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Effects of ethanol addition on the water sorption/solubility and percent conversion of comonomers in model dental adhesives

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Abstract

Objectives—This study evaluated the kinetics of water uptake and percent conversion in neat *versus* ethanol-solvated resins that were formulated to be used as dental bonding agents.

Methods—Five methacrylate-based resins of known and increasing hydrophilicities (R1, R2, R3, R4 and R5) were used as reference materials. Resins were evaluated as neat bonding agents (100% resin) or they were solvated with absolute ethanol (95% resin/5% ethanol or 85% resin/15% ethanol). Specimens were prepared by dispensing the uncured resin into a circular mold (5.8 mm × 0.8 mm). Photo-activation was performed for 80 s. The water sorption/diffusion/solubility were gravimetrically evaluated, while the degree of conversion (DC) was calculated by Fourier-transform infrared spectroscopy.

Results—Water sorption increased with the hydrophilicity of the resin blends. In general, the solvated resins exhibited significantly higher water sorption, solubility and water diffusion coefficients when compared to their corresponding neat versions ($p < 0.05$). The only exception was resin R1, the least hydrophilic resin, in which neat and solvated versions exhibited similar water sorptions ($p > 0.05$). Addition of ethanol increased the DC of all tested resins, especially of the least hydrophilic, R1 and R2 ($p < 0.05$). Despite the increased DC of ethanol-solvated methacrylate-based resins, it occurs at the expense of an increasing in their water sorption/diffusion and solubility values.

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Significance—Negative effects of residual ethanol on water sorption/solubility appeared to be greater as the hydrophilicity of the resin blends increased. That is, the use of less hydrophilic resins in dental adhesives may create more reliable and durable bonds to dentin.

Keywords

dental adhesives; residual ethanol; water sorption/solubility; percent conversion

Introduction

In contemporary dental adhesives, high concentrations of relatively hydrophilic methacrylate monomers (i.e. HEMA, BPDMA, PENTA) are generally blended with relatively hydrophobic adhesive monomers (i.e. Bis-GMA, UDMA) to enhance bonding to intrinsically water-wet dentin. To facilitate the mixing of hydrophilic with hydrophobic monomers and to avoid phase separation between these components, manufacturers have also added volatile solvents such as ethanol and acetone when formulating dental adhesives [1]. The presence of hydrophilic monomers and volatile solvents improves the wetting performance of dental adhesives when applied to acid-etched dentin that is intentionally saturated with water. Volatile solvents facilitate the displacement of water from the acid-etched dentin matrix [2], ensuring better monomers penetration into the micro- and nanoporosities left between the collagen fibrils [3] and, thus, improving their micro-retention to the tooth substrate [4,5].

Conversely, the presence of residual solvent/water before the photo-activation of adhesives and formation of hybrid layers has been thought to be responsible for producing localized areas of incomplete monomer polymerization [6–8], generating porosities within bonded interfaces that, in turn, may permit inward diffusion of oral fluids [9–13]. Recent reports have shown, however, that water uptake is dependent not only on the presence of residual solvent but is also determined by the degree of hydrophilicity of the materials [14–16]. The high concentration of hydrophilic comonomers in dental adhesives alters the colligative properties of the entire mixture, lowering the vapor pressure of volatile components, such as nonpolymerizable solvents (i.e. acetone, ethanol, water) [17]. It is reasonable to consider, therefore, that the presence of residual solvent, combined with the use of hydrophilic comonomers applied to wet dentin may synergistically compromise the requirements for perfect sealing and durable coupling between resin composites and resin-bonded dentin

Although the influence of residual volatile solvent on the kinetics of water sorption/solubility in dental adhesives has been theoretically considered [11,12,15, 18,19] or, even indirectly studied [20], to the best of our knowledge there are no studies where the relationship among these variables (i.e. presence of solvent, degree of resin hydrophilicity and water sorption/solubility behavior) has been investigated together. This lack of information is probably related to the fact that is quite impractical to investigate commercial adhesives of unknown quantitative composition. Thus, the purpose of this study was to analyze whether the addition of 5 or 15% ethanol to experimental dental adhesives of known composition and hydrophilicity could affect their water sorption and percent conversion. The amount of added ethanol simulated the clinical condition where complete elimination of the solvent was not reached [21]. Thus, the tested hypotheses were that addition of 5 or 15% ethanol to experimental, methacrylate-based adhesives of increasing hydrophilicity can: 1) increase their water sorption, solubility and water diffusion coefficients and 2) decrease their degree of conversion.

