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Improved degree of conversion of model self-etching adhesives through their interaction with dentin

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Abstract

Objective—To investigate the correlation of the chemical interaction between model self-etching adhesives and dentin with the degree of conversion (DC) of the adhesives.

Methods—The model self-etching adhesives contained bis[2-methacryloyloxyethyl] phosphate (2MP) and 2-hydroxyethyl methacrylate (HEMA) with a mass ratio of 1/1, and 0–40% water contents, respectively. The adhesives were applied either onto the prepared dentin surface or unreactive substrates (such as glass slides), agitated for 15s, then light-cured for 40s. The DCs of the adhesives were determined using micro-Raman spectral and mapping analysis.

Results—The DCs of the adhesives cured on the dentin substrate were found to be significantly higher than those on the unreactive glass substrate. Moreover, the DCs of the adhesives displayed a decreasing trend as the distance from the dentin surface became greater. The chemical interaction of the acidic 2MP/HEMA adhesives with the mineral apatite in dentin was proposed to play a significant role for the observations. The chemical interaction could be validated by the spectral comparison in the phosphate regions of 1100 cm^{-1} and 960 cm^{-1} in the Raman spectra. The results also revealed a notable influence of water content on the DC of adhesives. The DCs of the adhesive at 10% water content exhibited the highest DC level for both substrates.

Conclusions—Interaction with dentin dramatically improved the degree of conversion of self-etching adhesives. Our ability to chemically characterize the a/d interface including *in situ* detection of the DC distribution is very important in understanding self-etching adhesive bonding under *in vivo* conditions.

Keywords

Self-etching; dentin; micro-Raman spectroscopy; photo-polymerization; degree of conversion

1. Introduction

Since the advent in the 1990s, self-etching adhesives have shown great advantages including simplification of the bonding procedure and reducing the potential for tooth sensitivity.^{1, 2} A typical self-etching adhesive composition is based on phosphorylated methacrylate monomers or phosphoric acid esters (PAE) that ionize when combined with water.^{3, 4} These acidic adhesive monomers could de-mineralize the hard dental tissue while simultaneously

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creating a strong micromechanical bond.^{5, 6} In addition, a particular chemical interaction⁷⁻⁹ formed between the functional monomers of self-etching adhesives and dental mineral (hydroxyapatite, HAp) was also reported. While most of the investigations focused on the relationship of the interaction/etching with interfacial strengths and morphology, or hydrolytic stability of the bonding,¹⁰⁻¹⁴ there has been little research regarding the influence of the interaction/etching on polymerization so far.

The degree of conversion (DC) of adhesive resin is one of the determining factors for a durable dentin bonding. A suboptimal DC might be responsible for the reduced interfacial strength and inherent interface instability.¹⁵ Studies^{12, 16-18} have indicated that the presence of unreacted monomers within the hybrid layer or dentin tubules was associated with the adhesive permeability and continuing etching. Therefore, obtaining a higher DC is very important to the quality of adhesives bonded to the dental hard tissues. In self-etching adhesive systems, the acidic monomers are capable of performing the etching and polymerization functions simultaneously through a unique design that combines the unsaturated double bond with phosphoric (or carboxylic) acid groups in a single molecule.^{3, 4} However, this might also offer the possibility that the polymerization is affected by the etching process, because the polymerizable reagents or initiators are especially sensitive to the environmental alterations (such as pH).^{3, 19, 20} Currently, detailed investigations about the correlation of the etching with polymerization are still not available despite of its theoretic and clinical importance.

In the present study, the DCs of the model self-etching adhesives containing bis[2-(methacryloyloxy) ethyl] phosphate (2MP)/2-hydroxyethyl methacrylate (HEMA) were investigated by using micro-Raman spectroscopy. To investigate the influence of the chemical interaction on the DC of the adhesive system, the polymerization was conducted on two substrates: reactive dentin and unreactive glass (as control). The spectral analysis was performed in order to confirm the existence of chemical interaction and its molecular origin. The objective of this study was to understand the relationship between chemical interaction and DC of the self-etching adhesives. The null hypothesis tested was that the chemical interaction of functional monomers with dental mineral would not affect the DC of the adhesive.

2. Materials and methods

2.1. Adhesive/dentin specimen preparation

The monomer mixtures used in this study were 2MP (Aldrich, Milwaukee, WI) and HEMA (Acros Organics, Morris Plain, NJ) with a mass ratio of 1/1. The photoinitiator system (all from Aldrich, Milwaukee, WI) consisted of camphorquinone (CQ) as photoinitiator and ethyl 4-dimethylaminobenzoate (4E) as coinitiator. The amount of CQ or 4E used in the experiment was 0.022 mmol per gram of monomer mixture. Different amount of water was also incorporated into the adhesive system to prepare solutions with water concentration of 0, 10, 20, 30, 40 wt.%.

