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Composites dentaires

Frédéric Chaput, Anne-Charlotte Faure

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Dental composites

by **Frédéric CHAPUT**

PhD in ceramic materials science, Research director at the French national scientific research centre (CNRS)
Laboratoire de Chimie, Ecole Normale Supérieure de Lyon, France

Anne-Charlotte FAURE

PhD in inorganic chemistry
Head of research and development
ITEN, Dardilly, France

Abstract Dental composites are organo-mineral filling biomaterials used for the restoration of damaged teeth. They are, among other things, intended to replace amalgams, while preserving the healthy tissues to which they are bound via an adhesive. This field is at the crossroads of many disciplines: solid-state chemistry, organic chemistry, materials chemistry, colloid chemistry, soft chemistry, solid mechanics, optics, rheology, physics of granular media and biology. This contribution describes the evolution of dental composites from their origins, with emphasis on their structures, preparations, properties and clinical indications.

Keywords : restorative dentistry ; composite ; polymers ; (nano)particles.

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In addition to the constraints related to chewing, our teeth are subjected to multiple stresses day after day that can cause irreversible damages. Shocks or inappropriate mechanical stresses can lead, in the medium to long term, to the fracture of a tooth. A sugar rich diet, poor oral and dental hygiene, certain types of addictions can cause tooth decay with multiple health consequences. Tooth decay is the third most common pathology in the world. For example, 92% of French people have already suffered from caries, and eight out of ten on several occasions! All of these inconveniences require more or less complicated to implement care, depending on the extent of damage to the tooth and their position thereon. In the past, practitioners only had amalgam or poorly controlled or expensive restorative materials at their disposal. The unsightly nature of the resulting repairs, combined with the necessary sacrifice of healthy tissue led researchers to develop, since the mid-1950s, an alternative and high-performance solution: dental composites. These biomaterials have been developed in conjunction with the chemical treatment of teeth on the one hand and dental adhesives on the other

hand. It then became possible to make the restoration adherent, the healthy tissue economy in this field was born.

After a brief history of the field of dental restoration and some definitions, the article focuses on the different classifications of dental composites. It then aims to describe in details to the readers (and potential patients), to the practitioners or to the actors of the materials development, the composition and the properties of the dental composites. The article also aims to show the multidisciplinary nature of this topic that has led to the optimization of current dental composites and to the revolution that these materials represent in restorative dentistry.

Note: the reader will find at the end of the article a glossary of technical terms discussed throughout the article.

1 Background, definitions and locations of restorations

The development of viable solutions in the field of dental restoration has mainly been guided by the ease of implementation, availability and physico-chemical properties of the materials studied. Silver-mercury amalgams, still used today, have significant drawbacks for patients, including toxicity, poor aesthetics and lack of adherence to dental tissues. Furthermore, the implementation of this filling material requires the sacrifice of healthy tissues in order to obtain optimal cavity geometry. The first aesthetic alternatives to amalgam were based on silicate cements; however, the latter suffered from several defects including their delicate implementation, their poor mechanical properties (not all), their oral solubility and poor adhesion; they were quickly abandoned. From 1930 onwards the use of resins in particular acrylic and / or methacrylic was considered. These resins were tested with moderate success to reach the following conclusions: significant polymerization contraction (> 6% by volume), significant thermal expansion in comparison with the tooth, poor mechanical properties, lack of adhesion to dental tissues and carious resurgences. Despite their flaws these organic-based resins had desired qualities: ease of use, insolubility in the mouth and elasticity. The idea then came, in the middle of the twentieth century, to combine within the same material the advantages of mineral compounds (mechanical and optical properties, physico-chemical stability in particular) to those of organic resins (simplicity of implementation) [1]. Thus, a number of research projects were initiated on composite resins composed of several elements of different nature and whose physicochemical properties are far superior to those of their components taken individually. In this research, the optimization of monomers dedicated to dental applications (Synthesis of Bis-GMA for example by Bowen) played a preponderant role [2]. In addition, the advent of adhesive dentistry (etching and adhesives), combined with this research, has opened the door to tissue economy [3]: the practitioner adapts to the cavity and no longer adapts the cavity to the material. The convergence of all these key points has given birth to a multitude of high-performance dental composites and a wide range of possible restorations. Finally, the enamel and dentine that support these synthetic composites are themselves composite materials consisting of hydroxyapatite crystals ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, 70-96% by weight) associated to an organic part (collagen, proteins, phospholipids). Figure 1 shows the evolution over time of materials for direct dental restoration by emphasizing the evolution of dental composites and related issues.

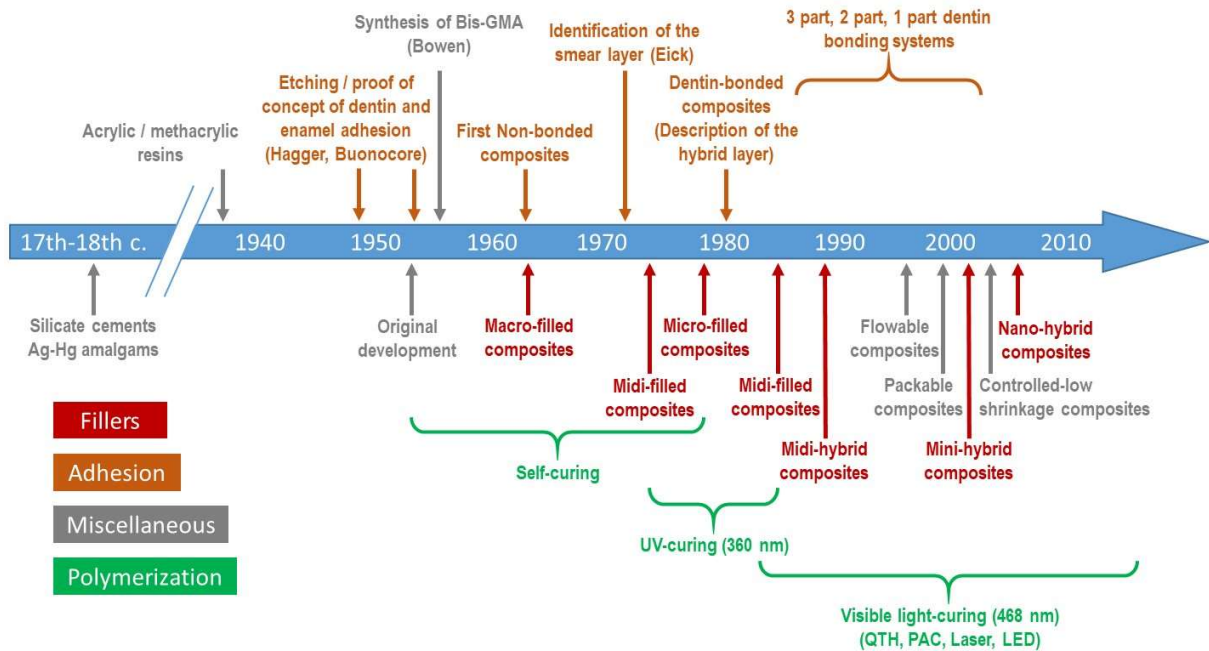


Figure 1 - Evolution over time of materials for direct dental restoration (Adapted from [4]).

A dental composite is by definition an organo-mineral biomaterial composed of a resinous matrix in which predominantly mineral fillers are dispersed. The binding of the latter with the matrix is provided by a coupling agent. The composites are bound to the dental tissues via an adhesive (Figure 2).

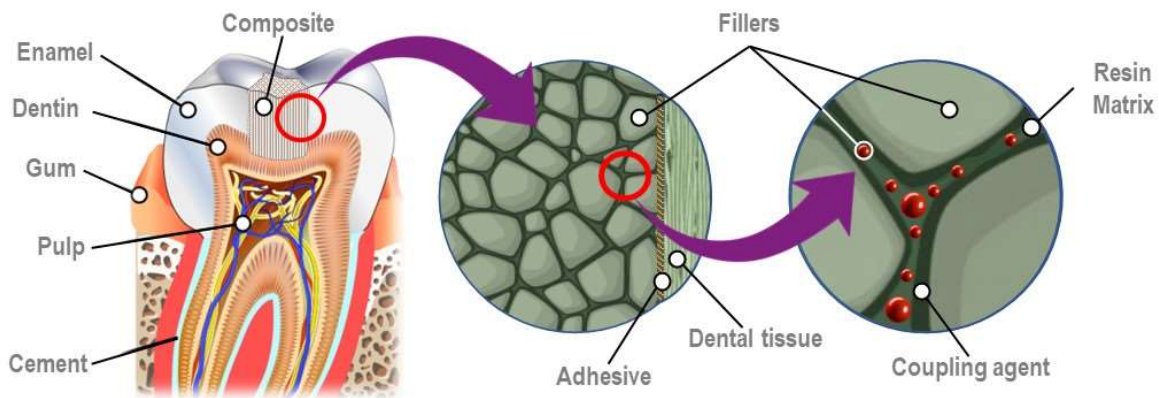


Figure 2 - The different components of the dental composite and the interface with the dental tissues.

Before acquiring all of their properties, modern dental composites are in the form of a paste of variable consistency depending on the type of restoration envisaged. Indeed, the choice of the restorative material among the different categories available, will depend on the nature of the lesion (mainly caries). A strictly topographical classification of carious lesions has been proposed by G.V. Black in 1908 [5]. This is the standard method used to identify carious lesions based on their location on the tooth surface (Figure 3). The following six classes of cavities are defined:

- Class I: cavity in pits or fissures on the occlusal surfaces of molars and premolars; facial and lingual surfaces of molars; lingual surfaces of maxillary incisors
- Class II: cavity on proximal surfaces of premolars and molars,
- Class III: cavity on proximal surfaces of incisors and canines that do not involve

the incisal angle,

- Class IV: cavity on proximal surfaces of incisors or canines that involve the incisal angle,
- Class V: cavity on the cervical third of the facial or lingual surfaces of any tooth,
- Class VI: cavity on incisal edges of anterior teeth and cusp tips of posterior teeth (class added later by W.J. Simon in 1956).



Figure 3 - Black's Classification of Caries Lesions (from illustrations of reference [6]).

However, this classification does not take into account the size of the lesions and their progression inside the tooth. This may be related to the fact that the dentist's act once consisted in eliminating the carious substance by shaping a filling cavity to the detriment of healthy tissue (very invasive model). The shape of the resulting cavity was dictated by the nature of the filling materials with scant regard for the durability of the repaired tooth. This strategy leads unavoidably to unnecessary tissue sacrifices. Silver amalgam and gold were at the time the only filling materials which, it should be reminded, have no adhesion property to dental tissues. With the evolution of dentistry, both in terms of materials and care, practices have changed markedly since the early 1970s. The bottom line is now the preservation of dental structures and the use of a composite is the result of an in-depth diagnosis described, for example, in the therapeutic decision guide of the SiSta concept (for Site/Stage) [7]. This concept, based on the Mount and Hume proposal, was born in 2006. The resulting classification is based on the principles of tissue economy, adhesion and biointegration. It defines carious lesions by site and by stage of development. It includes an initial stage (stage 0) for lesions which do not require invasive treatment (application of fluoride). Figure 4 shows the areas concerned and the degree of advancement of the carious lesions.







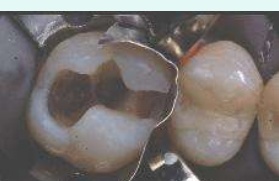

Stages ↓		Sites of carious lesions		
				
		Site 1 : Occlusal	Site 2 : Proximal	Site 3 : Cervical
0	 No cavity	This initial stage of demineralization, called white spot, refers to reversible enamel damage, without visible cavity. This is reflected in a surface porosity of the enamel. These lesions are usually found at the neck of the teeth, on the proximal surfaces and on smooth surfaces.		
1	 Minimum cavity	Microcavities on the surface that can reach the outer third of the dentin. Destruction of enamel, absence of pain.		
2	 Medium cavity	Medium-sized cavity up to the middle third of the dentin without weakening the cusps. Dentin, which is softer than enamel, is damaged. At this stage, the lesion will be able to progress deeply within the tooth. Hot, cold, sweet and acidity all cause pain.		
3	 Enlarged cavity	Large cavity that can reach the deep third of the dentin and weaken the cusps. The bacterial invasion progresses to attack the pulp. The toothache that can result from it will cause violent spontaneous pains.		
4	 Extensive cavity	Cavity that can reach the parapulpal zone ; part of the cusps is destroyed. Bacterial proliferation can progress to tissues close to the affected tooth (ligament, bone, gum) and cause tooth abscess with serious consequences.		

Figure 4 - Illustration of the SiSta concept (source of illustrations [8] [9]).

For large cavities, dental composites will not be used in direct restorations. When caries destroy the whole of a point of contact, the whole of a wall, or have weakened one of the cusps of a tooth, the damaged part must be reconstructed using a prosthetic part in composite resin (with thermopolymerizable matrix) or ceramic (inlay/onlay Figure 5). In this indirect restoration technique, the tooth is kept alive, devitalization

and the prosthetic crown are avoided. This approach will not be detailed in the rest of the article: only the direct restorative technique will be discussed, which only involves intraoral procedures performed in one single session.

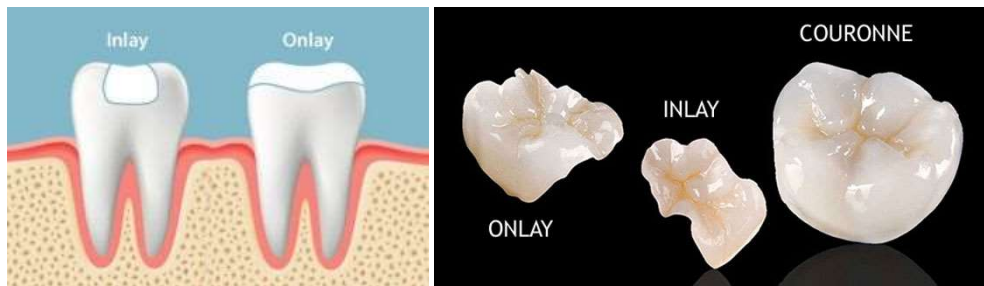


Figure 5 - Illustration of the concept of inlay/onlay and examples of prosthetic pieces (source of illustrations [10] [11]).

To remember

- Modern dentistry is based on the principle of tissue economy.
- A resinous matrix in which mineral fillers are dispersed, is the basis of dental composites.
- From the middle of the 20th century, the optimization of dental composites relied on innovative developments in various fields: monomers, mineral micro- and nanoparticles, polymerization initiators and dental adhesives.

2 Classifications

Currently, throughout the world, around forty manufacturers offer their customers no less than 200 dental composites [12]. In the latter, the resinous matrix is undoubtedly the weak link in the final materials. However, it plays a major role in the cohesion of all fillers, making its presence essential. Its proportion in the composites is minimized in favor of the fillers in order, on the one hand, to reduce the thermal expansion coefficient, the polymerization shrinkage and water absorption and on the other hand, to optimize the viscosity of the composite and the mechanical properties respectively before and after polymerization of the resin.

