

HYDROPHOBIC COATING OF DENTAL PMMA

Camila Gonçalves Duarte¹, Marina da Rosa Kaizer², Lisia Lorea Valente¹, Giana da Silveira Lima¹, Rafael R. Moraes¹

ABSTRACT:

Introduction: The purpose of the present study was to prepare and apply antiadherent, hydrophobic coatings on dental poly(methylmethacrylate) (PMMA). **Methods:** Microwave thermal-polymerized PMMA disc-shaped specimens were prepared (10 mm diameter × 2 mm thickness). Two hydrophobic solutions were used for the coatings: HS1 = 2.5 vol% hexadecyl-triethoxy-silane diluted in ethanol, and HS2 = 2.5 vol% perfluorodecyl-triethoxy-silane diluted in dimethyl sulfoxide. The PMMA discs were assigned into three groups, according to the surface treatment: control (C, no coating), HS1 and HS2 coatings. All groups were also subdivided into sandblasted groups (SB) and non-sandblasted groups (NSB). An additional subgroup was used as reference, in which the sandblasted specimens were coated with a conventional silane solution (2.5 vol% methacryloxypropyl-trimethoxy-silane diluted in dimethyl sulfoxide). Each subgroup (n=5) was subjected to water contact angle (θ , in degrees) and surface roughness (Ra, in μm) analyses. Contact angle data were statistically analyzed using two-way Analysis of Variance (ANOVA) and SNK's test (coating × treatment). Sandblasted groups (control, HS1, HS2,

and conventional silane) were subjected to one-way ANOVA and SNK's test. Roughness data before and after sandblasting were compared using paired t-tests ($\alpha = 0.05$). **Results:** Means (standard deviations) for θ were: C-SB = $88.7 \pm 9.3^\circ$; C-NSB = $61.1 \pm 5.2^\circ$; HS1-SB = $114.7 \pm 3.3^\circ$; HS1-NSB = $95.2 \pm 6.8^\circ$; HS2-SB = $106.9 \pm 2.6^\circ$; HS2-NSB = $106.4 \pm 4.2^\circ$; SS-SB = $89.4 \pm 4.3^\circ$. Sandblasted specimens presented higher θ than non-sandblasted specimens ($p < 0.001$). Roughness analyses showed $Ra_{\text{before}} = 0.80 \pm 0.04 \mu\text{m}$ and $Ra_{\text{after}} = 1.78 \pm 0.11 \mu\text{m}$. The effect of surface treatment (sandblasting or not) was dependent of the coating solution ($p < 0.001$). **Conclusion:** The hydrophobic coatings determined increased θ with water. The surface treatments tested, associating sandblasting and the hydrophobic solutions, had a synergistic effect on the increase of water contact angle, suggesting a surface with poorer wettability.

KEYWORDS: Hydrophobic and hydrophilic interactions. Polymethyl methacrylate. Surface properties.

1. Universidade Federal de Pelotas, Programa de Pós-graduação em Odontologia (Pelotas/RS, Brazil).

2. New York University, College of Dentistry, Department of Biomaterials (New York/NY, USA).

DOI: <https://doi.org/10.14436/2447-911x.15.2.148-157.oar>

INTRODUCTION

The use of dentures is often associated with oral pathologies. Among the infections of the oral environment, denture-related stomatitis is one of the most frequent¹. Denture-related stomatitis has a multifactorial etiology and its control is difficult since it does not depend only on plaque removal from the prosthesis but also on the commitment of the patient, who must remove the prosthesis at night, and on the use anti-fungal agents².

There are local causes often associated with these opportunistic infections, such as using dentures poorly adapted, uninterrupted use of the denture, presence of soft liners, and poor oral hygiene^{1,3}, which end up facilitating the formation and adhesion of oral biofilm on the base of the prosthesis. Although the exact mechanism of adherence of microorganisms to acrylic surfaces is unknown, some factors may be considered determinant in this process, such as the surface roughness and free energy of the acrylic resins⁴. The presence of salivary acquired pellicle as well as chemical and electrostatic interactions between the microorganisms

and polymethyl methacrylate (PMMA) of the denture base may also interfere in the surface adhesion⁴⁻⁷.

