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Hydroxyapatite Effect on Photopolymerization of Self-etching Adhesives with Different Aggressiveness

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Abstract

Objective—To understand the correlation of the acidic monomer/hydroxyapatite (HAp) reaction with the photopolymerization behavior of self-etching adhesives with different aggressiveness.

Methods—Two commercial self-etching adhesives the strong Adper Prompt L-Pop (APLP, pH~0.8) and the mild Adper Easy Bond (AEB, pH~2.5) were used. HAp powders were incorporated into both adhesives to acquire solutions with concentrations of 0, 1, 3, 5, 7 wt%. The attenuated total reflectance Fourier transform infrared (ATR/FT-IR) technique was employed to collect the *in-situ* spectra during light-curing, from which the degree of conversion (DC) and polymerization rate (PR) were calculated. The pH of each tested solution was also measured.

Results—Without HAp incorporation, the DC and PR of the strong APLP (7.8% and 0.12%/s, respectively) were much lower than those of the mild AEB (85.5% and 5.7%/s, respectively). The DC and PR of APLP displayed an apparent increasing trend with the HAp content. For example, the DC increased from 7.8% to 58.4% and the PR increased from 0.12 to 3.8%/s when the HAp content increased from 0 to 7 wt%. In contrast, the DC and PR of AEB were much less affected by the HAp content. The observations were correlated well with the spectral and pH changes, which indicated that APLP underwent a higher extent of chemical reaction with HAp than AEB.

Conclusions—The results disclosed the important role of the acidic monomer/HAp chemical reaction in improving the photopolymerization of the strong (low-pH) self-etching adhesives such as APLP. The phenomenon of polymerization improvement strongly depended on the adhesive aggressiveness.

Keywords

Self-etching; hydroxyapatite; FTIR; photo-polymerization; degree of conversion

1. Introduction

Self-etching adhesives have steadily gained growing popularity in today's dental practices due to their apparent advantages.^{1,2} The contemporary self-etching adhesives contain acidic functional monomers that condition and prime the dental tissues simultaneously.^{3,4} In order to achieve reliable binding, the acidic monomers are designed to de-mineralize (or pervade) the smear layer and penetrate into the superficial parts of dentin by dissolving or partially

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dissolving hydroxylapatite (HAp) crystallites.^{5–8} The interfacial reaction/interactions between the HAp-based dental tissues and acidic functional monomers were considered to be important for the actual adhesive performance.^{4, 9–13} The manner of the functional molecules interacting with dental mineral has been described as the “adhesion/ decalcification (A/D)” concept.^{14–16} It is proposed in this concept that initially all acids chemically bond to calcium of HAp at the adhesion step. Subsequently at the decalcification step, whether the molecules remain bonded or de-bonded depends on the stability of the formed calcium salts.

The functional, acidic monomer/dental mineral interaction is closely related to the classifications of the self-etching adhesives, especially to their aggressiveness (usually quantified by the pH value). Self-etching adhesives vary in their aggressiveness by virtue of the composition and functional monomer concentration in the systems.^{17, 18} Efforts have been made to classify the self-etching adhesives as mild (pH>2), intermediate (1< pH < 2), and strong (pH <1).^{4, 13, 19} Depending on their aggressiveness, the self-etching adhesives may differ in their ability of penetrating into dentin smear layers and the depth of demineralization. A more aggressive system could completely dissolve/de-mineralize the smear layer/plugs and produce etching patterns comparable to those achieved by phosphoric acid etching.^{18–20} Studies have disclosed variable interfacial properties and features such as bonding strength and durability^{9, 21–23} and morphology^{24, 25} among self-etching adhesives with different aggressiveness. As a determining factor for successful bonding, the conversion of monomers during the polymerization^{26–28} might be also interfered by the etching step and acidic monomer/HAp interaction,²⁹ since the processes of etching (on HAp-based tissues) and polymerization occur sequentially. Self-etching adhesives with different aggressiveness might demonstrate distinct polymerization behaviors. However, there has been little work reported in this regard so far.

