Do new matrix formulations improve resin composite resistance to degradation processes?

Abstract: The aim of this study was to determine the degradation resistance of three new formulations—silorane-, Ormocer- and dimer-acid-based materials—and compare them to the traditional dimethacrylate-based materials. One silorane- (Filtek P90, P90), one Ormocer- (Ceram-X, CX), one dimer-acid- (N’Durance, ND) and two dimethacrylate-based (Filtek P60, P60; Tetric Ceram, TC) materials were investigated. Water sorption (Wsp) and solubility (Wsl) were determined after the materials were immersed in water for 28 days. Knoop hardness (KH) was determined before and after 24 h immersion in pure ethanol. The flexural-strength (FS) was determined by the bending test after one-week storage in a dry environment or after one-week immersion in pure ethanol. Data were submitted to analysis of variance (ANOVA) and Tukey’s test (95%). The three new formulations showed lower Wsp than the dimethacrylate-based formulation. CX (0.50 ± 0.17%) and ND (0.72 ± 0.19%) exhibited the lowest Wsp, whereas P90 (0.02 ± 0.03%) and P60 (0.04 ± 0.03%) showed the lowest Wsl. All resins showed reduced Knoop hardness number (KHN) after ethanol immersion. P60 presented the lowest decrease in KH value (19 ± 5%). TC (48 ± 3%) and P90 (39 ± 9%) showed the highest KHN decrease after ethanol storage. The FS of CX, ND and TC were affected by ethanol storage. The new formulations did not improve the degradation resistance, as compared with the traditional methacrylate-based materials.

Descriptors: Solubility; Composite Resins; Water.

Introduction

Composite materials are well established for dental restorations, and are widely used in anterior and posterior teeth. One of the major concerns is the stability and the longevity of these materials. In the oral environment, many factors may affect the lifetime of the composites, such as secondary caries, fractures and staining, which may be associated with resin shrinkage and consequent stress. Thus, one of the goals of contemporary dentistry is to find solutions to such drawbacks. With this in mind, new formulations have been developed, such as those based on Ormocer (organic modified ceramic), dimer acid and silorane technology.

The combination of Ormocer and ether-methacrylate is an alternative monomer, because it contains organic and inorganic components potentially able to form a hybrid network where organic groups are linked to...
an inorganic backbone. In contrast, dimer acid is a fatty acid derived from linoleic acid, which may be used as a copolymer diluent instead of TEGDMA (triethylene glycol dimethacrylate) in a methacrylate resin-based composite to promote “polymerization-induced-phase-separation” (PIPS). PIPS is a physical phenomena created by a change in monomer polarity triggered by the onset of polymerization. When PIPS occurs, the volume expands to compensate volumetric shrinkage. Another approach that has been investigated is silorane-based technology. Silorane is the name given to a class of restorative materials with monomers derived from the combination of siloxane and oxirane. Polymerization takes place by a cationic ring opening, and the initial process differs from that of the methacrylate-based materials that use radical intermediates.

Although polymerization shrinkage is a determinate factor in restoration longevity, the degradation resistance might also be considered. However, there is a lack of information regarding the comparison of materials formulated with different approaches to reduce shrinkage stress. Therefore, the aim of this study was to evaluate Wsp and Wsl rates, as well as hardness (KH) and flexural strength (FS), before and after ethanol immersion, of Ormocer-, dimer-acid-, and silorane-based materials, in order to determine their degradation resistance. The following research hypotheses were tested:

1. the alternative matrixes (Ormocer-, dimer-acid-, and silorane-based) would promote lower Wsp and Wsl than dimethacrylate-based composites,
2. the ethanol challenge would not decrease the surface hardness of the alternative materials, and
3. the ethanol challenge would not decrease the FS of the alternative materials.

**Methodology**

**Materials**

Five restorative composites were selected for this study, as shown in Table 1.

Sorption and solubility. Specimens were made by placing the resin composite in a stainless-steel mold, 8.66 mm in diameter and 0.60 mm thick, and pressing the composite between clear matrix strips (n = 10). The measures were adapted from the ISO 4049 standards. Direct photoactivation (20 s × 1000 mW/cm²) was performed on each side with a light emitting diode (LED) source (Radii-call, SDI, Bayswater, Australia). Samples were stored for 24 h, and then transferred to a desiccator at 37 ± 1°C. After 22 h in the first desiccator, the specimens were removed, stored in a second desiccator at 25 ± 1°C for 2 h and weighed using an analytical balance (Mettler-Toledo, XS 205, Greifensee, Switzerland). These procedures were repeated until a constant mass (m₁) was obtained (with no more than a 0.0001 g variation). The dry specimens were then immersed in deionized water at 37 ± 1°C and readings were taken after 28 days (m₂). Afterwards, the specimens were reconditioned to constant mass (m₃), followed by the cycle described above for m₁. The percentage of water sorption (Wsp) and solubility (Wsl) were calculated as follows:

\[
\text{Wsp} = 100 \times \frac{(m_2 - m_1)}{m_1};
\]
\[
\text{Wsl} = 100 \times \frac{(m_1 - m_3)}{m_1}
\]