Several methods have been tested for reducing the problems associated with the accumulation of biofilm in dental PMMA, including increasing the surface smoothness⁸, modifying the surface with plasma treatment⁹, and depositing polyelectrolyte multilayers on the surface for reducing the wetting.¹⁰ Another possibility is to render the acrylic surface antiadherent¹¹. The ability to form a surface with antiadherent characteristics is directly related to the ability of a material or structure to have a low surface energy. In recent years, the possibility of developing hydrophobic and lipophobic surfaces has received much attention since controlling surface wetting is relevant to many areas of science¹².

Among the materials used to render surfaces with antiadherent effects, fluorocarbons, polytetrafluoroethylene, and polydimethylsiloxanes should be highlighted. These compounds are applied on the surfaces of materials and structures in order to modify their interaction

with water and other organic substances¹³. Hydrophobic surfaces have a contact angle formed with water (θ) between 90° and 150°, and thus are more resistant to microbial adhesion. Oral biofilms are formed by protein coating on solid surfaces and formation of the acquired pellicle, with the microbial adhesion depending on specific hydrophilicity of the microorganisms and other physical-chemical interactions between the microorganisms and solid surfaces¹⁴.

Recently, a patent application of an antiadherent composition for use in dental surfaces was requested by our research group¹⁵. Such composition involves surface coatings to render them (super) hydrophobic and/or lipophobic, by forming a siloxane network film. The compound that generates the siloxane network can have a linear, cyclic, or branched chain, containing two or more carbons and/or fluorocarbons associated with a functional group with the ability to connect to the structure of the substrate, usually an organo-silane.

The purpose of this study was to prepare solutions containing precursor of hydrophobic layers and deposit antiadherent films on the surface of dental PMMA, and evaluate the effect on reducing surface wetting. The tested hypothesis was that the wetting of PMMA would be reduced irrespective of the hydrophobic solution tested.

MATERIAL AND METHODS

Experimental design

This *in vitro* study involved a 3×2 factorial experimental design (n=5) to evaluate the factors: hydrophobic coating (three levels: control, hydrophobic solution 1, and hydrophobic solution 2 — groups C, HS1, or HS2) and surface treatment (two levels: PMMA sandblasted or non-sandblasted, groups S or NS). The control group did not receive any surface coating. An additional group (n=5) was tested as a reference and involved sandblasted PMMA specimens that were coated with a conventional silane solution (SS), which does not form a hydrophobic coating. The three silanes tested (HS1, HS2, SS) were selected in order to investigate the effect of the molecule structures with regard to the hydrophobic behavior of the coatings. The primary response variable was surface wetting assessed by means of water contact angle (θ) measurements.

Preparation of the hydrophobic solutions

Two distinct hydrophobic solutions (HS) based on silanes were prepared. HS1 was obtained by diluting 2.5 vol% hexadecyl-triethoxy-silane (Sigma-Aldrich, St. Louis, MO, USA) in ethanol, whereas HS2 was composed by 2.5 vol% perfluorodecyl-triethoxy-silane (Sigma-Aldrich) diluted in dimethyl sulfoxide. The reagents were used as received. A conventional silane solution was prepared diluting 2.5 vol% methacryloxypropyl-trimethoxy-silane in dimethyl sulfoxide and used as a reference. The concentration of silanes and the solvents employed were defined in pilot experiments. The molecular structures of the tested silanes are shown in Figure 1.

