FUNCTIONALIZED ORMOCER® RESINS AS BASIS FOR HIGHLY AESTHETIC, LOAD-STABLE AND BIOCOMPATIBLE DENTAL MATERIALS

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Keywords: ORMOCER®, composites, dental prostheses, biocompatibility, translucency

Abstract

Objectives: To be applicable as permanent dental prostheses suitable composite materials have to meet excellent biocompatibility, high mechanic characteristics and a tooth-like aesthetics/translucency adapted to the different areas of the tooth (dentine and enamel). To realize all these requirements the aim of this study was the development of monomer-free hybrid composites with high flexural strength and translucency based on ORMOCER®-resins with different functionalizations.
Methods: Flexural strength/Young's modulus of the ORMOCER®-resins/-composites were determined using a three point bending test according to ISO 4049. Translucency was measured by use of a spectrophotometer and the refractive indices by means of an Abbe-refractometer (589 nm, 20 °C). Investigations on biocompatibility were performed with the help of WST-1-/ BrdU-test [1].
Results: Compared to the basic resin/composite the functionalized analogues show a significantly higher flexural strength and translucency due to the higher amount of C=C-groups and the adapted refractive indices as well as an excellent biocompatibility according to WST-1-/ BrdU-test [1].
Conclusion: By functionalizing the monomer-free ORMOCER®-resins in combination with an individualized particle system biocompatible hybrid composites can be adjusted in their mechanical/optical characteristics for the different layers of teeth (dentine and enamel) and represent an excellent basis for a load-stable and highly aesthetic dental prostheses such as multilayered crowns or artificial teeth.

1. Introduction

For the care of severely damaged or lost teeth prefabricated materials for dental prostheses, such as artificial teeth for partial/full dentures or blocks for crown manufacturing using the established CAD/CAM-technology, are often used. To be suitable for a permanent indirect prosthetic restoration composites have to meet complex requirements. These are, in particular, the essential mechanical properties to withstand the high occlusal forces especially in the region of antagonistic teeth, an excellent biocompatibility and a tooth-like aesthetics (translucency adapted to dentine and enamel). For the latter the prefabricated materials for dental prostheses such as CAD/CAM-blocks or artificial teeth are often multilayered to emulate the optic of a natural tooth. With regard to the processability the ORMOCER®-resins/-composites also have to possess a suitable rheological behavior.
As a fundamental prerequisite for the implementation of appropriate dental composites a high quality resin/matrix has to be used. Due to a variety of advantages and an enormous variability to adjust e.g. mechanical and optical properties (flexural strength, refractive index, etc.) inorganic-organic hybrid

Excerpt from ISBN 978-3-00-053387-7

polymers (ORMOCER®s) [2] are an ideal material to realize the required properties. ORMOCER®s are based on multifunctional silanes which contain hydrolyzable/condensable alkoxysilyl groups, an organic polymerisable functional group (e.g. a methacrylate group) and an organic spacer unit as connecting element. In addition further modifications can be brought into the network by functionalizing the spacer unit (e.g. hydroxyl, carboxyl, phosphorus containing groups) [3]. The fundamental structure of a multifunctional silane is shown in Figure 1. The inorganic network of ORMOCER®s is formed first by the classical inorganic sol–gel-processing reactions. Thereby a controlled hydrolysis and condensation of the multifunctional silanes leads to an oligomeric Si-O-Si-nano structure. The second step of ORMOCER® synthesis is the crosslinking of the organic polymerizable functional groups during the final curing step [4]. In the case of dental materials the reactive organic unit of the precursor is often a methacrylate group that creates the three-dimensional polymer structure by a radical polymerization which can be initiated by light or thermal curing and by redox initiator systems. Finally, composites are formed by incorporation with organic or inorganic fillers.

