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Spatially resolved photopolymerization kinetics and oxygen inhibition in dental adhesives

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Abstract

A comparative study of three commercial dental adhesives was performed by ¹H nuclear magnetic resonance spectroscopy and Stray-Field magnetic resonance imaging. Spectroscopic evidence was found for the presence of solvent and unreacted methacrylate groups in photopolymerized adhesives. Spatially resolved photopolymerization kinetics and volumetric contraction (solvent evaporation and polymerization shrinkage) were obtained without solvent removal and in the presence of oxygen from the atmosphere. The oxygen and solvent inhibitor effects in the photopolymerization were found to be higher for water/ethanol based adhesives. However, was one of these adhesives that exhibited less spatially dependent irradiation time to start vitrification, higher concentration and a more uniform spatial distribution of rigid domains at the end of the photopolymerization. © 2004 Elsevier Ltd. All rights reserved.

Keywords: Dental adhesive; Photopolimerization kinetics; Oxygen inhibition; Volumetric contraction

1. Introduction

A number of new adhesive systems have been developed in an attempt to obtain a reliable bonding to enamel and dentin and simplify the clinical bonding procedures. Two different means are employed to achieve this goal. The first utilizes the total acid-etching technique to demineralize both enamel and dentin surfaces, followed by the application of a self-priming agent that combines the primer and the adhesive resin in one solution (e.g. Prime&Bond NT, Single Bond). The second approach is the use of self-etching primers, including the all-in-one adhesive systems (e.g. XENO III) [1]; their bonding mechanism is based upon the simultaneous etching, priming and bonding to the smear-covered dental tissue using one solution and in one step [2,3]. However, the benefit of saving time may be achieved at the expense of compromising the durability of resin-dentin bonds [4], as

these adhesives contain highly hydrophilic monomers that make hybrid layers more permeable and sensitive to water sorption and degradation [5].

It is known that free radical addition polymerization of vinyl monomers may be inhibited by oxygen [6,7]. Moreover, it has been speculated about the possibility of an incomplete polymerization of adhesives within the hybrid layer [8,9], due not only to oxygen inhibition, but also to the presence of intrinsic water of the dentin, primer solvents or even to the existence of chemical incompatibilities between the components of the adhesives, specially when all-in-one systems are used [10,11]. To help with water (in dentin) and solvent (in the adhesive) evaporation, manufacturers recommend to gentle air-dry the treated tooth for a few seconds. However, controversy exists about the benefits of this step. Indeed, solvent removal is only easily accomplished during the clinical procedure when acetonebased adhesives are used; once water/ethanol-based adhesives are applied, air-drying will not be able to induce significant solvent evaporation. Moreover, air thinning the bonding resin prior to light irradiation, significantly reduce dentin bond strength because a thinner layer of adhesive will be much more susceptible

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to oxygen inhibition of the polymerization [12]. This incomplete polymerization of the adhesives will accelerate the water degradation effects [13]. Due to these circumstances, the efficacy of polymerization of these self-priming and self-etching adhesives needs to be studied in order to assure a reliable and durable adhesion to a wet tissue like dentin.

Stray-Field Magnetic Resonance Imaging (STRAFI-MRI) has proved its reliability in the study of dental materials [14–17]. A comparative study of three adhesives (Prime&Bond NT, Single Bond and XENO III) by ¹H STRAFI-MRI is presented.

The objective of this work was to study the photopolymerization of self-priming and self-etching dental adhesives without performing any attempt to remove the solvent component, prior to the irradiation period. The null hypothesis to be tested was that there are no influence of the solvent component on the efficacy of the polymerization, the spatially resolved photopolymerization kinetics and the final volumetric contraction regardless of the type of dental adhesive.

2. Materials and methods

2.1. Materials

Chemical composition of the adhesives used in the present study is shown in Table 1.

2.2. Methods

The experimental data were acquired in the following sequence, using a Bruker MSL 300 P spectrometer (Bruker Spectrospin, Germany).