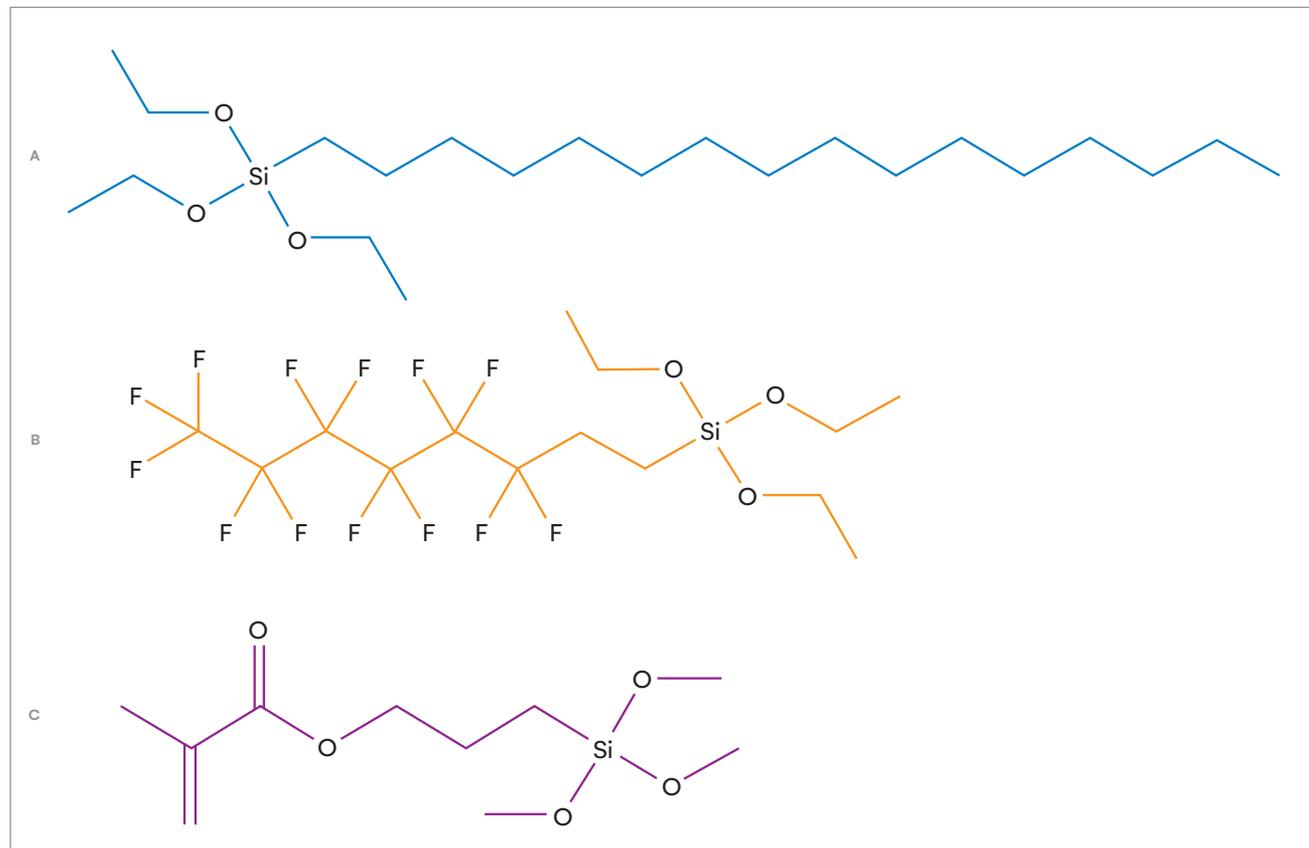


Figure 1:

Molecular structure of the tested silanes: **(A)** hexadecyl-triethoxy-silane, **(B)** perfluorodecyl-triethoxy-silane, and **(C)** methacryloxypropyl-trimethoxy-silane.

