Polymerization efficacy of simplified adhesive systems studied by NMR and MRI techniques

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ABSTRACT

Objective. To ascertain the efficacy of polymerization of self-etching dental adhesives in different solvent evaporation conditions.

Material and methods. Four self-etching adhesive systems were studied. Two of them are classified as mild two-step self-etching adhesives (Clearfil SE Bond, Protect Bond) and the other two are strong one-step systems (Xeno III, ADP-Prompt-L-Pop). The influence of temperature and duration of the air-drying period on photo-polymerization was followed by: gravimetry, 1H solid-state NMR spectroscopy and stray-field MRI. The evolution of proton magnetization with irradiation time was recorded and correlated with volumetric polymerization shrinkage and extent of reaction; evaporation and hardening effects were identified.

Results. Main variables determining water-solvent evaporation of the tested adhesives are: (1) water/HEMA relative concentration, (2) presence of photoinitiator compounds in the primer (SEB) and (3) presence of ethanol (XENO). SEB shows the highest extent of photo-polymerization of the tested adhesives. The lowest volumetric contraction was obtained for APLP and XENO and the attempt to remove the solvents did not increase the extent of polymerization significantly.

Conclusions. Temperature increase following photo-polymerization reaction is dominant towards the effect of the drying step for solvent evaporation in self-etching systems. Attempts to remove the solvents did not increase the extent of polymerization, so other problems are impairing the polymerization of one-step adhesives.

Clinical significance. The use of tested one-step adhesives is discouraged as the attained low extent of polymerization may lead to low bond strength, high susceptibility to degradation and also will favor a continuing etching effect on the underlying dentin.

1. Introduction

The durability of resin–dentin bonds is a key issue if resin composites are to be successfully used over long time periods [1]. Self-etching systems have been proposed as suitable adhesive agents for dentin bonding and this appears to be a promising approach for reducing technique sensitivity in dentin bonding. These systems must diffuse by demineralising through the smear layer and into sound underlying dentin, forming a hybrid layer (resin-infiltrated dentin) and leaving this intact dentin sealed [2]. When testing self-etching systems a high correlation has been encountered between degree of cure...
and bond strength [3]. Moreover, degradation of resin–dentin bonds created by these current hydrophilic adhesive systems has been revealed [1,4] and a relationship between degradation and degree of conversion of the monomers has been advocated [5].

Incomplete free radical addition polymerization of vinyl monomers does exist and has been assigned to the presence of oxygen [6], intrinsic water of the dentin smear layers that contain water-filled channels [7,8], water of the self-etching adhesives as it is an integral component necessary as a solvent and for ionization of the acidic resin monomers so that they can effectively demineralise cut dentin [9], presence of other solvents (ethanol) [10], or even to the existence of chemical incompatibilities between the components of the adhesives, specially when self-etching one-step adhesives are used [11,12]. To help with water and other solvent evaporation, manufacturers recommend gently air-drying the treated tooth for a few seconds after primer/adhesive application. However, controversy exists about the benefits of this step. Air-drying may not be able to induce significant evaporation of solvent and/or excess of water, and air thinning the bonding resin prior to light irradiation may reduce dentin bond strength, because a thinner layer of adhesive will be much more susceptible to oxygen inhibition of the polymerization [13]. This incomplete polymerization due to water presence and/or to oxygen inhibition of the adhesives will accelerate the degradation of the resin–dentin bonds [14]. Due to these circumstances, the efficacy of polymerization of these adhesives in different solvent evaporation conditions needs to be studied in order to assure a reliable and durable adhesion to a wet tissue like dentin.

