Properties of dental resins submitted to pH catalysed hydrolysis

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ARTICLE INFO

Article history:
Received 8 May 2012
Received in revised form
10 September 2012
Accepted 19 September 2012

Keywords:
Resin composite
Alkaline medium
Acid
Roughness
Microhardness

ABSTRACT

Objectives: This study evaluated the surface microhardness (SM) and roughness (SR) alterations of dental resins submitted to pH catalysed degradation regimens.

Methods: Thirty discs of each TPH Spectrum (Dentsply), Z100 (3M-ESPE), or an unfilled experimental bis-GMA/TEGDMA resin were fabricated, totaling 90 specimens. Each specimen was polymerized for 40 s, finished, polished, and individually stored in deionized water at 37 °C for 7 days. Specimens were randomly assigned to the following pH solutions: 1.0, 6.9 or 13, and for SM or SR evaluations (n = 5). Baseline Knoop-hardness of each specimen was obtained by the arithmetic mean of five random micro-indentations. For SR, mean baseline values were obtained by five random surface tracings (R s). Specimens were then soaked in one of the following storage media at 37 °C: (1) 0.1 M, pH 1.0 HCl, (2) 0.1 N, pH 13.0 NaOCl, and (3) deionized water (pH 6.9). Solutions were replaced daily. Repeated SM and SR measurements were performed at the 3-, 7- and 14-day storage time intervals. For each test and resin, data were analysed by two-way ANOVA followed by Tukey’s test (α = 0.05).

Results: There was significant decrease in SM and increase in SR values of composites after storage in alkaline medium. TPH and Z100 presented similar behaviour for SM and SR after immersion in the different media, whereas unfilled resin values showed no significant change.

Conclusion: Hydrolytic degradation of resin composites seems to begin with the silanized inorganic particles and therefore depend on their composition.

Significance: To accelerate composite hydrolysis and produce quick in vitro microstructural damage, alkaline medium appears to be more suitable than acidic medium. Contemporary resin composite properties seem to withstand neutral and acidic oral environments tolerably well.

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1. Introduction

The development of hydrolytically stable dental resin composites is an important goal in dental materials research. In the oral environment these materials encounter various challenges, since polymers are subjected to numerous stresses related to chemical and mechanical factors. Chemical degradation may lead to corrosive wear of the outer surface layers of resins. The first step in this process is absorption of...
water that diffuses internally through the resin matrix, pores and filler interfaces, which may lead to its softening and hydrolytic degradation. As the corroded layer is worn as a result of mastication or tooth brushing, a fresh surface is exposed and the corrosion cycle continues. Clinically, this may lead to loss of restoration contour, increase in surface roughness and plaque retention by the restoration, increasing susceptibility to wear, staining, caries and periodontal inflammation.2,3

The most significant and detrimental chemical event is hydrolytic degradation. Hydrolysis is a biomolecular reaction in which water and the functional group possessing the labile bond are involved. The fraction of the two reaction components determines the speed of reaction, which also depends on the type of chemical bond, pH, copolymer composition and water uptake. The pH particularly affects degradation rates through catalysis, being more unfavourable to hydrophilic resins.4

As all polymers degrade, it is the degradation time scale that dictates their biomedical applicability. From this aspect, there are polymers that are specially designed to degrade, such as the poly (lactic acid), poly (glycolic acid), poly (orthoesters) and poly (anhydrides) used as absorbable suture materials and drug delivery systems.1

Ideally, polymers for dental restorations should not degrade in the oral environment, which consists of an aqueous medium presenting pH fluctuations.5 Acids produced by bacterial metabolism such as acetic, propionic and lactic acid cause a variation in pH, with 4 being the lowest pH found in plaque.6 Usually, these are the media of choice used by researchers who want to catalyse hydrolysis in order to evaluate the longevity of dental resins.7–9

Dental composites consist of a mixture of monomers and silane-treated filler particles such as quartz, zirconia, borosilicate and silica. Although these materials undergo chemical degradation in the oral environment, there is still poor evidence to confirm whether acidic pH levels in the mouth significantly affect this process.10–12 Degradation of resin-based dental materials seems to progress at similar rates in water, artificial saliva and in neutral to slightly low pH media.5

Therefore, in order to induce polymer hydrolysis and accelerate micro-structural damage, alternative choices would be to soak test specimens either in very low (pH 1) or very high pH (pH 13) environments. This study investigated the effects of neutral and extremely acidic or alkaline pH storage media on dental resin surface properties. The null hypothesis tested was that there is no difference in the hardness and roughness of resins after storage in different pH media over time.

