Composite resins. A review of the materials and clinical indications

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ABSTRACT
The aim of this work is to present the different components of the composites currently used in dentistry and furnish dentists with a basis that can provide criteria for choosing one or another to suit their therapeutic requirements. Most composites used in dentistry are hybrid materials, so-called because they are composed of polymer groups reinforced by an inorganic phase of glass fillers with different compositions, particle sizes and fill percentages. Flowable or condensable composites have attempted to provide an answer to certain functional requirements, although they have not been too successful at improving properties. Turning to polymerisation initiators, both halogen lamps, whether conventional or high intensity, and LED curing lights which provide a gradual increase in light intensity are very useful for reducing shrinkage of the composite material. The clinical choice of a composite must consider whether priority should be given to mechanical or aesthetic requirements: if mechanical considerations are paramount the material with the greatest volume of filler will be chosen; if aesthetic considerations predominate, particle size will be the most important factor. Additional components such as opaques and tints make it possible to improve the aesthetic results. Equally, the spread of other therapeutic procedures, such as tooth bleaching, has made it necessary to design composite materials in shades that are suitable for the special colour situations found in teeth treated by these methods.

Key words: Composite resins, inorganic filler, organic matrix, polymerisation, clinical applications.

RESUMEN
El objetivo de este trabajo es presentar los diferentes componentes de los composites actualmente utilizados en Odontología y aportar al profesional las bases que puedan proporcionarle los criterios a tener en cuenta para seleccionar uno u otro en función de los requerimientos terapéuticos. La mayoría de los composites de uso en Odontología corresponden a materiales híbridos, se denominan así por estar conformados por grupos poliméricos reforzados por una fase inorgánica de vidrio de diferente composición, tamaño y porcentaje de relleno. Los composites fluidos o los condensables han tratado de dar respuesta algunos requerimientos funcionales, aunque sin demasiado éxito en la mejora de sus propiedades. Respecto a las fuentes de polimerización, tanto las lámparas halógenas, convencionales o de alta densidad de potencia, como las LEDs, que ofrecen un incremento gradual de la intensidad lumínica, son muy útiles para disminuir la contracción volumétrica del material. A la hora de la selección clínica de un material compuesto se valorará si priman los requerimientos mecánicos o los estéticos; en el primer caso seleccionaremos el material que tenga mayor volumen...
INTRODUCTION
Composite resins have been introduced into the field of conservative dentistry to minimise the drawbacks of the acrylic resins that replaced silicate cements (the only aesthetic materials previously available) in the 1940s. In 1955, Buonocore used orthophosphoric acid to improve the adhesion of acrylic resins to the surface of the enamel. In 1962 Bowen developed the Bis-GMA monomer in an attempt to improve the physical properties of acrylic resins, as their monomers only allowed linear chain polymers to be formed (1). These early, chemically cured composites required the base paste to be mixed with the catalyst, leading to problems with the proportions, mixing process and colour stability (2). From 1970, composite materials polymerised by electromagnetic radiation appeared, doing away with mixing and its drawbacks. At first, an ultraviolet light source (365 nm) was used to provide the required light energy, but its shallow polymerisation and iatrogenic side-effects led to its replacement by visible light (427-491 nm), which is currently in use and undergoing further development (3). Composite development has been and continues to be unceasing, making it necessary to keep abreast continually. The aim of this work is to present the different components of the composites currently used in dentistry and furnish dentists with a basis that can provide criteria for choosing one or another to suit their therapeutic requirements.

CHARACTERISTICS OF PRESENT DAY COMPOSITES
The physical, mechanical and aesthetic properties and the clinical behaviour of composites depend on their structure. Basically, dental composites are composed of three chemically-different materials: the organic matrix or organic phase; the inorganic matrix, filler or disperse phase; and an organosilane or coupling agent to bond the filler to the organic resin. This agent is a molecule with silane groups at one end (ion bond to SiO₂) and methacrylate groups at the other (covalent bond with the resin) (4).