In the present study, the influence of acidic monomer/HAp chemical reaction on the photopolymerization was investigated by employing two widely-used all-in-one self-etching adhesives: Adper Prompt L-Pop (APLP) and Adper Easy Bond (AEB). Both of the adhesives are methacrylated phosphoric esters-based and from the same manufacturer. However, they differ greatly in their aggressiveness: AEB has a pH of about 2.5 (classified as mild), while that of APLP is much lower as about 0.8 (classified as strong). The considerable difference in acidity provided a great opportunity to investigate the role of aggressiveness in the acidic monomer/HAp reaction and the photopolymerization behaviors. Different amounts of HAp powders were incorporated in the solutions of each adhesive so that the varying level of dentin demineralization or interaction with dental mineral could be mimicked. The objective of this study was to understand the correlation of the acidic monomer/HAp reaction with the photopolymerization behavior of self-etching adhesives with different aggressiveness. The null hypothesis tested was that there would be no difference in photopolymerization between the strong and mild self-etching adhesives with and without incorporation of HAp.

2. Materials and methods

2.1. Adhesive preparation

Two commercial all-in-one self-etching adhesives APLP (3M ESPE Dental Products, St Paul, MN) and AEB (3M ESPE Dental Products) were used in the study. The compositions of the adhesives are shown in Table 1. To investigate the effect of mineral content on photopolymerization, HAp ($\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$, the particle size ~0.5–5 μm , Aldrich, Milwaukee, WI, USA) powder was added to the neat adhesive systems to obtain mass fractions of 0, 1, 3, 5, 7 wt%. Shaking and sonication were required to yield well-mixed

solutions. All of the prepared solutions were kept on shaker for at least 24 hrs before any further characterization.

2.2. Real-time ATR/FT-IR measurement

The polymerization process was monitored by using a Fourier transform infrared spectrometer equipped with an ATR attachment (Spectrum One, Perkin-Elmer, Waltham, MA, USA) at a resolution of 4 cm^{-1} . A small volume ($\sim 0.03\text{ ml}$) of the adhesives (or adhesive/HAp solutions) was placed on the crystal top-plate of the ATR accessory, and covered with a clear, polyester film (Mylar, $22 \times 22 \times 0.25\text{ mm}$, Fisher Scientific, Pittsburgh, PA, USA). The ATR crystal was diamond with a transmission range between 650 and approximately 4000 cm^{-1} . Time-based spectral acquisition software (Spectrum TimeBase, Perkin-Elmer) was used for continuous and automatic collection of spectra for 180 s during polymerization at a rate of one spectrum every 0.4–0.6 s. Fifty spectra were initially acquired and acted to supply absorption parameters of the specimen in the uncured state, after which a 10-s exposure from a conventional dental light polymerization unit (Spectrum Light, Dentsply, Milford, DE, USA) emitting 550 mW/cm^2 was applied. The output of 550 mW/cm^2 was measured by using a visible curing light meter (CURE RITE, EFOS Inc., Williamsville, NY, USA) with a digital display. The distance from the top of the Mylar film to the distal end of the light guide was kept at $\sim 2\text{ mm}$. Three separate replications for each adhesive formulation were conducted.

2.3. Calculation of the degree of conversion (DC) and polymerization rate (PR)

Two characteristic bands 1637 cm^{-1} (stretching of methacrylate double bond $\text{C}=\text{C}$) and 1715 cm^{-1} (stretching of carbonyl group $\text{C}=\text{O}$) were employed to calculate the DC of photopolymerization. The intensities of these two bands were integrated based on band height methodology and the change of the band ratios profile $1637\text{ cm}^{-1}/1715\text{ cm}^{-1}$ was monitored. The DC was calculated by the following equation:³⁰

$$DC = \left(1 - \frac{\text{Absorbance}_{1637\text{ cm}^{-1}}^{\text{sample}} / \text{Absorbance}_{1715\text{ cm}^{-1}}^{\text{sample}}}{\text{Absorbance}_{1637\text{ cm}^{-1}}^{\text{monomer}} / \text{Absorbance}_{1715\text{ cm}^{-1}}^{\text{monomer}}}\right) \times 100\%$$

Two-point baseline and maximum band height ratio protocol were used to measure the absorption intensity. The last 20 spectra of time-resolved spectra were employed to generate a single mean DC value, and the three mean values were averaged to obtain the final DC of the adhesive formulation. The PR was determined using the maximum slope of linear region of the DC-time plots by using the least square linear fitting. The polymerization rate reported was the average of the three individual slopes for the individual runs for a given specimen group. A one-way analysis of variance (ANOVA, $\alpha = 0.05$) was used (GraphPad InStat version 3.06, GraphPad Software, Inc.) to analyze the data on the DC and PR.

