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Injection-type Denture Base Materials Surface Modification after Vapor Plasma Deposition

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Abstract: *The purpose of this study was to investigate changes of superficial topography and wettability of two injection-type denture base materials following low pressure plasma treatment. Samples of denture base materials (Polyan and Biodentaplast) were fabricate using dedicated technology and were exposed to plasma treatment. Resin surface topography and rugosity were evaluated using SEM and AFM, while wettability was determined through contact angle measurements. Artificial saliva was the testing liquid. Initial contact angles for the two materials are close (Biodentaplast-37.60°, Polyan-36.75°). Plasma treatment halves the values of the contact angle. 30-days measurement reveals a reduced bounce-back effect (Biodentaplast-20.68°, Polyan-20.11°). Surface topography modified differently for the two materials. Rugosity increased significantly for both materials ($p<0.05$). Surface rugosity values pre- and post-plasma treatment respect the biological threshold of fungal adhesion. Plasma exposure increased injection-type denture base materials wettability with artificial saliva and surface roughness. Injection-type denture base materials and artificial saliva can enhance prosthetic experience of xerostomic patients.*

Keywords*: vapor plasma deposition, denture base, wettability, roughness*

1. Introduction

Denture retention represents a complex phenomenon which has its foundation in a three-component system: mucosa, saliva and denture base. Mucosa and salivary characteristics degrade in the elderly. This population category is exposed to dry mouth and xerostomia due to age-based degenerescence of salivary glands and overmedication [1-3]. European (Eurostat) [4] and national statistics (Romanian National Institute of Statistics) [5] show that in 2014 approximatively 25% of the population was aged over 60 years. Increase of life-time and low birth rate are the factors that will contribute to a higher percent of elderly in the following decades, according to the same statistical data.

Improvement of denture base materials represents an important step towards a better quality of life for denture wearers, especially those with reduced salivary function. Close fit and maximum physiological extension of complete dentures are mandatory and can be obtained only trough perfect clinical and laboratory work. In addition, plasma surface treatments enhance denture base material's wettability [6-13] and can reduce microbial adherence to denture base materials [14,15]. Material's superficial rugosity remains an unclear issue regarding its influence on fungal adherence and material's wettability [14,16-18]. Injection-type denture base materials were recently introduced in the technology of removable dental prostheses and are currently less investigated than classical PMMA materials regarding their surface properties. Surface modification using plasma deposition involves physical and

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chemical actions that can meet the criteria of bioprophylaxis and superwettability for a better prosthetic experience. The association of this type of treatment with the use of artificial saliva can define a standard for xerostomic patients.

2. Materials and methods

2.1. Preparation of test specimens

Injection-type denture base materials (Table 1) were processed automatically using a dedicated injection unit (Thermopress 400 Injection Unit, Bredent, Germany). A 1.5 mm thick wax-plate (Superpink 660, YetiDental, Germany) was flasked and processed under accurate pressure and temperature control. The entire cooling process is automatic, the level of force is maintained for an optimum fit and prevention of porosity. All plates were sectioned in 10x10mm samples which were tagged and distributed for surface treatment. All specimens were kept in deionized water.

Table 1. Denture base materials tested

Brand name	Manufacturer	Polymerization type	Composition
Polyan	Polyapress, Germany	Injection-type, thermoplastic	Modified-PMMA
Biodentaplast	Bredent, Germany	Injection-type, thermoplastic	Polyacetal-Copolymer

*PMMA=Polymethylmethacrylate

2.2. Surface treatment techniques (low pressure plasma treatment)

The experiments for plasma deposition were performed in a Bell-Jar reactor. The capacitively-coupled discharge (RF, 13.56 MHz, max. 500W) was generated between two parallel planar electrodes. The upper electrode is connected to the RF power supply, while the grounded electrode is used as substrate holder. Argon was admitted into the chamber at a constant rate of 10 sccm. A preliminary vacuum of 0.02 torr was obtained using a rotary mechanical pump. Treatment time was set at 5 min. Low-pressure plasma treatment (VDP) was carried out in a capacitively coupled discharge between two parallel electrodes in the Bell-Jar configuration placed in a stainless-steel chamber. The upper electrode was RF powered (13.56 MHz, maximum power 500W) and designed as a shower for the uniform introduction of the gas. The lower electrode is grounded and supports the denture base material samples. Before deposition the reactor was evacuated to a pressure of 0.02 torr (2.66 Pa) using rotary pumps. Working gas (Ar) was introduced at a 10 sccm flow rate for 5 min.