2. Materials and methods

2.1. Experimental design

This study evaluated microhardness and surface roughness as response variables to the following factors: (1) different resins at three levels: two commercial composites, Z100 (3M-ESPE) and TPH Spectrum (Dentsply), and one experimental unfilled resin (UR); (2) storage media at three levels: pH 1, pH 6.9, pH 13 and, (3) storage time intervals at four levels: baseline, 3-, 7- and 14-day. The association between factors 1 and 2 resulted in 9 (3 × 3) groups and 90 specimens, of which half of them were randomly used for each test and storage media (n = 5). Repeated measurements were performed for hardness and roughness evaluation during the different storage time intervals.

2.2. Materials and specimen preparation

Two commercial resin composites and one experimental unfilled resin based on bis-GMA and TEGDMA were chosen for this study (Table 1). For the unfilled resin, the comonomer ratio used was 60 mol% of bis-GMA and 40 mol% of TEGDMA. Resins were gently hand mixed and activated for visible light polymerisation by the addition of CQ and DMPT, each at 0.2 wt%. Thirty specimens of each resin were fabricated using a cylindrical acrylic matrix with internal dimensions of 7 mm diameter × 2 mm height. Unpolymerized material was sandwiched between two polyester strips on a glass-mixing tablet. A microscope glass slide was placed over the top polyester matrix and a 1000 g load was applied for 15 s before polymerisation. A visible light curing unit (Degulux short-start; Degussa, GmbH, Germany) was used for polymerisation for 40 s, uninterruptedly delivering 550 mW/cm², verified by a radiometer (Model 100; Demetron Research, CT, USA).

The top surfaces of specimens were polished in a metallographic grinding machine (DPL-4; Arotec, SP, Brazil) using a series of #600, 1000 and 1200-grit abrasive papers followed by a series of 1, 0.3 and 0.05 µm-grit aluminium-oxide slurries (Arotec, SP, Brazil), applied with a velvet cloth (DPN; Struers, Copenhagen, Denmark). After being ultrasonically cleaned for 5 min between each polishing step, specimens were individually pre-stored in 8 mL of deionized water at 37 °C for seven days.

2.3. Baseline microhardness (SM) and surface roughness (SR) measurements

A hardness tester (HMV-2000; Shimadzu, Tokyo, Japan) combined with the CAMS-Win software (NewAge Inds., PA, USA), fitted with a Knoop diamond indenter was used under a

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filltek Z100 (3M-ESPE)</td>
<td>Bis-GMA, TEGDMA, Silica/zirconia (84.5 wt%); 0.6 µm average particle size, photoinitiator</td>
</tr>
<tr>
<td>TPH spectrum (Dentsply)</td>
<td>Bis-GMA, Bis-EMA, TEGDMA, Ba Al borosilicate glass (77 wt%); &lt;1.0 µm average particle size, colloidal silica, initiators/stabilizers</td>
</tr>
<tr>
<td>Unfilled Resin (Kerr Corp.)</td>
<td>Bis-GMA, TEGDMA, Camphorquinone (CQ), N,N-dimethyl-p-toluidine (DMPT), No filler content</td>
</tr>
</tbody>
</table>

a 2,2-Bis[4-(2-hydroxy-3-methacyloyloxypropyl)-1-oxy]phenyl]propane. 

b Triethylene glycol dimethacrylate.

< 2,2-Bis[4-(2-methacyloyloxyethyl)phenyl]propane.
load of 300 g for 15 s. After being wiped with absorbent paper, five measurements were taken on the top surface of each sample. The baseline Knoop hardness number was obtained by the arithmetic mean of these five micro-indentations. For surface roughness \( R_a \), each specimen was also wiped with absorbent paper and five roughness tracings were taken on top surface using a Hommel Tester rugosimeter (T1000-basic; Hommelwerke, GmbH, Germany). This contact equipment has a 5 μm Diamond Tip Stylus and Sensor Angle of 90°. The tracing parameters were established at \( L_r \) (assessment length): 4.8 mm, \( L_c \) (cut-off): 0.8 mm (ISO 4287/1), at a speed of 0.5 mm/s. Baseline \( R_a \) values were obtained by the arithmetic mean of these five readings.