2.4. pH measurement

The acidity of each test solution was measured with a pH meter (Accumet Excel XL15, Fisher Scientific, Pittsburgh, PA, USA). Prior to measuring, the pH electrode was calibrated with buffer solutions at pH 4.00 and 7.00. Three specimens were prepared for the measurements of each solution and the pH results were averaged.

3. Results

Figure 1 shows the representative real-time spectra of AEB and APLP (both with addition of 7 wt% HAp) during the photopolymerization. In the figure, only the spectra from 30 s to 60

s were demonstrated because the major monomer conversion took place within this time period. The figure displayed that the absorbance (or the height) of 1637 cm^{-1} band decreased while that of 1715 cm^{-1} band remained almost unchanged as polymerization proceeded. The decrease in absorbance at 1637 cm^{-1} indicates consumption of methacrylate C=C bonds during polymerization. By integrating the heights of 1637 and 1715 cm^{-1} bands, and normalizing with respect to their band heights at 0 s, the DC can be quantified. The DC plots as a function of time for two adhesives are shown in Figure 2. Without HAp incorporation, the DC-time plot for APLP remained flat, indicating very minimum monomer conversion took place. To study the influence of HAp on the polymerization of the two self-etching adhesives, HAp with concentration of 1, 3, 5, 7 wt% was incorporated into the systems. The results showed that the polymerization kinetics of APLP and AEB was significantly different. The DC of APLP increased consistently as the HAp content was enhanced from 0 to 5 wt%. If the HAp content was further elevated to 7 wt%, there was no additionally significant increase with the DC. In contrast, AEB exhibited similar DCs regardless of the amount of HAp added. In addition, the DCs of AEB were always higher than those of APLP. More quantitative data of the DC and PR for the two adhesives are presented in Figure 3, which clearly showed their distinct DC and PR dependence on the HAp content.

Figure 4 shows the spectra of two self-etching adhesives before and after the incorporation of HAp. The spectrum of HAp is also given in the figure for reference. The results indicated that after the addition of HAp, the spectral changes of AEB and APLP were dramatically different, especially in the phosphate region ($\sim 900\text{--}1100\text{ cm}^{-1}$). After the addition of 7 wt% HAp in APLP, the absorbance of 1074 cm^{-1} band (HPO_4^{2-} stretching) increased while that of 1034 cm^{-1} band (PO_4^{3-} stretching) decreased considerably. For AEB, the spectra in this phosphate region appeared identical before and after the addition of 7 wt% HAp. Only the band absorbance in this region was slightly enhanced.

The pH values of both adhesives with varying amounts of HAp were also measured to find out the role of the aggressiveness in the acidic monomer/HAp reaction and photopolymerization. As shown in Figure 5, originally (at 0 wt% HAp) AEB and APLP displayed different pH values, 2.5 and 0.8, respectively. As various amounts of HAp were added to the adhesives, distinct trends of the pH value changing with the HAp content were observed. The pH of APLP showed a constantly increasing trend with the HAp content. In contrast, The pH of AEB only slightly enhanced as 1 wt% HAp was incorporated, and then showed no significant change with further increasing the HAp content up to 7 wt%.

4. Discussion

The proposed null hypothesis was rejected. The present FTIR results have clearly revealed the distinct polymerization behaviors between the strong APLP and mild AEB self-etching adhesives without and with incorporation of HAp. Surprisingly, it was noticed that without incorporation of HAp, the strong APLP could barely polymerize (Figs. 2 and 3). The DC and PR of APLP were only 7.8% and 0.12%/s, respectively, which were much lower than those of AEB (85.5% and 5.7%/s, respectively). With the addition of various amounts of HAp, it was also interesting to discern that the DC and PR of the strong APLP displayed an apparent increasing trend with the HAp content. In contrast, there was much less effect of the HAp content on the DC and PR of the mild AEB.