One thus realizes the important role played by fillers, the volume concentration of which can vary between 25 and 70%. They also present a variety of sizes, compositions, shapes and combinations of assemblies, which ultimately lead to essentially classify dental composites on the basis of their reinforcements, which will be discussed in the section devoted to fillers (§ 3.2). Other classification criteria exist, detailed below.

2.1 Classification according to viscosity

For a given restoration, the consistency of a composite is one of the practitioner's selection criteria. During the same operation, the practitioner can use several composites with very different consistencies. These are the result of an adjustment of the compositions by the manufacturers. Composites currently available on the market can be classified into three categories:

2.1.1 Medium viscosity composites:

These easy-to-handle composites (microhybrids) are said to be “universal”. Their viscosity is suitable for a large number of indications, both anterior and posterior. Moreover, their opacity is adjusted, by the manufacturers, according to the targeted clinical indication and/or the complexity of the colour shades to be reproduced (enamel,

dentin and intermediate opacity). The filler loading of these composites is of the order of 78% by weight; 60% by volume.

2.1.2 Flowable composites

These composites, which are mostly hybrids, are recommended for specific clinical indications (occlusal microcavities, slot cavities, cervical cavities or dentine substitutes, for example). Due to their fluidity, they show easy spreading, associated with good adaptation to cavity walls. These composites are useful for thin films. They are preferred in the step consisting in covering the bottom of the cavity before adding a more viscous composite. Moreover, it must be taken into account that they exhibit significant polymerization induced shrinkage (up to 5% by volume) and reduced mechanical properties (compared to universal composites) due to their low level of fillers (between 50 and 70% by weight and less than 50% by volume).

2.1.3 Condensable/packable composites

These composites were developed in the 1990s for posterior restorations in order to replace amalgams while trying to maintain their conditions of use (ease and speed of handling). Due to a high failure rate in clinical use, this type of composite has been phased out.

2.2 Classification according to the polymerization mode of the resinous matrix

For most monomers, polymerizations are carried out via the radical route, the first step of which, called initiation, consists of the reaction of a primary radical with the first molecule of monomer. Primary radicals are generally obtained by homolytic decomposition of an initiator. The steps of propagation (successive additions of monomer molecules to the active center) and of termination (disappearance or transfer of the active center to another molecule in the medium) subsequently terminate the polymerization. In the dental field, there are two modes of initiation that allow differentiating between composites:

- Chemical initiation after thermal or redox decomposition of an initiator
- Photochemical initiation after photochemical decomposition of an initiator

We can thus distinguish 2 + 1 classes of composites.

2.2.1 Composites with a chemopolymerizable matrix

In these composites, the generation of primary radicals is initiated chemically, generally from a peroxide type initiator (benzoyl peroxide for example). However, for these compounds the production of radicals is only optimal within a certain temperature range incompatible with the dental field ($T=85^{\circ}\text{C}$ for benzoyl peroxide). To accelerate the decomposition of the peroxides and thus allow their use in a more favorable temperature range, a decomposition induced by reducing agents is used. The latter (considered as coinitiators) together with the peroxides, constitute redox systems which must imperatively operate in a non-aqueous medium. The systems composed of peroxides (benzoyl peroxide, cumyl peroxide, tert-butyl hydroperoxide) and tertiary amines (N,N-Dimethyl-p-toluidine, 4-(Dimethylamino)phenylacetic acid) are the most commons. Figure 6 shows the schematic of the redox initiation reaction with benzoyl peroxide and N,N-Dimethyl-p-toluidine. The redox reaction takes place using the heat of the medium.

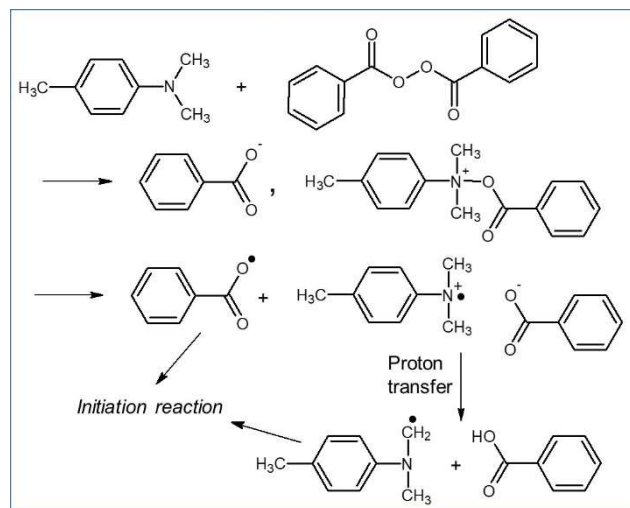


Figure 6 - Decomposition of benzoyl peroxide in the presence of N,N-Dimethyl-p-toluidine [13].

Composites with a chemopolymerizable matrix are available in the form of two components (either two pastes or one powder and one liquid), one containing the initiator, the other containing the coinitiator. The practitioner proceeds to their mixing at the time of his intervention. Mixing during this step results in the inclusion of air bubbles, which affect both the aesthetics and the strength of the material (oxygen being a polymerization inhibitor). After mixing, the processing time of the composite is limited.

2.2.2 Composites with a photopolymerizable matrix

In these composites the generation of primary radicals is photochemically initiated. Photochemical initiation resulting from the mere activation of monomers by photons is difficult to achieve. This is why these single-component composites contain a photoinitiator (usually camphorquinone, $\lambda_{\max}=466.5\text{nm}$). However, camphorquinone alone cannot photoinitiate polymerization effectively. Thus, for an efficient production of the radicals the photoinitiator is used in combination with a co-initiator, most often a tertiary amine such as 2-Dimethylaminoethyl methacrylate. The initiator radicals (a ketyl radical and a second radical) are then produced by hydrogen transfer between the excited species and a hydrogen donor as shown in Figure 7 in the case of camphorquinone in the presence of a tertiary amine. Among the most reactive donors are, in fact, tertiary aliphatic amines (hydrogen in alpha position of nitrogen).

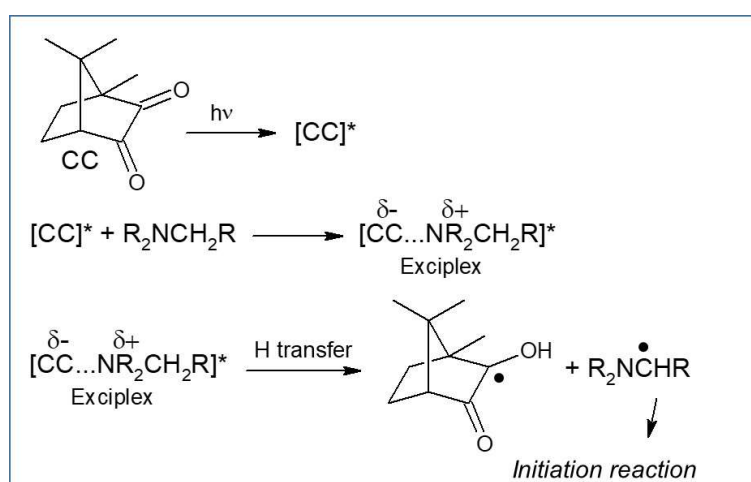


Figure 7 - Free radical formation assisted by a hydrogen donor in the camphorquinone-tertiary amine system [13] [14].

Composites with a light-curing matrix are in the form of a paste that can be used straightaway. The absence of mixing prevents the incorporation of bubbles within the paste. The practitioner also has complete freedom over the setting time. He can multiply the inputs of matter and shape the material as he wishes before irradiation. The latter is done today with LED curing lights (Figure 8).



Figure 8 - Photopolymerization step during the implementation of a dental composite [15].

2.2.3 Dual-cured resin-based composites

In these composites the generation of primary radicals is initiated both photochemically and chemically.

Finally, it should be noted that composites with a thermopolymerizable matrix have also been developed for the preparation of prepolymerized fillers or prosthetic parts (inlay/onlay). Primary radicals are initiated during thermal decomposition (between 50 and 150 ° C for peroxides) of the initiator (Figure 9).

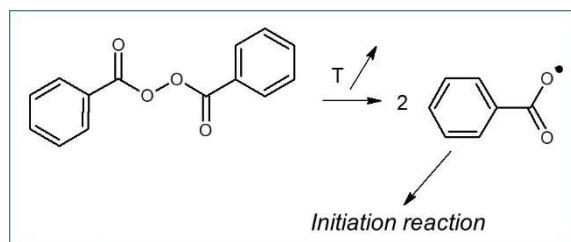


Figure 9 - Thermal decomposition mechanism of benzoyl peroxide [13].

2.3 Classification according to the clinical indication

For a medical professional, classification by clinical indications may be more appropriate. Each step of the planned restorations must follow a precise protocol, in particular the association of the right adhesive system with the right composite(s). Figure 10 summarizes this classification.

Clinical indication	Type of composite	Set-up of the composite	Example
---------------------	-------------------	-------------------------	---------






Furrow sealing	<ul style="list-style-type: none"> - Nano-hybrid fluid composite - Opaque white - May contain fluor 	<ul style="list-style-type: none"> - Tooth cleaning - Enamel etching - Rinsing / drying - Application of the sealing composite - Light-curing (1 layer) - Possible polishing 	
Obturation for teeth of the anterior sector	<ul style="list-style-type: none"> - Universal nano-hybrid composites - Shapeable - Opaque (dentin) - Translucent (enamel) 	<ul style="list-style-type: none"> - Etching - Application of the adhesive - Application of composites, layering is carried out from the palatal face to the vestibular face - Light-curing of each increment - Finishing + polishing 	
Obturation for teeth of the posterior sector (small cavity)	<ul style="list-style-type: none"> - Nano-hybrid fluid composites - Opaque (dentin) - Translucent (enamel) 	<ul style="list-style-type: none"> - Etching - Application of the adhesive - Application of the composite (one to two layers) - Light-curing - Finishing + polishing 	
Obturation for teeth of the posterior sector (large cavity)	<ul style="list-style-type: none"> - combination of fluid nano-hybrid Bulk Fill composite and shapeable Bulk Fill composite. or - combination of fluid nano-hybrid Bulk Fill composite and shapeable nano-hybrid universal composite. - Opaque (dentin) - Translucent (enamel) 	<ul style="list-style-type: none"> - Etching - Application of the adhesive - Application of the fluid nano-hybrid Bulk Fill composite - Light-curing - Placing the shapeable Bulk fill composite or the universal nano-hybrid composite that can be shaped incrementally. - Light-curing of each increment. - Finishing + polishing 	
Stump reconstruction	<ul style="list-style-type: none"> - Dual-cured fluid Bulk-Fill composite. or - Shapeable Bulk Fill composite. 	<ul style="list-style-type: none"> - Placing the dental post - Injection of the dual-cured fluid Bulk Fill composite around the dental post or - Positioning of the shapeable Bulk Fill composite around the dental post - Light-curing - Sculpture of the stump 	

Figure 10 - Use of the different types of composites according to the clinical indication - examples associated with this classification (source of the illustrations [16]).

To remember
<ul style="list-style-type: none"> - Four types of classifications currently exist for dental composites according to their viscosity, their polymerization method, clinical indication and type of fillers. - The composites currently used have a medium to low viscosity. - Composites with a photopolymerizable matrix can be used without prior preparation, while their counterparts with a chemopolymerizable matrix require an indispensable preliminary phase, of mixing several components.

3 Compositions of dental composites

3.1 Resin

In small proportion compared to mineral fillers, this essential component causes degradation of some mechanical properties of the composite (resistance to wear for example). It is also the source of polymerization induced shrinkage and the stresses it generates. In the most commonly used photopolymerizable dental composites, the resinous matrix is obtained by polymerization of dimethacrylate monomers. The presence of two polymerizable functions borne by the same molecule makes it possible to generate an organic network with a high crosslinking density.

3.1.1 Polymerization of methacrylates

Methacrylates polymerize according to a chain polymerization reaction by a free-radical mechanism. The latter takes place in three stages: initiation, propagation, termination [J 5 830].

Various factors will depend on the nature of the monomer. The lower the molar mass of the monomer and the less rigid its structure, the higher its final degree of conversion will be [17]. Conversion of free monomers into macromolecules then into a polymer generates a reduction in the volume of the reaction medium called polymerization shrinkage. For the same functionality, the higher the molar mass of the monomer and/or the more crowded the molecule, the less the shrinkage will be. On the contrary, the higher the degree of conversion, the greater the shrinkage will be [17]. Since the dental composite is, at least in part, bound to its environment through the dental adhesive, polymerization shrinkage results in the development of stresses. These two phenomena, the consequences of which are detailed in Figure 11, are among the main sources of failure in restorations [18].

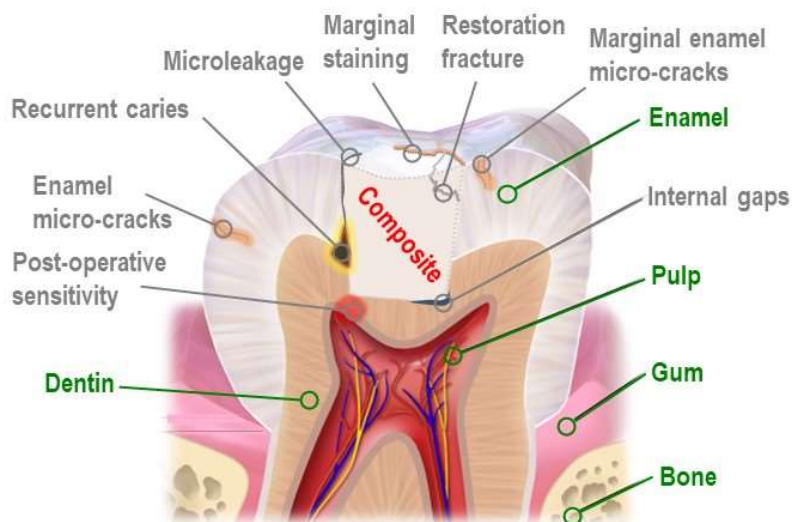


Figure 11 - Damage (marked in gray) caused by polymerization shrinkage and contraction stresses.

The appearance and intensity of these stresses are related to the change in the properties of the material formed during the polymerization process. This process can be divided into three phases [18] [19]. During the pre-gel phase, the molecules and macromolecules are mobile in a liquid medium, the viscosity of which initially depends on the mixture of monomers. The network continues to grow until it forms a macrogel that covers the full extent of the deposited composite. The gel point is then reached (at a degree of conversion equal to 5% for the methacrylates). The three-dimensional network formed is not yet rigid, it exhibits rubber-like behavior. From this point, the

volume shrinkage induces contraction stresses. When the degree of conversion continues to increase to a value close to its maximum the network becomes completely rigid. This phase is called **vitrification**. Network rearrangements are no longer possible or only possible to a limited extent. The volume shrinkage generated in this state of the material results in a very strong increase in contraction stresses. Thus, the more the gel point appears at high conversion degree and the more flexible the material formed (low Young's modulus), the lower the contraction stresses will be.

