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Hydrolytic and Biological Degradation of Bulk-fill and Self-adhering Resin Composites

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Clinical Relevance

The interaction between different substances on resin composite surfaces is a critical issue in the assessment of the clinical longevity of restorative materials.

SUMMARY

Objectives: This study aimed to evaluate the hydrolytic degradation (*in vitro*) and biodegradation (*in situ*) of different resin composites: bulk-fill (XTra Fill, XTF/VOCO; Tetric EvoCeram Bulk Fil, TBF/ Ivoclar Vivadent), self-adhering (Vertise Flow, VTF/ Kerr; Fusio Liquid Dentin, FUS/ Pentron Clinical), and a conventional resin composite (Filtek Z250, Z250/ 3M ESPE), which was used as a control.

Methods and Materials: Seventy-five cylindrical specimens (7 × 1 mm) were desiccated and immersed into distilled water (DW), artificial saliva (AS), and 0.1 M lactic acid (LA) (n=5) for 180 days. Specimens were weighed after 180 days, after which they were desiccated again. The sorption (μg/mm^3) and solubility (μg/mm^3) were calculated based on ISO 4049. For the *in situ* phase, an intraoral palatal device containing five cylindrical specimens (5 × 1.5 mm) was used by 20 volunteers for seven days. Surface roughness was evaluated before and after this period to analyze the superficial biodegradation. Sorption and solubility data were submitted to Kruskal-Wallis and Mann-Whitney tests. The Wilcoxon signed-rank test was used to compare roughness at different observation times. The statistical significance for all tests was considered α=0.05.

Results: For *in vitro*, self-adhering resin composites (VTF and FUS) showed, respectively, higher sorption values independent of the solution (62.55 and 50.81 μg/mm^3 in DW, 67.26 and 50.46 μg/mm^3 in AS, and 64.98 and 59.86 μg/mm^3 in LA). Self-adhering VTF also had a greater solubility value in DW (22.18 μg/mm^3) and FUS in LA (65.87 μg/mm^3). In AS, the bulk-fill resin composite XTF showed higher solubility (22.13 μg/mm^3). All resins were biodegraded, but the XTF specimens were more resistant (*p*=0.278) to chemical attack.

Conclusions: The self-adhering resin composites showed the highest hydrolytic degradation, and the bulk-fill resin composites exhib-

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ited comparable or superior results to the conventional resin composites. Not all resin composites underwent biodegradation in the *in situ* environment. The storage environment influenced the final characteristics of each material tested.

INTRODUCTION

The complexity of the oral environment is a significant challenge for restorative materials. The presence of water, saliva, and the acid metabolites produced by the cariogenic biofilm may lead to physical and hydrolytic degradation of the dental restorations. Moreover, surface damage such as softening and increased surface roughness can also occur as part of the biodegradation process.[1-3] The clinical desire for more straightforward restorative procedures leads to the development of new restorative materials. New monomer technologies, photoinitiators, or bonding mechanisms have been introduced such as bulk-fill and self-adhering resin composites. However, there is limited knowledge about the influence of cariogenic biofilms on the hydrolytic and biological degradation of these resin composites.[4]

The resistance to degradation in the oral environment has a significant impact on the longevity and clinical success of dental materials.[5] Sorption and solubility are inherent bulk properties of the polymeric materials. Besides the deleterious effects on the structure of the material, these properties may predict material behavior and clinical performance, as they are precursors to a variety of physical and chemical processes of biological concern.[5,6] The degree of sorption and solubility can influence the restorative's integrity, esthetic appearance, and surface properties.[7]

The sorption through polymeric materials is considered a diffusion-controlled phenomenon that is influenced by the hydrophilicity of the polymer network,[8] degree of conversion,[9] and cross-link density[10]; it is inversely proportional to the amount of filler particles.[11,12] Sorption is a result of absorption and adsorption. Adsorption is a surface phenomenon, whereas absorption involves the whole volume of the material.[13] Dental polymer networks based on dimethacrylate monomers absorb moisture, which may result in the enlargement of the spaces between the polymer chains.[14] These areas allow free unreacted monomers trapped in the polymer network to diffuse out into the storage media, depending on their molecular size and their affinity to the solvent.[15] The solvent can reduce the siloxane bonding energy between the filler particle and the resin matrix, and with time, can break this bond and allow the solvent adsorption to the particle.[13] Thus, the solubility can compromise the biocompatibility of the material and lead to mechanical property reduction.[8,14]

