Effects of curing protocols on fluid kinetics and hardness of resin cements

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The effects of polymerization protocols on water sorption/solubility, the diffusion coefficient (D), the flux (J), and the hardness (JH) of two resin cements were evaluated. The materials were manipulated and divided into three groups (n=6) according to the curing protocol: PA=photoactivation (40 s); DP=delayed photoactivation (10 min self-curing plus 40 s photoactivated); CA=chemical activation. After desiccation, the specimens were weighed, stored in water (37°C), evaluated over 28-days, and hardness recorded. Chemical activation resulted in lower net water uptake, D, and J for RelyX ARC (RX). For Variolink II (VL), CA yielded equivalent D and lower J; however, photoactivation resulted in lower net water uptake. Hardness of VL was less affected by the water storage, irrespective of the polymerization protocol. Considering the water diffusion parameters, VL demonstrated immediate photoactivation dependence; for RX, a chemical activation. Different polymerization protocols affect the fluid kinetics and the hardness of the resin cements tested.

Keywords: Resin cement, Hardness, Water sorption, Diffusion coefficient, Diffusion flux

INTRODUCTION

Recent developments in resin-based dental materials have focused on the need for the longevity of restorations by not only considering their mechanical resistance but also their chemical stability. Currently, many discussions in the literature address the degradation and leaching of monomers after simulated aging in various solvents, including saliva, water, and ethanol1-4. Water absorption was previously deemed beneficial to filling materials, as the consequent swelling was believed to compensate for polymerization shrinkage5-6. However, absorbed water is now known to result in internal strains, facilitating the extraction of free monomers or polymerization residues in resin-based materials8. Water molecules can also cluster7 inducing a plasticization effect and softening of the surrounding matrix, thus lowering the restoration rigidity9-11. Depending upon the extent of water uptake, the hoop stresses around the filler particles can be reduced, facilitating filler pulling-out by breaking down the resin-filler bond8-10, or by causing the erosion of the surface of filler particles8.

Water may infiltrate the polymer network by means of porosities and intermolecular spaces in the organic matrix. The existence of microporosities in the inorganic phase can also contribute to this phenomenon7, as the extent and rate of water uptake is dependent upon the density of the polymer network and on the potential for hydrogen bonding and polar interactions, which provide paths for facile diffusion. The amount of water absorbed is regulated by the diffusion coefficient and the thickness of the specimen12. Depending upon these characteristics, two different mechanisms may take place: (1) an uptake of water resulting in an increased weight and (2) the dissolution of fillers and monomers in water, leading to a weight reduction13. The fluid kinetics can be slower for certain resins and may not reach equilibrium, even after several days as the speed of this process primarily depends upon water molecules’ ability to diffuse into the matrix, a concept known as hydrophilicity10.

Resin-based cements are also subjected to the oral environment, in spite of the thin layer that results from seating indirect restorations. Considering this clinical scenario, the polymerization protocol of resin cements is of paramount importance in the restoration performance. It has been claimed that the best mechanical properties are achieved when base and catalyst pastes are mixed and immediately photoactivated14. On the other hand, the chemical cure progresses slowly and is expected to ensure polymerization in those areas that light is unable to reach15. However, the question has recently been raised as to whether or not immediate photoactivation might restrict the window of time available in which the polymer can grow, resulting in the formation of an overly rigid network that “freezes” the cement15. As these materials induce physical (photoactivation) and chemical curing, it makes dual-cured resin cements less effective with respect of their conversion potential16. As the polymerizing network develops further, the rate of radical propagation eventually becomes limited by diffusion, and the polymerization rate decelerates, providing only a limited conversion even in the presence of unreacted monomer and free radicals16. Conversely, under conditions yielding a delayed amount of time in which the photoactivation can occur, the opposite should take place, resulting in a higher end conversion17.
The hardness test has been used for composite dental materials to evaluate their physical properties and predict their clinical performance\(^\text{29}\). In addition, the increase in the hardness correlates well with increases in the degree of conversion during setting\(^\text{20}\).

Drawing upon two hypotheses, this study attempts to investigate the effects of polymerization protocols on the fluid kinetics (mass uptake, diffusion coefficient, water flux, and solubility) and the Knoop hardness of two current dual-cured resin cements. The hypotheses tested were as follows: (1) different polymerization protocols affect the fluid kinetics of resin cements; (2) different polymerization protocols affect the hardness, depending upon the stages of water sorption and solubility.

