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Invited Review

New Inorganic Components for Dental Filling Composites

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Summary. Dental composite filling materials are improved by incorporating nanofillers. They impart increased hardness and wear resistance to composites. In addition, they produce better polishing results than macrofillers. If the particles are sufficiently small, transparent composite pastes are obtainable, independent of the refractive index of the polymerisable monomers. In this context, organosols, non-agglomerated nanoparticles in organic liquid media, are especially interesting. Some of our own results on organosols are presented in this paper. Their relatively low viscosity enables the preparation of composites with a high filler load, thus reducing the shrinkage of the dental composite during polymerisation and improving the mechanical properties. Inorganic–organic hybrids are an attractive class of materials for dental fillings. The synthesis of different polymerisable ormocers for dental composites is reviewed in the second part. Ormocers can be applied as a polymerisable matrix, improving biocompatibility and wear resistance. Their use as inorganic fillers improves the thermodynamic compatibility of the filler with the matrix and enhances the polishability. Functionalised inorganic clusters used as new additives combine the properties of very small nanoparticulate fillers and well-designed highly functional monomers with high crosslinking capabilities. Xerogel colour pigments are advantageous alternative additives to conventional pigments. 3-D structural colour pigments, which are obtained by the self-assembly of monodisperse spherical particles, produce an opalescent effect resembling that of the natural enamel in highly aesthetic composites.

Keywords. Composites; Polymerisation; Dental; Clusters; Sols.

Introduction

The introduction of resin-based composite technology to restorative dentistry was one of the most significant contributions to dentistry in the last century [1, 2]. Nowadays tooth-shaded dental restorations are well-accepted and becoming more and more popular in general practice. For the restoration of anterior lesions, as well as for the treatment of smaller and medium-sized defects in the posterior region,

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Table 1. Typical composition of dental composites

	Dental composites	
Inorganic fillers	*ca.* 75–85% *w*/*w*	– radiopaque silicate glasses – fumed oxides/mixed oxides – *etc.*
Organic matrix	*ca.* 15–25% *w*/*w*	– polymerizable monomers – initiator system – stabilizers, pigments

direct resin composite filling materials are used. By definition, a composite is a material that consists of two or more components. Typically, dental resin filling composites contain 15–25% *w*/*w* of a free-radically polymerisable organic matrix and 75–85% *w*/*w* of a mixture of different inorganic fillers, in addition a photoinitiator system or in some cases other curing systems and further additives as shown in Table 1.

Composition of Resin-Based Filling Composites

In currently used resin filling composites, the organic matrix is based on methacrylate chemistry, with the most popular monomers being cross-linking dimethacrylates, for example, 2,2-bis[4-[2-hydroxy-3-(methacryloyloxy)propyl]phenyl] propane (Bis-*GMA*), 1,6-bis[2-(methacryloyloxy)ethoxycarbonylamino]-2,4,4-trimethylhexane (*UDMA*), or decanediol dimethacrylate (*D_3MA*) [3, 4] (Fig. 1). The dimethacrylates demonstrate different properties such as molecular weight, polarity, polymerisation shrinkage (ΔV_P), or viscosity (η).

Therefore, the selection of the monomers substantially influences the reactivity, viscosity, and polymerisation shrinkage of the composite paste, as well as the mechanical properties and water uptake of the cured composite. In most of the commercially available direct filling resin composites the free-radical polymerisation of the matrix monomers is caused by free-radical-forming photoinitiators where the dentists induce photopolymerization by irradiation with halogen lamps of blue light. For this purpose, 0.2–0.5% *w*/*w* of a mixture of camphorquinone (*CC*) and *tert.* amines,

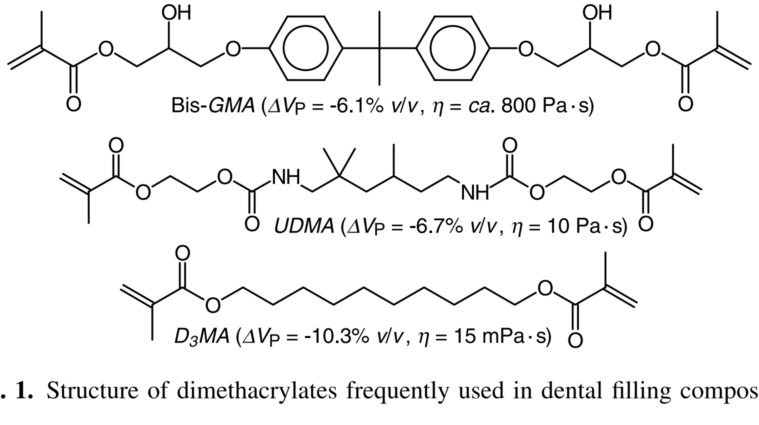


Fig. 1. Structure of dimethacrylates frequently used in dental filling composites

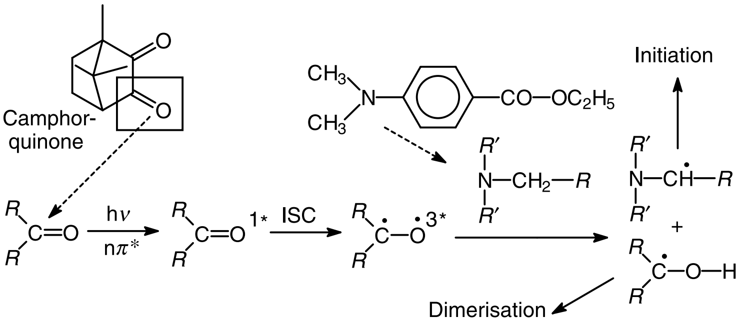


Fig. 2. Mechanism of initiating radicals of the *CC/EDAMB* photoinitiator system

for example, ethyl *p*-dimethylaminobenzoate (*EDAMB*) are usually applied in direct filling resins, because *CC* decomposes at low temperature, the system is highly reactive, but has a good storage stability and shows no discolouration, no toxicity, and is odourless. The mixture is activated by visible light in the region of 450–480 nm. In the photoinitiator system comprising *CC* and *EDAMB* as the coinitiator, α-aminoalkyl radicals are formed, which initiate the free-radical polymerisation, whilst the ketyl radical mainly dimerises or disproportionates (Fig. 2) [5]. The free-radical polymerisation of the matrix monomers leads to the stepwise formation of a three-dimensional network [6, 7] in which the filler particles are dispersed. After the initiation of the polymerisation by the α-amino-alkyl radicals, linearly propagating macro radicals are formed because only one double bond per monomer molecule is involved at that time in the polymerisation process.

During the subsequent course of polymerisation, the macro radicals form micro gel particles. At what is known as the gel point, a three dimensional polymer network is built up. For dimethacrylates, the time between the initiation and the gel point is only in the range of a few seconds. However, to achieve a nearly complete monomer conversion and a high double bond conversion, a longer polymerisation time is needed (20–60 s). After the gel point, the polymerisation system behaves like a visco-elastic solid. Because of the gel effect, the change in density is accelerated, resulting in an increase in internal contraction stress. About 80% of the polymerisation shrinkage of cross-linking dimethacrylates is responsible for the internal stress build-up that may cause the formation of a marginal gap between the resin-based filling composite and the dental hard tissue.

