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Research Paper

Strengthening of dental adhesives *via* particle reinforcement

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ARTICLE INFO

Article history:
Received 12 February 2014
Received in revised form
24 April 2014
Accepted 3 May 2014
Available online 11 May 2014

Keywords:
Nanoparticles
Bond strength
Elasticity
Adhesives
Dentin

ABSTRACT

The bond between methacrylic polymer adhesives and dental restoratives is not perfect and may fail either in the short or in the long term. This study aims to evaluate the effects of particle incorporation in a self-etch model adhesive on mechanical and physical properties that are relevant during application and service. Filled adhesives containing 5, 10, 15 or 25 wt% glass fillers were compared to their unfilled counterpart in terms of water sorption and solubility; viscosity and dynamic viscosity during polymerization were recorded using rheological measurements and compared to FTIR analysis of the real-time degree of cure. Elastic modulus and ultimate tensile strength measurements were performed in uniaxial tension; the energy to fracture was used to calculate the fracture toughness of the adhesives. Finally, the experimental adhesives were applied on dentin substrate to test the bond strength using the microtensile test. Results showed that the incorporation of 5–10 wt% nanofiller to self-etching dental adhesives is efficient in accelerating the polymerization reaction and increasing the degree of cure without compromising the film viscosity for good wettability or water sorption and solubility. Fillers increased the elastic modulus, tensile strength and fracture toughness to a plateau between 5 and 15 wt% filler concentration, and despite the tendency to form agglomerations, active crack pinning/deflection toughening mechanisms have been observed. The bond strength between resin composite and dentin was also improved when adhesives with up to 10 wt% fillers were used, with no additional improvements with further packing. The use of fillers to reinforce dental adhesives may therefore be of great practical benefit by improving curing and mechanical properties.

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http://dx.doi.org/10.1016/j.jmbbm.2014.05.007
1751-6161/

1. Introduction

Tailoring of mechanical and physical properties of materials through changes in formulations is a process based on compromises between desirable and undesirable effects. For dental adhesives that join restoratives to tooth tissues, mechanical stiffness and stability are the goals in order to endure shrinkage stresses and cyclic mastication forces (Braga et al., 2005; Frankenberger et al., 2005). The initial state of this bond has shown to reach satisfactory levels for currently marketed adhesives (Van Meerbeek et al., 2010). Its degradation, however, is rather expedited by the susceptibility to water diffusion from the underlying wet substrate and the environment, and is mainly dictated by the hydrophilicity of the adhesive composition (Tjäderhane et al., 2013). Prevailing strategies to preserve the bond integrity focus on minimizing the polymer water uptake by using more hydrophobic compositions (Tay et al., 2007; Tjäderhane et al., 2013). This should be achievable using monomer solutions that maintain a fluidic character for proper substrate wettability and still reach adequate degrees of cure.

Improvements in bond strength can also be accomplished by reinforcing the adhesive polymer with fillers. In a previous report (Lohbauer et al., 2010a) we showed that uncoated spherical zirconia (ZrO_2) nanoparticles can be added to either components of a particular 3-step dental adhesive as an attractive strategy to improve the dentin-composite bond. That study corroborated previous attempts to reinforce the bond between resin-based restoratives and tooth tissues through filler incorporation into dental adhesive agents (Miyazaki et al., 1995; Kim et al., 2005b; Sadat-Shojai et al., 2010). Meanwhile nano- and micro-sized particles (mainly colloidal silica or glass fillers) compose many marketed dental adhesives in concentrations between 5 and 48 wt% (Van Landuyt et al., 2007).