2.2.1. Nuclear magnetic resonance spectroscopy

Spectroscopic data (¹H nuclear magnetic resonance (NMR) spectra obtained from the liquids and from the photopolymerized adhesives) were acquired in order to assist in the interpretation of STRAFI-MRI results

(a) ¹H NMR spectroscopic studies of the adhesives were performed in solution. The spectra were obtained from the adhesive after the addition of ethanol-d₆ or as received, in which case the lock solvent (acetone $-d_6$) and the reference compound for the chemical shifts (TMS) were kept in a capillary, inside the NMR tube; the acquisition conditions for each adhesive are indicated in Fig. 1 caption. (b) The adhesives were photopolymerized at about 22°C following the instructions from the manufacturers, using an Optilux 401 (~470 nm, Demetron, Kerr, USA) to irradiate the samples with about $500 \,\mathrm{mW/cm^2}$ light intensity, over the indicated periods: 10+10s for Prime&Bond NT, 20s for Single Bond and 40 s for XENO III. Subsequently, ¹H NMR spectroscopic studies of the photopolymerized crushed samples were performed using the magic angle spinning (MAS) technique with spinning rates of 6 or 8 kHz, except for Xeno III, in which case only 1.2 kHz was reached. Either a 70° one-radio frequency (RF) pulse (the pulse duration corresponding to a 90° magnetization tip angle was 1.9 μ s) or a Hahn-echo RF sequence (90° x-time delay– 180°_{ν} -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 (T_2) , like protons in mobile groups. Ethanol signals were used as external references for the chemical shifts. A MAS spectrum of the mixture of the two XENO III components was also acquired at a spinning rate of about 890 kHz.

Table 1

Composition of the adhesives used in the present study, according to the manufacturers

Self-priming adhesives	Composition		
Prime&Bond NT (Dentsply DeTrey, Konstanz, Germany)	Dipentaerythritol penta acrylate monophosphate (PENTA), di- and tri-methacrylate resins, urethane dimethacrylate resin (UDMA), nanofillers (amorphous silicon dioxide), photoinitiators, stabilizers, cetylamine hydrofluoride and acetone.		
Single Bond (<mark>3M-ESPE</mark> , Dental Products, St Paul, MN, USA)	2,2-bis-[4-(2-hydroxy-3-methacryloyl-oxypropoxy)] phenyl propane (Bis-GMA), 2-hydroxyethyl methacrylate (HEMA), di-methacrylate resins, polyacrylic polyitaconic copolymer, initiators, water and ethanol		
All-in-one self-etching adhesive			
Xeno III (Dentsply DeTrey, Konstanz, Germany)	<i>Liquid A</i> : HEMA, butylated hydroxy toluene (BHT), highly dispersed silicon dioxide, water and ethanol. <i>Liquid B</i> (with the highest viscosity): phosphoric acid modified methacrylate resin, mono fluoro phosphazene modified methacrylate resin, UDMA, BHT, camphorquinone (CQ), ethyl-4-dimethylaminobenzoate.		



Fig. 1. ¹H spectra of the adhesives: (1) Prime&Bond NT: (a) Spectrum obtained from the liquid with the lock solvent (acetone–d₆) and the reference (TMS) introduced in a capillary placed inside the NMR tube; (b) MAS spectrum from the adhesive photopolymerized over 20 s ($\sim 500 \text{ mW/cm}^2$). (2) Single Bond: Spectra obtained as (1a) and (1b). (3) XENO III: Comparison of the spectra of the liquid components in ethanol–d₆ with the spectrum of the mixture of the A and B components (recorded in MAS mode) and with the spectrum of the adhesive photopolymerized over 40 s ($\sim 500 \text{ mW/cm}^2$).

2.2.2. ¹H STRAFI-MRI

One-dimensional STRAFI images, projections along an axis, were acquired from the liquid and from the photopolymerized adhesives:

¹H STRAFI-MRI observations were performed as previously described [14,15], 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 Tm^{-1} near the edges of the coil. The STRAFI probe was tuned to 123.4 MHz, which gives ¹H resonance at 2.9 T; this field strength was obtained just outside the bore of the magnet. Each liquid sample was introduced in a cylindrical glass vial (9.0 mm length and 6.0 mm inner diameter) filled up to 3 mm height and irradiated in situ (25 mW/cm^2) , while positioned at the magnet stray-field region, using an optical fiber cable connected to the light curing unit and guided to the top of the probe-head radiofrequency coil. One-dimensional images (profiles) were acquired along the container axis after each irradiation period up to a total of 180s was reached. A reference signal for the intensities was obtained from a plastic disc, about 0.5 mm thick, placed near the bottom of the glass vials, which is shown on the right side of the adhesive profile. The magnetization was recorded as multiple 16 spinecho trains (see [14] for details) with echo time (TE) $35 \,\mu\text{s}$, RF pulse duration (90°) 10 μs and slice thickness <100 µm. The photopolymerization was carried out at room temperature (about 22° C). The spatially resolved kinetics was obtained and the final volumetric contraction, which includes polymerization shrinkage and solvent evaporation, was determined (in %) as: \sum (magnetization of slices of the unpolymerized adhesive, MUP) $-\sum$ (magnetization of adhesive slices polymerized over 180 s, MP) \times 100]/ \sum (MUP). The highest intensity of MP was used as a reference for the intensity normalization of MUP and MP.