The above different trends with the HAp content could be associated with the variation in chemical reaction/interaction of the two adhesives with HAp. A higher extent of chemical reaction with HAp took place in APLP than AEB. This could be verified by the spectral comparison of the two adhesives before and after the addition of HAp. As indicated in

Figure 4, the absorbance of HPO_4^{2-} band (1074 cm^{-1}) increased relative to that of PO_4^{3-} band (1034 cm^{-1})^{31, 32} in the spectrum of APLP with 7 wt% HAp, compared with that of APLP without HAp. The spectral change suggested the occurrence of chemical reaction between the strong self-etching adhesive (APLP) and HAp.^{33, 34} However, such spectral change was not observed for AEB. Instead, the IR spectral absorbance in this phosphate band region of AEB was only slightly elevated. If the spectrum of HAp was also compared, it could be seen that the elevated spectral absorbance was mainly due to overlapping with the major bands of HAp at 1028 cm^{-1} and 1092 cm^{-1} (PO_4^{3-} stretching).³² The result clearly indicated that mixing of HAp with AEB involved much less extent of chemical reaction (and more extent of simply physical mixing) compared with APLP. The present spectral comparison was consistent with our visual observation of HAp solubility in the two adhesives: HAp could easily dissolve in APLP to obtain a clear solution, while it barely dissolved in AEB with the resultant solution being opaque all the time.

The discrepancy of their chemical reaction with HAp can be also demonstrated by the pH changes of the two adhesives as a function of the HAp content (Figure 5). As shown in Figure 5, the pH dependence on the HAp content for two adhesives was substantially different. The pH of APLP increased consistently with the addition of HAp, while that of AEB was raised only in the case that 1 wt% HAp was incorporated (that was, no significant increase of pH when the HAp content was $>1\text{ wt}\%$). Within the investigated HAp content range (0 to 7 wt%), the overall pH enhancement of APLP was 0.80 (from 0.84 to 1.64), in contrast to a much lower value of 0.34 (from 2.50 to 2.84) for AEB. The observed difference in the pH changes (with the HAp incorporation) was most likely ascribed to their originally distinct pHs (0.8 and 2.5 for APLP and AEB, respectively). Our results indicated that the chemical reaction of the self-etching adhesives with HAp strongly depended on the aggressiveness of the adhesives.

The variation in chemical reaction of the two adhesives with HAp and the pH changes most likely influenced their respective initiator systems differently, thus their resulting DC and PR. An inherent problem^{17, 35, 36} with photopolymerization of the self-etching adhesives is the compromised initiating efficacy arisen from the reaction of the acidic monomers with amines used in the initiator systems, such as camphorquinone/amine system in the current AEB and APLP adhesives. The reaction with an acidic monomer can reduce the concentration of the amine, and thus the amount of the formed amine radical that initiates the photopolymerization. Therefore, high acidity would negatively influence the degree of monomer conversion and the polymerization rate. This influence from the acidic monomer(s) had, to a great extent, contributed to the observed extremely low levels of DC and PR for APLP when no HAp was added. As different amount of HAp was incorporated into APLP, the chemical reaction with HAp could consume the hydrogen ions from the acidic functional monomer and increase the pH of the system.^{5, 19} The more HAp was added, the higher level of the chemical reaction would occur, thus the more enhanced pH would be achieved. (Figure 5) As a result, the initiation efficacy and polymerization of the APLP system were also dramatically improved.

It was noticed that the PC and PR of AEB were always higher than those of APLP despite of the HAp content (Fig. 3). Besides its higher pH which is favorable for photopolymerization as discussed above, the specific chemical composition of AEB may also play important roles.^{13, 17, 18, 37} For example, contemporary self-etching adhesives usually contain a widely used component of Bis-GMA. This reagent can produce a cross-linked, three-dimensional resin network due to its high reactivity.^{38, 39} Therefore, the higher content of Bis-GMA enables the adhesives to achieve more optimized polymerization. The presence of Bis-GMA in the current two adhesive systems can be confirmed from the characteristic IR bands at 1608 and 1510 cm^{-1} (phenyl ring C=C stretching, Figure 4). However, the

intensities of these two bands were different between two adhesives, with AEB showing higher intensities than APLP. This fact suggested that AEB contained higher amount of Bis-GMA than APLP, which most likely also contributed to the higher DC and PR. Another compositional difference that might be responsible for the different polymerization efficacy was related to silica filler. Compositional comparison (Table 1) showed that the formulation of AEB included silica filler, whereas that of APLP did not. Silica fillers are added to improve mechanical properties of resins, while reducing their polymerization shrinkage. The addition of these materials, at the same time, could raise the viscosity of the system, thus likely lead to the improvement of the polymerization.^{40, 41} Similarly, the greater content of viscous Bis-GMA in AEB than APLP might produce a higher viscosity, therefore benefited the polymerization. Furthermore, other compositional discrepancies such as in water and photoinitiator contents, might be also closely associated with the polymerization potential of the two self-etching adhesives. How these factors affect photo-polymerization of self-etching adhesives certainly deserves further studies.