MATERIALS AND METHODS

Specimen preparation

Two commercial dual-cured resin cements [RelyX ARC (RX), and Variolink II (VL), shade A3\(^\text{3}\)] were selected for this study (Table 1). Materials were manipulated according to the manufacturer’s directions and inserted into Teflon molds (6 mm in diameter × 0.5 mm thick). Subsequently, a Mylar strip was applied to the surface of the non-polymerized materials, and a microscope slide was used to adapt them completely to the confines of the molds, providing the same material volume and also a flat top and bottom surfaces. The small amount of excess material was then removed from the specimens towards the mold outer edges. Three groups were categorized and treated (n=6) according to the polymerization protocol (Table 2). Specimens of groups PA and DP were photoactivated for 40 s on the top surface. After photoactivation (PA and DP groups), the specimens were removed from the molds and stored in lightproof recipients for 24 h at room temperature (22°C). For the light-curing procedure, the power density of the quartz-tungsten-halogen light (QTH light) (3M ESPE XL3000, St. Paul, MN, USA) was assessed by means of a hand-held radiometer (Curing Radiometer; Demetron Research Corp., Danbury, CT, USA) in order to standardize 600 mW/cm\(^2\) for all of the light-cured specimens. Specimens from the chemically activated group (CA group) were kept in the mold for 24 h at room temperature in the dark prior to their removal.

Water sorption and solubility

Water sorption and solubility tests were based on the 4049 ISO standard with the exception that the period of water immersion was extended up to 28 days. After 24 h, the specimens were placed in a desiccator containing silica gel and were stored at 37°C. The specimens were repeatedly weighed every 24 h, until a constant mass (\(m_1\)) was obtained (i.e. a mass in which variation amounted to less than 0.2 mg within any 24 h period)\(^\text{21}\). The specimens were measured using a digital caliper (Absolute Digimatic, Mitutoyo, Tokyo, Japan) and the volume (V) of each specimen (in mm\(^3\)) was calculated. Specimens were then individually placed in test tubes containing 10 mL of distilled water (pH 7.2) at 37°C. The distilled water was daily replaced in order to keep constant the pH and the volume into the test tubes. Once each storage time interval, up to 28 days had passed, the tubes were removed from the oven and then the specimens were washed in running water, gently wiped with a soft absorbent paper, weighed by means of an analytical balance (m\(_2\)) and returned to vials containing 10 mL of fresh distilled water. Following the 28 days of storage, the specimens were dried inside a desiccator containing fresh silica gel and weighed daily until a constant mass (m\(_3\)) was obtained. The initial mass determined after the first desiccation process (m\(_1\)) was used to calculate the change in mass after each fixed time interval of the 28 days of storage in water. The variation in the mass at a certain evaluation time (m\(_n\)) was calculated as a function of the initial mass (m\(_1\)) [(m\(_n\)−m\(_1\))/m\(_1\)\(\times 100\)]\(^\text{21}\). Changes in mass were plotted against the storage time in order to obtain the kinetics of water sorption and solubility for the entire period of water storage.

The water sorption (WS) and solubility (SL) over 28 days of water storage\(^\text{21}\) were calculated by means of the following formula\(^\text{7}\):

\[
WS = \frac{m_2 - m_3}{V} \\
SL = \frac{m_1 - m_3}{V}
\]

(1)

where \(m_1\) refers to the initial dry constant mass (mg) prior to immersion in water; \(m_2\) describes the mass (mg) after water immersion at various time periods; \(m_3\) is the mass (mg) after drying the specimens that had reached their maximum water sorption and V refers to the specimen’s volume in mm\(^3\). Net water uptake (%) was also calculated as the sum of water sorption and solubility.

Diffusion coefficient

Six new disks of each material were prepared as previously described. Once a constant mass (m\(_1\)) was obtained the disks were immersed in distilled water at 37°C. At fixed time intervals, the specimens were removed from the tubes, washed in running water, blot-dried, weighed, and returned to the water. Several readings were taken during the first day (every hour), and at increasing intervals (every 12 h) thereafter, until equilibrium (repeated mass after two readings), was attained. These are the reasons why new specimens were prepared in which it was considered the mass variation only during the period of water sorption. The kinetics of water sorption was analyzed in terms of diffusion theory\(^\text{22}\). According to Fick’s second law, when the diffusion coefficient \(D\) is constant, the equation for diffusion in one dimension (x) can be expressed as follows:

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2},
\]

(2)

where \(C\) refers to the concentration of the diffusing
species at time $t$.

The diffusion coefficients of water into the resin cements were determined by plotting the $M_t/M_\infty$ ratios as a function of the squared root of time (where $M_t$ was the mass gain after time $t$ and $M_\infty$ describes the final mass gain). The diffusion coefficient of water ($D$) in the resin cements was calculated by means of Stefan’s approximation, using the Eq. (2):

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

where $L$ is the thickness in cm.

