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Nanofiller loading level: Influence on selected properties of an adhesive resin

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ABSTRACT

Objectives: To evaluate the effect of the filler content in the cohesive strength (σ), Weibull modulus (*m*) and degree of conversion (DC) of an experimental adhesive system.
Methods: A HEMA/Bis-GMA/TEGDMA-based adhesive was formulated and filled with silica nanofillers in the following weight percentages (wt%): R0 = 0%; R1 = 1%; R3 = 3%; R5 = 5% and R10 = 10%. The adhesive of Adper Scotchbond Multi-Purpose (SBMP) system was used as a commercial reference. Twenty dumbbell-shaped specimens with cross-sectional area of 0.5 mm^2 were made per group and tensile tested with a crosshead speed of 0.5 mm/min until fracture. The cohesive strength was calculated in MPa. DC was obtained through FTIR after light curing for 25 s. Data were submitted to one-way ANOVA and Tukey's test ($\alpha = 0.05$) and to Weibull analysis.
Results: Mean σ results were: R0 = 65.4 ± 8.4; R1 = 73.2 ± 8.8; R3 = 72.0 ± 8.4; R5 = 73.1 ± 9.7; R10 = 85.5 ± 13.1 and SBMP = 79.0 ± 11.0 MPa. R10 presented the highest σ, while R0 showed the lowest. R5 and SBMP did not differ significantly ($p < 0.05$). Weibull analysis revealed no significant difference in structural reliability between groups. The experimental adhesives presented similar results of DC, which, in turn, were significantly higher than the SBMP.
Conclusions: The addition of 10% filler in weight improves the cohesive strength of the adhesive, not interfering in the structural reliability or the degree of conversion.

1. Introduction

Composites nowadays are considered a reliable alternative for either anterior or posterior restorations. This became possible due to the latter developments in composites microstructures and mechanical properties, and to factors such as the aesthetic appeal and the adhesiveness to the dental structure.

Adhesion of such restorations is driven by the adequate penetration of a fluid resin into the collagen network. The role of the adhesive layer is to withstand the stress caused by the shrinkage of the composite during setting and all the mechanical challenges imposed by the oral dynamics to the restoration, keeping it in place.[1] Add to that, it is also responsible for the marginal sealing of the restoration. Consequently, the breakage of the adhesive bonds results in poor marginal sealing, inducing tooth sensitivity and pulpal damages.[2]

Within the adhesive zone, the adhesive layer located above the hybrid layer is considered the weakest spot of an

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adhesive restoration[3] and, thus, is more likely to fail.[4] Microcracks may propagate within the adhesive layer, leading to interfacial opening. Besides, adhesives also undergo hydrolytic degradation through time, resulting in elution of their components to the wet oral environment[5] and weakening even more the interface. These situations are highly related to the nature of the polymer network that constitutes the adhesives.

Attempts to improve the mechanical properties of polymer-based materials, especially of dental composites, have been made by adding a percentage of silanized inorganic filler particles.[6,7] Previous reports on composites have shown considerable improvement of properties such as elastic modulus, fracture toughness, flexural strength and hardness with the increase of the filler volume.[8] The presence of closely spaced filler particles has been suggested also to increase the strength and the fracture energy of brittle polymers through creation of crack stopping steps.[6,9,10]

Several recent commercial adhesive systems present filler particles in their constitution.[11] However, whether the addition of filler particles improves the mechanical behavior of these adhesives still remains unclear, since their mechanical properties rely on other factors that cannot be studied isolated using commercial adhesive systems.[12,13] Only a few studies have systematically studied the effect of the filler content on the strength of the adhesives. Kim et al.[13] observed a significant increase in flexural strength of an ethanol-based one bottle adhesive by adding up to 1% of filler.