2.4. pH-storage regimen and subsequent hardness and roughness evaluations

The following aqueous solutions were used in the study: (1) 0.1 M, pH 1, hydrochloric acid (140 g sodium bisulphate, 30 mL sulphuric acid, 60 g sodium chloride; Sigma Aldrich, St. Louis, MO, USA); (2) 0.1 N, pH 13, sodium hydroxide; and (3) pH 6.9, deionized water. Specimens were individually immersed in 8 mL of each solution and stored at 37 °C for 14 days. The solutions were replaced daily. Repeated hardness and roughness measurements were performed on each specimen at the 3-, 7- and 14-day storage time intervals. The tests were carried out as described for baseline measurements.

2.5. Statistical analysis

For each test and resin, data were analysed by 2-way ANOVA (factors: storage media and storage time interval) followed by Tukey’s test. In addition, ANOVA followed by Tukey’s test were used to evaluate differences among different media at each storage time interval. Level of significance was set at 5%.

2.6. Surface microscopic observation

Representative specimens of each group and testing condition were selected for qualitative scanning electron microscopy observation (SEM, LEO-VP, Cambridge, UK). Specimens were dried in a desiccator at 37 °C for 24 h, sputter-coated with gold (MED 010, Balzers, Liechtenstein) and analysed at 3000× magnification.

3. Results

Table 2 shows the mean hardness and standard deviation values. The Z100 resin composite stored in the acidic pH medium showed no changes in hardness after 14 days. In the neutral medium, values oscillated and were slightly, but significantly lower at day 14. The drop in hardness of specimens stored in an alkaline solution progressed gradually and significantly at each evaluated time interval \( p < 0.001 \). In all storage periods, TPH composite at pH 1 and pH 6.9, showed no significant differences in comparison with the respective baseline means. In the alkaline medium, however, hardness dropped gradually and significantly from one storage period to another \( p < 0.001 \). In all pH media, UR groups remained statistically unchanged up to day 14. For each resin, the baseline means were the same among the different media. For the two composites at 3 and 7 days, and TPH at the 14-day evaluation, acidic and neutral values were statistically the same differing significantly from the mean alkaline value. For Z100 at day 14, all values differed statistically from each other in the following order: acidic > neutral > alkaline. In each storage period, UR showed no statistical differences in mean hardness values among the different media.

Table 3 shows the mean roughness and standard deviation values. The two composites in pH 1 and pH 6.9 media, and UR in all pH media showed no significant changes in roughness after 14 days. Z100 and TPH at an alkaline pH showed similar behaviour, and values at 3, 7, and 14 days were statistically the same, but differed significantly from baseline values \( p < 0.001 \). The mean roughness values of all resins at baseline, and UR at 3, 7 and 14 days were the same among the different media. For both composites at the 3-, 7- and 14-day evaluation, acidic and neutral values were statistically the same, and differed significantly from the mean alkaline value \( p < 0.001 \).

4. Discussion

As shown by the present findings, the evaluated resin composites underwent significant softening and became rougher after immersion in a highly alkaline medium during the 14-day evaluation time interval, leading to rejection of the
proposed null hypothesis. On the other hand, all SM and SR values of the unfilled resin remained statistically unchanged after storage in media with different pH values. The aqueous environment of the mouth, conducive to chemical degradation and softening, and therefore to corrosion-wear, is a critical factor that affects the mechanical properties of resin composite. In this mechanism, there is the conjoint action of chemical and mechanical forces. In composites, this process starts with absorption of water that diffuses internally through resin matrix, pores and most probably through the filler interfaces. The internally corroded subsurface layer is soft and porous creating conditions for corrosive-wear. As the corroded layer is mechanically removed, a fresh surface is exposed and the cycle continues.\textsuperscript{13,14}

Moreover, it has been reported that one of the main water diffusion pathways exists at the interface between filler particle and the organic matrix. Water uptake by filled specimens is about twice that which would be expected to occur in an unfilled resin counterpart.\textsuperscript{15} This path of facile diffusion (or ‘grain boundary diffusion’\textsuperscript{16}) leads to hydrolytic degradation of silane couplers and fillers. It compromises their reinforcing effect and surface properties such as the SM and SR of composites, as seen in the present findings for groups Z100 pH 13 and TPH pH 13. The strong influence of the alkaline medium on composite properties is due to its interaction with OH\textsuperscript{−} ions during the hydrolysis process. With its pH at 13, the alkaline medium provides a million times as many hydroxyl ions as are present in solutions at neutral pH or low pH. This accelerated degradation caused by a catalysed hydrolytic process was observed in the SEM images. Figs. 1 (Z100 composite resin) and 2 (TPH composite resin) show a continuous process of surface deterioration characterized by particles exposure (Figs. 1a and 2a), dislodgement at the 3-day (Figs. 1b and 2b) and 14-day time interval evaluations (Figs. 1c and 2c), leading to the decrease in hardness and change in surface topography, with consequent increase in roughness values.