Many immersion media have been tested such as water,[8,16] saliva,[17,18] lactic acid,[17] and esterases,[15] each with well-established protocols. The acid metabolites produced by cariogenic biofilm can cause increased surface roughness.[19] *Streptococcus mutans* has higher affinity to resin composites than enamel and other restorative materials such as ceramics and metals.[20] Organic acids may degrade methacrylate-based polymers, changing their surface hardness.[21,22] The biostability of resin composites impacts the prevalence of secondary caries.[23,24]

The bulk-fill resin composites are based on new monomer technology and polymerization modulators[9] that reduce the effect of polymerization shrinkage stress.[10] The self-adhering restorative resin composites are based on traditional methacrylate systems, with the incorporation of functional acidic monomers typically found in dentin bonding agents, such as glycerolphosphate dimethacrylate (GPDM). According to the manufacturers, such monomers may be capable of bonding through mechanical and chemical interactions with the tooth structure.[19]

Therefore, the objective of this study was to analyze the *in vitro* hydrolytic degradation and the *in situ* biodegradation of bulk-fill and self-adhering resin composites in different immersion media generally present in the oral environment. The null hypotheses tested were: (i) there is no difference in the sorption and solubility between evaluated materials; (ii) after 180 days of storage, there is no difference in the influence of storage medium on the restorative materials tested; and (iii) biofilm interaction does not promote increase in surface roughness.

METHODS AND MATERIALS

This study was conducted in two parts: *in vitro* (Figure 1) and *in situ* (Figure 2). All tested materials are listed in Table 1.

The sample calculation was performed using BioEstat 5.3 (Mamirauá Sustainable Development Institute, Manaus, Brazil). An $\alpha = 0.05$ and a 0.80 power was considered. For the *in vitro* test, the results from the study of Alshali and others[14] were considered. The ideal sample size per group was four to note

