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Effect of nonthermal plasma treatment on surface chemistry of commercially-pure titanium and shear bond strength to autopolymerizing acrylic resin

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ABSTRACT

The effect of nonthermal plasma on the surface characteristics of commercially pure titanium (cp-Ti), and on the shear bond strength between an autopolymerizing acrylic resin and cp-Ti was investigated. A total of 96 discs of cp-Ti were distributed into four groups (n = 24): Po (no surface treatment), SB (sandblasting), Po + NTP and SB + NTP (methane plasma). Surface characterization was performed through surface energy, surface roughness, scanning microscopy, energy dispersive spectroscopy, and X-ray diffraction tests. Shear bond strength test was conducted immediately and after thermocycling. Surface treatment affected the surface energy and roughness of cp-Ti discs ($P < .001$). SEM–EDS showed the presence of the carbide thin film. XRD spectra revealed no crystalline phase changes. The SB + NTP group showed the highest bond strength values (6.76 ± 0.70 MPa). Thermocycling reduced the bond strength of the acrylic resin/cp-Ti interface ($P < .05$), except for Po group. NTP is an effective treatment option for improving the shear bond strength between both materials.

1. Introduction

Acrylic resins — polymers based on polymethylmethacrylate (PMMA) — are widely used as a superstructure material for implant-supported fixed dentures [1,2] because of their similarity to oral soft tissues, low cost, biocompatibility, easy handling [3,4], and its assumed "cushion effect" on masticatory loadings to the peri-implant hard tissue [1,5]. Despite these advantages, denture durability might be affected by the adhesion of PMMA to the metal framework [6]. Frameworks of implant-supported fixed dentures are mainly fabricated with commercially pure titanium (cp-Ti) due to advances in the casting procedures [7] and the favorable properties such resistance to corrosion, biocompatibility and relatively low cost [3].

In vitro studies show that acrylic resins have poor bonding to metal alloys [3,6–10]. Failure at the metal-resin interface may lead to significant clinical complications [3,7,10]. In general, the failures are adhesive in nature and allow the micro-leakage of oral fluids, microorganisms and oral debris [3,7,8], resulting in biodegradation of the PMMA material [4]. As a consequence, the strength of this bonding, which is relatively low, decreases, and fractures of the resin material may occur [8]. This might be the major factor that is responsible for the high incidence (from 43.75% to 66.6%) of resin superstructure fractures (most common clinical problem) and prosthesis maintenance after 15 years of follow up [11,12].

The use of autopolymerizing acrylic resins is considered to be an economical and non-time-consuming method for performing repairs of dentures with PMMA-based materials as superstructures [6,9,10]. However, the resin-metal interface may not be durable because the strength of this chemical bonding decreases (≈60%) in the short-term [6]. Therefore, developing treatments to improve the bonding of resins to metal alloys has been the goal of some studies [3,7,8].

Several methods for improving the bonding between acrylic resin superstructures and metal frameworks have been proposed [6–8,10]; sandblasting with aluminum oxide particles (Al_2O_3) is one of the most effective methods for increasing the bond strength between these two materials [8]. In addition, some studies have used nonthermal plasma (NTP) treatments to improve the bonding values in dental ceramics; these treatments are considered an alternative solution for the clinical problems related to adhesion [13–17]. The plasma technique may increase the adhesion of a substrate to new molecules through improving its wettability by inducing strong chemical bonds and new chemically reactive sites [13–17]. NTP treatments are widely used in industry [18,19], and a previous study demonstrated that the plasma created by

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methane gas (CH_4) associated with ion bombing through high-energy electro-pulses has a satisfactory result for improving the contact angle and free surface energy of some metals (Ti and Ti–6Al–4V alloy) and polymers (Teflon, silicone rubber, nylon, polyvinyl-chloride and polyurethane) used in biomedical devices [17]. Moreover, it has been shown that high-energy electro-pulsing treatment also improves the mechanical properties of Ti–6Al–4V (i.e. ductility and strength-toughness), as well as its corrosion behavior [20,21].

Because the CH_4 plasmas might improve the Ti wettability, it is assumed that they might be used to improve the adhesion between this material and other materials. However, to the best of the author's knowledge, no study evaluated the NTP created by CH_4 to improve the chemical bonding of PMMA to cp-Ti. Artificial aging through thermocycling is necessary for evaluating the performance of an adhesive interface because this condition affects the bond strength of two different materials and is considered a clinically relevant aging parameter [22,23]. Thus, the aims of this study were as follows: (1) to characterize the surface of cp-Ti discs with or without NTP treatment based on surface energy, scanning electronic microscopy associated with energy dispersive spectroscopy (SEM–EDS), and X-ray diffraction (XRD) analyses; and (2) to evaluate whether the NTP treatment improves the shear bond strength between an autopolymerizing acrylic resin and cp-Ti before and after thermocycling. The tested hypotheses were that the NTP treatment would modify the surface characteristics of cp-Ti and would improve the shear bond strength between PMMA and cp-Ti.