Teeth used in this study were extracted non-carious, un-erupted human third molars, which were stored at 4°C in phosphate buffered saline (PBS) containing 0.002% sodium azide before use. The teeth were collected after the patients' informed consent under a protocol approved by the University of Missouri Kansas City adult health sciences institutional review board. The occlusal one-third of the crown was removed by means of a water-cooled low-speed diamond saw (Buehler Ltd, Lake Bluff, IL, USA). A uniform smear layer was created on the dentin surface by using wetted 600-grit silicon carbide sandpaper for 30 s. The tooth specimens were then sectioned equally perpendicular to the abraded surfaces to obtain rectangular slabs (10 × 2 × 1.5 mm). Each slab was notched from the middle position

of the bottom side opposite to the abraded surface. Each notch stopped approximately 0.5 mm beneath the abraded surface. The prepared dentin slabs were then treated with the 2MP/HEMA adhesives by applying the solutions onto the abraded dentin surfaces and agitated evenly for 15 s using a brush applicator. After being gently air-dried (10 s), the adhesive-coated dentin surfaces were light-cured for 40 s (600 mW/cm², Spectrum 800 halogen light, Dentsply, Milford, DE) with cover glass slips on the top. All of the prepared slabs were stored in an environment that keeps the specimens away from moisture and light for 24 hr. To avoid water contamination and potential release of un-reacted monomers during cutting, the slabs were not cut by the water-cooled saw used above, instead, they were fractured from the notches. The exposed adhesive/dentin interfaces were characterized by micro-Raman spectroscopy. As comparison, the 2MP/HEMA adhesives were also coated on glass slides following the same procedures as above.

2.2. Micro-Raman spectroscopy

To collect the Raman spectra of the specimens, a LabRam HR 800 Raman spectrometer (Horiba Jobin Yvon, Edison, NJ) using monochromatic radiation emitted by a He-Ne laser (a wavelength of 632.8 nm and excitation power of 20 mW) was employed. It was equipped with a confocal microscope (Olympus BX41), a piezoelectric (PI) XY stage with a minimum step width of 50 nm, and an air-cooled CCD detector of 1024X256. The spectra were Raman-shift-frequency calibrated with known lines of silicon. The laser of the Raman spectrometer was focused through a 100X Olympus objective to obtain a beam diameter of ~1 μm. For the specimens cured on dentin, Raman spectra were acquired starting from the a/d interface towards the adhesive layer at a 1-μm interval. For the specimens cured on glass, spectra were collected from the adhesive surfaces in contact with both the glass slide and glass cover slip. All the spectra were obtained over the spectral region of 200-2000 cm⁻¹ and with an acquisition time of 60 s. The degrees of conversion of the 2MP/HEMA adhesives were calculated based on the band ratios of 1640 cm⁻¹ (C=C stretching) and 1458 cm⁻¹ (CH₂ deformation). The intensities of these two bands were measured and the change of the band ratios with 1640 cm⁻¹/1458 cm⁻¹ was monitored. The DC was calculated by the following equation:

$$DC = \left(1 - \frac{Intensity_{1640cm^{-1}}^{sample} / Intensity_{1458cm^{-1}}^{sample}}{Intensity_{1640cm^{-1}}^{monomer} / Intensity_{1458cm^{-1}}^{monomer}} \right) \times 100\%$$

Two-point baseline and maximum band height ratio protocol were used to measure the band intensities. Each DC value was determined and averaged based on at least three Raman spectra. Data on the DC were analyzed using analysis of variance (ANOVA), together with the *T* test (*p*<0.05).

3. Results

Representative Raman spectra of the 2MP/HEMA adhesives with different amount of water light-cured on glass and dentin are shown in Figure 1. For the adhesives cured on glass, the spectra were collected from the adhesive surfaces in contact with glass slides. For the adhesives cured on dentin, the spectra were acquired from the adhesives in contact with dentin. The two Raman bands 1640 and 1458 cm⁻¹ (indicated by the arrows in Figure 1) were employed to determine the DC of the adhesive. It can be discerned from the figure that the band intensities of 1640 cm⁻¹ relative to those of 1458 cm⁻¹ for adhesives cured on dentin showed apparently different levels when compared with those on glass. More quantitatively, Figure 2 shows the comparison of DCs for the 2MP/HEMA adhesives with varying water amount cured on the two different substrates. The data indicated that the

adhesives cured on dentin substrates had significantly higher DCs than those on glass substrates regardless of the water content. The DCs of the adhesives cured on dentin all exceeded 90% (from 95.5% to 98.7%), while those of the adhesives on glass ranged from 19.1% to 85.7%. In addition, the DCs of the adhesives cured both on dentin and glass increased as the water content increased to 10%, and decreased with further increasing water content. However, less dependence on the water content was observed for the adhesives on dentin than those on glass.

