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The effect of hydroxyapatite presence on the degree of conversion and polymerization rate in a model self-etching adhesive

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Abstract

Objective—The effect of hydroxyapatite (HAp) content on photopolymerization of a model self-etching adhesive was studied by using attenuated total reflectance Fourier transform infrared (ATR/FT-IR) spectroscopy.

Materials and methods—The model adhesive contained two monomers: bis[2-(methacryloyloxy)ethyl] phosphate (2MP) and 2-hydroxyethyl methacrylate (HEMA) using a 1:1 mass ratio, representing an acidic formulation. Camphorquinone and ethyl 4-dimethylaminobenzoate were added to enable visible light photopolymerization in a constant concentration of 0.022 mmol per gram monomer. HAp [$\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$] powder were added to the test solutions to obtain mass fraction of 0, 1, 2, 3, 4 wt%. The degree of conversion (DC) and the polymerization rate (PR) with/without HAp were determined using ATR/FT-IR with a time-based spectrum analysis.

Results—Monomer DC and PR were significantly enhanced by addition of HAp. Incorporation of 4 wt% of HAp increased DC from 20.8 (± 0.3) % to 93.4 (± 1.1) %, and PR from 0.42 (± 0.01) %/s to 3.21 (± 0.07) %/s. The pH of adhesive solutions was measured and correlated with DC and PR. The pH of test solutions was also controlled using a base (sodium hydroxide, NaOH) to similar values as when using HAp. Results indicated that both the DC and PR increased with increasing pH, regardless of additive, confirming the role of pH on polymerization. From the IR spectral comparison, changes in molecular structures of the self-etching adhesive after the addition of HAp were observed, which were correlated with the specific interaction between 2MP and HAp. The effect of viscosity was also proposed to be another possible reason for the improved polymerization.

Significance—The photopolymerization of a self-etching adhesive was enhanced / accelerated in the presence of HAp. The results provide the critical information for understanding the interactions/bonding between self-etching adhesives and tooth substrates.

Keywords

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

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1. Introduction

During the past two decades, the field of adhesive dentistry has undergone remarkable progress. In particular, development of self-etching adhesives has attracted considerable interest, because these materials simplify the clinical application procedure without compromising the bond strength and retention in dental restoration [1–5]. There is a trend toward eliminating as many steps as possible in the bonding protocol. Self-etching adhesives are designed to combine both an etching function and resin-forming function, thus eliminating a separate rinsing step. Compared with early generation dental adhesives, self-etching adhesives are less time-consuming, less technique sensitive, and easier to achieve an acceptable seal [6, 7]. Currently self-etching adhesives can be found in numerous applications in daily dental practice, due to their outstanding characteristics and advantages.

Contemporary self-etching and priming adhesives usually incorporate specific monomer molecules that combine unsaturated polymerizable functions with either carboxylic or phosphoric acid groups [8, 9]. After being applied, self-etching adhesives can penetrate into the intact, underlying enamel or dentin, and polymerize *in situ*. Simultaneously, enamel and dentin are partly decalcified and dissolved in self-etching adhesive monomers [4, 5, 10, 11]. Hydroxyapatite (HAp), which accounts for more than 70 wt% and 90 wt% of dentin and enamel respectively, is easily dissolved in a self-etching adhesive and is redeposited within the demineralized dentin collagen network and demineralized enamel substrate [12]. Residual HAp may also serve as a template for additional chemical interaction with the adhesive's functional monomer, and is regarded as especially essential for long-term stability of the bonded interface [12, 13]. However, the role of HAp in polymerization of the self-etching adhesives has not been elucidated. Previous work [14] has shown that the degree of conversion (DC) of self-etching monomers at the interface (with higher level of HAp) was consistently greater than that within the tubules, which indicated that, besides water content, HAp might directly affect polymerization of self-etching adhesives. However, detailed information of polymerization process of self-etching resin in the presence of mineral (HAp) has not been reported.

