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Gedalias Custódio Martim, Vicente Lira Kupfer, Murilo Pereira Moisés, Andressa dos Santos, Andrelson Wellington Rinaldi, et al.. Physical-chemical properties of dental composites and adhesives containing SBA-15 silanized with 3-methacryloxypropyltrimethoxysilane. Journal of the mechanical behavior of biomedical materials, 2018, 80, pp.277-284. <10.1016/j.jmbbm.2018.02.009>. <hal-03915996>

HAL Id: hal-03915996

<https://hal.science/hal-03915996v1>

Submitted on 6 Feb 2024

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Physical-chemical properties of dental composites and adhesives containing SBA-15 silanized with 3-methacryloxypropyltrimethoxysilane

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Abstract

The aim of this study was to synthesize and characterize mesoporous materials SBA-15 and SBA-15 modified with 3-(methacryloxy)-propyl-trimethoxysilane (MPS) to be used as the inorganic filler in restorative dental composites and adhesives, and evaluate the main physical-chemical properties of the resulting material. The SBA-15 and SBA-15/MPS were characterized by FTIR, BET and X-Ray in order to be combined with TEGDMA, bis-GMA and commercial spherical silica to fabricate composites dental and combined with TEGDMA, bis-GMA and HEMA to fabricate adhesives. In order to compare the results was prepared composite and adhesive containing only commercial spherical silica as control. The physical-chemical properties degree of conversion (DC), flexural strength (FS) and modulus (FM), water sorption and solubility (W_{sp} and W_{sl}), specific area (BET), leachable components were evaluated. The SBA-15/MPS can be used to prepare dental restorative materials, with some foreseeable advantages compared with pure SBA-15 dental materials and with improved properties compared with commercial spherical silica dental materials. One significant advantage is that the dental materials based on SBA-15

modified have the potential to be less toxic, once they presented a reduction of more than 50% in leaching of unreacted monomers extracted by solvent compared to the control.

Keywords: SBA-15, 3-methacryloxypropyltrimethoxysilane, Composite resin, Adhesives, Physicochemical phenomena.

1. Introduction

Several works have been published using mesoporous silica in order to be used in different materials. These materials based on mesoporous silica can be used as catalytic systems, adsorption as well as used for medicinal purpose, for example, drug delivery [1-5]. Furthermore, it behaves similarly as bioactive glasses, when in contact with body fluid can develop an apatite layer like of natural bone [6]. However, few researches have been listed using mesoporous silica as inorganic filler in dental composite and adhesives, those works reported did not show in details important physical-chemical properties required to evaluate the restoratives dental materials.

It is worth emphasizing some reports using mesoporous silica applied on restorative dentistry. Zhang and cols. [7] presented the antimicrobial effects from delivery of chlorhexidine inserted in mesoporous silica (SBA-15) applied on dental composites. This study compared the results of mechanical properties of composites containing chlorhexidine without mesoporous silica and composites containing chlorhexidine with mesoporous silica, the results showed that the materials based on chlorhexidine encapsulated in mesoporous silica did have its mechanical properties significantly decreased, differently of the materials containing only chlorhexidine.

Can be find on the literature studies about dental composites containing antimicrobial agents immersed in dental monomer instead of included in the inorganic filler, for these materials, the

results reveals a significantly decrease of mechanical properties to the final polymers obtained [8-11]. Therefore, the use of antimicrobial agent inserted in mesoporous silica seems to be the way to solve the problem of bacteria growth on dental composites without impairing its mechanical properties.

Samuel et al. evaluated the mechanical properties values of experimental dental composite prepared with mesoporous silica mixed with spherical silica. These authors defend the use of mesoporous silica without the common treatment with silane agents. It is well known that the silane agents containing methacrylate groups linked on dental fillers and surely improve the mechanical properties of the restorative dental materials due to the chemical interaction between the filler and the organic monomers [12].

Even though the silane agents improve mechanical properties of the composites, these agents can be hydrolyzed in the oral environment bringing consequences as decreased durability of the materials. In this way, the problem of hydrolysis could be avoided with the utilization of mesoporous silica, for before the cure the monomers would be inserted into the porous. After the polymerization, would exist a strong mechanical interaction between polymer and silica, it would lead to have a material with good mechanical properties without concerning with the hydrolysis of silane agents [12].

Bing et al. inserted one of the most common dental monomers, the triethyleneglycoldimethacrylate (TEGDMA) into the porous of mesoporous silica, the SBA-15. These authors also defend the use of silica without treatment without silane agents. It was observed that the composition having below 40% of SBA-15 mixed with TEGDMA had no free volume and decreased the thermal expansion. The decrease of thermal expansion is excellent to dental composite, but what calls attention is, in this study was used only TEGDMA as organic matrix [13].

It is well known many disadvantages of using only one monomer as organic matrix, mainly TEGDMA, TEGDMA is the worst monomer to be use alone, for it has high value of polymerization shrinkage which lead to marginal infiltration, secondary caries, micro-crack and post-restoration pain. Thereby, the dental restoratives materials are fabricated by copolymerization using monomer with high molecular weight combined with TEGDMA.

In another work, Bing and Cols. [14] elaborated composites using SBA-15, however, at this time, the composites were made with TEGDMA and bisphenol-A-diglycidylmethacrylate (bis-GMA). In this study, the authors report that the focus of the work was more focused on the filling process than to the study of the properties of composites. In general, those worked quoted bring innovation and good perspective to the restorative dentistry area, nevertheless, many details has to be investigated.

Although these studies advocated the use of mesoporous silica without silane agents in dental composites, there is no study based on the degree of conversion, extraction in organic solvents, water sorption and water solubility to prove the effectiveness of the presence of mesoporous silica with or without silane agents. Obviously, the absence of silane agents does not bring concerning about hydrolysis in the oral environment, however, the lack of chemical interaction between the monomers (which are toxic) and fillers could lead the final composite to release more unreacted monomers than composites treated with silane agents.

The aim of this study was synthesize dental composite and adhesives containing mesoporous silica: SBA-15, SBA-15 treated with 3-methacryloxypropyltrimethoxysilane and commercial spherical silica in order to investigate its physical-chemical properties, especially as the release of the components in organic solvent and water. The null hypothesis is that the composites and adhesives formulated with modified SBA-15 will not show improvement in properties compared to SBA-15 and controls.