To understand the mechanism of the above observations, representative Raman spectra of the 2MP/HEMA adhesive containing 30% water content cured on glass and dentin were compared as shown in Figure 3. It indicated that the spectrum of the adhesive cured on dentin showed stronger phosphate bands near ~ 1100 - 1070 and 960 cm^{-1} . Meanwhile, the relative band intensity of the 1640 to 1458 cm^{-1} was much lower than that of the adhesive on glass, indicating a much higher DC.

The DCs of the 2MP/HEMA adhesives as a function of distance from the dentin surface were also investigated. Figure 4(a) shows the typical micro-Raman mapping spectra in the region of 1300 - 1900 cm^{-1} across from the dentin surface into the adhesive layer (The adhesive contains 30% water content). The DCs of the adhesives containing different water content as a function of location are shown in Figure 4(b). It indicated a consistent decreasing trend over location for all of the adhesives. Within the location range studied, all of the DCs obtained were greater than 90%. In terms of the influence of water content, the data displayed that the DC increased as water content increasing from 0% to 10%, and decreased when the water content was further raised to 20, 30, and 40%.

Figure 5(a) shows representative micro-Raman mapping spectra in the region of 900 - 1600 cm^{-1} across from the dentin surface into the adhesive layer. It showed that the intensity of the phosphate band at $\sim 960\text{ cm}^{-1}$ band decreased as a function of distance away from the dentin surface. The quantitative plot of 960/1458 ratios as a function of location is shown in Figure 5(b). The result indicated that the calculated 960/1458 ratios declined gradually and then leveled off as the location from the dentin surface interface became farther.

4. Discussion

The proposed null hypothesis was rejected. The present micro-Raman investigation has clearly revealed the difference in the photopolymerization efficacy of 2MP/HEMA self-etching adhesives cured on two different substrates of dentin and glass. The DCs of the adhesives cured on dentin were considerably higher when compared with those cured on the glass substrate (Figures 1, 2). Glass can be considered as chemically “inert” to the current self-etching adhesive system and thus should not impose influence on the DC of the adhesives. The observed differences in DCs between the two substrates likely were arisen from dentin.

The major component in dentin is hydroxyapatite (HAp), which accounts for more than 90 wt % and 70 wt % of enamel and dentin, respectively.²¹ The contemporary self-etching adhesives have been designed to penetrate through the smear layer into the intact underlying enamel and dentin by dissolving HAp crystallites.²²⁻²⁵ The penetration and demineralization process neutralize the acidic functional monomers in the adhesives.^{4, 8} In the current study, the Raman spectra have shown significant information about the neutralization (or chemical reaction) of the 2MP/HEMA adhesive by HAp. In the spectral comparison (Figure 3), new or higher bands near ~ 1100 - 1070 and 960 cm^{-1} were seen in the spectrum of the adhesive cured on dentin. These bands are associated with $\nu_3\text{ PO}_4$ and $\nu_1\text{ PO}_4$ of calcium phosphate complexes respectively.^{26, 27} The appearance of these bands was attributed to the reaction of

the acidic monomer 2MP with the mineral HAp. The neutralization reaction also leads to increase of the adhesive pH value due to the buffering effect induced by HAp. In a separate investigation²⁸ with the 2MP/HEMA adhesive, the pH value of the adhesive system (with 20 wt.% water content) increased from 0.3 to 1.2 by incorporating 4 wt.% HAp. Previous results showed that low pH could considerably affect the initiating efficiency of amines (such as 4E as co-initiators used in the current study), thus resulted in poor polymerization.^{3, 19, 20, 29} Therefore, under a circumstance of high acidity (without buffering of HAp) like on the glass substrate, the DCs of the adhesives were relatively lower. However, when the adhesives were applied onto the dentin, the buffering effect by HAp would repress the negative influence of monomer's acidity on the initiating efficiency of co-initiator 4E. As a result, the degrees of monomer conversion during polymerization were significantly improved.

The buffering effect of HAp can be also employed to understand the position dependence of the DC as presented in Figure 4. The figure indicated a decreasing trend of DC as the distance from the dentin surface increased. Since the resulting DC of the current adhesive system strongly depended on the chemical reaction between the functional monomer and HAp (Figures 2 and 3), the result in Figure 4 might have suggested a similar decreasing extent of the chemical reaction (to that of the DC) within the adhesives. This was validated by the plot of 960/1458 ratios as a function of location away from the dentin surface (Figure 5). As mentioned above, the 960 cm^{-1} band is related to the formation of calcium phosphate complexes,^{26, 27} thus the 960/1458 (1458 cm^{-1} band as an internal standard) can serve as the measure of the extent of chemical reaction between acidic monomers and HAp. The observation indicated that there might be relatively higher amount of calcium involved in the reaction at the locations closer to the dentin surface. Consequently, a higher degree of monomer conversion was obtained. The consistent trend of the DC (Figure 4) and extent of chemical reaction (Figure 5) demonstrated again the significant role of the acidic monomer interaction with mineral in the polymerization of the present self-etching adhesives.