Thus, the purpose of the current study was to elucidate the role of HAp on the photopolymerization process of a model, self-etching adhesive. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR/FT-IR) was employed, which provided real time information regarding adhesive solutions before, during, and after light-curing. Since the buffering effect of HAp on self-etching monomers might modify acidity of the adhesive system, the pH of test solutions was monitored and correlated with DC and PR. Solutions with controlled pH using sodium hydroxide (NaOH) were also prepared to evaluate the effect of pH on polymerization. The hypothesis tested was that presence of HAp in a model self-etching adhesive would increase the pH of the system and significantly increase both the degree of conversion as well as the polymerization rate.

2. Materials and methods

2.1. Self-etching model adhesive preparation

The monomer mixtures were based on a model self-etching dentin adhesive consisting of bis[2-(methacryloyloxy)ethyl] phosphate (2MP) (Sigma-Aldrich, Milwaukee, WI, USA) and 2-hydroxyethyl methacrylate (HEMA) (Acros Organics, Morris Plain, NJ, USA), in a mass ratio of 1/1. This composition is similar to those of commercial two-step, self-etching dentin adhesives, such as Clearfil Liner Bond 2V (Kuraray America, Inc., New York, NY, USA). The photoinitiator system (all from Aldrich, Milwaukee, WI, USA) consisted of camphorquinone (CQ) as a photoinitiator and ethyl 4-dimethylaminobenzoate (4E) as a coinitiator, present in 0.022 mmol per gram each of all monomer mixtures.

Twenty weight percent content of deuterium oxide (D₂O, Cambridge Isotope Laboratories, Inc., Andover, MA, USA) was used to activate monomer acidity. In addition, use of D₂O instead of H₂O avoided any potential interference of IR absorption within the wavenumber bands of interest. To investigate the effect of mineral content on photopolymerization, HAP (Ca₁₀(OH)₂(PO₄)₆, Aldrich, Milwaukee, WI, USA) powder was added to the neat model adhesive system to obtain mass fractions of 1, 2, 3, 4 wt%. Shaking and sonication were required to yield well-mixed solutions.

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 [15–18]. A small volume of the adhesive/water mixtures was placed on the diamond crystal top-plate of the ATR accessory, and covered with a clear, polyester film (Mylar, 22 × 22 × 0.25 mm, Fisher Scientific, Pittsburg, 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 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 40-s exposure from a conventional dental light polymerization unit (Spectrum Light, Dentsply, Milford, DE, USA) emitting 550 mW/cm² was applied. The output of 550mW/cm² 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 ~2 mm. Real-time IR spectra were continuously recorded for 300s after light activation began. 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 C=C) and 1715 cm⁻¹ (stretching of carbonyl group C=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 with 1637 cm⁻¹ /1715 cm⁻¹ was monitored. The DC was calculated by the following equation [17]:

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

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 solution at pH 7.00. Three specimens were prepared for the measurements for each solution and the pH results were averaged.

2.5 Ancillary pH-adjusting additive

In order to validate the influence of pH on the polymerization behavior, the acidity of the neat model adhesive solution was adjusted to pH values near those when using HAp by incorporating controlled amounts of a laboratory base: 0.2, 0.4, 1, 2 wt% of sodium hydroxide (NaOH, Sigma-Aldrich, Milwaukee, WI, USA).

3. Results and discussion

Figure 1(a) shows a typical IR spectrum of the 2MP/HEMA model adhesive with 20 wt% water and 3 wt% HAp at a time point before the photo irradiation commenced. The molecular structures of both monomers are also given for reference along with the spectra. The characteristic IR band of C=C at 1637 cm^{-1} can be clearly discerned from the figure, which ensures that the polymerization kinetics of the adhesive system can be quantitatively tracked by the changes in IR absorbance of this band. In addition, the IR band of C=O at 1715 cm^{-1} can be used as an intrinsic standard band for the DC calculation [17]. Figure 1(b) displays the evolution of the IR absorbance of the 1637 cm^{-1} band as a function of time. As expected, the absorbance decreased with the polymerization time. 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 real-time plots of the DC of the 2MP/HEMA model adhesive are shown in Figure 2. In the present model adhesive system, different amount of HAp (1, 2, 3, and 4 wt%) powder was incorporated to study the effect of HAp on the photopolymerization behavior. The results indicated that the DC of the 2MP/HEMA adhesive was distinctly enhanced by the addition of HAp for all of the HAp fractions studied. Moreover, the dependence of DC on HAp content was also significant: the DC increased with the increasing HAp content.