The strength of the adhesives should be sufficient to resist the polymerization shrinkage of the composite without creating microcracks, voids or any other discontinuity in the tooth/restoration interface.[13] It is expeculated whether the addition of filler particles could not only improve the strength of adhesives but also reduce the number of structural flaws that could lead to catastrophic failure. The Weibull statistics have been employed to verify the effect of the flaw distribution on the mechanical properties of several materials,[14–18] and is perfectly suitable to determine the effect of microstructural alterations on the distribution of failure stress. Besides, parameters others than the Weibull modulus (m) and the characteristic strength (σ_0), which help to visualize the extremes of the stress distribution, are provided by such approach.[15,18]

The mechanical behavior and the likelihood of failure of the adhesives are strongly affected by the degree of conversion (DC), which represents the consumption of the aliphatic C=C bonds during the setting of the material[19] and is determined by infrared spectroscopy.[20,21] A high percentage of non-reacted C=C bonds indicates that the material presents a more open structure and, therefore, is more susceptible to degradation[22] and to compromising of the mechanical properties.[23,24] Variations of filler percentage have been shown to significantly affect the DC in some studies,[21] while other studies found no significant influence.[13]

The aim of this study was to evaluate the effect of different filler content on the cohesive strength, degree of conversion and structural reliability of an experimental dental adhesive. The null hypothesis tested was that the inorganic filler content does not influence the properties evaluated.

2. Material and method

The experimental adhesive resins were formulated by mixing the monomers 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropyl)phenyl]-propane (Bis-GMA), 2-hydroxyethyl methacrylate (HEMA) and trietilenoglicol dimethacrylate (TEGDMA) (Esstech Inc., Essington, PA, USA), which were used as received, in a 50/25/25 wt% ratio. To make the materials light curing, a binary light-curing system constituted by 0.4% of camphorquinone (CQ, Esstech) and 0.8% of ethyl 4-dimethylaminebenzoate (EDAB, Fluka, Milwalkee, WI, USA) were dissolved in the mixture. The reagents were used as received, without further purification.

The silica nanofillers (7 nm average particle size, Aerosil 380, Degussa, Germany) were silanized by gamma-methacryloxypropyltrimethoxysilane (γ-MPTS, Aldrich Chemical Co., Milwalkee, WI, USA). The nanofiller were added in an acetone (Labsynth Ltda., Diadema, SP, Brazil) solution containing γ-MPTS (10% of the filler wt) and a slurry was formed. The mixture was stored for 24 h at 37 °C to assure the complete solvent removal. After storage, the fillers were sieved through a 150 μm sieve.

Five experimental resins were formulated according to the filler weight percentage (wt%): 0, 1, 3, 5 and 10%. The filler was added to the resin and mechanically mixed by a motorized mixer (stirring). In order to assure the adequate dispersion of the filler, the experimental resins were ultrasonicated during 1 h.

The adhesive resin of the three-step etch-and-rinse adhesive system (Adper, Scotchbond Multi-Purpose, batch no. 6BB, 3 M ESPE, St. Paul, MN, USA—SBMP), with no filler in the composition, was used as commercial reference.

2.1. Cohesive strength (σ)

Specimens of 10.0 mm length × 10.0 mm of width × 1.0 mm thick were produced using a silicone based mold. Twenty dumbell-shaped specimens with cross-sectional area of 0.5 ($\pm$1.0) mm^2 were made for each group. The specimens were light cured for 25 s in both, top and bottom surfaces, using a LED light-curing unit (Radii, SDI, Bayswater, Victoria, Australia) with irradiance of 1400 mW/cm^2, measured with a power meter (Ophir Optronics, Danvers, MA, USA).

The specimens were carefully examined in light microscopy at 40× magnification in order to identify any defect close to or in the constriction zone. Thereafter, the area of the constriction zone was measured with a digital caliper. The specimens were dry-stored for 24 h at room temperature. Following, they were fixated in the metallic device with cianoacrylate-based glue and tensile tested in a universal testing machine (EMIC DL 500, São José dos Pinhais, PR, Brazil) at a 0.5 mm/min crosshead speed till fracture. The σ was calculated and expressed in MPa.

2.2. Degree of conversion

Degree of conversion from experimental materials were evaluated using real time Fourier Transform infrared spectroscopy at a Shimadzu Prestige21 spectrometer (Shimadzu Corporation, Kyoto, Japan) equipped with a attenuated total