Apart from the possibility of debonding, it is also possible to evoke hydrolysis of the inorganic particles themselves with an excess of OH\textsuperscript{−} ions. The stress-corrosion theory proposed by Charles\textsuperscript{17} is based on how easily metal ions, melted into the glass, can leach into the surrounding water and be replaced by the smaller H\textsuperscript{+} ions in the silicone and oxygen network. This is especially detrimental to sodium containing glasses, whereas quartz seems to be more resistant. Reports have indicated that barium oxide glass produced a pH around 9.3 when suspended in distilled water. This alkaline reaction may adversely affect the stability of organo-functional silane agents in the presence of water.\textsuperscript{18}

The reaction in which siloxane bonds are attacked by

Table 3 – Mean values for surface roughness average (Ra – μm) according to period of exposure to the different pH media.

<table>
<thead>
<tr>
<th>Groups</th>
<th>Baseline (SD)</th>
<th>3-day (SD)</th>
<th>7-day (SD)</th>
<th>14-day (SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z100 pH 1.0</td>
<td>0.04900 (0.011)\textsuperscript{AA}</td>
<td>0.04408 (0.010)\textsuperscript{AA}</td>
<td>0.04256 (0.008)\textsuperscript{AA}</td>
<td>0.04076 (0.008)\textsuperscript{AA}</td>
</tr>
<tr>
<td>Z100 pH 6.9</td>
<td>0.05024 (0.007)\textsuperscript{AA}</td>
<td>0.05468 (0.009)\textsuperscript{AA}</td>
<td>0.05032 (0.007)\textsuperscript{AA}</td>
<td>0.04812 (0.008)\textsuperscript{AA}</td>
</tr>
<tr>
<td>Z100 pH 13.0</td>
<td>0.05228 (0.012)\textsuperscript{AA}</td>
<td>0.09216 (0.019)\textsuperscript{AA}</td>
<td>0.09880 (0.013)\textsuperscript{AA}</td>
<td>0.09696 (0.014)\textsuperscript{AA}</td>
</tr>
<tr>
<td>TPH pH 1.0</td>
<td>0.06092 (0.014)\textsuperscript{AA}</td>
<td>0.06152 (0.013)\textsuperscript{AA}</td>
<td>0.05936 (0.014)\textsuperscript{AA}</td>
<td>0.05940 (0.014)\textsuperscript{AA}</td>
</tr>
<tr>
<td>TPH pH 6.9</td>
<td>0.06388 (0.012)\textsuperscript{AA}</td>
<td>0.06484 (0.014)\textsuperscript{AA}</td>
<td>0.06236 (0.012)\textsuperscript{AA}</td>
<td>0.06320 (0.012)\textsuperscript{AA}</td>
</tr>
<tr>
<td>TPH pH 13.0</td>
<td>0.05492 (0.009)\textsuperscript{AA}</td>
<td>0.08756 (0.019)\textsuperscript{AB}</td>
<td>0.08340 (0.007)\textsuperscript{AB}</td>
<td>0.08268 (0.005)\textsuperscript{AB}</td>
</tr>
<tr>
<td>UR pH 1.0</td>
<td>0.03780 (0.006)\textsuperscript{AA}</td>
<td>0.04104 (0.010)\textsuperscript{AA}</td>
<td>0.03840 (0.005)\textsuperscript{AA}</td>
<td>0.04028 (0.006)\textsuperscript{AA}</td>
</tr>
<tr>
<td>UR pH 6.9</td>
<td>0.03916 (0.004)\textsuperscript{AA}</td>
<td>0.03936 (0.009)\textsuperscript{AA}</td>
<td>0.03924 (0.002)\textsuperscript{AA}</td>
<td>0.03816 (0.003)\textsuperscript{AA}</td>
</tr>
<tr>
<td>UR pH 13.0</td>
<td>0.04508 (0.007)\textsuperscript{AA}</td>
<td>0.03824 (0.006)\textsuperscript{AA}</td>
<td>0.03808 (0.005)\textsuperscript{AA}</td>
<td>0.03684 (0.007)\textsuperscript{AA}</td>
</tr>
</tbody>
</table>

Same superscript upper case letters indicate no statistical significance among values in column view. Same lower case letters indicate no statistical significance among values in line view. SD, standard deviation.

