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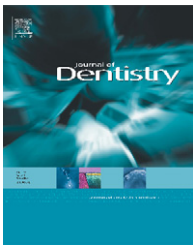

Degradation resistance of ormocer- and dimethacrylate-based matrices with different filler contents

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ABSTRACT

Objectives: To investigate the influence of matrix and filler content on degradation resistance of an experimental pure-ormocer and an dimethacrylate-based composite derived from a commercially available material.

Materials and methods: A dimethacrylate- Grandio (GR) and a model pure ormocer-based-matrix ORMOCER (ORM) were used. Each material had three different types according to their filler content (% w/w): regular (87% and 86%), flowable (80% and 79%) and fissure sealer (70% and 69%) for GR and ORM respectively. Disc-shaped (1 mm thickness × 10 mm diameter) samples were prepared for each material ($n = 6$). Water sorption and solubility tests were adapted from ISO4049. To evaluate porosity, specimens were scanned at a resolution of 19.4 μm and 3D reconstructions were made. The volume ratio of pores in the specimens were calculated and expressed as percentages. The results were submitted to 2-way ANOVA (factors: matrix and filler content) and Tukey post-hoc statistic test ($p = 0.05$).

Results: Filler content influenced the water sorption for the ormocer-matrix and the water solubility for the dimethacrylates. ORMOCER regular was a less porous material compared to flowable and sealer formulations. On the other hand, the filler content had no effect on porosity for Grandio.

Conclusion: Modifications made in the pure ormocer-matrix formulation were not significantly important to produce a more water-stable material compared to the dimethacrylate-matrix composite materials.

1. Introduction

By using a technology combining organic and inorganic components at nanoscopic scale through the sol–gel method the ORganically MOdified CERamics (ormocers-matrix-based composite) is a hybrid structure that can be an alternative dental restorative. The main characteristic of this type of material is the incorporation of organic groups linked to the inorganic backbone.[1] The combination of organic and inor-

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ganic networks in the ormocers can enhance and improve resistance to chemical degradation.[2,3]

In Dentistry, admixed (a material mixture of dimethacrylate and ormocer-organic matrix) and pure ormocer-matrix has been used to overcome some drawbacks of conventional dimethacrylate-matrix composites, such as elution of monomers that can cause toxic and/or allergenic reactions.[4–6] A pure ormocer-matrix composite,[7] according to manufacturer information, has no free monomers, thus eliminating the risk of allergic reaction. A pure Ormocer-matrix formulations are believed to offer enhanced clinical performance through high wear resistance, reduced polymerization shrinkage, enhanced biocompatibility, and long-lasting polymer-matrix stability.[8,9] In our previous study the results obtained through a softening test demonstrated that this material formulation was the only material amongst conventional dimethacrylate resin-based and admixed-ormocer that preserved surface integrity after water storage and had the greatest resistance to the ethanol-challenge.[2]

Several factors such as formulation, filler content and the amount of porosity influence the water stability of resin-based materials.[2,10] The long-term stability of the filling material plays an important role in the enduring success of the restoration. There are several degradation mechanisms of resin-composite restorations, and possible deleterious effects created by leached components that cannot be ignored.[11] However, there is a lack of evidence in literature that can confirm these properties especially for this type of resin-matrix composite. The objectives of the present study were to investigate the degradation resistance of pure-ormocer and dimethacrylate-based composites with different filler contents through measurements of water sorption, water solubility and porosity

The specific hypotheses tested were that:

a) The higher the filler content the lower the sorption and solubility in water;
b) The filler amount affects the porosity level due to the different viscosity;
c) Ormocer-based materials would exhibit, relative to the dimethacrylate-based composites lower degradation throughout lower water sorption and lower solubility in water.

2. Methods

The materials studied including their resin-matrix composition, ller type and content are listed in Table 1.

Disc-shaped (1 mm thickness × 10 mm diameter) samples were prepared for each material ($n = 6$). All samples were photoactivated (40 s × 550 mW/cm^2) with halogen LCU (Optilux 501, Demetron). Irradiance was periodically measured by a radiometer built into the Optilux 501. A thin glass cover slip was used to eliminate the presence of oxygen during the polymerization procedure. All samples were measured for water sorption, water solubility and porosity. All measurements were performed with the same sets of specimens.