Diffusion flux ($J$)

The Fick’s first law was used in this study to calculate the diffusion flux ($J$). This law describes the flow facility or the rate of flow of energy or particles across a given surface as follows:

$$J = \frac{\partial M}{A \times \partial t},$$

where $J$ is in kg/m$^2$ $M$ refers to the mass in diffusion, $A$ describes the area through which diffusion occurs and $t$ is the elapsed diffusion time. In the present study, the diffusion flux was calculated for all of the corresponding diffusion coefficients.

Knoop hardness evaluation

Another six resin cement disks of each material were prepared from a Teflon mold (6 mm in diameter x 0.5 mm thick), as previously described. After photoactivation (PA and DP groups), the specimens were removed from the molds and their irradiated top surface was identified with an indelible mark prior to being stored into lightproof recipients for 24 h. Chemically-cured specimens (CA group) were kept in the mold for 24 h at room temperature in the dark prior to their removal. The top surfaces were then marked and stored as described above. Three hardness readings were recorded for each sample in a longitudinal manner in order to identify a trend over a period of time, following the water sorption/solubility storage steps (at $m_1$, $m_2$, and $m_3$) by means of a digital Knoop hardness-measuring instrument (Shimadzu HMV-M Microhardness Tester; Newage Testing instruments Inc., Southampton, PA, USA) and a load of 50 g for 5 s. The objective was to determine hardness changes as a function of the specimens’ water sorption and desorption. For randomization, specimens were arbitrarily rotated before the indentations, which were made exclusively on the marked, top surface. A mean value was determined for each sample at each time interval.

SEM observation and Energy-dispersive X-ray spectroscopy (EDS) analysis

In order to evaluate the microstructure of the resin
cements, four disks of RX or VL were prepared using Teflon molds (6 mm in diameter × 2 mm thick). After photoactivation, the specimens were immersed in acetone p.a. (99.5%, Fisher Scientific, Fair Lawn, NY, USA) for 24 h and then dehydrated in silica gel for 2 h. Next, half of the processed specimens were sputter-coated (40 mA for 120 s) with gold/palladium (SCD 050; Balzers, Schaan, Liechtenstein) in order to characterize the inorganic phase of the resin cements by means of SEM (JSM 5600LV, JEOL, Tokyo, Japan) under secondary electron mode; meanwhile, the other half of the specimens was submitted to carbon evaporation (SCD 050, Balzers, Schaan, Liechtenstein) for the elemental analysis using EDS under a backscattered electron mode, both operated at 15 kV. Representative images of selected regions of the specimens were taken in order to observe the morphological aspect of the filler particles, the distribution/packing, and the proportional percentage (by weight) of the chemical elements. The aim of this method did not encompass quantifying any composition parameters, such as the inorganic phase of the resin cements. Instead, the goal was to conduct a qualitative analysis based on the morphological aspects of the materials evaluated in order to support the interpretation of the results.

**Statistical analysis**

The mean and standard deviation of water sorption and solubility were calculated for each material group, and all of the data were analyzed by means of two individual two-way ANOVA (one for water sorption and the other for solubility data), using the materials and polymerization protocols as factors. Subsequently, changes in the mass observed within each material as a function of the increasing storage time in water were also tested for significance using a two-way ANOVA, and the polymerization protocol and storage time as the two factors. Post-hoc multiple comparisons were performed by means of Tukey’s test. In the same manner, the mean and standard deviation of hardness values were calculated for each material group, and all of the data was submitted to three-way ANOVA and Tukey’s HSD post-hoc test for pair-wise comparisons. A three-way ANOVA was performed in order to evaluate the influence of the three variables tested: the material (RX and VL), the polymerization protocol (PA, DP, and CA), and the evaluation time (at m1, m2, and m3). The diffusion coefficients and fluxes for each group of material were analyzed by means of a one-way ANOVA which sought for significant differences between materials. Post-hoc multiple comparisons were performed using Tukey’s test. All of the statistical testing was performed with α=5%. Correlations between net water uptake (%) and hardness, water sorption (WS) and flux ($J$), water sorption (WS) and diffusion coefficient ($D$) and also diffusion coefficient ($D$) and flux ($J$) were performed and the Pearson correlation coefficient ($r$) was calculated in order to measure the strength of linear dependence between the variables.