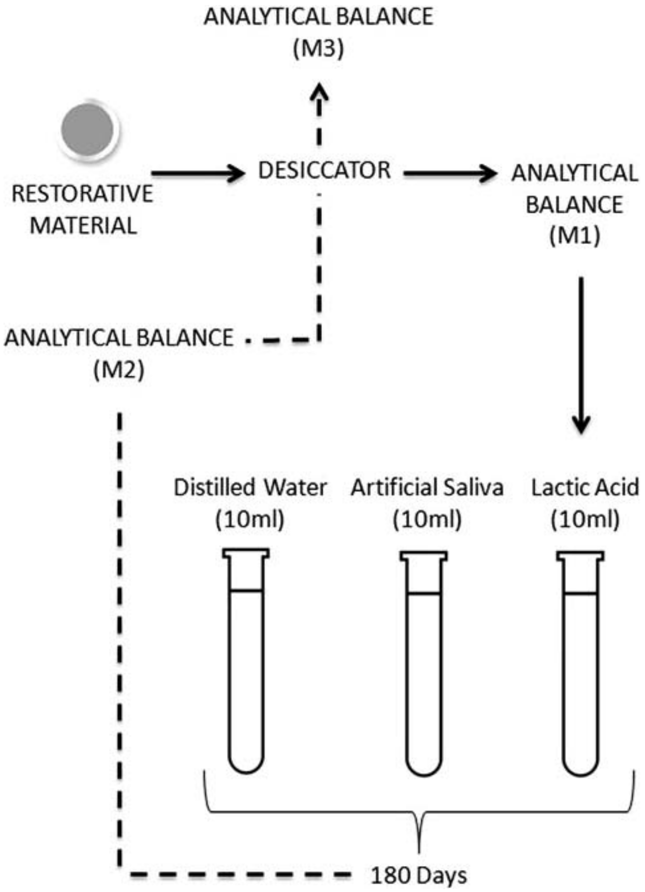

Figure 1. *Schematic illustration of the* in vitro *experimental design.*

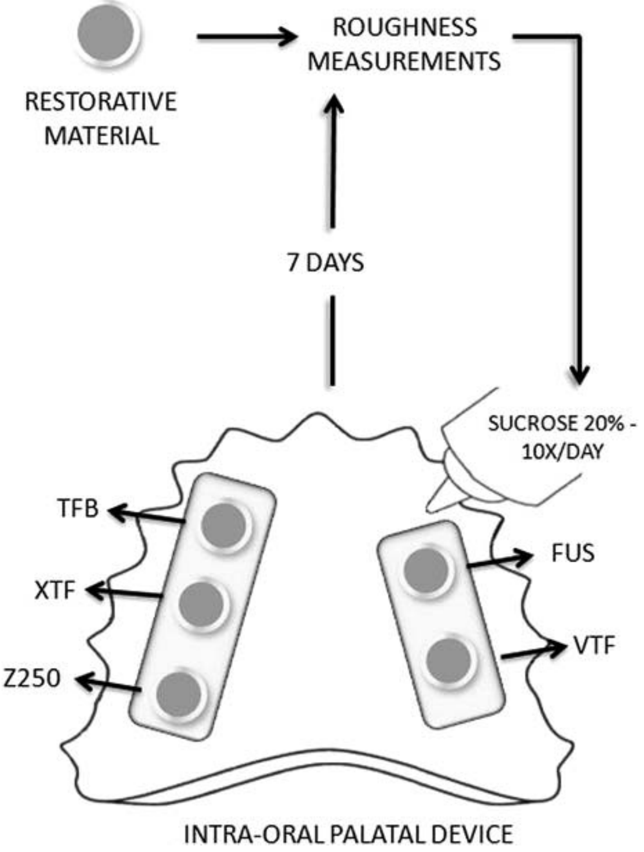

Figure 2. *Schematic illustration of the* in situ *experimental design and the intraoral palatal device model.*

significant differences. In this study, a sample size of five was used. For the *in situ* phase, the sample calculation was based on the study of Padovani and others.[3] A sample size of 17 was found to note significant differences; however, a sample size of 20 volunteers was used to compensate possible outlying values that might lead to specimen loss.

Preparation of Specimens for the *In Vitro* Phase

Seventy-five disc-shaped specimens of each resin composite were made using a Teflon mold (7×1 mm). The mold was filled to excess and a Mylar matrix strip under a microscope glass slab were placed on top. Slight digital pressure was applied to the glass to minimize voids.

Each specimen was cured at the specimen's central area according to the manufacturers' instructions using an LED light curing unit (Radii-Cal, Dental Product SDI, Bayswater, Victoria, Australia) with 1200 mW/cm^2 irradiance. Specimens were removed from the mold, and the flash was removed using a sharp blade and silicon carbide papers (#600 and #1200).

Sorption and Solubility

The specimens were individually stored in plastic vials, placed in a desiccator containing freshly dried silica gel, and transferred to an incubator at 37°C. After 24 hours, the discs were repeatedly weighed on an analytical balance (AUW 220D/0.01 mg, Shimadzu Analytical Balance, Tokyo, Japan) until specimen mass variation was less than ±0.1 mg to obtain m_1, the initial mass of each specimen. The dimensions of the specimens were measured at four points using a digital caliper (Digimess, São Paulo, SP, Brazil) with a precision of 0.01 mm, and the volume (V) was calculated in mm^3 using the mean diameter and thickness of each specimen. Specimens were divided into three groups (n=5) according to the immersion media used: distilled water, artificial saliva (Table 2), or lactic acid 0.1 M. The pH of lactic acid was adjusted to 4.0 with 40% sodium hydroxide (Dilecta, Compounding Pharmacy, João Pessoa, Brazil). Each specimen was placed in a plastic vial, and 10 mL of immersion medium was added and kept at 37 ± 1°C during all experimental phases.

