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# Composite materials: Composition, properties and clinical applications

## A Literature Review

Key words: Composite, silorane, ormocer, compomer

**Summary** Various composite materials are available today for direct restorative techniques. The most well-known materials are the hybrid composites. This technology, based on methacrylates and different types of filler coupled with silanes, has been continuously improved. Disadvantages such as polymerisation shrinkage, bacterial adhesion and side effects due to monomer release still remain. The aim of material development is to eliminate or at least reduce these negative factors by adapting the individual components of the material. With ormocers, the methacrylate has been partially replaced by an inorganic network. According to recent studies, the biocompatibility was not improved in all cases. The development of compomer was an attempt to

combine the positive properties of glassionomers with composite technology. This has only partially succeeded, because the fluoride release is low. In an in-situ study, a caries protective effect could be shown at least in the first days following filling placement with concurrent extra-oral demineralisation. By replacing the chain-monomers in the composite matrix by ring-shaped molecules, a new approach to reduce polymerisation shrinkage was investigated. A new group of materials, the siloranes, has been developed. Siloranes are hydrophobic and need to be bonded to the dental hard tissue using a special adhesive system. Long-term clinical studies are still needed to prove the superiority of this new group of materials over modern hybrid composites.

## Introduction

After the establishment of composite as a restorative material, there was an attempt to categorise the different composite types according to filler size (LUTZ & PHILIPS 1983). This classification does not do justice to today's composites, since most of the composite materials belong to the nanocomposites, nano-filled composites, nano-filled hybrid composites or micro-hybrid composites. Although knowledge of filler shape and composition are still important, the development of various matrix components necessitates an additional material classification (Tab. I). For many dentists, there is a lack of practical information about subgroups such as siloranes and ormocers. The present paper aims to describe the properties of the restor-

ative resin materials currently on the market and offer assistance with regard to handling and indications.

## Materials and methods

With the help of currently available literature, this paper has attempted to identify and characterise the properties of the different composite materials. Furthermore, advantages and disadvantages of the different materials were pointed out. The electronic database PubMed was searched for scientific articles on the different filling materials. The search was carried out between March and May 2009. The search words "composite restoration", "ormocer", "silorane" and "compomers" were used. After examining the articles, a further search using the

Tab.1 Classification of composites according to matrix components

| Matrix                     | Chemical system          | Group            | Example of material  |
|----------------------------|--------------------------|------------------|----------------------|
| Conventional matrix        | Pure methacrylate        | Hybrid composite | Tetric EvoCeram®     |
|                            |                          | Nano composite   | Filtek supreme XT®   |
| Inorganic matrix           | Inorganic polycondensate | Ormocers         | Admira®<br>Definite® |
| Acid modified methacrylate | Polar groups             | Compomers        | Dyract eXtra®        |
| Ring opening epoxide       | Cationic polymerisation  | Silorans         | Filtek Silorane®     |

option “related articles” was carried out as well as a hand search to complete the literature search.

### Filling material requirements

In all material development, the basic requirements of a dental filling material should not be forgotten: Every filling material should have good optical characteristics, and the physical properties should correspond with those of dental hard tissue. Wear resistance and the effect on the antagonist should be similar to the properties of enamel. It is also important that the material is easily distinguishable from dental tissue on x-ray. The material should be easy to handle and easy to polish. Likewise, the material should form a sufficient bond with dental tissue or at least with a dental adhesive. The material should, of course, be tasteless and biocompatible. Most of these requirements are recorded in the ISO standards (ISO 4049). However, the range allowed for dental products is very wide and this may lead to the approval of products, which only narrowly meet the requirements.

### Composite

Composite (componere = to combine) is the universally used tooth-coloured direct restorative material (Fig. 1a and 1b). Composites were developed in 1962 by combining dimethacrylates (epoxy resin and methacrylic acid) with silanized quartz powder (BOWEN 1963). Thanks to their properties (aesthetics, and advantages of adhesive technology) composites have taken over the place that was occupied by amalgam.