3. Results

3.1. ¹H NMR spectroscopy

The ¹H NMR spectra of the unpolymerized adhesives are shown in Fig. 1. In the spectrum of Prime&Bond NT, the most intense signal is observed at 2.2 ppm and is due to the methyl groups of acetone $(CH_3)_2CO$; some of the other resonances are assigned to the methylenic groups in methacrylate moieties (at 6.1 and 5.6 ppm) and in the chain (4.3 ppm and about 3 ppm). In the spectrum of Single Bond the major signals are from ethanol and water (1.17, triplet, 3.61, quartet, and 4.90, broad), Bis-GMA (for example, doublets at 6.8 and 7.1 ppm, multiplets at 6.1 and 5.6 and singlets at 1.9 and 1.6 ppm) and HEMA (6.1, 5.5, 4.2, 3.8 and 1.9 ppm). The spectrum of XENO III component A shows HEMA, ethanol and water dominant signals, while in the spectrum of component B the major signals are from methacrylate monomers. The ¹H solid-state MAS spectra of the photopolymerized adhesives are also shown in Fig. 1. Due to the selected acquisition mode, the signals of more mobile groups appear strongly enhanced in these spectra. Therefore, for Prime&Bond NT, while methylenic and methyl groups of more mobile photopolymerized methacrylate moieties are recorded at $\sim 0.5-2.6$ ppm, new resonances are clearly observed at 3.9 and 4.8 ppm (Fig. 1(1b)). The major signals identified in the solid state spectrum of Single Bond (Fig. 1(2b)) are from ethanol, water and unreacted methacrylate groups. The spectrum of photopolymerized XENO III is shown in Fig. 1.3; the dominant resonances are from methacrylate monomers, mainly HEMA, ethanol and water.

3.2. ¹H STRAFI-MRI

In order to obtain the spatially resolved kinetics for the curing of the adhesive, profiles were acquired prior irradiation and after each of the successive irradiation times, 5, 5, 10, 10, 10, 20, 20 s (1 h post-cure), 20, 20 and 60 s (24 h post-cure), until a total cumulative irradiation period of 180s was reached. In order to get preliminary information on the adhesive post-curing evolution, profiles were also acquired after waiting periods of 1 and 24 h, following the second 20 s and the total irradiation periods, respectively. Figs. 2a, 3a and 4a show the superimposed profiles obtained from the adhesives before being light-cured and after the indicated cumulative irradiation periods. It is observed that the ¹H signal intensity decreases with the irradiation time. Some profiles show higher signal intensity near the surface, which is explained by the presence of highly mobile groups, like unreacted methacrylate groups, and solvent molecules; for example, a more mobile surface region was obtained for Single Bond (Fig. 3a) and for XENO III (Fig. 4a) after 60s total irradiation time. Nevertheless, when the total irradiation time of 180s was reached, only the profile obtained from XENO III still showed higher surface signal intensity; only small intensity variations were observed in the corresponding projection recorded for Single Bond. Single Bond and XENO III data show unambiguously the inhibition effect of oxygen, which is expected to be higher near the adhesive surface in contact with air. A different behavior was observed when comparing these data with the evolution of Prime&Bond NT as a function of irradiation time (Fig. 2a); in this case, for each profile of the irradiated adhesive, the highest signal intensity was always obtained from a slice near the bottom of the container. This observation may be explained by a contribution of solvent (acetone) evaporation to the observed decreased mobility, which consequently is dominant as compared to the oxygen inhibitor effect.