Preparations of PMMA specimens

A total of 35 discs (diameter 10 mm × 2 mm thickness) of microwave thermal-polymerized PMMA (VIPI WAVE, Pirassununga, SP, Brazil) were prepared. The material was prepared by mixing the powder and liquid in a glass container in accordance with the manufacturer's recommendations. In the plastic phase, the material was included in a microwave flask that contained a mold previously prepared using silicone (Zetalabor, Zhermack, Badia Polesine, Italy),

and the PMMA was covered with a high-density polyethylene film. The opposite side of the flask contained plaster. The flask was closed and initially pressed using 500/1000 kgf. The flask was then opened for removal of the plastic film and PMMA flashes, then closed again and subjected to final pressing for 15 min (1000/1250 kgf).

The flask was taken to the microwave oven, with 1300 W power, for the curing cycle: early stage for 20 min with 10% power + final stage for 5 min with 30% power, in accordance with the manufacturer's recommendations. After bench cooling, the PMMA specimens were removed. The excesses around the specimens were trimmed using a milling cutter and polishing to obtain final surface smoothness was standardized using #600, 1200, 1500, and 2000-grit SiC papers. After polishing, the specimens in the SB groups were submitted to airborne-articles abrasion using 50 μm aluminum oxide particles for 10 s at a distance of 15 mm. The specimens were then cleaned in ultrasonic bath with distilled water for 30 min.

Surface roughness

The evaluation of the surface roughness was carried out using a contact surface profilometer (Surfcorder SE1200; Kosaka lab., Tokyo, Japan)

equipped with a diamond tip (0.5 μm radius) with 0.01 μm accuracy. Each specimen was subjected to three readings and the mean value was recorded as the surface roughness for each specimen (R_a , μm).

Hydrophobic coating of the surfaces

Surface coating was performed by applying three layers of each silane solution to the PMMA surfaces with intervals of 1 min. The specimens were heated at 150°C for 1 h in an oven (INTI FL 1300; São Carlos, SP, Brazil), at a 10°C/min heating rate, for condensation of a crosslinked siloxane layer on the surfaces via sol-gel process.

Water contact angle

The contact angle formed with the water (θ) was evaluated by means of photographs obtained with a digital DSLR camera (T1i; Canon, Tokyo, Japan), using 105-mm macro lens (Sigma, Ronkonkoma, NY, USA) and circular flash (Canon). A 10- μL drop of distilled water was dispensed over the specimen using a micropipette (LM-100; PZ HTL, Warsaw, Poland) with its tip positioned at a distance of 5 mm from the surface of the specimen. The photographic record was taken 5 s after the drop was dispensed.

The contact angle was calculated in the images by averaging the angles obtained between the surface of the specimen and the left and right limits of the water droplet. The calculation was carried out using the imaging software Image J (NIH, Bethesda, MA, USA).

Statistical analysis

Surface roughness data before and after sandblasting were compared by paired t-tests. Contact angle data comparing the hydrophobic solutions HS1 and HS2 and the control group were subjected to two-way Analysis of Vari-

ance (ANOVA, coating × surface treatment). In a distinct analysis, the contact angle data of all sandblasted groups (control, HS1, HS2, and SS) were subjected to one-way ANOVA. All pairwise multiple comparison procedures were performed by the Student–Newman–Keuls' method. The significance level was set at $\alpha=0.05$.

RESULTS AND DISCUSSION

Table 1 shows results for the contact angle of the hydrophobic solutions compared to the control, for both sandblasted and non-sandblasted groups. The statistical analysis indicated that

Table 1:

Means (standard deviations) for water contact angle (θ) (n=5).

COATING	SURFACE TREATMENT	
	NON-SANDBLASTED	SANDBLASTED
Control	61.1 ± 5.2 ^{Bc}	88.7 ± 9.3 ^{Ac}
SH1	95.2 ± 6.8 ^{Bb}	114.8 ± 3.4 ^{Aa}
SH2	106.4 ± 4.2 ^{Aa}	106.9 ± 2.6 ^{Ab}

Distinct capital letters in the same line indicate significant differences between the surface treatments; distinct lowercase letters in the same column indicate significant differences between the coatings ($\alpha=0.05$).

the factors 'coating' and 'surface treatment' were both significant, as well as interaction between the two factors ($p < 0.001$). The contact angles formed on the surfaces treated with HS1 and HS2 were significantly higher than in the control group, irrespective of the prior use of sandblasting. Thus, the tested hypothesis was confirmed.

