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Surface analysis and shear bond strength of zirconia on resin cements after non-thermal plasma treatment and/or primer application for metallic alloys

Aljomar José Vechiato-Filho [a,*], Adaias Oliveira Matos [b], Richard Landers [c], Marcelo Coelho Goiato [d], Elidiane Cipriano Rangel [e], Grace Mendonça De Souza [f], Valentim Adelino Ricardo Barão [g], Daniela Micheline dos Santos [h]

[a] Department of Dental Materials and Prosthodontics, Aracatuba Dental School, Univ. Estadual Paulista - UNESP, Aracatuba, Sao Paulo, Brazil
[b] Department of Prosthodontics and Periodontology, Piracicaba Dental School, University of Campinas (UNICAMP), Piracicaba, Sao Paulo, Brazil
[c] Institute of Physics Gleb Wataghin, University of Campinas (UNICAMP), Cidade Universitária Zeferino Vaz, Barão Geraldo, Campinas, Sao Paulo, Brazil
[d] Department of Dental Materials and Prosthodontics, Aracatuba Dental School, Univ. Estadual Paulista - UNESP, Aracatuba, Sao Paulo, Brazil
[e] Laboratory of Technological Plasmas (LaPTec), Engineering College, Univ. Estadual Paulista - UNESP, Sorocaba, Sao Paulo, Brazil
[f] Department of Clinical Sciences, Faculty of Dentistry, University of Toronto, Toronto, ON, Canada
[g] Department of Prosthodontics and Periodontology, Piracicaba Dental School, University of Campinas (UNICAMP), Piracicaba, Sao Paulo, Brazil
[h] Department of Dental Materials and Prosthodontics, Aracatuba Dental School, Univ. Estadual Paulista - UNESP, Aracatuba, Sao Paulo, Brazil

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ABSTRACT

There is no established protocol for bonding zirconia (Y-TZP) with resin cements. Non-thermal plasma (NTP) may be an alternative for the clinical problems related to adhesion. The purpose of the present study was to characterize the surface of Y-TZP exposed to methane (CH_4) NTP or coated with a layer of primer for metal alloys and the association between the two methods and to evaluate the effect of NTP treatment on bond strength between Y-TZP and two resin cements. A total of 235 Y-TZP discs (8 × 2 mm) were distributed into five groups: Co (no surface treatment), Pr (primer), NTP (methane plasma), Pr + NTP and NTP + Pr. The effect of the treatment type on the surface free energy, morphology, topography and chemical composition of the Y-TZP discs was investigated. The discs were cemented to composite resin substrates using Panavia F2.0 or RelyX U200. Shear bond strength (n = 10) analyses were performed (1 mm/min) before and after thermocycling (5–55 °C, 2000 cycles) on the bonded specimens. The data were analyzed with one and three-way ANOVAs and Bonferroni tests (α = 0.05). NTP reduced the surface energy and roughness of the Y-TZP discs. SEM-EDS and XPS analyses showed the presence of the organic thin film, which significantly improved the bond strength results when Rely X U200 was used, whereas the primer treatment was more effective with Panavia F2.0. Thermocycling significantly reduced the bond strength results of the NTP and Pr + NTP groups cemented with Rely X U200 and the Pr and NTP + Pr groups cemented with Panavia F2.0. Nonthermal plasma improves the bond strength between Rely X U200 and Y-TZP and also seems to have water-resistant behavior, whereas Panavia F2.0 showed better results when associated with primer.