2.1. Water sorption and solubility

The water sorption (W_{sp}) and water solubility (W_{sl}) measurements were done according to the International Standards Organization ISO 4049 (2000). After the porosity analysis, the specimens were transferred to a desiccator maintained at 37 (±1) °C. After 22 h, specimens were removed and stored in a second desiccator maintained at 22 (±1) °C, to normalize temperature with the room's conditions, for 2 h then weighed. This cycle was repeated until a constant mass, m_1, was obtained. After final drying, specimen dimensions were measured to calculate volume (V) in mm^3. Then specimens were immersed in distilled water at 37 °C for 30 d, after which, the resin-composite discs were removed and washed with water. Excess water was removed by blotting with a tissue and specimens were re-weighed (m_2). The specimens were reconditioned to constant mass (m_3) in the desiccators using the cycle described above for m_1. The following calculations were applied to obtain W_{sp} and W_{sl} (μg/mm^3):

$$W_{sp} = \frac{m_2 - m_3}{V}$$

and

$$W_{sl} = \frac{m_1 - m_3}{V}$$

The results were analysed with one-way analysis of variance (ANOVA) followed by the Tukey post-hoc statistic test ($p = 0.05$).

2.2. Porosity

Twenty-four hours after cure and dry-storage the samples were scanned at a resolution of 19.4 μm using the Sky Scan 1072 micro-CT (SkyScan Micro-CT 1072, Kontich, Belgium). The machine operated at a voltage of 104 kV and current of 98 μA. 50 sliced images were obtained horizontally along the length of the specimens. Three-dimensional reconstructions

Table 1 – Materials studied including their resin-matrix composition, ller type and wt%.

Material	Type	Matrix	Fillers wt% (SiO_2 and glass-ceramic)	Manufacturer
(OR)	ORMOCER *regular*	ORMOCER[a] matrix with no additional	86	Voco, Germany
(OF)	ORMOCER *flowable*	dimethacrylate monomers	79	
(OS)	ORMOCER *sealer*		69	
(DR)	Dimethacrylate *regular*	Bis-GMA, UDMA, TEGDMA	87	
(DF)	Dimethacrylate *flowable*		80	
(DS)	Dimethacrylate *sealer*		70	

[a] ORMOCERS are inorganic/organic hybrid structures incorporating covalently-bonded methacrylate end-groups for free-radical cross-linking developed by the Fraunhofer-Institute, Germany. Information provided by the manufacturer.

were made using image analysis software (Sky Scan - NRecon). The porosity (%) in each specimen was measured. The results were submitted to 2-way ANOVA (factors: matrix and filler content) and Tukey post-hoc statistic test ($p = 0.05$).

3. Results

3.1. Water sorption and solubility

Fig. 1a and b respectively show the materials' water sorption and water solubility after 30 d. Water sorption was inversely proportional to the amount of filler content for both composite matrices and was affected by the type of organic matrix. Dimethacrylate- presented lower water sorption than ormocer-based regardless the filler content.

Solubility in water was not influenced by the filler content for the ormocer-based materials, however it was for the dimethacrylate. The dimethacrylate-based composite in regular consistency was the material that exhibited the lowest water solubility but the same was not observed for sealer and flowable ones which presented higher solubility than the ormocers.

3.2. Porosity

According to the results expressed in the type of matrix had no influence on the porosity ($p = 0.118$), whilst filler content had ($p = 0.049$). The interaction filler × matrix was significant ($p = 0.042$). Filler content affected the porosity only for ormocer-based materials. Porosity values ranged from 0.04 to 0.06% for the dimethacrylates and 0.03 to 0.08% for the ormocers (Table 2). Typical micro-CT images are shown in Figs. 2 and 3. No significant correlation was detected between filler content and porosity ($r^2 = 0.20$).