Conventional Magnetic Resonance Imaging (MRI) and Stray-Field Nuclear Magnetic Resonance Imaging (STRAFI-MRI) have been used as efficient tools to determine the depth of cure [15] and the degree of conversion of light cured dental resins [16–19]. However, while conventional MRI is well suited for the observation of mobile molecules, like monomers or short-chain oligomers, STRAFI-MRI allows mapping molecules from monomers to rigid polymers. This technique permits the determination of bulk or stepped spectroscopic data (1H NMR spectra obtained from the liquids major species and to identify the residual solvent and unre-acted monomers in uncured versus light-cured adhesives. (a) 1H NMR spectroscopic studies of the adhesives were performed in solution. The spectra were recorded from each adhesive after the addition of a lock solvent and the reference compound for chemical shifts (TMS). (b) Subsequently, 1H NMR spectroscopic studies of the photo-polymerized samples were performed using the MAS (magic angle spinning) technique with spinning rates of about 7 kHz. Either a 70° one-radio frequency (RF) pulse (the pulse duration corresponding to a 90° magnetization tip angle was 1.9 μs) or a Hahn-echo RF sequence (90°-time delay–180°-time delay–signal acquisition) were used for the signal acquisition; this sequence, with a long time delay, is used as a simple spin filter for the selective excitation of resonances with long spin–spin relaxation times (T2), like protons in mobile groups. Ethanol signals were used as external references for chemical shifts.

2. Materials and methods

Two two-step self-etching adhesives Clearfil SE Bond (SEB) and Protect Bond (PRB), and two one-step self-etching adhesives Adper Prompt-L-Pop (APLP) and Xeno III (XENO) were tested. Chemical compositions of the adhesives according to manufacturers are shown in Table 1. After the air-drying period, the adhesives were irradiated using an Optilux 401 light-source (Demetron, Kerr, USA, ∼470 nm). Cylindrical glass vials (9.0 mm length and 5.0 mm inner diameter) were used to follow-up the solvent evaporation by gravimetric analysis and 1H STRAFI-MRI.

2.1. Gravimetric measurements

Four sets of primers (PRB and SEB, about 20–30 mg each) and four sets of adhesives (APLP and XENO, about 35–80 mg each) were gently air-dried for 5 s and accumulated periods reaching 20, 30 or 40 s, by blowing air at 21 or 38 °C, guided to the adhesive surface through a tube of 1 cm diameter. The corresponding weight losses were obtained using an analytical balance (Metler, MXS, 0.001 g readability). The manufacturers usually recommend 5 s air-drying at 21 °C. Four other sets of each of the four uncured adhesives (about 30–80 mg each) were submitted to 5 or 20 s or 30 or 40 s drying time at 21 °C, followed by light-curing (500 mW/cm²) over 10 s at 22 °C, and the consequent weight losses were obtained; the drying step was repeated with other adhesive sets under air at 38 °C, and subsequent adhesive curing was also performed at 22 °C.

2.2. NMR spectroscopy

Spectroscopic data (1H NMR spectra obtained from the liquids and from the photo-polymerized adhesives) were acquired using a Bruker MSL 300 P spectrometer (Bruker Spectrospin, Germany), operating at 300.13 MHz, in order to assign the major species and to identify the residual solvent and unre-acted monomers in uncured versus light-cured adhesives.
light-intensity of about 250 mW/cm² (the distance from the which was filled up to 4–5 mm height, and irradiated with a of the coil. Each liquid sample was introduced in a glass vial, using 1H STRAFI-MRI. 1H STRAFI-MRI observations were adhesives, in the presence of the primers, was performed on each adhesive, which are indicated in Table 1. Aiming to erates a magnetic field gradient of 37.5 T m⁻¹, which gen-

The follow-up of the photo-polymerization reaction of the adhesives, in the presence of the primers, was performed using 1H STRAFI-MRI. 1H STRAFI-MRI observations were performed at 123.4 MHz as previously described [17], using the same Bruker MSL 300 P NMR spectrometer with an 89 mm diameter bore superconducting solenoid magnet, which generates a magnetic field gradient of 37.5 T m⁻¹ near the edges of the coil. Each liquid sample was introduced in a glass vial, which was filled up to 4–5 mm height, and irradiated with a light-intensity of about 250 mW/cm² (the distance from the light-source to the liquid surface was about 4–5 mm) (Fig. 1). Two sets of 1H STRAFI-MRI observations were performed on each adhesive, which are indicated in Table 1. Aiming to compare the corresponding induced volumetric adhesive contractions with those promoted by the recommend protocols, light-irradiation or air-drying evaporation periods at 38 °C were also extended to 40 s, that is, well beyond the indications of the manufacturers (10 and 5 s at 21 °C, respectively). Hence, one-dimensional images (profiles) were obtained along the container axis from Primer/Bond liquids (either previously mixed or left unmixed, according to manufacturer instructions for the application of one-step or two steps adhesives), before or after being gently air-dried over the indicated periods at 21 or 38 °C, after each of the indicated, cumulative, irradiation periods and after the indicated post-cure periods. A reference signal for the magnetization intensities was obtained from a plastic disc, about 0.5 mm thick, placed under the glass vials, which is revealed on the right side of the adhesive profiles shown in Figs. 5 and 6. Photo-polymerization was carried out at room temperature (about 22 °C). The magnetization was recorded as multiple eight spin–echo trains (see [17] for details) with echo time (TE) 35 ms, RF pulse duration 90° (t_p) 10 μs. In STRAFI-MRI, the linear resolution Δx can be estimated by \( \sqrt{3 \pi / (t_p \times \gamma_H \times G_z)} \), with \( t_p \) the RF pulse duration that is related to the frequency range to be excited, \( \gamma_H \) the proton gyromagnetic ratio (267.5 Mrad T⁻¹) and \( G_z \) the magnetic field.