Obtaining a dense three-dimensional rigid network quickly limits the mobility of species and prevents the conversion of the monomers in their entirety. Thus, the maximum degree of conversion achieved for formulations based on dimethacrylates, used in direct restoration, is 75%. The unreacted C=C bonds (25%) are distributed on the one hand in the pendant bonds linked to the network (90%) and on the other hand in the free monomers (10%).

3.1.2 Specification of monomers

The specifications must meet several criteria [20]

- High degree of conversion (ideally > 60%) and high crosslinking properties (functionality ≥ 4): this will lead to an improvement in mechanical properties and reduction in unreacted monomers.
- The lowest possible volume shrinkage (ideally <7% for basic monomers) or expansion during the polymerization process: improving this property has been the main source of innovation in the field of monomers.
- Optimal mechanical properties and wear resistance once polymerized, especially in oral conditions.
- Glass transition temperature of the formed polymer above 60°C: the composite must not exhibit a rubber-like character under the conditions of use.
- Low water absorption of the polymer formed: this property is required to limit the passage of molecular species from the composite to saliva and vice versa.
- Stability of the polymer towards surrounding light over time (absence or limitation of degradation, possible sources of additional coloring): this is a required property in the case of anterior restorations where aesthetic character is essential.
- Stability during storage in the presence of inorganic fillers and additives: the monomers must neither degrade nor polymerize before use.
- Low oral toxicity, no mutagenic or carcinogenic effect of the monomers and the corresponding polymer.

Most of the commercial formulations are prepared from a small number of monomers (two to three), the chemical formulas of which are shown in Figure 12.

3.1.3 Commonly used monomers

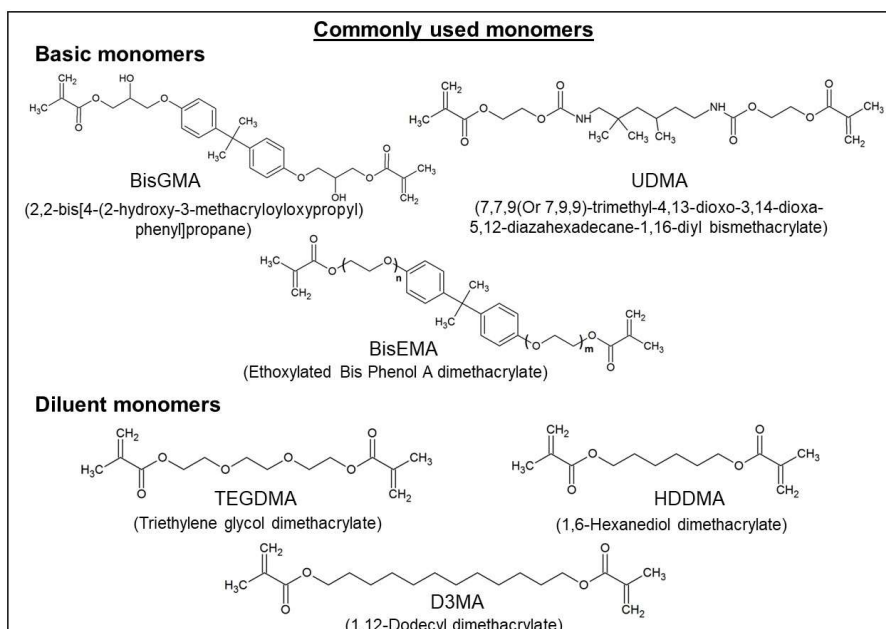


Figure 12 - Monomers commonly used for the preparation of resinous matrices.

The properties of the most common monomers are listed in Table 1 [20] [21].

Table 1: selected physico-chemical properties of dental monomers.

Monomer	Molecular weight (g/mol)	Degree of conversion (at room temperature)	Polymerization shrinkage (in volume %)	Viscosity (Pa.s)	Refractive index
BisGMA	512	56-66	6,1-6,6	500-800	1,550
UDMA	470	78-82	5,6-6,7	5-10	1,485
BisEMA	452-540	82-86	6,0	0,75-1,00	1,535
TEGDMA	286	68-85	13-14,3	0,008-0,100	1,461
HDDMA	254	74-78	10,7	0,007	1,458
D3MA	338			0,012	1,459

The historic monomer of dental composites, still widely used today is BisGMA (Figure 12).

Present in most formulations on the market, its use is currently under debate for public health reasons. Indeed, it is suspected of releasing bisphenol A (BPA), an endocrine disruptor, either as a synthesis residue or after degradation of the composite. The elution of BPA molecules from a BisGMA-based dental composite, however, remains widely controversial in the literature. Indeed, it is difficult to quantify such rates, that would be in any case very low. In addition, the results achieved depend on the test protocol implemented, especially with respect to the degradation of BisGMA. Currently, the only case where a high release rate of BPA molecules could be suspected would be the simultaneous presence of numerous and large composite-based restorations [18].

BisGMA was synthesized and patented by Bowen in 1962 [2]. The high molar mass as well as the rigidity of the molecule allow limiting the polymerization shrinkage [17]. However, this monomer exhibits too high a viscosity due to hydrogen bonds that establish between the alcohol functions. This viscosity as well as the molecular

crowding greatly reduces the mobility of BisGMA and therefore its reactivity (degree of conversion between 56 and 66%). Despite the high rate of unconverted functions, the mechanical properties of the obtained polymer are acceptable for a dental composite. Hydrogen bonds strengthen, for example, the structure of the material [19].

The UDMA monomer (Figure 12) was developed in 1974 by Foster and Walker [22]. It is used alone or in combination with other monomers. Its molar mass is close to that of BisGMA. Its more flexible structure than that of BisGMA would improve the resistance of the obtained polymer [17]. The reactivity of UDMA is higher than that of BisGMA and its viscosity is much lower (Table 1). There therefore remains less free monomers at the end of polymerization. In contrast, its low refractive index, which differs greatly from that of the fillers used, limits polymerization depth. **In terms of biocompatibility, degradation of UDMA would release HEMA (2-hydroxyethyl methacrylate) reported as being highly cytotoxic [17].**

BisGMA and UDMA are considered to be basic monomers in formulations, sometimes in combination with each other. BisGMA and to a lesser extent UDMA are not used in their pure form but rather in combination with diluent monomers which facilitate the introduction of mineral fillers and the handling of the formulations. Among the most common diluent monomers is TEGDMA (Figure 12) [17]. It is not very viscous and has a high reactivity. In return, the volume shrinkage that it generates is very high compared to BisGMA and UDMA (Table 1). **It is also toxic [23].** Due to the very strong affinity of polyether chains for water molecules, the presence of this monomer increases water absorption. To avoid this effect, hydrophobic diluents have been proposed such as HDDMA and D3MA (Figure 12) [23]. Among the basic monomers derived from BisGMA, BisEMA (for the most common molecule $n + m = 3$) (Figure 12) has a rigid structure associated with a lower viscosity than that of BisGMA (absence of alcohol functions). Thus, its presence lowers the viscosity of the mixture without too much increasing the shrinkage [18].

3.1.4 New monomers marketed / envisaged

The development of new monomers, some examples of which are shown in Figure 13, is driven by a constant concern to improve the properties of dental composites. The main motivation is to increase the durability of restorations with a reduction in collateral damage caused by polymerization shrinkage (between 2.2 and 3.2% for current microhybrid composites) and more specifically the constraints associated with this shrinkage [18] [24]. The objective of eliminating BisGMA (in relation with its potential toxicity) has also led to the development of new monomers.

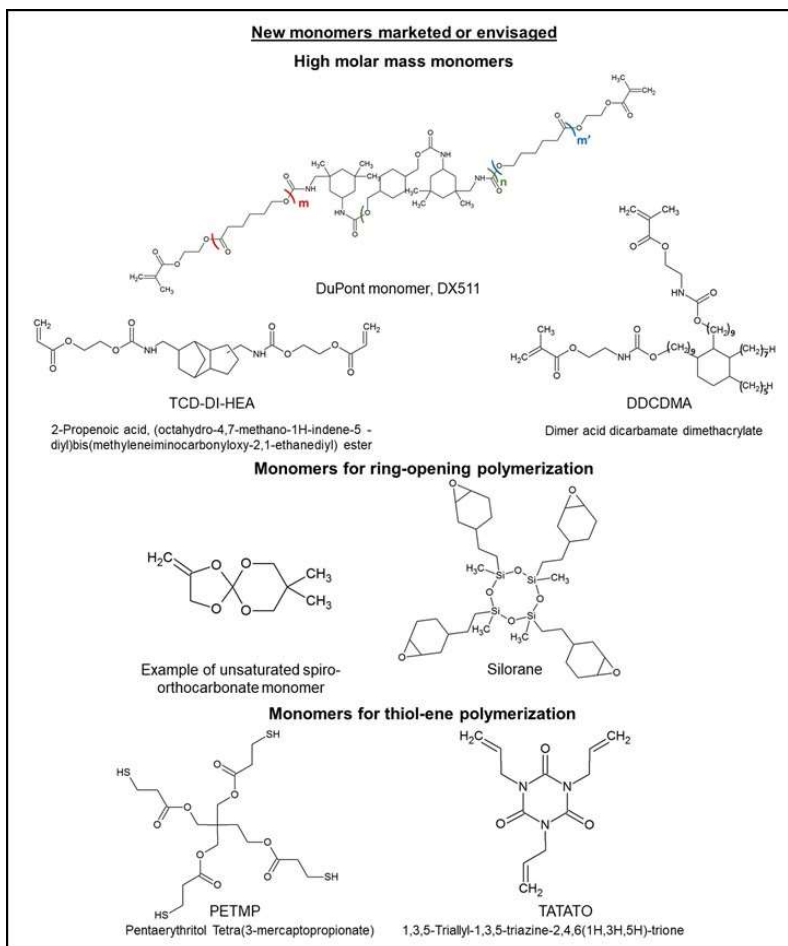


Figure 13 - New monomers, marketed and envisaged for the development of resinous matrices.

One of the ways envisaged for reducing shrinkage is to develop monomers combining a high molar mass and a rigid structure similar to that of BisGMA. The DX511 monomer (Figure 13) developed by Dupont has, for example, been introduced into formulations without BisGMA recently marketed. The molar mass of this dimethacrylate monomer ($\geq 1077\text{g/mol}$) is twice that of BisGMA. The lack of reactivity observed for monomers with high molar masses is here solved by the introduction of flexible arms carrying the methacrylate functions [18]. TCD-DI-HEA (Figure 13), another high molecular weight monomer (465g/mol), has also been developed for the preparation of new resinous matrixes [25]. This molecule includes three cycles which stiffen its structure. Its low viscosity allows it be used without diluent in combination with UDMA (20%) [18]. Despite the presence of terminal acrylate functions, studies have established the low toxicity of the monomer and the biocompatibility of the composite after polymerization [23]. DDCDMA (843g/mol), a hydrophobic monomer, is used as a diluent for a BisEMA/UDMA mixture in a commercial formulation [21] [26]. The latter exhibits a high degree of conversion ($> 80\%$, 72h after photoinitiation) associated with low shrinkage (2.4%) and low water absorption ($18\mu\text{g}/\text{mm}^3$) [27].

Unsaturated spiro orthocarbonate monomers [28] and siloranes [29] also constitute an interesting alternative to limit the polymerization shrinkage (Figure 13). Their ring-opening polymerization mechanism (example of the oxirane group borne by the silorane monomer in Figure 14) induces an expansion of the network which opposes the shrinkage. The commercial silorane-based formulation thus exhibits very low polymerization shrinkage, between 0.94% and 1.5% [27] [29].

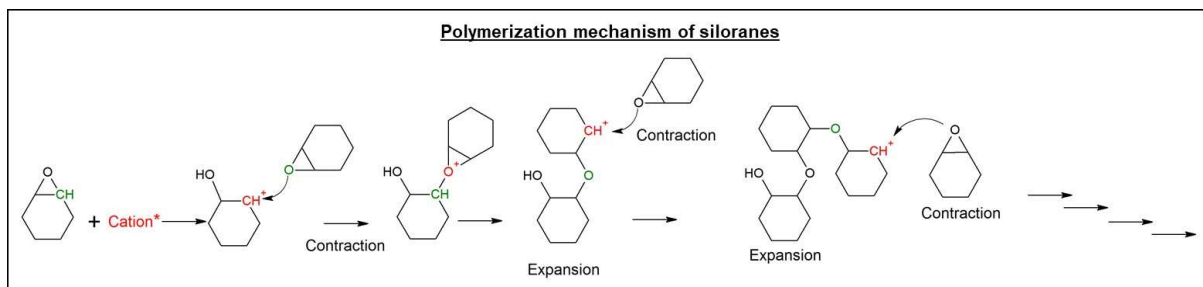
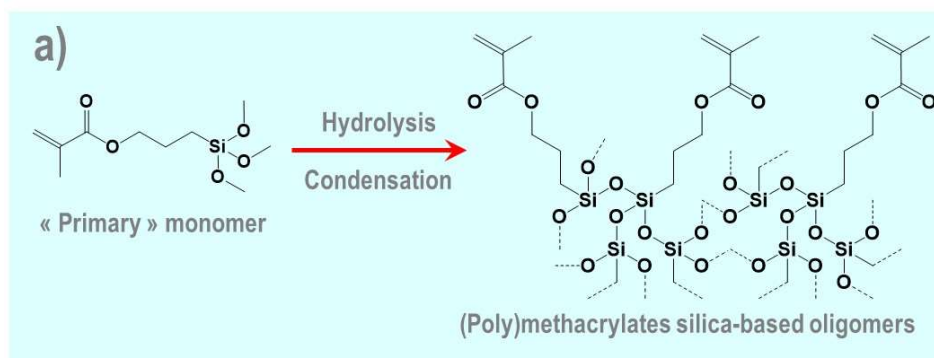


Figure 14 - Polymerization mechanism of siloranes (adapted from reference [30]).

The combination of PETMP and TATATO has also been considered to manufacture dental composites with low shrinkage (Figure 13). The polymerization of these compounds, called thiol-ene polymerization, proceeds according to a stepwise addition mechanism [AM3044]. This type of formulation achieves high degree of conversion while minimizing polymerization shrinkage and contraction stresses [31]. However, the strong smell of thiol-containing molecules and the instability of the components during storage have, among other things, doomed the development of purely thiol-ene resinous matrices. However, a strategy has been considered to take advantage of the benefits of thiol-ene polymerization by combining the PETMP and TATATO monomers with methacrylate monomers. The resinous matrix resulting from this mixture is obtained by a combination of chain polymerization and step polymerization [23].

