DENTAL MATERIALS 24 (2008) 1194–1200

available at www.sciencedirect.com

ScienceDirect

journal homepage: www.intl.elsevierhealth.com/journals/dema

Degree of conversion of resin blends in relation to ethanol content and hydrophilicity

Milena Cadenaro[a,*], *Lorenzo Breschi*[a,b], *Francesca Antoniolli*[a], *Chiara O. Navarra*[a], *Annalisa Mazzoni*[c], *Franklin R. Tay*[d], *Roberto Di Lenarda*[a], *David H. Pashley*[d]

[a] *Department of Biomedicine, Unit of Dental Sciences and Biomaterials, University of Trieste, Via Stuparich 1, I-34125 Trieste, Italy*
[b] *IGM-CNR, Unit of Bologna c/o IOR, Bologna, Italy*
[c] *Department of SAU & FAL, University of Bologna, Bologna, Italy*
[d] *Department of Oral Biology & Maxillofacial Pathology, School of Dentistry, Medical College of Georgia, Augusta, GA 30912-1129, USA*

ARTICLE INFO

Article history:
Received 13 April 2007
Received in revised form
23 January 2008
Accepted 29 January 2008

Keywords:
Degree of conversion
Dental bonding agents
DSC
Ethanol
Hydrophilicity

ABSTRACT

Objectives. To evaluate the degree of conversion of five experimental adhesive systems in relation to their hydrophilicity. The resin blends ranged from hydrophobic to hydrophilic and were tested as neat bonding agents, or solvated with increasing percentages of ethanol. The hypothesis tested was that extent of polymerization of resin blends is affected by resin hydrophilicity, solvent concentrations or time of polymerization.

Methods. Five light-curing versions of neat experimental resin blends were submitted to investigation: (1) 70% E-BisADM, 28.75% TEGDMA; (2) 70% BisGMA, 28.7% TEGDMA; (3) 70% BisGMA, 28.7% HEMA; (4) 40% BisGMA, 30% TCDM, and 28.75% TEGDMA; (5) 40% BisGMA, 30% BisMP, and 28.75% HEMA. All blends included 1% EDMAB and 0.25% CQ. Ethanol in different weight percentages (A: 0%, B: 30%, C: 50%, D: 70% and E: 90%) was added to these resin blends simulating different formulation of adhesives. A differential scanning calorimeter was used to measure the degree of conversion of resin blends as a function of resin hydrophilicity, solvent concentration and time of curing. Data were analyzed with three-way ANOVA and Tukey's post hoc test.

Results. Exotherms showed that degree of conversion was influenced by the hydrophilicity of the blends resin ($p < .05$), percentage of ethanol dilution ($p < .05$) and time of curing ($p < .05$). 30% ethanol dilution increased degree of conversion compared to neat compounds irrespective to resin type and curing time, showing the highest degree of conversion values of the study design.

Significance. This study supports the hypothesis that high ethanol percentages (>50 mass%) may compromise extent of polymerization kinetics of dental adhesives.

1. Introduction

Dentin bonding agents (DBA) are solvated blends of hydrophilic and hydrophobic comonomers designed to bond to intrinsically wet surfaces (such as vital dentin). DBA can be divided in etch-and-rinse [1] or self-etch (i.e. etch-and-dry) [2] adhesives, being either multi-step (i.e. three-step etch-and-rinse and two-step self-etch) or simplified by combining the number of steps required for the clinical application (i.e. two-step etch-and-rinse and one-step self-etch) [1–3]. Since

* *Corresponding author.* Tel.: +39 040 662744; fax: +39 040 662744.
E-mail address: m.cadenaro@fmc.units.it (M. Cadenaro).
0109-5641/$ – see front matter © 2008 Academy of Dental Materials. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.dental.2008.01.012

simplified DBA formulations involve mixing of nonsolvated adhesives with solvated primers (i.e. two-step etch-and-rinse) or with self-etching/primers (i.e. one-step self-etch), DBA simplification strongly increases the hydrophilicity of the mixture, and of the bond [3]. This process of simplification led to the formation of hydrophilic bonded interfaces that behave as permeable membranes after polymerization [4], allowing water to flow from the underlying dentin substrate to the top of the adhesive layer [5–7].

Recent studies [8,9] evaluating the degree of polymerization of DBA using differential scanning calorimetry (DSC) revealed a direct correlation between the extent of polymerization of the adhesive films and their permeability. Simplified adhesives (two-step etch-and-rinse and one-step self-etch systems) exhibited lower degrees of polymerization than conventional adhesives (three-step etch-and-rinse and two-step self-etch systems), and a direct relation was found between adhesive permeability to water and the extent of polymerization of the adhesive. As the water permeability of resins is directly correlated with both hydrophilicity and extent of polymerization of DBA [10], we speculated that there is a direct correlation between hydrophilicity of adhesive blends and their degree of conversion (DC). However, since the exact composition of commercially available resin blends are never disclosed by manufactures, previous reports failed to relate the DC of each adhesive to its hydrophilicity.