Material and Methods

Five experimental comonomer resin blends (R1, R2, R3, R4 and R5) were evaluated as potential dentin/enamel adhesive systems. These experimental resin blends were purposely formulated to be ranked in an increasing order of hydrophilicity ($R1 < R2 < R3 < R4 < R5$), based on their Hoy's solubility parameters for hydrogen bonding or total cohesive energy [12,22], as listed in Table 1. Resins R4 and R5 contain comonomers with acidic functional groups that are methacrylate derivatives of carboxylic or phosphoric acids, respectively. They are similar to one-step self-etch adhesives [14,22] and very hydrophilic when compared to resins R1 and R2, which consist of relatively more hydrophobic dimethacrylates. Resins R1 and R2, therefore, are similar to non-solvated bonding agents of three-step etch-and-rinse and two-step self-etch adhesive systems [22]. Resin R3 has an intermediary hydrophilicity and contains a typical composition of two-step etch-and-rinse adhesives [22]. These experimental resins were used in the form of either neat or solvated resins that were mixed with absolute ethanol to produce primers, containing 95% comonomers/5% ethanol or 85% comonomers/15% ethanol (w/w %). Freshly prepared mixtures were ultra-sonicated for 5 minutes in closed containers to ensure homogeneity.

Resin disk preparation

Twenty resin disks ($n=20$) of each experimental comonomer resin blend (neat and solvated) were produced in a brass mold (5.8 mm diameter, 0.8 mm thick). The liquid comonomers (approximately 50 μL) were directly dispensed to completely fill the mold. Solvent evaporation was not performed as the aim of the study was to evaluate the effect of known ethanol concentrations on the kinetics of water diffusion and percent conversion of such experimental resins. A glass cover slip was then placed on the top of the resins to exclude atmospheric oxygen, ethanol evaporation and displace excess solution. Photo-activation was immediately performed using a quartz-tungsten-halogen-light source at delivered 650 mW/ cm^2 for 40 s (Elipar TriLight, ESPE, Germany). After removal from the mold, the bottom of the resin disks was further photo-cured for another 40 s. Selection of curing time was determined in a pilot experiment by measuring a baseline microhardness of the surface of the resin disks (unpublished data). With the adopted total curing time (80 s) resins exhibited a mean Knoop microhardness of 20 ± 2 KHN that was sufficient to allow specimens to be removed from the brass mold without undergoing permanent deformation. The twenty specimens produced with each experimental neat and solvated resin were randomly divided into 4 groups of five specimens ($n=5$ per group) to evaluate the diffusion coefficient of water, the water sorption and solubility in two different periods (after 7 days and 6 months of storage in water) and the degree of conversion.

Diffusion coefficient of water

After preparation, the resin disks were all pre-dried in a sealed desiccator containing fresh silica gel (at 37 °C) and repeatedly weighed at 24-h intervals, until a constant mass (m_1) was obtained (i.e. variation lower than 0.02 mg in 24 h). They were individually immersed in deionized water at 37 °C for measurement of the diffusion coefficient of water in the resins. At fixed time intervals, the specimens were removed from the vials, washed in running water for 5 s, blot-dried, weighed and returned to water. Several readings were taken during the first day (every 30 minutes for 12 hours), and then at increasing intervals (every 12 hours) until equilibrium of specimen mass was attained. The diffusion coefficients of water in the experimental resins were determined by plotting the M_t/M_∞ ratios as a function of the square root of time (where M_t was the mass gain after time t and M_∞ was the final mass gain). Since all plotted curves were linear when $M_t/M_\infty < 0.5$ (not shown), the diffusion coefficients of water (D) in the resins could be calculated using the Stefan's approximation [23]:

$$\frac{M_t}{M_\infty} = \frac{4}{L} \cdot \left(\frac{Dt}{\pi} \right)^{1/2} \quad (1)$$

where L is the thickness of the specimen (in cm).

The calculation of the diffusion coefficient of water was based only on the increases in wet mass due to water sorption, that is, loss of specimen mass by release of resin compounds/water was not included. The diffusion coefficients of water in neat and solvated resins were analyzed by two-way ANOVA, with the type of resin blend and the amount of solvent present in the mixture as the main factors. Post-hoc multiple comparisons were performed using Tukey's test. Statistical significance was preset at $\alpha=0.05$.

Water sorption and solubility evaluation

Water sorption and solubility were determined using the following modifications to ISO 4049, which includes smaller specimen dimensions (5.8 mm in diameter, instead of 15 mm) and longer periods of water gain/loss measurements (i.e. besides the analysis after the seventh day of storage in water, they were also tested after 6 months of storage in water). After a constant dry mass (m_1) was obtained (as described previously), the resin disks were individually immersed in deionized water at 37 °C for water sorption and solubility evaluation. After time intervals of 7 days and 6 months, the resin disks were washed in running water, gently wiped with absorbent paper, and weighed in an analytical balance for m_2 determination. The disks were then re-dried in a desiccator, as previously described, and weighed daily up to a dried constant mass (m_3) was obtained. Water sorption (WS) and solubility (SL) were calculated after 7 days (7 d) or 6 months (6 m) of water immersion using the following formulae [24]:

$$WS = \frac{m_2 - m_3}{V} \quad SL = \frac{m_1 - m_3}{V} \quad (2)$$

where V is the volume of each resin disk (in mm³).

