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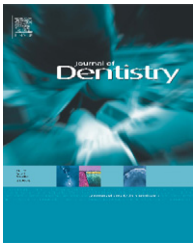

Hydroxyapatite effect on photopolymerization of self-etching adhesives with different aggressiveness

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ABSTRACT

Objective: To understand the correlation of the acidic monomer/hydroxyapatite (HAp) reaction with the photopolymerization behaviour 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.

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 dentine by dissolving or partially 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

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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 dentine 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 behaviours. 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 behaviours. Different amounts of HAp powders were incorporated in the solutions of each adhesive so that the varying level of dentine 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 behaviour 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 ($Ca_{10}(OH)_2(PO_4)_6$, the particle size $\sim$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 h 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 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 mm × 22 mm × 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 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 metre (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 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 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

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 methacryate (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