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Zirconia nanoparticles prepared by laser vaporization as fillers for dental adhesives

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ABSTRACT

Zirconia nanoparticles prepared by laser vaporization were incorporated into the primer or into the adhesive of a commercial adhesive system in order to evaluate its effect on bond strength to dentin. Zirconia nanoparticles (20–50 nm) were prepared using a particular laser vaporization technique and incorporated into the primer (P) or into the adhesive (A) of the Adper Scotchbond Multi-Purpose (SBMP) system at 5, 10, 15 and 20 wt.% by means of mechanical mixing (stirring) and ultrasonication. Control (unfilled) and experimental groups (filled) were applied, according to the manufacturer's instructions, onto flat mid-coronal human dentin. Composite crowns were built up, stored in distilled water for 24 h at 37 °C and cut into 0.65 ± 0.05 mm^2 beams following a non-trimming microtensile technique. Specimens were fractured in tension using a universal testing machine (Zwick) and examined by scanning electron microscopy for fractographic analysis. Microtensile bond strength (μTBS) data were analyzed using a two-way ANOVA and modified LSD test at $\alpha = 0.05$. Analysis of the nanofiller distribution and ultramorphological characterization of the interface were performed by transmission electron microscopy (TEM). Zirconia nanoparticle incorporation into the primer or into the adhesive of SBMP significantly increased μTBS to dentin. Filler concentration only affected μTBS significantly in the P group. Statistically significant differences between groups P and A occurred only at 20 wt.% filler content, with a significantly higher μTBS in group P. TEM micrographs revealed nanoparticle deposition on top of a hybrid layer when incorporated into the primer, whereas they remained dispersed through the adhesive layer in group A. Zirconia nanoparticles incorporation into SBMP increased bond strength to dentin by reinforcing the interface adhesive layer. Nanofiller incorporation into the primer solution showed a tendency of increasing bond strength with increasing concentration. At high concentrations (20 wt.%) nanofiller incorporation was more efficient in increasing bond strength if incorporated in the primer solution. Adding nanofillers to the primer and to the adhesive solutions resulted in different particle distributions at the interface.

1. Introduction

Filler incorporation induces toughening mechanisms in crystalline, semi-crystalline and amorphous materials [1–4]. In polymers particle incorporation has shown a reinforcing effect by crack deflection and local plastic deformation around the particle [5,6]. Reducing the particle size down to the nanoscale, closer to polymer chain size, chain/filler interactions are affected, due to the increased surface to volume ratio of the fillers, with a direct impact on polymerization dynamics and internal stress development. Under loading, nanoparticles have the ability to reorient in a stress dissipation mechanism in order to inhibit crack extension in semi-crystalline and amorphous polymers [7,8]. For surface coating polymers "crack healing" mechanisms have been described, in which nanofillers are attracted to the substrate, filling surface defects through a "depletion attraction" phenomenon [9].

In dental adhesives fillers are incorporated to increase viscosity, as radiopaque components or as a means of improving the mechanical properties of the neat polymer blend. Significant increases in flexural and tensile strength by incorporating 1–10 wt.% silica nanofillers into adhesive resins have been reported [10,11]. Recently it has been shown that the addition of hydroxyapatite nanorods significantly increases the diametral tensile strength and flexural strength of an experimental adhesive when added at 0.2–0.5 wt.% [12].

At the dentin–composite interface level, cohesive failure within the adhesive resin has been often attributed to higher dentin–composite bond strength values [13,14]. Strong adhesion to tooth substrates shifts the fracture plane from the interface to the next weakest element, so that stronger adhesives should render stronger bonds between tooth and composite resins. However, different

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studies yield diverging conclusions regarding nanoparticle incorporation into adhesive resins and dentin bond strength increase. Miyazaki et al. [15] found a significant shear bond strength increase with the addition of up to 20 wt.% filler addition and bond strength deterioration when the filler content exceeded 50 wt.%. When hydroxyapatite was used as a nanofiller bond strength increased significantly at 0.2 wt.% content, but decreased to the initial level with further packing [12]. Conversely, filled adhesives have failed to increase dentin bond strength in comparison with their unfilled counterparts in several studies [11,16,17].

The purpose of this study was to evaluate the effect of adding spherically shaped, laser evaporated zirconia nanofillers into the primer or into the adhesive resin of a commercial three-step etch and rinse adhesive on dentin bond strength and correlate it with interfacial morphological characteristics. The null hypotheses tested were that: (1) the incorporation of nanofillers does not increase bond strength to dentin; (2) the filler content has no influence on bond effectiveness to dentin; (3) there is no difference when incorporating the fillers into the primer or into the adhesive resin.

2. Materials and methods

2.1. Preparation of zirconia (ZrO_2) nanoparticles

Zirconia (ZrO_2) nanoparticles were prepared using a particular CO_2 laser evaporation (LAVA) technique. This highly versatile and potent method allows the continuous production of a multiplicity of nanoscaled particles and nanopowders under well-defined and stable conditions. The LAVA process and the laboratory set-up have been described in detail elsewhere [18–20]. Briefly, a CO_2 laser beam is focused onto the surface of a coarse raw powder. Its chemical composition commonly is the same as that of the desired nanopowder.