Means of water sorption and solubility were analyzed by two individual three-way ANOVA (one for water sorption and other for solubility data), having as main factors: the type of resin blend (R1, R2, R3, R4 or R5), the amount of solvent present in the mixture (none, 5% or 15% ethanol) and the storage time (7 d or 6 m). Post-hoc multiple comparisons were performed using Tukey's test. Statistical significance was preset at $\alpha=0.05$.

Degree of resins conversion

Following curing and storage in a desiccator for obtaining a constant dry mass, the resin disks were pulverized into fine powder using an agate mortar and pestle. Resin powder was mixed with infrared grade potassium bromide (KBr) powder at a ratio of 3:180 mg [25]. Five KBr pellets were obtained from each of tested cured resins. Infrared-spectra of KBr/resin pellets were collected in transmission mode using a Fourier transform infrared spectroscopy (FTIR Shimadzu 8300, Shimadzu, Tokyo, Japan) equipped with a KBr beam splitter and a mercury cadmium telluride detector. A blank KBr pellet was used for the collection of the background spectrum. For each specimen, multiple spectra were collected in the range of 4000 ~ 650 cm⁻¹ at a resolution of 4 cm⁻¹. FTIR-spectra of uncured resins were also obtained as reference for calculation of the degree of conversion (DC). From the absorbance of uncured resins, a calibration curve was generated allowing for correlation of (C=C) absorption ratios with known molar concentration ratios. The degree of conversion was calculated from the equivalent aliphatic (absorbance peak located at 1638 cm⁻¹)/

aromatic (absorbance peak located at 1608 cm^{-1}) molar ratios of cured (C) and uncured (U) specimens [26]. Percentage of degree of conversion (%DC) of all neat and solvated resin blends was estimated based on the formula:

$$\%DC = \left(\frac{1 - C}{U} \right) \times 100 \quad (3)$$

Degree of conversion for neat and solvated resins was analyzed by a two-way ANOVA with the amount of solvent present in the mixture and the resin type as the two factors. Post-hoc multiple comparisons were performed using Tukey's test. Statistical significance was preset at $\alpha=0.05$.

Results

Diffusion coefficient of water

Results of measurements of the diffusion coefficients of water in the neat and solvated resins are summarized in table 2. In general, the neat versions of the experimental resins exhibited diffusion coefficients of water that were significantly lower compared to their correspondent ethanol-solvated version ($p<0.05$). It was not possible to calculate a precise diffusion coefficient of water in resin R1, since it did not present a significant mass gain during the whole period of storage in water. Both solvated versions of resin R5 (5% and 15% ethanol), the most hydrophilic among the tested mixtures (Table 1), exhibited the greatest water diffusion coefficient ($p<0.05$). Conversely, the lowest water diffusion coefficient was observed for neat resin R2 ($p<0.05$), one of the least hydrophilic resins (Table 1). Water diffusion coefficients for resins R3 and R4 were in the same order of magnitude ($p>0.05$) that, in turn, were significantly higher in comparison to resin R2, considering the neat and 5% ethanol-solvated versions ($p<0.05$); while R3 and R4 had water diffusion coefficients significantly lower when compared to resin R5 ($p<0.05$), regardless their state of solvation (neat or solvated). Differences between the solvated versions of experimental resins (5% and 15% ethanol) were significant only for resin R2, with R2 + 15% ethanol exhibiting a greater diffusion coefficient for water than R2 + 5% ethanol ($p<0.05$).

Water sorption

Results of water sorption of the neat and solvated experimental resins are summarized in table 3. In general, the neat resins exhibited values of water sorption that were significantly lower when compared to their correspondent ethanol-solvated version ($p<0.05$), except for resin R1 (neat=solvated; $p>0.05$) and for resin R5 when analyzed after 6 months of storage in water (neat=solvated; $p>0.05$). The highest values of water sorption were exhibited by neat and solvated versions of resin R5, for both periods of storage in water (7 days and 6 months). The higher the concentration of ethanol present in resin R5, the higher the water sorption. However, such increase in water sorption due to increasing concentrations of ethanol addition into R5 was only significant at the 7th day of water storage ($p<0.05$). Conversely, the lowest water sorption was shown by neat and solvated versions of resin R1 ($p<0.05$). The presence of ethanol (5 or 15%) and the period of storage in water (7 days or 6 months) did not alter significantly the water sorption behavior of resin R1 ($p>0.05$). For resins R2, R3, R4 and R5, the larger the concentration of ethanol present in the mixture, the greater was the amount of absorbed water. For all these resins, the increase in water sorption due to the increasing in ethanol concentration was significant when specimens were tested at the seventh day of storage in water ($p<0.05$). However, after 6 months of water immersion, the increase in water sorption was significant only for the groups composed by resins R2 and R3 ($p>0.05$) (Table 3). Mass variation curves during 7 days of immersion in water are

