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Degradation resistance of silorane, experimental ormocer and dimethacrylate resin-based dental composites

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Abstract: There are several degradation mechanisms of resin-composite restorations and possible deleterious effects created by leached components cannot be ignored. Additionally, the surface integrity influences the long-term clinical performance of resin-composite restorations and can be affected by several factors. Novel technologies have been proposed, but there is a lack of information considering the degradation resistance of such materials. The aim of this study was to investigate the degradation resistance of silorane (SIL), pure-ormocer (ORM) and dimethacrylate (ELS and GRD) resin-based dental composites. Water sorption and solubility tests were adapted from ISO4049, color change through the CIELab parameters after 24h and 30d immersion in distilled water. Knoop hardness readings were performed at the aforementioned periods and the percentage of hardness decrease was considered. Results were analyzed with one-way ANOVA followed by Tukey's test ($P = 0.05$). SIL and GRD produced lower water sorption than ORM and ELS. SIL presented the lowest solubility. All materials demonstrated acceptable results for color stability. SIL demonstrated the more stable surface, when considering surface hardness, in aqueous environment. It can be concluded that i) silorane and ormocer-based materials did not

produced higher color stability than dimethacrylates in distilled aqueous media; and ii) silorane-based materials exhibited lower water solubility and lower hardness decreases after water immersion than dimethacrylate-based resin-composites, while the pure-ormocer-based material not. (J Oral Sci 53, 413-419, 2011)

Keywords: resin-composite; silorane; ormocer; dimethacrylate; color stability.

Introduction

The stress development resulting from the polymerization process is considered one of the major drawbacks of dental composite restorations (1,2). In order to diminish the stress development in photoactivated composites, clinical application techniques have been developed and studied, but the results are somehow controversial. Consequently, modifications in the resin matrices formulations have been made with a view to overcome such problem, and two examples are the "siloranes" and "ormocers".

The silorane-based material is based on the combination of a siloxane backbone, that provides hydrophobic characteristics, with cycloaliphatic oxirane rings that open during the cationic polymerization process, causing expansion, which might produce lower volumetric shrinkage (3) and stress (4) without compromising the final mechanical properties (5). An ormocer-resin-based composite is a hybrid molecular structure. This combines organic and inorganic components at nanoscopic scale

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Table 1 Tested materials and corresponding formulations

Material	Type	Matrix	Fillers
Filtek Silorane*	Silorane	3,4-epoxycyclohexylethycyclo polymethylsiloxane, Bis 3,4-epoxycyclohexylethylphenylmethysilane	76 wt.% Quartz, yttrium fluoride
ExperimentalOrmocer **	Ormocer ⁺	ORMOCER, matrix with no additional dimethacrylate monomers	87 wt.% SiO ₂ and glass-ceramic
ELS - Extra-low shrinkage ***	Dimethacrylate	BisGMA, BisEMA, catalyst, inhibitors, pigments	74 wt. % Silanized barium glass
Grandio**	Dimethacrylate	Bis-GMA, UDMA, TEGDMA	87 wt.% SiO ₂ and glass-ceramic

*3M/ESPE, Seefeld, Germany; **Voco, Cuxhaven, Germany; ***Saremco Dental AG, Rebstein, Switzerland.

ORMOCERS are inorganic/organic hybrid structures incorporating covalently-bonded methacrylate end-groups for free-radical cross-linking developed by the Fraunhofer-Institute, Würzburg, Germany.

BisGMA = bisphenol A glycol dimethacrylate, BisEMA = ethoxylated bisphenol A glycol dimethacrylate, UDMA = urethane dimethacrylate, TEGDMA = triethylene glycol dimethacrylate

through the sol-gel method and the main characteristic of this type of material is the incorporation of organic groups linked to the inorganic backbone (6,7). Ormocers were initially used together with dimethacrylates, but a recent material formulated with a pure-ormocer-based resin matrix has been developed.

Besides polymerization shrinkage, the long-term stability of resin composite restorations also plays an important role in the long-term success of the restoration. There are several degradation mechanisms of resin-composite restorations and possible deleterious effects created by leached components cannot be ignored (8). Additionally, the surface integrity influences the long-term clinical performance of resin-composite restorations and can be affected by several factors. These include degradation due to agents in the oral environment. There is scarce published information about the degradation behavior of silorane and “pure”-ormocer-based materials.