2. Experimental procedures

2.1. Materials

All reagents used in this work were purchased from Sigma-Aldrich Inc. These reagents were used without further purification. The commercial reagents used to synthesize the SBA-15 and modifications were: hydrochloric acid (HCl, 2 M), pluronic P123 (EO₂₀PO₇₁EO₂₀), Tetraethyl orthosilicate (TEOS, 99,99%), 3-methacryloxypropyltrimethoxysilane (MPS, 98%). The photoinitiator system was camphorquinone (CQ, 97%) and 2-(N,N-dimethylamino)ethyl methacrylate (DMAEMA, 99%), the inhibitor system was *p*-hydroxyanisole (*p*-HA, 98%). The commercial monomers used to prepare the composites and adhesives were: 2-hydroxyethylmethacrylate (HEMA, 99%), bisphenol-A-diglycidylmethacrylate (bis-GMA), and triethyleneglycoldimethacrylate (TEGDMA, 95%). Barium glass (V258 2507, SP 345, 5% silane, 0.7 μ m) and fumed silica (OX-50, 5% silane, 50 nm) were used as inorganic fillers and were obtained from ESSTECH.

2.2. Synthesis of SBA-15

The SBA-15 was synthesized according to the method described by Zhao et. al. [15] with slightly modifications. Mesoporous silica phases were synthesized at 40 °C by using nonionic surfactants as the structure-directing agents. In a typical preparation, 4.0 g of pluronic P123 was dissolved in 125 mL of 2 M HCl solution with stirring at 40 °C for 4 h. After 4h was added 25 mL of water in order to guarantee the total solubilization of the pluronic. Then 8.5 g of TEOS was added to that homogeneous solution with stirring at 40 °C for 24 h. After that, the final product was led to hydrothermal process at 90 °C for 24 h. The porous material obtained was washed with water and dried at 40° C for 24h. The dried material was calcined at 550 °C for 6h with a heat rate of 1 °C/min.

2.3. Modification of SBA-15 with 3-methacryloxypropyltrimethoxysilane

The functionalization of SBA-15 with MPS was performed as follow: 3 g of SBA-15 was mixed with 12 mL of MPS and toluene, the mixed was added in a 100 mL flask equipped with a magnetic stirrer and reflux system, which was immersed in a thermobath for temperature control. Next, the reaction was kept at 60 °C at 24h. After that, the material obtained was centrifuged at 3500 rpm for 20 min, washed 6 times with ethanol and dried at 60 °C for 24h. Then, the remaining solvent was removed from the material under vacuum with 500 mmHg at 40 °C for another 3h.

2.4. Characterization by Fourier transform infrared (FTIR)

FTIR experiments were carried out using a BOMEM-MB-100 Hartmann & Braun Québec, Canada spectrometer. For liquid samples the spectra were obtained using NaCl plates, and for solid samples the spectra were obtained using KBr pellets prepared with 3.0 mg of the sample to 100 mg of the KBr. Each spectrum was acquired with 32 scan and resolution of 4.0 cm⁻¹ [16].

2.5. Composites formulation and curing conditions

The composites and adhesives (*etching-and-rinse adhesive*) were mixed at 50 °C for 3 h and kept at room temperature 24 h before the polymerization process, following the compositions listed in Table 1. 0.8 wt% of camphorquinone (CQ) and 3.2 wt% of dimethylamino ethyl methacrylate (DMAEMA) were added to all materials as the photo-initiator system and the inhibitor system to formulate the adhesives was *p*-hydroxyanisole. The Table 1 also shows the acronym of each formulation. The subscribed numbers are the percentage of each component added on the mixture and the numbers ahead of the acronym are the percentage of total amount of filler present. The meaning of each letter on the formulation are presented as: B = bis-GMA, T

= TEGDMA, H = HEMA, SSM = spherical silica microparticulate, SBA-15 = pure SBA-15, SBP-15/MPS, = SBA-15 modified with MPS, C = composites, A = Adhesives.

Table 1 – Compositions and its acronym to all composites and adhesives elaborated.

Composition	Acronym
$C(B_{0.5}-T_{0.5})_{30}(SSM_1)_{70}$	(CBT-SSM)-70
$C(B_{0.5}-T_{0.5})_{30}(SSM_{0.95}SBA-15_{0.05})_{70}$	(CBT-SSM-SBA-15)-70
$C(B_{0.5}-T_{0.5})_{30}(SSM_{0.95}SBA-15/MPS_{0.05})_{70}$	(CBT-SSM-SBA-15/MPS)-70
$A(B_{0.6}-H_{0.4})_{100}$	(ABH)-0
$A(B_{0.6}-H_{0.4})_{90}(SSM)_{10}$	(ABH-SSM)-10
$A(B_{0.6}-H_{0.4})_{90}(SBA-15)_{10}$	(ABH-SBA-15)-10
$A(B_{0.6}-H_{0.4})_{90}(SBA-15/MPS)_{10}$	(ABH-SBA-15/MPS)-10
$A(B_{0.6}-H_{0.4})_{85}(SSM)_{15}$	(ABH-SSM)-15
$A(B_{0.6}-H_{0.4})_{85}(SBA-15)_{15}$	(ABH-SBA-15)-15
$A(B_{0.6}-H_{0.4})_{85}(SBA-15/MPS)_{15}$	(ABH-SBA-15/MPS)-15

2.6. Characterization by X-ray diffraction (XRD)

Low-angle X-ray diffraction (XRD) patterns were obtained using Bruker D8-Advance equipment operated with a source emission cathode copper, a wavelength of 1.5406 Å, current of 30 mA and 40 kV power, a 0.01° step size and 2 s per step over the range $0.5^\circ < 2\theta < 5^\circ$.

2.7. Nitrogen adsorption-desorption techniques (BET)

The specific surface area was determined by N₂ physisorption at 77 K (Quantachrome NOVA-1200E) using BET method and the pore size distributions were calculated using the Barrett–Joyner–Halenda (BJH) method.

2.8. Mechanical properties in flexure

Flexural strength and flexural modulus of the samples were measured according to the 3-point bending method carried out with a universal test machine (Lloyd Instruments, modelo LR 10K plus) at a cross-head speed of 0.5 mm/min. The bar specimens were prepared in dimensions of 2 mm × 2 mm × 25 mm according to ISO 4049 [17]. The specimens were

fabricated between glass slides and photopolymerized with three overlapping 60-second exposures at 700 mW/cm² (Bluephase). The specimens (n = 5) were stored in water for 24 h at 37 °C before being tested in three-point bending. The flexural strength (FS) in MPa was then calculated as: $(FS(\sigma) = 3Fl/2bh^2)$, where F stands for load at fracture (N), l is the span length (20 mm), and b and h are the width and thickness of the specimens in mm, respectively. The elastic modulus (FM) was determined from the slope of the initial linear part of stress–strain curve. $(FM = Fl^3/4bh^3d)$, where F is the load at some point on the linear region of the stress–strain curve; d is the slack compensated deflection at load F ; l , b , and h are as defined above [18].