shown in Figure 1a–e. Changes in mass were plotted against the storage time in order to obtain the kinetics of water absorption during the first week of water storage. Then, the initial mass determined after the first desiccation process (m_1) was used to calculate the change in mass after each fixed time interval during the first 7 days (i.e. 168 hours) of storage in water. All materials showed the greatest increase of mass within the first 12 or 24 hours of storage in water, except for R1 specimens that did not exhibit a significant mass variation during the whole period of water storage (Figure 1a). A continued increase of mass was observed for neat and ethanol-solvated resins R2, R3 and R4 until the equilibrium was reached, which occurred for all these resins between the first and second day of storage in water (Figure 1b, 1c and 1d). Conversely, after the first 12- or 24 hours of water storage, a constant and significant decrease of mass was seen in neat and solvated resin R5 (Figure 1e).

Solubility

Results of solubility of the neat and ethanol-solvated resins are summarized in table 4. For most resin blends, the neat resins exhibited solubility values that were significantly lower compared to their corresponding solvated versions ($p < 0.05$), except for resin R5, when analyzed after 6 months of storage in water (neat=solvated; $p > 0.05$). The highest values of solubility were exhibited by neat and solvated versions of resin R5, regardless of the period of storage in water (7 days and 6 months). The higher the concentration of ethanol present in resin R5, the higher was the solubility value ($p < 0.05$). However, differences between the ethanol-solvated versions of resin R5 (5% and 15%) were significant only when the solubility measurement was performed at the seventh day of storage in water ($p < 0.05$). Neat resin R1, the least hydrophilic tested material (Table 1), exhibited a solubility value that was significantly higher than neat resins R2, R3 and R4 ($p > 0.05$), regardless of the period of storage in water. However, for specimens that were tested at the seventh day of storage in water, the increasing concentration of ethanol (5% *versus* 15%) in R2, R3 and R4 made these resins to exhibit solubility values that were similar (R1+5% ethanol = R2+5% ethanol, R3+5% ethanol and R4+5% ethanol, $p > 0.05$) or even superior (R2+15% ethanol, R3+15% ethanol and R4+15% ethanol > R1+15% ethanol, $p < 0.05$) to the solubility of ethanol-solvated R1 (Table 4). After 6 months of water storage, it was shown that increasing the concentration of ethanol (5% *versus* 15%) in resin R1 resulted in an increased solubility of the specimens, with the following statistical significance ($p < 0.05$) between the solubilities of solvated resins: R1+5% ethanol > R3+5% ethanol and R1+15% ethanol > R2+15% ethanol, R3+15% ethanol and R4+15% ethanol.

Degree of resins conversion

Results of measurements of the degree of conversion of the neat and solvated experimental resins are summarized in table 5. The percent conversion for neat and solvated resins R1–R5 ranged from 43.1 % (neat resin R1) to 71.3 % (5% ethanol-solvated R4). In general, the addition of ethanol into the resin blends increased the conversion of monomers into polymers (Table 5). The highest increase in the percentage of degree of conversion, due to the presence of solvent, was observed for the least hydrophilic resins R1 and R2. For all resins, the degree of conversion of blends solvated with 15% ethanol was significantly higher when compared to their respective neat version ($p < 0.05$). Differences in the degree of conversion of resins solvated with 5 *versus* 15% ethanol were significant only for resins R1 and R2 ($p < 0.05$). There was no significant correlation between percent conversion and the water sorption/solubility of any of the resins, regardless the period of evaluation (i.e. 7 days or 6 months) (data not shown).

Correlations between water sorption/solubility and hydrophilicity of resins

Our previous publications of the water sorption/solubility of neat resins R1–R5 reported highly significant positive correlations between water sorption and Hoy's solubility

parameters χ_h , χ_p or χ_t values. The same is true for these relationships in the current paper for water sorption of neat and solvated resins R1–R5 after both 7 days and 6 months. Figure 2 summarizes these data only for 15% ethanol-solvated resins R1–R5 and their total cohesive density parameters χ_t ($p < 0.05$). However, similar highly significant results were obtained especially when water sorption of 5% ethanol-solvated resins R1–R5 was plotted against χ_t (after 7 days of water immersion $R^2 = 0.95$, $p < 0.05$; after 6 months of water immersion $R^2 = 0.93$, $p < 0.05$ – data not shown).

There were weak and insignificant correlations between the solubility of neat or solvated resins R1–R5 and their respective Hoy's solubility parameters (data not shown).

Correlations between Hoy's solubility parameters χ_h , χ_p or χ_t values and the other test variables (i.e. diffusion coefficient of water and degree of conversion) were not performed.