The material consists of three components: resin matrix (organic content), fillers (inorganic part) and coupling agents.

The resin matrix consists mostly of Bis-GMA (bisphenol-A-glycidyl dimethacrylate). Since Bis-GMA is highly viscous alone, it is mixed in different combinations with short-chained monomers such as TEGDMA (triethylenglycol-dimethacrylate). The lower the Bis-GMA content and the higher the proportion of TEGDMA, the higher the polymerisation shrinkage (GONÇALVES ET AL. 2008). Replacing Bis-GMA with TEGDMA increases the tensile but reduces the flexural strength of the material (ASMUSSEN & PEUTZFELDT 1998). Monomers can be released from the restorative material. Longer light polymerisation improves the rate of conversion (chain-linking of the individual monomers) and thus leads to less monomer release (SIDERIOU & ACHILIAS 2005).

The fillers are made of quartz, ceramic and or silica. With increasing filler content the polymerisation shrinkage, the linear expansion coefficient and water absorption are reduced. On the other hand, with increasing filler content, the compressive and tensile strength, the modulus of elasticity and wear resistance are generally increased (KIM ET AL. 2002). The filler content of a composite is sometimes determined by the shape of the filler. In a study with different types of composite, those materials with pre-polymerised composite fillers were shown



Fig. 1a Initial situation: Loss of tooth substance due to wear and obvious staining. The patient was not satisfied with the aesthetics.



Fig. 1b Aesthetic improvement after home bleaching and direct composite veneers (hybrid composite: Miris®). The crown of tooth 43 was left and the discoloured tooth margin was masked using an opaque coloured hybrid composite.

to have the lowest filler content and thus also the lowest flexural strength and hardness. Composites with round fillers had the highest filler content, which was associated with higher hardness and high flexural strength. For mixed filler particles (hybrid composites) there was no linear relationship between filler content and flexural strength (KIM ET AL. 2002). In one study of 72 restorative materials it was also shown that filler volume had a significant influence on the mechanical properties. The relationship between filler content, flexural strength and modulus of elasticity was most obvious (LIE & HICKEL 2009a).

The stable bond between the filler and matrix further influences the material properties. The quality of the bond affects

Tab. II Classification of composites according to filler particles (LUTZ & PHILIPS 1983)

| Filler   | Macro-filler (>10 µm)  | Micro-filler (0.01–0.1 µm)  | Micro-filler complexes  |
|--|--|---|---|
| <b>Composite type</b>  | Macro-filler composite   | Hybrid composite  | Homogenic Micro-filler composite  |
| <b>Properties</b>  | + physical properties<br>+ radiopacity<br>– polishability<br>– wear resistance | + radiopacity<br>+ polishability<br>+ physical properties<br>– polymerisation shrinkage | + polishability<br>– wear resistance<br>– water absorption<br>– radiopacity<br>– polymerisation shrinkage |
| <b>Purpose</b>   | Core build-up material under indirect restoration?<br>No longer indicated      | All classes of restoration  | Small anterior restorations Class V   |
| <b>Example</b>   | Prisma-Fil®  | Tetric Ceram®   | Palfique®   |
| +: positive property, performance acceptable    -: negative property, performance unacceptable |  |   |   |

the abrasion resistance of the restorative material (MANHART ET AL. 2000). The compound phase molecules have a silane group at one end and a methacrylate group at the other end and can bond with both the filler and the resin matrix. Silanisation of the filler is important for material strength (IKEJIMA ET AL. 2003).

The LUTZ & PHILIPS (1983) classification, which is still popular, allows composites to be ordered according to filler size (Tab. II). Nanofillers and nanoclusters enhance the long-term stability and the polishing properties of micro-filler composites are made possible by the use of nanoparticles and nanoclusters. The mechanical stability achieved in hybrid composites is due to larger filler particles or “nanoclusters”. Superficial filler particles are lost due to abrasion. The nanoclusters of the nanocomposites are hereby broken down into nanoparticles. These particles are smaller than the wavelengths of visible light. It has been shown that surface polish is preserved longer after wear tests in composites with filler particles <0.4 µm (MITRA ET AL. 2003). Nanoparticles can be incorporated into cells but their toxic potential is still largely unknown (KOENEMAN ET AL. 2009).