The DC of dental adhesives is an important parameter since low mechanical properties are related with low percentage of monomer to polymer conversion within resin-based materials [11]. In addition, sub-optimally polymerized resin specimens exhibited higher elution of monomers over time [12,13]. To investigate DC in relation to hydrophilicity of dental adhesives, five experimental resin blends with a known monomer composition that ranged from more hydrophobic to more hydrophilic were prepared and ranked by their Hoy's solubility parameters. Since the resin blends composition is known, the degree of conversion calculated from exotherms obtained with the DSC analysis can be correlated in relation to their respective Hoy's solubility parameters, to test the relationship between DC, degree of hydrophilicity and permeability or mechanical properties [14–17].

DBA are usually solvated in ethanol, acetone or water [18] to promote the infiltration into the wet dentin substrate and substitute polar solvent for residual unbound water during substrate impregnation. A limited number of studies investigated the relation between the presence of solvent and DC [19,20] of dental adhesives. It has been demonstrated that presence of porosities within the hybrid layer [21] and early failures of the bonded interface [22] are correlated with excess solvent in the adhesive layer after polymerization. In addition, high percentages of solvent within the adhesive layer, if poorly evaporated, causes phase separations within the adhesive layer compromising the stability of resin–dentin bonds [23].

The aim of the present study was to correlate polymerization of five experimental DBA with their hydrophilicity and solvent content. The hypothesis tested was that the DC of the five tested resin blends is correlated with the respective Hoy's solubility parameters or with their ethanol content.

2. Materials and methods

Five light-curing versions of neat experimental resin blends with increasing hydrophilicity were investigated (R1, R2, R3, R4 and R5). Their composition is listed in Table 1. All blends included 1% EDMAB and 0.25% canphoroquinone, the most commonly used photoinitiator in dental adhesives. R1 and R2 are similar to nonsolvated hydrophobic resins used in the formulation of the bonding agent of three-step etch-and-rinse and two-step self-etch adhesives. R3 is representative of a typical two-step etch-and-rinse adhesive, while R4 and R5 contain methacrylate derivatives of carboxylic and phosphoric acids, respectively, and are very hydrophilic, similarly to a one-step self-etch adhesive. Resin blends R1–R5 were purposely formulated to be ranked in an increasing order of hydrophilicity, based on their Hoy's solubility parameters (Table 1), that can be considered as a useful method to rank the hydrophilicity of dental adhesive systems.

Absolute ethanol in different mass percentages (A: 0%, B: 30%, C: 50%, D: 70% and E: 90%) was added to the resin blends simulating different formulation of dentin bonding systems and compared with their neat counterparts. A DSC device (Q10 TA Instruments, New Castle, DE, USA) was used to measure the extent of polymerization of resin blends as a function of resin hydrophilicity, solvent content and time of curing. The resins/ethanol mixtures were placed in pans with a transparent cover to avoid solvent evaporation and polymerized in the DSC chamber. Curing was performed at a constant temperature of 35 °C in a nitrogen-purged environment using a curing unit (600 mW/cm^2). To normalize DSC data, for each specimen the mass of the resin mixtures (average mass = 5.0 mg) was measured immediately after mixing, prior to polymerization. The curing procedure was performed for up to 120 s. DSC analysis was conducted in accordance with Cadenaro et al. [8]. In brief, two aluminum pans were placed in the sample holder of the calorimeter chamber: one with the tested specimens and the other empty as a reference. The DSC chamber was covered by an aluminum cover with a round hole and a thin quartz glass to allow light to pass through and permit curing of the specimen inside the calorimeter at a minimum distance of 5 mm. A custom made support held the lamp during polymerization to fully irradiate the specimen-containing pan. The irradiance of the curing unit through the quartz glass at a distance of 5 mm (i.e. as to simulate the actual irradiance on the specimen surface) was 498 mW/cm^2 (measured using a power meter PM100, Thorlabs, Karlsfeld, Germany). Calorimetric analysis consisted of two consecutive light exposures: the first light exposure to the specimens to produce complete polymerization, and the second exposure to the same fully cured specimens to evaluate irradiation heat flow from the light-curing unit. The heat of reaction obtained from the first scan represented the sum of the exothermic effect due to monomer conversion plus the heat flow from the curing unit, while the heat flow measured in the second scan was attributed to the irradiation heat output of the lamp [8]. The heat of resin polymerization can be calculated by subtracting the heat value of the second exotherm from the value obtained after the first light exposure [9]. Extent of polymerization expressed as percentage and normalized by the sample