Structural Properties and Resistance against Abrasion of Some New Dental Materials

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Abstract. Experimental dental composite materials were obtained using urethane aliphatic dimethacrylate monomers (isophorone diisocyanate 2-hydroxyethyl methacrylate) and Bis GMA respectively as organic phase. Glass containing barium oxide and colloidal silica, and quartz and colloidal silica respectively was used as inorganic fillers. X ray diffraction spectra showed that the inorganic barium glass is a vitreous amorphous phase embedding crystalline SiO\textsubscript{2}. For the related composites, the wear depth and the morphology (using SEM) were determined. The micrographs of the specimens illustrated the influence of the composition of inorganic filler on the morphology of obtained composites, as well as that of the organic matrix on the shiny composite surface. C3 composites, that contain the greatest amount of glass, reported a good smoothness of composites surface and good wear behavior. The abrasion test of each material shows that the wear depth depends on: the composition of inorganic filler, the size and distribution of particles for each sample. A material submitted to abrasion may have its roughness increased or reduced, depending on the proportion organic matrix/inorganic fillers and particle size in its composition.

Keywords: dental composite materials; abrasion; structure.

INTRODUCTION

Over the past three decades, there have been extensive experimental and theoretical studies directed towards understanding the relationship between the structure and the unique properties of polymer-based composite formulations designed for various dental appliances (Buruiana \textit{et al.}, 2006, Tarumi \textit{et al.}, 1995, Anseth \textit{et al.}, 1995, O’Connor, 2003). The development of this new class of materials is motivated by unique advantages in terms of desired aesthetic and mechanical characteristics, which can be customized according to the particular application, by varying the proportions and properties of the structural components. Besides the important benefits and shortcomings of commercial materials, the open questions still limiting a wide clinical acceptance of polymer composites, are mainly related to their behavior at long term exposure in the oral environment.

Dental composite materials are obtained using an organic phase (liquid) that embeds an inorganic one as filler. Fillers are irregular or spherical in shape, depending on the manufacture techniques. Spherical particles are easier to incorporate into a resin matrix and to fill more space, leaving less resin. One size spherical particle occupies a certain space. Adding smaller particles, these fill the space between the larger particles to take up more space. There
is less resin remaining and therefore, less shrinkage on curing when particles with different sizes are used in a proper distribution. Today, the inorganic filler types mainly influence the properties, and therefore they are the basis of the composite classification (Hickel et al., 1998).

Among mechanical properties, the abrasive wear is very important. There are several mechanisms of composite wear including adhesive wear, abrasive wear, fatigue, and chemical wear. Extremely small contacts and therefore extremely high forces, of the two opposing surfaces, create adhesive wear. When small forces release, the material is removed. All the surfaces have microscopic roughness, which is where extremely small contacts occur between opposing surfaces.

Resistance to abrasion is an important property of dental materials in terms of the quality of the restoration. Materials that are highly resistant to abrasion yield more durable restorations, with a smaller marginal leakage and higher color stability. Depending on the type, particle size, characteristics and composition of the inorganic filler, composite resins may present different behaviors in terms of mass loss (abrasion) and surface roughness after tooth brushing, with no direct relation between them (Martinelli et al., 2006).

A material submitted to abrasion may have its roughness increased or reduced, depending on the proportion organic matrix/inorganic fillers and particle size in its composition (Braem et al., 1987, Martins et al., 2002, Cavalcante et al., 2009, Le Roux et al., 2008). Therefore, materials with a greater amount of organic matrix, comparatively to the amount of filler, tend to have greater mass loss upon abrasion. The Bis-GMA based resin composites have been proved to be a successful material in esthetic restorations. There is still a major shortcoming with Bis GMA resins, i.e. marginal leakage due to volume shrinkage during polymerization and insufficient abrasion resistance (Zhengfei, 2005). Therefore some new monomers have to be also studied. The purpose of this study is to characterize/describe some composites based on urethane aliphatic dimethacrylate monomer (as organic phase) and barium oxide glass and colloidal silica (as inorganic phase) compared to composites obtained using Bis-GMA (65%) and TEGDMA (35%) with quartz and colloidal silica fillers.