2.9. Extraction, water sorption and water solubility (E, W_{sp} and W_{sl} in µg/mm³)

The amount of leachable components was determined according to the methods described previously by Stansbury and Dickens [19]. Briefly, The composites (n = 3) were poured into a steel mold (disc specimens (0.8 mm thickness and 10 mm diameter)), covered with a glass cover slip, clamped and photoactivated through the glass using 700 mW/cm² (Bluephase) for 60 s. and the conversion values were determined. Then, the specimens were weighed until a constant mass (m_1) was achieved prior to the immersion in 8 mL of methylene chloride containing 0.01 wt% *p*-hydroxyanisole (*p*-HA) for 7 days. The *p*-HA is added to avoid further conversion due to the increased molecular mobility produced in solvent-swollen networks. After 7 days, the solvent from the extraction solutions was removed under rotary evaporation to constant mass. The remaining discs were dried to constant mass (m_2) and weighed after extraction as well. The mass extracted was then calculated as: $Mass\ extracted\ (\%) = (m_2 - m_3) / V$. The sorption (W_{sp}) and solubility (W_{sl}) measurements (in µg/mm³) were tested following a similar method described to the extraction procedure but based on standard ISO 4049 [17]. The resins (n = 5) were poured into a steel mold (disc specimens (0.8 mm thickness and 10 mm diameter)), covered with a glass cover slip, clamped and photoactivated through the glass using 700 mW/cm² (Bluephase) for 60

s. The polymerized resins were dried in a desiccator at 37 °C for 24h and kept into the desiccator until a constant mass (m_1) was achieved. The volume of the discs was calculated by measuring the diameter and thickness with the aid of a digital caliper. The specimens (each disc) were then put into containers with distilled water (8 mL) and stored for 7 days at 37 °C. After 7 days, excess of water was removed with absorbent paper and the disc mass was weighted once again. The weight measured is referred to as (m_2). The procedure of placing samples in a desiccator until each one reached constant mass (m_3) was repeated. The water sorption (W_{sp}) and water solubility (W_{sl}) are then calculated as: $W_{sp} = (m_2 - m_3) / V$ and $W_{sl} = (m_1 - m_3) / V$ [20].

2.10. Degree of conversion (DC%)

The degree of double bond conversion (DC) was determined by using an FTIR spectrometer (Spectrum Two PerkinElmer). The experimental and control samples were polymerized in a mold that was 0.5 mm deep and 6.0 mm in diameter, after that, it was macerated in order to be mixed with KBr. First, the spectrum of the unpolymerized sample (approximately x g) was measured through the mixture of each sample with KBr. Then the sample was irradiated for 60 s on each side with a LED visible light-curing unit (SDI/Australia, Radii model, $\lambda = 470 \text{ nm}$ and an intensity of 1200 mW/cm^2). To determine the percentage of remaining unreacted double bonds, the intensities of aliphatic C=C peak absorption at 1637 cm^{-1} and the aromatic C=C peak absorption at 1608 cm^{-1} were calculated by using a baseline method. The aromatic C=C vibration was used as an internal standard. The ratios of absorbance intensities were calculated and compared before and after polymerization. The degree of conversion was calculated by the equation mentioned by [21].

2.11. Atomic-force microscopy (AFM) and Scanning Electron Microscopic (SEM)

The samples were polymerized in a mold that was 0.5 mm deep and 6.0 mm in diameter to obtain topographical images of the composite. The surface of each disc was cleaned with a jet of isopropyl alcohol under N₂ flux. The images were obtained on a Nanosurf FlexAFMC3000 Controller (Nanosurf®, Switzerland). The analysis was conducted using a Tap-190AL-G (Resonant Frequency 190 ± 60 kHz) probe in intermittent contact (topography and phase contrast), with scan covering an area of about 20 µm x 20 µm containing 512 x 512 pixels at maximum resolution. The Gwyddion® 245 software package was used to analyze AFM images.

Scanning Electron Microscopic was carried out by a Quanta 250 from FEI Company (Hillsboro, OR, USA) with an accelerating voltage of 5 kV. The fractured surface of the composite samples were investigated after carbon sputtering.

2.12. Statistical analyses

All statistical analyses were carried out with Sigma Stat 3.5 (Systat Software, Inc., Point Richmond, CA, USA). Assumptions of equality of variance and the normal distribution of errors were checked with Kolmogorov-Smirnov test ($\alpha = 0.05$). The data were analyzed using one-way analysis of variance (ANOVA) followed by Tukey's test at a global level of significance of 95%.

3. RESULTS AND DISCUSSION

3.1. Characterization by FTIR

Figure 1 shows the FTIR spectra of MPS (1), SBA-15 (2) and SBA-MPS (3). The band at ca. 2947 cm⁻¹, 1720 cm⁻¹ and 1637 cm⁻¹ in spectrum (1) is assigned to C-H sp³ bonds, C=O stretching and aliphatic C=C bonds, respectively. The broad signal at ca. 3400 cm⁻¹ and 1640 cm⁻¹ in spectrum (2) is assigned to the OH group stretching and Si-O bonds, respectively. After the modification of SBA-15 with MPS, it is observed that all the signals belonging to MPS and SBA-15 also appear in spectrum (3), indicating that the modification happened successfully.

