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Effect of adhesive hydrophilicity and curing time on the permeability of resins bonded to water vs. ethanol-saturated acid-etched dentin

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ABSTRACT

Objective. This study examined the ability of five comonomer blends (R1–R5) of methacrylate-based experimental dental adhesives solvated with 10 mass% ethanol, at reducing the permeability of acid-etched dentin. The resins were light-cured for 20, 40 or 60 s. The acid-etched dentin was saturated with water or 100% ethanol.

Method. Human unerupted third molars were converted into crown segments by removing the occlusal enamel and roots. The resulting crown segments were attached to plastic plates connected to a fluid-filled system for quantifying fluid flow across smear layer-covered dentin, acid-etched dentin and resin-bonded dentin. The degree of conversion of the resins was measured using Fourier transform infrared spectroscopy.

Result. Application of the most hydrophobic comonomer blend (R1) to water-saturated dentin produced the smallest reductions in dentin permeability (31.9, 44.1 and 61.1% after light-curing for 20, 40 or 60 s, respectively). Application of the same blend to ethanol-saturated dentin reduced permeability of 74.1, 78.4 and 81.2%, respectively ($p < 0.05$). Although more hydrophilic resins produced larger reductions in permeability, the same trend of significantly greater reductions in ethanol-saturated dentin over that of water-saturated dentin remained. This result can be explained by the higher solubility of resins in ethanol vs. water.

Significance. The largest reductions in permeability produced by resins were equivalent but not superior, to those produced by smear layers. Resin sealing of dentin remains a technique-sensitive step in bonding etch-and-rinse adhesives to dentin.

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1. Introduction

The observation that resin-bonded dentin is not as well sealed as dentin covered with a smear layer [1–6] raises concerns as to whether dental adhesives can ever seal dentin as well as cementum or enamel. Confocal laser scanning microscopy (CLSM) studies have shown that fluorescent tracers can pass between resin tags and the walls of acid-etched dentin [7–12]. This has been termed micropermeability. Apparently, there are nanometer-sized spaces that remain filled with water after resin infiltration or are the result of the solvent evaporation step, where more water is pulled from dentin into the bonded interface [13]. It is likely that the relatively low solvent concentrations (14–17 mol/L) and comonomer concentrations (ca. 2–3 mol/L) cannot displace the high concentration (55.6 mol/L) of very small water molecules from rinsed, acid-etched collagen fibrils. Although it is known that >9% water lowers the percent conversion of adhesives [14], there are other issues that may play a role in attempts to seal dentin with solvated comonomers. All contemporary "simplified adhesives" whether used in etch-and-rinse or self-etch adhesive systems, contain mixtures of hydrophilic monomethacrylates and more hydrophobic dimethacrylates to permit sufficient cross-linking to make the adhesives strong enough to serve as bonding agents. Through careful formulation, the manufacturers add sufficient solvents to create a single phase solution. The goal is to have the hydrophilic and hydrophobic comonomers copolymerize with each other to create uniformly cross-linked copolymerized chains. However, when bonded resins are stained by ammoniacal silver nitrate and examined by transmission electron microscopy, the resin films are not homogeneous. Instead, they contain water-filled voids and channels called water trees [15]. We speculated that the resin films created by most simplified adhesives, when applied to moist dentin, create heterogeneous adhesive films due to sequestration of domains of hydrophobic stiff copolymers from domains of more flexible hydrophilic copolymers. Depending upon the relative concentrations of hydrophilic vs. hydrophobic comonomers, the "matrix" of the film could be hydrophilic or hydrophobic. Regardless of the composition, we speculate that there will be hydrophilic regions in the film that span the entire thickness of the adhesive film. The boundaries between the hydrophilic and hydrophobic domains may contain microphase separations that are too small to be identified using conventional methods. What are called water trees may represent the interfaces of these invisible phase boundaries. When miniature impressions are taken of resin films bonded to dentin, many such surfaces are covered with micrometer size water droplets [16–20]. We speculated that each water droplet is at the top of a water tree that makes these resin films permeable to water. Additional support for that idea was the high correlation between the hydraulic conductance of resin-bonded dentin and the number of water droplets per unit surface area on the surface of resin-bonded dentin [12].

Another reason why resin films are more or less permeable to water is due to their degree of conversion [21]. Under-cured adhesives are more permeable [21,22] than optimally cured adhesives. Under-curing can be due to inadequate irradiation or due to dilution by too much solvent, inadequate solvent evaporation and other variables.

The purpose of this study was to evaluate the effects of different curing times using a quartz halogen light, on the permeability of resin-dentin bonds made with experimental model adhesives of increasing hydrophilicities to water or ethanol-saturated acid-etched dentin. The test null hypotheses were that the degree of conversion has no effect on the permeability of resin-bonded dentin and that the permeability of the experimental resins bonded to water-saturated dentin was no different than when bonded to ethanol-saturated dentin.

2. Materials and methods

2.1. *Teeth preparation*

One hundred-fifty non-carious unerupted human third molars were collected after the patients' informed consent had been obtained under a protocol reviewed and approved by the Human Assurance Committee of the Medical College of Georgia. Crown segments were prepared by sectioning the occlusal enamel and roots of each tooth, using a slow-speed diamond saw (Isomet, Buehler Ltd., Lake Bluff, IL, USA) under water-cooling. The pulpal tissue was removed with a pair of small forceps. Care was taken to avoid scratching or damaging the predentin. The dentin surface was further abraded with 240-grit silicon carbide paper, down to a residual dentin thickness of 0.6 ± 0.2 mm from the ground surface to the highest pulp horn. The crown segments were attached to Plexiglass slabs (1.8 cm × 1.8 cm × 0.7 cm) using a viscous cyanoacrylate cement (Zapit, Dental Ventures of America, Corona, CA, USA) which also covered the peripheral cementum. Each Plexiglass slab was penetrated by a short length of 18-G stainless steel tubing, which ended flush with the top of the slab. This tube permitted the pulp chamber to be filled with water and to be connected to a fluid-filled automated flow-recording device (Flodec System, De Marco Engineering, Geneva, Switzerland).

2.2. *Experimental resins*

Five light-curing versions of experimental adhesive resin blends (R1, R2, R3, R4 and R5) were investigated (Table 1). R1 and R2 are similar to nonsolvated hydrophobic resins used in the formulation of contemporary commercial bonding agents of three-step etch-and-rinse and two-step self-etch adhesives systems [23]. R3 is representative of a typical two-step etch-and-rinse adhesive [24], R4 and R5 contain methacrylate derivatives of carboxylic and phosphoric acids, respectively, which are very hydrophilic, and are similar to a one-step self-etch adhesive [24]. These resin blends, with known compositions and concentrations, were purposely formulated so that they could be ranked in an increasing order of hydrophilicity, based on their Hoy's solubility parameters (Table 1).

Absolute ethanol (10% ethanol/90% resin mass%) was added to the resin blends simulating the formulation of lightly solvated dentin bonding system [25]. In a previous report [26], we found that resins 1 and 2 were too hydrophobic to permeate water-saturated dentin. However, by saturating acid-etched