It is known that both surface wetting and the successful obtaining of hydrophobic layers depend on the type of material, surface topography, and chemistry of the substrate^{13,14,16}. For a better performance of hydrophobic coatings, the coated surface should present a minimum of roughness to maximize the hydrophobic effect, because a rough surface allows better interaction with the layer deposited via sol-gel process. A possible manner to obtain surface roughness on PMMA is sandblasting it with aluminum oxide particles. In this study, sandblasting determined a significant increase ($p < 0.001$) in surface roughness (Ra, μm) of the tested specimens: Ra_{before} = 0.80 (0.04); Ra_{after} = 1.78 (0.11).

The sandblasting was important to further increase the contact angle obtained by using HS1, which contained only a long carbon chain, without fluorine. However, sandblasting did not affect the contact angle formed on surfaces treated with HS2. This finding was observed before¹⁴

and can be explained by the distinct three-dimensional arrangement of the precursor molecules in the formation of the hydrophobic crosslinked coatings when using different silanes in the solutions. For HS2, which presents fluorine in the silane molecule, the increase in the water contact angle with PMMA (compared to the control group) was independent of the previous surface sandblasting. Fluorinated polymers are of great relevance when aiming at achieving surfaces with a hydrophobic character, due to their low surface energy¹³. In this sense, the prior use of sandblasting was not necessary to enhance the antiadherent coating. This finding can be considered interesting from the point of view of simplifying the coating process.

Figure 2 presents a comparison of the wetting obtained in the control, HS1, and HS2 groups, and the surfaces treated with the conventional silane (SS), which did not have a long carbon chain or contained a fluorocarbon. This comparison was carried out to observe if the simple coating of the surface with a silane layer would lead to lower wetting. It can be clearly observed that application of a conventional silane did not interfere with the contact angle formed with water, as compared with the control group ($p = 0.835$). This finding confirms that the hydrophobic solutions were effective in altering the wetting of the PMMA, since the groups HS1 and HS2 had significantly lower wetting than the control group ($p < 0.001$).