To obtain more quantitative understanding on the effect of each experimental variable on polymerization, the final DC and PR as a function of concentrations of HAp in the adhesive solutions are given in Figure 3 and Table 1. The results clearly showed that by incorporating HAp to the adhesives, both the DC and PR of the system were significantly improved. Compared with those of the 0 wt% HAp system, the DC and PR could be increased from $20.8 (\pm 0.3)\%$ to $61.1 (\pm 5.8)\%$ and $0.42 (\pm 0.01)$ to $0.94 (\pm 0.01)\%$ /s, respectively, by the addition of only 2 wt% HAp. If the HAp amount was increased to be 4 wt%, the DC can be further enhanced to $93.4 (\pm 1.1)\%$, while the PR to $3.21 (\pm 0.07)\%$ /s (Table 1).

The remarkable improvement of the polymerization for the 2MP/HEMA adhesive by the addition of HAp might be attributed to multiple reasons. Firstly, the pH change of the system due to HAp could be an important factor. Self-etching adhesives usually have low pH values and significant acidity, and are capable to produce prominent etching patterns on dentin or enamel that are comparable to those achieved by phosphoric-acid etching [19–21]. During the self-etching adhesive application, hydrogen ions from acidic functional monomers diffuse across the dentin or enamel. The activity of a self-etching adhesive might be stopped by a neutralization reaction with mineral apatites and/or by polymerization of the adhesive itself [22, 23]. It is believed that the balance between the acidity and chemical reactivity of the functional monomers and the buffering capacity of dentin are important to create stable bonding between the dentin and adhesive resin [21]. Under a circumstance of high acidity, there is possibility that polymerization of the bonding agent is affected by the acidic moieties, because tertiary amines in the adhesives might be neutralized by the acidic functional monomers. This acid-base reaction of acidic monomers with amines used in the initiator systems is believed to be an intrinsic problem of self-etching adhesives [24, 25].

The chemical reaction might contribute to the decrease of amine concentration, and therefore the concentration of formed amine radicals that is responsible for the initiation of polymerization [26]. In the current study, considering possible sensitivity of the co-initiator 4E (one of amines) on acidity of the functional monomer, it is reasonable to suppose that pH also has an effect on the initiating efficiency of 4E thus resulting in poor polymerization.

To validate this hypothesis, the polymerization behavior of the present self-etching system in different pH environments was investigated. The adhesive solutions with different pH were prepared by incorporating variable NaOH amounts of 0.2, 0.4, 1, and 2 wt% to achieve pH values of 0.6, 0.7, 1.0, and 1.2 accordingly (Table 1). Figure 4 shows the real-time plots of the DC for the 2MP/HEMA adhesive system as a function of NaOH content. The result showed a pronounced trend of the DC increasing with the NaOH content. The increasing trend of the DC and PR with the NaOH amount can be discerned more quantitatively in Figure 5. The observed dependence of DC or PR on NaOH content was similar to that of adhesives with HAp, and most likely reflected the influence of pH on both systems. The relationship between NaOH or HAp content and pH of the solutions is shown in Figure 6. The results indicated that the pH values for both HAp and NaOH-containing adhesives increased as the increasing content of additives. Despite of the capacity to achieve a considerably higher pH for NaOH as a strong base than HAp, the current result clearly demonstrated the similar buffering effect of HAp to that of NaOH. Figure 7 shows the DC and PR as a function of pH for the adhesives incorporating either NaOH or HAp. The data indicated that the dependences of DC and PR on pH for both NaOH and HAp were consistent with each other. Both DC and PR increased as the pH value. Even if the mechanism of enhancement in pH by using NaOH is not exactly same as that of HAp, the current experimental results suggested that the pH change was probably one of important reasons for the increase of the DC and PR by adding HAp in the self-etching adhesive.