2.3. Evaluation of wettability by contact angle measurements

The changes of wettability were assessed by measurement of contact angle at room temperature with CAM101 (KSV Instruments, Finland). For each drop 21 recordings were performed at 1 second interval with the mean contact angle value automatically computed and stored. Three drops were analyzed on each sample. The plasma treated samples were measured immediately and after 30 days from the surface treatment. Overall data was processed using a dedicated statistical software.

Artificial saliva was used as testing liquid for the contact angle measurements. Xerostom® with Saliactive (Biocosmetics laboratories, Spain) was the artificial saliva (AS) used for contact angle determinations. This mouth-spray is designed for dry mouth or xerostomic patients.

2.4. Evaluation of surface topography

The surface topography of acrylic samples was analyzed by using SEM (JEOL, JSM-6510, Tokyo, Japan). Micrographs both before and after polishing were taken to compare the change in surface roughness of each specimen. Acrylic specimens were mounted on a metal stuband coated with 10nm of gold in a sputter coater system (SPI, Gold Sputter Coater, Watford, UK) and surfaces topography was observed by SEM at a magnification of 100, 500, 1000, 2000 and 5000. All resin specimens were mounted on a metal stub and assessed directly at the same magnification.

2.5. Surface roughness measurements by Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) images on denture base samples surfaces were taken before and after plasma/sandblasting treatment with a Park XE-100 instrument from Park Systems (S. Korea). Areas of 5 × 5 μm and 40 × 40 μm were scanned in the non-contact mode with a silicon tip of 10-20 nm radius with a resonance frequency of 265 -400 kHz and a force constant of 20 - 75 N/m. Values of root mean square (RMS) roughness were calculated from the height values in the AFM images using a commercial software.

3. Results and discussions

3.1. Contact angle measurements

Low-pressure plasma deposition induced significant wettability changes in both materials. Investigation of the bounce-back effect mentioned in the literature was investigated trough contact angle measurement after 30 days from low-pressure plasma deposition (Table 2).

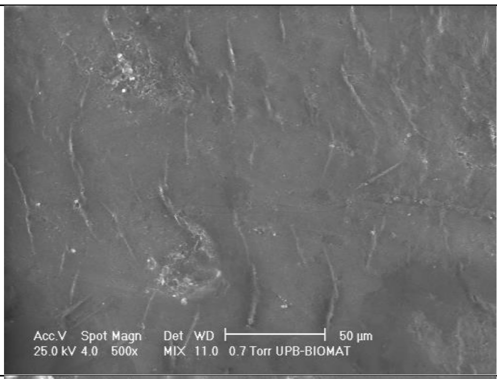
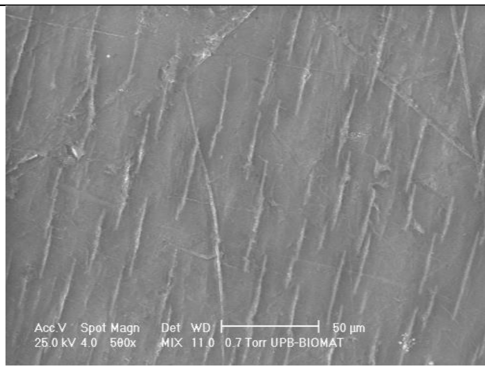
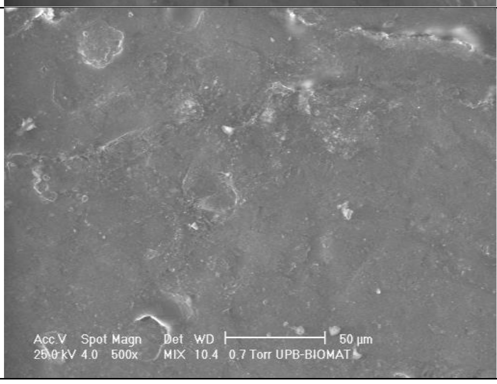
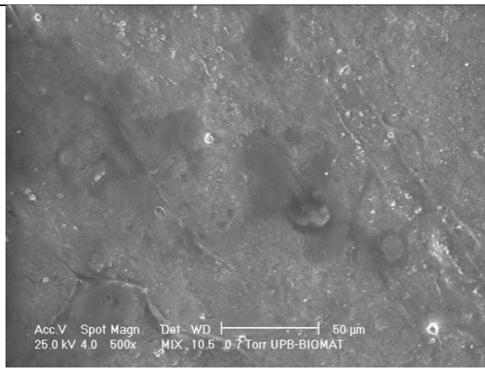
Material	Initial	Final	30 days after plasma deposition
Polyan	36.75	16.06	20.68
Biodentaplast	37.60	18.93	20.11