Discussion

The results of this study demonstrated that, even in relatively low concentrations (5 or 15%), the addition of ethanol into the tested experimental methacrylate-based dental adhesives increased the ability of these materials to absorb and transport water. The only exception was neat resin R1 which absorbed the lowest amount of water and exhibited a water sorption value that did not differ from those observed for its corresponding ethanol-solvated pairs (R1+5% ethanol; R1+15% ethanol). In general, the extent and rate of water sorption, water diffusion and resin solubility increased with the hydrophilicity of the resin blends. Water uptake profiles showed that, when present, the highest amount of absorbed water occurred at the first 12 hours of the immersion of the test resins in water (Figure 1). Undoubtedly for most of tested conditions, water sorption, solubility and diffusion coefficients were clearly dependent on the hydrophilicity (χ_t) of resins and the presence of residual ethanol. Nevertheless, based on the described exception (data of resin R1), the first tested hypothesis of this study that the addition of ethanol to experimental adhesives of increasing hydrophilicity increases their water sorption, solubility and water diffusion coefficients was only partially supported.

If addition of ethanol had increased the uptake and diffusion of water in all resins, it would have created a linear relationship between the cohesive energy density of the polymer network and their ability to absorb and be permeated by water. In this case, water diffusion could be considered as being more likely dependent on the balance between the macromolecular packing density and the effective free-volume of the formed polymer. However, the low water uptake in the least hydrophilic resins R1 and R2 (neat or solvated), comparatively to the most hydrophilic resins R3 – R5, confirms that resin hydrophilicity is fundamental in determining the rate and extent of water diffusion into these methacrylate-based materials. Thus, we believe that water may have diffused freely through the nanoporosities that were left after evaporation of residual ethanol/unreacted monomers during the desiccation cycle of the specimens, but it may have also diffused as “bound” water, that is, attached to the polar domains present in these experimental resins, as previously described [12,14–16,27].

Since the presence of residual solvent is thought to influence the conversion of monomers into polymer [6,8,21,28–30] by increasing the effective free volume of the formed polymer [15], there was an expectation that ethanol-solvated resins would form specimens that were more prone to absorb water than those formed by non-solvated resins. In fact, such expectation was confirmed. For most resins, the rate and extent of water diffusion in solvated resins was significantly higher than in the neat counterparts (Tables 2 and 3). However, this was not related to the fact that solvated resins were more poorly converted

than neat resins (Table 5). Addition of ethanol, indeed, improved the percent conversion of all tested resins, especially of the more hydrophobic resins, R1 and R2. With low concentrations of ethanol (e.g. 15%) the viscosity of the resins may have been reduced to a level where increased intermacromolecular spacing (i.e. increased resin free volume), molecular mobility and growing polymer chain segments might occur [21,28–30]. Such occurrences, in concert, could have been responsible for enhancing the degree of conversion of the model adhesives, which lead us to reject the second tested hypothesis of this study.

The fact that the presence of low concentrations ethanol increased the degree of conversion of the model resins does not mean, however, that one should ignore the requirement of removing as much solvent as possible before dental adhesives polymerization. Increasing the free volume of resins due to the presence of low concentration of ethanol, or any other non-polymerizable polar solvent, may have increased the degree of conversion but it may not be beneficial to the polymer cross-linking. Our results suggest that the concentrations of ethanol used in the present study may have increased the water sorption/diffusion and solubility of solvated model adhesives by interfering with their optimal macromolecular packing density (i.e. homogeneous macromolecular cross-linking), instead of purely affecting their percent of conversion. In other words, we suggested that while small concentrations of ethanol decreases the viscosity of comonomers blends and allows radical propagation to increase the degree of conversion [20, 28–30]; its presence and non-polymerizable condition also increase the effective free volume of the resin and can prevent the approximation between reactive pendant species, making the cross-linking reaction more difficult [31]. The well-documented correlation between effective removal or complete absence of volatile solvent in dental adhesives and increase in their mechanical properties [7,31,32] is another good reason for not polymerizing these materials in the presence of residual solvent. Polymer networks with homogeneous packing density (i.e. restricted free volume) tend to exhibit at least two desirable properties for a durable function: higher mechanical properties [7,31,33] and lower ability to absorb water [34–36].

Theoretically, solvent and water elimination should be achieved by allowing sufficient evaporation time before polymerization of adhesives. However, complete solvent/water evaporation has shown to be clinically problematic [21,37,38], especially when using the evaporation times recommended by manufacturers [39,40]. In a recent study, for instance, it was shown that experimental adhesives solvated with 50 wt% acetone, 50 wt% ethanol, 50 wt% acetone/water or 50 wt% ethanol/water mixtures retained from 5 to 10% of the added solvent, even after blowing air for 120 s [20], a period 10 times longer than that recommended by the majority of manufacturers of dental adhesives. That study also concluded that the percentage of residual solvent retained in experimental adhesives was significantly influenced by the degree of hydrophilicity of resin monomers, that is, the more hydrophilic was the resin, more solvent it retained [20].