2. Materials and methods

2.1. Experimental design

The materials used in the present study are listed in Table 1. A total of 96 discs of cp-Ti (8 mm in diameter × 2 mm in thickness) that were grade IV according to the American Society for Testing Materials (ASTM) were obtained (Conexão Sistemas de Prótese Ltd., Arujá, SP, Brazil). The discs were randomly divided into 4 groups (n = 24) as follows:

- Po group = control; no surface treatment was conducted.
- SB group = sandblasting with aluminum oxide particles (Al_2O_3).
- NTP group = nonthermal plasma treatment.
- SB + NTP group = sandblasting with Al_2O_3 + nonthermal plasma treatment.

The cp-Ti discs were positioned in the center of cylinder cups (SamplKups; Buheler, Lake Bluff, IL, USA) and embedded in an autopolymerizing acrylic resin (JET, Classico, Sao Paulo, SP, Brazil). After acrylic resin polymerization, the embedded cp-Ti discs were sequentially polished with 320-, 400- and 600-grit abrasive papers (CarbiMet 2; Buehler, Lake Bluff, IL, USA) with constant water irrigation in a semi-automatic polishing machine (Aropol 2V; Arotec, Cotia, SP, Brazil). Then, the cp-Ti discs from the SB and SB + NTP groups (n = 48) were sandblasted with 120 μm particles of Al_2O_3 (Polidental Industria Comercio Ltd., Cotia, SP, Brazil) deposited from a 50 mm distance with 90° of angulation using 0.45 MPa bar pressure for 30 s [24]. The cp-Ti discs were then cleaned with alternate ultrasonic baths in deionized water (1 min), 99.3% ethyl alcohol (5 min), and again in deionized water (1 min) to remove the smear layer from the specimen surface [14].

2.2. NTP treatment

The cp-Ti discs from the NTP and SB + NTP groups were subjected to NTP treatment. Plasma treatment was performed inside a stainless steel chamber by using a custom-made reactor from the Technological Plasma Laboratory (LaPTec; Sao Paulo State University — Engineering College, Sorocaba, SP, Brazil) 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) applied in the sample-holder for 600 s under a constant work pressure of 1.67×10^{-1} Torr. Immediately after this cleaning procedure, Ar was stopped, and the chamber was evacuated again to the background pressure. Then, the plasma depositions were prepared from mixtures of 92% of CH_4 gas and 8% of Ar at 13.56 MHz (70 W) applied in the superior electrode for 600 s under 1.67×10^{-1} Torr. The plasmas were created with the ion implantation and deposition by immersion in plasmas (IIDIP) technique using the following conditions: 3.12 kV, 299 Hz, 25 μs and 0.75% of working cycle. In IIDIP, high pulses of negative tension are applied in the sample-holder so that ions are accelerated and implanted (ionic bombing) on the surface and subsurface of the cp-Ti discs, creating thin-films with improved mechanical and tribological properties. The cp-Ti discs were removed from the stainless glass chamber at a temperature of 33 °C, thereby preserving the surface integrity.

2.3. Surface energy

Three cp-Ti discs from each group were subjected to surface energy analysis using a goniometer (Ramé-Hart 100–00; Ramé-Hart Instrument Co., Succasuanna, NJ, USA). A 0.5-μL drop of deionized water (polar component) and diiodomethane (dispersive component) was dropped through a 50-μL glass syringe. The contact angle was calculated by means of the Young equation: $\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \Theta$; where Θ is the contact angle and g is the surface energy of the solid–vapor (sv), solid–liquid (sl) and liquid–vapor (lv) interfaces. The surface energy was calculated using the Owens–Wendt–Rabel–Kaelble method. The relationship between the contact angle and the surface energy was evaluated using the formula $\gamma L = \gamma^D L + \gamma^P L$, where γL is the total surface energy, $\gamma^D L$ is the dispersive (apolar) component and $\gamma^P L$ is the polar component. Ten measurements were performed per disc (n = 100 total readings).

2.4. Surface roughness

Surface roughness was measured with a profilometer (Dektak D150; Veeco, Plainview, NY, USA). Three discs from each experimental group were used for the roughness test. The Ra (arithmetic mean of surface roughness), Rq (root-mean-square roughness), Rz (height between the maximum and minimum profiles over evaluation length), and Rt (vertical distance between the highest peak and the deepest pit) values were obtained by using a *cutoff* of 500 μm for 12 s. Three readings were taken: 1 at the center of the specimen and 2 parallel readings to the

Table 1
Materials used for the present study.

Material (identification)	Composition (in % of weight)	Batch number	Manufacturer
Commercially pure titanium (cp-Ti) (grade IV)	0.03 N, 0.1 C, 0.0125 H, 0.3 Fe, 0.25 O, balance Ti	142440	Conexao Sistemas de Protese Ltd.
Autopolymerizing acrylic resin (JET)	Powder: methyl ethyl methacrylate copolymer, organic pigments (medium pink hue), peroxide Liquid: methyl methacrylate monomer, dimethacrylate	015070	Classico
Methane (CH_4)	100% methane vapor	USLY001027	White Martins
Argon (Ar)	100% argon vapor	15116/12	White Martins