The properties of composite restoratives are considerably influenced by the fillers that are used. Therefore, the composite restoratives have been classified according to the type of filler employed (Fig. 3) [8]. Although this classification is twenty years old, it is still valid for modern composite filling materials. Nevertheless, macrofilled composites with an average particle size between 5 to 30 μm are less frequently used nowadays because of aesthetical reasons. The fillers used are characterized by different manufacturing techniques, the average particle size, and the chemical composition. The macrofillers are mechanically prepared by grinding larger particles of radiopaque glass, quartz, or ceramics into smaller particles. Macrofiller particles are purely inorganic, usually splinter-shaped. Today, they have an average particle

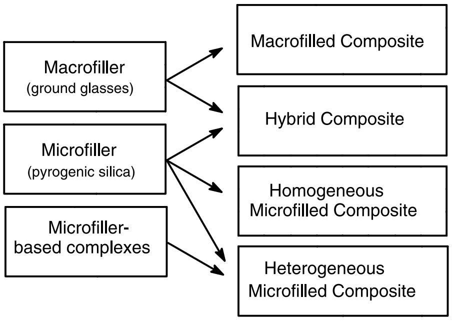
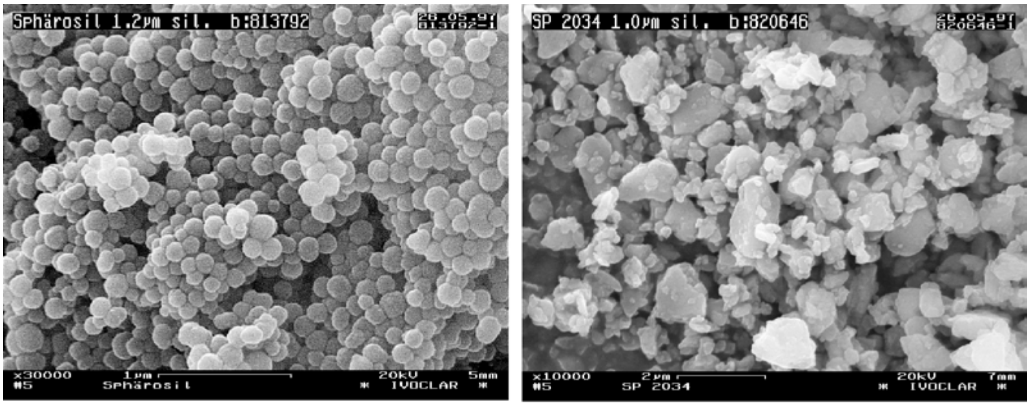
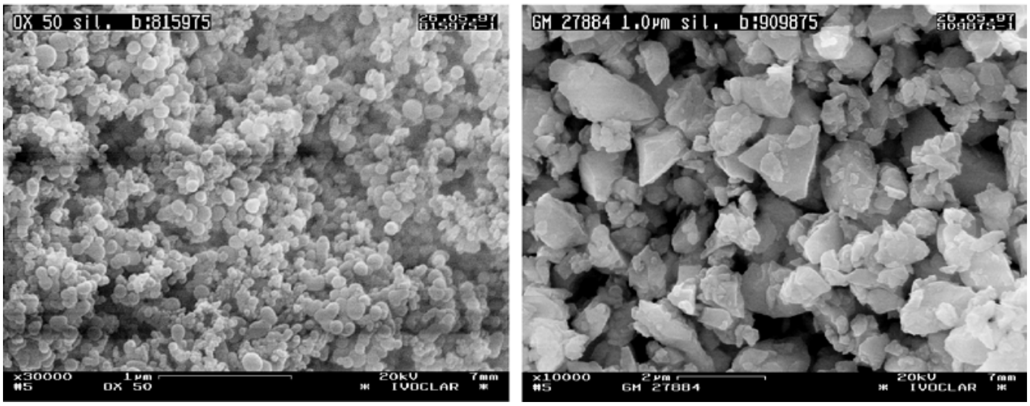


Fig. 3. Classification of resin-based filling composites

size between 0.2 and 5.0 μm. Pyrogenic silica is an important representative of a microfiller. Other microfillers are prepared, for example, via the sol–gel route, starting from tetraalkyl orthosilicates or metal alkoxides such as titanium(IV) and zirconium(IV) ethoxide or mixtures thereof. Inorganic microfillers consist of spheri-



Spherical Zr/Si mixed oxide **Ba-F silicate glass**



Silica **Ba-silicate glass**

Fig. 4. SEM pictures of different fillers used in dental composites

cal primary particles with an average particle size of approximately 5 to 100 nm. Therefore, nowadays the term nanofiller can also be used for such particles. Often, the primary particles of these fillers are agglomerated and the formed agglomerates may influence the transparency of the composite. Because of the large specific surface area of the micro- or nanofiller particles, they can show a pronounced thickening effect. Therefore, microfiller-based complexes have been developed in order to increase the microfiller loading in heterogeneous microfilled composites. They can be produced, for example, by incorporating pyrogenic silica into a resin matrix, curing this mixture, and milling the obtained microfilled composite into splinter-shaped particles, which show a particle size of 10 to 100 μm. Usually, the inorganic part of hybrid composites consists of about 70–80% w/w of glass fillers and 20–30% w/w of microfillers. Figure 4 shows the scanning electron micrographs (SEM) of different fillers used in dental composites. In general, the surfaces of silicate fillers are conditioned with methacrylate-functionalised silanes, such as the frequently used 3-(methacryloyloxy)propyltrimethoxysilane (*MPTMS)*, to create covalent links between the inorganic filler particles and the organic resin matrix by radical copolymerisation. The fillers used in dental composites directly influence their radiopacity, abrasion resistance, flexural modulus, and thermal coefficient of expansion. Polymerisation shrinkage largely correlates with the volumetric amount of the filler in the composite. Many modern dental composites use the fillers listed in Table 2. In general, dental filling composites contain a mixture of at least two different fillers. In this context, ytterbium fluoride (YbF_3) may serve as a radiopacifier. Yttrium fluoride (YF_3), fluorosilicate glasses, or sparing amounts of soluble fluoride salts are added to composites for the release of fluoride ions.

Dental filling composites contain a number of further additives. Inhibitors, such as phenols, *e.g.* 2,6-di-*tert*-butyl-methylphenol (*BHT*) and hydroquinone monomethylether (*MEHQ*), are added to the resin formulation in amounts of 200 to 1000 ppm to prevent premature polymerisation during the storage of the composite and avoid uncontrolled photopolymerisation by normal room light during the preparation and filling of the cavity. In this context, we were able to show [9] that anaerobic inhibitors, such as 2,2,6,6-tetramethylpiperidinyl-1-oxyl (*TEMPO*) radicals are also very efficient and enable the preparation of composites with reduced daylight sensitivity and improved vacuum stability. In addition, UV photostabili-

Table 2. Type of fillers and filler size used in dental composites

Filler composition	Particle size
Highly dispersed SiO_2	10–40 nm
Radiopaque, finely ground Ba or Sr silicate glasses	0.7 μm, 1.0 μm, 1.5 μm, or larger
Radiopaque, finely ground Ba/Sr fluoro silicate glasses	1.0 μm, 1.5 μm, or larger
Ground quartz glass	1.0–1.5 μm
YbF_3, YF_3	0.10–3.0 μm
Si/Zr mixed oxide	250–500 nm
Ti, Zr, and Al oxide used as opacifier	250–500 nm
Splinter polymerisate mainly based on SiO_2	10–100 μm

zers, such as commonly available 2-hydroxybenzophenones or 3-(2-hydroxyphenyl)-benzotriazols, in amounts of 0.10 to 0.50% *w/w* protect the composites against photodegradation. The photodegradation of the organic matrix may cause changes in the colour of the filling material. Finally, colour pigments are added in amounts of 0.001 to 0.05% *w/w* in order to meet the aesthetic demands for composite fillings. For this purpose a mixture of different inorganic pigments (yellow, red, white, and black) is most commonly used to imitate the colour of the natural teeth.

Properties of and Requirements for Dental Filling Composites

In Table 3 some of the physical properties of composite filling materials are listed in correlation with the type of filler, particle size of the filler, and filler load. Flexural strength and flexural modulus were measured by a three point bending test using a *Zwick* universal testing machine (BZ 2.5/TS1S, Germany) with samples ($2 \times 2 \times 25$ mm) after 24 h immersion in water at 37°C. In the case of hybrid composites, the filler load has an effect on the flexural strength and the flexural modulus (compare fine particle hybrid of a mean particle size of 1.0 μm with a flowable fine particle hybrid with the same mean particle size in Table 3). Hetero-

Table 3. Correlation between the type of filler, filler load, and the physical properties of a composite

Type of composite	Filler load/% *w/w*	ΔV_P^{a}/% *v/v*	Flexural strength/MPa	Flexural modulus/GPa
Fine particle hybrid	81	2.7	135	11.0
Flowable fine particle hybrid	69	3.6	95	5.1
Microfill composite	78	2.4	110	6.5
Flowable microfill composite	59	4.8	110	4.1

[a] Polymerisation shrinkage after 24 h was calculated from the difference of the density of the composite paste and the cured composite determined by dilatometry

Processing requirements:
- *optimum consistency (handling)*
- *easy shade selection*
- *high polishability*
- *optimum reactivity*
- *limited light sensitivity*