It has been hypothesized that during the first stage of water diffusion, the polymer network is softened by water sorption that causes polymer swelling. Polymer swelling by water reduces the frictional forces between polymer chains [41] (i.e. plasticizes resins). At a high level of absorbed water, polymer chains can undergo a relaxation process, thereby facilitating the elution of unreacted monomers and/or solvents trapped in the polymer network. More hydrophilic polymers, that have a superior capacity of relaxation, may permit faster elution of unreacted monomers/solvents than more hydrophobic polymers [42,43]. This was probably why the most hydrophilic resins R4 and R5 – neat or solvated - showed a high and long-lasting solubility when compared to less hydrophilic resins, such as R2 and R3 (Table 4). Resins R4 and R5 (both neat and solvated) were the only resins that continued to lose mass after 6 months of water immersion (data not shown). At a long-term, the continuous solubility of hydrophilic resin blends may represent a factual hydrolytic

breakdown of resin compounds, instead of a simple release of unreacted and/or pendent monomers.

Theoretically, our calculated water diffusion coefficients may have been under-estimated, since they were based on water sorption data alone (i.e. increases in wet mass). Since net increase in wet mass may include loss of dry mass due to simultaneous solubilization of unreacted monomers, the true gain in wet mass may have been greater than was reported. This error would be proportional to the degree of solubilization that, in the current study, varied widely.

Nevertheless, resin hydrophilicity cannot explain, in principle, why the least hydrophobic neat resin R1 exhibited higher solubility than neat resins R2, R3 and R4. In that case, the structural features of the copolymers formed by neat resin R1 may provide a better explanation for their solubility behavior. Apart from the resin hydrophilicity, the relaxation capacity of a polymer network may be also dependent on the degree of conversion and homogeneity of polymer cross-links [34]. It is clear that neat resin R1 exhibited the lowest percent of conversion (43.1% - Table 5) of all five test resins. Neat resin R1 is basically composed of ethoxylated Bis-GMA (Bis-GMA-E) and TEGDMA (Table 1), while the other neat resins are composed by different combinations of Bis-GMA with HEMA, 2MP, TCDM and/or TEGDMA. In high concentration, Bis-GMA-E was reported to give lower degrees of conversion compared to Bis-GMA, UDMA and TEGDMA [44]. In addition, the absence of hydroxyl groups in the backbone of Bis-GMA-E leads it to the formation of polymers that are more flexible than those formed by Bis-GMA [34]. Lower degree of conversion and higher flexibility may explain the high solubility of ethoxylated Bis-GMA-based resins [15,34] (Table 4).

From the profile of the mass variation seen in resins R1–R5 during immersion in water (Figure 1), it was shown that, in general, more water could enter into solvated resins than into neat resins, at least within the first 12–24 hours of water immersion. Likewise, after obtaining maximum water sorption, the rapid loss of mass observed for solvated resins indicates that they formed less compacted polymer networks that, in turn, imposed lower resistance to the elution of residual ethanol and/or unreacted monomers than did the neat resins. In fact, the presence of solvents (i.e. ethanol, water, acetone), either dispersed among the polymer chains or hydrogen-bonded to polar domains, it is thought to cause additional plasticization by increasing swelling and/or relaxation of polymer network [45,46], which also explains why the experimental ethanol-solvated adhesives showed higher solubility than their neat counterparts (Table 4).

While lower polymer chain cross-linking in these ethanol-solvated methacrylated-based resins seems to offer a theoretical explanation for their higher susceptibility when immersed in water (i.e. water sorption, diffusion and solubility), the effect of the degree of polymers cross-linking on the kinetics of water diffusion should be accurately investigated in future studies.

Under the limited conditions of this study, the present results suggest that there are competing trends operating in resin bonding. Increases of the degree of conversion of adhesives by ethanol addition are not sufficient to form impervious polymerized adhesives. Accordingly, even well-converted adhesives might keep allowing water/moieties diffusion (i.e. solvated resin R4, Table 5), especially if they exhibit a patent hydrophilic nature. The negative effect of residual ethanol on water sorption/diffusion appeared to be even more critical for hydrophilic resin blends. Thus, the amount of solvent incorporated in resins is a critical step in formulating dental adhesives. While solvent should be sufficient to increase the percent conversion of resins, decrease the viscosity of the comonomers and facilitate the

displacement of water from dentin, it should not increase the capability of these resins for water sorption/diffusion and solubility. Since hydrophobic resins are less permeable to water and may have their degree of conversion increased by small amounts of ethanol (i.e. 5 – 15%), studies should be performed in order to test whether solvated-hydrophobic monomers could create reliable and durable bonds to dentin.

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Figure 1.

Mass variation of experimental neat and solvated resins over 7 days of water storage.