As the temporal evolution of ¹H magnetization (essentially spin-spin relaxation, T_2 , dependent) is correlated with the extent of reaction, the spatially resolved photopolymerization kinetics was obtained for the three adhesives, without solvent removal and in the presence of oxygen from the atmosphere. The irradiation time dependence of the intensity at three different positions (slices) through the profile was fitted with a sigmoidal (Boltzmann) function, $M = (M_1 - M_2)/[1 +$ $e^{(t-t_0)/t_c}] + M_2$, where M_1 and M_2 are the magnetizations, in arbitrary units, recorded before and after the irradiation period, respectively, and t_c is the reaction time constant; in order to facilitate the comparison of the present results with relevant data obtained using other techniques Figs. 2b, 3b and 4b show the intensity as (10 - M) and the curves obtained using the fitting function

$$10 - M = \frac{(10 - M_2) - (M_1 - M_2)}{[1 + e^{(t - t_0)/t_c}]}.$$
 (1)

The reaction rate, M' = d[M]/dt, was obtained from the derivative of Eq. (1): $M' = (M_1 - M_2) \times (e^{(t-t_0)/t_c}) \times$



Fig. 2. Evolution of ¹H magnetization profiles of Prime&Bond NT with the following cumulative irradiation periods (25 mW/cm^2) recorded up to a total 180 s irradiation time was reached: 0, +5 s, +5 s, +10 s, +10 s, +20 s+20 s+1 h post-cure +20 s+20 s+60 s and +24 h post-cure. A signal of a plastic disc kept near the bottom of the container was used as a reference for the intensity normalization.



Fig. 3. Evolution of ¹H magnetization profiles of Single Bond with cumulative irradiation periods (25 mW/cm^2) recorded up to a total 180 s irradiation time was reached: 0, 5+5 s, +10 s+10 s, +20 s, +20 s, +20 s, +1 h post-cure +20 s+20 s+60 s+24 h post-cure. A signal of a plastic disc kept near the bottom of the container was used as a reference for the intensity normalization.

 $(1/t_c)/[1 + e^{(t-t_0)/t_c}]^2$. The corresponding curves are shown in Figs. 2b, 3c and 4c. Table 2 shows the irradiation times that correspond to the maxima of these



Fig. 4. Evolution of ¹H magnetization profiles of XENO III with cumulative irradiation periods (25 mW/cm^2) recorded up to a total 180 s irradiation time was reached: 0, 5+5 s, +10 s+10 s, +20 s, +20 s, +20 s, +1 h post-cure +20 s+20 s+60 s+24 h post-cure. A signal of a plastic disc kept near the bottom of the container was used as a reference for the intensity normalization.

curves, the reaction time constants and the reaction rate at the irradiation time t_0 (at which the magnetization reaches half of the initial value; $M' = (M_1 - M_2)/4t_c$), obtained for three different slices of the adhesives. The limiting degree of conversion, expressed as the fraction of less mobile domains (in %), was obtained from Eq. (1) with t equal ∞ : $(M)_{\text{limit}} = M_2$.

The volumetric contractions, which include solvent evaporation and photopolymerization contributions, are: $52.4\pm0.1\%$ (Prime and Bond NT), $31.1\pm0.1\%$ (Single Bond) and $22.8\pm0.1\%$ (XENO III). Fig. 5 shows the superposition of the initial and the last profiles, recorded for each one of the three adhesives during the follow-up of the solvent evaporation/photopolymerization; regions I, II and III are the projections of the volumetric contractions. XENO III, which presents the more spatially anisotropic curing reaction, causes a more rigid region, region IV, to be formed near the bottom of the sample; the observed signal intensity variation is consistent with different degrees of vitrification.

4. Discussion

The STRAFI MRI technique allows the observation of both solids (e.g. glassy polymers) and liquid components (e.g. monomer mixtures); the signal intensity depends on hydrogen concentration, but is also strongly affected by relaxation. The relaxation processes are mainly spin-spin and spin-lattice in the rotating frame relaxations, which are correlated with molecular mobility in the kHz range. They have time constants T_2 and $T_{1\rho}$, which are very short for rigid solids, longer for liquid components. When the total concentration is approximately constant, as occurred during a photopolymerization reaction without significant evaporation of any of the starting components, the decrease of the signal is thus determined by the liquid–gel and gel–solid phase transitions. As the curing progresses, the viscosity increases and the material becomes more rigid; it is then expected that the average ¹H T_2 decreases, thereby inducing a decrease of the intensity of the profile [15]. The spatial dependence of the signal intensity is thus correlated with the spatial dependence of the fractional of less mobile domains.