3.1.5 Monomers for OrmoCer / new approach

For the preparation of matrices based on Ormocer, (an acronym for “ORganically MOfified CERamics”), the “primary” monomers are hetero-bi-functional molecules of the alkyl-trialkoxysilane type bearing one or more polymerizable organic groups (methacrylates) [32] [33] [34]. These monomers can undergo a hydrolysis-condensation step which leads to the formation of (poly)methacrylates silica-based oligomers (Figure 15-a). These consist of a three-dimensional polysiloxane network to which are attached, via an Si-C bond, the organic parts terminated by the methacrylate groups. During the implementation of Ormocers composites, micron-sized fillers (barium glass for example) as well as functionalized nanoparticles (SiO₂ for example) are dispersed in the Ormocer resin (Figure 15-b). The composites obtained after polymerization of methacrylates exhibit very low shrinkage (<1.5%) as well as high biocompatibility owing, in particular, to the absence of free methacrylate monomers (abundance of polymerization sites). In addition to the organic polymer, the presence within the resinous matrix of a polysiloxane network improves the wear resistance of the final material [35].



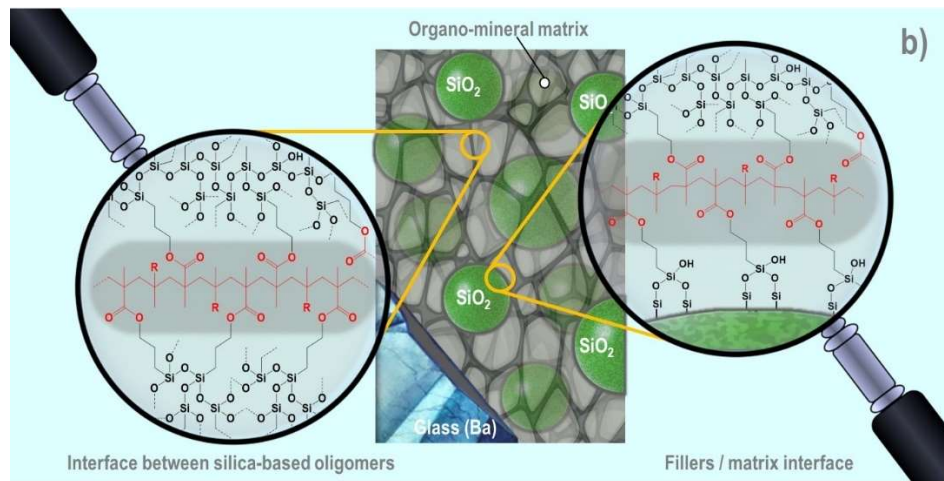


Figure 15 - a) Synthesis of (poly)methacrylates silica-based oligomers from 3-(Trimethoxysilyl)propyl methacrylate ; b) Schematic structure of an Ormocer (the organic polymer is shown in red).

3.2 Fillers

Currently-marketed composites differ mainly in the characteristics of the fillers they contain. The role of these fillers is to overcome the shortcomings (poor mechanical and thermal properties, for example) of the host matrix to which they are linked (chemically and/or physically). In addition, the fillers have a significant impact on the polymerization shrinkage and on the water sorption of composites. Thus, the composition, size, size distribution and mass or volume percentage of the fillers within the organic matrix define a wide range of composites. Table 2 gives an overview of the composition of these fillers [18] and specifies the terminology adopted to classify them according to their size. The term micro-filler, historical but ill-suited, is very often used to designate fillers in the size range 10-100nm.

Nano-filler <i>1-100nm</i>	Mini-filler <i>0,1-1µm</i>	Midi-filler <i>1-10µm</i>	Macro-filler <i>10-100µm</i>
<ul style="list-style-type: none"> - Colloidal SiO₂, - Colloidal ZrO₂, - Colloidal YbF₃, - Pyrogenic SiO₂ 	<ul style="list-style-type: none"> - Silicate, borosilicate or fluorosilicate glasses containing various elements (Li, Al, Ba, Sr, Zn, Yb, etc.), - Quartz, - SiO₂/ZrO₂, ZrO₂, Al₂O₃, TiO₂, - Glass ceramic, - Pre-polymerized filler, - Aggregates or agglomerates of nanoparticles (Silica, zirconia...), - YbF₃, YF₃, 	<ul style="list-style-type: none"> - Glasses, - Quartz, - Pre-polymerized fillers, - Porous fillers 	

The fillers are prepared by different techniques that the target size may impose. To this end, two approaches can be considered: the so-called top-down approach and the so-called bottom-up approach. The "top-down" approach is by far the oldest and most tested for the preparation of powders. The ceramics industry, for example, frequently uses this approach for the development of its raw materials. It consists of gradually fragmenting a coarse micron powder until the size of its particles reaches the submicron scale. This is done using mills, the efficiency of which has improved significantly over time. High-energy grinding is one of the main techniques used in this context. The coarse particles are subjected to huge mechanical stresses in the grinding

chamber (shocks, friction, shearing, compression, etc.) which result in the appearance of defects (broad particle size distribution, pollution, sharp-edged particles, etc.) the presence of which can be constraining for some applications. Moreover, these techniques, which are often long, are restricted to fragile materials and do not allow control of the morphology of the obtained particles. A step to select a size range may then be necessary, by sieving for example. Thus, in the case of glasses, the obtained particles appear in the form of angular objects with no noticeable shape. A less sharp-edged (rather spheroidal) geometry is however sought to limit the areas of stress concentration within the final material. Even if current size reduction technologies allow these geometries to be obtained, the latter can be advantageously prepared by other techniques, in particular by a bottom-up approach. The "bottom-up" approach comes from research laboratories and has become more and more sophisticated with the advent of nanoscience. As its name implies, materials are built atom by atom, molecule by molecule, or cluster by cluster. The assembly of atoms, molecules or clusters is carried out in a perfectly controlled manner, thus allowing the development of functional objects whose structure and morphology can be fully mastered. The sol-gel process or the colloidal synthesis for example, representatives of "soft chemistry" and the bottom-up approach, are mature techniques for the development of fillers (SiO_2 , ZrO_2 , TiO_2 , YbF_3 , etc.) used in dental composites. Figure 16 shows examples of silica, ytterbium fluoride and zirconia nanoparticles, prepared by colloidal synthesis.

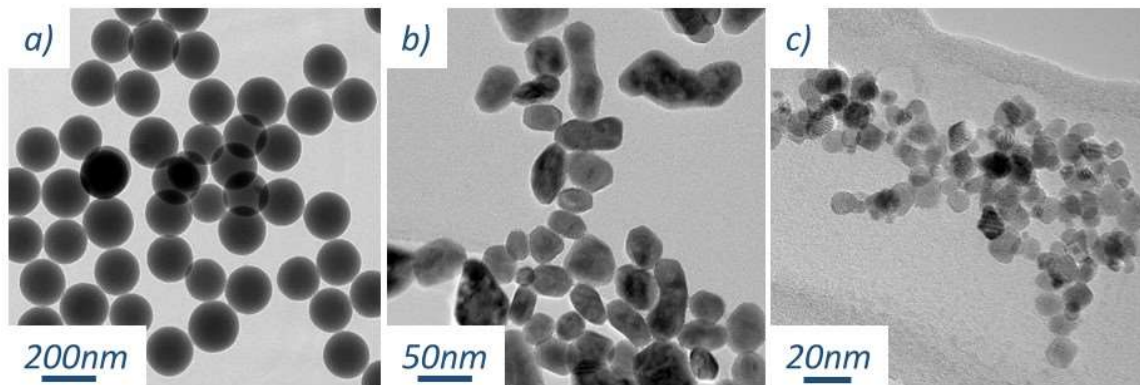


Figure 16 - Nanoparticles of : a) Silica; b) Ytterbium fluoride; c) Zirconia (source of illustrations : Chemistry Laboratory of the Ecole Normale Supérieure de Lyon).

Some of these nanometric fillers (SiO_2 , $\text{SiO}_2/\text{ZrO}_2$) can be assembled into more or less porous structures, at the time of their synthesis or by subsequent sintering (Figure 17a) [36]. Introduced into the resins, as micron or submicron sized fillers, these aggregates or agglomerates of nanoparticles combined with isolated nanoparticles, make it possible to achieve high filler loading while maintaining an acceptable viscosity for easy handling. The resulting composites demonstrate attractive aesthetics and polished state retention, similar to their micro-filled counterparts, while maintaining high physical properties comparable to those of hybrid composites [37].

With the same purpose, prepolymerized fillers are also used as complex fillers. They are developed using a top-down or bottom-up approach [38]. In the case of the top-down approach, a block of composite material containing a high concentration of micro-fillers (70% by weight), is prepared by thermal polymerization. The block is then ground in the form of micron sized powder with sharp-edged geometric shapes (Figure 17b).

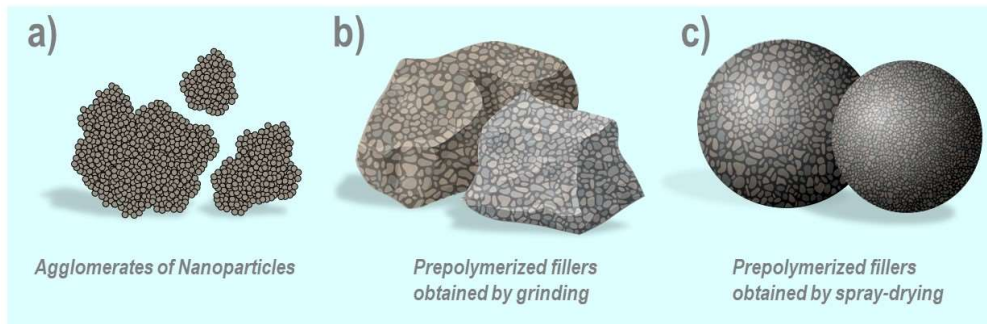


Figure 17 - Pre-assembled nanoparticles in a) agglomerates, b) prepolymerized fillers obtained by grinding and c) prepolymerized fillers obtained by spray-drying.

In the bottom-up approach, spherical particles are obtained after spray-drying a solution containing submicron glass particles and/or nanoparticles suspended in a mixture of monomers and a solvent. The particles thus produced are heat treated to complete the polymerization initiated during atomization (Figure 17c). Figure 18 shows an example of such prepolymerized fillers and their embedding into a composite.

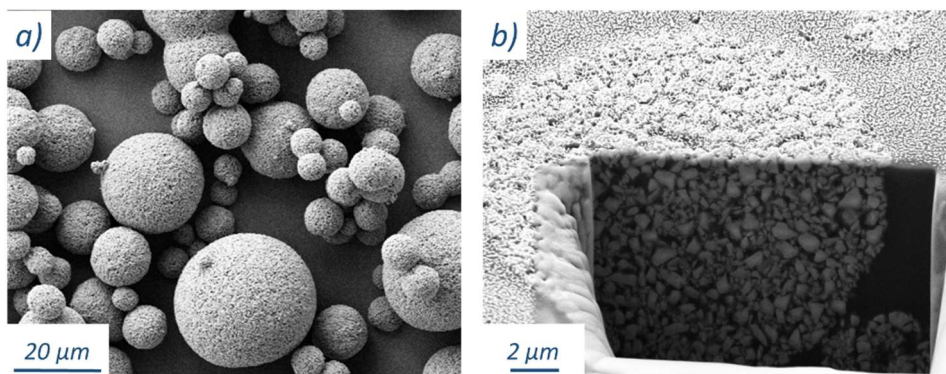


Figure 18 - Prepolymerized fillers observed by scanning electron microscopy: a) Individualized and b) Inserted in a resinous matrix (from the Dentsply Sirona illustrations).

Fillers dispersion in the monomers is a key step in the preparation of a composite. When formulating a composite, it is important not to overload it, since the wetting of the surface of all particles is essential, and this point is exacerbated when the fillers are very small. A material containing only partially wetted fillers would then exhibit poor physical and mechanical properties. The monomer concentration required to cover the filler per unit area varies from matrix to matrix and from filler to filler. This step of intimate mixing between fillers and monomers is carried out using tools that are adapted to the nature of the fillers. Thus, the smallest fillers (nanometric) are, in the most favorable cases, introduced into the monomers mixture in the form of colloidal solutions. We are then in the presence of two perfectly miscible liquids. The solvent in the colloidal solution, which is used to transfer the nanofillers into the mixture of monomers, is removed under vacuum using a rotary evaporator. After this step, the stability of the particles is ensured by coupling and/or compatibilizing agents which will be detailed below. Subsequently, the largest fillers are introduced into the colloidal solution made up of the nanofillers dispersed in the mixture of monomers. The homogenization and deaeration (removal of air bubbles) of the paste obtained are carried out in a planetary mixer (Figure 19) or in devices with equivalent functions.

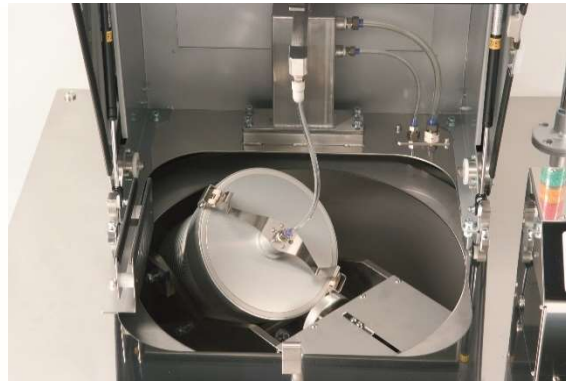
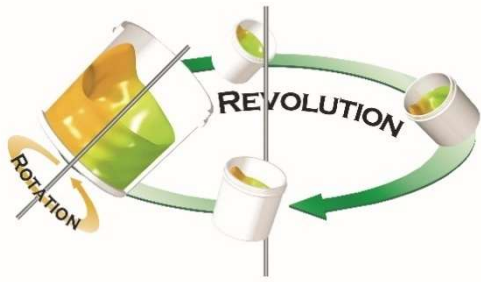


Figure 19 - Operating principle of a planetary mixer and photograph of a commercial model (source of the illustrations [39]).

The more or less viscous pastes resulting from these different sub-steps also contain additives that are necessary to preserve the product and to adjust the properties related to aesthetics. The pastes thus formulated are packaged into syringes (Figure 20). These are installed in a dispensing gun and equipped with tips of different geometries to facilitate the laying of the composite (Figure 20).

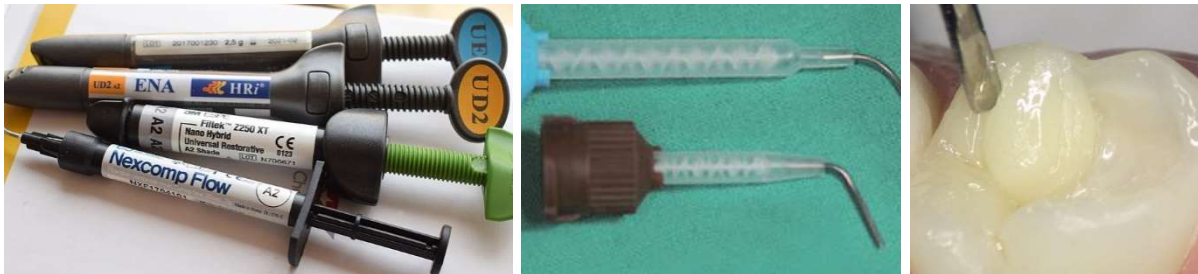


Figure 20 - Dental composite conditioning syringes, examples of dispensing tips and step of laying a composite (source of the illustrations [16] [40] and Dentsply Sirona).