Our finding of improved adhesive polymerization on dentin might expand current understanding on the binding mechanism of self-etching adhesives with dentin. The adhesion of self-etching adhesives to dentin was thought to be arisen from different processes.⁵⁻⁹ An established mechanism is micro-mechanical interlocking. Based on high-resolution microscopic analysis, Nakabayashi et al.⁶ proposed that the bonding performance of self-etching adhesives depended on micro-mechanical interlocking of resin and collagen through the formation of hybrid layer. Recently, it was found that the interaction of the acidic functional monomer with the dental minerals could also be important in creating an effective bond between dentin/enamel and self-etching adhesives.⁷⁻⁹ Fu et al.⁷ confirmed the existence of specific interaction between the phosphoric acid ester (PAE) and HAp by using ¹³P CP-MAS NMR spectroscopy and FTIR. Thermo-cycling and micro-tensile bond strength testing conducted by Yoshida et al.⁹ further demonstrated the hydrolytic stability of the chemical bonding (through the specific interaction) induced by 10-methacryloyloxydecyl dihydrogen phosphate (MDP) and dentin. The highly improved DC of the self-etching PAE adhesives on dentin found in this study may be another important process/mechanism to be considered, since the polymerization of adhesives directly determines the quality of the bonded interface. Due to the importance of the interaction between the acidic monomers and dental mineral, rubbing or massage during self-etching adhesive application is especially necessary to ensure thorough contact and mixing.

Water plays a critical role in the performance of self-etching adhesives binding to dental substrates.³⁰⁻³² The presence of water is generally an interfering factor for the polymerization of adhesives.^{18, 33} This can be validated from the data presented in Figure 2. It was found that both adhesives cured on dentin and glass showed a similar DC trend of

first increasing (at 0-10% water content) and then decreasing (at 10-40% water content) with the water amount. A prescribed amount of water could reduce the viscosity and increase the DC of the water-compatible resin.¹⁸ This explained the increase of DC as the water content increased from 0% to 10% in the system. As the water content was further raised up to 40%, the dilution of the system might have reached an extent that there were no adequate free radicals for polymer chain propagation. As a result, the degree of conversion would decrease. The results in Figure 2, however, also disclosed that the DCs of the 2MP/HEMA adhesives cured on dentin showed much less dependence on water content as compared with those on glass. This was ascribed to the enhancement of polymerization induced by HAp, which universally elevated the DCs of all the adhesives (to the levels all higher than 90%) despite of the different water content.

In summary, the micro-Raman spectroscopy results disclosed that the DCs of self-etching adhesives were significantly higher when light-cured on dentin than on unreactive substrate (glass). In addition, the DCs of the monomers cured on dentin showed a decreasing trend as the distance from the dentin surface increased. The influence of water content on the DCs was also elucidated. Raman spectral analysis indicated that the results were most likely ascribed to the chemical interaction between the acidic monomer and HAp in dentin. The current finding suggested that the chemical interaction was especially essential for the acidic self-etching adhesives to achieve higher DC and thus better binding.

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Figure 1.

Representative Raman spectra of the 2MP/HEMA adhesives with different amount of water light-cured on glass and dentin for 40 s, respectively. The arrows indicate the Raman bands used for the DC calculation. For the specimens cured on glass, the spectra shown were collected from the adhesive surface in contact with glass slides. For the specimens cured on dentin, the spectra were acquired from the adhesive in contact with dentin.

Figure 2. Comparison of degree of conversions for the light-cured 2MP/HEMA adhesives (with different amount of water) on glass and dentin

Figure 3.
Representative Raman spectra of the light-cured 2MP/HEMA adhesive (containing 30% water) on glass and dentin

Figure 4.

(a) Representative micro-Raman mapping spectra in the region of $1300\text{--}1900\text{ cm}^{-1}$ across from the dentin surface into the adhesive layer (containing 30% water); the arrows indicate the Raman bands used for the DC calculation. (b) Degree of conversion plots of the light-cured 2MP/HEMA adhesives with different amount of water as a function of location across the dentin surface and bulk adhesive layer.

Figure 5.

(a) Representative micro-Raman mapping spectra in the region of $900\text{--}1600 \text{ cm}^{-1}$ across from the dentin surface into the adhesive layer (containing 30% water); the arrows indicate the Raman bands used for the 960/1458 calculation. (b) 960/1458 plot of the light-cured 2MP/HEMA adhesive (containing 30% water) as a function of location across the dentin surface and bulk adhesive layer.