During the early stages of the irradiation period, the viscosity of the adhesive is governed by three competing mechanisms: (a) the increase in temperature, which will reduce the viscosity, (b) the solvent's evaporation and (c) the polymer's increasing molecular weight, which will increase viscosity. Over the early irradiation periods, Prime&Bond NT profiles are mainly controlled by solvent evaporation (a contraction due to solvent loss was observed): acetone evaporation occurs over the first 5s irradiation time, in spite of the employ of a lightsource intensity about 20 times less that the one general used in clinical applications. Due to solvent evaporation, the signal intensity increases immediately after the first irradiation period, in agreement with an increase in the hydrogen concentration (Fig. 2). On the other hand, a much slower solvent evaporation was detected subsequent to the irradiation of water/ethanol based adhesives, as expected. This effect was more pronounced for XENO III than for Single Bond; thus, for XENO III, the evaporation front changes very little up to an irradiation time of 60 s. It must be pointed out here that, similar shapes were obtained for XENO III and Single Bond profiles recorded prior the irradiation periods; thus, the different behaviour of XENO III may not be

Table 2					
Adhesive	Irradiation time to start vitrification (t_0) (s) Reaction time constant (s) Reaction rate at t_0 (arb units s ⁻¹) Fraction of less mobile domains (%)			Volumetric contraction (%)	
					Surface slice
	Prime&Bond NT	a	a	$22.9 \pm 4.0 \\ 6.8 \pm 3.3 \\ 0.042 \pm 0.002 \\ 38.2$	52.4±0.1
Single Bond	$\begin{array}{c} 65.8 \pm 2.4 \\ 10.3 \pm 1.9 \\ 0.044 \pm 0.001 \\ 46.7 \end{array}$	$\begin{array}{c} 47.7 \pm 1.5 \\ 10.5 \pm 1.2 \\ 0.030 \pm 0.001 \\ 63.2 \end{array}$	$\begin{array}{c} 40.7 \pm 1.8 \\ 7.8 \pm 1.7 \\ 0.033 \pm 0.001 \\ 65.9 \end{array}$	31.1±0.1	
Xeno III	$64.5 \pm 9.6 \\ 30.2 \pm 9.1 \\ 0.022 \pm 0.003 \\ 18.0$	148 ± 72 17.8 ± 29.5 0.025 ± 0.008 48.4	<5 13.4±4.1 ≈1	22.8±0.1	

^a Due to solvent evaporation, the adhesive contraction is very high immediately after the first irradiation period and only one slice is clearly defined outside the meniscus region.



Fig. 5. Superposition of the ¹H magnetization profile obtained from the adhesives before being irradiated with the profile recorded after cumulative irradiation periods up to a total 180 s irradiation time with a light intensity of 25 mW/cm^2 ; the highest magnetization of this profile was used as a reference for the intensity normalization. (a) Prime&Bond NT, (b) Single Bond and (c) XENO III.

explained by the non-homogeneity of the starting twocomponent solution, in which case a more intense signal would be obtained from the bottom layers due to higher proton density of the more viscous monomers, as compared with solvents. Conversely, as the adhesive curing progresses, less signal is obtained from those layers, which become more rigid that the ones near the surface; this observation is related to uncompleted solvent evaporation and also to the oxygen inhibitor effect.

From the analysis of the STRAFI data may be observed that, during the photopolymerization, there are two processes occurring: one corresponding to the initial gelation phase, and the other to the vitrification phase. The curves obtained for the reaction rates as a function of the irradiation time (Figs. 2b, 3c and 4c) show an increase of the rate until a maximum is reached; this period corresponds to the gelation-phase [18]. The curves in Figs. 2b, 3c and 4c also show a rate decrease corresponding to the vitrification phase. It is worth noting that, in the case of XENO III, only this phase could be observed by STRAFI-MRI for the slice near the bottom of the container (slice 3 in Fig. 4c), what means that, in this region, gelation has occurred in less than 5 s, which was the duration of the first irradiation period. A similar shape of the rate curve was reported on Bis-GMA and UDMA photopolymerizations, followed by FT-IR spectroscopy [18].