The current results suggested that photopolymerization of the strong APLP self-etching adhesive greatly depended on the interaction/reaction with HAp. The chemical reaction with the dental mineral (HAp) could considerably benefit the photo-polymerization of strong self-etching adhesives such as APLP. For example, The DC of APLP was only 7.8% at 0 wt% HAp, but was increased to 58.4% at 7 wt% HAp. However, such dramatic polymerization improvement or strong dependence on the HAp content was not observed in the mild AEB self-etching adhesive (Figure 3). The DC of AEB was 87.5% at 0 wt% HAp, was only slightly increased to 89.6% at 7 wt% HAp. Such distinct polymerization behaviors should be taken into account when applying the adhesives to dental bonding substrates.

To further understand ramifications of current findings, more detailed *in-situ* micro-Raman studies are in progress to investigate the effect of chemical reaction/interaction with dentin surface on polymerization of the adhesive layer. It would be interesting to see how the two adhesives with different aggressiveness polymerize on the dentin surface. For APLP, the maximum DC value was 60.3% at 5 wt% HAp, slightly dropped to 58.4% when the HAp content increased to 7 wt% (Fig.3). It would be desirable to know if the DC value of this adhesive would be different (i.e., higher) when interacting with dentin surface, and if there would be a lack of curing throughout the adhesive layer. For AEB, the polymerization improvement of the adhesive solutions in the presence of HAp was not observed in general by using FTIR. It should be noted that limited amount of acidic monomers in AEB should have also chemically reacted with HAp if considering its pH increase from 2.50 to 2.84 with addition of 1 wt% HAp (Figure 5). The reaction might be ascribed to superficial dissolution of HAp that induced by the adhesive adsorption and subsequent deposition of adhesive-calcium salt.^{14–16} If this is the case, it would be interesting to see if the local reaction/interaction would further increase the DC of the adhesive in contact with dentin. The results may expand the current understanding on the binding mechanism of self-etching adhesives with dental mineral.

5. Conclusion

The polymerization behaviors of APLP and AEB with incorporation of various amount of HAp were significantly different. The strong APLP could barely polymerize without incorporation of HAp. The DC and PR of the strong APLP displayed an apparent increasing trend with the HAp content. Such notable polymerization improvement or strong dependence on the HAp content was not observed in the mild AEB self-etching adhesive. In contrast, the PC and PR of the mild AEB were always much higher than those of APLP despite of the HAp content. There was much less effect of the HAp content on the photopolymerization of AEB. The results were correlated with the spectral changes, which

indicated that APLP underwent a higher extent of chemical reaction with HAP than AEB. The chemical reaction/interaction and the polymerization strongly depended on the aggressiveness of the adhesives.

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Figure 1. Representative time-resolved FTIR spectra in the C=O and C=C regions of (a) Adper Easy Bond; and (b) Adper Prompt L-Pop collected at different times (from 20 s to 60 s, every 3 s are shown here). Both adhesive solutions of (a) and (b) contained 7 wt% HAp.

Figure 2. Real-time degree of conversion (DC) plots of (a) Adper Easy Bond; and (b) Adper Prompt L-Pop in the presence of different content of HAp.

Figure 3.
Degree of conversion (DC) and polymerization rate (PR) for Adper Easy Bond and Adper Prompt L-Pop in the presence of different content of HAp.

Figure 4. Representative FTIR spectra of Adper Easy Bond and Adper Prompt L-Pop before and after the addition of 7 wt% HAp. Representative spectrum of hydroxylapatite (HAp) is also given for reference.

Figure 5.
pH values of Adper Easy Bond and Adper Prompt L-Pop in the presence of different content of HAp.

Table 1

Compositions of one-step self-etching adhesives used in this study

Adhesive	Composition
Adper Prompt L-Pop (APLP, 3M ESPE Dental Products, St Paul, MN)	Methacrylated phosphoric esters, bis-GMA, initiators based on camphorquinone, stabilizers, water, 2-Hydroxyethyl methacrylate (HEMA), polyalkenoic acid
Adper Easy Bond (AEB, 3M ESPE Dental Products, St Paul, MN)	2-hydroxyethyl methacrylate (HEMA), bis-GMA, methacrylated phosphoric esters, 1,6 hexanediol dimethacrylate, polyalkenoic acid (Vitrebond copolymer), finely dispersed bonded silica filler, ethanol, water, initiators based on camphorquinone, stabilizers