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Hydroxyapatite induces spontaneous polymerization of model self-etch dental adhesives

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Abstract

The objective of this study is to report for the first time the spontaneous polymerization phenomenon of self-etch dental adhesives induced by hydroxylapatite (HAp). Model self-etch adhesives were prepared by using a monomer mixture of bis[2-(methacryloyloxy)ethyl] phosphate (2MP) with 2-hydroxyethyl methacrylate (HEMA). The initiator system consisted of camphorquinone (CQ, 0.022 mmol/g) and ethyl 4-dimethylaminobenzoate (4E, 0.022–0.088 mmol/g). HAp (2–8 wt.%) was added to the neat model adhesive. In a dark environment, the polymerization was monitored in-situ using ATR/FT-IR, and the mechanical properties of the polymerized adhesives were evaluated using nanoindentation technique. Results indicated that spontaneous polymerization was not observed in the absence of HAp. However, as different amounts of HAp were incorporated into the adhesives, spontaneous polymerization was induced. Higher HAp content led to higher degree of conversion (DC), higher rate of polymerization (RP) and shorter induction period (IP). In addition, higher 4E content also elevated DC and RP and reduced IP of the adhesives. Nanoindentation result suggested that the Young's modulus of the polymerized adhesives showed similar dependence on HAp and 4E contents. In summary, interaction with HAp could induce spontaneous polymerization of the model self-etch adhesives. This result provides important information for understanding the initiation mechanism of the self-etch adhesives, and may be of clinical significance to strengthen the adhesive/dentin interface based on the finding.

Keywords

Dental adhesives; Spontaneous polymerization; Hydroxyapatite; Aromatic amine; Real-time FTIR

1. Introduction

Today's dental adhesives follow either an “etch-and-rinse” or a “self-etch” approach [1,2], which differ significantly in the manner they deal with tooth tissues. Clinically, self-etch is becoming the most promising approach with regard to user-friendliness and technique-

sensitivity [3]. The general strategy of a self-etch adhesive functioning on a dentin substrate is through two processes [1,4]: 1) dentin demineralization by acidic functional monomers, along with simultaneous infiltration of cross-linking monomers or other functional monomers as well as components of initiators. 2) subsequent interfacial polymerization of infiltrated monomers. While as the major advantage of the self-etch approach, the former process has been extensively investigated [3,5–7], there has been relatively less emphasis placed on the latter one. In fact, adequate polymerization is a prerequisite for overall clinical success and longevity of the adhesive bonding [8–10]. In order to better understand the mechanism by which dental adhesives function, it is necessary to also understand the mechanism by which they polymerize. The mode of polymerization, which can be of various categories, will have essential influence on both strength and durability of the formed self-etch adhesive/dentin interface [11,12].

The polymerization of common, commercial self-etch adhesives usually adopts photo irradiation as the major activation mode [13]. A typical photoinitiator system used in these adhesives contains camphorquinone (CQ) and aromatic amines. Despite good clinical acceptance, CQ/aromatic amine-based photoinitiating systems exhibit significant problems of compatibility with acidic monomers in self-etch adhesives [4,14–16]. As aromatic amines are nucleophilic, an acid–base reaction between the amine coinitiator and the acidic monomers cannot be excluded. This reaction will lead to protonization of a moiety of the amines, and thus, to the decrease of the formed amine radicals responsible for the initiation of photopolymerization. Another effect of the acid–base reaction is associated with possible spontaneous polymerization. Previous studies [17–19] have shown that polymerization of acrylic monomers could be chemically activated with a combination of various carboxylic acids and aromatic amines such as n-phenylglycine (NPG) and n-p-tolylglycine (NTG). The mechanism for the polymerization was speculated to involve the intermediacy of an unstable complex that formed due to the interaction of the carboxylic acid and amine functional groups of the reactants, and subsequent decomposition by an electron transfer process to produce initiating radicals.