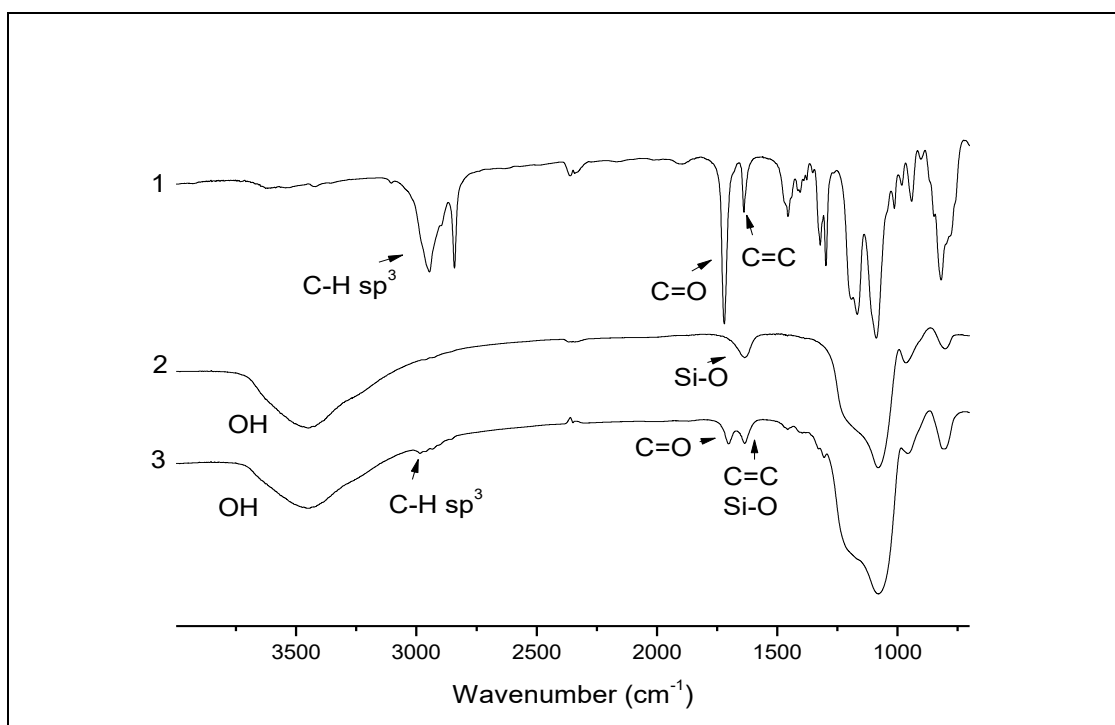


Figure 1. FTIR spectra of MPS (1), SBA-15 (2), SBA-15/MPS (3). Tirar graficos?

3.2. Characterization by Ray-x

Figure 2 presents the XDR of SBA-15 (straight solid) and SBA-15/MPS (straight short dash). It can be observed that the data from SBA-15 and SBA-MPS are similar related to the amount of signals and region of it, that is, there was change only in the peak's intensity after the modification. Both showed a peak with high intensity at 0.9 in 2θ and two peaks with low intensity at 1.6 and 1.7 in 2θ , these peaks are attributed by reflection of high order in a hexagonal dimension (P6mm), where all these peaks belong to (100), (110) and (200) reflection plan, respectively.

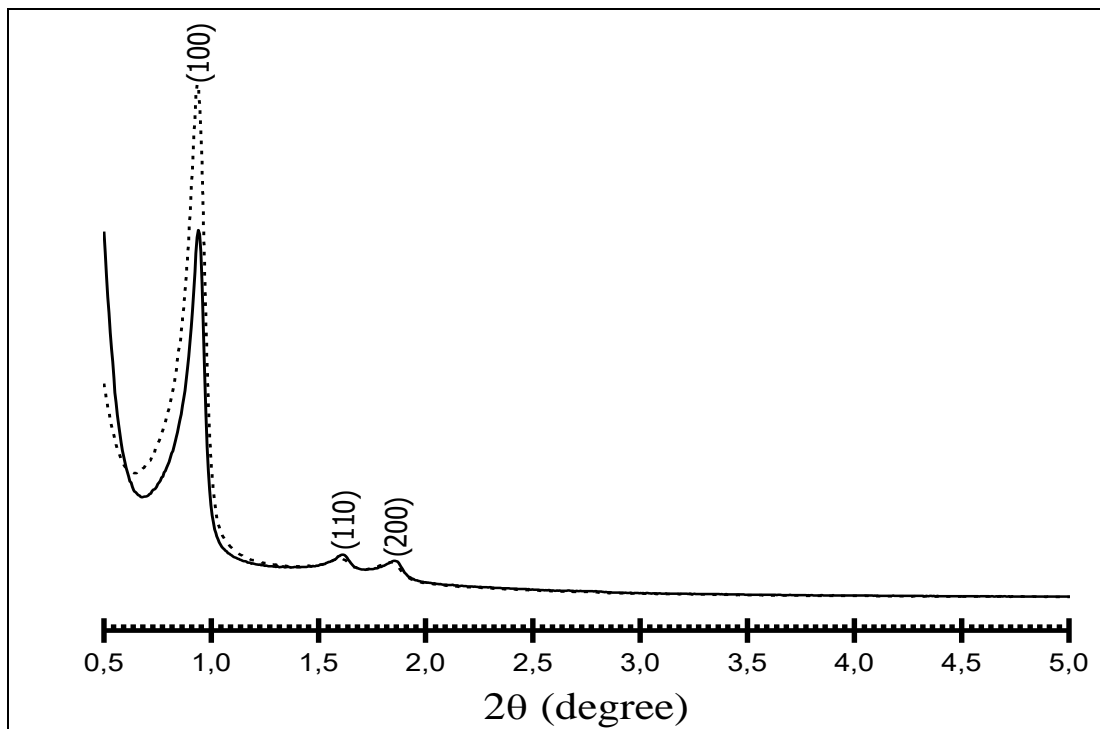


Figure 2. X-ray diffraction to SBA-15 (straight solid —) and SBA-MPS (straight short dash ...).

3.3. Characterization by Nitrogen adsorption-desorption techniques

Figure 3 shows the hysteresis loop in N_2 adsorption and desorption to SBA-15 and SBA-15/MPS. Both presented H1 hysteresis loop in N_2 adsorption and desorption isotherms type IV according to IUPAQ [22]. Could be seen through the isotherm of SBA-15/MPS a significant reduction of specific surface area ($BET = 513.2 \text{ m}^2/\text{g}$) compared to the isotherm of SBA-15 ($BET = 843.7 \text{ m}^2/\text{g}$). The reduction of specific surface area to SBA-15/MPS is due to a lower N_2 concentration adsorbed, that is, after the modification the porous was partially blocked with MPS. Furthermore, the pores diameters of SBA-MPS ($BJH = 50.4 \text{ \AA}$) also reduced significantly compared to the size of the pores diameters of SBA-15 ($BJH = 57.9 \text{ \AA}$). This result showed the efficiency of functionalization method. The specific surface area from pure SSM was ($BET = 13.33 \text{ m}^2/\text{g}$).

