



Hydroxyapatite induces spontaneous polymerization of model self-etch dental adhesives



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ARTICLE INFO

Article history:

Received 23 January 2013

Received in revised form 4 April 2013

Accepted 25 April 2013

Available online 3 May 2013

Keywords:

Dental adhesives

Spontaneous polymerization

Hydroxyapatite

Aromatic amine

Real-time FTIR

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.

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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

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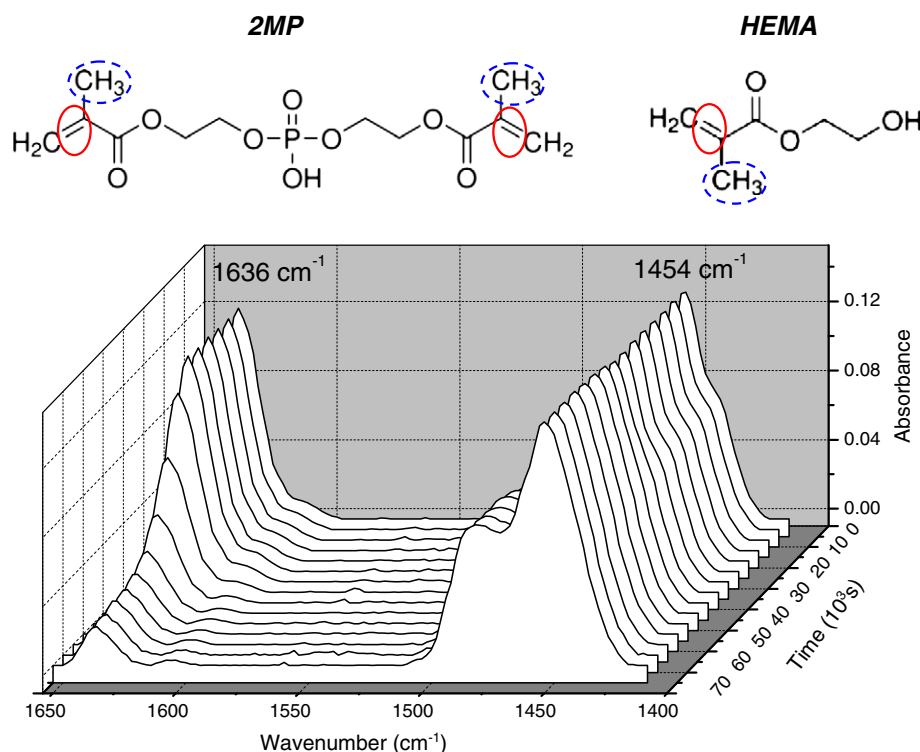


Fig. 1. Representative time-resolved IR spectra in the CH₃ (1454 cm⁻¹, indicated by blue dash ovals from chemical structures of 2MP and HEMA) and C = C (1636 cm⁻¹, indicated by red solid ovals from chemical structures of 2MP and HEMA) regions of the 2MP/HEMA system. (HAp content: 6 wt.%, water content: 20 wt.%, CQ or 4E content: 0.022 mmol/g).

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, 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 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.

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