### Table 1 – Composition of the adhesives according to the manufacturers

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Composition</th>
<th>Samples observed by 1H stray-field MRI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two-steps</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clearfil SE bond (pH 2, primer, Kuraray Co. Ltd., Osaka, Japan)</td>
<td>Primer: 10-methacryloyloxydiethyl dihydrogen phosphate (MDP) (0.6), 2-hydroxyethyl methacrylate (HEMA) (1), hydrophilic dimethylacrylate, dl-camphorquinone (CQ), N,N-diethanol-p-toluidine (DET), water (40) Bond: MDP (0.04), HEMA (1), bis-GMA (0.75), hydrophobic dimethylacrylate, CQ, DET, silanated colloidal silica</td>
<td>(1) Unmixed primer and bond liquids gentle air-dried at 21 °C over 5 s (2) Sample 1: light-cured over 10 s (3) Sample 2: light-cured over 30 s (4) Post-cure over 16 h of (3)</td>
</tr>
<tr>
<td>Protect bond (pH 2, primer, Kuraray Co. Ltd., Osaka, Japan)</td>
<td>Primer: Methacryloyloxdodecylpyridinium bromide (MDPB) (0.04), MDP (0.2), HEMA (1), hydrophilic dimethylacrylate, water (2.5) Bond: MDP (0.06), HEMA (1), bis-GMA (0.75), hydrophobic dimethylacrylate, CQ, DET, silanated colloidal silica, surface treated sodium fluoride</td>
<td>(1) Unmixed primer and bond liquids (2) Sample 1: gentle air-dried at 21 °C over 5 s and light-cured over 10 s (3) Sample 2: light-cured over 30 s (4) Post-cure over 2 h of (3)</td>
</tr>
<tr>
<td>All-in-one</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adper Prompt-L-Pop (pH &lt; 1, mixed, 3M ESPE, Seefeld, Germany)</td>
<td>Red blister: Methacrylated phosphoric esters (3.3), bis-GMA (1), initiators based on CQ, stabilizers Yellow blister: water (5), HEMA (1), Polyalkenoic acid (0.7%), stabilizers</td>
<td>(1) Mixture of liquids (three blisters) (2) Sample 1: gentle air-dried at 21 °C over 5 s and light-cured over 10 s (3) Sample 2: light-cured over 30 s (4) Post-cure over 18 h of (3)</td>
</tr>
<tr>
<td>Xeno III (pH 1, mixed, Dentsply DeTrey, Konstanz, Germany)</td>
<td>Liquid A: HEMA (1), butylated hydroxy toluene (BHT), highly dispersed silicon dioxide, water (8) and ethanol (1.2) Liquid B: phosphoric acid modified methacrylate resin, mono fluoro phosphazene modified methacrylate resin, urethane dimethacrylate resin, BHT, CQ, ethyl-4-dimethylaminobenzoate</td>
<td>(1) Mixture of liquids (A and B), gentle air-dried at 21 °C over 5 s (2) Sample 1: light-cured over 10 s (3) Sample 2: light-cured over 30 s (4) Post-cure over 16 h of (3)</td>
</tr>
</tbody>
</table>

Concentrations (mol, italicised) of some compounds included in the adhesive formulations obtained by 1H NMR spectroscopy using deuterated lock solvents (chloroform-d₆ and ethanol-d₆, which was used for Xeno III and for the bond in Clearfil SE Bond). 1H stray-field MRI experiments were performed on sample sets I and II.

a Monomer units.
b With the highest viscosity.