The objectives of the present investigation were to investigate the degradation resistance of silorane, pure-ormocer and dimethacrylate-based composites through measurements of:

- water sorption and water solubility,
- color stability, and
- surface hardness changes with time.

The specific hypotheses tested were that silorane and ormocer-based materials would exhibit, relative to the dimethacrylate-based resin composites:

- lower water sorption,
- lower solubility in water,
- higher Color stability, and
- lower surface hardness changes upon water immersion.

Materials and Methods

The materials used in the current study, their formulations and manufacturers are listed in Table 1.

Disc-shape (0.8 mm thickness ×10 mm diameter) samples were prepared for each material ($n = 6$). All samples were photoactivated ($40 \text{ s} \times 550 \text{ mW/cm}^2$) with halogen LCU (Optilux 501, Demetron). A thin glass cover-slip was used to avoid the presence of oxygen during the polymerization procedure. All samples were measured for water sorption, water solubility, Color and Knoop hardness analyses; as detailed below. All measurements were performed with the same sets of specimens.

Water sorption and solubility

Twenty-four hour after curing, the specimens were transferred to a desiccator maintained at $37 \pm 1^\circ\text{C}$. After 22 h, specimens were removed and stored in a second desiccator maintained at $25 \pm 1^\circ\text{C}$ for 2 h and weighed. This cycle was repeated until a constant mass, m_1 , was obtained. After final drying, specimen dimensions were taken to calculate volume (V) in mm^3 . Then specimens were immersed in distilled water at $37 \pm 1^\circ\text{C}$ 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 the 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 water sorption (W_{sp}) and water solubility (W_{sl}) in micrograms per cubic millimeter:

$$W_{\text{sp}} = (m_2 - m_3) / V$$

and

$$W_{\text{sl}} = (m_1 - m_3) / V.$$

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

Color stability analyses

A chromameter (CR-221, Minolta Corp., Ramsey, NJ, USA) was used to determine CIE Lab tristimulus param-

Table 2 Mean values (standard deviation) of water sorption, water solubility and color changes for the materials tested

Material	Water sorption in $\mu\text{g}/\text{mm}^3$	Water solubility in $\mu\text{g}/\text{mm}^3$	Color change, ΔE
Filtek Silorane	14.9 (1.1) ^B	1.4 (0.3) ^D	1.9 (0.5)
ExperimentalOrmocer	17.8 (0.9) ^A	6.5 (0.5) ^B	1.7 (0.4)
ELS - Extra-low shrinkage	18.4 (0.7) ^A	10.1 (1.0) ^A	1.3 (0.9)
Grandio	14.5 (0.5) ^B	4.2 (0.5) ^C	1.6 (0.4)

Mean values followed by distinct letters in the same column denote statistical differences.

eters (Illuminant D65, specular component included): L^* (lightness, from 0 = black to 100 = white), a^* (from $-a$ = green to $+a$ = red) and b^* (from $-b$ = blue to $+b$ = yellow). The color changes (ΔE) were calculated from:

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}.$$

Surface readings were made 24 h after the photoactivation procedure and repeated after 7 d storage at $25 \pm 1^\circ\text{C}$ dry and with protection from further light exposure. Subsequently, the samples were immersed in distilled water ($37 \pm 1^\circ\text{C}$) and readings were taken after 24 h and 30 d.

The parameter ΔE was calculated from the differences between $L^*a^*b^*$ values obtained at 24 h and 30 d, as described above. These data were analyzed with one-way analysis of variance (ANOVA) followed by the Tukey *post-hoc* test ($P = 0.05$).

Knoop hardness

Twenty-four hours after the photoactivation procedure, hardness was measured on the irradiated surface with a Knoop indenter (Future Tech FM-700, Tokyo, Japan) under a load of 50 g for 15 s. Measurements were performed at five locations and the average Knoop Hardness Number (KHN) was recorded for each specimen. This evaluation was repeated after 30 d in water, the same time when m_2 was obtained for water sorption. Due to the plasticizing effect of water there were changes in the surface hardness. The percent Knoop hardness decrease after water storage was obtained, for each specimen. The data were analyzed by one-way analysis of variance (ANOVA) followed by the Tukey *post-hoc* test ($P = 0.05$).

Possible correlations between water sorption and ΔE , water solubility and ΔE , water sorption and % of KHN decrease; water solubility and % of KHN decrease were analyzed by the Pearson's correlation test ($P = 0.05$).