Figure 21 shows the evolution of the micro (nano) structures of composites over time as a function of the fillers incorporated. The choices made regarding the fillers incorporated within the final materials have been largely driven by the availability of these fillers at the time of the composites manufacture. Thus, the first so-called "macro-filled" composites used large-sized fillers, the interparticle space of which was occupied by the polymer matrix. This mismanagement of the optimization of granular stacking led to poor properties of the composite. As with high performance concretes, the approach adopted to improve the compactness of fillers and therefore their physicochemical properties, refers to that followed by the Ancient Greek geometer, Apollonius of Perga. The latter asked himself the following question: "How to pave a flat space with disks of all sizes, ensuring that the gaps between the disks occupy a minimum area?". The scientist then proposed a basic pattern made up of three circular elements between which is inscribed a fourth which is tangent to them (Figure 22). Of course, in the case of dental composites, the industrial context requires the use of fillers with often irregular shapes but whose size distribution remains relatively narrow. Thus, a mixture of fillers of controlled size and of different nature cemented by the polymer matrix makes it possible to obtain composites with performances matching the dental field requirements.

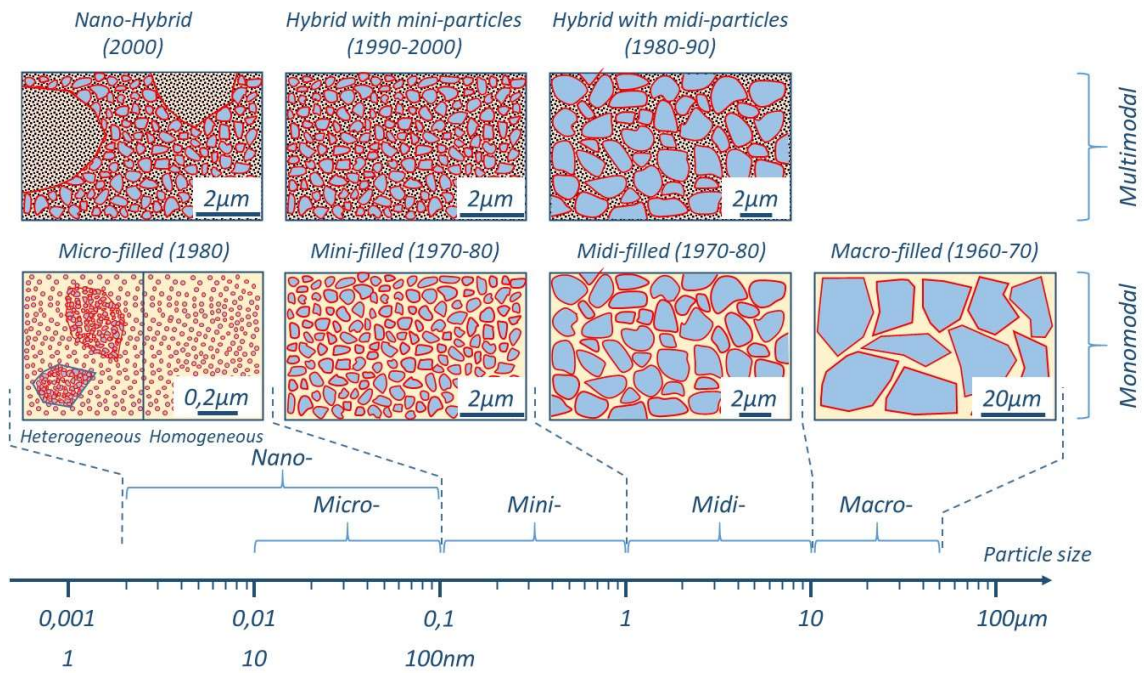


Figure 21 - Types of structures encountered in the field of dental composites as a function of the size of the fillers; the part in red represents the interphase in which the coupling agent is engaged (Adapted from [41]).

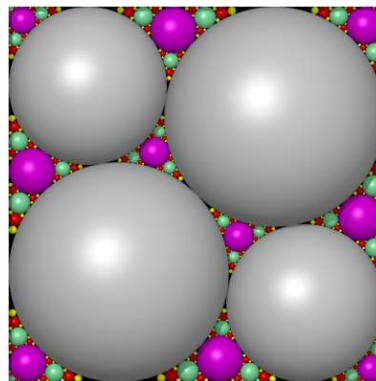


Figure 22 - Example of Apollonian packing (from illustrations [42]).

Thus, through a wise choice in the mixture of inorganic fillers available, the mechanical and optical properties of the composites can be perfectly optimized according to the restorations to be carried out. Depending on their size, particulate fillers can be divided into macro-fillers (10–100 μm , used in early restorative composites), midi-fillers (1–10 μm), mini-fillers (0.1–1 μm) and nano-fillers (1–100nm). As a reminder, composites incorrectly referred to as "micro-filled" contain particles in the 5–100 nm range. To improve handling properties and achieve a high filler loading, heterogeneous micro-filled composites may contain prepolymerized fillers obtained from a homogeneous micro-filled material. Micro-filled composites have poor properties due to their relatively low fillers content. They have been developed to meet the need for aesthetically pleasing composites with good polishability. Therefore, the currently available universal composites, usable for most anterior and posterior applications, are hybrids based on a mixture of mini-fillers and nano-fillers. They have sufficient mechanical properties as well as a satisfactory polishing ability. These micro-hybrid composites are called nano-hybrids when their filler level is enhanced by the addition of nanoparticles and possibly prepolymerized charges [23] [43].

Bulk Fill composites have been designed to simplify the implementation of posterior restorations, especially for the treatment of large cavities. The aim is to replace conventional composites, the installation of which is carried out using an incremental technique (superimposition of layers whose thickness is limited to 2 mm). This technique, complicated to implement, is time consuming and can generate discomfort and additional costs for the patient. The currently developed Bulk Fill type composites have a significant depth of cure (from 4 to 5 mm), a rather limited volume shrinkage (1.6 to 2% for materials of medium viscosity, 2.5 to 4.1% for fluid materials) as well as a restricted choice of shades (four shades maximum). The increase in the depth of cure was obtained by improving the materials translucency (perfect match between the refractive indices of the matrix and the fillers, use of nanometric fillers, reduction of the filler loading for fluid composites, etc.) and in some cases by optimizing the photoinitiator (high absorption coefficient at λ_{max}). Medium viscosity Bulk Fill composites may require prior installation of a layer of fluid composite which will release contraction stresses. Fluid composites, for their part, must be combined with a conventional micro-hybrid composite which will be polymerized on the surface of the restoration (2 mm thick layer) in order to reinforce the mechanical properties (stress resistance and wear resistance in particular) and the aesthetic properties, compromised in some cases by the high translucency of the Bulk Fill material [44].

The dispersion of fillers within the monomers requires modifying their surface with a coupling agent in order to ensure compatibility of the inorganic part with the organic part. This agent is often a hetero-bi-functional molecule which ensures the cohesion between the mineral fillers and the organic phase [45]. A purely mechanical anchoring of fillers was also envisaged using, for example, porous or rough fillers [46]. If there is no bond between the resinous matrix and the fillers, the fillers become stress concentrators and there can be no stress transfer within the material. Apart from the fact that the coupling agent allows anchoring of the fillers to the organic part, it improves their hydrophobic character and minimizes their aggregation. Thus, an optimal fillers distribution can be obtained, which is very important for the properties of the final material. All the points mentioned above become crucial and the coupling agent plays a major role when nanoparticles are present within the composite. In fact, the filler/matrix interfacial area then becomes significant. For nanoparticles, the extremely high surface/volume ratio leads to the incorporation of a higher percentage of coupling agents compared to composites containing fillers of micrometric size. Obviously, the bifunctional molecules used as coupling agent must have an affinity for the surface of the mineral fillers. Thus, for silicate fillers, the coupling agents are evidently silanes, some examples of which are shown in figure 23 [47].

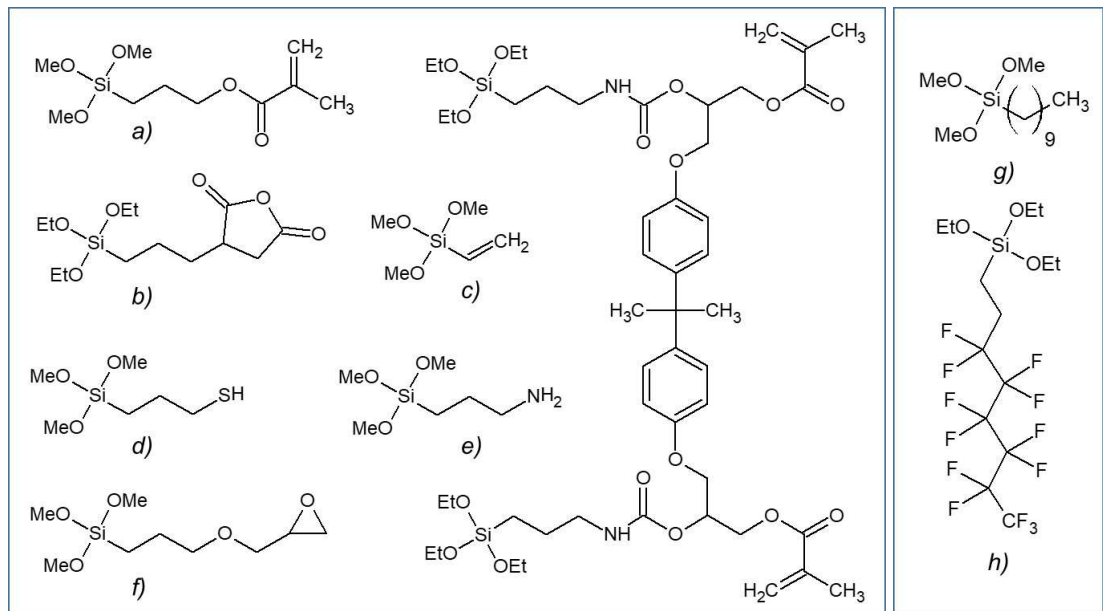


Figure 23 - Examples of coupling agents.

Alkyl-trialkoxysilanes with various functional groups:

a) 3-Methacryloxypropyltrimethoxysilane, b) 3-(Triethoxysilyl)propylsuccinic anhydride, c) Vinyltrimethoxysilane, d) (3-Mercaptopropyl)trimethoxysilane, e) (3-Aminopropyl)trimethoxysilane, f) (3-Glycidyloxypropyl)trimethoxysilane;

Alkyl-trialkoxysilanes without functional group:

g) n-Decyltrimethoxysilane, h) 1H,1H,2H,2H-Perfluorooctyltriethoxysilane.

The fillers functionalization is carried out in most cases in solution from the dry powders in a solvent medium and in the presence of water and a catalyst. The type of solvent (polar vs non-polar), the nature of the catalyst (acid vs base), the amount of water, the amount of silane, the temperature are important parameters that will determine the type of interphase generated. The grafting mechanism consists first of all in the hydrolysis of the alkoxy groups of the silicon alkoxide. The hydrolysis products can then condense on themselves and/or adsorb via hydrogen bonds to the surface of the particles. In a final step, the condensation between the hydrolyzed molecules and the silanol groups of the particles occurs. There is formation of a covalent bond between the inorganic structure and the organic group. This link anchors the mineral part to the organic network and prevents its release. Figure 24 shows the mechanism of grafting of a trialkoxysilane to the surface of a silicate material [48].

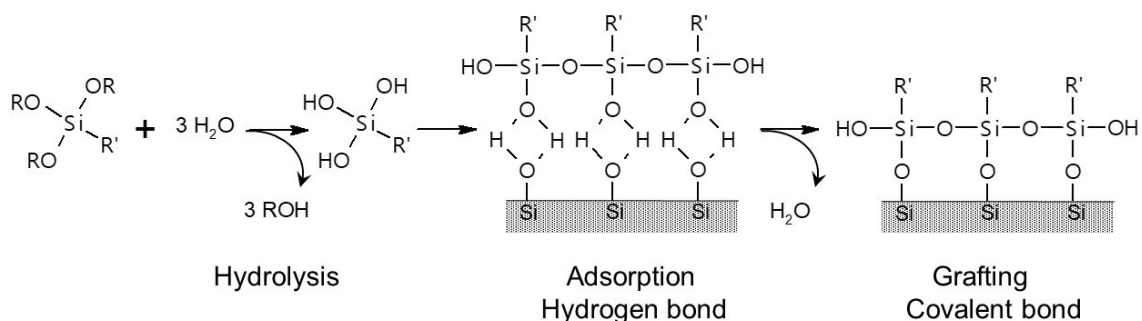


Figure 24 - Grafting mechanism of a trialkoxysilane to the surface of a silicate material [48].

However, this ideal representation poorly reflects the complexity of real reactions. For

multifunctional alkoxy-silanes, silanol groups remain in the grafted oligomers. They are likely to subsequently react with their counterparts to form siloxane bridges within oligomers or between oligomers without interacting with the surface of the particles. Thus, if the experimental conditions are poorly controlled, an extended three-dimensional layer will be present on the surface of the fillers, very far from the ideal coating presented in figure 24. Moreover, the hydrolysis of the bonds established between the fillers and the matrix can lead to the loss of cohesion of the organic and mineral phases, resulting in a premature and rapid aging of the composite resin. Hetero-bi-functional molecules of phosphonate or phosphate type have also been grafted onto the surface of particles of metal oxides or lanthanide fluorides. Examples of these coupling agents are given in figure 25 [49].

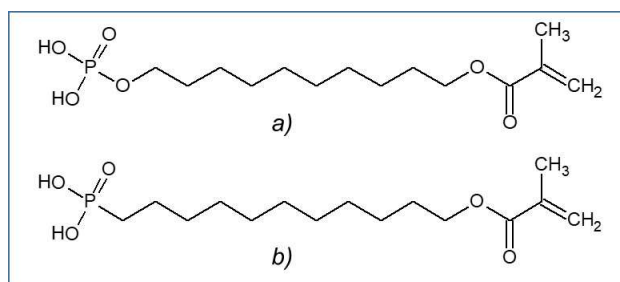


Figure 25 - Phosphate and phosphonate coupling agents with functional group: a) 10-Methacryloyloxydecyl dihydrogen phosphate, b) 11-Methacryloyloxyundecylphosphonic acid.

While functionalization of the micron or submicronic fillers takes place rather “easily”, functionalization of the nanoparticles requires some precautions, in particular as regards their dispersion in the reaction solvent. It will, of course, be better in this case to start with colloidal solutions rather than strongly agglomerated dry powders

Regarding the use of nanoparticles in the biomedical field, it should be recalled that in one of its latest reports the French Agency for Food, Environmental and Occupational Health Safety (ANSES) pleaded in favor of a strengthened regulatory framework. The agency specifies that health effects have been observed (carcinogenic, genotoxic effects, accumulation in the body, impact on the nervous system).