Table 1: *Tested Materials, Composition, and Specifications*

Materials	Classification	Monomers*	Inorganic Filler	Filler, wt/vol %	Cure Time, s	Manufacturer Batch Number
X-Tra Fil (XTF)	Bulk Fill Sculptable Resin Composite	Bis-GMA, UDMA, TEGDMA	Barium aluminum silicate vitreous particles	86/70.1	10	VOCO, Cuxhaven, Germany, 1443074
Tetric EvoCeram Bulk Fill (TBF)	Bulk Fill Sculptable Resin Composite	Bis-GMA, UDMA, Bis-EMA	Vitreous particles of barium aluminum silicate, Ytterbium trifluoride, Mixed oxide	62.5/61	10	Ivoclar Vivadent, Ontario, Canada, T32776
Vertise Flow (VTF)	Self-Adhering Flowable Resin Composite	GPDM, HEMA	Prepolymerized filler, barium glass, nano-sized colloidal silica, nano-sized ytterbium fluoride	70/NA	20	Kerr, Orange, CA, USA, 5245261
Fusio Liquid Dentin (FUS)	Self-Adhering Flowable Resin Composite	UDMA, TEGDMA, HEMA, 4-MET	Amorphous silica nanoparticulate, silane treated with barium glass, minor additives, photoactivating particles	65/52	10	Pentron Clinical, Orange, CA, USA, 5224286
Filtek Z250 (Z250)	Universal Sculpable Resin Composite	UDMA, Bis-GMA, Bis-EMA, TEGDMA	Particles of zirconia and silica	82/60	20	3M/ESPE, St Paul, MN, USA, 269759

** Bis-EMA, bisphenol A ethoxylate dimethacrylate; Bis-GMA, bisphenol A glycidyl dimethacrylate; GPDM, glycerolphosphate dimethacrylate; HEMA, 2-hydroxyethyl methacrylate; TEGDMA, triethylene glycol dimethacrylate; UDMA, urethane dimethacrylate; 4-MET, 4 methacryloxyethyl trimellitic acid.*

After a 180-day period, the specimens were blotted dried with absorbent paper until moisture could no longer be observed and the recorded mass was registered as m_2. All the specimens were then reconditioned in the desiccator and then weighed until the mass variation was smaller than 0.1 mg (m_3). The sorption (S_p) and solubility (S_l) of the resin composites (mg/mm^3) were calculated according to the following equations:

$$S_p = \frac{(m_2 - m_1)}{V}$$

$$S_l = \frac{(m_1 - m_3)}{V}$$

Preparation of Specimens for *In Situ* Phase

For this phase, 100 disc-shaped specimens were made (5×1.5 mm) as previously described. However, these specimens had their surfaces polished by using fine and superfine aluminum oxide abrasive discs (Sof-Lex 3M ESPE, St. Paul, MN, USA) for 20 seconds in the same direction with intermittent movements. The specimens were then washed in an ultrasonic cleaner (1440D, Biodont, São Paulo, SP, Brazil) with water for 30 seconds.

Roughness Measurements

The mean surface roughness (Ra) was measured (µm) using a contact profilometer (SURFTEST SJ 310, Mitutoyo Corp, Kanagawa, Japan). Four successive in-line measurements were performed in the horizontal direction of each disc at the constant speed of 0.5 mm/s with a load of 0.7 mN, and a cutoff value of 0.25 mm, to maximize filtration of surface waviness, and a trace length of 4.0 mm. Calibration was done periodically to monitor the instruments' performance.

Table 2: *Chemical Composition of Artificial Saliva*

Saliva 1 Composition	Saliva 2 Composition	Saliva Final Composition
0.625% potassium chloride	10% sodium benzoate	10% of saliva 1 composition
0.865% sodium chloride	42.74% sorbitol	10% of saliva 2 composition
0.0558% magnesium chloride	1.1295% potassium acid phosphate	0.5% carboxymethil cellulose
0.1662% calcium chloride	0.0043% sodium fluoride	0.1% phenonip
Distilled water Q.S.P 100%	Distilled water Q.S.P 100%	Distilled water Q.S.P 100%

Abbreviation: Q.S.P, French for quantitié suffisante pour.

Panelists and Ethical Aspects

This study protocol was approved by the Local Research and Ethics Committee (protocol 895.899/2014) where 20 individuals, ages 21 to 30 years and dental students in graduate and undergraduate courses, participated in this study. The inclusion criteria were as follows: good general and oral health, the absence of antibiotic use two months before the experiment, no signs of gingivitis or caries, and ability to comply with the study. Volunteers using a dental prosthesis or orthodontic devices, with diabetes, palatine torus, chronicle oral breathing, or with motor difficulties were excluded from the experiment. Visual and oral examinations were carried out by a dentist. All the volunteers agreed to participate and signed an informed written consent form.