Symbols represent means values ($n=5$). Since the standard deviations around all means are smaller than the symbols, they have not been indicated. **A:** Neat and solvated resin R1; **B:** Neat and solvated resin R2; **C:** Neat and solvated resin R3; **D:** Neat and solvated resin R4 and **E:** Neat and solvated resin R5. (Neat resin:—●—; Resin + 5% ethanol:—□—; Resin + 15% ethanol:—▲—).

WATER SORPTION - RESINS + 15% ETHANOL

Figure 2.

Correlations between the water sorption of 15% ethanol-solvated resins R1–R5 and their respective Hoy's solubility parameter for total cohesive density (δ_t).

Table 1

Composition and Hoy's solubility parameter of the experimental polymers used in the study.

Resin	Composition	Hoy's solubility parameters (MPa) ^{1/2}					
		% (w/w)	d	p	h	t	
R1	Bis-GMA-E	70.00					
	TEGDMA	28.75	15.44	10.59	6.17	19.71	
	CQ	0.25					
	EDMAB	1.00					
R2	Bis-GMA	70.00					
	TEGDMA	28.75	15.58	12.1	8.64	21.54	
	CQ	0.25					
	EDMAB	1.00					
R3	Bis-GMA	70.00					
	HEMA	28.75	15.37	13.02	9.94	22.46	
	CQ	0.25					
	EDMAB	1.00					
R4	Bis-GMA	40.00					
	TEGDMA	28.75					
	TCDM	30.00	16.21	12.61	9.3	22.55	
	CQ	0.25					
R5	Bis-GMA	40.00					
	HEMA	28.75					
	2MP	30.00	15.76	14.37	10.75	23.88	
	CQ	0.25					
R1 + 5%E	Bis-GMA	40.00					
	HEMA	28.75					
	R1	95.00	15.30	10.62	6.86	19.85	
	Ethanol	5.00					

Resin	Composition	Hoy's solubility parameters (MPa) ^{1/2}					
		% (w/w)	d	p	h	t	
R2 + 5%E	R2	95.00	15.43	12.05	9.21	21.64	
	Ethanol	5.00					
R3 + 5%E	R3	95.00	15.23	12.93	10.44	22.54	
	Ethanol	5.00					
R4 + 5%E	R4	95.00	16.03	12.54	9.84	22.60	
	Ethanol	5.00					
R5 + 5%E	R5	95.00	15.60	14.21	11.21	23.90	
	Ethanol	5.00					
R1 + 15%E	R1	85.00	15.02	10.68	8.24	20.19	
	Ethanol	15.00					
R2 + 15%E	R2	85.00	15.14	11.96	10.34	21.89	
	Ethanol	15.00					
R3 + 15%E	R3	85.00	14.96	12.74	11.45	22.74	
	Ethanol	15.00					
R4 + 15%E	R4	85.00	15.67	12.39	10.91	22.76	
	Ethanol	15.00					
R5 + 15%E	R5	85.00	15.29	13.89	12.14	23.96	
	Ethanol	15.00					

Abbreviations: 2MP: Bis[2-(methacryloyloxy)ethyl] phosphate; Bis-GMA: bisphenol A diglycidyl ether dimethacrylate; Bis-GMA-E: ethoxylated bisphenol A diglycidyl ether dimethacrylate; CQ: camphorquinone; EDMAB: ethyl N,N-dimethyl-4-aminobenzoate; HEMA: 2-hydroxyethyl methacrylate; TCDDM: di(hydroxyethylmethacrylate) ester of 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2dicarboxylic anhydride; TEGDMA: triethylene-glycol dimethacrylate; d: dispersion forces; p: polar forces; h: hydrogen bonding forces; t: total cohesive energy density

Table 2

Diffusion coefficient ($\times 10^{-8} \text{cm}^2 \text{s}^{-1}$) of water into the different neat and solvated comonomer mixtures.

	Neat	Solvated - 5% ethanol	Solvated – 15% ethanol
R1	**	**	**
R2	4.1 (0.72) ^{c,C}	11.6 (1.53) ^{b,C}	18.6 (2.05) ^{a,B}
R3	7.1 (0.27) ^{b,B}	18.9 (2.66) ^{a,B}	23.6 (0.30) ^{a,B}
R4	6.2 (0.67) ^{b,B}	14.8 (1.54) ^{a,B}	19.2 (1.41) ^{a,B}
R5	21.5 (1.50) ^{b,A}	79.3 (9.40) ^{a,A}	84.7 (14.98) ^{a,A}

Values represent mean (SD), n=5/group. Groups identified by different superscript lower case letters (analysis in lines) and upper case letters (analysis in columns) represent statistically significant differences ($p < 0.05$).

Specimens of R1 did not show a significant mass gain over the preset period to evaluate the coefficient of water diffusion, thus it was not possible to calculate a precise water diffusion coefficient for this resin blend.