3.3 Initiators and inhibitors of polymerization

Only photoactivatable initiators will be mentioned in this paragraph. In the formulation of composites, they represent a percentage by mass that lies between 0.1 and 1%. To be effective, they must satisfy a number of criteria [50]. In particular, they must display:

- High absorption in the emission range of the curing light used,
- A short lifetime for the reactive excited state in order to avoid side reactions with other molecules,
- A high radical formation quantum yield,
- High reactivity of the formed radicals towards monomers.

The very first light-curing dental filling materials contained ultraviolet (UV) initiators. Polymerization using UV radiation has several notable drawbacks. UV rays can, in particular, damage the mucous membranes or the eyes of patients, and are also strongly scattered by mineral fillers so that for tinted composite resins, the depths of cure are less than 1mm. In order to overcome these drawbacks, composite resins containing alpha-diketones as photoinitiators have been developed, which are cured using visible radiation [51]. Benzil (BZ), 1-phenyl-1,2-propanedione (PPD) or camphorquinone (CQ) are examples of commercially available alpha-diketones

(Figure 26). Due to its properties (optical, toxicity, etc.) CQ is almost the only alpha-diketone used in dentistry [52]. As mentioned in paragraph 2.2.2, it needs a co-initiator (tertiary amine) to form radicals. These CQ-amine systems have been extensively studied, alone or in combination with other photoinitiators (Lucirin TPO, Irgacure 819, cationic photoinitiators, etc.) (Figure 26) [53].

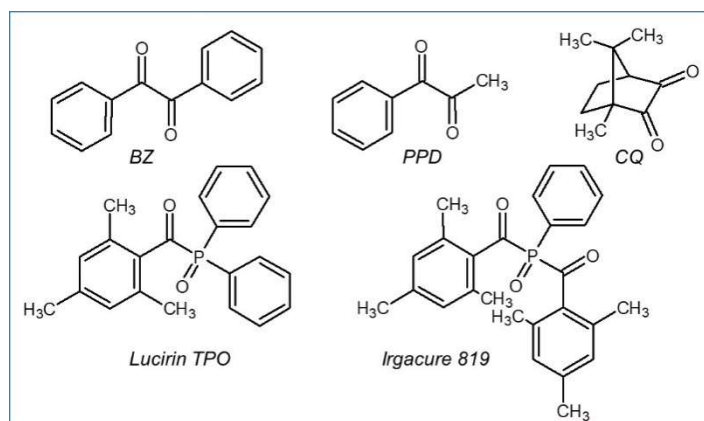


Figure 26 - Examples of photoinitiators used in the visible range.

These photoinitiating systems nevertheless have several drawbacks including [54]:

- An extremely low quantum yield of conversion of CQ per absorbed photon (<0.1).
- Coloring of composite resins (oxidation of the remaining amine molecules).
- A low molar absorption coefficient of CQ ($\epsilon = 28 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ at $\lambda_{\text{max}}=467\text{nm}$),
- Toxicity of the amines used.

In order to eliminate some of these disadvantages, various substances have been studied, for example, substitutes for amines. Molecules as alternatives to QC have also been evaluated (Irgacure 819, titanocene, cationic dye/borate anion complex, etc.) [55]. But a significant progress in the field concerns the photoinitiators of the acylgermane type (Figure 27). Among these compounds operating under visible light, benzoyltrimethylgermane (BTMGe), dibenzoyldiethylgermane (DBDEGe) or Ivocerin are very effective photoinitiators for methacrylate resins [56].

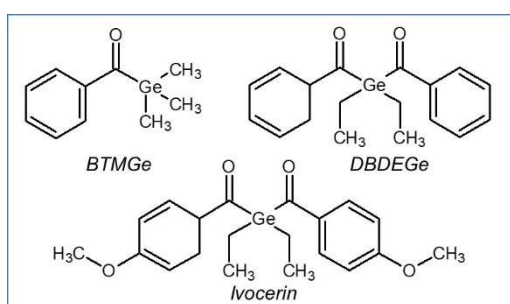


Figure 27 - Examples of acylgermane type photoinitiators [57].

Compared to Lucirin TPO ($\lambda_{\text{max}}=385\text{nm}$) or Irgacure 819 ($\lambda_{\text{max}}=379\text{nm}$), these germanium compounds show a pronounced red-shift of their absorption spectra ($\lambda_{\text{max}}=411\text{nm}$ for BTMGe ; $\lambda_{\text{max}}=418\text{nm}$ for DBDEGe ; $\lambda_{\text{max}}=408\text{nm}$ for Ivocerin). Compared to CQ they show a much greater absorption in the visible region (ϵ_{CQ} at $\lambda_{\text{max}}=28 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$; ϵ_{BTMGe} at $\lambda_{\text{max}}=137 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$; ϵ_{DBDEGe} at $\lambda_{\text{max}}=490 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$; $\epsilon_{\text{Ivocerin}}$ at $\lambda_{\text{max}}=724 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). The quantum yields of decomposition of the acylgermans mentioned here are for DBDEGe 0.83 and for Ivocerin 0.83, significantly higher than that of Irgacure 819 which is 0.59.

An analysis of dental composites containing acylgermans has shown that these photoinitiators offer significant advantages over CQ-amine systems [58]:

- Faster hardening of resinous matrices,
- Excellent whitening behavior,
- Much lower photoinitiator concentration to obtain comparable mechanical properties,
- Increased stability during storage of composites,
- Very low toxicity.

Among these acylgermans, Ivocerin, the result of optimizations in this field, is currently used by Ivoclar Vivadent [58].

In addition to photoinitiators, inhibitors are added (200 to 1000ppm) in dental composites to stabilize the monomers. The role of these molecules is to prevent any premature polymerization, by trapping the primary radicals formed (light, heat, etc.), during storage or handling of the composite [59]. Thus, the polymerization of methacrylates cannot really start until the total amount of inhibitor is consumed. The most common inhibitors in the field of dental composites are phenol derivatives: hydroquinone monomethyl ether (MEHQ) or 2,6-di-tert-butyl-4-methylphenol (BHT) (Figure 28).

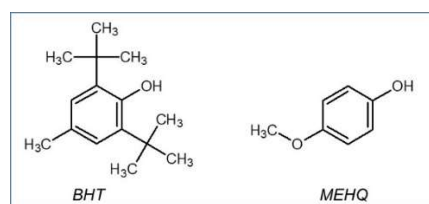


Figure 28 - Polymerization inhibitors used in dental composites.

Oxygen in the air is a potent polymerization inhibitor. Thus, the surface layer of the composite after irradiation is only partially polymerized. This layer is rich in double bonds which, in the case of an incremental restoration, will be able to ensure the chemical bond between each increment [60]. However, this is a major drawback for the polymerization of very thin restoration layers. Thus, to avoid contact with air, some practitioners take care to deposit a thin film of glycerin on the surface of the restoration before the irradiation step [16].

3.4 Additives for the management of aesthetics

Certain additives are important elements in the composition of dental composites in order to meet aesthetic requirements [61]. They are needed to match the color, but also the opacity, the translucency or the fluorescence of the restoration to that of natural teeth. For example, Figure 29 shows how the shade selection of a composite restorative is made using a shade guide for an anterior tooth for which the concept of aesthetics is crucial. For posterior tooth restoration, attention to detail also drives practitioners to use colored composites (Figure 29).



Figure 29 - Use of a shade guide to best adjust the shade of the restorative composite. Colored composite mimicking dentin for the restoration of a posterior tooth (source of illustrations [16]).

Pigments are added in amounts of from 0.001 to 0.05% by weight. For this purpose, a mixture of different inorganic pigments (Fe_2O_3 , FeOOH ...) is most often used. They must be stable in the oral environment and their features must not change over time. These inorganic pigments are finely divided and their surface is generally modified (polysiloxane with polymerizable groups) in order to enhance their dispersion in the resinous matrix. Organic pigments are advantageous alternatives (range of colors, ease of processing, etc.) to so-called conventional pigments. However, these organic pigments suffer from a lack of stability. To address this issue, the dye molecules can be incorporated into a sol-gel matrix. In order to increase their concentration in the sol-gel matrix and their stability, the chromophores are covalently grafted to the silica network. An example of a grafted chromophore is shown in Figure 30 [62].

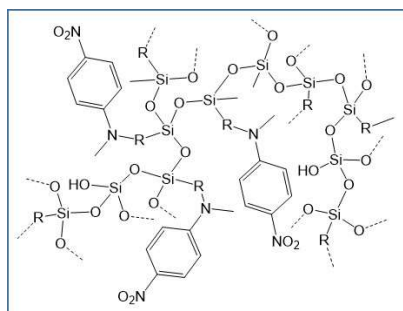


Figure 30 - Diagram showing the insertion of a chromophore into a sol-gel matrix [62].

The resinous matrix also contains (0.001-0.007% by weight) opacifiers (TiO_2 , Al_2O_3 ...) to adjust the optical transmission of the restorations. Finally, it should be noted that the opalescence management of composites, qualified as highly aesthetic, can be obtained by self-assembly of spherical and monodisperse oxide nanoparticles as is the case in natural opal [61].

To remember

- The decrease in polymerization shrinkage is one of the main drivers of monomer development.
- The fillers limit the polymerization shrinkage and play the role of mechanical reinforcements.
- The increase in the filler loading owes a lot to the optimization of the fillers as well as their dispersions in the monomers.
- Polymerization initiators and inhibitors as well as additives for the management of aesthetics are present in the formulations.

4 Properties of dental composites

Dental composites are materials whose properties must be close to those of the dental tissues (enamel and/or dentin) they are going to replace. Mechanical properties below those required would for example cause fracture of the restorative material. On the contrary, mechanical properties exceeding those required can induce damage to healthy tissues [60]. The final composite characteristics depend on the one hand on its composition and on the other hand on the polymerization conditions. The know-how of the practitioner as well as the implementation procedure of the restoration (layer by layer, thickness of the layers, irradiation time, curing lamp, etc.) are all factors which influence the properties of the cured composite. Furthermore, it is difficult to simulate the variety of constraints to which the material will be subjected (chewing in the

presence of various foods, friction with the opposing tooth, etc.) as well as the oral environment, the characteristics of which (pH, temperature, composition of the saliva...) are dependent on the patient and evolve during his lifetime. In this context, clinical studies are the most relevant to evaluate the performance of a composite as a dental restorative material, particularly in terms of longevity. However, these tests are expensive and time consuming and are not always all available when a new product is brought to the market [60]. The most relevant properties are therefore laboratory rated and subsequently clinically validated [63] [64].

The physical, mechanical and optical properties studied on dental composites are listed in the tables below (Tables 3, 4 and 5). Standard ISO 4049, which compiles the requirements for polymer-based restoration products, mentions only a limited number of them. These are indicated in the tables, accompanied by their threshold value. All the characterization techniques that can be considered on these materials have been listed in the literature [65] [66]. For illustration purposes, one or two of these test methodologies and / or the standard used have been mentioned here for each of the properties.

4.1 Physical properties

Table 3 - Physical properties of dental composites.			
Property	Measurement technique	Clinical interest	Note
Polymerization shrinkage	Method based on Archimedes' principle (ISO 17304:2013*)	Shrinkage and the stresses it generates are among the main causes of failure of direct restorations. Various factors have an effect on shrinkage and contraction stresses: the nature of the resinous matrix, the filler loading of the composite, the volume of the polymerized material, the shape of the cavity, as well as the polymerization mode [60]. The damage caused by polymerization shrinkage and contraction stresses are detailed in Figure 11.	Intrinsic property of the material.
Contraction stress	Bioman Method (University of Manchester, UK)		Extrinsic property of the material.
Water sorption	ISO 4049:2019** : Determination of the mass difference before and after drying, following immersion in water for 7 days at 37±1°C	The material swelling induced by the absorption of water reduces its mechanical properties, in particular the resistance to stress. High water sorption facilitates the release of free monomers and composite degradation products into saliva. It also facilitates the insertion of pigments from food and drink into the composite with a significant risk of staining the material [67].	ISO 4049 : Value ≤ 40 µg/mm ³
Water solubility	ISO 4049 : Determination of the mass loss caused by immersion in water for 7 days at 37±1°C	This type of degradation leads to a loss of material that is detrimental to the restoration [67]. It may cause biological hazards linked to the passage of degradation products in saliva.	ISO 4049 : Value ≤ 7,5 µg/mm ³
Coefficients of thermal expansion (CTE)	Thermo-mechanical analysis (TMA) (There is no standard method for the dental	The difference with the CTE of enamel and dentin (2 to 4 times lower than that of the composite) leads to the emergence of stresses at the interface between the materials during sudden temperature changes (from 5°C to 55°C depending on the food).	Property of minor importance because composites as well as dentin and enamel are very poor thermal conductors.

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* Dentistry - Polymerization shrinkage: Method for determination of polymerization shrinkage of polymer-based restorative materials.

** Dentistry - Polymer-based restorative materials.

4.2 Mechanical properties

Table 4 - Mechanical properties of dental composites.			
Property	Measurement technique	Clinical interest	Note
Fracture toughness	ISO 13586:2018* : 3-point bending on a pre-cracked specimen [M4166 V1]	The relatively low fracture toughness of composites classifies them among brittle materials. There are more marginal chipping for composites with the lowest K_{1c} [63].	A systematic review has revealed a weak positive correlation between fracture toughness and clinical fractures of posterior resin composite restorations [66].
Fatigue resistance	ASTM E606/E606M-12** : Test specimens subjected to uniaxial forces	The recurrence of the mechanical stresses during chewing can induce cracks (if they are not present) or promote their propagation (if they are present). Obviously, the repetition of these stresses can lead to a fracture of the restoration. This is particularly critical in the occlusal contact zones	Fatigue mechanisms are difficult to simulate by in vitro tests. Tests are generally abandoned in favor of stress strength or toughness measurements.
Compressive strength	ASTM D695-15*** : Compression test	This property is easy to measure but it is difficult to relate this property to the clinical behavior of the composite [60].	Low correlation with fracture rate.
Tensile strength	ASTM D638-14**** : Tensile test in uniaxial state of stress	Tensile stresses are among the most common causes of fractures [60].	Difficult to measure on fragile materials. Good correlation with bending strength.
Bending strength	ISO 4049 : Three point bend test	High flexural strength is essential in particular in the case of posterior restorations to withstand chewing forces. This property of the material is affected by the oral environment. The tests are therefore carried out after immersion for 24 hours in a water bath at 37°C. Aging is simulated by thermocycling between 5°C and 55°C.	ISO 4049 : value ≥ 80 MPa This measurement is preferred over compression and traction tests. It is the only one recommended in the standard.
Young's modulus or modulus of elasticity	Determined from the bending test	The higher it is, the more rigid the material is, and therefore less likely to deform under stress. <u>Interest of a high Young's modulus in the following cases:</u> - Restoration directly subjected to chewing stresses, otherwise risk of induction of cracks in the tooth. - Large volume of the restoration, otherwise risk of flexion of the remaining cusps. <u>Interest of a weak Young's modulus in the following cases:</u> - Class V restoration, because there is a risk of expulsion of too rigid materials. - Use as an underlay between the adhesive and a more rigid composite to dissipate stress during the latter's shrinkage.	

