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Influence of nanogel additive hydrophilicity on dental adhesive mechanical performance and dentin bonding

Valeria B. Gotti [a,*,1], *Américo B. Correr* [a], *Steven H. Lewis* [b],
Victor P. Feitosa [c], *Lourenço Correr-Sobrinho* [a], *Jeffrey W. Stansbury* [b]

[a] *Department of Restorative Dentistry, Division of Dental Materials, Piracicaba Dental School, State University of Campinas, 901 Limeira Ave., 13414-903 Piracicaba, Brazil*
[b] *Department of Craniofacial Biology, University of Colorado—School of Dental Medicine, 12800 E 19th Ave./RC1-North—Rm. 2104, Mail Stop 8310, Aurora, United States*
[c] *Department of Restorative Dentistry, Dental School, Federal University of Ceará, Monsenhor Furtado St., 60430350 Fortaleza, Brazil*

ABSTRACT

Objective. To assess the influence of hydrophilicity of reactive nanogels on the mechanical performance of dental adhesives and microtensile bond strength (μTBS) to dentin after 24 h or 3 months of aging.

Methods. A series of three nanogels were synthesized: NG1—IBMA/UDMA; NG2—HEMA/BisGMA; NG3—HEMA/TE-EGDMA. The nanogels were dispersed in solvent, HEMA or BisGMA/HEMA. The degree of conversion (DC) of the materials was measured and the flexural modulus of these polymers was evaluated in dry or wet conditions. For μTBS analysis, a model adhesive was used without nanogel (control) or with the incorporation of nanogels. μTBS was evaluated after storage in distilled water for 24 h or 3 months. The analysis of the fracture was performed after μTBS testing. Data were analyzed using ANOVA and Tukey's test ($\alpha = 0.05$).

Results. Water significantly increased the modulus of NG1 and NG2 dispersed in solvent, while significantly decreased the stiffness of NG3. All polymers dispersed in HEMA and Bis-GMA/HEMA had significantly lower modulus when stored in water. NG2 showed the highest DC in solvent and BisGMA/HEMA. In HEMA, NG1 and NG3 produced the highest DC. After three months, NG2 showed the best μTBS. The μTBS of NG2-containing adhesive resin significantly increased after 3 months, while storage had no effect in the control group, NG1 and NG3.

Significance. The more hydrophobic IBMA/UDMA nanogel showed higher bulk material mechanical property results, but the best dentin bond strength values, and notably strength values that improved upon storage, were obtained with the amphiphilic nanogel based on BisGMA/HEMA.

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* *Corresponding author.*
  E-mail addresses: val_bisinoto@hotmail.com (V.B. Gotti), amerbc@yahoo.com.br (A.B. Correr), steven.lewis@ucdenver.edu (S.H. Lewis), victorpfeitosa@hotmail.com (V.P. Feitosa), sobrinho@fop.unicamp.br (L. Correr-Sobrinho), jeffrey.stansbury@ucdenver.edu (J.W. Stansbury).
  [1] Present address: 1700 Jaime Ribeiro da Luz Ave., Apt. 203, Uberlandia, 38408-188, Brazil.

1. Introduction

Although high quality adhesive systems are available for applications in restorative dentistry, the great immediate results of bond strength typically decline with storage time. The adhesive interface remains the weakest component of dental restorations based on varied degrees of degradation over relatively short times [1]. This seems to be due to several factors such as substrate characteristics, technical limitations, aging conditions in the oral environment (i.e., temperature, moisture and chewing load) and the composition of adhesives [2–6].

To ensure appropriate hybridization of wet collagen matrix, increasing concentrations of hydrophilic and ionic monomers have been added to adhesives [7]. Furthermore, simplified adhesive systems also have a large concentration of solvents and hydrophilic monomers [8,9], which interferes in the polymerization and decreases the degree of conversion [10–12]. The addition of hydrophilic monomers forms a network with low cross-linking density, and increases water sorption/solubility and resin plasticization [13,14]. These factors are thought to contribute directly to the hydrolytic and potential enzymatic degradation of the polymer resin.

Different strategies have been developed to control and prevent the degradation of the hybrid layer, such as ethanol wet bonding [13–17], chlorhexidine [18], and antioxidants/crosslinking agents [19–23]. Moreover, good results have also been obtained using nanomaterials in adhesive formulations [24].