The proposed hypothesis that presence of HAp in a model self-etching adhesive would increase the pH as well as the DC and PR of the system was verified. However, pH should not be the only factor responsible for the improvement in polymerization. From Figure 7 and Table 1, it can be noticed that both DC and PR for HAp-containing adhesives were higher than those of NaOH-containing adhesives at comparable pH values. For example, both the 2 wt% HAp and 0.4 wt% NaOH solutions showed a pH value of 0.7, while the DC values for the two adhesives were different, which were 61.1 (± 5.8) % and 33.6 (± 2.2) %, respectively. The results indicated that besides the pH change, other factors might have also played a role in the improvement of photopolymerization for the 2MP/HEMA adhesives.

As one of important self-etching adhesive monomers, phosphoric acid esters (PAEs, 2MP used in this study is an example of PAEs) have been widely used for composite-to-tooth bonding. However, inherent mechanism of the interaction between PAEs and HAp in enamel and dentin is quite complicated [12, 13]. In a study by Fu et al. [12], it was found that reactions of PAEs with HAp were not simple acid-base reactions like those with $\text{Ca}(\text{OD})_2$ in either liquid or solid. Instead, PAEs-HAp complexes were observed to be produced from the reactions. Their study further revealed that the chemical reaction of self-etching adhesives with enamel took place concomitantly with the chemisorption of the adhesives onto the enamel surfaces. Yoshida et al. [13] also discovered an intense chemical interaction between 10-methacryloyloxydecyl dihydrogen phosphate (MDP) and HAp. In the present study, representative spectra of the 2MP/HEMA adhesive system with and without HAp addition were compared and shown in Figure 8. Both spectra were randomly picked from time-resolved IR spectra collected before the light activation, thus the interference by possible spectral changes due to photopolymerization was avoided. From the spectra, differences can be seen from two IR regions: the carbonyl group region at 1650–1750 cm^{-1} , and the phosphoric group region at 900–1110 cm^{-1} . In the first IR region, the

C=O band shifted from 1704 to 1713 cm^{-1} after the addition of 3 wt% HAp. Usually it is believed that the electro-statically inductive effect might cause the IR shift of C=O towards a higher wavenumber [27]. In a proposed chemical interaction model [13] of MDP with HAp, it is stated that ionic binding could be formed by means of MDP interacting electro-statically with the Ca^{2+} ions of HAp. In this case, the ionic binding will indeed cause the C=O band shift to a higher wavenumber due to the inductive effect [27, 28]. Furthermore, the changes of IR bands in the phosphoric group region after adding 3 wt% HAp were also noticeable. For example, both the band positions and relative intensities of PO_4^{3-} and HPO_4^{2-} [29, 30] became different after the addition of HAp (Figure 8). These changes in IR spectra revealed the corresponding alterations in molecular structures of the self-etching adhesive by incorporating HAp.

Based on an established mechanism [13] for the HAp decalcification and the PAE adsorption on HAp, a possible process for the interaction of the current adhesive system with HAp can be described as follows:

Where R represents the 2-(methacryloyloxy) ethyl group in 2MP. The equations indicated that the ionization of 2MP (2) and the decalcification of HAp (1,2) might contribute to the decrease in PO_4^{3-} content and the increase in HPO_4^{2-} content, which was consistent to our IR results. The amount of the deposited salts in formula (3) depends on the equilibrium of the three reactions as well as their solubility in solvent. [13]The current results also indicate that there may be correlation of the 2MP/HAp interaction to the improvement of polymerization. The chemical interaction probably imposed a positive influence on polymerization thus contributed to the enhancement of DC and PR. More detailed investigations on the relationship between the 2MP/HAp interaction and the polymerization improvement are in progress.