**RESULTS**

**Water sorption and solubility**

Mass variation curves for the 28 days of immersion in water are presented in Fig. 1. The results for water sorption and solubility are summarized in Table 3. Water sorption and solubility varied significantly ($p<0.05$) between materials. When mass gain (i.e. water sorption) and mass loss (i.e. solubility) of resin cement disks were plotted against time, the lowest water sorption was determined for Variolink II, irrespective of the polymerization protocol applied ($p<0.05$). The means of solubility for VL were lower than that observed for RX, but no significance was noted the chemical protocol (CA group) were compared ($p>0.05$). When polymerization protocols were compared, no significance in the water sorption was observed for VL when the DP and CA groups were compared with the PA group ($p>0.05$). The same occurred for solubility ($p>0.05$). For RX, significantly higher water sorption was seen when the photoactivation was delayed (DP group, $p<0.05$), whereas a significantly higher solubility was observed for the chemical-cured as opposed to the light-cured groups ($p<0.05$). The net water uptake for VL was determined to be lower than that seen for RX cement, irrespective of the polymerization protocol. For RX, the chemical-cured group (CA group) resulted in the lowest net water uptake while for VL, the light-cured group rendered the lowest net water uptake.

**Diffusion coefficient and diffusion flux**

The results for $D$ and $J$ are summarized in Table 4. The diffusion coefficient and flux were always higher for RX than for VL, regardless of curing protocol. For VL, the curing protocol did not affect $D$. For both resin cements, a
significantly lower flux was observed when the chemical protocol was employed ($p<0.05$). Despite the equivalence with the control group (PA group), DP protocol yielded the highest $D$ and $J$ for both materials. In general, $D$ and $J$ values can be ranked for both materials as follows: DP>PA>CA. Correlation between the diffusion coefficient ($D$) and Flux ($J$) was strong ($r=0.97$) and positive. Another strong positive correlation ($r=0.83$) was found between the water sorption and the diffusion coefficient ($D$). A moderate and positive correlation was also found between the water sorption ($WS$) and Flux ($J$) ($r=0.51$).

**Hardness test**
A significantly higher hardness ($p<0.05$) was observed (Table 5) when both resin cements were polymerized according to the manufacturer’s instructions (calling for immediate photoactivation for 40 s after manipulation − PA group). The resin cement VL was less affected by the water sorption (hardness at $m_2$), irrespective of the polymerization protocol. The lowest hardness mean was observed for the specimens that were chemically activated (CA group), irrespective of resin cement, when compared to other polymerization protocols.

For RX, a significant decrease in the hardness was observed after the 28-day storage period (hardness

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**Table 3** Water sorption after 28 days of water storage and solubility ($\mu g/mm^3$)

<table>
<thead>
<tr>
<th>Material</th>
<th>Technique</th>
<th>RX Water sorption $\mu g/mm^3$ (%)</th>
<th>VL Water sorption $\mu g/mm^3$ (%)</th>
<th>Solubility</th>
<th>Net water uptake (%)**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$(\mu g/mm^3)$</td>
<td>$(\mu g/mm^3)$</td>
<td>$(%)$</td>
<td>RX $(\mu g/mm^3)$ $(%)$</td>
</tr>
<tr>
<td>PA</td>
<td></td>
<td>51.9 (7.3)$^{ab}$ 5.19</td>
<td>8.7 (0.71)$^{A}$ 8.7</td>
<td>−10.6 (3.9)$^{a}$ 1.06</td>
<td>−0.2 (0.54)$^{B}$ 0.02</td>
</tr>
<tr>
<td>DP</td>
<td></td>
<td>64.9 (5.3)$^{ab}$ 6.49</td>
<td>9.5 (0.53)$^{A}$ 9.5</td>
<td>−8.3 (5.3)$^{a}$ 0.83</td>
<td>−0.6 (0.73)$^{B}$ 0.06</td>
</tr>
<tr>
<td>CA</td>
<td></td>
<td>50.7 (5.3)$^{ab}$ 5.07</td>
<td>10.1 (0.79)$^{A}$ 10.1</td>
<td>4.7 (5.8)$^{a}$ 0.47</td>
<td>3.8 (1.33)$^{B}$ 0.38</td>
</tr>
</tbody>
</table>

Values are mean (standard deviation), $n=6$, $\mu g/mm^3$. Water sorption is given in absolute terms ($\mu g/mm^3$) and in relative terms (%) to provide comparisons to literature values which include both expressions. Different small letters in column and capital letters in row: significant ($p<0.05$).

*51.9 $\mu g/mm^3=0.0519$ mg/mm$^3\times100=5.19$ mg/100 mm$^3=5.19$ %.