Physico-chemical requirements:
- *good mechanical properties*
- *low polymerisation shrinkage*
- *limited water absorption/solubility*
- *low thermal expansion*
- *high monomer conversion*
- *good storage stability*

Clinical and toxicological requirements:
- *excellent resistance to oral conditions*
- *good shade stability*
- *abrasion resistance similar to enamel*
- *excellent adaptation to margin edges*
- *long-term marginal stability*
- *sufficient radiopacity*
- *compatibility with adhesive systems*
- *minimum toxicological risk*

Fig. 5. Selected requirements of composite restorative materials

geneous microfilled composites show only a correlation between the filler load and the flexural modulus. Beside the physical properties, a composite restorative material must also meet certain chemical, processing, clinical, and toxicological requirements (Fig. 5) [10]. The clinical performance of a filling material largely depends on the indication for which it is used. The stress exerted on restorations in the posterior region is much higher than that exerted on anterior restorations. According to the literature [11], the average life cycle of hybrid composite posterior restorations placed in general practices is four years compared to eight years for amalgam restorations. Efforts to improve the clinical performance of composite filling materials are focused on the following main topics:

- reduction of the polymerisation shrinkage to improve marginal adaptation and prevent recurrent caries,
- improvement of the mechanical properties, especially wear resistance, and
- improvement of biocompatibility by reducing the elution of components.

These improvements can be achieved by changing both the organic matrix and the inorganic fillers. In this paper, which is focused on inorganic components for dental filling composites, we will outline new nanofillers, especially silica organosols and their application in dental composites. Subsequently sol–gel derived inorganic–organic hybrid materials as the monomer matrix of dental restoratives as well as their utilization as fillers will be described. Finally, the application possibilities of the new inorganic additives, such as inorganic building blocks, sol–gel based opalescent fillers and colour pigments will be discussed.

Nanosized Dental Fillers

Today, macrofillers, which are surface-modified with a silane, are not as widely used in dental composites due to the resulting rough surface, especially after repeated tooth brushing. The soft resin matrix abrades faster than the filler particles which then protrude from the surface or even break off. This also leads to the tendency to lack lustre, it reduces the aesthetic properties and increases wear of the material and the antagonistic tooth by chewing. Finally, a rough surface promotes plaque adhesion. Therefore, microparticles (*i.e.* nanoparticles) below 0.1 μm particle size have become popular over the last few years [12]. They cannot be produced by grinding glasses. Microfillers, commercially available in high amounts, are highly dispersed pyrogenic silica consisting of agglomerated nearly spherical nanoparticles (*e.g.* available under the tradenames Aerosil (Degussa), HDK (Wacker), Cab-O-Sil (Cabot Corp.)). Other methods include flame spray processes and sol–gel processes. Due to the small particle size, the specific surface area of the particles increases dramatically. More monomers are necessary to wet the surface of the particles. In addition, the interaction between the matrix and the filler surface is increased. This raises the viscosity of the uncured material and reduces the attainable filler load, thus leading to poorer mechanical properties of the composite.

The thickening effect can be reduced by using discrete, unassociated nanoparticles, which are well dispersed in the matrix on a nanoscale level [13–16]. For good dispersion of the particles in the matrix, a thorough surface modification of the particles is necessary [12, 14, 16]. Due to the well-dispersed nanoscale filler, no settling occurs even in low viscosity monomers. The low viscosity is retained as will be shown in detail below. Furthermore, the formed nanocomposites (the nanofilled polymers) show improved hardness and abrasion resistance. A relatively low viscosity of nanofilled monomers also allows the addition of other fillers and enables high filler loads. Favourable rheological properties of the uncured materials also facilitate the handling and placement of the filling material in the desired location on a tooth. In dental bonding agents [12] the nanoparticles are said to increase the adhesion to both enamel and dentin and improve the marginal integrity. In addition, cured materials with nanoparticles (1–50 nm) show increased strength and decreased polymerisation shrinkage, while still maintaining low viscosity. Nanoparticles may also be prepared from trialkoxysilanes bearing polymerisable and acidic groups, *e.g.* phosphonic or sulfonic acid groups [17].

If the particles or aggregates are below 50 nm, transparent materials are obtained independent of the refractive index of the matrix. This leads to highly aesthetic materials, in which the transparency can be adapted to the special applications. The transparency of the composite paste considerably influences the curing depth upon irradiation with visible light.

Polymerisable Silica Organosols

Stable colloidal silica dispersions of nanoparticles in organic media (organosols) are of special interest because they contain discrete almost non-agglomerated particles. They are prepared, for example, by condensation of silicic acid in water under special conditions. The water of the resulting aqueous silica sol is subsequently replaced by an organic solvent that is at least partly water soluble, such as ether or alcohols [18, 19]. Organosols can also be prepared by *Stöber*'s method using alkoxysilanes as precursors [20, 21]. The organic solvents can be exchanged for polymerisable monomers. Before the nanoparticles are incorporated into the polymerisable monomers they are thoroughly silanised with a polymerisable silane to stabilise the particles in the dispersion and to obtain a covalent bond between the filler and the matrix after curing the material. Silica organosols are commercially available in alcoholic solvents or in a few mono- or dimethacrylates, *e.g.* as Highlink® Nano G (Clariant) or as Nanocryl® (hanse chemie). An example of a thin film of a cured resin with silica nanoparticles is shown in Fig. 6. The particles are well dispersed and no large agglomerates are observed. The monodispersed nanoparticles in reactive resins lead to nanocomposite materials with increased mechanical properties, good processability, and high filler loads, as well as high transparency [22].

We prepared different dental dimethacrylate monomer organosols and investigated their viscosity as a function of varying amounts of nanofiller of 13 nm in diameter. It was demonstrated that the capacity of the filler load is strongly dependent on the kind of monomer involved. The initial viscosity of the dimethacrylate is important, but also the hydrophilicity and polarity of the monomer as well as a suitable surface modification of the SiO_2 nanoparticles. For example, the monomer triethyleneglycol dimethacrylate can be filled with 50% w/w of silica nanoparticles without showing any pseudoplastic behaviour. The viscosity does not depend on the shear rate as shown in Fig. 7.

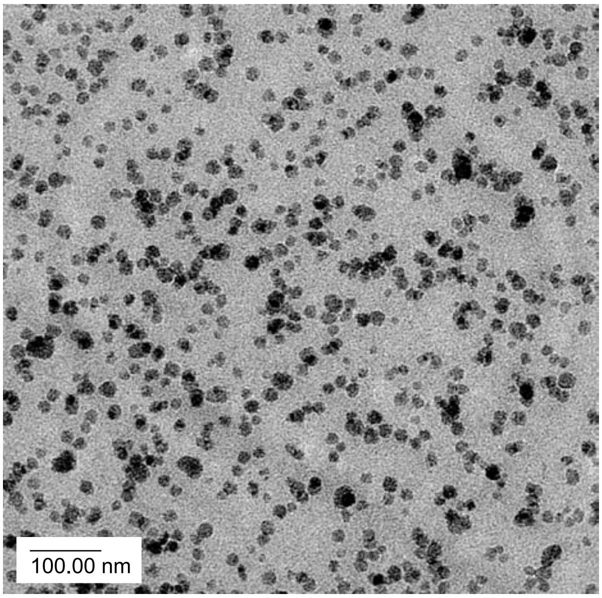


Fig. 6. TEM image of silica nanoparticles in an ultrathin film of a cured resin with the friendly permission of hanse chemie

With 60% *w/w* of silica, the viscosity significantly increases and becomes dependent on the shear rate. In organosols based on the more viscous and hydrophobic monomer ethoxylated bisphenol A dimethacrylate (SR348C, Sartomer),