Wear resistance	<p>ISO/TS 14569-1:1999****: Wear by Tooth Brushing</p> <p>ISO/TS 14569-2:2001*****: Wear by two- and/or three body contact</p>	<p>Wear is considered a major source of dental restorative failure.</p> <p>The actual wear mechanism of dental material is very complex. It is linked to a set of processes (see [TRI 501] for the theory of wear and [68] for the specific case of dental composite) which can occur, simultaneously or successively, more or less repeatedly.</p>	Lack of correlation between the results obtained in vitro and clinical observations.
Hardness	Vickers hardness Knoop hardness	<p>It is related to the ease of polishing of the surface. Indeed, the harder the material, the more difficult it is to polish.</p> <p>Hardness gives an indication of the material's resistance to abrasion wear.</p>	
Polishing ability	Study of the roughness parameter Ra	<p>It must be significant in order to allow a good aesthetic finish of the restoration.</p> <p>The value of Ra should tend towards a threshold value of 0.2µm which corresponds to the retention threshold of dental plaque without exceeding 0.62µm which is that of human enamel [69].</p>	

* Plastics — Determination of fracture toughness (GIC and KIC) — Linear elastic fracture mechanics (LEFM) approach.

** Standard Test Method for Strain-Controlled Fatigue Testing.

*** Standard Test Method for Compressive Properties of Rigid Plastics.

**** Standard Test Method for Tensile Properties of Plastics.

***** Dental Materials - Guidance on Testing of Wear Resistance - Part 1: Wear by Tooth Brushing.

***** Dental materials — Guidance on testing of wear — Part 2: Wear by two- and/or three body contact.

4.3 Optical properties

Table 5 - Optical properties of dental composites.

Property	Measurement technique	Clinical interest	Note
Radio-opacity	ISO 4049 : Evaluation from an aluminum step wedge – tests according to ISO 13116 :2014*	<p>Essential property for the visualization, on an X-ray, of the restoration and its marginal adaptation.</p> <p>The radio-opacity of the composite is expressed in mm of aluminum. It should be greater than that of dentin (1-1.8mm) and enamel (2-3.1mm). Too much radiopacity, however, risks creating negative interference for secondary caries.</p>	
Depth of cure	ISO 4049 : Measurement of the material height after removal of the unpolymerized portion	<p>The higher this value, the greater the volume of the material, polymerized at one time, will be. This represents a time saving for the practitioner and more comfort for the patient.</p> <p>But beware of the shrinkage generated by the polymerization of a large volume of material</p>	<p>ISO 4049 : Value ≥ 1 mm for opaque composites</p> <p>ISO 4049 : Value ≥ 1,5 mm for other composites</p>
Sensitivity to ambient light	ISO 4049 : Behavior under irradiation by a Xenon lamp at 8000 ± 1000 Lux	If the material is too sensitive to ambient light, the light sources in the dental office (operating lights, sunlight) can trigger premature polymerization of the composite before it is placed in the patient's mouth.	The light intensity recommended by the ISO 4049 standard for this test appears relatively low compared to actual operating conditions.
Color, translucency, refractive index	Color measurement with a colorimeter, Refractometry,	These properties affect the aesthetic character of the restoration. They must match the properties of the teeth of the patient being treated so that the	Properties particularly important for anterior restorations

	Measurement of the light intensity (Lux) transmitted through the sample	restoration does not stand out from healthy teeth (see paragraph 3.4).	
Color stability over time	ISO 4049 : Comparison of the color before and after a week of a treatment described in ISO 7491:2000** .	This property influences the aesthetic character of the restoration.	The color change of the materials shall not be more than slight after treatment.

* Dentistry - Test Method for Determining Radio-Opacity of Materials

** Dental materials – Determination of colour stability.

4.4 Figures on current composites

Table 6 lists some physical and mechanical properties for each class of composites and for Bulk Fill composites currently on the market [23] [70] [71] [72] [73]. The values of these properties for enamel and dentin are given for comparison. The Young's modulus of composites is close to that of dentin (case of microhybrids and Bulk Fill composites) but remains very far from that of enamel. Similarly, the hardness of composites is comparable to that of dentin but much lower than that of enamel.

Composite type	Filler loading (% by weight)	Volume shrinkage (%)	Bending strength (MPa)	Bending Young's modulus (GPa)	Hardness (VHN)
Micro-filled	40-56	3,0-8,1	60-120	3-7	20-50
Micro-hybrid	76-81	2,3-3,0	100-170	8-10	32-111
Fluid Micro-hybrid	60-68	3,0-4,5	90-120	5-8	12 -55
Nano-hybrid	70-86	1,6-2,2	80-170	4,5-7	35-120
Fluid Nano-hybrid	55-65	1,9-2,5	70-120	4-6	28,4
Bulk-Fill	77-86	1,6-2,0	115-185	4-12,9	88 -142
Fluid Bulk Fill	65-75	2,5-4,1	110-141	2,8-9,3	40-100
Enamel			8-35	84,1-90,6	240-440
Dentin			30-65	10,3-18,1	50-87

The composition of the restorative material as well as the physicochemical characteristics of its components influence its various properties. Due to their high percentage in the material, mineral fillers play a predominant role. Thus, a high concentration of fillers (case of microhybrids, nanohybrids and Bulk Fill of medium viscosity) limits the polymerization shrinkage and the water absorption, makes the material more rigid (high Young's modulus), reinforces its bending strength and increases its toughness and hardness. Fluid compositions, generally having a lower filler loading, lead to more flexible materials and therefore more likely to deform under stress. They undergo greater polymerization shrinkage but their viscoelasticity allows better stress dissipation during and at the end of the polymerization process. The composites obtained are less resistant to bending and exhibit lower toughness than materials resulting from the polymerization of compositions of medium viscosity. Fillers size influences the curing depth. The latter is greater the smaller the charges,

with a refractive index close to that of the matrix. It is greatly increased in Bulk Fill composites (≥ 4 mm) compared to other composites (≤ 2 mm). A decrease in the fillers size associated with an increase in their mass percentage improves the surface finish of the material and its resistance to wear.

In terms of composition, it is essential that part of the mineral fillers be based on materials composed of at least one element of high atomic number in order to make the composite radiopaque. Indeed, the organic matrix does not have an intrinsic property of radiopacity.

Finally, regarding the wear of dental restorative materials, it is considered acceptable below 40 to 50 $\mu\text{m}/\text{year}$, knowing that the wear of the enamel is estimated at 50 $\mu\text{m}/\text{year}$ and 30 $\mu\text{m}/\text{year}$, respectively for molars and premolars. According to clinical studies, the wear of composite materials is 10-20 $\mu\text{m}/\text{year}$ for the marginal areas of a posterior restoration. In some cases, this wear can drop below 5 $\mu\text{m}/\text{year}$. In contrast, it can be 3 to 5 times greater for areas with contact resulting in a significant loss of the height of the restoration [60].

To remember

- As a substitute for enamel and/or dentin, dental composites must exhibit properties similar to those of these two tissues.
- The final properties of restorative materials depend on their composition but also strongly on the conditions of their implementation.
- Clinical studies remain the most relevant for studying the performance of dental composites because the real conditions of use are very variable and difficult to simulate in vitro.

5 Examples of restorations

5.1 Anterior tooth restoration

Some representative steps in the restoration of a fractured anterior tooth are shown in Figure 31.



Initial situation.



Test of the silicone mold properly positioned.



Cleaning of the affected dentin (ceramic bur).



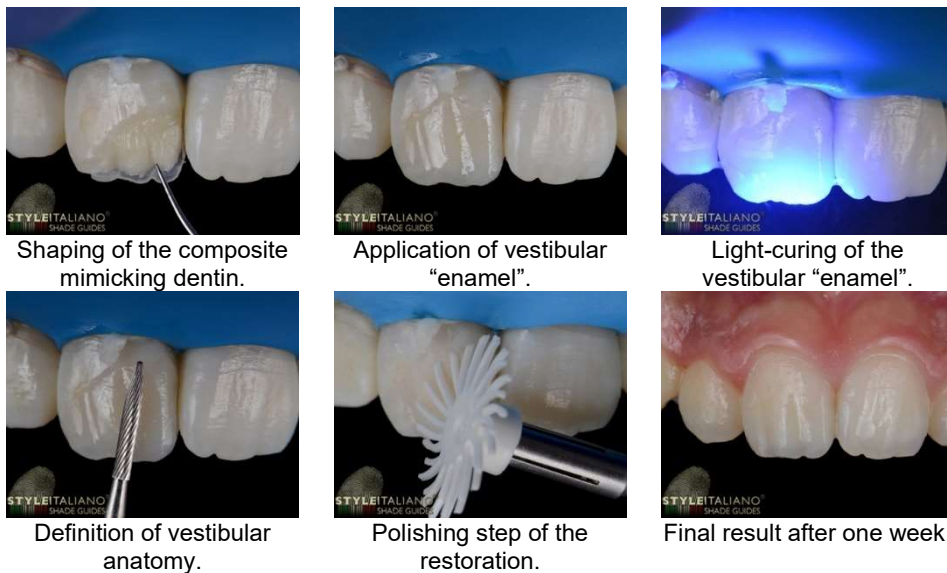
Application of a universal adhesive (enamel and dentin).



Implementation of the palatal "enamel".



Palatal "enamel" after light-curing.



Shaping of the composite mimicking dentin.

Application of vestibular "enamel".

Light-curing of the vestibular "enamel".

Definition of vestibular anatomy.

Polishing step of the restoration.

Final result after one week.

Figure 31 - Steps in direct restoration of a fractured anterior tooth (source of illustrations [16]).

5.2 Posterior tooth restoration

Some representative steps in the restoration of decayed posterior teeth are shown in Figure 32.



Initial situation.

Removal of previous restorations.

Etching step.

Application of an adhesive.

Fabricating the distal walls with a composite imitating enamel.

Overview of the tooth after polymerization of the distal wall.

Laying of the composite imitating dentin.

Shaping of the composite imitating dentin.

Laying of the composite imitating enamel.

Shaping of the composite
imitating enamel.

Finishes after
polymerization of the
enamel.

Final result after complete
restoration.

Figure 32 - Steps in direct restoration of decayed posterior teeth (source of illustrations [16]).

To remember

- Restorations using dental composites involve many steps in order to obtain the optimal properties of the final materials, on the one hand, and to ensure their esthetic results, on the other.
- Obtaining an optimal result for the patient will require the use of one or more composites depending on the case.
- Dental composites have certainly been the subject of numerous optimizations, but the practitioner plays a key role in the success of dental restoration.

Conclusion

In this paper, we illustrated the degree of sophistication of current composites whose successive optimizations have taken advantage of advances in different scientific disciplines. Practitioners have had to improve their skills in the field of restorative dentistry and also became, for most of them, real artists with regard to the aesthetic demands of patients (See for example the website of "Style Italiano" [16]). As the reader may have already realized, the laying of dental composite is really a matter for specialists and it has in fact very little in common with the laying of an amalgam. Poorly controlled dental restoration with a composite, can rapidly evolve into serious complications (secondary decay, release of monomers, etc.) and seriously limits the restoration lifetime. All of this, of course, regardless of the high performance of the material in vitro. Regarding biocompatibility, the presence of "toxic" monomers as well as the concerns about nanoparticles safety have directed research in the field to other approaches. Ormocers have been developed to this end as well as new mineral-based dental restorative materials. Another way currently explored concerns the development of biogenic dental products. In theory, they allow teeth to be reconstructed and caries to be treated by eliminating treatment based on synthetic materials [74].

Glossary

Adhesive

Interface biomaterial that helps form an adherent and tight bond between dental tissue (enamel and dentin) and restorative biomaterials.

Amalgam

Alloys of mercury and other metals (mainly silver, tin, copper and zinc), used for over 150 years as a dental restorative material, primarily for filling molars. In this case, the restoration consists of placing this alloy in the plastic phase in a cavity prepared as an undercut without an adhesive agent. This unaesthetic material requires a retentive cavity preparation, therefore more mutilating by its lack of adhesive power, it is, moreover, corrosive in the presence of other metallic materials. They can release a small amount of mercury during their placement, their removal or in case of normal wear and tear.



Examples of restorations with amalgam (source of illustrations [16]).

Configuration factor (or c-factor)

It corresponds to the ratio of the number of composite surfaces bonded to the cavity walls over the number of its free surfaces (which are not in contact with the tooth). It has been shown that the higher the c-factor, the greater the stresses at the tooth-material interfaces.



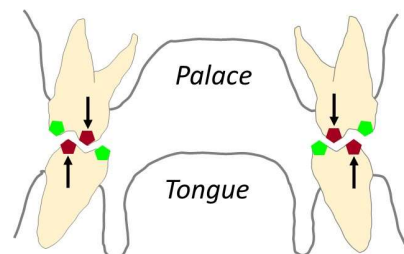
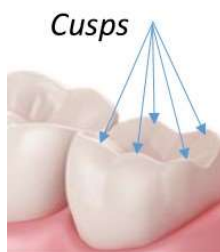
c-factor=1



c-factor=0.5

Cusp

Coronal eminence of convex shape and variable volume which is present on the occlusal surface (upper surface of the teeth, which fits with that of the opposite tooth) of a tooth (premolar or molar) or on the one of the edges of a canine.



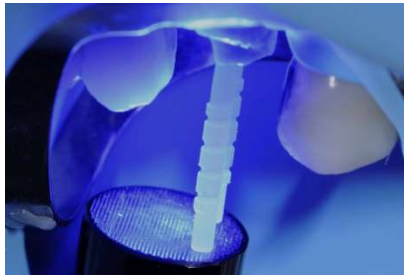
In red, supporting cusps and in green, non-supporting cusps.

Degree of Conversion (DC)

It corresponds to the number of moles of carbon-carbon double bonds having reacted relative to the total number of moles of carbon-carbon double bonds initially present. FTIR Spectroscopy is one of the most widely used techniques for measurement of DC in dental composites. This parameter will affect many properties including mechanical properties, solubility, color change and biocompatibility of the composite.

Dental post

Small fiber-reinforced composite or metal shaft implanted in a devitalized tooth whose role is to improve the retention of restorations in root filled teeth.



Sealing of a dental post in a devitalized tooth by light-curing of a resin cement (source of illustrations [16]).

Etching

Acid attack of dental tissues, mainly the mineral part, to facilitate the adhesion of restorations.

Functionality of a monomer

Number of covalent bonds that a monomer molecule or monomeric unit in a macromolecule or oligomer molecule can form with other reactants [AM 3040].

Inlay/onlay

Prosthetic pieces that are placed, as their prefix indicates, on or in the tooth. Their role is to help rebuild a tooth that has suffered from oral hygiene problems, cavities or cracks.



Examples of prosthetic pieces in zirconia (source of illustrations [16]).

Tooth decay

Disorder affecting the teeth which undergo an alteration of the enamel and then of the dentin. It leads to the formation of holes and the progressive destruction of the tooth with potentially serious consequences.



Extension of a lesion caused by tooth decay (source of illustrations [16]).

