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Polymerization efficacy of simplified adhesive systems studied by NMR and MRI techniques

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ABSTRACT

Objective. To ascertain the efficacy of polymerization of self-etching dental adhesives in different solvent evaporation conditions.

Material and methods. Four self-etching adhesive systems were studied. Two of them are classified as mild two-step self-etching adhesives (Clearfil SE Bond, Protect Bond) and the other two are strong one-step systems (Xeno III, ADP-Prompt-L-Pop). The influence of temperature and duration of the air-drying period on photo-polymerization was followed by: gravimetry, ^{1}H solid-state NMR spectroscopy and stray-field MRI. The evolution of proton magnetization with irradiation time was recorded and correlated with volumetric polymerization shrinkage and extent of reaction; evaporation and hardening effects were identified.

Results. Main variables determining water-solvent evaporation of the tested adhesives are: (1) water/HEMA relative concentration, (2) presence of photoinitiator compounds in the primer (SEB) and (3) presence of ethanol (XENO). SEB shows the highest extent of photo-polymerization of the tested adhesives. The lowest volumetric contraction was obtained for APLP and XENO and the attempt to remove the solvents did not increase the extent of polymerization significantly.

Conclusions. Temperature increase following photo-polymerization reaction is dominant towards the effect of the drying step for solvent evaporation in self-etching systems. Attempts to remove the solvents did not increase the extent of polymerization, so other problems are impairing the polymerization of one-step adhesives.

Clinical significance. The use of tested one-step adhesives is discouraged as the attained low extent of polymerization may lead to low bond strength, high susceptibility to degradation and also will favor a continuing etching effect on the underlying dentin.

1. Introduction

The durability of resin–dentin bonds is a key issue if resin composites are to be successfully used over long time periods [1]. Self-etching systems have been proposed as suitable adhesive agents for dentin bonding and this appears to be a promising approach for reducing technique sensitivity in dentin bonding. These systems must diffuse by demineralising through the smear layer and into sound underlying dentin, forming a hybrid layer (resin–infiltrated dentin) and leaving this intact dentin sealed [2]. When testing self-etching systems a high correlation has been encountered between degree of cure

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and bond strength [3]. Moreover, degradation of resin–dentin bonds created by these current hydrophilic adhesive systems has been revealed [1,4] and a relationship between degradation and degree of conversion of the monomers has been advocated [5].

Incomplete free radical addition polymerization of vinyl monomers does exist and has been assigned to the presence of oxygen [6], intrinsic water of the dentin smear layers that contain water-filled channels [7,8], water of the self-etching adhesives as it is an integral component necessary as a solvent and for ionization of the acidic resin monomers so that they can effectively demineralise cut dentin [9], presence of other solvents (ethanol) [10], or even to the existence of chemical incompatibilities between the components of the adhesives, specially when self-etching one-step adhesives are used [11,12]. To help with water and other solvent evaporation, manufacturers recommend gently air-drying the treated tooth for a few seconds after primer/adhesive application. However, controversy exists about the benefits of this step. Air-drying may not be able to induce significant evaporation of solvent and/or excess of water, and air thinning the bonding resin prior to light irradiation may reduce dentin bond strength, because a thinner layer of adhesive will be much more susceptible to oxygen inhibition of the polymerization [13]. This incomplete polymerization due to water presence and/or to oxygen inhibition of the adhesives will accelerate the degradation of the resin–dentin bonds [14]. Due to these circumstances, the efficacy of polymerization of these adhesives in different solvent evaporation conditions needs to be studied in order to assure a reliable and durable adhesion to a wet tissue like dentin.