There have been attempts to improve the antimicrobial and caries inhibiting properties of the filling material using specific modifications. The caries protective effect of fluoride has been known for some time in dentistry. First fluoride salts (NaF, KF, SrF<sub>2</sub>, SnF<sub>2</sub>) were added to the matrix (SWARTZ ET AL. 1976). While these salts release fluoride at first, this effect decreases quickly. Furthermore, the fluoride salts adversely affect the mechanical properties of the restorative material. Later filler materials containing fluoride were used (fluoroaluminumsilicate-glass, YbF<sub>3</sub>) (XU & BURGESS 2003). At the moment nearly all fluoride containing composites and compomers use this filler type. The use of fluoride containing fillers in addition to tetrabutylammonium fluoride (TBAF) in the monomer matrix has led to an improved release and storage of fluoride in the filling material in in-vitro tests (XU ET AL. 2006). In addition, the mechanical and physical properties of the restorative material are acceptable, whereas the solely addition of TBAF to the matrix results in deterioration of these properties (GLASSPOLE ET AL. 2001, XU ET AL. 2006). It has also been attempted to introduce antimicrobial substances into the filling material. The addition of chlorhexidine has a negative effect on the mechanical properties of the material. Similarly, silver ions were added to the material. The addition of silver ions has been shown to have a very good protective effect against *S. mutans* (YOSHIDA ET AL. 1999). These antimicrobial qualities have been exploited for some time in the impregnation of carious deciduous teeth.

However silver has an unfavourable influence on the colour of the restorative material, which in turn must be masked by other substances.

Thanks to the many modifications since their introduction nearly 50 years ago, modern composite materials are, when used correctly (dry operation field, application in layers, sufficient polymerisation), a reliable restorative material for nearly all applications.

### Ormocers

Ormocers, a word originally derived from organically modified ceramic, were originally developed for science and technology (e.g. for special surfaces like protective coatings, non-stick surfaces, anti-static coatings and non-reflective coatings). In contrast to conventional composites, the ormocer matrix is not only organic but also inorganic. Therefore monomers are better embedded in the matrix what reduces the release of monomers.

Ormocers basically consist of three components – organic and inorganic portions and the polysiloxanes. The proportions of those components can effect the mechanical, thermal and optical qualities of the material:

1. The organic polymers influence the polarity, the ability to cross link, hardness and optical behaviour.
2. The glass and ceramic components (inorganic constituents) are responsible for thermal expansion and chemical stability.
3. The polysiloxanes influence the elasticity, interface properties and processing.

The inorganic components are bound to the organic polymers by multifunctional silane molecules. After polymerisation the organic portion of the methacrylate groups form a three-dimensional network.

In spite of all efforts to create a better restorative material using ormocers, their performance (cervical and occlusal marginal adaptation) was significantly worse when compared to today's hybrid composites, after cyclical loading in a laboratory test (KOURNETAS ET AL. 2004). However, no significant differences were found in a five-year clinical comparison of Admira® (ormocer) and Tetric Ceram® (hybrid composite) (BOTTENBERG ET AL. 2009). At the same filler content, ormocers have a reduced polymerisation shrinkage compared to hybrid composites (YAP & SOH 2004) or at a lower filler content of the ormocer the polymerisation shrinkage is equal to that of a conventional composite (CATTANI-LORENTE ET AL. 2001).

ROSIN ET AL. (2003, 2007) investigated the “in-vivo” quality of ormocer restorations in a clinical trial over one and two years. The clinical application was acceptable, but there were concerns about the marginal adaptation and the indication for class V restorations due to poor adhesion. In contrast, another study found no difference in longevity of restorations between ormocers and Bis-GMA-based systems (BOTTENBERG ET AL. 2007, 2009). However, the five-year control showed a much stronger tendency to discolouration with one of the two ormocer materials compared to the other materials (BOTTENBERG ET AL. 2009). Another one-year study found that an ormocer (Definite®) failed to meet the requirements for restoration longevity compared to a conventional composite resin for class II restorations. Numerous restorations had to be replaced within the first year (OBERLÄNDER ET AL. 2001).