** Net water uptake (%) is the sum of water sorption and solubility (%); i.e. RX (PA): 5.19 (WSorption)+1.06 (WSolubility)=6.25%

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**Table 4** Diffusion coefficients ($D$) ($\times10^{-13}cm^2s^{-1}$) and Flux ($F$) ($\times10^{-8}$ Kg/m$^2$s)

<table>
<thead>
<tr>
<th>Material</th>
<th>Technique</th>
<th>RX $\times10^{-13}cm^2s^{-1}$</th>
<th>VL $\times10^{-13}cm^2s^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$D$</td>
<td>$J$</td>
</tr>
<tr>
<td>PA</td>
<td></td>
<td>1.49 (0.41)$^{a}$</td>
<td>1.29 (0.17)$^{A}$</td>
</tr>
<tr>
<td>DP</td>
<td></td>
<td>1.90 (0.45)$^{a}$</td>
<td>1.51 (0.15)$^{A}$</td>
</tr>
<tr>
<td>CA</td>
<td></td>
<td>0.70 (0.25)$^{a}$</td>
<td>0.94 (0.12)$^{A}$</td>
</tr>
</tbody>
</table>

Different small letters in column and capital letters in row: significant ($p<0.05$)

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**Table 5** Knoop Hardness values (KHN) of resin-cements

<table>
<thead>
<tr>
<th>Material</th>
<th>Technique</th>
<th>RX $m_1$</th>
<th>$m_2$</th>
<th>$m_3$</th>
<th>$m_1$</th>
<th>$m_2$</th>
<th>$m_3$</th>
<th>$m_1$</th>
<th>$m_2$</th>
<th>$m_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA</td>
<td></td>
<td>55.1 (6.6)$^{a}$</td>
<td>35.5 (1.3)$^{B}$</td>
<td>50.7 (5.2)$^{A}$</td>
<td>43.0 (5.4)$^{B}$</td>
<td>31.2 (3.8)$^{A}$</td>
<td>47.6 (6.1)$^{B}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DP</td>
<td></td>
<td>42.3 (7.7)$^{a}$</td>
<td>30.9 (5.9)$^{B}$</td>
<td>43.0 (7.1)$^{A}$</td>
<td>39.0 (5.5)$^{B}$</td>
<td>36.6 (2.2)$^{B}$</td>
<td>45.8 (4.7)$^{A}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CA</td>
<td></td>
<td>36.4 (5.8)$^{a}$</td>
<td>28.4 (1.3)$^{B}$</td>
<td>30.7 (2.3)$^{A}$</td>
<td>21.6 (1.9)$^{B}$</td>
<td>23.3 (2.5)$^{B}$</td>
<td>35.9 (3.2)$^{A}$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Different small letters in column and capital letters in row: significant ($p<0.05$)
at $m_2$). The hardness significantly increased after the second period of desiccation (hardness at $m_3$) compared to $m_2$ ($p<0.05$), which did not differ significantly from the baseline $m_1$. For VL, the same results were obtained when the specimens were immediate photoactivated for 40 s after manipulation (PA group); the hardness decreased significantly at $m_2$ and no significance in the hardness means was observed in comparison with the baseline ($m_1$). In the DP and CA groups, hardness did not decrease significantly after water sorption ($m_1$ vs. $m_2$); nevertheless, hardness significantly increased beyond the baseline after desiccation ($m_3$) ($p<0.05$).

Moderate and negative correlation ($r=0.62$) was found between net water uptake (%) and hardness variation ($m_3-m_i$). Considering the hardness at $m_3$, it was noted a moderate positive correlation ($r=0.48$) between net water uptake (%) and hardness.

**SEM/EDS analysis**

Representative SEM/EDS analysis are presented in Figs. 2-a and b. The illustrations revealed that RX contains filler particles that are quite large and sparsely distributed, characteristics of a non-uniform particle size distribution (Fig. 2-a). The EDS analysis revealed

![Representative SEM/EDS analysis](image)

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Fig. 2 Representative SEM/EDS analysis of the inorganic phase of the resin-cements are illustrated.

(a) The fillers of RelyX ARC show a non-uniform particle size distribution. This discrepancy in size and the irregular shape of the fillers contributes to its sparsely dispersed packing in the organic matrix. The EDS analysis revealed higher incidence of Si, followed by a considered amount of Zr. The chemical element Na was also detected, even though in reduced amount. (b) The disparity of the fillers size-distribution of the Variolink II is less pronounced than in RelyX ARC and its irregular shape is evidently more pronounced. This characteristic provides a better packing of the fillers, allowing higher incorporating in the cement composition. The EDS analysis detected strong signals of Si and a reduced amount of Zr. Other chemical elements were detected in different amounts, showing the complexity of the composition of the inorganic phase of the Variolink II.
calculated from the initial curve slope, which indicates that the sorption/desorption rate of the composites follows Fickian's diffusion only until this value. Beyond this value, certain curves demonstrate non-Fickian behavior indicating that these materials mostly likely generated micro-cracks or defects at the surface that favored the water sorption. This phenomenon was primarily observed among the Rely X groups.