Nanotechnology in the form of reactive nano-scale prepolymeric particles that can be swollen by monomer has attracted substantial interest due to the versatile structures with multiple applications in the drug delivery, tissue engineering and polymer composites [25,26]. While a large number of biomedical applications envolve nanogels as freely dispersed particles, recent studies have applied nanogels as functional fillers or additives in the preparation of nano-composite polymer networks [24–27].

In general, incorporation of nanogels in dental adhesive systems and composites reduced shrinkage and improved mechanical properties such as flexural modulus and flexural strength, both in dry and wet conditions, due to the strengthening of the polymeric network by the presence of the crosslinked particles [24]. Furthermore, water solubility was reduced, and short-term bond strength to dentin was improved significantly with the inclusion of the nanogels, without need to modify the existing application techniques [24].

Despite the use of nanogels as an interesting option for the modification of dental materials, the effects of comonomer combinations within the nanogels that produce different levels of hydrophilicity have not been studied with regard to adhesive formulations and bonding to a dentin substrate. The interaction between materials and substrates is very important for the establishment of efficient and effective adhesive bonds. It is reasonable to expect that specific types of nanoparticles may be able to influence the properties and durability of polymers. Thus, the aim of this study was to compare three nanogels that systematically differ in terms of hydrophilicity and assess how the incorporation of these nanostructures into dental adhesives will influence the mechanical performance of materials and bond strength to dentin over early storage times. The null hypotheses to be tested were: (1) nanogels with different hydrophilicity would not affect the mechanical performance when exposed to water; (2) nanogels with different hydrophilicity would not interfere with dentin bond strength.

2. Materials and methods

2.1. Nanogel synthesis

Three nanogel (NG) copolymers were synthesized at a 70:30 molar ratio of: isobornyl methacrylate (IBMA; TCI America, Portland, OR, USA) and urethane dimethacrylate (UDMA; Sigma–Aldrich Co., St. Louis, MO, USA) (NG1); 2-hydroxyethyl methacrylate (HEMA; TCI America) and bisphenol A glycerolate dimethacrylate (BisGMA; Esstech, Essington, PA, USA) (NG2); 2-hydroxyethyl methacrylate (HEMA) and tetraethylene glycol dimethacrylate (TE-EGDMA; TCI America) (NG3). 2-Mercaptoethanol (ME; Sigma–Aldrich) was added (10 mol% for NG1, 40 mol% for NG2, and 15 mol% for NG3 relative to monomers) as a chain-transfer agent to avoid macrogelation, control molecular weight/nanogel particle size, and provide sites for post-polymerization refunctionalization with reactive groups. Free radical polymerization was conducted in solution (six-fold excess for NG1, eight-fold excess for NG2, seven-fold excess for NG3 of methyl ethyl ketone (MEK; Fisher Scientific, Waltham, MA, USA) relative to monomer) with 1 wt% 2,2′-azobisisobutyronitrile (AIBN; Sigma–Aldrich) as thermal initiator. A 100 mL round-bottom flask was used as the reactor with monomer batch sizes of approximately 10 g with reaction conditions of 80 °C and a stirring rate of 200 rpm. Methacrylate conversion during nanogel synthesis was calculated from mid-IR spectra (Nicolet 6700, Thermo Scientific, Waltham, MA, USA) before and after polymerization.

Nanogels were purified by precipitation from hexanes (10-fold excess; Fisher Scientific) and filtration. Resulting precipitates were re-suspended in dichloromethane (BDH Chemicals, VWR Analytical, Radnor, PA, USA) for NG1 and NG3, and acetone (Fisher Scientific) for NG2, and reacted at room temperature with a 10 mol% for NG1, 10 mol% for NG2, and 15 mol% for NG3 of 2-isocyanoethyl methacrylate (IEM; TCI America) with a trace amount of dibutyltin dilaurate (Sigma–Aldrich) as catalyst. The polymer precipitation method was repeated to isolate the methacrylate-functionalized reactive nanogel. Residual solvent was removed completely under vacuum until the nanogels were obtained as dry powders.

2.2. Nanogel particle characterization

Polymeric nanogels were characterized by triple-detector (refractive index, viscosity, light scattering) gel permeation chromatography—GPC (GPCmax; Viscotek, Malvern Instruments, Malvern, UK) in tetrahydrofuran (EMD Millipore, Billerica, MA, USA). The glass transition temperature (Tg) of nanogel powders was determined by dynamic mechanical analysis (DMA 8000, PerkinElmer, Waltham, MA, USA) by