1. Introduction

In recent years, dental ceramics with a high crystalline content have been widely used as a core material for fixed restorations because of their high fracture resistance, chemical stability and superior aesthetic properties when compared to other low-fusing ceramic systems [1–7]. However, as the crystalline content increases, the glass phase of the ceramic composition is reduced [6]. As a consequence, the etching effect caused by the hydrofluoric acid gel on the glass phase of low-fusing ceramic is not obtained, and this protocol cannot be recommended for yttria-tetragonal zirconia polycrystals (Y-TZP). Although the acid-resistant surface does not seem to be problematic when Y-TZP cores are cemented on ideally anatomic preparations, high bond strength may be required for milled, cast or pressed restorations, which have with misfit of ≈100 μm and can be considered lesser retentive restorations [1]. Therefore, the development of any approach that could result in a stronger adhesive interface would be useful for those clinical scenarios.

Several approaches have been investigated for enhancing the resin bond to zirconia-based restorations [1,6,8–12]. However, some studies

* Corresponding author at: Department of Dental Materials and Prosthodontics, Aracatuba Dental School, Univ. Estadual Paulista - UNESP, Jose Bonifacio, 1153, 16015-050 Aracatuba, Sao Paulo, Brazil.
E-mail address: aljomarvechiatoflo@gmail.com (A.J. Vechiato-Filho).

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have indicated that some of them may create critical flaws in the ceramic surface, leading to their catastrophic failure [6,9,11–13]. These findings may explain the reports of clinical failures [13–16], in spite of the fracture strength values being well above the stresses estimated for the posterior areas of the mouth [13]. Moreover, previous studies have suggested that some primers containing 10-methacryloyloxydecyl dihydrogen phosphate (MDP) showed no significant benefit compared to zirconia bonding because this surface treatment does not create a hydrolysis-resistant interface, which results in reductions in bond strength up to 87% for Panavia cements after 5 months of water storage [6,11].

In addition, nonthermal plasma (NTP) treatments have been considered an alternative solution for clinical problems related to adhesion [17,18,19]. In summary, the plasma technique may improve the adhesion by creating new reactive sites onto a substrate surface, which chemically bond to another substrate [17–20]. A previous study demonstrated that thin films created by methane (CH_4) plasma indeed reduce the contact angle and increase free surface energy of some materials used in biomedical devices [20–22].

Considering that the plasma may be generated containing reactive and energetic species and that the exposure of a material to this environment will inevitably change the properties of the outermost layers, it is speculated that organic films deposited from methane may improve the adhesion between zirconia and resin cements because they would be well connected to the ceramic and possess an affinity to cement. However, to the best of the authors' knowledge, no study has evaluated CH_4–based NTP to improve the chemical bonding of Y-TZP to resin cements. Moreover, the association of promising surface treatments has already been investigated by an *in vitro* investigation, but not for MDP-based primers and plasma methods [8]. Undoubtedly, the durability of this new interface has to be tested through artificial aging [1,23]. A thermocycling challenge in an aqueous environment is commonly used to simulate mechanical fatigue in the wet oral environment [1,21,23–27]. Indeed, the hydrolytic stability of the bonding may affect the clinical performance of an indirect restoration because the humidity of the oral environment accelerates the degradation of the adhesive interface. Therefore, thermocycling is considered to provide clinically relevant information [1,21,23–27].

Thus, the aims of this study were: (1) to characterize the surface of Y-TZP discs with or without nonthermal plasma or primer and the association of both based on surface energy, surface roughness, scanning electronic microscopy (SEM), energy dispersive spectroscopy (EDS), and X-ray dispersive spectroscopy (XPS) analyses, and (2) to evaluate the bond strength between Y-TZP-treated surfaces and two resin cements before and after thermocycling. The null hypotheses were that both treatments would not modify the surface characteristics of Y-TZP and affect the bond strength between this ceramic system and tested resin cements.