The nature of the resin matrix (mainly resin polarity and network topology)\textsuperscript{21} is a fundamental parameter that may control not only the rate of water diffusion, but also the extent of water sorption\textsuperscript{24}. Diluent monomers favor the water uptake of the resin and the release of low molecular weight substances\textsuperscript{25,26}. Based on information provided by the manufacturer, VL contains a mixture of urethane dimetacrylate (UDMA=UEDMA) and Bis-GMA among other components. The presence of UDMA diluted with TEGDMA in VL cement results in a high degree of crosslinking for this cement\textsuperscript{27} thereby enhancing the mechanical properties in comparison with those which are exclusively Bis-GMA-based\textsuperscript{19,28}. Water uptake is higher in materials that contain TEGDMA as a sole diluent monomer\textsuperscript{27}, as is the case for RX cement\textsuperscript{29}. The solvent effect is higher when a minimal solubility parameter mismatch is present between the solvent and the polymer itself\textsuperscript{9,30,31}.

Higher diffusion coefficients ($D$), in molecular terms, could result in a lower degree of crosslinking and a more rapid uptake of water\textsuperscript{3}, which is, in fact, in accordance with the results obtained for RX. Although the physical and mechanical properties of resin-based materials are also strongly influenced by the degree of conversion\textsuperscript{20}, increased crosslink density has been associated with increased physical properties and stability\textsuperscript{32}, which has also been attributed to the plasticizing effect of water in a polymeric matrix. This phenomenon highlights $D$'s dependence on the water content. Malacarne-Zanon \textit{et al.}\textsuperscript{23} pointed out that the diffusion coefficient is also dependent on many aspects such as the polymer crystalinity, cross-linking, and swelling. According to these authors, a correct explanation for the higher susceptibility of resin-based materials to water (i.e. water sorption, diffusion and solubility) and the effect of the degree of polymer cross-linking on the kinetics of water diffusion still need to be accurately investigated in future studies. According to the present study, as seen in the Table 4, values for $D$ ranged from 0.24 to 1.90, with the highest $D$ observed for RX when photoactivation was delayed (DP group) and the lowest for VL under the CA protocol. RX exhibited significantly lower diffusion coefficients (Table 4) when photoactivation was omitted (CA group). Significantly lower $J$ means were also observed when both cements were chemically polymerized ($p<0.05$) (Table 4). A strong and positive correlation ($r=0.97$) was found between the diffusion coefficient ($D$) and Flux ($J$).

In the present study, the hardness test revealed VL cement to be less affected by water sorption (hardness at $m_3$), irrespective of the polymerization protocol used (Table 5). The hardness after desorption ($m_3$) was also

**DISCUSSION**

Resin degradation may be associated with either volumetric changes such as swelling, physical changes such as plasticization, chemical changes such as oxidation and hydrolysis\textsuperscript{8}. Figure 1 demonstrates that all resin cements showed the greatest increase of mass within the first day of storage in water, if $m_1$ is considered the baseline mass. After that period, a continued and significant increase of mass was observed for both resin cements, irrespective of the curing protocol. Only PA group for VL exhibited a final mass ($m_3$) similar to that observed at the baseline ($m_0$) (Fig. 1).

The analysis of the kinetics of water diffusion, which was determined from the association of water sorption and solubility, actually correlated with the behavior of the resin cements evaluated\textsuperscript{21}. According to ISO 4049 for dental restorative resins, a resin must display a water sorption lower than 50 µg/mm\textsuperscript{3} and a solubility lower than 5 µg/mm\textsuperscript{3} after a seven-day time period in order to be considered suitable for use as dental material\textsuperscript{7}. The variation in mass, due to both water penetration and the elution of low molecular weight material, revealed the resulting net water uptake (%) to be higher for RX than for VL, irrespective of the curing protocol. Since water sorption and solubility occur simultaneously\textsuperscript{23}, the sum of both values was used to estimate the total water uptake. These values ranged from 0.89% to 7.32% among the different experimental groups. In a previous study\textsuperscript{4}, in which the water sorption and solubility of a variety of commercial cements were evaluated, a similar fluid kinetics behavior was noted when the specimens were subjected to the same environment. Despite the differences in the methodology, water sorption and solubility results were found to be dependent on filler parameters such as type, size, content, and concentration. As these parameters also affects the diffusion of water through the material, it was expected to find a strong correlation between the water sorption and the diffusion coefficient ($r=0.83$).

