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ORIGINAL ARTICLE

Impact of monomer functional groups of resin-based materials on the interaction with water

Impacto de grupos funcionais de monômeros resinosos na interação com a água.

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ABSTRACT

Objective: The objective of this in vitro study was to compare dentin bonding systems and composite resins based on their functional groups in terms of water sorption (WS) and water solubility (WSB). **Material and Methods:** Three dentin bonding systems (Adper Single Bond 2 – 3M ESPE, Clearfil SE Bond – Kuraray, P90 Adhesive System – 3M ESPE) and three commercial composite resins (Filtek Z350 – 3M ESPE, Filtek Z250 – 3M ESPE, Filtek P90 – 3M ESPE) were tested. Eight specimens of each material were prepared to evaluate the WS and WSB. The discs were individually stored in a desiccator until constant mass was achieved. Specimens were then individually stored in distilled water until the mass was stabilized again. Finally, the specimens were dried again in the desiccator until constant mass was obtained. WS and WSB were calculated from these measurements. **Results**: Data were analyzed by one-way ANOVA and Tukey post hoc test ($p < 0.05$). Filtek Silorane-Bond presented the lowest values of WS, and Clearfil SE Bond presented the lowest WSB. Filtek Silorane resin showed the lowest WS and WSB results. **Conclusion:** Based on the results, it can be concluded that the WS and WSB were influenced by the composition of the materials. The main functional group of the materials determines their susceptibility to water and influences their performance.

KEYWORDS

Dental bonding; Composite resins; Sorption; Solubility.

RESUMO

Objetivo: O objetivo desse estudo in vitro foi comparar a sorção (SO) e a solubilidade (SB) em água de sistemas adesivos e resinas compostas baseados em seus grupos funcionais dos monômeros. **Material e Métodos:** Três sistemas adesivos (Adper Single Bond 2 – 3M ESPE, Clearfil SE Bond – Kuraray, sistema adesivo da P90 – 3M ESPE) e três resinas compostas (Filtek Z350 – 3M ESPE, Filtek Z250 – 3M ESPE, Filtek P90 – 3M ESPE) foram testados. Oito espécimes de cada material foram preparados para avaliar a SO e SB. Inicialmente, os discos foram individualmente armazenados em um dessecador até a obtenção de uma massa constante e, em seguida, armazenados individualmente em água destilada até a massa se estabilizar novamente. Finalmente, os espécimes foram secos novamente no dessecador até uma massa constante ser obtida. SO e SB foram calculadas a partir dessas mensurações. **Resultados:** Os dados foram analisados pelo teste de ANOVA a 1 critério e teste de Tukey ($p < 0,05$). O adesivo do sistema P-90 apresentou os menores valores de SO e o Clearfil SE Bond apresentou os menores valores de SB. A resina composta Filtek P-90 apresentou os menores valores de SO e SB. **Conclusão:** Baseado nos resultados, pode-se concluir que a sorção e a solubilidade foram influenciadas pela composição dos materiais. O principal grupo funcional dos materiais determina a suscetibilidade à água e influencia o seu desempenho.

PALAVRAS-CHAVE

Adesivos dentários; Resina composta; Sorção; Solubilidade.

INTRODUCTION

Despite the progress in dental bonding systems (DBSs) and composite resins (CRs) technology, there are shortcomings that still compromise their lifetimes [1]. Both of the characteristics of DBSs and CRs determine the performance of the restorations in advance.

Clinically, the main cause of adhesive restorations failures is attributed to marginal leakage that leads to marginal discoloration, secondary caries and consequently loss of retention [2]. In relation to composite resins, the methacrylate polymerization reaction causes volumetric shrinkage, which contributes to stress formation in the bond interface of the restorations [3]. All of these drawbacks, in an oral environment, force the replacement of these restorations in a short period of time.

Stability to resist to degradation by hydrolysis is of major concern. To overcome this challenge, their physicochemical properties and their strategies of interaction with enamel and/or dentin have been focused [4]. For DBS, functional groups as MDP (10-methacryloyloxydecyl dihydrogen phosphate) have been successfully employed as an alternative to conventional HEMA-based systems [5].