AL-HIYASAT ET AL. (2005) examined the cytotoxicity of three different filling materials and their flowables (Admira®, Z250®, Tetric Ceram®). The ormocer material (Admira®) had the highest cytotoxicity in the standard composites but the lowest regarding flowables. This has been rejected by another study, which showed that an ormocer (CeramX®) released significantly less monomers such as Bis-GMA, TEGDMA or UDMA compared to either a nanohybrid composite (Filtek supreme XT®) or a self-curing composite (Clearfil Core®) (POLYDOROU ET AL. 2009).

With respect to microhardness, the ormocers are comparable with hybrid composites, but their wear resistance is lower (SAY ET AL. 2003). This contradicts other studies, which have shown less wear for ormocers (TAGTEKIN ET AL. 2004, YAP ET AL. 2004a) (Fig. 2a–c).

### Compomer

The word “compomer” comes from **composite** and **glassionomer**. The material itself is a polyacrylic-/polycarboxylic acid-modified composite. Compomers are composed of composite and glassionomer components. It is an attempt to take advantage of the desirable qualities of both materials: the fluoride release and ease of use of the glassionomers and the superior

material qualities and aesthetics of the composites. In addition to the various polymerizable monomers (e.g. UDMA) the material also contains dicarboxylic acids, which in contrast to those in traditional glassionomers have polymerisable double bonds.

The reactive fluoroaluminumsilicate glasses from the glassionomer technology are found in compomers. The particle size of fillers in these products varies from 0.2 µm up to 10 µm (ZANTNER ET AL. 2004). Compomer restorations have been shown to have insufficient retention without pre-treatment of the dental hard tissue with an adhesive system (FOLWACZNY ET AL. 2001a, MOODLEY & GROBLER 2003).

The composition and properties of these adhesives do not differ fundamentally from adhesives used for composites. The setting reaction of the compomer is based primarily on the polymerisation of acidic monomers. The acid-base reaction, which starts only after water absorption, is limited to the superficial layers. Although, for a narrow range of indications, certain coloured compomer materials (Comp natur®) may be of interest for use in adults (KALWITZKI & KRÄSTL 2007) (Fig. 3a–c), compomers are most suitable for restorations in the deciduous dentition due to their low abrasion resistance (Fig. 4) (BERG 1998, ZANTNER ET AL. 2004, KRÄMER ET AL. 2006). In cervical restorations, compomer restorations performed better than resin-modified glassionomers but not as well as hybrid composites (FOLWACZNY ET AL. 2000, FOLWACZNY ET AL. 2001a, b). The fluoride release of compomers increased quickly initially (24 hrs), but decreased equally quickly (PRESTON ET AL. 1999, VERMEERSCH ET AL. 2001, ASMUSSEN & PEUTZFELDT 2002, ITOTA ET AL. 2004). The ability of compomer to be recharged with fluoride from its environment resulting in longer lasting caries prevention, has been discussed (VIEIRA ET AL. 1999). An in-situ experiment showed that caries development next to compomer restorations (Dyract eXtra®) was lower than next to composite restorations (Spectrum TPH®). The fluoride release over 28 days had an inhibitory effect on caries development in the adjacent tooth (LENNON ET AL. 2007). It has also been shown that fluoride release into saliva was less for young permanent teeth than



Fig. 2a Tooth-/restoration fracture in tooth 46.



Fig. 2b After excavation the high degree of tooth destruction is evident. The available financing is limited.



Fig. 2c Direct adhesive composite build-up (nano-filled hybrid composite in part with ormocer-matrix: CeramX®).



**Fig. 3a** Tooth 22 congenitally missing; tooth 23 needed endodontic treatment due to carious lesion. The available financing is limited.