When polymerization protocols were compared, the lowest net water uptake was noticed when the RX cement was chemically activated (CA group) whereas the photoactivated (PA group) demonstrated the lowest net water uptake for the VL cement. Despite the lowest net water uptake of PA group, the results observed for both experimental groups of VL were somewhat superior. The results obtained for net water uptake were in accordance with the diffusion coefficient for both materials. The curves represented in Fig. 1 are in accordance with the equations; consequently Fickian's diffusion theory can be assumed for these monomers for the entire sorption history\textsuperscript{7}. All curves were linear until $M_t/M = 0.5$, enabling the diffusion coefficients to be

a higher incidence of Si and a considerable amount of Zr in the composition of the RX-fillers. The irregular morphological aspect (shape) of the fillers in VL is more evident. The EDS analysis of the VL fillers detected a significant amount of Si and a reduced amount of Zr. 

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Malacarne-Zanon \textit{et al.}\textsuperscript{23} pointed out that the diffusion coefficient is also dependent on many aspects such as the polymer crystalinity, cross-linking, and swelling. According to these authors, a correct explanation for the higher susceptibility of resin-based materials to water (i.e. water sorption, diffusion and solubility) and the effect of the degree of polymer cross-linking on the kinetics of water diffusion still need to be accurately investigated in future studies. According to the present study, as seen in the Table 4, values for $D$ ranged from 0.24 to 1.90, with the highest $D$ observed for RX when photoactivation was delayed (DP group) and the lowest for VL under the CA protocol. RX exhibited significantly lower diffusion coefficients (Table 4) when photoactivation was omitted (CA group). Significantly lower $J$ means were also observed when both cements were chemically polymerized ($p<0.05$) (Table 4). A strong and positive correlation ($r=0.97$) was found between the diffusion coefficient ($D$) and Flux ($J$).
observed to be similar to (for RX) or even higher (for VL) than the hardness obtained at the baseline \( (m_i) \). A higher hardness was also observed when the cements were immediately photoactivated (PA group). Based on the PA group results, water storage appears to reduce hardness due to the plasticization effect, whereas the desiccation process seems to restore or even increase the hardness, perhaps due to the elution of unreacted monomers. Thus, the second hypothesis, which states that the polymerization protocols tested produce different hardness readings depending on the water uptake or the extent of desiccation, was accepted, although the correlation found between net water uptake (\%) and hardness variation \( (m_f-m_i) \) was moderate and negative \( (r=0.62) \). The hardness means differed depending on curing protocol as well as the water sorption and solubility. Considering the hardness at \( m_n \), a moderate positive correlation \( (r=0.48) \) was found between net water uptake (\%) and hardness.

In general, polymer networks prepared by means of free-radical polymerization of hydrophilic methacrylates reveal a spatial heterogeneity, in which certain parts are densely cross-linked and others are loosely crosslinked\(^{33}\). Such spatial heterogeneity is present from nearly the beginning of polymerization, with unreacted monomers dispersed in a pool of microgel domains with a variable density of cross-links\(^{33}\). The reduced potential for conversion after immersion in water has been attributed to the rapid decay of free radicals due to reactions with the oxygen in the water or with the oxygen present within the material as a contaminant\(^{35,34}\), which may also be related to the polymeric network crosslinking density\(^{29}\). Accordingly, the present study indicates that hardness does not discriminate between polymers with different extents of crosslinking. In spite of its higher hardness values, a higher net water uptake was noted for RX cement when compared to that of VL cement. In addition, regarding the same cement, although higher hardness means were observed for the same resin cement in the group immediately photoactivated (PA group), a lower net water uptake was observed for the chemically activated group (CA group).