Table 3

Water sorption ($\mu\text{g}/\text{mm}^3$) of neat and solvated versions of the experimental resins after 7 days and 6 months of water storage.

	7 Days			6 Months		
	Neat	Solvated - 5% ethanol	Solvated - 15% ethanol	Neat	Solvated - 5% ethanol	Solvated - 15% ethanol
R1	13.7 (0.16) ^{a,D}	12.5 (2.71) ^{a,D}	15.2 (3.93) ^{a,D}	12.9 (2.11) ^{a,D}	12.0 (2.96) ^{a,D}	11.2 (2.24) ^{a,D}
R2	34.1 (4.47) ^{c,C}	59.3 (3.43) ^{b,C}	83.0 (5.44) ^{a,C}	39.1 (3.00) ^{c,C}	55.6 (3.62) ^{b,C}	82.0 (5.35) ^{a,C}
R3	61.8 (4.20) ^{c,B}	77.6 (3.59) ^{b,B}	103.1 (5.71) ^{a,B}	65.2 (2.39) ^{c,B}	69.6 (1.64) ^{b,B}	101.5 (0.82) ^{a,B}
R4	68.6 (2.21) ^{c,B}	88.9 (4.72) ^{b,B}	110.7 (6.14) ^{a,B}	70.4 (2.04) ^{c,B}	73.1 (2.17) ^{c,B}	90.9 (3.37) ^{b,B}
R5	160.4 (7.65) ^{c,A}	175.9 (7.61) ^{b,A}	191.7 (6.81) ^{a,A}	143.6 (8.84) ^{a,A}	148.1 (6.31) ^{c,d,A}	155.7 (5.06) ^{c,d,A}

Values represent mean (SD), n=5/group. Groups identified with different superscript lower case letters (analysis in columns) and upper case letters (analysis in lines) represent statistically significant differences ($p < 0.05$).

Solubility ($\mu\text{g}/\text{mm}^3$) of neat and solvated versions of the experimental resins after 7 days and 6 months of water storage.

Table 4

		7 Days			6 Months		
	Neat	Solvated - 5% ethanol	Solvated - 15% ethanol	Neat	Solvated - 5% ethanol	Solvated - 15% ethanol	
R1	13.7 (0.16) ^{aLB}	28.0 (4.31) ^{c-BC}	27.8 (3.94) ^{c-D}	24.0 (1.97) ^{c-B}	46.1 (7.36) ^{b-B}	86.5 (10.88) ^{a-B}	
R2	- 3.5 (4.41) ^{c-C}	24.6 (4.30) ^{b-BC}	49.8 (3.12) ^{a-C}	- 1.7 (2.39) ^{c-C}	33.7 (7.61) ^{b-BC}	58.0 (4.08) ^{a-C}	
R3	- 3.5 (5.62) ^{c-C}	20.5 (2.49) ^{b-C}	68.4 (6.53) ^{a-B}	- 1.7 (4.01) ^{c-C}	26.0 (4.35) ^{b-C}	53.8 (2.88) ^{a-C}	
R4	4.4 (3.12) ^{d-B}	37.0 (4.76) ^{b-B}	59.5 (3.96) ^{a-BC}	12.7 (3.82) ^{c-B}	37.9 (3.85) ^{b-BC}	67.2 (4.48) ^{a-C}	
R5	68.1 (9.57) ^{a-A}	117.3 (6.76) ^{c-A}	141.3 (5.06) ^{b-A}	185.1 (5.06) ^{a-A}	188.5 (6.07) ^{a-A}	195.5 (4.18) ^{a-A}	

Values represent mean (SD), n=5 (per group). Groups identified with different superscript lower case letters (analysis in lines) and upper case letters (analysis in columns) represent statistically significant differences ($p<0.05$). Negative values indicate that after final desiccation the dried constant mass m3 was higher than m1, suggesting that the absorbed water may have not been completely eliminated.

Table 5

Degree of conversion (%) of neat and solvated versions of the experimental resins.

	Neat	Solvated – 5% ethanol	Solvated - 15% ethanol
R1	43.1 (2.16) ^{cD}	59.0 (0.93) ^{bC}	63.2 (1.10) ^{aB}
R2	47.2 (0.90) ^{cC}	65.3 (1.45) ^{bB}	69.8 (0.95) ^{aA}
R3	55.1 (1.18) ^{bB}	64.5 (1.05) ^{aB}	63.9 (1.75) ^{aB}
R4	56.5 (2.23) ^{bAB}	71.3 (1.27) ^{aA}	70.5 (1.22) ^{aA}
R5	58.5 (1.06) ^{bA}	62.5 (4.13) ^{abBC}	63.7 (2.24) ^{aB}

Values represent mean (SD), n=5/group. Groups identified with different superscript lower case letters (analysis in lines) and upper case letters (analysis in columns) represent statistically significant differences (p<0.05).