Table 1
Technical data of the LAVA laboratory set-up.

CO_2 laser type	FEHA SM 2000E, steady-state power up to P_{max} = 2 kW, wavelength λ = 10.59 μm, electrically pulsable
Focusing mirror	Focal length f = 1000 mm, focus intensity up to I_{max} = 0.15 MW cm^{-2}
Carrier gas	Air or gas mixtures, volume flow rates up to $\dot{V}_{tot} = 20$ m^3 h^{-1}
Powder separation	Metal bag filter or paper filter tube
Production rates	Dependent on material and process parameters up to several 10 g h^{-1}

Absorbing the intense laser radiation the raw material heats up and vaporizes. Superheating and ionization of the vapor leads to the formation of a plasma. Evaporation and plasma generation proceed in a continuously flowing carrier gas (condensation gas) under atmospheric pressure. Expanding into the flowing gas, the plasma and the hot vapor are rapidly quenched and ultrafine particles grow by gas phase condensation. Driven by the carrier gas flow they are transported out of the condensation zone into the filtering unit. From here the desired nanopowder is finally extracted. Table 1 summarizes technical data of the LAVA laboratory set-up.

Preparation of the ZrO_2 nanopowder in the LAVA laboratory set-up started from a coarse tetragonal zirconia powder (TZ-3YS-E, partially stabilized with 3 mol.% yttria (Y_2O_3), TOSOH Corp., Tokyo, Japan). The raw powder was vaporized under air as the carrier gas (constant flow rate $\dot{V}_{tot} = 14.5$ m^3 h^{-1}) applying continuous CO_2 laser radiation (output power P = 2 kW). The ZrO_2 nanoparticles were separated from the generated particle aerosol on a metal bag filter. Under these process conditions a production rate of 23 g ZrO_2 nanopowder per hour was achieved. Transmission electron microscopy (TEM) micrographs (Fig. 1) show the typical morphology of the resulting ZrO_2 nanoparticles. These particles (sizes range from about 20 to 50 nm) are of spherical shape and merely softly agglomerated by weak van der Waals forces. Only a marginal fraction of the particles was firmly bonded by solid-state bridges ("sinter necks"). Thus, it should be possible to deagglomerate the LAVA generated ZrO_2 nanoparticles by ultrasonication.

2.2. Nanoparticle incorporation into the adhesive system

The zirconia fillers were incorporated into the primer (P) or into adhesive solutions (A) of the Adper Scotchbond Multi-Purpose (SBMP) commercial adhesive system (3M ESPE, St. Paul, MN) in 5, 10, 15 and 20 wt.%. After being weighed using a high accuracy balance (YDK01, Sartorius, Goettingen, Germany), the fillers were added to the resin solutions and mechanically mixed with a motorized stirrer (Roti-Speed hand piece with conical micro pestle adapter, Roth, Karlsruhe, Germany). To further increase the dispersion of the fillers the resin mixtures were ultrasonicated for 1 h (Elmasonic Ultrasonication Bath, Elma, Singen, Germany) and subsequently applied to the etched dentin.

2.3. Bonding procedures, specimen fabrication and microtensile testing

Sound human third molars were stored in 0.5% chloramine solution and used within 3 months of extraction. Using a low speed

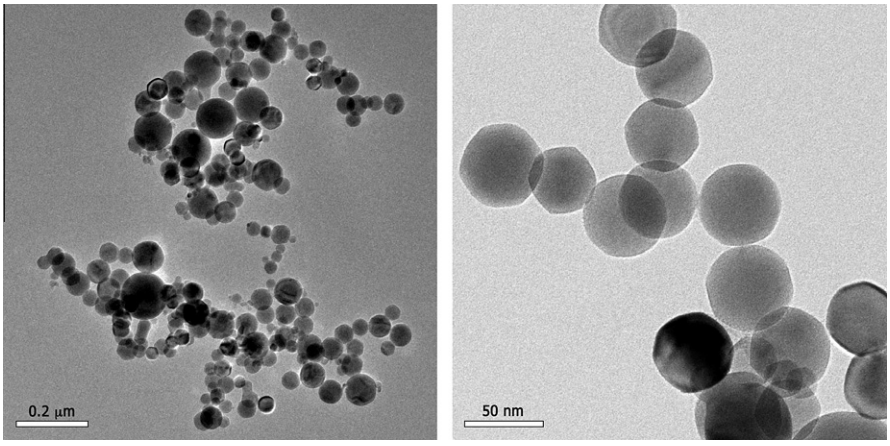

Fig. 1. TEM photomicrographs of the LAVA generated ZrO_2 nanoparticles. Raw material TOSOH TZ-3YS-E zirconia powder, continuous laser power 2 kW, process gas air, flow rate of the process gas 14.5 m^3 h^{-1}.

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