Even though the above-mentioned spontaneous polymerization was observed in the early generation dental bonding agents, the phenomenon was of great interest to the contemporary self-etch adhesives due to their compositional similarity: both are involved aromatic amines and acidic functional components. As disclosed from the available data [20–22], the spontaneous polymerization offered both negative and positive ramifications: the storage stability of the systems may be a problem, whereas the effectiveness in adhesive bonding can be probably improved. Therefore, it is important to understand the “spontaneous” reactivity of self-etch adhesives in order to potentially maximize both storage stability and adhesive bonding efficacy. In the present study, the feasibility of spontaneous polymerization of a model self-etch adhesive system was tested under a dark environment. To mimic the condition that self-etch adhesives interact with dentin mineral, various amounts of HAp were incorporated into the system. By using in-situ ATR/FT-IR and nanoindentation techniques, efforts were directed towards identifying the effect of HAp and aromatic amine contents on the possible spontaneous polymerization. The objective of the study was to gain more understanding on the initiation of spontaneous polymerization of self-etch dental adhesives. The null hypothesis tested was that the spontaneous polymerization would not take place in the model self-etch adhesive system.

2. Materials and methods

2.1. Model self-etch adhesives preparation

The monomer mixtures were based on a model self-etch dental 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-etch dentin adhesives, such as Clearfil Liner Bond 2V (Kuraray America, Inc., New York, NY, USA). The initiator system (all from Aldrich, Milwaukee, WI, USA) consisted of camphorquinone (CQ) / ethyl 4-dimethylaminobenzoate (4E), present in 0.022 mmol per gram monomers for CQ and 0.022, 0.044, 0.066, and 0.088 mmol per gram monomers for 4E.

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 spontaneous polymerization, HAp (Ca₁₀(OH)₂(PO₄)₆, Aldrich, Milwaukee, WI, USA) powder was added to the neat model self-etch adhesive system to obtain mass fractions of 2, 4, 6, 8 wt.%. Immediately after well-mixing of all components, ATR/FT-IR measurement was performed.

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 in the absence of light. A small volume of the adhesive solution 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, 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 during polymerization at a rate of one spectrum every 5 or 10 min. The deposited samples and the polyester films were then sealed to avoid moisture and light during the course of the measurement.

2.3. Determination of the degree of conversion (DC), rate of polymerization (RP) and induction period (IP)

Two characteristic bands 1636 cm⁻¹ (stretching of methacrylate double bond C=C) and 1454 cm⁻¹ (deformation of CH₃, as internal standard) were employed to calculate the DC of polymerization. The intensities of these two bands were integrated based on band height methodology and the change of the band ratio profile with 1636 cm⁻¹/1454 cm⁻¹ was monitored. The DC was calculated by the following equation [23]:

$$DC = \left(1 - \frac{\text{Absorbance}_{1636\text{cm}^{-1}}^{\text{sample}} / \text{Absorbance}_{1454\text{cm}^{-1}}^{\text{sample}}}{\text{Absorbance}_{1636\text{cm}^{-1}}^{\text{monomer}} / \text{Absorbance}_{1454\text{cm}^{-1}}^{\text{monomer}}} \right) \times 100\%. \quad (1)$$

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_{max} value. RP was acquired from the 1st derivative analysis of the DC/ time plot. IP of the polymerization was determined as the time interval between the starting point of the IR spectral collection and the point that the DC (or RP) of the adhesive significantly increases.

2.4. Nanoindentation measurement

The spontaneously-polymerized model self-etch adhesive films were subjected to nanoindentation tests. The tests were performed by using a nanoindenter (Triboscope, Hysitron Inc., Minneapolis, MN) attached to a Nanoscope IIIa atomic force microscope

(AFM, Digital Instruments Inc., Santa Barbara, CA). The diamond-tipped indenter (on an equilateral triangular base) was calibrated using quartz before the measurement. A peak force of 1000 μN , loading and unloading rates of 100 $\mu\text{N/s}$ and a holding segment time of 3 s were utilized during the mechanical data collection. The nanoindentation data were acquired from at least 3 points on the surface of the adhesive films.

By means of the obtained force-displacement curves from the nanoindentation tests, the initial part of the unloading curve was analyzed based on the Oliver–Pharr method [24] to generate elastic modulus (E) for each nanoindentation. The values of Young's modulus (E_r , reduced modulus) were obtained via Hysitron software based on the following equation:

$$\frac{1}{E_r} = \frac{1 - \nu_m^2}{E_m} + \frac{1 - \nu_i^2}{E_i} \quad (2)$$

where ν_m and E_m are the Poisson's ratio and the elastic modulus of the materials, respectively. ν_i and E_i are the Poisson's ratio and elastic modulus, respectively, for the indenter.