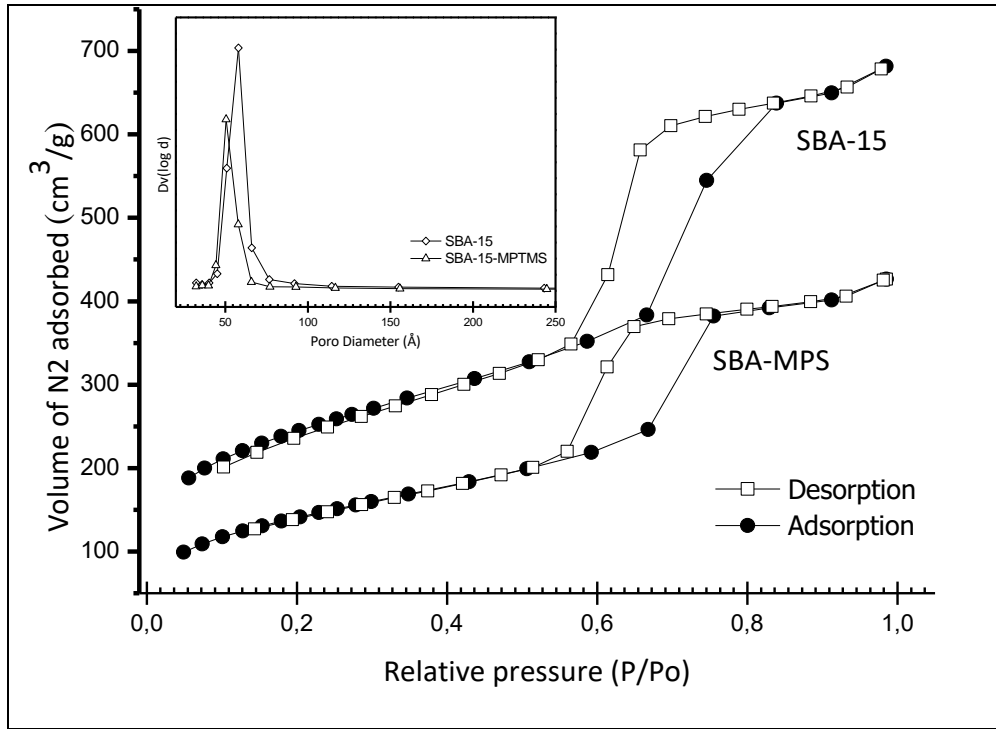


Figure 3. N₂ adsorption and desorption isotherms at 77 K from SBA-15 and SBA-15/MPS.

3.4. Physical-chemical properties

The Table 2 presents the results from degree of conversion, extractions studies, water sorption, water solubility, surface area, flexural strength and flexural modulus measurement for all composites prepared. In Table 3 the results for degree of conversion, surface area, flexural strength and flexural modulus for the adhesives fabricated are summarized.

Table 2. Mean and standard deviation of degree of conversion (DC in %), extractions studies (E in $\mu\text{g}/\text{mm}^3$), water sorption (Wsp in $\mu\text{g}/\text{mm}^3$), water solubility (Wsl in $\mu\text{g}/\text{mm}^3$), surface area (BET in m^2/g), flexural strength (FS in MPa) and flexural modulus (FM in GPa) for composites prepared with SBA-15 (5 wt% of total filler), SBA-15/MPS (5 wt% of total filler) and SSM (100 wt% of total filler). Values followed by the same superscript on the same column are statistically similar ($\alpha = 0.05$).

SAMPLE	Area (m^2/g)	FM(GPa)	FS(MPa)	DC(%)	Extraction ($\mu\text{g}/\text{mm}^3$)	Wsp ($\mu\text{g}/\text{mm}^3$)	Wsl ($\mu\text{g}/\text{mm}^3$)
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(CBT-SSM-70)	4.61	5.49±0.53 ^a	87.84±28.67 ^a	84.30±1.32 ^a	17.54±3.81 ^a	24.59±0.91 ^b	3.08±0.47 ^c
(CBT-SSM-SBA-15)-70	9.14	5.77±0.69 ^a	90.16±11.84 ^a	67.89±1.08 ^b	9.29±1.39 ^b	30.13±1.03 ^a	5.90±0.55 ^a
(CBT-SSM-SBA/MPS)-70	6.14	6.30±0.39 ^a	85.74±23.59 ^a	69.86±2.86 ^b	7.34±0.38 ^b	26.05±0.83 ^b	4.22±0.31 ^b
-		(<i>p</i> =0,097)	(<i>p</i> =0,953)	(<i>p</i> =8.60E ⁻⁵)	(<i>p</i> =0,004)	(<i>p</i> = 1,91E ⁻⁶)	(<i>p</i> =1,72E ⁻⁶)

Table 3. Mean and standard deviation of degree of conversion (DC in %), surface area (BET in m²/g), flexural strength (FS in MPa) and flexural modulus (FM in GPa) for adhesives prepared with SBA-15 (10 and 15 wt% of total filler), SBA-15/MPS (10 and 15 wt% of total filler) and adhesives prepared without fillers (100 wt% of monomers). Values followed by the same superscript on the same column are statistically similar ($\alpha = 0.05$).

SAMPLE	FS(MPa)	FM(GPa)	DC(%)	Area (m ² /g)
(ABH)-0	51.06±1.23 ^{ab}	0.99±0.05 ^d	51.74±2.28 ^c	9.17
(ABH-SSM)-10	49.05±2.75 ^{ac}	1.00±0.05 ^d	85.64±2.21 ^a	3.01
(ABH-SBA-15)-10	45.69±4.75 ^{bcd}	1.12±0.04 ^c	59.63±7.18 ^{bc}	5.91
(ABH-SBA-MPS)-10	54.34±4.38 ^a	1.43±0.05 ^a	66.79±1.95 ^b	6.52
(ABH-SSM)-15	41.78±1.98 ^d	0.86±0.06 ^e	69.72±4.85 ^b	4.86
(ABH-SBA-15)-15	46.35±3.33 ^{bcd}	1.19±0.06 ^{bc}	54.07±0.49 ^c	10.27
(ABH-SBA-15/MPS)-15	44.00±4.44 ^{bcd}	1.29±0.06 ^b	71.85±6.52 ^b	5.65
	(<i>p</i> = 1.01E ⁻⁴)	(<i>p</i> =1.66E ⁻¹⁵)	(<i>p</i> = 2.96E ⁻⁶)	-

It was visible observed the great decrease on viscosity of composites containing SBA-15 or SBA-15/MPS. It happened because these porous materials have low density confirmed by the lower specific surface area. The composites based on SBA-15 presented the higher specific surface area (BET = 9.14 m²/g), followed by composite containing SBA-15/MPS (BET = 6.14 m²/g) and composite base only on SSM (BET = 4.61 m²/g), these results followed the same behavior of pure powder fillers (Figure 3 and Table 2). When 10% m/m of SBA-15 or SBA-15/MPS was added over composite to have a composite containing 90% m/m of SSM and 10% m/m of porous filler, the final product had its aspect as solid materials instead resin. However, the additions of 5% m/m of porous filler was able to produce a resin and to improve some physical-chemical properties of the dental composites.