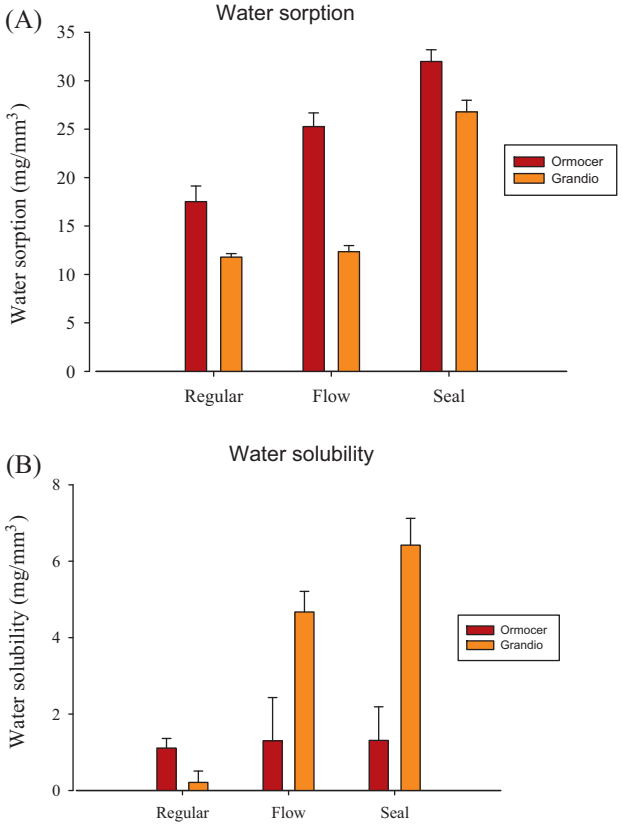

Fig. 1 – Water sorption (A) and water solubility (B) after 30 days.

Table 2 – Percentage (%) of porosity for ormocer- and dimethacrylate-based matrix composites.

Filler content	% of porosity	
	Ormocer	Dimethacrylate
Hybrid	0.031 (0.01) Ab	0.045 (0.02) Aa
Flow	0.071 (0.03) Aa	0.056 (0.03) Aa
Seal	0.080 (0.03) Aa	0.079 (0.03) Aa

Different letters indicate statistically significant difference for each material (capital letters horizontally and small letters vertically).

4. Discussion

Degradation induced by water influences the long-term clinical performance of resin-composite restorations. Identified as a formulation-dependent process, the degradation seems proportional to the degree of water sorption. In a previous study it was identified that pure ormocer-based composites preserved surface integrity after water storage and presented greater resistance to the ethanol-challenged than the dimethacrylate-based materials.[2] However, the literature is still scarce about water-stability and degradation behaviour of materials based on pure-ormocers with different filler contents.

An ormocer is a hybrid structure combining organic and inorganic components at nanoscopic scale through the sol–gel method.[1] First used in dentistry as an admixed ormocers-resin matrix (*Admira* from Voco GmbH, *Definite* from Degussa AG and

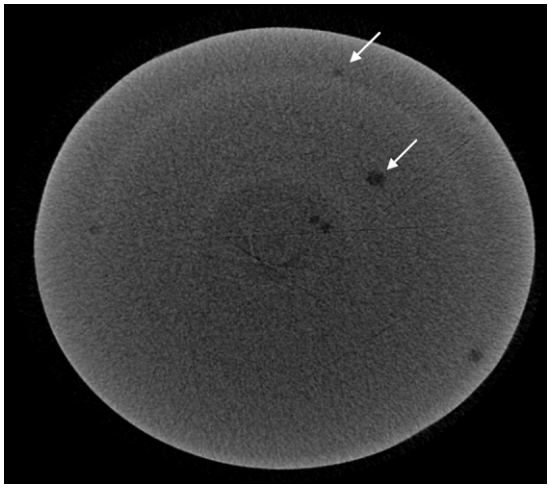

Fig. 2 – 2D slice of a sample, the white arrows are showing the pores as black dots.

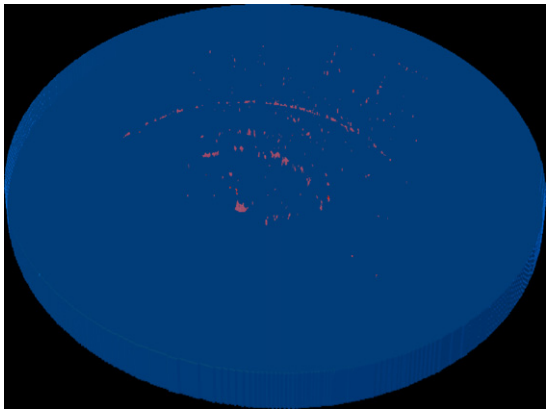

Fig. 3 – 3D reconstruction of a sample (in blue) showing the porosity (in red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Ceram-X from Dentsply), such materials still incorporate some dimethacrylate monomers so the long term stability of these materials could still be a concern. The manufacturing process of ormocers allows for many structural-design variables. These include: inorganic and organic network density, the spacer-length connecting the inorganic and organic cross-linking sites of functional monomers and many other possibilities.[7] The development of a pure-ormocer matrix was an attempt to improve the performance of the admixed ormocers and it has been previous reported as promising.[2,9,12] Consequently, the present study was designed to investigate the influence of the type of organic matrix and filler content on the physical and chemical parameters water sorption and solubility and porosity over the time.