![Table 1 - Dental composites used in the current study (composition as stated by the manufacturers).](image)

<table>
<thead>
<tr>
<th>Material/lot</th>
<th>Matrix composition</th>
<th>Filler composition</th>
<th>Filler fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filtek P90¹</td>
<td>Silorane</td>
<td>Quartz Yttrium Fluoride</td>
<td>55 vol%</td>
</tr>
<tr>
<td>Ceram-X²</td>
<td>Methacrylate</td>
<td>Silanized Ba-Al-borosilicate glass silanized pyrogenic SiO₂ (nano particle size)</td>
<td>57 vol%</td>
</tr>
<tr>
<td>N'Durance³</td>
<td>Bis-GMA, UDMA, DDCDMA</td>
<td>Ytterbium-fluoride, barium glass, quartz</td>
<td>65 vol%</td>
</tr>
<tr>
<td>Filtek P60⁴</td>
<td>Bis-GMA, Bis-EMA, UDMA, TEGDMA</td>
<td>Aluminum Oxide, Silica, Zirconium oxide</td>
<td>61 vol%</td>
</tr>
<tr>
<td>Tetric Ceram⁵</td>
<td>Bis-GMA, UDMA and TEGDMA</td>
<td>Barium glass, Yttrium Fluoride</td>
<td>60 vol%</td>
</tr>
</tbody>
</table>

Bis-GMA: bisphenol A diglycidyl ether dimethacrylate; TEGDMA: triethylene glycol dimethacrylate; Bis-EMA: bisphenol A polyethylene glycol diether dimethacrylate; UDMA: urethane dimethacrylate; DDCDMA: dimer-acid-derived dimethacrylate; 1: Silorane version sold in Brazil - 3M ESPE St. Paul, USA (Batch: N273780); 2: Dentsply DeTrey, Konstanz, Germany (Batch: 0901000199); 3: Septodont Louisville, USA (Batch: F0411-7); 4: 3M ESPE St. Paul, USA (Batch: N297134); 5: Ivoclar/Vivadent, Schaan, Liechtenstein (Batch: J16767).
Results
Sorption and solubility

The results for Wsp (Table 2) show that the alternative matrix materials tend to promote lower Wsp than those formulated with dimethacrylate-based matrixes.

Knoop hardness

All composites showed reduced KHN (Knoop hardness number) after ethanol immersion (Figure 1). Before ethanol storage, P60 exhibited the highest KHN values among the tested groups, whereas the other composites did not differ statistically. After ethanol storage, P60 showed the highest values whereas TC showed the lowest values. P60 demonstrated the lowest percentage of KH decrease (19 ± 5%), whereas TC (48 ± 3%) and P90 (39 ± 9%) demonstrated the most pronounced KH decrease after ethanol storage (Figure 2).

Flexural strength

The FS of CX, ND and TC were significantly affected after storage for one week in pure ethanol. P90 and P60 samples were not affected under the same conditions (Figures 3 and 4).

Discussion

Laboratory studies have demonstrated that water uptake plays an important role in dental composite degradation, and that monomer hydrophilicity, crosslink density and network porosity are important factors. Chemical characteristics like inorganic content, filler/matrix interface, concentration...
of catalyst and the initiator system are other factors that also influence the Wsp rate.\textsuperscript{11,13-17} In the current study, the percentage of mass variation was used to determine Wsp and Wsl after 28 days. CX and ND showed the lowest Wsp rates for this period. The organic-inorganic matrix of CX may yield a high hydrophobic polymer network. Furthermore, the ND matrix is a ternary resin formulation with Bis-GMA, UDMA and dimer acid dimethacrylate as a co-polymer. In a comprehensive study carried out by Trujillo \textit{et al.},\textsuperscript{7} the authors related lower water uptake by dimer acid. The same results of ND were presented in Bracho-Troconis’ study.\textsuperscript{18} The silorane-based material showed the highest Wsp among the new resin formulations, despite its hydrophobic property.\textsuperscript{9} Among all composites studied, silorane had the highest matrix percentage (45 vol\%). This could explain how it differed from the other new formulations. On the other hand, the CX with 43 vol\% matrix showed the lowest Wsp; its inorganic backbone probably accounts for its high hydrophobic behavior.