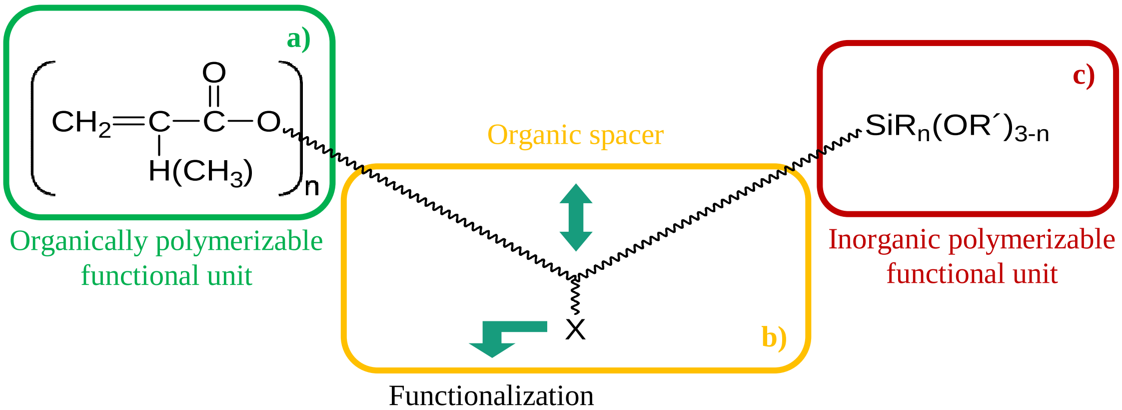

Figure 1. Basic structure of a multifunctional silane. Organically polymerizable functional unit (a), organic spacer unit with further functional groups → X: e.g. hydroxyl, carboxyl, phosphorus containing groups (b) and inorganic polymerizable functional unit → R = alkyl groups (c)

Because of the inorganic oxidic network in combination with the attached organic polymer structure there are additional advantages like high hardness and abrasion resistance, if needed, a comparably low polymerization shrinkage during the curing process and an excellent biocompatibility due to the absence of dental monomers (important for avoiding allergic reactions).
Therefore ORMOCER®-resins and composites thereof are an interesting material class, especially, if very demanding requirements have to be realized. In this study monomer-free hybrid composites based on ORMOCER®-resins with different functionalizations for an adapted translucency are a promising approach for the development of load-stable and biocompatible multilayered crowns or artificial teeth with high strength and highly aesthetic properties.

2. Materials and methods

Composites based on four ORMOCER®-resins (I-IV) were manufactured. Resin I is a basic resin system with coupling groups for functionalization in order to adapt the refractive index. Relating to this, resins II-IV are based on resin I and functionalized with different aromatic groups. The flowable resins (viscosity: 3.9 - 128/1.1 - 15 Pa·s at 25/40 °C) were synthesized following the general procedure of hydrolysis and polycondensation reactions using the above mentioned precursor silanes. The refractive indices of the cured resins are in a range of $n_D = 1.500$ to 1.525. In principle various inorganic surface functionalized filler particles are available to achieve composites with different variations of types, sizes, amounts and ratios of the filler components. Due to this, the filler combination has a high impact on the final properties of the resulting composites. To enable comparable results in this study, two components of one filler type are processed in each composite (see Table 1, I_C-IV_C). Those fillers with mean particle sizes of 0.4 µm, 0.7 µm and 3.0 µm are based

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on type GM27884, a barium containing dental glass, with a refractive index of n_D = 1.528. The fillers are irregularly shaped and surface-modified with the silane coupling agent 3-methacryloyloxypropyl-trimethoxysilane. The filler content of the composites is in a range of 60 - 70 wt.%. The incorporation of the fillers was performed by using a three roll mill and a planetary mixer. Polymerization of the material was carried out thermally (T = 100 °C) or light-induced (λ = 380 - 420 nm). The mechanical properties of the ORMOCER®-resins/-composites, such as flexural strength and Young's modulus, were determined using a three point bending test according to ISO 4049. The translucency was measured by means of a spectrophotometer and the refractive indices by use of an Abbe-refractometer (589 nm, 20 °C). Investigations on biocompatibility were made with help of WST-1-/ BrdU-test [1].

3. Results and discussion

As shown in Table 1 resins II-IV show with 111-115 MPa a significantly higher flexural strength compared to resin I with only 91 MPa. In addition to that the corresponding composites II_C (σ = 151 MPa), III_C (σ = 159 MPa) or IV_C (σ = 145 MPa) also achieve higher flexural strength than composite I_C (σ = 131 MPa). This can be explained by the higher amount of polymerizable C=C-groups of the functionalized resins II and IV or the corresponding composites II_C and IV_C. The higher flexural strength of resin III and composite III_C, respectively, might be explained by different arrangements of the C=C-groups in the organic structure. Also the Young's modulus of the functionalized resins reaches higher values than the basic resin. In the same way the composite II_C shows a higher Young's modulus compared to composite I_C which differs only in the matrix. For the other two composites III_C and IV_C with lower filler contents (60 wt.%) a comparison is not expedient because Young's modulus especially depends on the filler content. Due to the high viscosity of the corresponding resins III and IV a filler content of 60 wt.% is the maximum value to ensure a good processability with regard to the manufacture/application process.