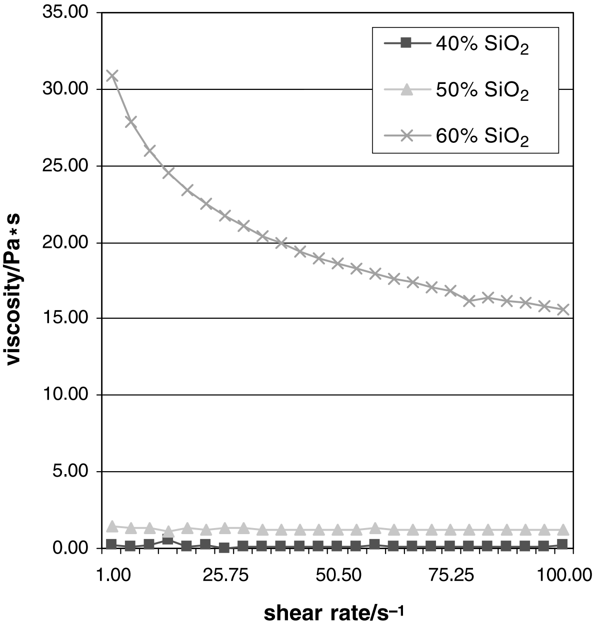


Fig. 7. Viscosity of *TEGDMA* with different amounts of silica nanoparticles; the viscosity was measured with a rotational viscosimeter (Bohlin CVO-120HRNF) using a cone-plate system of 2.5°/20 mm at 23°C

the limit at which pseudoplastic behaviour is observed is reached at 40% *w*/*w* of silica; for *UDMA* the limit is 50% *w*/*w* of silica. In the low viscosity but more hydrophobic decanediol dimethacrylate (*D$_3$MA*) the limit is even lower. Significant dependence of the viscosity on the shear rate is already observed with 30% *w*/*w* of the nanoparticles. Nanofilled *D$_3$MA* with 40% *w*/*w* of silica which is surface modified with the frequently used silane *MPTMS* is very stiff and the rotational viscosity is not measurable anymore. But if the surface of the nanoparticles is adapted to the matrix, for example by silanisation of the particles with a silane bearing a hydrophobic spacer such as 10-(methacryloyloxy)decyltrimethoxysilane (*MDTMS*), a transparent and smooth material with 40% *w*/*w* of silica is obtained with a viscosity from 2100–1.4 $\mathrm{Pa \cdot s}$ at a shear rate from 1–100 $\mathrm{s^{-1}}$. The viscosity still depends on the shear rate. The measurable viscosity indicates less interaction between the particles, better interaction with the dimethacrylate, as well as improved wettability of the particle surface and stability of the sol. With fumed silica nanoparticles like Aerosil 200 (Degussa, primary particle size 12 nm in diameter), which are highly agglomerated, these high filler contents of nanoparticles in the different monomers cannot be realized, because the viscosity increases much more rapidly and pronounced pseudoplastic behaviour is observed. In *UDMA*, 5% *w*/*w* of silica (Aerosil 200, silanised) increases the viscosity to 54–31 $\mathrm{Pa \cdot s}$ at a shear rate from 1–100 $\mathrm{s^{-1}}$.

The organosols may contribute to improved mechanical properties of a dental composite over those provided by the unfilled monomers. In particular the modulus of elasticity is increased by the addition of the nanofiller (Table 4). When the cured samples were stored in water a decrease in the flexural strength was observed in the composites with a high nanofiller content. The materials become brittle, probably as a result of overloading the composite. A monomer, which already shows brittleness after storage in water, for example, the hydrophilic monomer glycerol dimethacrylate, cannot be improved by the addition of the SiO_2 nanoparticles.

The mechanical properties also depend on the silane used for the surface modification. The decrease in the flexural strength upon storage of the composite sample in water can be reduced by surface modification with the more hydrophobic silane *MDTMS*. But the overall mechanical properties achieved with this silane bearing the flexible decyl spacer are worse than those attained with the silane possessing the propyl spacer. Another silane which shows promising results is the adduct of glycerol dimethacrylate and 3-(isocyanato)propyltriethoxysilane (*UDMS*) (Fig. 8) which has crosslinking properties. Less brittleness of the cured composites is observed after storage in water. Furthermore, the mechanical properties are better than those achieved with *MDTMS* (Fig. 9).

In summary the methacrylate-based silica organosols were transparent or translucent liquids with relatively low viscosity. The mechanical properties, especially the modulus of elasticity, were significantly improved by the nanoparticles. However, in the case of the cured composites the mechanical properties as well as the filler load capacity were influenced by the kind of silane used for the surface modification of the nanoparticles. Surface modification has to be carefully adapted to each kind of monomer to obtain optimal properties.

Table 4. Organosols were additionally filled with 75% *w*/*w* of conventional dental glass fillers and 1% *w*/*w* of photo-initiator; light curing was performed by 6 min. irradiation with a dental light source (Spectramat® Fa. Ivoclar Vivadent AG); polymerised samples were stored 24 h dry, 24 h in water, or 7 days in water before measurement of the flexural strength and the modulus of elasticity

Monomer	Silica/% *w*/*w*	24 h dry	24 h H_2O	7 d H_2O
Flexural strength/MPa				
TEGDMA	0	99	88	99
	40	87	78	92
	60	88	83	64
UDMA	0	85	93	128
	40	103	124	108
SR348C	0	116	98	103
	20	111	107	96
	40	108	106	89
GDMA	0	101	53	60
	20	95	62	46
	40	103	67	38
Modulus of elasticity/MPa				
TEGDMA	0	6330	6380	6840
	40	9660	9900	10900
	60	13260	12080	10490
UDMA	0	5930	6470	8550
	40	12670	12220	11330
SR348C	0	8620	8480	8520
	20	9720	9520	9130
	40	11490	11740	11450
GDMA	0	8540	8160	8420
	20	10580	11100	10780
	40	12560	11940	11940

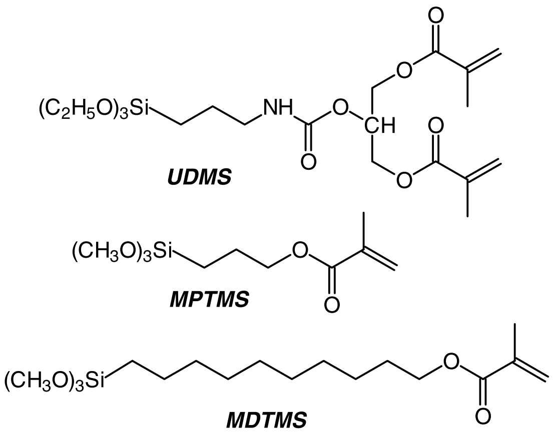


Fig. 8. Silanes used for surface modification

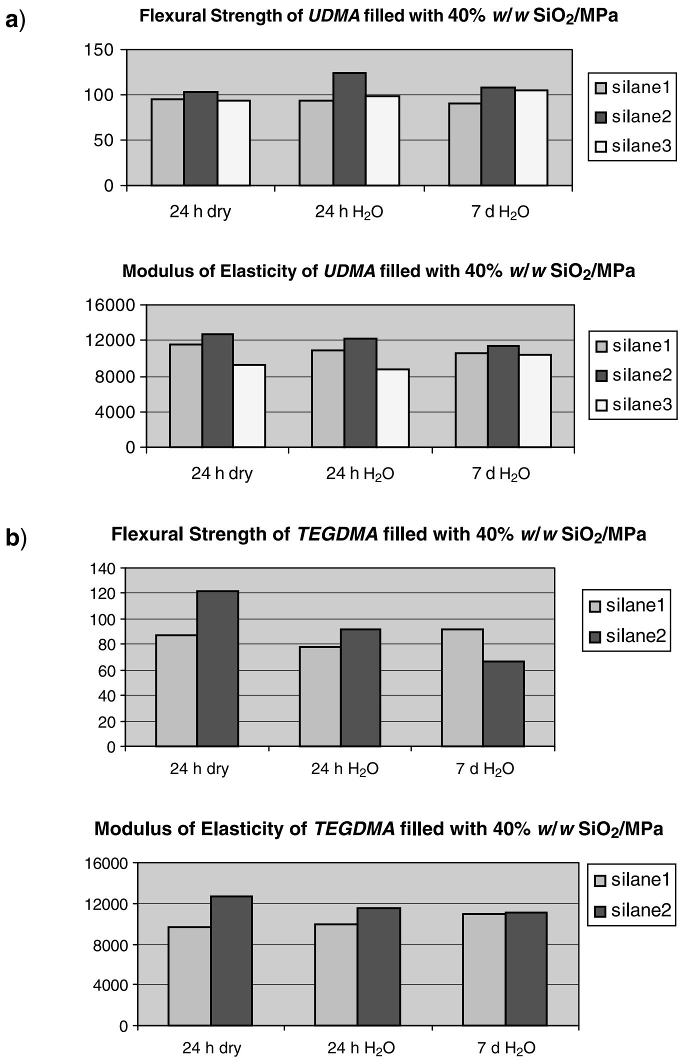


Fig. 9. Mechanical properties of different silanised nanoparticles a) in *UDMA*; b) in *TEGDMA*

Radiopaque Fillers

For dental materials, sufficient radiopacity is also required to allow the composite to be distinguished from the natural tooth on an X-ray photograph. The radiopacity of a compound increases with the use of heavy elements. Therefore, heavy metal compounds are applied. Conventional glass fillers contain heavy metal oxides such as BaO. Other ceramic fillers can also be used. Attractive radiopaque fillers include precipitated $BaSO_4$ and in particular YbF_3 [23]. The heavy metal oxides also increase the refractive index of the filler. By adapting the refractive index of the filler to that of the matrix a higher transparency can be achieved. This increases the cure depth of the filling composite when it is irradiated with visible light by the dentist.