In Situ Phase

The volunteers' teeth were impressed with alginate (Hidrogum 5, Zhermack, Rovigo, Italy), and type III gypsum models were obtained. An acrylic intraoral palatal device was made for each participant, each containing five wells (2.5 mm deep) as shown in Figure 2. A plastic mesh was fixed to the sides of the intraoral device covering each specimen. A 1.0-mm space was left between the mesh and the specimen to allow dental biofilm accumulation to form.

Oral and written instructions were given to the volunteers. No dietary restrictions were given, but participants were asked to remove the device before eating or drinking beverages and to keep the device moist in a plastic box provided. Oral hygiene was indicated three times per day with a standardized fluoride dentifrice (Colgate Maximum Cavity Protection, Colgate-Palmolive Company, New York, NY, USA). At this time, only the palatal region of the device was extraorally brushed to avoid disturbing the biofilm. The cariogenic challenge was provided by an extraoral application of a 20% sucrose solution on the specimens at 10 times per day. For this application, the devices were removed from the mouth, and the excess saliva was cleaned with gauze. One drop of the solution was placed on each specimen at 08:00, 09:30, 11:00, 12:30, 14:00, 15:30, 17:00, 18:30, 20:00, and 21:30 hours. The sucrose was then gently dried with gauze after five minutes, and the device was reinserted into the mouth. After seven days, the specimens were carefully removed from the device and washed in an ultrasonic bath for 10 minutes. The final roughness measurements were then performed as previously described.

Statistical Analysis

Data were analyzed using STATA/SE software 12.0 (StataCorp, College Station, TX, USA). Means and standard deviations were calculated. The presence of normal distributions was evaluated by the Kolmogorov-Smirnov test. The Kruskal-Wallis test determined differences between the sorption and solubility groups, and the Mann-Whitney test was applied when needed. The Wilcoxon signed-rank test was used to compare roughness. The statistical significance for all tests was considered $\alpha=0.05$.

RESULTS

The results for the *in vitro* sorption and solubility ($\mu g/mm^3$) are shown in Table 3. The Kruskal-Wallis test rejected the null hypothesis for all three storage mediums, indicating that at least one of the groups differed from the rest ($p<0.001$). All tested self-adhering resin composites showed higher and significant sorption for all three immersion media.

The self-adhering resin composites Vertise Flow (VTF) and Fusio Liquid Dentin (FUS) showed the highest sorption for all three immersion mediums. For FUS, statistically significant differences were only observed between lactic acid and artificial saliva. However, results showed that VTF's sorption had no statistical difference between tested media ($p=0.208$). Lower sorption was observed within the bulk-fill composites X-Tra Fil (XTF) and Tetric EvoCeram Bulk Fill (TBF). Their results were comparable to the control group Filtek Z250 (Z250).

The resin composites showed the same behavior for sorption in artificial saliva and lactic acid (XTF<TBF<Z250<FUS<VTF). Lower sorption was observed for TBF in distilled water (20.83 $\mu g/mm^3$). There was no statistical difference between the bulk-fill resin composites and the control group (Z250). However, self-adhering resin composites showed statistical differences between the bulk-fill and control groups ($p=0.009$).

The control group (Z250) showed significantly higher sorption in lactic acid ($p=0.006$) than bulk-fill composites. The sorption of XTF and TBF bulk-fill resin composites did not differ between tested media.

As for solubility, TBF showed the lowest values in all three media. Some high discrepancy values were observed for the bulk-fill resin XTF in artificial saliva (22.13 $\mu g/mm^3$) and the self-adhesive FUS in lactic acid (65.87 $\mu g/mm^3$). In general, solubility values obtained from the self-adhesive VTF were also higher than the control group.

Table 3: *Sorption (S_P) and Solubility (S_L) (μg/mm^3) Means (SD) After 180-Day Storage Period*