Also, efforts have been focused on minimizing the polymerization shrinkage and reduction of the stress that affects the bond interface as the monomeric matrix changes or the filler load increases [6]. Therefore, several low-shrinkage materials have been developed as an alternative to dimethacrylate resins [7,8]. Silorane-based composites present the cycloaliphatic oxirane functional groups, which are responsible for lower shrinkage when compared to methacrylate-based composites. Oxiranes, which are cyclic ethers, polymerize by a cationic ring-opening mechanism, while methacrylates polymerize via a free-radical mechanism, and the siloxane determines the highly hydrophobic nature of the siloranes [6]. However, the adhesive components are not silorane-based. It is a methacrylate-based, two-step “self-etch” system that contains a hydrophobic dimethacrylate monomer and promotes association with a covalent bonding to the hydrophobic oxirane-based composite.

In this scenario, water sorption and solubility are important parameters that can predict the behavior of the material [7,9].

Water sorption is thought to destabilize the adhesive-tooth bond [4]. In resin composites, it causes several effects, including the elution of leachable species [10], hydrolytic degradation of bonds (particularly at resin/filler interfaces), hygroscopic expansion, reduction in hardness [11], weakened mechanical properties [12] with decreased wear resistance [13], and a reduction in the longevity of the restorations. The solubility is reflected by the amount of leached unreacted monomers [7,9].

The aim of this study was to compare dentin bonding systems and composite resins based on their functional groups. The null hypothesis tested was that there is no difference of the effect of the functional group by means of water sorption and solubility.

MATERIAL AND METHODS

Experimental design

This *in vitro* study involved two categories of materials: three dentin bonding systems and three commercial composite resins, as outlined in Table 1. The response variables were water sorption (WS) and water solubility (WSB).

Table 1 - Composition of the materials used in this study

Material	Manufacturer		Composition
Adper Single Bond 2	3M ESPE. St. Paul, MN, EUA	DB	Bis-GMA, HEMA, diurethane dimethacrylate, polyalckenoic acid copolimer, camphorquinone, water, ethanol, 1.3 glycerol dimethacrylate, 10% silica particles (5 nm)
Clearfil SE Bond Primer Bond	Kuraray Co, Osaka/Japan	DB	Primer: MDP, HEMA, camphorquinone, hydrophilic dimethacrylates, N, N-diethanol p-toluidine, ethanol, water. Bond: MDP, Bis-GMA, HEMA, aliphatic hydrophobic dimethacrylates camphorquinone, N, N-diethanol p-toluidine, silica
P90 Adhesive System Primer Bond	3M ESPE. St. Paul, MN, EUA	DB	Primer: phosphate methacrylates, Vitrebond monopolymer, Bis-GMA, HEMA, ethanol, silica, stabilizers, camphorquinone. Bond: hydrophobic dimethacrylate, phosphate methacrylates, TEGDMA, silica, camphorquinone, stabilizers
Filtek Z350	3M ESPE. St. Paul, MN, EUA	CR	Bis-GMA, Bis-EMA, UDMA, TEGDMA, zirconia/sílica, silica, camphoroquinone
Filtek Z250	3M ESPE. St. Paul, MN, EUA	CR	Bis-GMA, Bis-EMA, UDMA, zirconia/sílica, silica, camphoroquinone
Filtek P90	3M ESPE. St. Paul, MN, EUA	CR	Siloxane, oxirane, camphoroquinone, iodonium salt, electron donor, quartz, itrium, fluoride, stabilizers, pigments

Bis-GMA (bisphenol glycidyl methacrylate); HEMA (2-hydroxyethylmethacrylate); MDP (10-methacryloyloxydecyl dihydrogen phosphate); TEGDMA (triethyleneglycol dimethacrylate); Bis-EMA (bisphenol ethyl methacrylate); UDMA (urethane dimethacrylate).

Specimens preparation

The water sorption (WS) and solubility (WSB) of each material (n = 8) were assessed during the hydration/dehydration cycling. All of the specimens were prepared according to ISO 4049:2000 [14] with adjustments [9,15].