As mentioned, conventional microfillers consist of silica. If the nanoparticles are small enough and if they are not aggregated or the primary and the secondary particle size is below 50 nm, the material becomes translucent or transparent independent of the refractive index. Nevertheless, X-ray opacity is required. Therefore efforts have been made to obtain microfillers with sufficient X-ray opacity in the past few years. Nanoparticles with mixed oxides were prepared in a sol–gel process for instance by co-condensation of silicium alkoxides with other metal oxide precursors. For example, spherical silica-zirconia particles were prepared as well as silica-titania mixed oxides [24]. Additional incorporation of barium oxide was possible. Pure metal oxide nanoparticles were prepared, for example, from zirconium propoxide [25]. Stabilization and surface modification of the metal oxides is crucial and not as simple as with silica. Surface modification was obtained with neopentyl(diallyl)methacrylate zirconate. However, it was necessary to increase the hydrophobicity of the surface to prevent phase separation with the matrix by adding a secondary surface agent such as dimethylethoxyvinylsilane. Another route for the preparation of non-agglomerated zirconia nanoparticles involved the synthesis of a polyether acid zirconium salt from a commercially available zirconium acetate sol (Nyacol) by addition of a polyether monocarboxylic acid [26, 27]. The isolated salt was redispersed in water. After hydrolysis, crystalline zirconia particles were obtained at temperatures of 150–200°C and 2–20 bar. After the concentration of the sol to 10–40% *w*/*w* and the removal of the free acid, the non-agglomerated particles were surface treated for stabilization. Suitable surface treatment agents were polymerisable carboxylic, phosphonic, and sulfonic acids. Dental materials containing this filler showed very high light transmission, a high refractive index, and high radiopacity. In some cases it may be desireable to form weak agglomerates from the heavy oxidic nanoparticles together with non-heavy oxidic nanoparticles to provide strong, highly aesthetic radiopaque materials that retain their polish after repetitive abrasive contact [28]. Further interesting heavy metal oxidic nanofillers include tantalum, niobium, indium, and tin oxide particles [29, 30]. For example, tantalum oxide nanoparticles were prepared using tantalum ethoxide produced by ester exchange with formic acid. To prevent high surface acidity and self-interaction of the particles, a polymerisable silyl phosphonate ester can be applied. Here, the phosphonate ester serves as a surface phosphonating agent, while the silyl group serves as a silanising agent thus rendering the surface hydrophobic (Fig. 10).

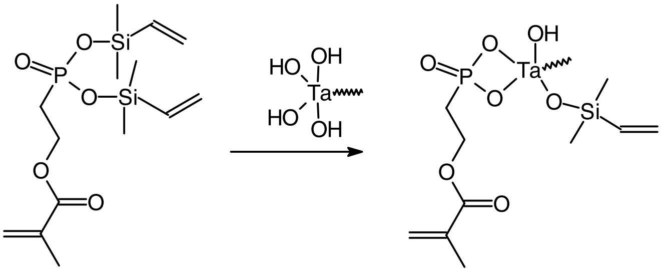


Fig. 10. Surface modification of tantalum oxide nanoparticles with a silyl phosphonate ester

Dental Composites Based on Sol–Gel Inorganic–Organic Hybrid Materials

Inorganic–organic hybrid materials [31–36], which have been synthesised by means of sol–gel processing, combine organic structures such as oligomers or polymers and inorganic oxides at a nanoscopic scale or even molecular level. The starting compounds are hydrolysable and condensable molecular precursors, especially metal alkoxides. Hydrolysis is catalysed by acids, bases, or other strong nucleophiles, such as fluoride anions. The organic parts can just be combined with the inorganic parts by weak interactions, such as *van der Waals* interactions, hydrogen-bridging interactions, or ionic interactions, for example, as interpenetrating networks [37–39] (class I materials). Alternatively, the organic parts can be covalently anchored to the inorganic network (class II materials). This class of hybrid materials can be easily synthesised stepwise starting from alkoxysilanes, which are functionalised with polymerisable groups by hydrolytic condensation or co-condensation with other organofunctionalised alkoxysilanes or metal alkoxides (first step). In the second step the obtained polycondensates are polymerised under formation of a cross-linked inorganic–organic hybrid [40–42]. The hybrid materials show interesting new properties in relation to the single components and can be fine-tuned by adjusting the composition and method of combination. This renders them very attractive for matrices of dental filling composites. The main reason for incorporating inorganic units in the organic matrix is to increase the biocompatibility and wear resistance of the filling composites. In addition, the mechanical properties can be improved and the polymerisation shrinkage reduced which may enhance the marginal adaptation of the filling composites. For this purpose, a number of hydrolysable and condensable trialkoxysilanes bearing methacrylate groups, which are covalently connected to the Si atom *via* different spacers, have been synthesised. On the basis of these silanes, polycondensates were produced, which are called ormocers (**or**ganically **mo**dified **cer**amics). They have already been successfully used in commercially available dental composites. Examples of corresponding silanes include *UDMS* and *EDMS* (Fig. 11). These silanes can be synthesised by the reaction of glycerol dimethacrylate with the commercially

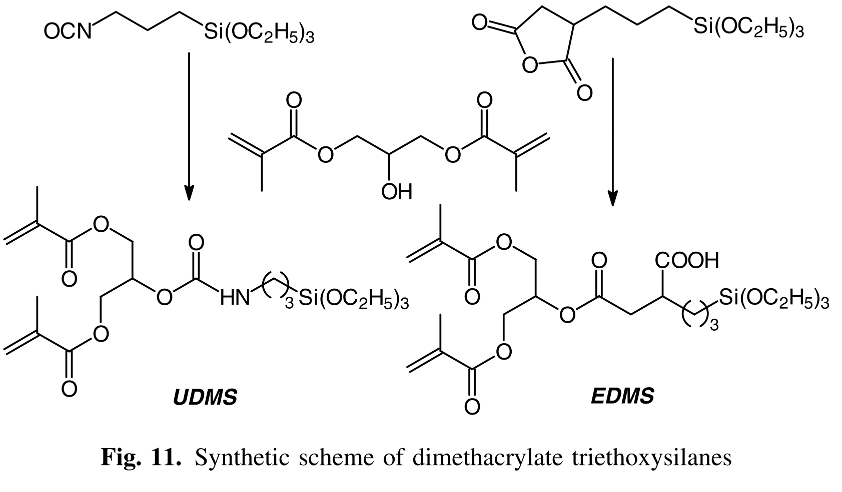


Fig. 11. Synthetic scheme of dimethacrylate triethoxysilanes

available isocyanato or carboxylic acid anhydride-functionalised propyltriethoxysilane. *UDMS* and *EDMS* consist of two methacrylate groups in the monomer structure and therefore enable the preparation of highly cross-linked inorganic-organic hybrid materials. For the composite production, the silanes were hydrolytically condensated, resulting in fluid polycondensates. Based on these polycondensates, composite pastes were prepared by adding the visible-light photoinitiator system, a mixture of conventional fillers and additionally required additives. Unfortunately, the monomer matrix of commercialised *UDMS*-polycondensate based restorative composites still contained a certain amount of dimethacrylates as diluents, for example, decanediol dimethacrylate, because of the high viscosity of the pure *UDMS*-polycondensate. Instead of ester and urethane units bearing spacers [43] between the two methacrylate groups and the hydrolytically condensable trialkoxysilyl group we used amide (Fig. 12, *AMDMS*) or amine linking groups (*ADMS*) [44, 45]. *ADMS* was easily synthesised by *Michael* addition of 3-aminopropyltriethoxysilane with 2-methacryloyloxypropyl acrylate. The hydrolytic condensation of the silane *ADMS*, bearing a more flexible amine spacer, in the presence of catalytic fluoride ions resulted in a polycondensate of relatively low viscosity. Therefore it was not required to add further diluents when the filling composite was prepared. This may further improve the material's biocompatibility, as conventional diluents are no longer required. Moreover, it was found [46] that the polycondensate of silane *ADMS* may increase the cross-linking density and decrease the part of dimethacrylates which is soluble in ethanol and therefore extractable, for example, *UDMA* in the cured composite. Low viscosity hybrid materials were also obtained starting from acrylate- or methacrylate-terminated macromers containing amine links, which were functionalised with hydrolytically condensable silane groups [47–49] (Fig. 13). If the condensation reaction was performed under special reaction conditions in a reactive diluent, stable nanoparticle dispersions with interesting properties were obtained.