2.3. 1H stray-field MR imaging

The follow-up of the photo-polymerization reaction of the adhesives, in the presence of the primers, was performed using 1H STRAFI-MRI. 1H STRAFI-MRI observations were performed at 123.4 MHz as previously described [17], using the same Bruker MSL 300 P NMR spectrometer with an 89 mm diameter bore superconducting solenoid magnet, which generates a magnetic field gradient of 37.5 T m⁻¹ near the edges of the coil. Each liquid sample was introduced in a glass vial, which was filled up to 4–5 mm height, and irradiated with a light-intensity of about 250 mW/cm² (the distance from the light-source to the liquid surface was about 4–5 mm) (Fig. 1). Two sets of 1H STRAFI-MRI observations were performed on each adhesive, which are indicated in Table 1. Aiming to compare the corresponding induced volumetric adhesive contractions with those promoted by the recommend protocols, light-irradiation or air-drying evaporation periods at 38 °C were also extended to 40 s, that is, well beyond the indications of the manufacturers (10 and 5 s at 21 °C, respectively). Hence, one-dimensional images (profiles) were obtained along the container axis from Primer/Bond liquids (either previously mixed or left unmixed, according to manufacturer instructions for the application of one-step or two steps adhesives), before or after being gently air-dried over the indicated periods at 21 or 38 °C, after each of the indicated, cumulative, irradiation periods and after the indicated post-cure periods. A reference signal for the magnetization intensities was obtained from a plastic disc, about 0.5 mm thick, placed under the glass vials, which is revealed on the right side of the adhesive profiles shown in Figs. 5 and 6. Photo-polymerization was carried out at room temperature (about 22 °C). The magnetization was recorded as multiple eight spin–echo trains (see [17] for details) with echo time (TE) 35 ms, RF pulse duration 90° (t_p) 10 μs. In STRAFI-MRI, the linear resolution Δx can be estimated by \( \sqrt{3 \pi / (t_p \times \gamma_H \times G_z)} \), with \( t_p \) the RF pulse duration that is related to the frequency range to be excited, \( \gamma_H \) the proton gyromagnetic ratio (267.5 Mrad T⁻¹) and \( G_z \) the magnetic field.
Fig. 1 – Dimensions of the cylindrical glass vials used as containers for the follow up of adhesive photo-polymerizations by $^1$H STRAFI-MRI. On the right-side is shown a typical profile, which includes the projection of a plastic disc that was used as a reference for the magnetization intensities and SEB projection, after being gently air-dried at 38 °C over 40 s and 10 s light-cured (250 mW/cm²).

Fig. 2 – The chemical structure of monomethacrylate monomers commonly found in some simplified adhesive formulations.

3. Results

3.1. Gravimetric measurements

Table 2 shows weight losses of the primers of two-steps systems and of one-step adhesives, which were obtained as a function of different evaporation times under applied air at controlled temperature (21 or 38 °C). At 21 °C, both primers evaporate very little, even after 40 s (1 ± 1 mg), while one-step adhesives lost about 4 and 2 ± 1 mg, respectively. By increasing air temperature to 38 °C, SEB primer lost about twice the weight of that of the PRB primer (2 ± 1 mg) while one-step adhesives showed the highest weight loss (5 ± 1 mg) at 21 °C, showing that air temperature did not influence the adhesive evaporation, within the range tested. After the combined effects of evaporation over different times (5–40 s) and photo-polymerization (irradiation over 10 s at 500 mW/cm²), weight losses of the adhesives were also obtained. In these conditions, only the one-step and alcohol-containing adhesives showed significant weight losses, which were about 2 ± 1 mg (Table 2).