MATERIALS AND METHODS

The organic phase consists of urethane diacylates (75% wt), including hydrophilic urethane diacrylate oligomers (synthesized in our laboratory):

These monomers were diluted with triethylene glycol dimethacrylate (25% TEGDMA) (Aldrich), camphorquinone (CQ) (Aldrich), in concentration of 0,5% and dimethylamino-ethylmethacrylate (DMAEM) (Aldrich), in concentration of 1% as a photoinitiator system, related to the amount of monomers and BHT (Merck), tertbuthyl hydroxy toluene 0,1% as polymerisation inhibitor.

The filler was either, glass modified for radio-opacity by adding BaO (barium oxide glass) with colloidal silica, in different concentrations or quartz and colloidal silica. The experiments were based on obtaining a vitreous mass (G) through the conventional melting...
The chemical composition of (G) and the condition for synthesization are: 45% SiO₂; 10% Al₂O₃; 17% B₂O₃; 20% BaO; 8% NaF-CaF₂; melting temperature: 1350 °C. The chemical bond between the organic and inorganic phases was assured by the silanization of fillers with an aciddulated water containing ethanol, with 3-methacryloyloxypropyl 1-trimethoxysilane (A-174, Merck). The composites were prepared as a paste, by dispersing the colloidal SiO₂ and glasses (G) or quartz in the monomer mixture (Table 1).

### Tab.1

<table>
<thead>
<tr>
<th>Composites code</th>
<th>Organic phase % wt</th>
<th>Inorganic Phase % wt</th>
<th>Mean wear (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Glass G</td>
<td>Colloidal SiO₂</td>
</tr>
<tr>
<td>C1</td>
<td>18</td>
<td>61.5</td>
<td>20.5</td>
</tr>
<tr>
<td>C2</td>
<td>21</td>
<td>63.25</td>
<td>15.75</td>
</tr>
<tr>
<td>C3</td>
<td>19</td>
<td>68.85</td>
<td>12.15</td>
</tr>
<tr>
<td>C4</td>
<td>25 (65 % Bis-GMA+35 % TEGDMA)</td>
<td>60- quartz</td>
<td>15</td>
</tr>
</tbody>
</table>

Sample C4 had been prepared using Bis-GMA (65%) (synthesized in our laboratory) and TEGDMA (35%) with quartz filler.

**Characterization of the inorganic phase (G)** was made by X-ray diffraction. The X-ray scattering patterns were obtained using a standard DRON-3M powder diffractometer, working at 40 kV and 30 mA The CuKα (l=1.54178 Å) radiation, Ni filtered, was collimated with Soller slits.

**Characterization of the composites.** Cylindrical specimens were obtained in Teflon moulds by light curing, for abrasion determinations (4 mm diameter, 8 mm length) and for structure determinations (6 mm diameter, 3 mm length). Abrasive wear tests were made using a Stall Universal Abrader machine. The difference between the initial and final mass was calculated to determine the composite wear (abrasion). For morphology determination, a Philips XL 30 ESEM scanning electronic microscope was used.

The standard abrasion interval was set at 1500 cycles with a two cycle per second speed. Each one of these cycles move the specimens horizontally on a 25.65 mm distance and spins the specimen’s support with 1½ degree. Specimens were eroded with silicon carbon paper No.220 A. The abrasive paper is pressed upon the specimen with a 1.13 kg weight upon the balance arm, thus giving each specimen a weight of about 0.7 kg/cm². All specimens were tested after being kept under water for 24 hours at a 37°C. The tested ends of the specimens were polymerized between glass plaques. Their weight was measured before and after the abrasion interval, after the cylinders were cleaned of the loose particles, being measured dry.

**RESULTS AND DISCUSSIONS**

The X-ray diffraction patterns (Fig. 1) show the amorphous and crystalline phases developed in these samples. The main diffraction maximum points for the G compound are very wide, characteristic to an amorphous system (Fig.1a). In Fig. 1b there are marked the main maximums of diffraction for the SiO₂ filler. This crystalline compound gives diffraction lines situated at 20 diffraction angle of 26.15° for the 4.04 Å interplanar distance; 33.65° for the 2.84 Å interplanar distance and 42.75° for the 2.45 Å interplanar distance.
The hybrid composites consist of glass and silica fillers with diameters smaller than the original quartz filler (1-10µ). Barium oxide glasses are considerably softer than quartz and shaping and finishing the surface is much easier. It may be mentioned that there is a natural self-polishing when the composites with Ba glasses are used to restore occlusal surfaces.

