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Optimization of the concentration of photo-initiator in a one-step self-etch adhesive

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ABSTRACT

Objectives. The objective of this study was to determine the optimal concentration of photo-initiator (camphorquinone) in an experimental one-step self-etch adhesive and to investigate the role of the photo-initiator.

Methods. Seven experimental one-step adhesives with a varying amount of camphorquinone ranging from 0 to 5.25 wt% were prepared. Their micro-tensile bond strength to enamel and dentin was determined. In addition, the bond strength was also determined when the adhesive was not light-cured prior to the application of the composite. SEM and TEM were used for further evaluation of the resultant interfacial ultrastructure.

Results. The bond strength to enamel was not influenced by the amount of photo-initiator, whereas the bond strength to dentin dropped significantly when concentrations below 0.35 wt% camphorquinone were used. Besides phase-separation droplets, electron microscopy revealed the presence of many small droplets at the bottom of the adhesive layer when the adhesive contained no or only a low concentration of initiator, or when the adhesive was not light-cured.

Significance. Since polymerization is severely hampered by oxygen inhibition in thin layers, one-step self-etch adhesives depend greatly on the polymerization of the first layer of lining composite to achieve their ultimate mechanical strength. Consequently, the bond strength to enamel is not influenced by the amount of photo-initiator, but on dentin, bond strength is compromised by droplets, probably due to water absorption, and additionally by the negative effect of water on polymerization and by continuing demineralization of unpolymerized acidic monomers. Overall, it was found that minimally 0.7 wt% camphorquinone was needed.

1. Introduction

Initiators are added to adhesives to obtain a high degree of conversion, and should hence provide good mechanical properties to the adhesive layer. Low degrees of conversion have also been associated with high susceptibility to degradation due to increased leaching of uncured adhesive components and due to augmented water uptake [1,2]. Additionally, high

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polymerization rates should prevent continued etching of dentin by the demineralizing monomers in self-etch adhesives [3].

Generally, adhesives are cured before the application of the composite in order to prevent overly thinning of the adhesive layer and to provide enough mechanical strength to withstand volumetric shrinkage stresses [4].

In methacrylate-based resin systems that polymerize following a radical-polymerization reaction, camphorquinone is the most commonly used photo-initiator. Usually, only minute amounts of photo-initiator are added to adhesives [4].

The newest generation of adhesives, the one-step self-etch adhesives (1-SEAs), however, have been documented with relatively low degrees of conversion [5,1]. Besides suboptimal mechanical strength of the adhesive layer, this may result in accelerated degradation of the adhesive, in excessive leaching of adhesive components and in higher permeability of the adhesive layer.

The objective of this study was (1) to evaluate the role of the photo-initiator in one-step adhesives, and (2) to determine the optimal concentration of camphoroquinone in an experimental one-step adhesive.

2. Materials and methods

Seven experimental one-step adhesives with different concentrations of camphorquinone (CQ) were prepared by GC (Tokyo, Japan). These nearly identical adhesives differed only in the amount of photo-initiator and contained respectively 0, 0.07, 0.35, 0.70, 1.75, 5.25, 3.50 and 5.25 wt% of CQ. They should be categorized as 'mild' self-etch adhesives as they exhibited a pH of 2 (Table 1). As all adhesives exhibited phase separation, an adapted application protocol including strong air-blowing was used [6].

2.1. *Bond-strength testing*

The bond strength to enamel and dentin was determined using a standardized micro-tensile bond-strength (μTBS) protocol. Non-carious human third molars (gathered following informed consent approved by the Commission for Medical Ethics of KULeuven) were stored in 0.5% chloramine/water at 4 °C and were used within 1 month after extraction. To prepare dentin samples, the occlusal crown third was removed with a diamond saw (Isomet 1000, Buehler, Lake Bluff, IL, USA), thereby exposing a flat mid-coronal dentin surface. A standardized bur-cut smear layer was produced by removing a thin layer of the surface using a Micro-Specimen Former (University of Iowa, Iowa City, IA, USA), equipped with a high-speed regular-grit (100 μm) diamond bur (842, Komet, Lemgo, Germany). For enamel, a flat surface was ground using the same bur at the buccal and lingual surface of a tooth. The adhesives were applied according to the instructions described in Table 1 on air-dried (but not desiccated) enamel and dentin. In order to determine the exact role of the photo-initiator, two additional groups were added in which Exp-0.07%CQ and Exp-3.5%CQ were applied onto enamel and dentin, but were not light-cured prior to the application of the composite. Composite build-ups were made with Gradia Direct Anterior (GC, shade A2) in three or four layers to a height of 5–6 mm. After 24 h storage in distilled water (37 °C), rectangular sticks (2 mm × 2 mm wide; 8–9 mm long) were sectioned perpendicular to the adhesive-tooth interface using the Isomet saw. Only the four central dentin sticks were used to eliminate substrate regional variability. The sticks were trimmed at the interface into an hourglass shape (diameter of ±1.1 mm) using the Micro-Specimen Former, equipped with a fine-grit (30 μm) diamond bur (5835KREF, Komet) in a high-speed handpiece under air/water coolant. The specimens were fixed to Ciucchi's jig with cyanoacrylate glue (Model Repair II Blue, Dentsply-Sankin, Ohtawara, Japan) and stressed in tension at a crosshead speed of 1 mm/min using a universal testing device (LRX, Lloyd, Hampshire, UK). The μTBS was derived by dividing the imposed force at the time of fracture by the bond area (mm^2). Statistical differences were examined using Kruskal–Wallis non-parametric statistical analysis ($\alpha = 0.05$). The mode of failure was determined with a stereomicroscope at 50× magnification. Representative dentin and composite μTBS-fracture planes, exhibiting the most frequently observed failure mode and a μTBS close to the mean, were processed for field-emission gun scanning electron microscopy (Feg-SEM; Philips XL30, Eindhoven, The Netherlands), using common specimen processing described previously [7].

2.2. *TEM interface characterization*

Dentin specimens of the seven experimental adhesives that were applied according the instructions were prepared for TEM according to a procedure described in detail by Van Meerbeek et al. [8]. Non-demineralized and demineralized ultra-thin sections were cut (Ultracut UCT, Leica) and examined unstained and positively stained (5% uranyl acetate for 20 min/saturated lead citrate for 3 min) with a Zeiss EM900 electron microscope. Additional adhesive-enamel/dentin interfaces, stained with 50 wt% ammoniacal silver-nitrate solution, were prepared according to the nanoleakage detection protocol described by Tay et al. [9].

3. Results

There were no significant differences in bond strength between the experimental adhesives when they were bonded to enamel (Table 2 and Fig. 1). In contrast, the bond strength to dentin of the experimental adhesives without photo-initiator (Exp-0%CQ) or with a very low concentration of camphorquinone (Exp-0.07%CQ) was significantly lower as compared to the dentin bond strength of the experimental adhesives with higher concentrations of camphorquinone. In Exp-0%CQ, the variance in bond strength was remarkably higher as well. When Exp-0.07%CQ and Exp-3.5%CQ were not light-cured, no differences in bond strength to enamel were observed (Table 2 and Fig. 2). However, the bond strength to dentin dropped significantly (Fig. 2).

Failure analysis revealed a predominantly mixed failure pattern, involving both regions that failed adhesively and region exhibiting failures cohesive in the adhesive and/or composite. However, Exp-0%CQ, Exp-0.07%CQ, and the non-light-cured adhesives exhibited a mainly adhesive failure