**Fig. 4** Treatment of caries in a deciduous tooth using a glittering green compomer material (Twinky star®).



**Fig. 3b** Cosmetic coronal extension of the gingival margin of tooth 23 using a gingival coloured compomer (Comp natur®). Tooth 24 was also endodontically treated and provisionally restored with a temporary material.



**Fig. 3c** The cervical margin of tooth 23 was restored using compomer (Comp natur®). The remaining crown was built up using a hybrid composite (Miris®).

for deciduous teeth. It is assumed therefore that young permanent teeth can store more ions in the enamel (GJORGIEVSKA ET AL. 2008). However, a clinical study showed no difference in new caries development in children who received compomer restorations compared to those who had amalgam restorations (TRACHTENBERG ET AL. 2009). The fluoride regeneration is mainly determined by the glass component and the hydro-gel layer. The hydro-gel layer is, in turn, dependent on the acid-base

reaction (HAN ET AL. 2002, ITOTA ET AL. 2004). Therefore, both the fluoride release and the fluoride re-uptake are greatest in glassionomers followed by compomers and then by composites (ASMUSSEN & PEUTZFELDT 2002, ITOTA ET AL. 2004).

The increased water absorption of the compomer compared to conventional composite results in marginal discolouration interfering with aesthetics particularly in the anterior teeth. Compomers are also contraindicated for large core build-ups due to their poor abrasion resistance (HSE & WEI 1997, WUCHER ET AL. 2002, YAP ET AL. 2004b).

#### Silorane

The name of this material class refers to its chemical composition from **Siloxanes** and **Oxirans**. This product class aims to have lower shrinkage, longer resistance to fading and less marginal discolouration. The silorane monomer ring differs obviously from the chain-monomers of hybrid composites.

The hydrophobic properties of the material are caused by siloxanes. Exogenous discolouration and water absorption are reduced. The oxirane rings are responsible for the physical properties and the low shrinkage. Siloranes are polymerized by a cationic reaction in contrast to methacrylates, which cross-link via radicals. The photoinitiator system is based on three components: light absorbing camphor chinon, an electron donor (eg amine) and an idonium salt. The camphor chinon is excited and reacts with the electron donor, which reduces the idonium salt to an acidic cation in the process. This starts the opening process of the oxirane ring. The opening of the oxirane rings during the polymerisation process compensates to some degree for the polymerisation shrinkage. The fillers in Filtek Silorane®, the only silorane material on the market at the moment, consist of 0.1–2.0 µm quartz particles and radiopaque yttrium fluoride.

A comprehensive study of Filtek Silorane® was carried out by WEINMANN ET AL. (2005): It confirms the low shrinkage (<1%) and found that the light stability of the silorane was seven times longer than for methacrylates. The siloranes low shrinkage leads to a lower contraction stress (ERNST ET AL. 2004, BOUILLAGUET ET AL. 2006, ILIE ET AL. 2007). The silorane-based filling material was shown to have both low water absorption and water solubility (PALIN ET AL. 2005). The adhesion of streptococci observed on the surface of silorane restorations was low, maybe because of its hydrophobic properties (BÜRGERS ET AL. 2009a). Siloranes have been shown to have good storage stability in various media and compared to conventional com-

posites they are less susceptible to changes if stored in ethanol (LIE & HICKEL 2009b). Filtek Silorane® has good polishing characteristics. The material showed little colour change after artificial ageing and the surface gloss was retained (FURUSE ET AL. 2008).

The clinical application of these materials is limited to the posterior teeth because few low translucent colours are available (Fig. 5a, b). Because of the hydrophobic properties the appropriate adhesive system must be used for silorane restorations. Dentists both value and recognise the challenge of the relatively high viscosity. At the moment the weak radiopacity is a disadvantage since the limitations of the restoration are difficult to recognise on radiographs (Fig. 5c, 5d).