Table 1. Composition and overview of optical, mechanical and biological data of ORMOCER®-resins (I-IV) and corresponding composites (I_C-IV_C)

		Resins				Composites			
		I	II	III	IV	I_C	II_C	III_C	IV_C
Filler content [wt.%]		-	-	-	-	70	70	60	60
C=C-groups / Si		0.95	1.29	0.95	1.14	0.95	1.29	0.95	1.14
Refractive index (cured material)		1.500	1.525	1.525	1.520	-	-	-	-
Flexural strength [MPa]		91±6	115±4	111±3	112±3	131±8	151±11	159±5	145±12
Young's modulus [GPa]		2.0±0.06	2.5±0.11	2.3±0.10	2.5±0.15	7.0±0.30	7.9±0.33	6.5±0.32	6.2±0.39
Translucency [%]		86	77	82	85	22	47	61	44
Relative growth [%]	WST-1-test	102±13	99±7	90±6	97±4	N/A	102±6	N/A	N/A
	BrdU-test	107±12	97±5	98±5	97±8	N/A	100±6	N/A	N/A

Because of the size of the used fillers (possibly partially agglomerated) it is necessary to achieve adapted refractive indices of the filler-matrix-combination to receive translucent composites. Functionalization allows a very precise modulation of the refractive index n_D of the resins in the range of 1.500 – 1.525 leading to an individualized adaption to the refractive indices of commercially available dental glass particles ($n_D \approx$ 1.500 – 1.530) as these are the main part of fillers used in dental composites. Due to the well-adjusted refractive indices of the used dental glass particles ($n_D \approx$ 1.528)

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and the functionalized ORMOCER®-resins II-IV the composites achieved high translucency values up to 61 %. In this way, ORMOCER®-composites with high translucency usable for the enamel region or with reduced translucency for the dentin region can be obtained to realize the multilayer structure for a tooth-like optic. If necessary, e.g. caused by incorporation of other filler types, the refractive index range may be extended by further very simple modification of the resins. Results of the biological examinations prove a non-toxic, especially not allergenic, behavior necessary for the use in dental applications. The materials show an excellent biocompatibility according to the BrdU-assay (DNA-synthesis activity) and the WST-t-assay (metabolic activity) [3].
Finally anatomically shaped crowns were manufactured from previously fabricated composite blocks by CAD/CAM-technology. The resulting crowns with very high translucency or with reduced translucency and their desired combination of a two-layer design (adapting the appearance of natural teeth) are shown in Figure 2a-c.

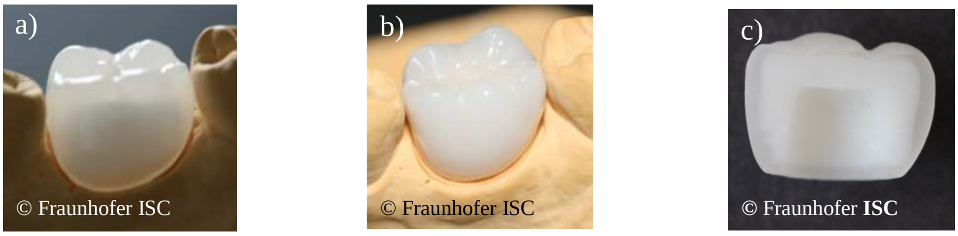

Figure 2a-c. A highly translucent crown (a), a more opaque crown (b) and a cross section of a crown with an opaque dentine core and a translucent enamel shell (c)

The adjustable translucency and high flexural strength, an excellent biocompatibility and the existing variation possibilities according to the resin/matrix systems as well as the usable filler types show the potential for an application as permanent indirect restoration. The teeth-like aesthetics were realized by multilayer construction of the prefabricated materials for dental prostheses such as CAD/CAM-blocks or artificial teeth.

4. Conclusion

By functionalizing the monomer-free ORMOCER®-resins with regard to the refractive index in combination with an individualized particle system it is possible to provide translucent composites for the different layers of the tooth (dentine and enamel). Due to the higher amount of polymerizable C=C-groups and the resulting increased values for mechanical characteristics such as flexural strength and Young's modulus the resins and the hybrid composites, respectively, are an excellent basis for a load-stable dental prostheses such as multilayered crowns or artificial teeth. Furthermore the ORMOCER®-resins show an excellent biocompatibility, because there is no diluting monomer (important for avoiding allergic reactions) which was confirmed by cytotoxicity tests. As an example for an applicable restoration with ORMOCER®-based composites anatomically shaped crowns created from previously fabricated composite blocks using the established CAD/CAM-technology were manufactured (see Figure 2a-c).

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Excerpt from ISBN 978-3-00-053387-7