3. Results

Representative time-resolved IR spectra in the wavenumber region of 1400–1650 cm^{-1} during spontaneous polymerization of the 2MP/ HEMA system (with the presence of 6% HAp) are shown in Fig. 1. The major IR bands in this wavenumber region are 1636 cm^{-1} (stretching of $\text{C}=\text{C}$) and 1454 cm^{-1} (deformation of CH_3), which decreased and remained almost unchanged with their absorbances, respectively, as time passed. The decrease in absorbance at 1636 cm^{-1} indicated consumption of methacrylate $\text{C}=\text{C}$ bonds during polymerization. By integrating the heights of 1636 and 1454 cm^{-1} (as internal standard) bands, and normalizing with respect to their band heights at 0 s, the DC can be quantified. Fig. 2(a) shows the real-time plots of the DC of the 2MP/HEMA model self-etch adhesives with the presence of 0–8 wt.% HAp. The result disclosed that polymerization was not observed in case that no HAp was included in the model self-etch adhesive systems (The actual IR data collection time was up to 4 days, within which no polymerization was detected. Data are not shown here). However, as different amounts of HAp were incorporated into the adhesives, spontaneous polymerization was induced. The data also indicated that higher HAp content led to more pronounced spontaneous polymerization, evidenced by the higher DC_{max} and shorter IP. The RPs of the model self-etch adhesive systems with different amount of HAp were also determined, as shown in Fig. 2(b). The result revealed that the RP_{max} s were also strongly dependent on the content of HAp incorporated, displaying an increasing trend as the HAp content increased. The values of the DC_{max} , RP_{max} and IP as a function of HAp content were summarized in Fig. 3. The results showed that by incorporating 2–8 wt.% HAp into the model self-etch adhesive systems, the DC of the spontaneous polymerization could be enhanced from 0 to higher than 70%. The highest DC_{max} obtained was 90.2% for 8 wt.% HAp incorporation. RP_{max} was also enhanced to 0.0048%/s as up to 8 wt.% HAp were added. Moreover, addition of HAp could reduce the IP of the systems to 10511 s as up to 8 wt.% HAp was added.

Effect of 4E content on the spontaneous polymerization was also investigated. Fig. 4 shows the real-time plots of the DC and RP of the 2MP/HEMA model self-etch adhesives with the presence of 0.022–0.088 mmol/g 4E. It can be found that both DC_{max} and RP_{max} were elevated as the 4E content became greater. In addition, IP of the systems exhibited shorter as higher amount of 4E was added. Fig. 5 shows the detailed values of the DC_{max} , RP_{max} and IP as a function of 4E content. As the 4E content was enhanced from 0.022 to 0.088 mmol/g,

the DC_{max} and RP significantly increased from 77.2% and 0.0044%/s to 97.4% and 0.0137%/s, respectively. IP also dramatically reduced from 39610 s to 10 s.

Fig. 6(a) displays a representative load-displacement curve of the spontaneously-polymerized model self-etch adhesive film, from which the Young's modulus of the model self-etch adhesive systems with the presence of different contents of HAp and 4E can be determined [Fig. 6(b)]. The result indicated that the Young's modulus generally increased with HAp and 4E contents (except for the slight decrease of the datum for 0.088 mmol/g as compared with 0.066 mmol/g of 4E), which was generally consistent with the ATR/FT-IR data.