The strong inhibitor effect shown by XENO III is tentatively explained by the high concentration of solvents and HEMA, which is a highly hydrophilic monomer, in the starting solution, according to the spectral data shown in Fig. 1; near the adhesive surface, the presence of protic solvents (a) and high concentration of dissolved molecular oxygen (b) may particularly inhibit HEMA polymerization. Thus, at the surface region, a very slow process was observed (the rate was about 0.022 ± 0.003 arb units s⁻¹) and evaporation seems to be the dominant contribution; on the contrary, a very fast reaction occurred in a slice at about 1.5 mm distance from the surface (ca.1 arb units s^{-1}). Consequently, the conjugation of the effects (a, b) determines the spatial anisotropy of the curing kinetics. It was already shown that the rate of water evaporation from water-HEMA mixtures decreases as the HEMA concentration rises [19] and that the presence of excess residual water may adversely affect the polymerization of the adhesives [20]. This observation does not rule out the presence of other kind of chemical interaction-inhibition, which, if present, would affect uniformly the shape of the profile. XENO III also shows a long post-cure reaction because the intensity of the profile decreases significantly after a post-cure waiting period of 24 h, subsequent to an irradiation period of 180s (Fig. 4a); according to the spectroscopic studies, the more mobile compounds at the end of the irradiation period are HEMA, ethanol and water. The dominant signals from mobile molecules in photopolymerized Single Bond are from the solvents. The fact that a thin film ($< 500 \,\mu\text{m}$ thick) was obtained for Prime&Bond NT is explained by the very fast evaporation of high amount of acetone from the reaction onset. Prime&Bond NT vitrification starts very rapidly (after an irradiation time of about 22s) and, consequently, at the end of the irradiation period (180 s), the fraction of less mobile domains is lower than in the other photopolymerized adhesives; solvent evaporation (acetone, boiling point 56.3°C) appears to be complete after an irradiation time of 5s. Incomplete curing of the resin may cause certain components of the resin to leach into water, leaving minute spaces within the polymer matrix that would subsequently be replaced by water [21].

In Prime&Bond NT clinical uses, because acetone evaporation occurs during the first 5 s irradiation time, it

may be not necessary to gentle air dry after applying the adhesive. A slower solvent evaporation was observed for water/ethanol-based adhesives, as expected, and this effect that was more evident for XENO III than for Single Bond, may be explained by the higher HEMA concentration in XENO III.

The oxygen and solvent inhibitor effects in the photopolymerization of the adhesives follow the trend: XENO III > Single Bond > Prime&Bond NT. The lowest volumetric contraction was obtained for XENO III; however, the polymerization is more spatially anisotropic for this adhesive. For the ethanol/water-based adhesives, the highest amount of unreacted methacrylate groups were found in XENO III, explaining the important post-cure reaction. This reaction could be detrimental as the exposure to water could cause the extraction of uncured water-soluble monomers and low-molecular-weight oligomers, leading to degradation of the bond between the resin and dental tissues [22].

Single Bond attained less spatially dependent irradiation time to start vitrification, higher concentration and a more uniform spatial distribution of rigid domains at the end of the photopolymerization. These results agree well with the previously reported good performance yielded by this adhesive, when compared to other dental adhesive systems [23,24]. Moreover, Single Bond contains water and ethanol as solvents, which reduce the impact of the moisture condition of the dentin [25]. Furthermore, it contains polyalkenoic acid in its composition which is able to form Ca-polyalkenoic acid-base complexes that may have an intrinsic stress relaxation capacity and seems to withstand the detrimental effect of water in the bonding procedures and after the extreme challenges from environmental conditions of the oral cavity [26].

5. Conclusions

The oxygen and solvent inhibitor effects in the photopolymerization were found to be higher for water/ethanol based adhesives. However, was one of these adhesives that exhibited less spatially dependent irradiation time to start vitrification, higher concentration and a more uniform spatial distribution of rigid domains at the end of the photopolymerization: the adhesive with lower concentration of hydrophilic monomer HEMA. This adhesive showed the best probed properties for bonding to dental tissues as accounts for less shrinkage stress after a more isotropic and complete polymerization. The null hypothesis should be rejected as the all-in-one self-etching system presented less final volumetric contraction, when compared with the tested self-priming adhesives; however, longevity of the bonding sites and biocompatibility of the system may be lower as a consequence of the major

solvent/oxygen inhibitor effects in the photopolymerization of this adhesive.

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