The disadvantage of methacrylate functionalised silanes was the relatively high polymerisation shrinkage of their polycondensates. Nevertheless, marginal adaptation was comparable with that of conventional composites [50, 51]. Many efforts have been undertaken to apply principles of non- or low-shrinkage polyreaction systems. For this purpose, other polymerisable groups instead of methacrylate groups were involved in the sol–gel process. It is well known [52] that cyclic monomers, which undergo free-radical ring-opening polymerisation, show lower

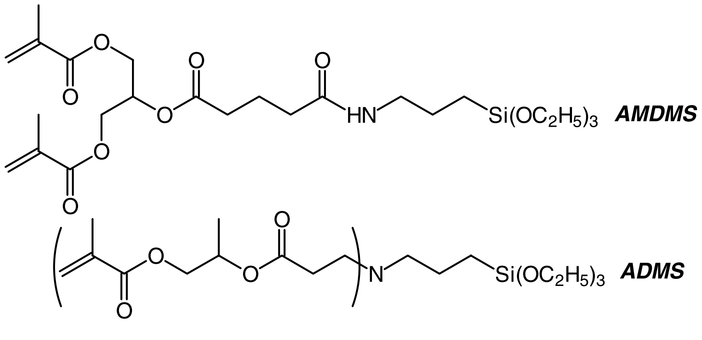


Fig. 12. Structure of amide and amine linked dimethacrylate triethoxysilanes

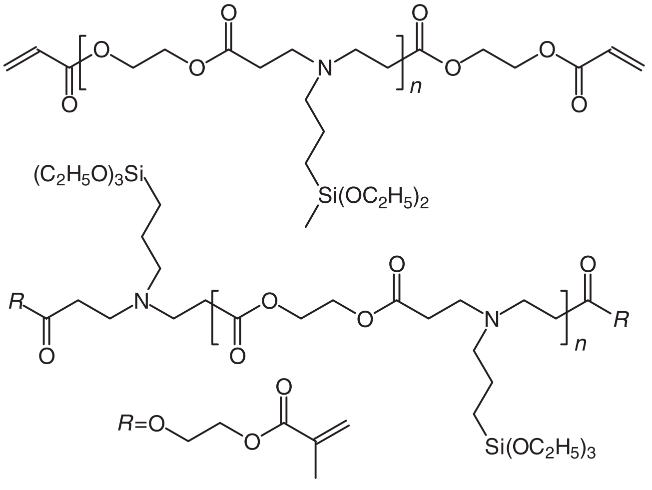


Fig. 13. Examples of macromeric silanes

polymerisation shrinkage than linear monomers. Therefore, silanes with radically ring-opening polymerisable groups such as vinylcyclopropane (*VCPS*) or methylene-1,4-dithiepane groups (*MDES*) (Fig. 14) were synthesised [53, 54]. Monomers that are cureable by cationic ring-opening polymerisation, for example, oxaspiro[4.4]nonane (*OSNS*) or oxetane derivatives (*OXS*) (Fig. 15) [55, 56] represent another promising class of low shrinking compounds. Another well-known approach for fabricating low-shrinking materials is that of thiol-ene polyaddition, *i.e.* the polyaddition of multifunctional thiols and olefinic compounds [57]. Norbornene-group containing silanes were shown to be highly suitable components enabling

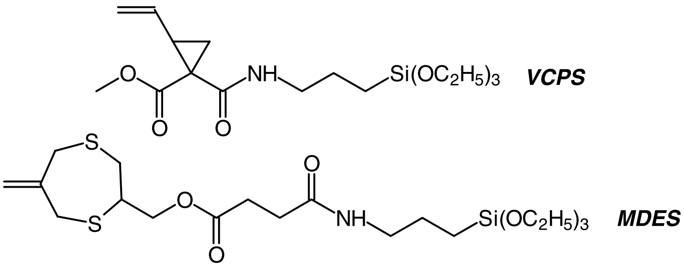


Fig. 14. Silanes containing free-radical ring-opening polymerisable groups

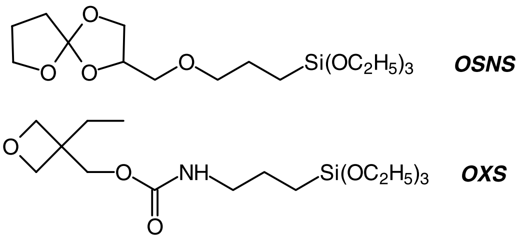


Fig. 15. Silanes containing cationic ring-opening polymerisable groups

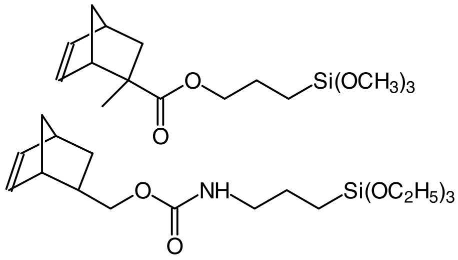


Fig. 16. Norbornene-silanes for thiole-ene polyaddition

the polyaddition with thiols (Fig. 16) [58, 59]. Thiol-ene resin mixtures show low viscosity and can be cured without the formation of an oxygen inhibition layer. However, the odour of the SH compounds prevents their application in dentistry.

Inorganic–organic hybrid materials can be used as a filler in the composite material, if they are milled down to the desired size. Conventional inorganic fillers are thermodynamically not very compatible with the organic polymer matrix. As mentioned above therefore, they are usually surface-modified with suitable silanes, for example, *MPTMS* to hydrophobise the particle surface and, by polymerisation, covalently anchor the filler to the matrix. However, the interface interactions increase significantly with small particles and incomplete silanisation has a dramatically adverse effect on filler loading in the matrix system. Increased numbers of silanol groups make the material more hydrophilic and aggregation of the particles results in phase separation and may reduce the mechanical properties. To overcome these problems, inorganic–organic hybrid materials based on polymerised methacrylates and silica have been prepared, which are called microfiller complexes. The polymeric methacrylate in the hybrid filler improves the thermodynamic compatibility with the matrix, resulting in enhanced wetting capabilities and a lower surface energy of the filler and therefore improves incorporation of the filler into the resin. Furthermore, the polymeric methacrylate improves the mechanical properties of the composite material. Suitable fillers were synthesised, for example, by co-condensation of a trimethoxysilyl-functionalised polymethacrylate precursor with tetraethoxysilane and hydrochloric acid as the catalyst [60]. A scanning electron micrographic study revealed less failures between the matrix and the filler than with pure silica, and the mechanical properties tended to be enhanced compared to those of silane-treated fused silica or pure silica fillers with the same amount of silica in the composite. *J. M. Yang et al.* [61] investigated poly(methyl methacrylate) silica, polystyrene silica, and poly(styrene-co-methyl methacrylate) silica hybrid material with covalent bonding of the polymer structure units to the silica as sol–gel hybrid fillers for dental composites. The best wear resistance was found with the poly(methyl methacrylate) silica. The hardness of the composite increased with increasing filler content, while the flexural strength decreased. The compressive strength was improved compared to that of unfilled resin, but decreased with increasing amounts of filler. Precursors of very different compositions were applied for the sol–gel processing of this kind of fillers, including alkyldialkoxysilanes and other metal alkoxides. Conventional methacrylate monomers such as triethyleneglycol dimethacrylate were also added to prepare the filler