The organic matrix of composite resins is made up, in essence, of a system of mono-, di- or tri-functional monomers; a free radical polymerisation initiation system, which in photocurable composite resins is an alpha diketone (camphoroquinone) used in combination with a tertiary aliphatic amine reducing agent (4-n,n-dimethylamino-phenyl-ethanol, DMAPE) and in chemically-curable ones is a per-compound, benzoyl peroxide, used in combination with an aromatic tertiary amine (n,n-dihydroxyethyl-p-toluidine);

an acceleration system (dimethylaminoethyl methacrylate or DMAEM, ethyl-4-dimethylaminobenzoate or EDMAB, or N,N-cyanoethyl-methylaniline or CEMA), which acts on the initiator, allowing curing to take place in a clinically acceptable time; a stabiliser or inhibitor system such as hydroquinone monomethyl ether to maximise the product’s storage life prior to curing and its chemical stability thereafter; and, lastly, absorbers of ultra-violet wavelengths below 350 nm, such as 2-hydroxy-4-methoxybenzophenone, to provide colour stability and eliminate the effects of UV light on the amine compounds in the initiator system that can cause discoulouration in the medium to long term (5).

The monomer system can be viewed as the backbone of the composite resin system. Bis-GMA continues to be the most-used monomer for manufacturing present-day composites; whether alone or in conjunction with urethane dimethacrylate, it constitutes around 20% (v/v) of standard composite resin compositions. As a general rule, it is accepted that the lower the mean molecular weight of the monomer or monomer combination, the greater the percentage of shrinkage. Because this resin is highly viscous, to facilitate the manufacturing process and clinical handling it is diluted with other low-viscosity monomers (low molecular weight) which are considered viscosity controllers, such as bisphenol A dimethacrylate (Bis-DMA), ethylene glycol dimethacrylate (EGDMA), triethylene glycol dimethacrylate (TEGDMA), methyl methacrylate (MMA) or urethane dimethacrylate (UDMA) (6, 7). Composite polymerisation always involves a degree of shrinkage, depending on the organic matrix. Consequently, to reduce this negative effect, the dental industry has tested a great variety of monomers, including spiroortho-carbonates (SOCs), which expand (8), epoxy-polyol system combinations, which show 40%-50% less shrinkage in vitro than traditional systems, the siloxane-oxirane based resins patented by 3M-Espe (9) or the use of high molecular weight molecules such as multiethylene glycol dimethacrylate and copolymers which manage to achieve 90%-100% conversion by reducing the C=C bonds. Ormocers (modified composites with organic and inorganic fillers) have also demonstrated their ability to reduce curing shrinkage, albeit minimally (10). Nonetheless, the main dental composite manufacturers currently still concentrate on the traditional systems, mostly adding a Bis-GMA/TEGDMA monomer or a Bis-GMA/UDMA/TEGDMA combination to the organic matrix.

Palabras clave: Resinas compuestas, relleno inorgánico, matriz orgánica, polimerización, aplicaciones clínicas.
The disperse phase of composite resins is made up of an inorganic filler material which, in essence, determines the physical and mechanical properties of the composite. The nature of the filler, how it is obtained and how much is added largely decide the mechanical properties of the restoration material. The filler particles are added to the organic phase to improve the physical and mechanical properties of the organic matrix, so incorporating as high a percentage as possible of filler is a fundamental aim. The filler reduces the thermal expansion coefficient and overall curing shrinkage, provides radio-opacity, improves handling and improves the aesthetic results (11).

The filler particles used vary widely in their chemical composition, morphology and dimensions. The main filler is silicon dioxide; boron silicates and lithium aluminium silicates are also commonly employed. In many composites, the quartz is partially replaced by heavy metal particles such as barium, strontium, zinc, aluminium or zirconium, which are radio-opaque. The search is currently on for materials, such as calcium metaphosphate, which are less hard than glass ones and therefore cause less wear on the opposing tooth (12).

Nanotechnology has led to the development of a new composite resin characterised by containing nanoparticles measuring approximately 25 nm and nanoaggregates of approximately 75 nm, which are made up of zirconium/silica or nanosilica particles. The aggregates are treated with silane so that they bind to the resin. The distribution of the filler (aggregates and nanoparticles) gives a high load, up to 79.5% (13).