Table 2 – Weight losses (mg) of the indicated primers and adhesives due to evaporation after being gentle air-dried over 5 s or accumulated periods reaching 40 s, at 21 or 38 °C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Evaporation over 5 or 40 s (cumulative periods)</th>
<th>Evaporation over 5 or 40 s and 10 s photo-polymerization</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>21 (°C)</td>
<td>38 (°C)</td>
</tr>
<tr>
<td>SEB primer</td>
<td>0.4; 1.3</td>
<td>0.8; 3.2</td>
</tr>
<tr>
<td>PRB primer</td>
<td>0.4; 0.9</td>
<td>0.4; 1.5</td>
</tr>
<tr>
<td>APLP</td>
<td>0.9; 2.2</td>
<td>0.6; 1.0</td>
</tr>
<tr>
<td>XENO</td>
<td>2.5; 4.7</td>
<td>1.5; 3.8</td>
</tr>
</tbody>
</table>

Weight losses (mg) of the indicated adhesives due to evaporation after being gentle air-dried over 5 or 40 s, at 21 or 38 °C, and light-cured over 10 s (500 mW/cm²). The error was ±1 mg.

3.2. NMR spectroscopy

Liquid state Nuclear Magnetic Resonance (NMR) spectroscopy was used to identify the major compounds and their relative concentration in the adhesive components. Fig. 2 displays the chemical structure of monomethacrylate monomers commonly included in some simplified adhesive formulations. Fig. 3 shows typical $^1$H spectra obtained from adhesive components, which were obtained from PRB Primer and from the bond, using chloroform-d$_1$ as lock solvent. The concentrations...
Residual solvents, 1H solid state MAS spectra were also air-dried for 40 s at 38°C and subsequently photo-polymerized over 10 s (500 mW/cm²); because all the adhesives contain HEMA, a wide chemical shift range. Signals from protons in vinyl moieties (chemical shift range 5.5–6.3 ppm). Fig. 4 shows typical 1H MAS spectra obtained from adhesives after being gently air-dried and subsequently photo-polymerized over 10 s (500 mW/cm²); (b) PRB, (c) XENO, (d) SEB and (e) APLP. The 1H spectrum of HEMA in acetone-d₄ is also shown, for comparison (a).

In order to identify dominant unreacted monomers and residual solvents, 1H solid state MAS spectra were also recorded from the cured adhesives, previously gently air-dried. In these experiments, narrow resonances are assigned to more mobile compounds (solvents, unreacted monomers and pendant methacrylate groups, contribution (a)) while broader signals are mainly from trapped molecules in the rigid network (contribution (b)), which very broad contribution spans over a wide chemical shift range. Signals from protons in vinyl groups were identified in all the spectra, indicating the presence of important contributions of unreacted methacrylate moieties (chemical shift range 5.5–6.3 ppm). Fig. 4 shows typical 1H MAS spectra obtained from adhesives after being gently air-dried for 40 s at 38°C and subsequently light-cured over 10 s (500 mW/cm²); because all the adhesives contain HEMA, at least in one component, the spectrum of this monomer (in acetone-d₄) is also shown for comparison. In PRB and SEB spectra (Fig. 4b and d) narrow signals are mainly from HEMA and MDP; broader resonances, particularly observed for SEB, may be from free and bound water molecules (at about 4.4 and 2.3 ppm, respectively). Ethanol, water and HEMA signals are identified in the spectrum of the one-step alcohol-containing adhesive (Fig. 4c). Very intense signals are identified in one-step systems spectra at about 7.2 and 4.4 ppm, which are assigned to protons in acidic groups and in free water molecules (Fig. 4e).

### 3.3. STRAFI-MRI

Figs. 5 and 6 show typical 1H STRAFI-MRI profiles obtained for the adhesives. It must be noted that, in these figures, the profiles are rotated 90° and, consequently, the sample surfaces and the reference signals obtained from plastic discs, are shown on the left- and on the right-side of the plots, respectively. The gaps observed between the plastic discs and the adhesives correspond to the glass containers, which do not have hydrogen. The presence of the meniscus at the liquid surface and at the liquid bottom (due to the glass meniscus) can be observed on the left- and on the right- side of the profiles, respectively. While in I and II plots, the magnetizations were normalized assigning 1 arb unit to the reference signal, the highest intensity of the cured adhesive was used as a reference for the intensity normalization of the magnetization recorded from uncured and cured adhesives shown in A and B. The first general observations are the decrease in signal intensity and the narrowing of the profiles after exposure to light. The latter effect is clearly associated with contractions during polymerization and hence overall volume reduction. Because cured systems exhibit extensively lower magnetization, an estimate of the extent of the reaction, which must not be considered here as the degree of double bond conversion, could be directly drawn from magnetization measurements.