To know more

Dental composites

by **Frédéric CHAPUT**

PhD in ceramic materials science, Research director at the French national scientific research centre (CNRS)
Laboratoire de Chimie, Ecole Normale Supérieure de Lyon, France

Anne-Charlotte FAURE

PhD in inorganic chemistry
Head of research and development
ITEN, Dardilly, France

Literature sources

- [1] BOWEN (R.L.) - The Journal of the American Dental Association, 66, p. 57-64 (1963).
- [2] Dental filling material comprising vinyl silane treated fused silica and a binder consisting of the reaction product of bis phenol and glycidyl acrylate – US Patent 3066112 (1962).
- [3] SOFAN (E.) et al. - Annali di Stomatologia, VIII, p. 1-17 (2017).
- [4] BAYNE (S.C.) - The Journal of the American Dental Association, 144, p. 42S-46S (2013).
- [5] BLACK (G.V.) - A work on operative dentistry, vol. I and II, Chicago: The Medico-Dental Publ.Co, (1908).
- [6] DENTODONTICS. - Dental students blog. G.V. Black's classification of caries (2015) <https://dentodontics.com/2015/02/26/g-v-blacks-classification-of-cariou-lesions/>
- [7] LASFARGUES (J.J.) – EMC, Elsevier SAS, Odontologie, Paris, 23-069-A-10, p. 1-19 (2006).
- [8] DECUP (F.). – Le guide de décision thérapeutique des lésions carieuses. Dental Espace (2002) <https://www.dentalespace.com/praticien/formationcontinue/guide-decision-therapeutique-lesions-carieuses/>
- [9] YOUSSEF (A.). – Cuspide – Anatomie dentaire. Studio dentaire (2007) <https://www.studiodentaire.com/fr/glossaire/cuspide.php>
- [10] Inlay core ou onlay : le guide complet, Dentaly.org (Updated in 2018) <https://www.dentaly.org/inlay-core-ou-onlay-le-guide-complet/>
- [11] Composite dentaire, <https://www.implants-dentaire-hongrie.com/composite-dentaire>
- [12] LASFARGUES (J.J.) - *Les résines composites : Applications en dentisterie restauratrice*. SNPMD (2007).
- [13] SIDERIDOU (I.D.) - Dental polymer composite, Chapter in : Encyclopedia of Polymer Composites: Properties, Performance and Applications. Editor: Mikhail Lechkov and Sergej Prandzheva. Nova Science Publishers, Inc. NY 11788 USA, p. 593-619 (2010).
- [14] VAIDYANATHAN (T.K.) et al. - Dental Materials, 33, p. 1-11 (2017).
- [15] Dentist examining patients teeth with dental curing light.

<https://pikwizard.com/photo/dentist-examining-patients-teeth-with-dental-curing-light/aa3abf7121b73358c7a9d8be22301722>

[16] Website « STYLEITALIANO » : <https://www.styleitaliano.org/> ;

<https://twitter.com/styleitaliano>

[17] PEUTZFELD (A.) - European Journal of Oral Sciences, 105, p. 97-116 (1997).

[18] MILETIC (V.) - *Dental Composite Materials for Direct Restorations*, Springer (2018).

[19] STANSBURY (J.W.) - Dental Materials, 28, p. 13-22 (2012).

[20] MOSZNER (N.) et al. - Composites for Dental Restoratives dans *Polymers for Dental and Orthopedic Applications*, CRC Press Taylor and Francis Group, p. 13 (2007).

[21] TRUJILLO-LEMON (M.) et al. - Journal of Polymer Science: Part A: Polymer Chemistry, 44, p. 3921–3929 (2006).

[22] FOSTER (J.) et WALKER (R.). - Dental filling materials. US Patent 3825518 (1974).

[23] MOSZNER (N.) et al. - Journal of Polymer Science Part A: Polymer Chemistry, 50, p. 4369-4402 (2012).

[24] ILIE (N.) et al. - Australian Dental Journal, 56, p. 59-66 (2011).

[25] UTTERODT (A.), RUPPERT (K.), SCHAUB (M.), DIEFENBACH (C.), REISCH (K.), HOHMANN (A.), ECK (M.) et SCHÖNHOF (N.). - Compositions for Dental composites with tricyclo[5.2.1.0^{2.6}]decane derivatives. US Patent 2010/0076115 (2010).

[26] STANSBURY (J.), BOWMAN (C.) et TRUJILLO (M.). - Dimer acid-derived dimethacrylates and use in dental restorative compositions. US Patent 11568383 (2004).

[27] BOARO (L.C.) et al. - Dental Materials, 29, p. 398-404 (2013).

[28] STANSBURY (J.W.) - Journal of Dental Research, 71, p.1408-1412 (1992).

[29] WEINMANN (W.) et al. - Dental Materials, 21, p. 68-74 (2005).

[30] SAKAGUCHI (R.L.) et al. - *Craig's restorative dental materials*, 13th edition, Elsevier (2012).

[31] MOSZNER (N.) et al. - Macromolecular Materials and Engineering, 292, p. 245-271, (2007).

[32] CANCEILL (T.) et al. - Biomatériaux Cliniques, 2, p. 14-16 (2017).

[33] FRAUNHOFER ISC. – - Dental Applications

<https://www.isc.fraunhofer.de/en/fields-ofactivity/applications/dental-applications.html>

Bifunctional starting compounds <https://www.ormocere.de/en.html>

[34] WOLTER (H.) et al. - Materials Research Society Symposium Proceedings, 346, p. 143-149 (1994).

[35] PAGES (P.) - Concept et applications des Ormocers en odontologie : Une véritable alternative aux résines d'obturation conventionnelles ? Doctoral dissertation from the University of Paul Sabatier (2018).

[36] RANDOLPH (L.D.) et al. – Dental Materials, 32, p. 1586–1599 (2016).

[37] MITRA (S.B.) et al. – JADA, 134, p. 1382-1390 (2003).

[38] British Dental Journal, 220, p. 213 (2016).

[39] Poly dispensing system. – Mélangeurs planétaires

<http://polydispensing.com/products/melangeurs-planetaires/>

[40] Wikipedia. – Composite dentaire

https://fr.wikipedia.org/wiki/Composite_dentaire

[41] RANDOLPH (L.D.) et al. - Developing a more appropriate classification system for modern resin-based composite technologies, chapitre dans *Dental Composite Materials for Direct Restorations*, Springer (2018).

[42] FERRÉOL (R.). – Baderne d'Apollonius et empiement Apollonien. Mathcurve <https://www.mathcurve.com/fractals/baderne/baderne.shtml>

- [43] FERRACANE (J.L.) - Dental Materials, 27, p. 29-38 (2011).
- [44] MANHART (J.) et al. - Swiss Dental Journal, 124, p. 29-37 (2014).
- [45] KLAPDOHR (S.) et al. - Monatshefte für Chemie, 136, p. 21-45 (2005).
- [46] ZE BING (L.) et al. – Microporous and Mesoporous Materials, 175, p. 1-7 (2013).
- [47] ANTONUCCI (J.M.) et al. - Journal of Research of the National Institute of Standards and Technology, 110, p. 541-558 (2005).
- [48] DE MONREDON-SENANI (S.) - Interaction Organosilanes / Silice de précipitation, du milieu hydro-alcoolique au milieu aqueux, Doctoral dissertation from the University of Pierre et Marie Curie (2004).
- [49] TANAKA (R.) - Journal of Dental Research, 87, p. 666-670 (2008).
- [50] TELITEL (S.) - Des systèmes amorceurs hautes performances pour les photopolymérisations radicalaires, cationiques ou radicalaires contrôlées, Doctoral dissertation from the University of Haute Alsace (2015).
- [51] Method of repairing teeth using a composition which is curable by irradiation with visible light - US Patent 4,089,763 (1978).
- [52] STANSBURY (J.W.) – Journal of Esthetic Dentistry, 12, p. 300-308 (2000).
- [53] SINGH (S.) - International Journal of Applied Dental Sciences, 3, p. 17-20 (2017).
- [54] CHEN (Y.C.) - Dental Materials, 23, p. 655-664 (2007).
- [55] TEHFE (M.A.) - Etude de nouveaux systèmes amorceurs pour des polymérisations radicalaires ou cationiques, Doctoral dissertation from the University of Haute Alsace (2011).
- [56] MOSZNER (N.) - Dental Materials, 24, p. 901-907 (2008).
- [57] HAAS (M.) - Chem. Eur. J., 24, p. 8258-8267 (2018).
- [58] Ivoclar Vivadent R&D Report, N°19, (2013).
- [59] RANDOLPH (L.D.) et al. - Composition of dental resin-based composites for direct restorations chapitre dans Dental Composite Materials for Direct Restorations, Springer (2018).
- [60] VREVEN (J.) et al. - EMC (Elsevier SAS, Paris), Odontologie, 23-065-E-10, 2005.
- [61] LEE (Y.K.) - Dental Materials Journal, 35, p. 845-854 (2016).
- [62] SPANGE (S.) et al. - Angew. Chem. Int. Ed., 41, pp. 1729-1732 (2002).
- [63] FERRACANE (J.L.) - Dental Materials, 29, p. 51–58 (2013).
- [64] BAYNE (S.C.) - Dental Materials, 28, p. 52-71 (2012).
- [65] FERRACANE (J.L.) et al. - Dental Materials, 33, p.1171-1191 (2017).
- [66] ILIE (N.) et al. - Dental Materials, 33, p.880-894 (2017).
- [67] FERRACANE (J.L.) - Dental Materials, 22, p. 211–222 (2006).
- [68] CAZALAS (T.) - Traitement des lésions d'usure : survie des restaurations par méthodes directes et indirectes en matériaux composite. Revue systématique de la littérature, Doctoral dissertation from the University of Bordeaux (2017).
- [69] JAGER (S.) - Les résines composites fluides : données actuelles, Doctoral dissertation from the University of Lorraine (2011).
- [70] ALESSANDRI (M.) - Propriétés physico-mécaniques comparées des composites Bulk à travers une revue systématique de la littérature, Doctoral dissertation from the University of Nice-Sofia Antipolis (2017).
- [71] ILIE (N.) et al. - Operative Dentistry, 38-6, p.618-625 (2013).
- [72] ILIE (N.) et al. - Clinical Oral Investigations, 17, p.185–193 (2013).
- [73] NGUYEN (P.) - Les polymères utilisés dans les composites dentaires : concept, développement et perspectives, Doctoral dissertation from the University of Nantes (2006).
- [74] DOGAN (S.) et al. - ACS Biomater. Sci. Eng., 4, p.1788-1796 (2018).

Also read in our databases

DECKER Christian. - *Polymérisation sous rayonnement UV*. [AM3044 V1], Plastiques et composites (2000).
FELDER Eric et MONTMITONNET Pierre. - *Théorie de l'usure -Mécanismes d'usure* [TRI501 V1], Frottement, usure et lubrification (2016).
FONTANILLE Michel et VAIRON Jean-Pierre. - *Polymérisation* [AM3040 V1], Plastiques et composites (2009).
FRANCOIS Dominique. - *Essais de mesure de la ténacité - Mécanique de la rupture* [M4166 V1], Etude et propriétés des matériaux (2007).
HAMAIDE Thierry. - *Polymérisations en chaîne- Mécanismes* [J5830 V2], Plastiques et composites (2017).

Books

DIETSCHI (D.) et al. - *Restaurations esthétiques collées*. Quintessence International, Paris (1997).

LASFARGUES (J.J.) - *Les résines composites : Applications en dentisterie restauratrice*. SNPMD (2007).

MILETIC (V.) - *Dental Composite Materials for Direct Restorations*. Springer (2018).

MOUNT (G.J.) et al. - *Préservation et restauration de la structure dentaire*. DeBoeck Université (2002).

RASKIN (A.) - *Les résines composites*. Université Médicale Virtuelle Francophone, support de Cours (2010).

Events

Trade Show : International Dental Show (IDS), the largest European dental fair, takes place every two years in Cologne (Germany) (on every odd-numbered year) <http://english.ids-cologne.de/>

Congress and trade fair: ADF, every year in Paris. <http://www.adfcongres.com/fr/>

Norms and standards

ISO Dentistry: Polymer-based restorative materials ISO 4049 : 2019 ISO, 2019.

ISO Medical devices: Quality management systems - Requirements for regulatory purposes ISO 13485 : 2016 ISO, 2016.

ISO Plastics: Determination of fracture toughness (GIC and KIC) - Linear elastic fracture mechanics (LEFM) approach ISO 13586 : 2018 ISO, 2018.

ISO Dental materials: Guidance on testing of wear — Part 1: Wear by toothbrushing

ISO/TS 14569-1 : 2007 ISO, 2007.

ISO Dental materials: Guidance on testing of wear — Part 2: Wear by two- and/or three body contact ISO/TS 14569-2 : 2001 ISO, 2001.

ISO Dentistry: Polymerization shrinkage: Method for determination of polymerization shrinkage of polymer-based restorative materials ISO 17304 : 2013 ISO, 2013.

ISO Dentistry: Test Method for Determining Radio-Opacity of Materials ISO 13116:2014 ISO, 2014

ISO Dental materials: Determination of colour stability ISO 7491 : 2000 ISO, 2000.

ASTM Standard test method for tensile properties of plastics ASTM D638 – 14, ASTM International, 2014.

ASTM Standard test Method for compressive properties of rigid plastics ASTM D695 - 15, ASTM International, 2015.

ASTM Standard test method for strain-controlled fatigue testing ASTM E606/E606M-12, ASTM International, 2012.

Patents

Dental filling material comprising vinyl silane treated fused silica and a binder consisting of the reaction product of bis phenol and glycidyl acrylate – US Patent 3066112 (1962)

Dental filling materials – US Patent 3825518 (1974)

Compositions for Dental composites with tricyclo[5.2.1.0^{2.6}]decane derivatives – US Patent 2010/0076115 (2010)

Dimer acid-derived dimethacrylates and use in dental restorative compositions – US Patent 11568383 (2004)

Polysiloxane compound and dental materials that can be prepared from it US9532931B2

Directory

Manufacturers of dental composites:

3M : https://www.3mfrance.fr/3M/fr_FR/dentisterie/

Bisco : <https://www.bisco.com/>

Centrix : <https://www.centrixdental.com/>

Coltène : <https://www.coltene.com/fr/>

DMG : <http://fr.dmg-dental.com/>

Denmat : <https://www.denmat.com/>

Dentsply : <http://www.dentsply.fr/>

GC Europe: <https://www.gceurope.com/fr/>

Ivoclar Vivadent : <http://www.ivoclarvivadent.fr/fr/>

J. Morita : <https://www.jmoritaeurope.de/>
Kerr : <https://www.kerrdental.com/>
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Kuraray : <https://kuraraydental.com/>
Septodont : <http://www.septodont.fr/>
Tokuyama : <http://www.tokuyama-dental.com/>
Shofu : <http://www.shofu.com/>
Ultradent : <https://www.ultradent.com/>
Voco : <https://www.voco.dental/fr/accueil.aspx>