2.10) and can serve to increase light scattering and diffuse reflection for an improved optical matching with dentin and enamel tissues. Resin composites containing PPFs are also known to exhibit higher polishability and luster and usually designed for anterior application [48]. Adding PPFs however decreases the elastic



**Fig. 2.10** EDX analysis of a polished resin composite commercial material containing pre-polymerized fillers (PPF). Two different types of PPF are outlined in the micrograph. In *red* is a nano-filled particle (carbon-rich, with some silicon but no glass, i.e., Al, K, Na, Yb-poor),

and in *blue* is a nano- and micro-filled particle (from a hybrid resin composite, i.e., carbon-poor and composed of glasses containing silica, alumina, sodium, and ytterbium oxides). The *arrows* in magnified areas point to alumina particles. The scale bar is 30  $\mu\text{m}$  in all pictures

moduli and resin composites with PPFs that typically absorb more water than those which do not [29]. Further, the PPF integration in the resin is poor without treatment as the functional groups already reacted during their preparation.

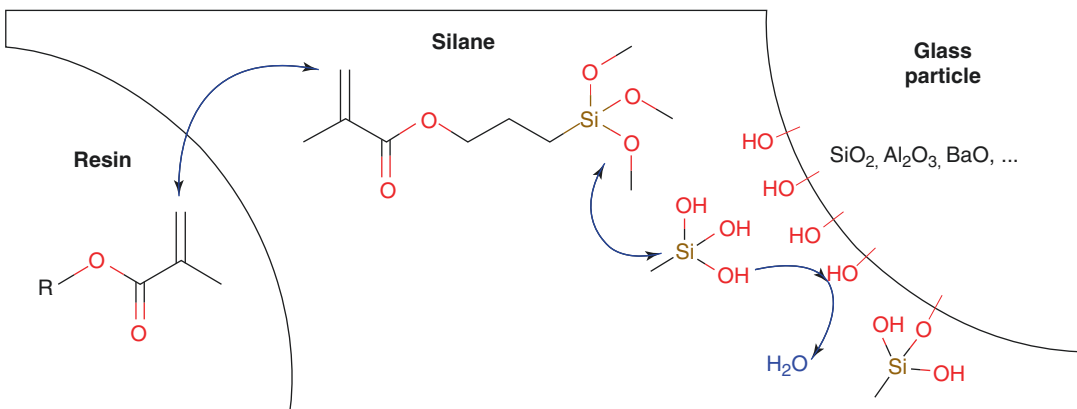
## 2.4 Functional Silane Chemistry

The mechanical performance of dental resin composites depends largely on the interaction, or lack thereof, between filler particles and the resin matrix. When stressed, the phases in a composite share the forces applied to different extents depending on their relative intrinsic mechanical properties. Stress distribution and transfer between phases are crucial in the performance of resin composites. In dental composites, the disparity in elastic modulus between the fillers ( $\gg 10$  GPa) and that of the resin (1–3 GPa) indicates that under iso-stress, i.e., a homogeneously distributed stress, the matrix will deform to a greater extent [49]. This may compromise particle-resin cohesion, creating voids and/or accelerating the deterioration of the material. To promote the interaction between the inorganic and organic phases, fillers are silanized, to enhance particle wetting and chemical binding to the matrix. Silanization increases the overall strength of a resin composite by about 50% [50].

Most silanes used in dentistry are difunctional molecules: one end presents one or more reactive groups (methacrylate, acrylate, epoxy, etc.) to bind with the resin phase, while the other end can bind to –OH groups at the surface of the glass (oxides, mostly silica) or metals. A typical structure of a methacrylate-functional silane is presented in Fig. 2.11.

Both the core and ends of silanes can be modified to adapt their suitability with regard to resin or filler composition:

- Regarding the resin phase, the chemistry of silanes greatly influences particle wetting and is hence a crucial parameter. For relatively hydrophobic resin blends such as BisGMA/TegDMA, the silane  $\gamma$ -MPS has been deemed suitable for decades. A longer alkyl spacer, more hydrophobic, may be even better suited. Extending chain length to ten carbons was associated with improved flexural strength and, equally important, higher filler loading due to improved wetting by the resin [51]. Further, the structure of silanes influences water sorption and potentially the stability of a composite. For example, water sorption of experimental resin composites based on  $\gamma$ -MPS is lesser than with UDMS (shown in Fig. 2.4) [52]. Reducing the hydrophilicity of



**Fig. 2.11**  $\gamma$ -(methacryloxy)propyltrimethoxy silane ( $\gamma$ -MPS), a typical molecule used in dental materials, with one methacrylate end to react with the resin phase and

another, hydrolysable  $\text{Si}(\text{OCH}_3)_3$ , that can react with conventional silica-based glass particles

the silane layer may be associated with increased durability [53].

- In order to improve the efficiency of silanes, the number of functional groups per molecule can be increased such as with UDMS (Fig. 2.4). This higher functionality and cross-linking potential may be associated with composite that is less prone to swelling [52].

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