Related to dental materials, the formation of clustering from particles aggregates can be an obstacle when is added fillers and it contributes to easier bond strength deterioration. One

factor that leads to more agglomeration is the geometries which improve the potential area for contact with others inorganic particles [23]. Once SBA-15/MPS decreased its specific surface area compared with SBA-15, it will decrease the potential area for contact among fillers becoming a greater candidate to decrease agglomeration and consequently a better material to be used in dental composite and adhesives than SBA-15 without functionalization.

Although there was no significant difference related to the mechanical properties results, the results showed that the combination of fillers SSM with SBA-15 or SBA-15/MPS increases the flexural modulus compare with composite containing only SSM. These results show that porous fillers with interconnecting pores are promising materials to prepare stronger dental composites [12] and the material with additional filler containing MPS associated with interconnecting pores are more promising than materials containing only interconnecting pores. Regarding to the flexural strength results all composite had comparable values.

Table 2 also shows that the degree of conversion for all composites group containing the addition of SBA-15 or SBA-15/MPS a statistically significant decrease when compared to those composites containing only SSM. The reduction on the degree of conversion is due to the increase of viscosity when is added SBA-15 or SBA-15/MPS [24,25]. In fact, the monomer viscosity influences mobility at very early stages in polymerization, thus the more viscous monomers tend to reach the diffusion-limited stage of reaction at lower conversions, which in general means that the final conversion will also be lower [26].

The water sorption was measured to analyze the hydrophilicity or hydrophobicity of the material fabricated and water solubility and methylene chloride extraction studies were designed to determine the amount of leachable components. Methylene chloride was used as the solvent to avoid the disparity in physical interaction parameters among these filler in water, the solvent most commonly used to analyze the elution of the dental composites [17]. The addition of SBA-15 reduced approximately 47% and SBA-15/MPS reduced approximately 58% of leachable

components after extraction compared to composite having only SSM. The reduction of leachable components to the composites based on porous materials is due to the insertion of polymeric network inside the porous instead only among fillers. Once the polymers go inside the porous, more resistant composite against solvent are made because of the mechanical interaction between fillers and polymers. Additionally, composites containing porous filler treated with MPS showed to be more resistant than composites containing only porous fillers. This may be explained by the likely greater crosslinking density due to the presence of MPS, which contains the methacrylate groups, the methacrylate increases the odds of polymerization between methacrylate monomer and methacrylate filler. In fact, it is statistically more likely that the unreacted functionalities in the composite with SBA-15/MPS filler are represented by trapped double bonds in the polymeric network formed due to chemical interaction filler-polymer, rather than extractable unreacted monomers.

Regarding to the water sorption and water solubility, composites made with SBA-15 increased significantly the water sorption and composites with SBA-15/MPS also had the water sorption increased, but not statistically different when compared with composite made with only SSM. Composites made with SBA-15 and SBA-15/MPS increased significantly the water solubility compared with composite made with only SSM. When is compared composites made with SBA-15 and SBA-15/MPS can be observed that those composites fabricated with SBA-15/MPS presented water solubility lower than composites prepared with SBA-15.

It is well known that the water sorption is directly related to the hydrophilicity or hydrophobicity. The more hydrophilic is the material the higher will be its water sorption. To the dental composites, in general, those materials with higher water sorption present higher water solubility, especially due to the hydrolysis of methacrylate groups. In this work, the theory previously mentioned about water sorption and its association with water solubility is true.

However, not always the materials with higher water sorption will show higher water solubility [27].

Siderous et. al. [28] showed that the water sorption to the dental materials depend not only on the chemical structure of monomer used, but also depend on the physical structure of polymeric network formed, for example, the higher is the heterogeneity of the polymeric network the more will be free volume of the material, this can allow great deposition of water and increase the water sorption. Specifically, poly-TEGDMA presents more water sorption than poly-bis-GMA, interesting that TEGDMA monomer not contain hydrophilic OH group as bis-GMA presents. It was expected to poly-bis-GMA would present higher water sorption than poly-TEGDMA. The opposite occurs because TEGDMA is capable to easily form cyclization of polymerization leading to the great heterogeneity of its polymeric network and great free volume. In another words, poly-TEGDMA present great amount of porous among its polymeric chains.

Therefore, the facts directly concludes that composite based on SSM reached lower water sorption and water solubility because of its lower specific surface area (less porous size) due to the presence of only spherical silica and its hydrophobic silane group. The same is true when is compared composite containing SBA-15 and SBA-MPS, those composite made with SBA-MPS reached lower water sorption and water solubility than those composites made with SBA-15 because of its lower specific area and the additional MPS that increases the hydrophobicity of the final material. The more is the water sorption and water solubility the less will be the longevity by reducing its mechanical properties and the more will be the capacity of toxicity to the dental composites because of higher hydrolytic degradations [29].

Related to the results from adhesives showed in Table 3, it can be observed that the addition of 10 wt% of fillers on the adhesives had the tendency of decrease flexural strength, except to the adhesive ABH-SBA-MPS-10 (which one increased the flexural strength), although no significant statistical difference between the unfilled adhesive and adhesives with 10 wt%. The

addition of 15 wt% of filler also showed the same behavior of decreasing the flexural strength compared to unfilled adhesives, showing statistically significant difference to the sample (ABH-SBA-15)-15. The addition of 10 and 15 wt% of fillers increased with statistically significant difference the flexural modulus to those composites made with SBA-15 and SBA-15/MPS, and decreased significantly to the composite containing SSM ((ABH-SSM)-15), but did not show statistical difference when is added 10% of SSM (ABH-SSM)-10).

Regarding to the degree of conversion, when is added 10 and 15 wt% of filler all adhesive showed a significant statistical increase on the degree of conversion, except for groups containing SBA-15. Furthermore, all adhesive had its surface area decreased, except to the adhesive ABH-SBA-15. The results of flexural strength, flexural modulus, degree of conversion and specific surface are from the adhesive show that those adhesive based on SBA-15/MPS is more promising to be used than SBA-15 or SSM because none composite containing SBA-15/MPS decreased significantly the flexural strength or modulus neither the degree of conversion and has comparable surface area to SSM.