As the particle size is smaller, resins made with this type of particle give the restoration a better finish, which is observed in its surface texture, and the likelihood of the material’s biodegrading over time is reduced. This technology has also achieved sufficiently competent mechanical properties for the resin to be indicated for use in the anterior and posterior sectors. It should also be mentioned that the lower size of the particles leads to less curing shrinkage, creates less cusp wall deflection and reduces the presence of microfissures in the enamel edges, which are responsible for marginal leakage, colour changes, bacterial penetration and possible post-operative sensitivity (14).

The drawback is that since the particles are so small they do not reflect light, so they are combined with larger-sized particles, with an average diameter within visible light wavelengths (i.e. around or below 1μm), to improve their optical performance and act as a substrate.

Composite resins have been classified in different ways, depending on their composition, to make it easier for dentists to identify and use them for therapeutic purposes. A very popular classification which is still valid is that of Lutz and Phillips, which is based on filler particle size. These authors divided composite resins into macro filler composites (particles from 0.1 to 100 µ), micro filler composites (0.04 µ particles) and hybrid composites (fillers of different sizes) (15). A more detailed classification by Willems et al is based on a number of parameters such as Young’s module, the percentage (by volume) of inorganic filler, the size of the main particles, surface roughness and compressive stress (16) (Table 1).

### Table 1. Classification of composites (Willems, 1993) (16).

<table>
<thead>
<tr>
<th>Composite type</th>
<th>Filler</th>
</tr>
</thead>
<tbody>
<tr>
<td>Densified composites</td>
<td></td>
</tr>
<tr>
<td>- Midway-filled</td>
<td>&lt; 60% by volume</td>
</tr>
<tr>
<td>Ultrafine</td>
<td>Particles &lt; 3 μm</td>
</tr>
<tr>
<td>Fine</td>
<td>Particles &gt; 3 μm</td>
</tr>
<tr>
<td>- Compact-filled &gt; 60% by volume</td>
<td>&gt; 60% by volume</td>
</tr>
<tr>
<td>Ultrafine</td>
<td>Particles &lt; 3 μm</td>
</tr>
<tr>
<td>Fine</td>
<td>Particles &gt; 3 μm</td>
</tr>
<tr>
<td>Microfine composites</td>
<td></td>
</tr>
<tr>
<td>- Homogeneous</td>
<td>Average particle size = 0.04 μm</td>
</tr>
<tr>
<td>- Heterogeneous</td>
<td></td>
</tr>
<tr>
<td>Miscellaneous composites</td>
<td>Blends of densified and microfine composites</td>
</tr>
<tr>
<td>Traditional composites</td>
<td>Equivalent to what are termed macrofill composites in other classifications</td>
</tr>
<tr>
<td>Fiber-reinforced composites</td>
<td>Industrial-use composites</td>
</tr>
</tbody>
</table>
HYBRID COMPOSITE RESINS.
These composites are so called because they are made up of polymer groups (organic phase) reinforced by an inorganic phase, comprising 60% or more of the total content, composed of glasses of different compositions and sizes, with particle sizes ranging from 0.6 to 1 micrometers, and containing 0.04 micrometer sized colloidal silica. They make up a large majority of the composites currently used in dentistry.

The characteristic properties of these materials are: availability of a wide range of colours and ability to mimic the dental structure, less curing shrinkage, low water absorption, excellent polishing and texturing properties, abrasion and wear very similar to that of tooth structures, similar thermal expansion coefficient to that of teeth, universal formulas for both the anterior and posterior sector, different degrees of opaqueness and translucency in different tones and fluorescence (17, 18).

FLOWABLE COMPOSITES
These are low-viscosity composite resins, making them more fluid than conventional composite resins. The percentage of inorganic filler is lower and some substances or rheological modifiers which are mainly intended to improve handling properties have been removed from their composition. Their main advantages are: high wettability of the tooth surface, ensuring penetration into every irregularity; ability to form layers of minimum thickness, so improving or eliminating air inclusion or entrapment (19); high flexibility, so less likely to be displaced in stress concentration areas (cervical wear processes and cavitated dentine areas); radio-opaqueness and availability in different colours. The drawbacks are: high curing shrinkage, due to lower filler load, and weaker mechanical properties.