Water uptake was influenced by the filler content. For ormocer and dimethacrylate, the regular viscosity absorbed less water than the flowable and seal viscosities. Only in ormocer formulations water solubility was not affected by the filler content. Grandio in regular viscosity was less soluble in water than the flowable and seal viscosities, respectively. Thus the hypothesis was partially accepted that the higher the filler content the lower the sorption and solubility in water.

Comparing both types of matrix, dimethacrylate-based materials presented lower water uptake than the ormocer ones. This can be probably related to the combination of the monomers used and to the hydrophilic characteristics of the material. Bis-GMA and TEGDMA contained in Grandio lead to the formation of a rigid network, which absorb less water than more flexible matrices.[13,14] The sorption is directly related to the amount and the type of organic phase available in the materials[15] for solvent diffusion and also to the porosity observed inside the samples after setting and cure. According to Sideridou et al., 2011, two contradictory processes occur during water uptake.[16] The solvent will extract unreacted components, resulting in shrinkage, loss of weight and reduction in mechanical properties. On the other hand, solvent diffuses into the polymer network and separates the chains creating expansions, swelling and an increase in weight. However, since the polymer network contains micro-voids created during polymerization and free volume between chains, a part of the solvent is accommodated without creating any change in the volume.[15,16]

The micro-voids inside the materials were measured in the current study through a novel approach, using X-ray micro-CT scanning for quantifying porosity in the samples. It showed that the volume ratio of pores (%) increases with decrease of ller fraction for ormocers. As for the preparation of samples, fluid compared to viscous materials can produce more bubbles during insertion into the cavity increasing porosity in a clinical situation. So the hypothesis that filler amount affects the porosity level due to the different viscosity was accepted only for ormocer-based composites.

The mass of components eluted from the composite may be found through the water solubility data. Ormocer material had greater solubility than the conventional dimethacrylate-composite (Grandio) only for the regular viscosity. This might be due to a lower degree of conversion. Lower conversion of ormocer-based composites, compared to the dimethacrylate-based composite Tetric Ceram, has been reported.[7] This was explained by noting that ormocers are highly functionalized compounds and, consequently, the higher degrees of functionality promote denser networks[17] where the double bonds are less accessible to polymerization, leaving a large proportion of unreacted double bonds. Polydorou et al., 2009 observed that curing time directly influenced monomer elution of an ormocer material.[12] The longer the exposure time, the higher the monomer elution at 24 h and 1 year and this type of negative effect may be a disadvantage of this material's special chemistry.[12]

On the other hand, dimethacrylates in flowable and sealer viscosities presented higher solubility than all ormocer-matrix materials evaluated. It is still unclear whether or not the size and distribution of fillers could affect monomer elution from composite materials since there are conflicting statements in the literature.[12,18,19] Even though, it has already been reported that higher concentrations of monomers eluted from flowable dimethacrylates-matrix composites compared to regular viscosity or ormocers-matrix.[20,21] Consequently, the hypothesis that ormocer-matrix would exhibit, relative to the dimethacrylate-based composites lower degradation throughout lower water sorption and lower solubility in water was partially rejected and was dependent on the filler amount.

5. Conclusions

Within the limitations of the current study, the authors conclude that:

- Filler content influenced water sorption for the ormocer-matrix and water solubility for the dimethacrylates.
- Ormocer-based composite with higher filler content produced a less porous material compared to flowable and sealer material. The filler content had no effect on dimethacrylate-based-matrix.
- Modifications made in the pure ormocer-matrix formulation were not significantly important to produce a more water-stable material compared to the dimethacrylate-matrix composite materials.