2. Materials and methods

2.1. Experimental design

The materials used in the present study are listed in Table 1. A total of 235 discs of Y-TZP (8 mm diameter × 2 mm thickness) were cut and sintered according to manufacturer's instructions. The treatment applied to the Y-TZP disc surfaces were: control (Co, no surface treatment), alloy primer application (Pr), non-thermal plasma treatment (NTP), primer application followed by non-thermal plasma treatment (Pr + NTP), and non-thermal plasma treatment followed by primer application (NTP + Pr). Seven discs per group (n = 7) were used for surface energy and surface roughness, SEM-EDS and XPS analyses immediately after surface treatment. Forty discs per group were used for the shear bond strength test, distributed as follows: 20 discs cemented with MDP-based resin cement (Panavia F2.0) and 20 cemented with ester phosphoric methacrylate-based cement (Rely X U200). Ten discs from each group were tested after the bonding procedure, and the remaining 10 were aged by means of thermocycling before being tested for shear bond strength. The flowchart shown in Fig. 1 schematizes the experimental procedures adopted here.

For the sample preparation, the Y-TZP discs were embedded in the center of cylinder cups (SamplKups, Buehler) fabricated by using autopolymerizing acrylic resin (JET, Classico). After its polymerization, the embedded Y-TZP discs were sequentially polished with a pre-established protocol [18]. Discs were then cleaned and degreased with a sequence of alternate ultrasonic bath [18]. The primer was applied onto the Y-TZP surface of the Pr, Pr + NTP and NTP + Pr groups using microbrushes (Microbrush; Microbrush International) for 60 s. Then, the solvent was removed with gentle air jets.

2.2. NTP treatment

The Y-TZP discs from the NTP, Pr + NTP and NTP + Pr groups were subjected to NTP treatment. Plasma treatment was performed inside a stainless steel chamber. The system was evacuated to a background pressure of 3.6×10^{-2} Torr. Before the CH_4 plasma depositions, argon (Ar) gas was admitted into the chamber, and cleaning plasmas were prepared at a radiofrequency of 13.56 MHz (70 W) and applied in the sample-holder for 600 s under a constant work pressure of 1.67×10^{-1} Torr. The depositing plasma, maintained for 1800 s, were then established by applying a radiofrequency signal (13.56 MHz, 70 W) to the top electrode while biasing the sample holder with negative pulses (3.12 kV, 299 Hz, 25 μs and 0.75% of duty cycle). Under these conditions, positive ions from the plasma were attracted by the negative potential and implanted on the surface and subsurface region of the samples placed in the biased electrode simultaneously to the film deposition and according to the Plasma Immersion Ion Implantation and Deposition (PIIID) approach. In the first stages of the process, ion

Table 1
Characteristics of materials used in the present study.

Materials	Composition	Fabricant
Ceramill zi system	99% of Y_2O_3/HFO_2/Al_2O_3/1% of other oxides	ARMANGIRRBACH
Z100 composite resin	Bis-GMA/TEDGMA/zirconia/silicon	3M ESPE
Rely X U200 (Base Catalyst)	Vitreous powder/silicon/calcium hydroxide/methacrylate phosphatide ester/di methacrylate/initiators	3M ESPE
Panavia F2.0 (Paste A Paste B Oxyguard II)	BPEDMA/MDP/DMA/silica/barium sulfate/dibenzoylperoxide N,N-Diethanol-p-toluidine/silica sodiumfluoride Polyethyleneglycol/glycerine/sodium benzenesulfinate cont. gel 3-Methacryloxypropil trimethoxy silane/MDP/ethanol phosphoric acid	Kuraray America Inc.
Alloy primer	MDP, VBATDT, 98.5% acetone	Kuraray America Inc.
CH_4, O_2 and Ar	Methane, oxygen and argon	White Martins

*Information provided by the manufacturer: Bis-GMA: bis-phenol-A diglycidyl dimethacrylate; TEDGMA: Triethyleneglycoldimethacrylate; BPEDMA: bisphenol-A-polyethoxy dimethacrylate; DMA: aliphatic dimethacrylate; MDP: 10-methacryloxydecyl dihydrogen phosphate; VBATDT: 6-(4-vinylbenzyl-n-propyl)amino-1,3,5-trizaine-2,4-dithiol.