Table 2. Mean contact angle values before and afterlow-pressure plasma treatment

3.2. SEM results

SEM micrographs were evaluated before and after the vapor plasma deposition. Both materials presented surface irregularities. Regarding the pre-treatment surface aspect, modified-PMMA samples presented surface irregularities resembling lines, while the polyacetal-copolymer samples had mostly round prominent areas. Post treatment micrographs of Polyan samples show the accentuation of the pre-existing linear irregularities. The surface of Biodentaplast samples presented a fading of round prominences and the deepening of several areas (Table 3).

Table 3. Pre- and post-vapor plasma deposition SEM micrographs (x500) for the investigated materials

	Before VDP	After VDP
Polyan		
Biodentaplast		

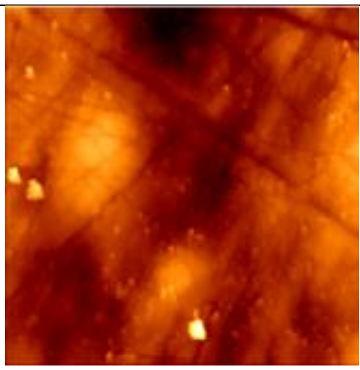
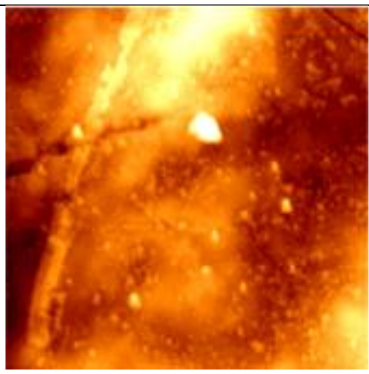
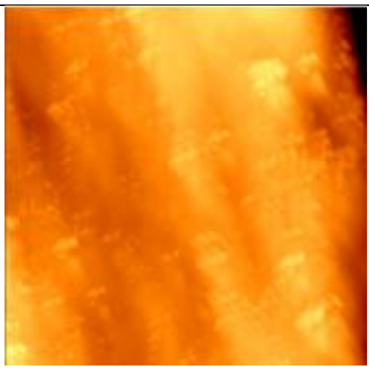
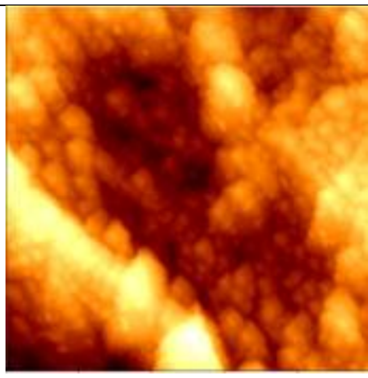
3.3. AFM results and roughness measurements

The mean value of surface roughness (Ra) before VDP treatment is similar for the two materials. VDP produced a significant increase of surface roughness (p=0.027) in Polyan samples, all of them presenting an increase of roughness. Also, a significant increase of Ra mean value was observed (p=0.036) in Biodentaplast samples though these samples presented showed both increases and decreases of surface rugosity (Table 4). The AFM images before and after VDP treatment are presented in Table 5.