**The wear depth** values are presented in Table 1. Our studies showed that composite materials with hybrid fillers (C1, C2, C3) have lower abrasion coefficients than those of composite with quartz filler and Bis GMA as organic phase (C4). Increasing the concentration of glass, from 61.5 % to 68.85 %, the abrasion coefficient decreased from 0.0405 mm to 0.0134 mm. These observations are in concordance with (Martinelli et al., 2006).

**The micrograph shows** at the same time the particle polydispersion and sizes. Figures (2, 3, 4, 5) show that the inorganic filler particle concentration influences the composites properties among which the surface texture before, as well as after the abrasion process. In each case, imagine was taken from the center of the worn area. The C3 containing 68.85 % glass as filler, following the abrasion process, confers a smooth shiny surface to the composite, this thing being extremely beneficial regarding their use in dentistry, even if the particles embedded in vitreous phase were bigger. An increase of filler content in resin matrix improves the mechanical properties of dental composites, such as: compressive and diametrical tensile strengths, abrasion resistance, and coefficient of thermal expansion and modulus of elasticity (Peutzfeldt, 1997, Mayworm et al., 2008, Barkmeier et al., 2008).
SEM examination has also been used to show that the individual microfiller particles clump together into clusters as large as 1 µm in diameter, apparently as a result of the silanization process (Taylor et al., 1998). For composites that contain the same amount of liquid and fillers, particle sizes influence abrasive wear. According to (Martinelli et al., 2006, Cavalcante et al., 2009), the composite resin with greater size of inorganic fillers shows the lowest mass loss and surface roughness means, indicating a higher resistance to toothbrush abrasion.

Our results show better handling facing abrasion of composites based on barium glass (fig 2, 3, 4), then for the quart based composite (fig 5) although in the experimental composites series, based on similar components, a better handling on abrasion was showed by the composite with a higher particles’ sizes average (fig 4). In the attrition wear region fatigue-like crack (fig 5b) were observed. Large cracks can be observed running through the
resin matrix, which may be due to the failure within the matrix or at the interface bond between the resin matrix and the agglomerated fillers (Moldovan et al., 2007). In the case of C4 sample obtained with quartz and colloidal silica, particle shape and sizes are less uniform.

The obtained results can be explained through the different make of the two phases’ components, meaning: the urethane monomers system – barium glass and colloidal silica (correspondent to the C1-C3 samples) compared to the Bis-GMA/TEDGMA – quartz and colloidal silica (the C4 sample), which allows a better bonding between components. As for the C1-C3 series, based on similar components but used in different amounts are according to literature data (Martinelli et al., 2006).

The formation of vitreous phase (use barium glasses) influences the abrasion processes of the final composite, improving their properties. In general, surface degradation was much more severe in the attrition than the abrasion region. In the current study, wear resistance of microfilled composites was significantly enhanced by filler weight with an increase from 60-68.89%. The experimental composites were all composed of the same resin matrix, so the differences in wear pattern must be due to the filler component differences.

CONCLUSIONS

In this work, we studied the relationship between the abrasive wear and the composites’ structure and composition. The study results illustrate that the wear depth of dental composites depends on both two phases of composition.

The values obtained for abrasion showed that the composites with glass filler (C1-C3) have a lower abrasion than the quartz composite (C4) and that can explain the good smoothness of the composites’ surface and a good bond between the components of the composites.

For the composite based on the same organic phase the wear depth depends on: the composition of the inorganic filler, the size and distribution of particles for each sample. The composites with a larger amount of barium glass within their inorganic phase show better wear depth through friction results.

By studying the wear abrasion upon experimental dental composites calculating both wear depth and SEM links between results were observed. For composites that have recorded a lower wear depth the SEM studies show slight differences between the images recorded before and after the abrasion.

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REFERENCES