The obtained profiles are hydrogen density maps, strongly weighted by mobility in the kHz frequency range. Hence, for similar proton density, higher mobile adhesive domains correspond to more intense profile regions; conversely, the decrease of profile intensity is due to solvent evaporation and/or mobility loss due to the viscosity increase that goes along with ongoing curing reactions. For example, similar fast spin-echo decays were recorded from glassy PMMA (atactic) slices and, consequently, the corresponding profile shows a uniform intensity, i.e., is not spatially dependent; conversely, an intensity variation was observed in the curing adhesive profiles, in agreement with a spatial molecular dynamics dependence, showing the presence of, at least two dominant regimes (from mobile and rigid domains, respectively). Hence, it is straightforward, for instance, to compare the contribution...
Fig. 5 – 1H STRAFI-MRI profiles of SEB showing the influence of air-drying period (duration and temperature), cumulative and post-curing irradiation periods. Two sample sets were observed (Table 1): (I) (1) primer and bond (unmixed) 5 s air-dried at 21°C, (2) sample 1: irradiated over 10 s and (3) sample 2: irradiated over 30 s; (II) (1) primer and bond (unmixed) 40 s air-dried at 38°C, (2) sample 1: irradiated over 10 s and (3) sample 2: after a post-curing period of 16 h. 1H STRAFI-MRI profiles of SEB showing volumetric contractions (VC) corresponding to I1–I3 and II1–II3 evolutions and represented in A and B, respectively.

of the more rigid domains in the curing adhesive, which correspond to less intense slices in the profiles. A close observation of the intensity variation of the profiles allows identifying the main process for profile narrowing; for example, evaporation is clearly the dominant effect for the one-step adhesive (APLP) because the intensity decrease was low (Fig. 6). From the profiles (like the ones shown in Figs. 5 and 6A and B) it was possible to estimate the volumetric polymerization contractions (VC). Table 3 summarizes the most relevant data obtained from 1H STRAFI-MRI experiments; it shows VC obtained for the adhesives after being submitted to gentle air-drying at 21 or 38°C over 5 or 40 s, respectively, and after 10 + 30 s or 10 s light-irradiation. Table 3 also shows preliminary results for the post-cure contractions.

All the profiles from the cured adhesives show the presence of highly mobile molecules; particularly in the case of one-step systems, where the extent of photo-polymerization was extremely low after 10 s light-irradiation. SEB presents a strong oxygen inhibitor effect, which is specially visible in Fig. 5II; for instance, in profile 4, a surface layer about 1 mm thick is

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Volumetric contraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>SEB</td>
<td>6.8</td>
</tr>
<tr>
<td>PR8</td>
<td>5.7</td>
</tr>
<tr>
<td>APLP</td>
<td>6.8</td>
</tr>
<tr>
<td>XENO</td>
<td>12.4</td>
</tr>
</tbody>
</table>

* Post-curing period was shortened, as compared with the other adhesives, due to experimental constraints.
observed showing that highly mobile adhesive regions remain even after 40 s air-drying at 38 °C followed by 10 s irradiation period and 16 h post-curing. In fact, solvent evaporation seems to be the main effect during this period. VC increased by a factor of about 1.6 by raising the temperature to 38 °C during the drying step. Two-step systems showed similar behavior, but SEB was less viscous after a 10 s irradiation period, most probably due to lower double-bond conversion.

One-step systems show mainly evaporation effects, which become predominant at 38 °C; in this condition, the curing appears to be very low. The one-step and ethanol-containing adhesives present a higher post-cure effect, even after being gently air-dried at 38 °C for 40 s.

4. Discussion

According to Table 1, while the primers of two-step adhesives contain water, other hydrophilic compounds (like HEMA and MDP) are included in both components; furthermore, SEB contains photoinitiators in the two components [21]. In one-step adhesive formulations, only one component contains hydrophilic compounds, which are not mixed with photoinitiators present in the other component.