Results

Water sorption and solubility

The materials tested exhibited different water sorption and water solubility behaviors ($P < 0.01$ for Wsp and for Wsl). Table 2 shows the materials' water sorption and

water solubility after 30 d. The Silorane and Grandio materials had lower water sorption than the experimentalOrmocer and ELS. For water solubility, Silorane had the lowest mean, whereas the experimentalOrmocer had higher solubility than the dimethacrylate-based Grandio.

Color stability

The analysis of variance of the results obtained for color change (ΔE) demonstrated that the results were statistically similar ($P = 0.580$). Table 2 also shows the final color change of each material after 30 d in distilled water. All materials had $\Delta E < 2.0$ and ELS had the lowest ΔE . Figure 1 details the gradual changes in L^* , a^* and B^* over time. For all materials, these changes were minor.

Knoop hardness

Figure 2A illustrates the Knoop hardness values obtained after 24 h dry and 30 d in distilled water. After 30 d in distilled water, all materials were significantly softer than after 24 h dry. For ELS after 30 d in water, the hardness was now so low that it was not possible to give a quantitative result for KHN. Since the initial Knoop hardness values differ among the distinct materials due to differences in composition, the percentage of Knoop hardness decrease was used to compare them. Silorane showed the most stable surface, whereasOrmocer and Grandio produced similar outcomes (Fig. 2B).

Possible correlations between properties

Pearson's correlation tests demonstrated that water sorption and hardness decrease, as well as water solubility and hardness decrease exhibited positive correlation coefficients ($r = 0.3422$ and $r = 0.866613$, respectively). On the other hand, water sorption and color changes, as well as water solubility and color changes presented inverse relationships ($r = -0.66186$ and $r = -0.92507$, respectively). However, none of the relationships analyzed were statistically significant ($P > 0.05$).

Discussion

Degradation resistance to aqueous media is important for the clinical longevity of resin-composite restorations.