Groups	Distilled Water		Artificial Saliva		Lactic Acid		p*	
	S_P	S_L	S_P	S_L	S_P	S_L	S_P	S_L
Z250	21.46 (2.43)^{Aa}	4.79 (4.51)^{Aa}	23.49 (1.18)^{Ba}	−1.70 (3.28)^{Ab}	27.46 (1.55)^{Bb}	5.10 (5.00)^{ADab}	0.006	0.055
XTF	23.17 (13.54)^{Aa}	8.65 (8.70)^{ABa}	14.52 (1.60)^{Aa}	22.13 (40.50)^{BDCa}	14.56 (5.04)^{Aa}	11.99 (3.48)^{Aa}	0.566	0.221
FUS	50.81 (5.69)^{Bab}	6.89 (6.24)^{ACa}	50.46 (3.80)^{Ca}	7.19 (2.88)^{Ca}	59.16 (2.30)^{Cb}	65.87 (6.85)^{Bb}	0.037	0.009
VTF	62.55 (4.01)^{Ba}	22.18 (1.94)^{Ba}	67.26 (3.21)^{Da}	15.16 (1.24)^{Db}	64.98 (3.82)^{Ca}	26.86 (2.78)^{Cc}	0.208	0.003
TBF	20.83 (2.68)^{Aa}	−1.56 (3.15)^{Cac}	20.90 (2.45)^{Ba}	−6.61 (4.31)^{Ab}	22.25 (3.02)^{Ba}	1.69 (1.55)^{Dc}	0.827	0.009
p value*	0.001	0.005	<0.001	0.001	<0.001	<0.001		

Different superscript letters indicate statistically significant differences between groups through the Mann-Whitney test. Uppercase letters indicate differences between resin composites within each solution (columns); lowercase letters indicate significant differences between solutions (lines).
** Kruskal-Wallis test.*

In distilled water, VTF and XTF showed significantly higher solubility values of 22.18 and 8.65 μg/mm^3, respectively, than the other materials (p=0.005). For artificial saliva, XTF showed the highest sorption value (22.13 μg/mm^3), which was statistically similar to the VTF and FUS values (15.16 and 7.19 μg/mm^3, respectively), but there was a difference between the control group and TBF (p=0.001). In general, solubility values obtained from the self-adhesive VTF were also higher than the control groups.

Negative solubility values were seen when TBF (−6.61 μg/mm^3) and Z250 (−1.70 μg/mm^3) were immersed in artificial saliva and when TBF (−1.56 μg/mm^3) was immersed in distilled water. These values can be attributed to the incomplete dehydration of these materials. There was no statistical difference between the tested mediums for XTF (p=0.221). However, for VTF, there was a difference for solubility in each tested medium (p=0.009).

The results for the *in situ* phase are shown in Table 4. Initially, 20 volunteers were selected. However, only 16 volunteers completed the study. One volunteer presented an allergic reaction in the palatal mucosa, two lost the intraoral palatal device, and one did not complete the established protocol. All the materials showed significantly increased roughness after biodegradation, except for the XTF group (p=0.278). The results obtained for the FUS and TBF groups were on the threshold of significance (p=0.049). The final roughness of the resin composites tested followed the order: FUS = VTF = Z250 = TBF < XTF.

Table 4: *Mean Surface Roughness (μm) and SD Before and After Biodegradation*

Groups	Initial	Final	p*
Z250	0.25 (0.08)^{BC}	0.31 (0.09)^{B}	0.001
XF	0.44 (0.15)^{A}	0.47 (0.15)^{A}	0.278
FLD	0.24 (0.04)^{BC}	0.28 (0.08)^{B}	0.049
VF	0.21 (0.05)^{C}	0.28 (0.09)^{B}	0.005
TECBF	0.26 (0.09)^{B}	0.33 (0.09)^{B}	0.049

Different superscript letters indicate differences between groups within each observation moment, according to the Mann-Whitney test.
** Wilcoxon signed-rank test was used to compare roughness in different moments of observations.*

DISCUSSION

All three null hypotheses were rejected. Differences were observed between the sorption and solubility of the evaluated restorative materials, with different results within storage media. Also, the biofilm interaction resulted in a roughness increase for some of the restorative materials.

Even after polymerization, resin composites are not stable. Different substances may affect their integrity by diffusion into the polymer matrix. The polymer absorbs substances to varying degrees, which are influenced by the polarity of molecular structure, the degree of cross-linking in the continuous matrix, and the presence of hydroxyl groups. The sorption may result in an expansion of the gap between the polymer chains, allowing free unreacted components trapped in the polymer matrix to diffuse out into the storage media. The storage medium and the immersion period strongly influence the sorption and the solubility.[14,24] Their interaction in the oral cavity with the surface of the restorative materials also favors biodegradation because they are capable of penetrating the polymeric matrix and enhancing the release of the unreacted monomers.[25]