Conventional Magnetic Resonance Imaging (MRI) and Stray-Field Nuclear Magnetic Resonance Imaging (STRAFI-MRI) have been used as efficient tools to determine the depth of cure [15] and the degree of conversion of light cured dental resins [16–19]. However, while conventional MRI is well suited for the observation of mobile molecules, like monomers or short-chain oligomers, STRAFI-MRI allows mapping molecules from monomers to rigid polymers. This technique permits the determination of bulk or stepped measurement of the degree of conversion of cured resins in a non-destructive mode. Hydrogen nuclei are caused to resonate and those in the liquid (mobile) phase can be differentiated from those in the solid (rigid) phase because the intensity of the STRAFI signal, usually a spin–echo train, depends on the molecular mobility in the kHz range. ^{1}H STRAFI-MRI enabled, namely, measurement of the adhesive volumetric contraction (due to solvent evaporation and photo-polymerization shrinkage) *in non-invasive and non-destructive modes*, in the presence of oxygen from the atmosphere [20]; the adhesives were neither subjected to any treatment prior to the MRI acquisitions nor the solvent component removed, prior to the irradiation period.

The aim of the study was to evaluate the influence of the duration and air temperature of the drying step on solvent evaporation and on the efficacy of the photo-polymerization process of four different self-etching adhesives. The null hypothesis to be tested was that there is no influence of the solvent component on the efficacy of photo-polymerization, spatially resolved photo-polymerization kinetics and final volumetric contraction, regardless of the type of dental adhesive.

2. Materials and methods

Two two-step self-etching adhesives Clearfil SE Bond (SEB) and Protect Bond (PRB), and two one-step self-etching adhesives Adper Prompt-L-Pop (APLP) and Xeno III (XENO) were tested. Chemical compositions of the adhesives according to manufacturers are shown in Table 1. After the air-drying period, the adhesives were irradiated using an Optilux 401 light-source (Demetron, Kerr, USA, ~470 nm). Cylindrical glass vials (9.0 mm length and 5.0 mm inner diameter) were used to follow-up the solvent evaporation by gravimetric analysis and ^{1}H STRAFI-MRI.

2.1. *Gravimetric measurements*

Four sets of primers (PRB and SEB, about 20–30 mg each) and four sets of adhesives (APLP and XENO, about 35–80 mg each) were gently air-dried for 5 s and accumulated periods reaching 20, 30 or 40 s, by blowing air at 21 or 38 °C, guided to the adhesive surface through a tube of 1 cm diameter. The corresponding weight losses were obtained using an analytical balance (Metler, MX5, 0.001 g readability). The manufacturers usually recommend 5 s air-drying at 21 °C. Four other sets of each of the four uncured adhesives (about 30–80 mg each) were submitted to 5 or 20 s or 30 or 40 s drying time at 21 °C, followed by light-curing (500 mW/cm^2) over 10 s at 22 °C, and the consequent weight losses were obtained; the drying step was repeated with other adhesive sets under air at 38 °C, and subsequent adhesive curing was also performed at 22 °C.

2.2. *NMR spectroscopy*

Spectroscopic data (^{1}H NMR spectra obtained from the liquids and from the photo-polymerized adhesives) were acquired using a Bruker MSL 300 P spectrometer (Bruker Spectrospin, Germany), operating at 300.13 MHz, in order to assign the major species and to identify the residual solvent and unreacted monomers in uncured versus light-cured adhesives. (a) ^{1}H NMR spectroscopic studies of the adhesives were performed in solution. The spectra were recorded from each adhesive after the addition of a lock solvent and the reference compound for chemical shifts (TMS). (b) Subsequently, ^{1}H NMR spectroscopic studies of the photo-polymerized samples were performed using the MAS (magic angle spinning) technique with spinning rates of about 7 kHz. Either a 70° one-radio frequency (RF) pulse (the pulse duration corresponding to a 90° magnetization tip angle was 1.9 μs) or a Hahn-echo RF sequence (90°_x-time delay–180°_y-time delay–signal acquisition) were used for the signal acquisition; this sequence, with a long time delay, is used as a simple spin filter for the selective excitation of resonances with long spin–spin relaxation times (T_2), like protons in mobile groups. Ethanol signals were used as external references for chemical shifts.