The DBS samples were prepared using metallic molds (0.8 mm in thickness and 5.0 mm in diameter) until they were filled completely. Only for the simplified DBS (Adper Single Bond 2) and for Filtek P90-primer, gentle air-stream was applied for 5 s to evaporate the solvent. For the two other systems, as only the adhesive properly was used, no evaporation was need, following the manufacturers' instructions. A polyester matrix strip was overlapped on its top and light-cured using a LED unit (Radical-SDI, Victoria, Bayswater, Australian) at 1,000 mW/cm2 for 10 s, following the manufacturer's instructions. Similar steps were performed for the preparation of specimens of each composite resin (0.5 mm in thickness and 15.0 mm in diameter), using the same light-curing unit for 20 s. After 15 min, the specimens were removed from the molds, and the excess was removed with a scalpel blade #15. The thickness of each specimen was measured using a digital caliper (Mitutoyo, Japan).

Immersion and dehydration cycles

The discs were individually stored in a desiccator at 37 ºC. The masses of the samples were recorded daily in an accurate balance, and the conditioning cycle was repeated until the mass loss of each specimen (m1) was constant (stable at 0.1 mg). Specimens were then individually stored in 6 mL of distilled water at 37 °C, and the water-saturated mass was measured (m2), until it was stabilized again. Finally, the specimens were dried again in the desiccator until constant mass was obtained, and their masses were once again determined (m3). WS and WSB were calculated according to the formulas:

$$WS = \frac{m2 - m3}{V}$$

$$WSB = \frac{m1 - m3}{V}$$

For the calculation of the volume, each specimen was measured (thickness and diameter) after m1 was obtained.

Data were analyzed by one-way ANOVA and Tukey post hoc test ($p < 0.05$), as they presented homogeneous and normal distribution according to Barlett and Kolmogorov-Smirnov tests, respectively.

RESULTS

Dentin bonding systems

Table 2 describes the means and standard deviation for WS and WSB for the DBS tested.

All DBS were statistically different in terms of WS ($p < 0.001$). Adper Single Bond 2 and Filtek Silorane-Bond presented the greatest and lowest values of WS, respectively (Figure 1).

Regarding WSB, significant differences were detected in the comparisons, except between Filtek Silorane-Bond and Clearfil SE Bond, which presented the lowest WSB ($p > 0.001$) (Figure 2). Filtek Silorane-Primer was the most affected DBS presenting greater WSB.

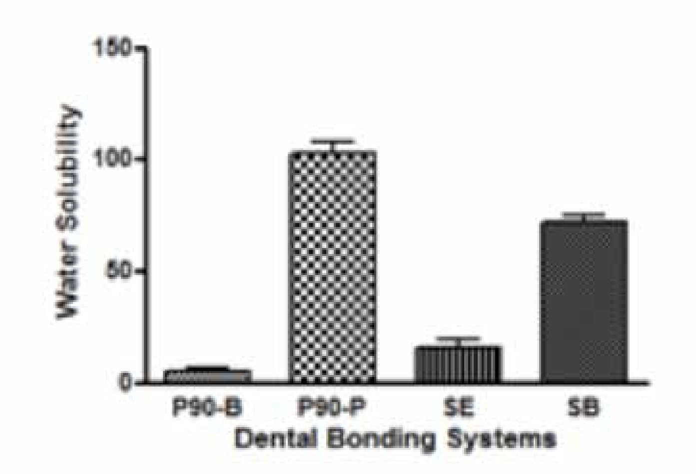

Figure 1 - Mean of the Water Sorption for Dental Bonding Systems (µg/cm^3).