Solubility is influenced by the leachable species, the solvent and composite solubility parameter, the quality of the resin-filler interface, immersion time periods and temperature.\textsuperscript{16,19,20} The solubility values, obtained in this study by mass variation percentage, showed that P90 (0.02\%) and P60 (0.06\%) were stable; there were no significant differences between them. The low solubility and stability of silorane in aqueous systems has been reported before.\textsuperscript{21-24} Filtek P60 had the highest Wsp and one of the lowest Wsl results; this may be related to its filler composition. Therefore, it may be hypothesized that hybrid composites with zirconia-derived fillers could lead to a freer volume among the fillers, considering
that some water could be trapped without reacting with the polymer or becoming water bound within the resin matrix. The lowest values were recorded for TC (0.14%), CX (0.16%), and ND (0.17%), with no statistical differences. The new CX and ND matrix showed low sorption but high solubility, whereas P90 demonstrated intermediate performance for sorption and the lowest solubility. Therefore, the first hypothesis was rejected.

KH is a mechanical property that may be related to the wear resistance of materials and their ability to remain stable.\textsuperscript{25} The solubility parameter of absolute ethanol is near that of some dimethacrylate resin composites. The extent that a composite may be affected depends on the crosslink density formed in the polymerization processes.\textsuperscript{21} Sideridou and Krabela\textsuperscript{26} observed that Bis-GMA, UDMA, and Bis-EMA showed high sorption rates when submitted to pure ethanol; however, TEGDMA was an exception. The solvent affects the polymer, modifying its mechanical properties. With this in mind, in the current study, KH was assessed before and after immersion in absolute ethanol for 24 h, to observe how the new matrix formulations behaved.

All composites presented KHN loss after ethanol storage. Therefore, the second hypothesis was rejected. Comparing all the materials, the new formulations presented intermediate values for the percentage of KHN decrease (Figure 3). Thus, degradation resistance should consider not only the resinous phase but also the inorganic characteristics. P60 showed the highest hardness values and the lowest percentage of KHN decrease after 24 h immersion in absolute ethanol, perhaps attributable to UDMA, Bis-EMA and especially a little TEGDMA in its formulation. This could ensure lower ethanol uptake.\textsuperscript{26}

The inorganic phase composed of a zirconia filler could explain the highest hardness values of P60 among all the other materials tested.

P60 demonstrated the highest FS values, regard-
less of the storage conditions. As cited before, this could be explained by the inorganic content of zirconia in its formulation. Considering the samples immersed in ethanol, only the silorane-based material and P60 (a dimethacrylate-based material) did not demonstrate different values from those of non-immersed samples. On the other hand, the materials based on Ormocer, dimer acid and TC (another dimethacrylate-based material) demonstrated a significant reduction in FS. Consequently, the third hypothesis should be partially accepted, since the FS properties of silorane were maintained.

Considering all the outcomes aforementioned in the current research, it should be considered that composite water sorption depends on the chemical properties of monomers and the physical structure of the polymer network.\(^\text{11}\) Traditional dimethacrylate-based composite structures are formed by a free-radical polymerization process where the C=C provides the network chain resistance. Depending on the monomer system of each composite, the physical configuration and the crosslink density are likely determinants for the physical and mechanical restoration properties. The new matrix formulations associate traditional monomers with new functional dimethacrylate-monomers, promoting changes in the polymerization dynamics. In the Ormocer derivate composite, the inorganic backbone is formed first, and then the organic reaction takes place, giving rise to low double-bonds, unlike traditional dimethacrylate.\(^\text{27}\) As for the ND material, where dimer acid is the co-polymer, when PIPS occurs, it triggers a physical separation of monomers, and radical polymerization results in different reactive centers, with different kinetics, and with an initial low double-bond.\(^\text{28}\) P90 is the only material with no dimethacrylate monomer and the polymerization process occurs by cationic ring opening. After the degradation test, the silorane-based material presented a significant decrease in KNH, suggesting low crosslink density. On the other hand, there was no change in FS after degradation. Lien and Vandewalle\(^\text{29}\) assessed the physical properties of silorane and then compared them with five dimethacrylate-based restorative materials, and observed the relative higher FS and lower KH of silorane. In the present study, this mixed mechanical behavior was pronounced by accelerated aging of ethanol. The different effects of this solvent could be related to the conversion rate, filler distribution, and chemical/physical characteristics of surface, subsurface, and network formation of the silorane composite. How the polymerization process and degree of conversion affects the degradation resistance of silorane is still an open question, despite the considerable amount of research that has been conducted on silorane.

**Conclusion**

According to the results obtained from the current study, it can be concluded that:

- The new CX and ND matrix formulations showed the lowest Wsp but the highest Wsl, and P90 showed the lowest Wsl but intermediate Wsp values.
- All materials presented a Knoop hardness decrease after ethanol soaking.
- Among the new formulations, silorane was the only material that showed no decrease in FS.

In general, the current study demonstrated that the overall content (organic and inorganic) of the resin composites may dictate the behavior of the materials, and that recent developments may not improve degradation resistance.

**References**

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