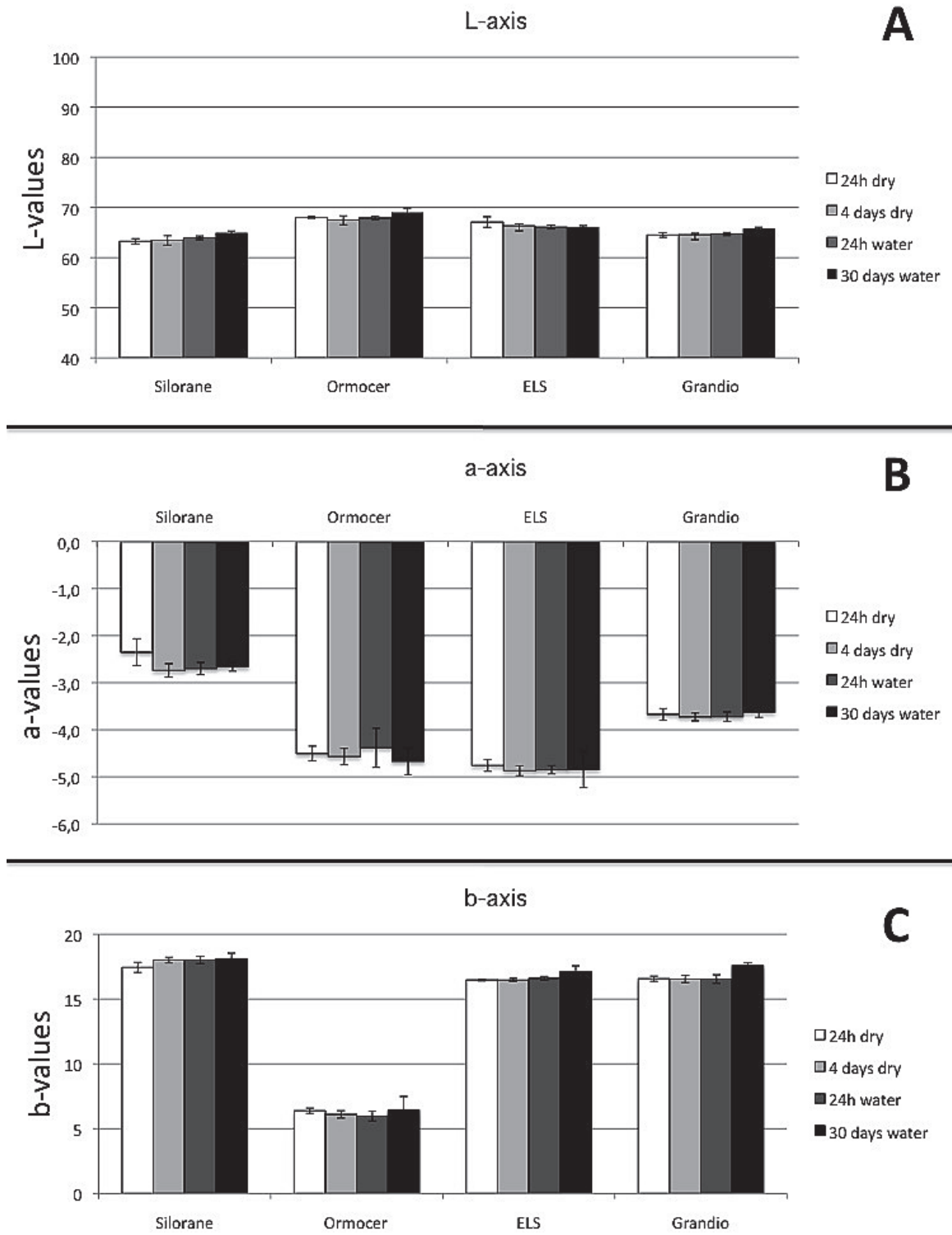


Fig. 1 (A) L*, (B) a*, and (C) b* values of the materials over time and storage conditions.

Previously there was scarce information about the water-stability and degradation behavior of materials based on siloranes and “pure”-ormocers. Consequently, the present study was designed to investigate water sorption and solubility, Color stability and the surface hardness over

time compared with two dimethacrylate-based products.

Water sorption and solubility

For dental resin-composites, water uptake is mainly dependent on the hydrophilicity of the constituent

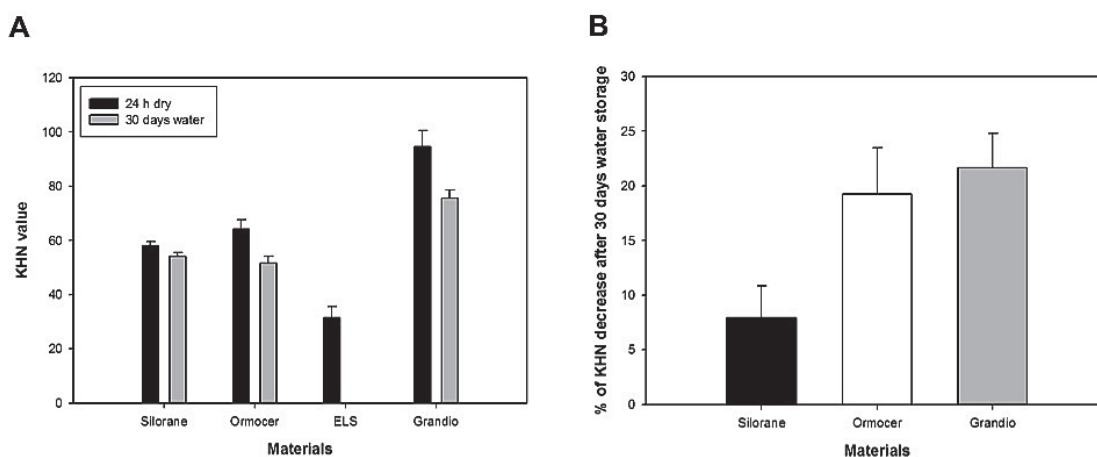


Fig. 2 (A) Knoop hardness and standard deviations obtained after 24 h dry and 30 d in distilled water. (B) Percentage Knoop hardness decrease after 30 d in distilled water.

monomers (9,10). This explains the behavior of the silorane material. Due to the hydrophobic siloxane backbone, Filtek Silorane had lower water sorption than the experimental-ormocer and the dimethacrylate-based ELS. However, some other factors - such as the degree of conversion, the combination of monomers used and the filler loading - may also be significant, since the dimethacrylate-based material Grandio was similar in this respect to Filtek Silorane. Consequently, the first hypothesis was partially rejected as both Grandio and Silorane had lower water absorption than the dimethacrylate-based ELS.