The weight losses of primers and adhesives after being air-dried for 40 s under controlled temperature (a and b) follow the trends: (a) 21 °C: PRB primer < SEB primer < APLP ≪ XENO and (b) 38 °C: APLP < PRB primer < SEB primer ≪ XENO (Table 2). SEB primer, which contains the highest water/HEMA relative concentration, always presents higher evaporation than PRB primer, at both air-drying temperatures. The drying step affects APLP less than XENO, which is explained by the presence of ethanol in this adhesive. The trends obtained for the weight losses of the adhesives after 5 s evaporation under controlled temperature and subsequent curing (c and d), were: (c) 21 °C and photo-polymerized: PRB < APLP < SEB < XENO and (d) 38 °C and photo-polymerized: APLP < PRB ≈ SEB < XENO (Table 2). Overall, the one-step and alcohol-containing system is the adhesive that shows higher evaporation. PRB is less affected by the drying step and curing, when the protocol
indicated by the manufacturers is followed. This observation may be explained by a relative low concentration water/HEMA in the primer (2.5, Table 1) that becomes even lower after the application of the bond, which also contains HEMA. It has been already shown that the rate of water evaporation from water–HEMA mixtures decreases as the HEMA concentration rises [22]. However, by increasing air temperature to 38 °C, APLF was the adhesive that evaporated less (with water–HEMA relative concentration equal to 5 in the primer, Table 1). In fact, according to the water–HEMA relative concentration for water-based primers, it should be expected that evaporation follows SEB < PRB; this trend is only verified for the photo-polymerized adhesives. Nevertheless, it must be pointed out that, after a drying step followed by curing, all the water-based adhesive weight losses were very similar. This is an indication that the temperature increase following photo-polymerization reaction is dominant towards the effect of the drying step. Hence, the lesser photo-polymerization efficacy encountered for PRB, when compared to SEB, may be due not only to a reduction in water evaporation, but also to a lower CQ content (CQ is not present in PRB primer).

The observation of cured adhesives by solid state NMR spectroscopy, in the presence of the primers, allowed the identification of unreacted vinyl groups in all the samples, particularly from HEMA and MDP. In one-step adhesive spectra, strong signals from protons in acidic groups and water were identified. The present results agree well with data previously obtained for the same one-step and alcohol-containing adhesive without any attempt to remove the solvents, in which case a volumetric contraction of 22.8 ± 0.1% was reported after a light-curing period of 180 s at 25 mW/cm² [20]. The extent of polymerization of the mentioned adhesive was lower in the present study, where the total duration of the irradiation period was either 40 or 10 s, at 250 mW/cm², after a drying period at 21 °C (5 s) and 38 °C (40 s), respectively: 12.4 and 13.5% (Table 3). These findings may be explained by the convenient use of longer irradiation periods at lower light intensity. In fact, the attempt to remove the solvents did not increase the extent of polymerization significantly, suggesting that other problems are impairing polymerization of these one-step adhesives.

The spatial dependence of the extension of the curing reaction was obtained by 1H STRAFI-MRI and the distribution of more mobile molecules (such as liquids, pendant unreacted groups and oligomers) within a polymeric solid matrix was revealed. A closer examination of the profiles reveals that in some cases the magnetization increases slightly at the beginning of irradiation. This effect is particularly observed for PRB and XENO and is explained by lowered viscosity (hence increased molecular mobility) due to sample heating, which dominates over the decrease in mobility due to reaction at the early stages of polymerization. There are two sources of heat in the present experiments: that resulting from the light absorption and the heat released during polymerization, calculated to be 56 kJ/mol·s per methacrylate double bond [23]. Some profiles also show, after the irradiation period, much lower intensities of adhesive slices near the bottom of the container (after being treated at 21 °C); this observation is in agreement with a higher extent of reaction in these regions (1H STRAFI-MRI signal intensity decreases with increasing viscosity, following the curing reaction). Conversely, for the one-step adhesive (APLF) treated at 38 °C, the intensity remains very similar after the curing period showing a very low extent of reaction, and VC is mainly due to evaporation; in fact, VC has remained low, independently of the air-drying temperature. It has been hypothesized that some one-step adhesives do not polymerize properly so low initial bond strength and rapid hydrolytic degradation is usually encountered when testing these systems [24,25]. These adhesives have also been shown to easily permit water transportation through them increasing nanoleakage and accelerating resin–dentin bond degradation [26]. Moreover, adhesives with strong acidity (mainly one-step systems) have been shown to exhibit the formation of a non-resin infiltrated demineralized collagen layer under the resin-hybridized dentin [27], which will be highly susceptible to degradation. It is probably a consequence of the continuing demineralization effect on dentin due to the poor polymerization of the adhesive [24]. Present results may in part, explain recently published in vitro and clinical data, stating that “strong” self-etch adhesive (e.g. APLF, XENO pH < 1) performed very poorly, in contrast to “mild” two-step self-etch adhesive (e.g. SEB, PRB pH ≥ 2) [28].