The solutions used as storage media in this study were chosen because they represent common liquids present in the oral environment. Organic solutions exhibit greater uptake and sorption/solubility values than water-based media.[14,26,27] In this study, differences in the sorption and the solubility of the evaluated materials was observed within each storage medium, with higher values when immersed in lactic acid. However, differences between storage media were only found in the sorption of Z250 and FUS. For the solubility, differences were observed in the groups FUS, VTF, and TBF. The lactic acid molecule presents functional groups in its composition such as -OH and -COOH, which may increase interaction with the polar sites of dimethacrylate monomers.[17]

Materials that highly absorbed water did not necessarily demonstrate high solubility and vice versa.[14,28] This phenomenon is attributed to leaching of residual monomers, additives, and filler content, which strongly depends on the degree of conversion, monomer hydrophilicity, mobility and molecular size as smaller molecules will decompose faster.[24,29-31]

The hydrolytic degradation mechanism is enhanced in the presence of filler particles containing metallic ions (ie, barium and zinc). Some ions are electropositive and tend to react with water. This reaction changes the balance inside the silica network, and the spaces occupied by zinc and barium are reestablished with the penetration of hydrogen ions of water. The siloxane bonds (Si-O-Si) of the silica network start to break with the increase of the concentration of hydroxyl ions, and there is the formation of an autocatalytic cycle of surface degradation that could explain the continuity of superficial softening with aging time.[32]

The release of unreacted monomers highly depends on the degree of conversion. It was reported that the degree of conversion of different monomer systems increases in the following order: Bis-GMA < Bis-EMA < UDMA < TEGDMA.[33] The higher the degree of conversion, the lower the number of unreacted monomers, and therefore, the lower the solubility.[14] TEGDMA is a hydrophilic low-molecular-weight monomer with high mobility. It decomposes more quickly than larger molecules, such as Bis-GMA.[34] The TEGDMA-resin network has high flexibility and is also more heterogeneous, with larger spaces between the polymers that can therefore accommodate a higher quantity of water inside the micropores.[29] Apart from TBF and VTF, all other studied resin composites contain TEGDMA in their composition. UDMA is also present in most of the studied resin composites (except for VTF). UDMA seems to have lower sorption compared with Bis-GMA due to its higher reactivity, degree of conversion,[35] and higher resistance to chemical degradation.[36] The higher water sorption of Bis-GMA is due to the hydrophilic characteristics of its monomer units. Also, hydroxyl groups form stronger hydrogen bonds with the water molecules than the urethane groups of UDMA-resin or the ester groups of Bis-EMA resin.[37]

Monomers with adhesive properties have polymerizable groups with an additional functional group that is linked by a custom-made spacer group. This molecular design influences the hygroscopic expansion of the resulting polymer.[38,39] The expansion observed in the VTF specimens is due to the presence of a hydrophilic acid phosphate group and a shorter spacer group in the adhesive monomer, GPDM.[39] Also, the presence of HEMA makes this material more susceptible to matrix disintegration due to the molecules high hydrophilicity.[40] As for FUS, besides the adhesive monomer 4-MET, the material contains UDMA, TEGDMA, and HEMA. A previous *in vitro* study[41] evaluated the hygroscopic absorption characteristics of different resin-based materials. Due to the incorporation of hydrophilic monomers, the self-adhering resins were the least dimensionally stable.

Previous studies have confirmed that sorption is highly influenced by the polymeric matrix properties.[8,14,42-44] Because sorption is a phenomenon associated with the polymeric phase, a negative correlation between sorption and filler loading content[45] explains that, when weight percentage of fillers increase, the polymeric matrix and the sorption decreases.[46] The higher sorption values for FUS and VTF could be justified based on their flow characteristics, which require more diluent monomers and filler content. Apart from Z250, the inorganic phase of the evaluated resin composites is based on barium glass and particles such as strontium, which contains leachable ions.[39]

Resin composites containing barium glasses (XTF, TBF, VTF, FUS) and zirconia silicate fillers (Z250) seem to be more prone to aqueous attack than those containing quartz in their composition. The substantial softening observed in Z250 may be attributed to the smaller surface area and the spherical shape of zirconia/silica fillers that may decrease the filler-matrix bonds.[32]

Some materials produced negative solubility values, which can be attributed to incomplete dehydration of the materials. These negative values do not indicate that no solubility occurred but may hint to their low solubility. Possible hydrolytic chemical reactions of glass fillers and metal oxides with water results in the formation of metal hydroxides within the composite.[14,27] Negative solubility results have also been reported in other studies.[27,41,47]

The *in vitro* methods can also differ over the need to replace the storage medium.[17,46,48,49] The replacement would favor the maintenance of a constant pH throughout the experiment.[14,27] It would be interesting to assess further the variation of the pH on sorption and solubility similar to what occurs in the oral cavity.