The flexural strength is directly related to the capacity of break resistance, thus the tendency of decreasing the flexural strength is probably due to the increase of heterogeneity of the final material containing few concentrations of fillers. Figures 4 and 5 show the images of SEM and AFM to the unfilled adhesive and adhesives containing 10 wt% of fillers. These images show the difference of homogeneity between unfilled adhesive and adhesives with fillers. When is compared the images SEM and AFM from the adhesives based on SBA-15, SBA-MPS and SSM can be seen better load distribution, homogeneity and interaction between filler and polymer (filler more attached to the polymer) to SSM than SBA-MPS and better load distribution, homogeneity and interaction between filler and polymer to SBA-MPS than SBA-15.

In general, the higher is the flexural strength the lower will be the flexural modulus, as showed by Barszczewska-Rybarek [30], the flexural strength to poly-bis-GMA and poly-TEGDMA

was approximately 110 and 85 MPa, respectively, the flexural modulus to poly-bis-GMA and poly-TEGDMA was approximately 3.7 and 3.9 GPa, respectively. The results shows higher flexibility from poly-bis-GMA than poly-TEGDMA, which is more resistant to fracture and shows lower rigidity from poly-bis-GMA than poly-TEGDMA, which is less resistant to impact (impact strength approximately to poly-TEGDMA = 8.9 KJ/m² and poly-bis-GMA = 6.3 KJ/m²).

The trend of having material with higher values from flexural strength and lower values from flexural modulus was found to the adhesives made in this work. As the flexural strength decreased due to the presence of fillers, the flexural modulus increased. The higher values of flexural modulus are due to mainly by the presence of more rigidity of silica. The higher values of flexural strength from the unfilled adhesives, beside greater homogeneity of material is a result of higher flexibility of polymer without rigid silica.

The degree of conversion increased for all adhesive after adding fillers (with either SSM or SBA-15 or SBA-15/MPS). An improvement in degree of conversion by the addition of fillers is due to the active role of fillers during the polymerization process which accelerates the reaction, the presence of fillers make the polymeric network reach higher level of rigidity earlier reaching high degree of conversion, this was observed through the viscosity measurement during polymerization [23]. Indeed, an improvement in degree of conversion happens greater when is used silanized filler because of the role of surface functionalization of particles in this mechanism, that is, the polymerization of monomers also happen on the surface. Thus, the inorganic fillers serve as fixed site in order to help the initiation of polymerization process [23, 31].

The fact of role of surface functionalization in the polymerization can explain why the adhesives based on SBA-15 without treatment reached lower degree of conversion, especially the adhesive captaining 15 wt% of filler, which had its degree of conversion statistically significant lower than the adhesives based on SBA-15/MPS and SSM (Table 3). Figure 4 shows how each filler presents different capacity of agglomerations, for adhesive with spherical silica (B) it can be

seen a higher homogeneity and no agglomerations of fillers due to spherical geometry and size of particles associated with silane agent that improve the interaction between filler and polymer. Unlike the spherical silica, the adhesive with pure SBA-15 (C) showed high heterogeneity and huge agglomeration of filler (mark by the arrow in the Figure 4) which is attributed to the lack of interaction between filler and polymer. When is made a material with SBA-15/MPS (D) we can see how the agglomeration tends to undo (it can be suggest because of absence of huge agglomeration in (D)) because of the increase in the chemical interaction between filler and polymer promoted by the presence of MPS agent.

In addition to that, in accordance with SEM image, the image of AFM to the adhesive containing SBA-15 (Figure 5) present the lack of interaction between polymer and filler (shown by its less load distribution and higher agglomerations spots), which contributes to decrease the degree of conversion. Furthermore, the visible aspect of adhesive based on SBA-15 had its aspect like slurry (not fluid), while the adhesives based on SBA-15 presented its aspect like fluid resin, these aspects show the importance of functionalization of fillers surfaces.