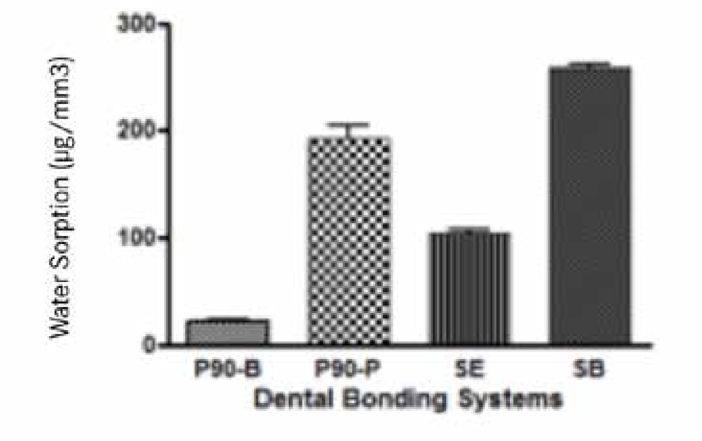

Figure 2 - Mean of the Water Solubility for Dental Bonding Systems (µg/mm^3).

Table 2 - Mean Water Sorption (WS) and Water Solubility (WSB) for Dental Bonding Systems (µg/mm^3)

Material	Adper Single Bond 2	Clearfil SE Bond	Filtek P90-Primer	Filtek P90-Bond
WS	259.50 (4.87)a	105.10 (6.73)c	193.30 (31.78)b	22.65 (4.16)d
WSB	71.82 (7.43)b	15.58 (9.00)c	102.40 (14.08)a	4.68 (5.17)c

N = 8, $p < 0.05$.

Different letter, in the same row, indicates statistical significance for the comparisons between materials.

Composite resin

A summary of the WS and WSB means for the composite resins is shown in Table 3 and Figures 3 and 4. The three composite resins exhibited significant differences in water sorption values ($p < 0.05$). Filtek Z350 reached greater WS, while Filtek Silorane resin showed the lowest WS mean.

The solubility (WSB) data did not reveal significant differences between the Filtek Z250 and Filtek Z350 composite resins ($p > 0.05$). Analysis of the data showed the lowest WSB means for Filtek Silorane ($p < 0.05$).

DISCUSSION

Overall results showed that all products, based on their composition, interacted with water specially to water sorption. Therefore, the null hypothesis is rejected.

Regarding DBS, Adper Single Bond 2 showed to be more prone to WS. This material is based on methacrylate and water content, turning it more hydrophilic. When simplified agents are tested under WS/ WSB, the presence of solvents optimizes their interaction [9,15]. Also, Filtek Silorane-Primer is based on HEMA and ethanol, which highlight its hydrophilicity [8]. Although Clearfil SE Bond contains HEMA in its composition, MDP is preponderant, which demonstrates to be less hydrophilic. According to the manufacturer, Filtek Silorane-Bond presents hydrophobic dimethacrylate that was confirmed by the lower water sorption [6,8].

Solubility parameters as Hoy's parameter are very relevant property. Hoy's triple solubility parameters may help to predict the relative contribution of dispersive (dd), polar (dp) and hydrogen bonding (dh) forces to the total cohesive energy density (dt) of polar solvents. Such method has been very useful to detail the interaction between solvent and collagen in order to improve resin infiltration [16].

There are several factors involved in the water sorption degree, which include the resin polarity, the network topology, the degree of cross-linking, the presence of residual monomers, the filler as particle size and morphology, and the properties of the resin-filler interface. The resin polarity is related to the concentration of polar sites available to form hydrogen bonds with water, and the network topology is related to the cohesive energy density of the polymer network [9,15]. While non-polar polymers permit water molecules to move through nanovoids as "unbound" water and do not cause dimensional changes of the polymer, water molecules that bind to the polymer chain via hydrogen bonding disrupt the interchain hydrogen bonding, inducing swelling and plasticizing the polymer