## Discussion

Clinical studies have shown that the different restorative materials have similar success rates (ERNST ET AL. 2006, MAHMOUD ET AL. 2008). The clinical outcome of Filtek Supreme® (nanocomposite), Tetric EvoCeram® (nano-hybrid composite), Tetric Ceram® (hybrid composite) and Admira® (Ormocer) was classified as equivalent on the basis of clinical parameters. A comprehensive study on the physical properties of different restorative materials (flexural strength, compressive strength and tensile strength) was able to demonstrate considerable differences in the same material group. The filler content had the greatest influence on the material properties (LIE & HICKEL 2009a). An investigation of the adhesion of *C. albicans* to the surface of the material showed less adhesion on the surface of compomers and ormocers (BÜRGERS ET AL. 2009b). No correlation was found between surface roughness, surface tension and adhesion. In contrast, the matrix composition appears to be crucial for adhesion (BÜRGERS ET AL. 2009b). The hydrophobic properties of Filtek Silorane® also appear to be unfavourable for the adhesion of *S. mutans* (BÜRGERS ET AL. 2009b). Jandt and Sigusch recently presented possible directions for future resin material technologies (JANDT & SIGUSCH 2009). The further development of nanotechnology and antimicrobial materials has a high potential. The realisation of “smart materials” would certainly be interesting. These are restorative materials, which are able to react directly to external stimuli (e.g. release of antimicrobial substances in the case of a drop in pH in the vicinity of the restoration). Research is also done in the area of self-repairing materials and in material science for bone and

dental hard tissue regeneration (JANDT & SIGUSCH 2009). Further material developments should be followed with interest but also with critical consideration. For clinical practice it is important, that sufficient clinical data are available before a new material is used clinically.

The development of high performance restorative materials is essential to the success of dental treatment. It must be noted that in addition to the restorative material, other aspects are important for success. These are a reliable and correctly applied adhesive, a patient with good oral hygiene, and last but not least a dentist who carefully and correctly handles the materials (HICKEL & MANHART 2001).

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## Résumé

Différents matériaux en composite sont aujourd'hui disponibles pour les restaurations directes. L'article donne une vue synoptique de la littérature actuelle et montre les différences. Les matériaux les plus populaires sont les *composites hybrides*. Cette technologie basée sur les méthacrylates et sur les différentes particules qui sont liées avec des silanes a sans cesse été améliorée. Les points négatifs sont toujours la rétraction durant la polymérisation, l'adhésion de bactéries et la possibilité d'effets secondaires liées aux monomères. Le but du développement des matériaux est d'éliminer ou au moins de réduire ces facteurs négatifs en changeant les différents composants. Avec les *ormocers*, la matrice des méthacrylates a été partiellement remplacée par une structure anorganique prépolymérisée. Malheureusement la littérature actuelle montre que la cytotoxicité n'a pas toujours pu être diminuée. Avec le développement des *compomères*, on a voulu combiner la diffusion de fluorides avec les propriétés du composite. Cela n'a réussi que partiellement parce que la diffusion de fluorides est très discrète. Cependant, on a quand même pu montrer un effet prévenant les caries – au moins au cours des premiers jours suivant l'application – dans les tests in situ. En échangeant certains monomères ayant une structure de chaînes par des molécules avec une structure d'anneau, on a analysé une nou-



**Fig. 5a** Tooth 17 with insufficient amalgam restoration with clearly erosive defect. Tooth 16 is root canal treated and has a temporary restoration.



**Fig. 5b** Class II mo silorane restoration in tooth 17 (Filtek Silorane®).



**Fig. 5c** Initial radiograph of the clinical case shown in Fig. 5a–b. The amalgam restorations are easily detectable due to the high radiopacity.



**Fig. 5d** Final radiograph of the case shown in Fig. 5a–b. The silorane restorations in teeth 17, 16 and 14 are difficult to distinguish from the tooth substance due to the poor radiopacity.

velle technique visant à réduire la rétraction durant la polymérisation. Une nouvelle catégorie de matériaux – les *siloranes* – a ainsi été développée. Les *siloranes* sont très hydrophobes et doivent être appliqués avec un adhésif spécifique à la surface

dentaire. Des études cliniques à long terme doivent montrer si ces nouveaux matériaux sont supérieurs aux composites hybrides.

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