4. Discussion

The proposed null hypothesis that the spontaneous polymerization would not take place in the model self-etch adhesive system was partially rejected. Our results suggested that, within the limitations of the current study, spontaneous polymerization could not carry out in the model self-etch adhesives without external additives. However, inclusion of HAp in the system was able to trigger the spontaneous polymerization (Figs. 2 and 3). Based on the present data and previously reported work [18,19,21], possible routes for the conduct of the spontaneous and photo polymerizations of the HAp-incorporated model self-etch adhesives were proposed in Fig. 7. The underlying mechanism (Fig. 7) for the initiation of spontaneous polymerization might consist of a two-step reaction between the acidic functional monomer 2MP and aromatic amine 4E. In the first step, a complex was formed through the interaction of hydrogen atom of 2MP with nitrogen atom of 4E. It is speculated that the obtained complex structure was relatively stable. Therefore, in order to proceed to the second step, that was, decomposition of the complex to generate the free radicals, involvement of external additives such as HAp was required. This proposed route is distinct from the reported studies [18,19,25] that employed carboxylic acids and NPG (or its analogs). In those systems, the interaction of the carboxylic acids with NPG produced rather unstable complex, probably due to the special chemical structure of NPG that combined both acid and amine groups. As a result, the complex could easily decompose (without external additives) and induce significant spontaneous polymerization, which at the same time led to unwanted gelation of acrylic monomers, so that the storage stability of the formulations remained as a major issue. Compared with the carboxylic acid/NPG systems, the spontaneous polymerization of the current model self-etch adhesives was more controlled. By adjusting the amount of HAp, preferred DC, RP as well as IP of the polymerization can be achieved. Especially, as the main component of which the dental enamel and dentin are comprised, HAp is highly available upon demineralization of the hard dental tissue by self-etch adhesives. This offers considerable possibility to strengthen the bonding of adhesives through the observed spontaneous polymerization as they are practically applied on dental substrates.

Recent studies have disclosed the active role of HAp in achieving an ideal bonding at the self-etch adhesive/dentin interface. Based on a recently proposed "A/D (adhesion/demineralization)" concept [2,3,26], HAp can serve as a template to form additional interaction with the acidic functional monomers of the self-etch adhesives, which is believed to particularly improve bond durability. Evidences also suggested that HAp was able to improve photopolymerization through its interaction with acidic functional monomers. In the previous studies [23,27] using the same model self-etch adhesive system and photopolymerization, dramatically enhanced DC was observed by either incorporating HAp powder into the adhesives, or applying the adhesives onto dentin surface. The results were attributed to the buffering effect of HAp to the acidic functional monomers, which meanwhile might have also released the coinitiator 4E from the formed 2MP/4E complex

(route b of Fig. 7). The present study further revealed that spontaneous free-radical polymerization could take place by virtue of the inclusion of HAp. The details regarding respective mechanisms for the generations of 4E (route b of Fig. 7) and 4E initiating radical (route a of Fig. 7) need further investigation. Despite of this, the spontaneous polymerization could enable the monomers achieve resultant DCs higher than 70% (Figs. 2 and 3), which are comparable to those achieved by photopolymerization [23]. Considering the potential complementary function of the spontaneous polymerization to the photopolymerization, the observed effect of HAp on spontaneous polymerization demonstrated again the importance of chemical interaction of HAp with the acidic functional monomer for strengthened dental bonding.

The amount of 4E also posed apparent influence on the observed spontaneous polymerization, which offers another opportunity to manipulate the process. As shown in Figs. 4 and 5, with the presence of 4 wt.% HAp, the efficacy of spontaneous polymerization was drastically improved by enhancing 4E content. The effect of the 4E content increase was especially significant to improve RP of the polymerization. Our data suggested that markedly elevated RP_{max} of 0.014%/s was obtained at 0.088 mmol/g 4E content as compared to 0.004%/s for 0.022 mmol/g 4E content. As a result, the overall period of time for the chemical cure to occur was reduced from ~83000 s (~23 h) to ~16000 s (~4 h). This role of 4E in spontaneous polymerization is in particular necessary to achieve a reasonable time frame for the potentially clinical applications. In addition, adjusting 4E content will be also important for a better spontaneous polymerization performance in case that only limited HAp can be obtained through demineralization of dental substrates.

The initiation systems of the dental adhesives and other resin-based dental materials, e.g., composites, sealants, cements, can be activated either chemically or by light/photo irradiation [4,12,13]. For bonding purposes, both chemical (or named as self or spontaneous) and photo polymerizations may be preferred, as each mode has its advantages and disadvantages. Generally, the major advantages of chemical over photo polymerization are the greater uniformity and depth of cure, as well as the capacity of the initiators to function in areas where curing light has limited access. Nevertheless, chemical polymerization has the drawback of requiring a prolonged setting time. Also, chemical initiators are not as storage-stable as photo initiators, so that they usually come with two-part systems. In contrast to the chemical initiator systems, the curing characteristics of photoinitiators allow rapid polymerization in the area within reach of the light energy to ensure adequate cure. However, insufficient irradiation may occur to the deeply infiltrated initiator components and monomers since the light is attenuated as it traverses to certain depths, especially in deep dentin tubules. As a result, suboptimal polymerization of the involved resin systems can be expected. In an attempt to overcome the limitations of both chemical cure and light cure, dual-cure initiators have been developed and used in some commercial bonding systems [12,28]. Our results suggested that the initiators of model self-etch adhesives were also able to activate polymerization following a dual-cure approach. However, this dual-cure approach differs markedly from the traditional ones in that separate chemical-cure initiators are not required (our model self-etch adhesives were formulated based on a typical photo-curing composition: camphorquinone with aromatic amine). Instead, the chemical cure can be performed through chemical interaction with dental mineral (HAp, Figs. 2 and 3). This unique way of chemical cure in the self-etch adhesives might expand our current understanding on the chemical cure or dual-cure mechanisms, and potentially inspires clinical applications based on the finding.