Fig. 1 – Representative micrographs of Z100 composite: (a) baseline, (b) 3-day pH 13, and (c) 14-day pH 13 (3000×).
hydroxyl ions leading to hydrolytic degradation has, for instance, been described as

\[
[\text{Si}–\text{O}–\text{Si}] + \text{NaOH} \rightarrow [\text{Si}–\text{OH}] + [\text{Si}–\text{O}–\text{Na}]
\]

The results of the present study support the theory that resin composite degradation is highly dependent on the silane-treated filler characteristics. The fact that Z100 pH 6.9 had a slightly decreased SM after 14 days of storage, as opposed to TPH pH 6.9 that showed no significant changes in SM, may therefore be related to their different filler particle compositions, such as type, size, and silanisation. In addition, recent studies that evaluated resin composites challenged by food-simulating media (such as citric acid pH 5\(^2\) and citric acid pH 3\(^2\)) agree that roughness changes are highly material dependent. According to their results, most of the evaluated composites were not affected by low pH after 6 months or 7-days storage periods, respectively. Materials containing alkaline metals such as barium showed more susceptibility to low pH after 6 months storage in citric acid\(^2\).

Degradation of resin-based dental materials seem to progress at similar rates in deionized water, neutral to slightly low pH media,\(^5\) and in a very low acidic medium (Fig. 3). After 14 days of storage, no remarkable qualitative differences were noted on the surfaces of Z100 composite stored in acidic medium (Fig. 3a) or deionized water (Fig. 3b), and those of TPH composite stored in acidic medium (Fig. 3c) or deionized water (Fig. 3d). Moreover, the different pH media affected none of the evaluated surface properties of the experimental unfilled resin. Fig. 4 exhibits a similar surface pattern of bis-GMA/TEGDMA comonomer at baseline (Fig. 4a), and after storage in acidic (Fig. 4b), neutral (Fig. 4c) or alkaline (Fig. 4d) pH media. Ester bonds in the polymeric structure of dimethacrylates are susceptible to degradation via hydrolysis.\(^2\) This leads to the formation of methacrylic acid and formaldehyde as by-products.\(^2\) Hence, it would be reasonable to expect that an alkaline pH would catalyse such a reaction. The SM and SR results, however, showed that a 14-day pH challenge was not sufficient to produce significant structural changes in the evaluated unfilled resin. The speed of this process depends on many other factors such as copolymer hydrophilicity, diffusivity of water inside the matrix, the degradation rate of the functional groups in

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**Fig. 2** – Representative micrographs of TPH composite: (a) baseline, (b) 3-day pH 13, and (c) 14-day pH 13 (3000×).

**Fig. 3** – Representative micrographs of composites at 14-day storage: (a) Z100 pH 1, (b) Z100 pH 6.9, (c) TPH pH 1, and (d) TPH pH 6.9 (3000×).
polymer chains, and matrix dimensions. Future studies should consider the evaluation of dental comonomers kept in alkaline solutions for longer storage periods, as well as by methodologies such as atomic force microscopy (AFM) nanoindentation or nanomechanical testing instruments. Conversely, in investigations where the purpose is to evaluate dental composite properties by accelerating hydrolysis and producing quick surface micro-structural damage, a highly alkaline solution seems to be the medium of choice. Contemporary resin composite materials seem to be designed to withstand neutral and acidic oral environments to an acceptable extent.

Acknowledgements

This study was supported by “Fundaç\’a˜o de Amparo \’a Pesquisa do Estado de S\’ao Paulo” – Brazil (Fapesp #2008/06170-7; RC), and by funds from the Faculty of Dentistry, University of Toronto – Canada (AP-FI) and Cononnaht Start-up Award (AP-FI). We thank Alvin Kobashigawa (Kerr Corporation) for supplying gift samples of some chemicals. The authors declare no conflicts of interest.

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