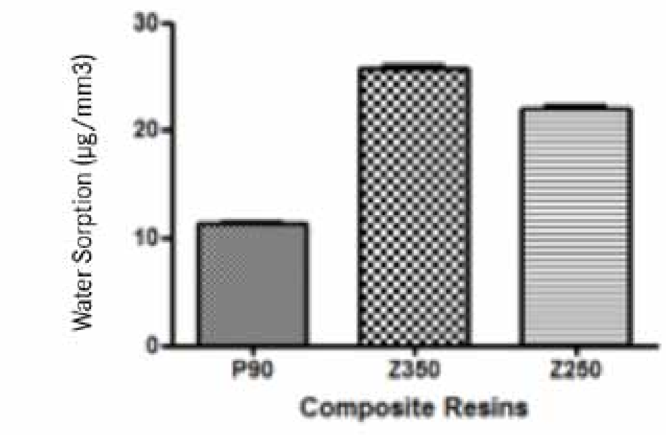

Figure 3 - Mean of the Water Sorption for Composite Resins (µg/mm^3).

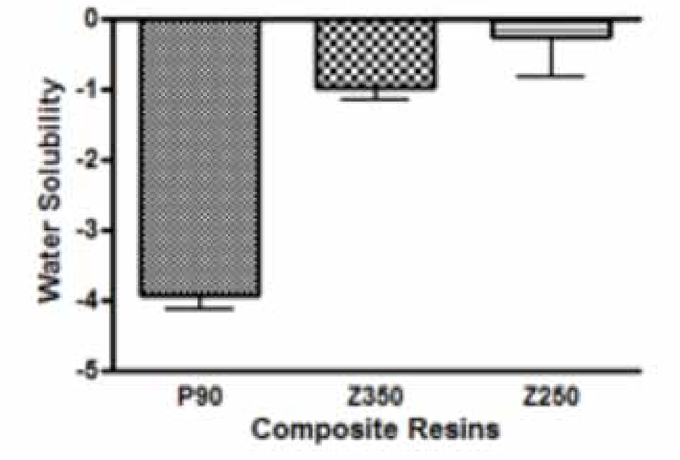

Figure 4 - Mean of the Water Solubility for Composite Resins (µg/mm^3).

[16-20]. The degree of cross-linking between the polymer chains generally results in a significant decrease in the water permeability of the polymer because they decrease the hole-free volume [19]. The water sorption can be influenced by the coupling agents and may be reduced in systems where filler particles and matrix are effectively coupled [20].

In terms of solubility, Filtek Silorane-Primer and Adper Single Bond 2 presented the higher values, which are in accordance with the water sorption results. Both materials are more hydrophilic, and the water may attack the polymer chains releasing non-reacted components.

The water sorption of the CRs showed that the polymer chain of the silorane-based materials is more stable and hydrophobic when compared to the methacrylate based-materials. In addition, the polymerization, which occurs by a cationic ring-opening mechanism, seems to increase the degree of conversion, despite some controversies [6,19]. This finding is in accordance with other studies in the literature that reported that the silorane-based material seems to be more hydrophobic than the methacrylate-based ones [7,12,22]. Another cause for the lower water sorption of the silorane-based composite resin may be due to the extensive cross-linking and rigid polymer chains, which is expected to increase the elastic modulus and limit chain movements [23]. The worst results presented by Z350 may be due to the inorganic matrix particles. The nanofillers present a greater surface area, which may reflect in the polymerization, causing lower degree of conversion and lower network density when compared to Z250 [22]. The monomer UDMA, present in Z350, absorbs more water than the aromatic-based material, which can explain the results obtained by this material [24].

Negative values were detected for WSB for all composite resins. The interpretation of the results, recommended by ISO, indicates that when the WS overlaps the WSB, it can mask the real solubility [9,15,25].

As water sorption, the variables that can influence the solubility may include the quality of resin-filler interface, the solvents, filler concentration and mean particle sizes, the surface area of the filler particle, and the chemical composition [25,26].

Based on the results and limitations of this study we can observe that the materials that are being formulated to optimize their stability under water condition presented better performance, even it still occurs. Dentin bonding systems based on MDP and with less amount of solvent react better than compositions based on BisGMA, especially when combined to solvents. For CR, the silorane based material also seems to resist better than BisGMA-based materials.

CONCLUSION

This in vitro study indicates that the main functional group of the materials may determine their susceptibility to water and influences their performance. BisGMA-based materials seem to be more fragile under water environment.

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