Other factors such as a change in viscosity [31, 32] by adding HAp in the adhesive system might also play a part during polymerization. Usually viscosity affects all diffusion processes. The termination reaction in radical polymerization is diffusion-controlled at the beginning of the polymerization reaction [33]. The greater the viscosity is, the lower the termination rate coefficient [33]. Therefore, initial viscosity of the reacting system determines the initial polymerization rate: a greater viscosity will result in a higher reaction rate and monomer conversion. In the present study, there is a possibility that the viscosity of solutions could be enhanced by physically mixing with HAp powder, or by chemical interaction between the HAp and 2MP monomer. As a result, both the polymerization rate and monomer conversion might also increase.

4. Conclusion

In summary, the photopolymerization behavior of the 2MP/HEMA model adhesive incorporating with various content of HAp has been investigated. The results showed that the addition of only small amount of HAp could lead to significant improvement in the DC and PR of polymerization. The mechanism of the improvement in photopolymerization was investigated. The factors such as pH change, interaction between 2MP and HAp, and

viscosity change, were suggested to be possible reasons for the observed phenomena. The results will provide the critical information for understanding the interactions/bonding between self-etching adhesives and tooth substrates.

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Figure 1.

(a) Representative FTIR spectrum of the 2MP/HEMA model adhesive before light activation; (b) Representative time-resolved FTIR spectra in the C=O and C=C regions of the 2MP/HEMA model adhesive collected at different times (from 20 s to 120 s, every 10 s). Both (a) and (b) are for the 2MP/HEMA adhesive system in the presence of 20 wt% water and 3 wt% HAp. (ν and δ represent stretching and deformation vibration, respectively)

Figure 2. Real-time degree of conversion (DC) plots of the 2MP/HEMA model adhesives in the presence of 20 wt% water and different content of HAp. Curing light exposure duration was 40 s.

Figure 3. Degree of conversion (DC) and polymerization rate (PR) for the 2MP/HEMA model adhesives in the presence of 20 wt% water and different content of HAp.

Figure 4. Real-time degree of conversion (DC) plots of the 2MP/HEMA model adhesives in the presence of 20 wt% water and different content of NaOH. Curing light exposure duration was 40 s.

Figure 5. Degree of conversion (DC) and polymerization rate (PR) for the 2MP/HEMA model adhesives in the presence of 20 wt% water and different content of NaOH.

Figure 6.
pH values of 2MP/HEMA model adhesives in the presence of 20 wt% water and different contents of NaOH and HAp.

Figure 7. (a) Degree of conversion (DC) and (b) polymerization rate (PR) as a function of pH value for the 2MP/HEMA model adhesives in the presence of 20 wt% water and different contents of NaOH and HAp.

Figure 8.

FTIR spectra of the 2MP/HEMA model adhesive before and after the addition of 3 wt% HAp in the presence of 20 wt% water. (ν and δ represent stretching and deformation vibration, respectively)

Table 1

The pH value, DC and PR of 2MP/HEMA model adhesive systems with different compositions

Adhesive system	PH value	DC(%)	PR(%/s)
Adhesive + 20 wt% water	0.3(±0.0)	20.8(±0.3)	0.42(±0.01)
Adhesive + 20 wt% water + 1 wt% HAp	0.5(±0.0)	32.0(±0.6)	0.67(±0.01)
Adhesive + 20 wt% water + 2 wt% HAp	0.7(±0.0)	61.1(±5.8)	0.94(±0.01)
Adhesive + 20 wt% water + 3 wt% HAp	0.9(±0.1)	89.8(±1.4)	2.57(±0.06)
Adhesive + 20 wt% water + 4 wt% HAp	1.2(±0.0)	93.4(±1.1)	3.21(±0.07)
Adhesive + 20 wt% water + 0.2 wt% NaOH	0.6(±0.0)	29.6(±0.4)	0.48(±0.01)
Adhesive + 20 wt% water + 0.4 wt% NaOH	0.7(±0.0)	33.6(±2.2)	0.67(±0.02)
Adhesive + 20 wt% water + 1 wt% NaOH	1.0(±0.1)	56.5(±4.6)	0.93(±0.02)
Adhesive + 20 wt% water + 2 wt% NaOH	1.2(±0.0)	73.1(±3.3)	1.04(±0.02)