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REFERENCES

1. Wolter H, Storch W, Ott H. New inorganic/organic copolymers (ORMOCERs) for dental applications. *Materials Research Society Symposium Proceedings* 1994;**346**:143–9.
2. Cavalcante LM, Schneider LF, Silikas N, Watts DC. Surface integrity of solvent-challenged ormocer-matrix composite. *Dental Materials* 2011;**27**:173–9.
3. Mortier E, Gerdolle DA, Dahoun A, Panighi MM. Influence of initial water content on the subsequent water sorption and solubility behavior in restorative polymers. *American Journal of Dentistry* 2005;**18**:177–81.
4. Stanley HR. Local and systemic responses to dental composites and glass ionomers. *Advances in Dental Research* 1992;**6**:55–64.
5. Meryon SD, Riches DW. A comparison of the in vitro cytotoxicity of four restorative materials assessed by changes in enzyme levels in two cell types. *Journal of Biomedical Materials Research* 1982;**16**:519–28.
6. Polydorou O, Trittler R, Hellwig E, Kummerer K. Elution of monomers from two conventional dental composite materials. *Dental Materials* 2007;**23**:1535–41.
7. Moszner N, Gianasmidis A, Klapdohr S, Fischer UK, Rheinberger V. Sol–gel materials 2. Light-curing dental composites based on ormocers of cross-linking alkoxysilane methacrylates and further nano-components. *Dental Materials* 2008;**24**:851–6.
8. Tagtekin DA, Yanikoglu FC, Bozkurt FO, Kologlu B, Sur H. Selected characteristics of an Ormocer and a conventional hybrid resin composite. *Dental Materials* 2004;**20**:487–97.
9. Pick B, Pelka M, Belli R, Braga RR, Lohbauer U. Tailoring of physical properties in highly filled experimental nanohybrid resin composites. *Dental Materials* 2011;**27**:664–9.
10. Cavalcante LM, Masouras K, Watts DC, Pimenta LA, Silikas N. Effect of nanofillers' size on surface properties after toothbrush abrasion. *American Journal of Dentistry* 2009;**22**:60–4.
11. Söderholm K. Degradation mechanisms of dental resin composites. In: Eliades G, Eliades T, Brantley WA, Watts DC, editors. *Dental materials in vivo, aging and related phenomena: quintessence*. 2003:99–1121.
12. Polydorou O, Konig A, Hellwig E, Kummerer K. Long-term release of monomers from modern dental-composite materials. *European Journal of Oral Science* 2009;**117**:68–75.
13. Sideridou I, Tserki V, Papanastasiou G. Study of water sorption, solubility and modulus of elasticity of light-cured dimethacrylate-based dental resins. *Biomaterials* 2003;**24**:655–65.
14. Ortengren U, Wellendorf H, Karlsson S, Ruyter IE. Water sorption and solubility of dental composites and identification of monomers released in an aqueous environment. *Journal of Oral Rehabilitation* 2001;**28**:1106–15.
15. Wei YJ, Silikas N, Zhang ZT, Watts DC. Diffusion and concurrent solubility of self-adhering and new resin-matrix composites during water sorption/desorption cycles. *Dental Materials* 2011;**27**:197–205.
16. Sideridou ID, Karabela MM, Vouvoudi E. Physical properties of current dental nanohybrid and nanofill light-cured resin composites. *Dental Materials* 2007;**27**:598–607.
17. Andrzejewska E. Photopolymerization kinetics of multifunctional monomers. *Progress in Polymer Science* 2001;**26**:60.
18. Sideridou ID, Achilias DS. Elution study of unreacted Bis-GMA, TEGDMA, UDMA, and Bis-EMA from light-cured dental resins and resin composites using HPLC. *Journal of Biomedical Materials Research Part B Applied Biomaterials* 2005;**74**:617–26.
19. Janda R, Roulet JF, Latta M, Ruttermann S. Water sorption and solubility of contemporary resin-based filling materials. *Journal of Biomedical Materials Research Part B Applied Biomaterials* 2007;**82**:545–51.
20. Seiss M, Langer C, Hickel R, Reichl FX. Quantitative determination of TEGDMA, BHT, and DMABEE in eluates from polymerized resin-based dental restorative materials by use of GC/MS. *Archives of Toxicology* 2009;**83**:1109–15.
21. Tabatabaee MH, Mahdavi H, Zandi S, Kharrazi MJ. HPLC analysis of eluted monomers from two composite resins cured with LED and halogen curing lights. *Journal of Biomedical Materials Research Part B Applied Biomaterials* 2009;**88**:191–6.