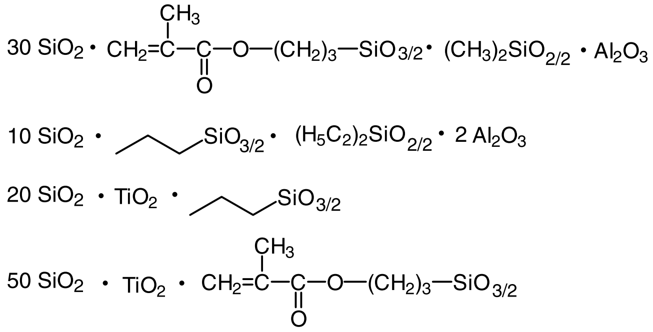


Fig. 17. Examples of inorganic–organic hybrid filler compositions

[62–66]. Some examples of filler compositions are given in Fig. 17. Metal alkoxides increased the hardness of the filler and caused a variation in the refractive index. The adaptation of the refractive index to the matrix prevented the material from being opaque. This is important as the translucency of the composite may influence the depth of cure of the resulting composite when visible-light induced photopolymerisation is used. Another advantage of this kind of hybrid fillers is that the abrasion of the filler and the matrix becomes similar, which helps to prevent the increase of roughness – a problem which tends to occur after some time because the matrix wears faster than the inorganic filler particles. Furthermore, highly polishable materials were obtained. The possibilities of milling hybrid filler glasses to obtain very small particles are limited. However, very small monodispersed soluble organopolysiloxane particles have been synthesized *via* sol–gel processing with methyltrimethoxysilane, vinyltrimethoxysilane, vinylmethyldimethoxysilane, and 1,3-divinyl-1,1,3,3-tetramethyldisilazane as precursors [67, 68]. The isolated particles with hydrodynamic radii of 10–12 nm were readily redispersible in organic solvents, resulting in translucent sols and were added to the resin matrix. With these nanofillers, a higher filler loading could be obtained compared to conventional glass fillers. Moreover, nanofiller-based composites were easier to process due to their lower viscosity [69]. Filler loadings of up to 95% w/w were achieved. As a result, polymerisation shrinkage was significantly reduced. Other curable dental materials contained organic fillers, *e.g.* cross-linked bead polymerisates based on methacrylates, with average particle diameters between 10–100 μm. However, if heavy loads were applied to these materials, their wear resistance decreased and their surface smoothness was not of a satisfying quality. If the bead polymerisates with particle diameters of 1–10 μm were cross-linked by Si–O–Si bridges, their wear resistance improved and smooth, highly polishable surfaces were obtained [70]. These polymerisates consisted of 2–25% w/w polymerised silane monomers such as *MPTMS*.

New Additives and Effects

Nanobuilding Blocks

Small inorganic particles as well defined polymerisable inorganic nanobuilding blocks, *e.g.* cubes or clusters, provide improved or even interesting new properties when they were incorporated into organic polymers or composite materials [71]. The incorporation of $R_8Si_8O_{12}$ cubes (or functionalised polyhedral oligomeric silsesquioxanes, POSS) into polymers has already been investigated for several materials [72]. These rigid cubic structures are prepared by hydrolysis and condensation reaction of silicon precursors with three hydrolysable groups and can be functionalised with polymerisable organic groups. Due to the very small size, the interfacial interactions contribute significantly to the materials properties, the so called interphase properties become important in the composite [73, 74]. In one case it was found that the incorporation of 5% *w*/*w* of methacrylate functionalised POSS monomer significantly reduced the shrinkage of a dental resin and improved the mechanical properties [75]. The cube may also contain four polymerisable groups (Fig. 18), therefore acting as a cross-linking monomer for hard and scratch resistant materials with a high silica content [76]. Other nanobuilding blocks with

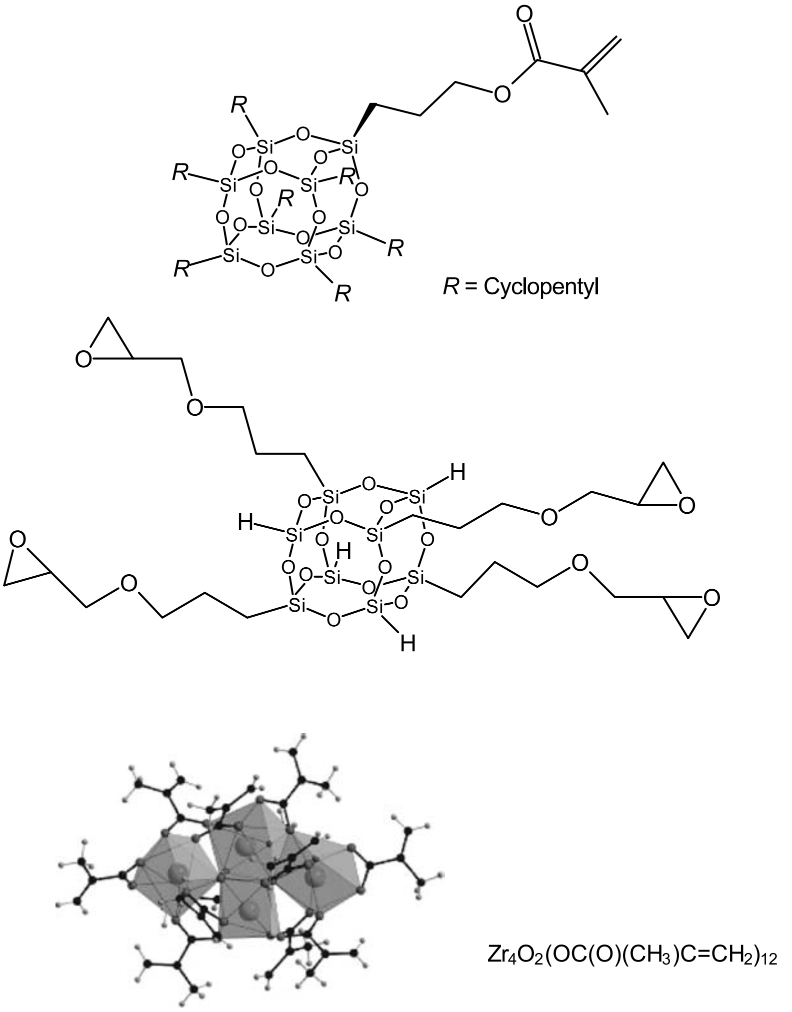


Fig. 18. Polymerisable nanobuilding blocks, Zr cluster with the friendly permission of Dr. Kickelbick (Technical University of Vienna)

great potential for dental applications are functionalised inorganic clusters, for instance the well-defined oxo-zirconium cluster coordinated by methacrylate groups, $Zr_4O_2(OC(O)(CH_3)C{=}CH_2)_{12}$. Due to its small size, it may act as a small nanoparticle in a polymerisable monomer matrix, thus increasing scratch and abrasion resistance. Furthermore, it raises the refractive index and the X-ray opacity. Additionally, a polymerisable oxo-zirconium cluster increases the mechanical properties of the dental compositions due to its high cross-linkability like that of highly functional monomers bearing 12 methacrylate groups [77]. By using the corresponding hafnium cluster instead of zirconium, the X-ray opacity of the monomer matrix is significantly increased. When urethane dimethacrylate was filled with 20% *w*/*w* of the oxozirconium cluster, an X-ray opacity of 25% Al was found, whereas a sample with only 10% *w*/*w* of the corresponding oxohafnium cluster showed an X-ray opacity of 58% Al.