The mass of components eluted from the composite may be found through the water solubility data. The siloxane backbone presented in the Filtek Silorane clearly provided a material with much lower solubility than the others studied here (11). This confirmed a previous finding that such material is stable in aqueous environments (12). The experimental ormocer material however had greater solubility than the conventional dimethacrylate-composite (Grandio).

An ormocer is a hybrid structure combining organic and inorganic components at nanoscopic scale through the sol-gel method (6,7). Ormocers are used in some other fields, such as optics, electronics and medical technology. In Dentistry, mixed ormocers-resin matrixes were previously developed, (*Admira* from Voco GmbH, *Definite* from Degussa AG and *Ceram-X* from Dentsply). However, such materials still incorporate some dimethacrylate monomers and so the long term stability of these materials could still be a concern. Some researchers found that ormocer-based materials (*Admira* and *Definite*) had lower abrasion resistance and higher roughness than some dimethacrylate-composite (13,14). Consequently, ormocer materials were in need of improvement.

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 crosslinking sites of functional monomers and many other possibilities (7,15). Therefore, experimental “pure-ormocer” matrix materials have been developed and one example was evaluated in the current study. However, this had higher solubility than the dimethacrylate-composite. 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 (15). This was explained by noting that ormocers are highly functionalized compounds and, consequently, the higher degrees of functionality promote denser networks (16) where the double bonds are less accessible to polymerization, leaving a large proportion of double bonds unreacted. Consequently, the second hypothesis was also partially rejected, since only the silorane-based material presented lower solubility in water than the dimethacrylate-based materials.

Color stability

Color changes of resin-composite restorations are affected by exogenous and endogenous factors. Exogenous aspects include plaque accumulation and absorption of dyes and pigments; these can be removed. However, endogenous discolorations are related to many aspects of the material composition, such as the resin matrix, filler particle content, initiator/co-initiator system, etc. This kind of discoloration cannot be removed. Since we aimed to analyze Color changes produced by differences in matrix composition, pigments or dyes were not used in aqueous solution.

Color stability may relate to water sorption and solubility. Resin-composite restorations are usually clinically acceptable when ΔE is smaller than 3.3 (17). As shown in Table 2, all materials had ΔE less than this value. So all the materials investigated had acceptable color stability in aqueous solution, regardless of their composition, water sorption or solubility. These outcomes were unexpected, since it is known that, among other conditions, resistance against discoloration is usually dependent upon low water sorption (18). Such a lack of significant color-stability difference among the materials tested (all $\Delta E < 2$) might be because pigments or staining dyes were not applied. Furthermore, the use of specific weathering lights might be useful in studies to accelerate discoloration, as recently seen in a study where silorane exhibited the best overall stability (19).

Knoop hardness

Water sorption causes polymer matrices to swell and reduces the frictional forces between polymer chains (20). Consequently, the surface hardness of resin composites can be significantly affected by the water plasticization and hydrolytic degradation (21). This was observed for all materials in this study, but to quite different extents. For ELS it was not possible to determine Knoop hardness after 30 d in water, due to the long width of the indentations. However, the experimental ormocer and silorane only slightly decreased in hardness. Besides lower water solubility, the silorane material was the most stable in surface hardness, corroborating with previous outcomes from Yesilyurt et al. (22).

Linear regression analyses did not demonstrate any significant relationships between Knoop hardness decrease vs. water solubility and vs. water sorption. Thus, some factors other than polymeric softening due to water penetration through the resin matrix must also influence the surface integrity of resin-composites. Degradation of particulate fillers may also be important, since resin-composites may leach components from stress corrosion around the inorganic particles (23,24). This depends on the filler composition. For example, materials formulated with zinc and barium glasses are more susceptible to aqueous degradation than those containing quartz (21). However, the exact relationship between filler type, size and composition on surface integrity is not yet fully elucidated. Therefore, conclusive interpretations of Knoop hardness decrease and filler composition are not yet possible.

The hypothesis that silorane and ormocer-based materials would exhibit greater Color stability than dimethacrylates in distilled aqueous media was rejected,

since all materials tested were Color-stable over time.

The hypotheses that silorane and ormocer-based materials would exhibit lower water sorption, lower water solubility and lower hardness decreases than dimethacrylate-based resin-composites were partially rejected, since only the silorane-based material was able to achieve such qualities. This latter material showed the best resistance to degradation among the set of materials examined.

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