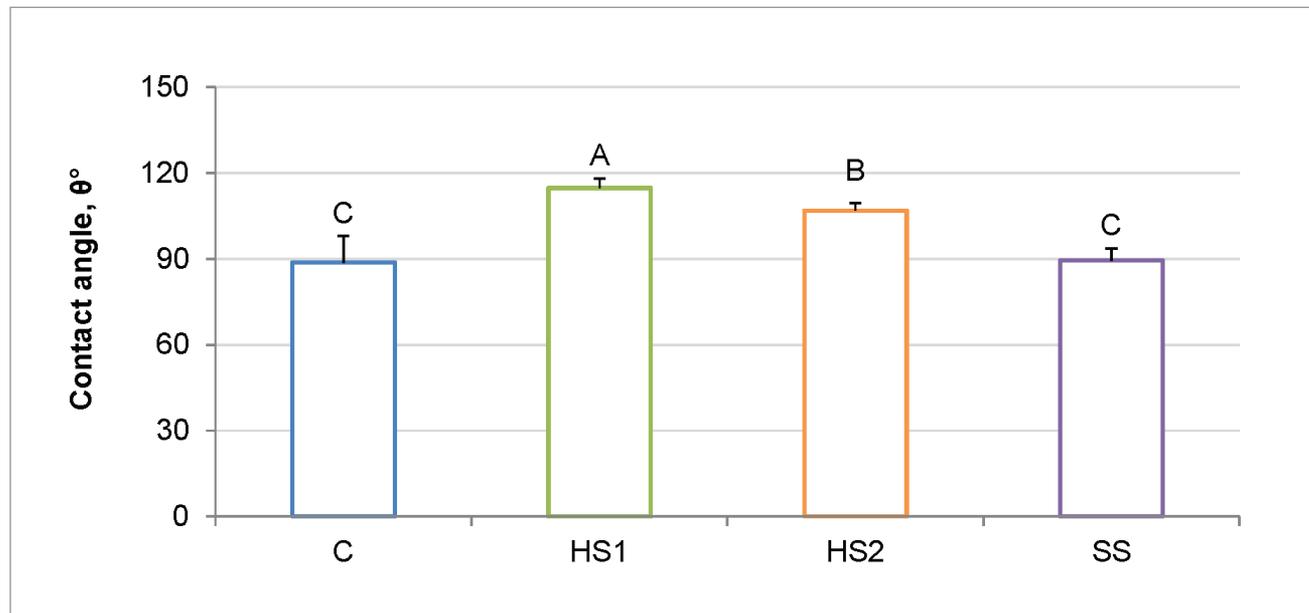


Figure 2:

Means (standard deviations) for water contact angle (θ) in all sandblasted groups. Distinct letters indicate significant differences between groups ($\alpha=0.05$). It can be observed that the conventional silane (**SS**), which has a small molecule without groups containing fluorine, did not modify the surface wetting of PMMA, in comparison with the control.

The effect of the hydrophobic coatings in reducing the surface wetting is explained by the fact that water, when meets a planar hydrophobic surface, forms a low-density layer by thermodynamic conduction, due to the low critical surface tension and low friction coefficient formed with the surface^{17,18}. Thus, there is a low attraction of the water molecules to the surface of the PMMA treated with the hydrophobic coatings, reducing wetting. In the untreated surfaces and in the surfaces treated with the conventional silane, the friction of water with PMMA is higher than the attractiveness between water molecules, generating a greater spreading of the water droplets over the surface.

As it has been shown elsewhere¹⁴, surfaces with less water affinity may reduce the formation of oral biofilms in the early stages of plaque accumulation. Thus, the hydrophobic coatings presented herein could contribute to the control of oral biofilms formed over PMMA-based prosthetic devices, either by reducing the formation of biofilms in the early stages or by facilitating the mechanical removal of plaque with brushing. However, the longevity of the coatings proposed herein as well as the long-term effects of the reduced surface wetting should be analyzed in future studies.

CONCLUSION

The assessment of surface roughness and water contact angle revealed that the surface treatment of PMMA with sandblasting using aluminum oxide particles and the subsequent application of the hydrophobic coatings had a synergistic positive effect in reducing the surface wetting of the PMMA. The hydrophobic coatings may aid in reducing the susceptibility to adhesion of oral biofilms in dental PMMA.

REFERENCES:

1. Barbeau J, Séguin J, Goulet JP, De Koninck L, Avon SL, Lalonde B, et al. Reassessing the presence of *Candida albicans* in denture-related stomatitis. *Oral Surg Oral Med Oral Pathol Oral Radiol Endod.* 2003 Jan;95(1):51-9.
2. Hilgert JB, Giordani JM, Souza RF, Wendland EM, D'Ávila OP, Hugo FN. Interventions for the management of denture stomatitis: a systematic review and meta-analysis. *J Am Geriatr Soc.* 2016;64(12):2539-45.
3. Webb BC, Thomas CJ, Wilcox MD, Harty DW, Knox KW. *Candida*-associated denture stomatitis. Aetiology and management: a review. Part 2. Oral diseases caused by *Candida* species. *Aust Dent J.* 1998 June;43(3):160-6.
4. Burgers R, Schneider-Brachert W, Rosentritt M, Handel G, Hahnel S. *Candida albicans* adhesion to composite resin materials. *Clin Oral Investig.* 2009 Sept;13(3):293-9.
5. Beldüz N, Kamburoğlu A, Yılmaz Y, Tosun I, Beldüz M, Kara C. Evaluation of *Candida albicans* biofilm formation on various dental restorative material surfaces. *Niger J Clin Pract.* 2017;20(3):355-60.
6. Sipahi C, Anil N, Bayramli E. The effect of acquired salivary pellicle on the surface free energy and wettability of different denture base materials. *J Dent.* 2001 Mar;29(3):197-204.
7. Yildirim MS, Hasanreisoglu U, Hasirci N, Sultan N. Adherence of *Candida albicans* to glow-discharge modified acrylic denture base polymers. *J Oral Rehabil.* 2005 July;32(7):518-25.
8. Nishioka M, Yamabe Y, Hisatsune K, Fujii H. Influence of polishing of denture base resin and metal surfaces on wettability with water and saliva. *Dent Mater J.* 2006 Mar;25(1):161-5.
9. Zamperini CA, Machado AL, Vergani CE, Pavarina AC, Giampaolo ET, Da Cruz NC. Adherence in vitro of *Candida albicans* to plasma treated acrylic resin. Effect of plasma parameters, surface roughness and salivary pellicle. *Arch Oral Biol.* 2010 Oct;55(10):763-70.
10. Etienne O, Picart C, Taddei C, Keller P, Hubsc E, Schaaf P, et al. Polyelectrolyte multilayer film coating and stability at the surfaces of oral prosthesis base polymers: an in vitro and in vivo study. *J Dent Res.* 2006 Jan;85(1):44-8.
11. Pareo P, De Gregorio GL, Manca M, Pianesi MS, De Marco L, Cavallaro F, et al. Ultra lightweight PMMA-based composite plates with robust super-hydrophobic surfaces. *J Colloid Interface Sci.* 2011;363(2):668-75.
12. Nosonovsky M, Bhushan B. Superhydrophobic surfaces and emerging applications: Non-adhesion, energy, green engineering. *Curr Opin Colloid Interface Sci.* 2009;14(4):270-80.
13. Ma M, Hill RM. Superhydrophobic surfaces. *Curr Opin Colloid Interface Sci.* 2006;11(4):193-202.
14. Oliveira AS, Kaizer MR, Azevedo MS, Ogluari FA, Cenci MS, Moraes RR. (Super) hydrophobic coating of orthodontic dental devices and reduction of early oral biofilm retention. *Biomed Mater.* 2015;10(6):065004.
15. Ogluari FA, Piva E, Oliveira IR, Silva AF, Moraes RR, Cenci MS. Composição odontológica anti-aderente. Brasil. Protocolo 0000221002087648. 2010. Depósito de pedido de patente ao Instituto Nacional da Propriedade Industrial.
16. Feng X, Jiang L. Design and creation of superwetting/antiwetting surfaces. *Adv Mater.* 2006;18:3063-78.
17. Poynor A, Hong L, Robinson IK, Granick S. How water meets a hydrophobic surface. *Phys Rev Lett.* 2006 Dec 31;97(26):266101.
18. Dimitrakellis P, Gogolides E. Hydrophobic and superhydrophobic surfaces fabricated using atmospheric pressure cold plasma technology: a review. *Adv Colloid Interface Sci.* 2018 Apr;1-21. doi: 10.1016/j.cis.2018.03.009.

How to cite: Duarte CG, Kaizer MR, Valente LL, Lima GS, Moraes RR. Hydrophobic coating of dental PMMA. *J Clin Dent Res.* 2018 May-Aug;15(2):148-57.

Submitted: April 20, 2018 - Revised and accepted: May 11, 2018.

Contact address: Rafael Moraes
 Faculdade de Odontologia, UFPel - Rua Gonçalves Chaves 457, sala 505
 CEP: 96.015-560 - Pelotas/RS - E-mail: moraesrr@gmail.com

» The authors report no commercial, proprietary or financial interest in the products or companies described in this article.

» Patients displayed in this article previously approved the use of their facial and intraoral photographs.
