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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 $[Ca_{10}(OH)_2(PO_4)_6]$ powder were added to the test solutions to obtain mass fraction of 0, 1, 2, 3, and 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.

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

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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 2 V (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 (D_2O, Cambridge Isotope Laboratories, Inc., Andover, MA, USA) was used to activate monomer acidity. In addition, use of D_2O instead of H_2O avoided any potential interference of IR absorption within the wavenumber bands of interest. To investigate the effect of mineral content on photopolymerization, HAp ($Ca_{10}(OH)_2(PO_4)_6$, Aldrich, Milwaukee, WI, USA) powder was added to the neat model adhesive system to obtain mass fractions of 1, 2, 3, and 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, $22 \times 22 \times 0.25$ 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 $550\,mW/cm^2$ 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 ~2 mm. Real-time IR spectra were continuously recorded for 300 s 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]:

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