Some of the indications for these materials that may be highlighted are: applications in class V restorations, cervical wear processes and minimal occlusal restorations or as liner materials in class I or II cavities or areas of cavitated enamel (20).

CONDENSABLE COMPOSITES
Condensable composites are composite resins with a high percentage of filler. The advantages are: condensability (like silver amalgam), greater ease in achieving a good contact point and better reproduction of occlusal anatomy. Their physical and mechanical behaviour is similar to that of silver amalgam, bettering that of hybrid composites (21); however, according to follow-up studies, their clinical behaviour is similar to that of hybrid composites (22). Their main disadvantages are difficulties in adaptation between one composite layer and another, difficult handling and poor aesthetics in anterior teeth. Their main indication is Class II cavity restoration in order to achieve a better contact point thanks to the condensation technique.

POLYMERISATION: IMPORTANCE AND SOURCES
Full polymerisation of the material is determined by the degree of conversion of monomers into polymers, indicating the number of methacrylate groups that have reacted with each other during the conversion process. The factors that influence the degree of conversion of the composite are shown in table 2 (23).

The shrinkage suffered by the composite during curing ranges from 1.35% to 7.1%. This, together with curing stress, leads to cohesion and adhesion failures, which are joined by the degree of monomer to polymer conversion as the main causes of composite resin restoration failures.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Clinical repercussions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curing time</td>
<td>It depends on: resin shade, light intensity, box deep, resin thickness, curing through tooth structure, composite filling.</td>
</tr>
<tr>
<td>Shade of resin</td>
<td>Darker composite shades cure more slowly and less deeply than lighter shades (60 seconds at a maximum depth of 0.5 mm).</td>
</tr>
<tr>
<td>Temperature</td>
<td>Composite at room temperature cure more completely and rapidly.</td>
</tr>
<tr>
<td>Thickness of resin</td>
<td>Optimum thickness is 1-2 mm</td>
</tr>
<tr>
<td>Type of filler</td>
<td>Microfine composites are more difficult to cure than heavily loaded composites.</td>
</tr>
<tr>
<td>Distance between light and resin</td>
<td>Optimum distance &lt; 1 mm, with the light positioned 90 degrees from the composite surface.</td>
</tr>
<tr>
<td>Light source quality</td>
<td>Wavelength between 400 to 500 nm. A power density about 600 mW/cm² is required to ensure that 400 mW/cm² reaches the first increment of composite in a posterior box.</td>
</tr>
<tr>
<td>Polymerisation shrinkage</td>
<td>Depends on the amount of organic phase.</td>
</tr>
</tbody>
</table>

Table 2. Factors that influence the composite resin polymerisation process.
Shrinkage depends solely on the organic matrix and, within this, on the number of reactions that take place. It rises with the degree of conversion and falls with increasing monomer molecular weight. The manufacturers try to develop light sources that will give the greatest conversion with the least curing stress, as this helps to improve the functional and aesthetic results of composite materials; using “soft-start” lamps (whether halogen, conventional or high intensity, or LED curing lights), which gradually increase the light intensity, is very useful for reducing composite shrinkage (24).

Nowadays, a number of sources for photo-initiating composite resins are available: halogen lamps, plasma arc lamps, laser and light-emitting diode (LED) lights. The most-used are halogen and LED lamps. LEDs are a promising alternative for photo-curing dental materials. Their use in dentistry has been discussed ever since blue diodes were developed in the 1990s. Research has shown that at a 100 mW/cm² intensity, the curing depth and the resin monomer conversion range is significantly better with an LED than with a halogen lamp.