Representative formulation of commercially available chemical (also known as chemical redox) curing systems usually consists of at least one oxidizing agent, such as peroxide (e.g., the frequently used dibenzoylperoxide (DBPO)), and one reducing agent such as tertiary

amines (e.g., n, n-diethanol-p-toluidine (DEPT) or n, n-diethyl-3,5-ditert-butylaniline) [13,29]. The basic initiating mechanism of the redox system is through a process that the reducing agent accelerates the cleavage of the peroxide to form free radicals, so that polymerization can be activated at room temperature. However, this process at the same time may lead to a storage-stability problem. In addition, these chemical initiators showed a serious disadvantage associated with the residual reaction products of DBPO with the amines, which [30] could change color upon light exposure. Such disadvantages can be avoided by using the discovered spontaneous polymerization of the current model self-etch adhesives. Nevertheless, further investigation is needed to find out the performance of spontaneous polymerization as compared to the commonly used chemical polymerization approach because essentially these two processes are different in mechanism and possibly also in their bonding potentials.

5. Conclusion

Our results have disclosed that addition of HAp could induce significant spontaneous polymerization of the model self-etch adhesives. Performance of the spontaneous polymerization strongly depended on the amount of HAp included. Higher HAp content led to enhanced DC, RP and reduced IP. In addition, higher content of coinitiator 4E also played a positive role in achieving higher performance of the spontaneous polymerization. The results expand our current understanding on the initiation mechanism of polymerization of self-etch adhesives, as well as the role of HAp in the processes. Furthermore, the finding may be of significance to inspire clinical applications in the areas of self-etch adhesive/dentin interfacial bonding.

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Fig. 1. Representative time-resolved IR spectra in the CH₃ (1454 cm⁻¹, indicated by blue dash ovals from chemical structures of 2MP and HEMA) and C = C (1636 cm⁻¹, indicated by red solid ovals from chemical structures of 2MP and HEMA) regions of the 2MP/HEMA system. (HAp content: 6 wt.%, water content: 20 wt.%, CQ or 4E content: 0.022 mmol/g). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 2. Real-time degree of conversion (DC, a) and rate of polymerization (RP, b) plots of the 2MP/HEMA system with the presence of different content of HAp. (Water content: 20 wt.%, CQ or 4E content: 0.022 mmol/g).

Fig. 3.

Degree of conversion (DC), maximum of rate of polymerization (RP), and induction period (IP) of the 2MP/HEMA system with the presence of different content of HAp. (Water content: 20 wt.%, CQ or 4E content: 0.022 mmol/g).

Fig. 4. Real-time degree of conversion (DC, a) and rate of polymerization (RP, b) plots of the 2MP/HEMA system with the presence of different content of 4E. (Water content: 20 wt.%, HAp content: 4 wt.%).

Fig. 5.

Degree of conversion (DC), maximum of rate of polymerization (RP), and induction period (IP) of the 2MP/HEMA system with the presence of different content of 4E. (Water content: 20 wt.%, HAp content: 4 wt.%).

Fig. 6.

(a) Representative load-displacement curve (HAp content: 4 wt.%, water content: 20 wt.%, CQ or 4E content: 0.022 mmol/g) and (b) Young's modulus of the 2MP/HEMA systems with the presence of different content of HAp (water content: 20 wt.%, CQ or 4E content: 0.022 mmol/g) and different content of 4E (water content: 20 wt.%, HAp content: 4 wt.%).

Fig. 7. Tentative routes for the conduct of the spontaneous and photo polymerizations of model self-etch adhesives with the addition of HAp.