Consequences of incorporating fillers into dental adhesives go beyond mechanical effects, and may further alter physical aspects that have a potential clinical relevance during application and service. One of these parameters is the film viscosity, which is increased by filler incorporation with the purpose of thickening the adhesive film and preventing full-thickness oxygen inhibition (Frankenberger et al., 2002). Overdoing in filler loading may increase the adhesive viscosity to a point that resin infiltration into the demineralized substrate is compromised. That represents a bigger issue for etch-and rinse adhesives, since the self-etching formulations promote resin infiltration at the pace of etching (Van Meerbeek et al., 2011). In increasing the viscosity, fillers may further affect the polymerization kinetics of the resin by acting as rigid centers for chain initiation during polymerization, with expected accompanying effects on the degree of cure.

The present study aims to clarify these questions. Here we address the effects of incorporating silanized sub-micrometer glass fillers into an experimental self-etch adhesive formulation in terms of viscosity, dynamic viscosity during curing, degree of conversion, water sorption/solubility, elastic modulus development, ultimate tensile strength, fracture toughness and bond strength to dentin. The null hypothesis tested was that filler concentration has no effect in the aforementioned parameters.

2. Materials and methods

2.1. Experimental adhesives

Due to the uncertainty surrounding the precise chemical composition and monomer concentrations of marketed dental adhesives, an experimental self-etching adhesive was produced specifically for this study (Voco, Cuxhaven, Germany). The following monomers/additives and corresponding weight concentrations were stirred until homogeneously mixed and stored in a PE beaker: Bis-2-methacryloyoxy)ethylphosphate (Bis-MEP; 33.3 wt%), Bisphenol A diglycidyl methacrylate (Bis-GMA; 33.3 wt %), 2-hydroxyethyl methacrylate (HEMA; 32.5 wt%), Camphoroquinone (0.3 wt%), Ethyl-4-dimethyllaminobenzoate (DABE; 0.45 wt%) and Butylhydroxytoluene (BHT; 0.01 wt%). From this composition, four filled versions (5, 10, 15 and 20 wt%, or 2.5, 5, 7.5 and 10 vol%, respectively) were produced by incorporation of SiO_2–BaO glass fillers (NanoFine® NF180 of glass GM27884, Schott, Landshut, Germany) with grain size of $d_{50}/d_{99}=180/500$ nm and irregular shape. Silanization of fillers was undertaken by the company delivering the fillers (Schott) by using 13 wt% relative to silica of the organosilane γ-methacryloxypropyltrimethoxysilane as a coupling agent. Further specifications of the used particles can be found in the product information sheet (Schott, 2010). Dispersion of filler in the resin was achieved in three steps via kneading, rolling and ultrasonification.

2.2. Water sorption and solubility

Five disc-shaped specimens (∅=15 mm; thickness=1 mm) were produced according to ISO 4049 for each adhesive. The adhesives were poured into a silicon mold, covered with a glass cover slip, clamped and light-activated for 5 min using a light-curing oven (Unilix AC, Heraeus Kulzer, Wehrheim, Germany). The specimens were dried in a desiccator at 37 °C for 22 h and transferred to another desiccator at 23 °C for 2 h. The specimens were subsequently weighted using a high accuracy balance (YDK01 model, Sartorius, Goettingen, Germany). After a stable mass reading was obtained, this value was taken as the initial mass ($m_{initial}$). The dimensions of the specimens were measured by taking 2 points for the diameter and 5 points for the height to calculate the volume V of the specimens. The specimens were then put in containers with distilled water and stored for 7 days at 37 °C. It was made ascertained that the minimum distance between the specimens was ≥3 mm and at least 10 ml water was supplied per specimen. After the storage period the specimens were rinsed, gently air-dried and weighted within 1 min. The weight measured is referred as m_{wet}. To determine the solubility in water (representing the amount of diluted monomer), the first step needed to be repeated with the wet samples, obtaining the weight m_{dry}. For the calculation of water sorption and solubility, the following equations were used:

$$W_{sorption} = \frac{m_{wet} - m_{initial}}{V} \quad (1)$$

$$W_{solubility} = \frac{m_{initial} - m_{dry}}{V} \quad (2)$$