According to the 1H STRAFI-MRI experiments, the inhibitor effect shown by the adhesives (which is lower for SEB) is due to the high concentration of solvents and HEMA (which is a highly hydrophilic monomer) in the starting solution, according to the NMR spectral data (Table 1). The presence of protic solvents (a) and high concentration of dissolved molecular oxygen (b) near the adhesive surface may particularly inhibit HEMA polymerization. Indeed, the spatially resolved curing kinetics depend strongly on effects (a and b), which determine the reaction rate spatial-isotropy. The STRAFI-MRI profiles presented here do not show the intensity of the curing light dropping significantly due to absorption by the adhesives, which is explained by the complexity of the adhesive formulations and ongoing phenomena; this effect is clearly observed on homopolymerizations [29]. It has already been shown that the presence of excess residual water may adversely affect polymerization of the adhesives [30]. Moreover, it is well known that functionality plays an important role in polymerization kinetics [31]. Reaction of monofunctional monomers, (e.g. HEMA and MDP), does not present an autocatalytic period at the initial stages of the reaction. Hence, at the beginning of the irradiation period, the fact that the rate is lower does not favor a high degree of conversion being reached if quenching of excited CQ triplet states by dissolved molecular oxygen occurs. Conversely, radical scavenging by oxygen is expected to slow down upon increasing the viscosity, and hence, to be constrained in the gelled and vitrified states. According to the present data, the two-step system containing photoinitiator in the primer shows the highest extent of photo-polymerization of the tested adhesives. However, the fact that a surface layer about 1 mm thick remains highly mobile even after 40 s air-drying at 38 °C followed by a 10 s irradiation period and 16 h post-curing, may explain published data showing that the demineralizing effect of this adhesive on dentin may continue over a long time (more than 12 h) after the recommended light-irradiation period [32].
5. Conclusions

Main variables determining the extent of water-solvent evaporation of the tested adhesives are the following: (1) relative concentration of water/HEMA, (2) presence of photoinitiator compounds in the primer and (3) presence of ethanol. Accordingly, the one-step and ethanol-containing adhesive shows the highest extent of evaporation and the rest of the adhesives follow the relative concentration water/HEMA (PRB < APLP < SEB). Solvent evaporation in non-ethanol containing adhesives is not affected by air-drying duration and temperature. A controversy remains about the benefits of the drying step on the photo-polymerization of most of the self-etching adhesives, because similar weight losses were obtained following the reaction. Temperature increase following photo-polymerization reaction is dominant towards the effect of the drying step for solvent evaporation in self-etching systems.

The spatial dependence of reaction extent was obtained by STRAFI-MRI and qualitatively correlated with major unreacted components within the polymeric solid matrix, using liquid- and solid-state NMR spectroscopy. The combined application of such techniques (NMR spectroscopy and STRAFI-MRI) provided information on how the variables applied to this experiment can affect the degree of conversion and residual solvents in the adhesives. The presence of a high relative water/HEMA concentration seems to improve the degree of conversion. The lowest volumetric contraction was obtained for one-step adhesives, where the extent of reaction appears to be extremely low and the profiles remain more spatially isotropic for these adhesives. Moreover, the attempt to remove the solvents did not significantly increase the extent of polymerization, suggesting that other problems are impairing polymerization of these one-step systems. The null hypothesis should be rejected as the all-in-one self-etching system presented less final volumetric contraction, when compared with the self-priming adhesives tested. However, longevity of the bonding sites and biocompatibility of the system may be lessened as a consequence of the major solvent/oxygen inhibitor effects in the photo-polymerization of this adhesive.

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