In vitro tests are not able to reproduce the complex process of biodegradation. The pH conditions in an *in vitro* environment may be different than observed in the oral conditions.[1,2] Therefore, *in situ* studies are alternatives to evaluate many situations within the oral cavity in a short period.[50] The aqueous environment, the salivary properties, the biofilm accumulation, and temperature fluctuations are conditions that can predict the restorative material's behavior[51]; lactic acid is the most crucial product metabolized by cariogenic bacteria such as *S. mutans* in the presence of sucrose.[52] This study model allows the observation of the consequences of biointeraction on the materials' surfaces under constant biodegradation.

Little is known regarding the surface degradation of restorative materials after biofilm interaction *in situ*[3] and the exact start time of the degradation process is still uncertain.[53] Results are observed at different experimental times: seven days,[3,54,55] 14 days,[50] and also periods over 14 days.[56] A seven-day *in situ* evaluation showed an influence of the biofilm formation on the materials with chemical and physical modifications due to the biodegradation process.[3,54]

Clinically, the biodegradation process of restorative materials involves the dissolution and disintegration in saliva and other types of physical/chemical degradation. The potential for mechanical and chemical dissolution may cause increased biofilm accumulation.[50] Most of the tested materials have a combination of BIS-GMA and the diluent monomer TEGDMA in their composition. These monomers are linked by the presence of unprotected esters linkage, which is strongly susceptible to hydrolysis by saliva enzymes generating bishydroxy-propoxy-phenyl-propane (BisHPPP), triethylene glycol (TEG), and methacrylic acid (MA). These degradation byproducts have a negative influence on microorganism cell function and metabolism.[57,58]

The surface roughness increased in all resin composites except for the XTF resin after seven days. The monomer composition can influence bacterial growth, reducing surface degradation by the presence of acid. The presence of TEGDMA increases the degree of conversion[59] and reduces the bacterial growth.[60] Moreover, UDMA presents low biodegradation probably due to the improvement of the chemical resistance.[36]

The complexity of the degradation process and the difficulty in simulating the intraoral environment *in vitro* shows the need for further analysis that could help understand this complex phenomenon. A resin-based material's surface free energy is a central topic regarding biofilm adhesiveness.[14] Restorative materials with higher surface energy show a decreased resistance to adhesive biofilm formation.[61] *In situ* studies based on caries adjacent to restorative materials still yield inconsistent results,[56] as many different factors are involved such as distinct diet and oral hygiene regimens, caries risk, salivary flow, and the buffer capacity of saliva.[3] It would be interesting for future studies to evaluate the ability of bacterial adhesion and the resulting degradation in the bonding interface of indirect restorations. The interfacial gap formed by acids and bacterial enzymes are sites with a higher level of biodegradation that could lead to interfacial seal compromise, increasing the risk of secondary caries and therefore affecting the clinical longevity.[57]

CONCLUSIONS

All of the resin composites tested demonstrated hydrolytic degradation during 180 days in an *in vitro* environment. However, not all of them showed biodegradation with increased roughness in the *in situ* environment.

The time and storage medium influenced the final characteristics of the resin composites tested. The sorption and solubility seemed to depend on the composition of each material. The self-adhering resin composites showed higher hydrolytic degradation, and the bulk-fill resin composites had similar behavior to the conventional microhybrid resin composite used as a control. The XTF resin presented higher solubility in the *in vitro* environment. However, it showed chemical resistance in the *in situ* environment.

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Regulatory Statement

This study was conducted in accordance with all the provisions of the local human subjects oversight committee guidelines and policies of the Local Ethics Committee from University of Pernambuco. The approval code for this study is 38778814.1.0000.5207.

Conflict of Interest

The authors of this manuscript certify that they have no proprietary, financial, or other personal interest of any nature or kind in any product, service, and/or company that is presented in this article.

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