Pigments

Further important additives for dental composites are pigments, which are necessary to match the colour of the natural tooth. The pigments have to be stable in the oral environment and the colour is not allowed to change over time. Oxidic pigments, such as ferric oxide (Fe_2O_3, red) or ferric hydroxide (FeOOH, yellow), are frequently used. Organic pigments often suffer from minor stability. If inorganic particles are used, they have to be ground to small particle sizes to allow them to be well dispersed. In addition, it is particularly difficult to stabilize such pigment particles when their surface area is high. To obtain uniform dispersion and a reproducable colour tone, the surface of the pigment particles can be covered with a polysiloxane film. Therefore coloured oxidic particles were treated with alkoxysilanes, preferably with polymerisable silanes [78]. Organic dyes can be homogeneously incorporated into silica materials and immobilised, for instance in a sol–gel process by preparing a trialkoxysilane with a covalently bonded chromophoric group and co-condensing it with a tetraalkoxysilane (Fig. 19). After hydrolytic condensation, altering, and drying, a strongly coloured xerogel powder is obtained [79].

These new chromophoric xerogels have some advantages in dental materials. They show high colour stability over a long period and improved chemical stability against oxidation and reduction. They are insoluble in oils, water, alcohols, and

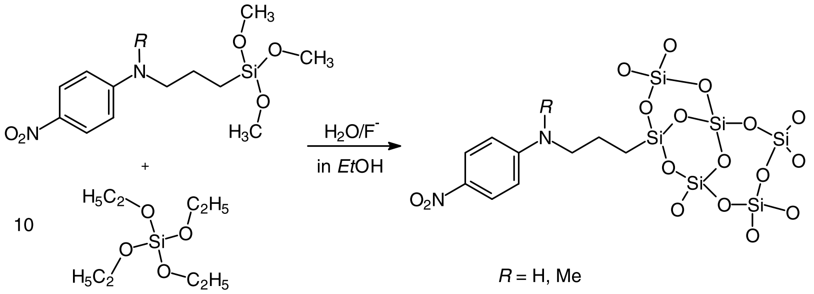


Fig. 19. Preparation of a xerogel pigment

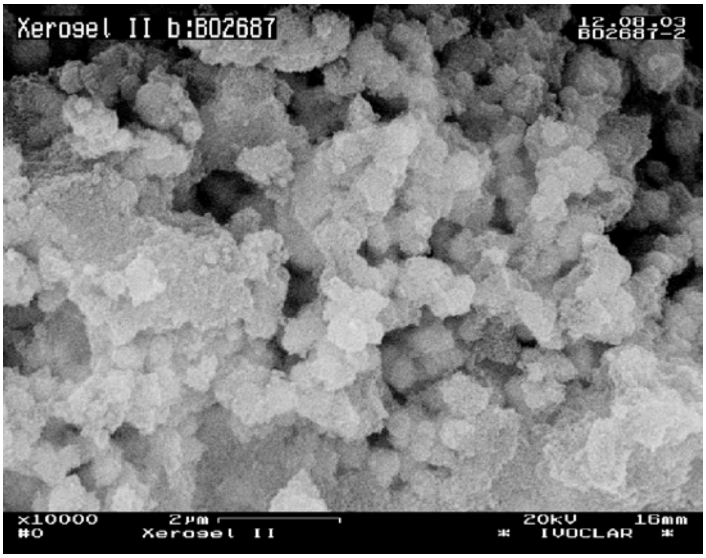


Fig. 20. Scanning electron micrograph of a xerogel pigment

other organic solvents and they are inert to the other dental components. Due to the immobilisation they are non-toxic. But the most important advantage is the significantly higher curing depths that are achieved during polymerisation with visible light, whereas the amount of pigment in the material is reduced by a factor of 10–30, resulting in the same colour intensity [80]. This may be caused not only by a different UV-VIS absorption characteristic of the chromophoric group ($\lambda_{max} = 410\,nm$) compared to that of camphorquinone ($\lambda_{max} = 468\,nm$), the photoinitiator used for visible light curing of the dental composites, but also by the good dispersability in the colouring paste due to the porous weakly agglomerated nanoparticulate structure of the xerogel (Fig. 20), which allows a very fine and homogeneous incorporation into the paste.

Apart from the fact that highly aesthetic dental materials have to match the colour tone of the natural teeth they must also mimic the opalescent effect of the enamel and the character of the living tooth. Materials with an opalescent effect appear reddish if visible light passes through them and they show a blue colour when light is back-scattered. The blue effect in dental enamel is usually mimicked with blue pigments or TiO_2 [81]. The natural colour of the tooth results from the dentin. The opalescent effect in the tooth is caused by the nearly transparent colourless enamel layer. Due to its crystalline structure of well-ordered enamel prisms, which form a lattice structure, the light is refracted in the visible light region causing an opalescent effect. This phenomenon of light diffraction according to *Bragg*'s law can also be obtained by a super lattice built up by monodisperse spheres of 200–250 nm in diameter (the lattice spacing should be about half of the wavelength of visible light), like the silica spheres in natural opal. If the spheres are monodisperse they tend to self-assemble in a lattice-like structure [82]. Monodisperse silica spheres can be prepared by *Stöber*'s method in a sol–gel process [20] (Fig. 21).

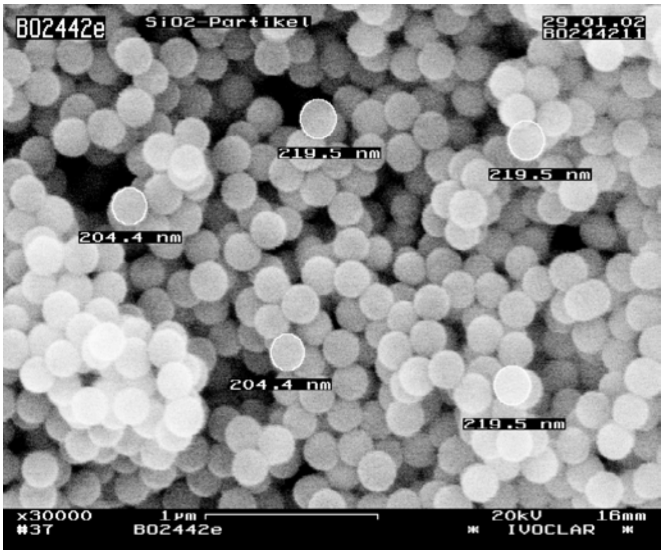


Fig. 21. Scanning electron micrograph of a powder of an opalescent filler

If these particles are surface modified with polymerisable alkoxysilanes and used as a filler in a dental composite, they create a pronounced opalescent effect in the cured material [83]. Colloidal crystals are known to be spontaneously formed by self-assembly of the particles also in nonaqueous dispersions [84]. They can function as a 3-D structural colour pigment. If the particle diameter varies by more than 6%, making the particles become more polydisperse, the opalescent effect is significantly reduced and soon lost. As described in the *Bragg* equations, the *Bragg* diffraction wavelength depends on the crystal volume fraction and the difference between the refractive indexes of the particles and the medium [84]. Therefore the refractive index of the matrix and the filler have to be well adapted to achieve good opalescence but also good transparency of the composite, *e.g.* by using a fluoroalkyl group bearing polymerisable monomers, or by increasing the refractive index of the silica filler by incorporating organic groups, preparing an inorganic–organic hybrid filler. With the monodisperse spherical particles, a much stronger opalescent effect can be observed than with conventional methods. The opalescence can also be adapted to a desired level by increasing the amount of monomer, reducing the crystal volume fraction, or by substituting the particles by much smaller spherical silica particles, *e.g.* of 100 nm in diameter, which reduces the buildup of a crystal, but does not significantly decrease the refractive index and thus the transparency of the composite.

Conclusions

The efforts to improve the performance of restorative composite filling materials is mainly focused on the reduction of polymerisation shrinkage as well as on the improvement of biocompatibility, wear resistance, and processing properties. In this context the use of new nanofillers, for example, SiO_2-based organosols, can contribute to the reduction of the polymerisation shrinkage and improvement of mechanical properties. Moreover, radiopaque nanofillers, for example, mixed oxides of silica and zirconia synthesised by sol–gel processes, enable an increase in the transparency and radiopacity of dental composites. Biocompatibility and wear resistance can be improved by means of polymerisable ormocers when they are used as a substitute for the conventional dimethacrylate matrix monomers. The properties of such composites can be further enhanced by the addition of reactive inorganic nanobuilding blocks, such as polymerisable clusters or POSS monomers. Furthermore, based on the variation of the composition of inorganic–organic hybrids, dental fillers can be tailor-made. Finally, the application of new inorganic additives, such as sol–gel based opalescent fillers or chromophoric xerogel pigment particles helps to meet the aesthetic demands for composites more efficiently.

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