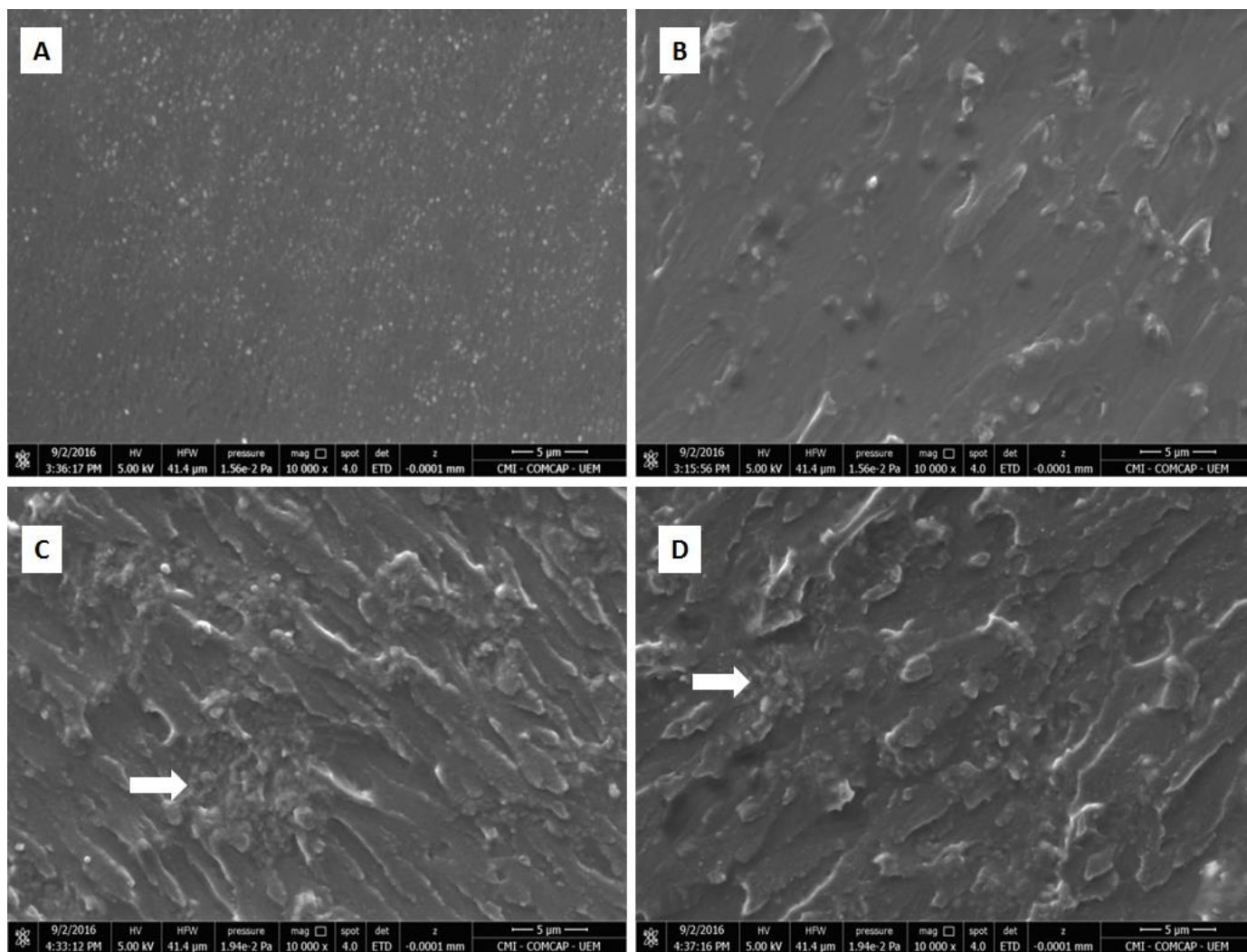


Figure 4. SEM images of adhesives to (ABH)-0 (A), (ABH-SSM)-10 (B), (ABH-SBA-15)-10 and (ABH-SBA-15/MPS)-10.

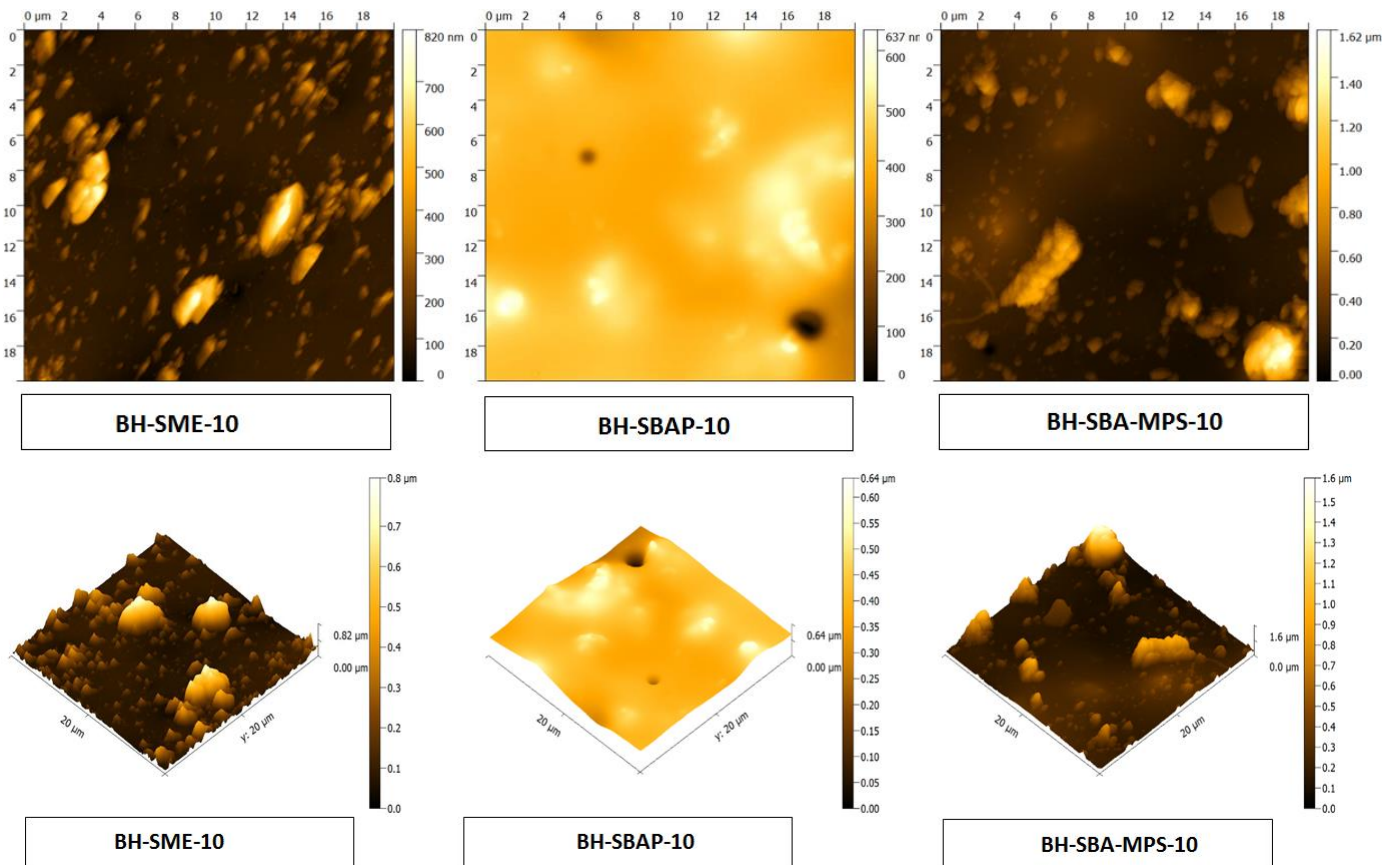


Figure 5. Typography and or not phase contrast images of the adhesives surfaces.

4. Conclusion

SBA-15 was successfully synthesized and modified with MPS. The modified SBA-15 showed significant reduction on its specific area compared with pure SBA-15. In overall, the dental materials based on pure SBA-15 and modified SBA-15 have shown lower degree of conversion due to the reduction on its viscosity, but better mechanical properties than dental materials based on commercial spherical silica because of the great capacity of porous material that improve the physical interaction between filler and polymer. The dental materials based on pure SBA-15 and modified SBA-15 have presented higher specific area than commercial spherical silica because of the presence of mesoporous that were not completely filled with polymer. Material containing modified SBA-15 had its specific area reduced compared with materials base on pure SBA-15 following the behavior of pure powder mesoporous silica.

Regarding to water sorption, the materials containing modified SBA-15 showed comparable values compared to those material based on commercial spherical silica and significant reduction compared to those material based pure SBA, this results are reflex of the hydrophobicity or size porous which are capable to retain less or more water. The water solubility is directly related with water sorption and follower the same trend of water sorption. More importantly, SBA-15 and modified SBA-15 have shown significantly greater resistance to leaching in organic solvents than commercial spherical silica due to the interconnecting pores, however the modified SBA-15 showed greater resistance to leaching than pure SBA-15 because of its better interaction between polymer and filler which is attributed to the presence of MPS, best interaction was shown by SEM and AFM.

Acknowledgements

The authors thank the Brazilian agencies CAPES and CNPq for the financial support and fellowship (GCM) and COMCAP – UEM department for SEM analyses.

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