Table 4. Mean values of Ra (μm) for tested materials

	Pre-treatment	Post-treatment	SS
Polyan	0.208 ± 0.254	0.267 ± 0.241	p=0.027
Biodentaplast	0.185 ± 0.162	0.195 ± 0.130	p=0.036

Table 5. Pre- and post-vapor plasma deposition AFM images for tested materials

	Before VDP	After VDP
Polyan		
Biodentaplast		

The thin film of saliva between mucosa and denture base was identified as one of the essential sources of denture retention. The liquid meniscus keeps air away from the denture and tissue surface. Both viscosity and surface tension affect the value of the retentive force [19]. Craig et al. [20] found high values for contact angles of water and saliva on denture resins, which denote a poor wettability of these resins because of their low surface energies. The contact angle represents a quantitative measure of the wetting process [21]. A liquid is considered to wet the substrate if the contact angle is lower than 90^0 while the perfect wetting corresponds to a 0^0 contact angle. Li et al. [22] investigated wettability of a PMMA-based resin with water (76.6^0) and natural saliva (74.1^0), similar values to our study. Also, Murray [23] reported some contact angle values: 79^0 with distilled water and 73.89^0 with fresh natural saliva. Etienne et al. [24] measured a higher contact angle (100^0) of distilled water with a PMMA-based denture base resin. Saliva substitutes have significantly better wetting capabilities than natural saliva presenting contact angles values of 20° to 40° on heat-polymerized acrylic resins or injection type resins [25-27].

Low-pressure plasma deposition is a time efficient process and induces surface modifications without affecting chemical and physical properties of the material. Many authors demonstrated the effectiveness of plasma treatment regarding the improvement of wettability. In similar plasma treatment and sample fabrication conditions, Zamperini et al. (2010) obtained a slightly higher contact angle with distilled water immediately after treatment (38.46^0) and a higher value after 48h in water (47.04^0). Ozden et al. [28] also found a lasting effect of plasma surface treatment, at least for 60 days. Yildirim et al. [29] presented similar values (22.30^0) of contact angle with distilled water for plasma exposure in oxygen atmosphere at 50W. We found a significant wettability increase for both materials submitted to plasma treatment and, most importantly, a good preservation of the effect in a 30-days period.

There is a larger variation regarding the rugosity of denture base materials due to different protocols used by authors for the fabrication of the samples. Zissis et al. reported a value of 3.4 μm to 3.8 μm for heat-cured materials without finishing. Slightly higher values were reported by Etienne et al. (4.0 μm). Abuzar et al. [30], testing samples obtained by molding of glass plates, found rugosity of a heat-cured resin to be 0.995 μm and of an injection-type polyamide 1.111 μm. Gungor et al. [31] reported a higher rugosity for an injection-type polyamide (1.64 μm) than a heat-cured PMMA-based denture base material (0.95 μm), both finished using a tungsten carbide bur at 10000 rpm. Wieckiewicz et al. investigated specimens smoothed with sandpaper, pre-polished with pumice slurry and polished with cotton polishers and polishing paste. These authors found a mean rugosity of 0.20 μm for a heat-cured PMMA-based resin, while an injection-type polyamide presented a rugosity of 0.28 μm. Zamperini et al. measured rugosity of heat-cured samples before plasma treatment and found a mean value of 1.76 μm. The 4 protocols applied by these authors produced an increase of rugosity in three cases and a decrease in one case. All these studies confirmed the decrease of rugosity by conventional laboratory polishing or by use of silicone finishing chairside kits. Scanning electron microscopy is a reliable and widely used surface topography investigation, [32,33] regarding denture base materials. SEM association with AFM measurement result in a more detailed picture of surface properties.

Within the limitations of this study, our results are similar to previous studies regarding injection-type denture base materials. Rugosity values before and after plasma treatment of these materials are lower than in polished, glazed or untreated heat-cured acrylic resins.

4. Conclusions

In our study, surface rugosity values pre- and post-plasma treatment were close to 0.2 μm, respecting the biological threshold of fungal adhesion. Plasma exposure increased injection-type denture base materials wettability with artificial saliva and surface roughness. Injection-type denture base materials and artificial saliva can enhance prosthetic experience of xerostomic patients.

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