The LED lamps that are commercially available nowadays are very similar in power to halogen lamps: about 755 mW/cm². Studies show that the curing light quality is not exclusively due to the intensity of the light, as initiator system absorption must also be taken into account, so the spectrum emitted is an important determining factor in the performance of a curing lamp. The camphoroquinone absorption curve covers a range from 360 to 520 nm, with a peak at 465 nm. The optimum emission spectrum of a polymerisation source therefore lies between 440 and 480 nm. In conventional curing units 95% of the light is emitted in wavelengths between 400 and 510 nm, whereas 95% of the spectrum emitted by blue LEDs lies between 440 and 500 nm with a peak at 465 nm, identical to the camphoroquinone peak, so a photon emitted by an LED curing lamp is more likely to be absorbed by the camphoroquinone than that of a halogen lamp (23).

**FACTORS THAT INFLUENCE THE CHOICE OF A COMPOSITE. CLINICAL CONSIDERATIONS**

**Position of the cavity**

The nature of the restoration work, in terms of its location and size, is decisive in the choice of one material or another. For fillings requiring high mechanical performance (class IV cavities with occlusal function, large class I, combination or complex class II, class VI) the most suitable composite is that with the highest inorganic load; in the case of the posterior sector it should be radio-opaque (25).

Restorations in anterior teeth are aesthetically more demanding, so composites with other properties are indicated in these cases: good polishing, suitable opacity for a natural look or fluorescence. Polishing depends on particle size and composites with submicronic fillers or nanoparticles are ideal. It should be remembered that materials can be combined, as in the case of a large class IV restoration, where a high-load densified composite (generally hybrid) covered by a microfine (microfiller) composite in the vestibular area would be indicated (26).

Cervical lesions, both in the posterior and in the anterior region, are best filled with highly polishing materials in order to avoid plaque accumulating on them; the material must also respond well to flexural stresses (25).

**Aesthetic requirements**

On occasion, the composites are primarily intended to solve an aesthetic rather than a functional problem: treatment of dysmorphias or discolorations, closing diastemas or camouflaging dental malpositions; at other times aesthetic requirements are added to mechanical ones: large carious lesions in anterior teeth or dental traumatisms in the anterior face of the tooth (27).

Consequently, consideration should be given to other components of the composites which facilitate the treatment and sometimes give rise to special products. Firstly, the role of the material’s opacity must be highlighted. Certain composites are presented as “universal”, which means that as well as being usable in both the anterior and the posterior sector, they can be used without adding any other product. It is also common to find composite presentations which contain both a standard material and a more opaque material. This is quite different from opaquers, which are resins materials that are used to hide the underlying tooth colour. Their use removes the transparency of the tooth, which then has to be reproduced artificially through a combination of materials, in this case a hybrid composite that covers the opaquer and is overlaid with a fine veneer of microfine composite: the different compositions of the successive layers achieve a type of reflection and refraction of the light falling on the tooth that improves its final appearance, which approaches that of the natural tooth (28).

At the opposite pole, translucent composites are useful for reproducing incisal edges in young patients Tints are resins with intense chromas that are used to improve the final aesthetic effect of the restoration; their purpose is to reproduce the specific morphological or chromatic characteristics of each patient, such as white spots, increment lines, fissures, etc., but it should be remembered that their use must be minimal: small quantities and sub-surface location (always covered by another composite, generally microfine) so that their use in the restoration is not noticeable.

Special composites for bleached teeth deserve a special mention. When a tooth requires a bleaching treatment, this is because it is more or less intensely discoloured. After bleaching, the perception of its colour may have improved but the final tone is unlike the more usual shades. This has led to the creation of special formulae for these situations, although they are not available for all the composites on the market (29).

**CONCLUSIONS**

Nowadays, composites have unquestionably acquired a prominent place among the filling materials employed in direct techniques. Their considerable aesthetic possibilities give rise
to a variety of therapeutic indications, which continue to grow as a result of the great versatility of the presentations offered; also, these materials conserve the tooth structure better because they are retained by adhesive methods rather than depending on cavity design (30). Nonetheless, it should not be forgotten that they are highly technique-sensitive, hence the need to control certain aspects: correct indication, good isolation, choice of the right composite for each situation, use of a good procedure for bonding to the dental tissues and proper curing are essential if satisfactory clinical results are to be achieved.

REFERENCES