Although the presence of hydrophilic monomers may influence the rate and the degree of water absorption, it is neither the only factor nor necessarily the dominant factor\(^{26}\). An important practical point emerges from the presence of hydrophilic monomers added to the luting cements with respect to particle shape, size, and distribution. The relative size and shape distribution of the filler particles is extremely important to the viscosity of the resin-cements. Considering the same resin-cement volume, very high packing densities can be achieved with an appropriate selection of the particle size and proportions. It has been suggested that a practical limit to the amount of filler particles in the resin cement formulations must exist well before the densest pack limit is reached\(^{19}\). A lower organic matrix content also helps to explain the lowest water uptake. Lower water sorption in high filler-loaded resins has previously been reported in the literature\(^{45,50}\). A highly filler-loaded composite may be more susceptible to disintegration once the matrix has degraded and a stable structure is no longer provided for the filler particles\(^{50}\). In a previous study\(^{29}\), it was pointed out that the polymerization of methacrylate-based materials produces densely crosslinked network and, during the polymerization period, part of the methacrylate groups involved in the formation of the cross-linked matrix remains unreacted, especially in the case of high-molecular-weight monomers. This associated with the amount of fillers influences the decrease of mobility of polymer radicals; as a consequence there is a decrease on the reactivity. The products with higher filler loading (such as Variolink II) react slower and this somehow also explains why the VL demonstrated immediate photoactivation dependence.

Figure 2 presents the RX (a) and VL (b) SEM/EDS analysis. Figure 2-a clearly indicates that Rely X ARC fillers are larger than those seen for VL. Moreover, these representative figures demonstrate that the fillers appear to be irregular in shape and size. The EDS analysis revealed predominance in Si and a considerable amount of Zr. Figure 2-b demonstrates that the fillers of Variolink II, despite their smaller size, is more regular in size than in shape. The circumstance represents a great advantage as the distribution/packing of the fillers assists in preventing the water sorption, as observed in the present study. For this material, the filler distribution appears to be more uniform than that observed for RX. Moreover, VL presents certain structures as small clusters or agglomerates, which, due to their greater size compared to the mean filler size, would provide for superior physical and chemical interaction with the silane, with the matrix as well, suggesting the possibility of a lower water sorption for this material. In addition, a possible explanation for the higher values of net water uptake for RX cement could be the weak bonding between the resin cement fillers and the resin matrix. The filler treatment and presence of interspacing caused by poor silanization process can affect the surface energy of the fillers, as any of those are considered defects into material and concentrate stress. The initiation of the crack/flow is facilitated under wet conditions leading to hydrolysis of adhesion of the fillers to the matrix\(^{56}\). This potential deterioration of the glass is one of the reasons why it is so important to form an organic layer of silane molecules on the surface of the fillers. Conversely, it has been found that the silane treatment remains stable for at least 6 months, even when specimens are stored at adverse conditions in distilled water\(^{57}\).

Clinically, restorative materials must set in a reasonably short amount of time in order to be practical, and immediate photoactivation may guarantee the initial stability necessary to withstand clinical tensions\(^{58}\). The chemical curing might be expected to guarantee the resin cement maximum properties over time in areas that light energy is unable to reach, thereby increasing the macromolecular packing density of the polymer\(^{59}\) and reducing the presence of nanovoids in the material and the effective volume for water diffusion. Conversely, a deficient chemical-cure may result in
higher concentration of unreacted double bonds, a lower hardness, and a higher solubility of the cements, which can influence chemical stability in an oral environment\(^3\). In a previous study\(^4\), it was found that neither the power density, nor the spectral irradiance seems to interfere in the bond strength of the RelyX ARC to dentin. On the other hand, according to the results of the present study, delaying photoactivation characterizes the most undesirable clinical scenario for both resin cements tested. For RX, despite its higher solubility, chemical activation alone resulted in a lower net water uptake and a lower \(D\) and \(J\) as well. Thus, the tested hypothesis, which states that different polymerization protocols affect the fluid kinetics of the resin cements, was accepted.

It is important to consider the detrimental conditions at the oral environment that favors a higher water sorption and solubility and may represent an important flaw in terms of resin cement properties. However, extrapolations to clinically support and validate the results using different resin cement categories need to be done with caution. The findings for the properties investigated in this study indicate that future studies that considering the net water uptake and its long-term effect are required, particularly in the light of the fact that the optimization of all aspects involved in the water sorption process is still a challenge.

CONCLUSIONS

In this study, a series of tests were performed with a view to examining and comparing the effects of polymerization protocols on net water uptake, the diffusion coefficient \((D)\), the flux \((J)\), and the hardness \((KH)\) of two resin cements.

Chemical activation resulted in lower net water uptake, \(D\), and \(J\) for RelyX ARC. For Variolink II, the chemical activation yielded similar \(D\) and lower \(J\); however, photoactivation resulted in lower percentage of net water uptake. Considering the water diffusion parameters, Variolink II demonstrated immediate photoactivation dependence whereas RX, a chemical activation dependence. Hardness of Variolink II was less affected by the water storage, irrespective of the polymerization protocol. Results of this study seemed to suggest that different polymerization protocols affect the fluid kinetics and the hardness of the resin cements tested.

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