Nanocomposites obtained by incorporation of silanized silver nanowires to improve mechanical properties and prevent fungal adhesion

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Abstract
In this work, the surfaces of silver nanowires (AgNWs) were modified by silanization process to improve the mechanical and antibiofilm properties of polymethylmethacrylate (PMMA) dental resins. A two-route methodology was used to silanize the AgNWs: first, a surface treatment using tetraethyl orthosilicate (TEOS) was performed to act as interface agent; and then, γ-methacryloxypropyltrimethoxysilane (MPS) was used to insert functional groups compatible to the acrylic resin. PMMA/AgNWs composites were obtained using pristine (AgNWp) and modified AgNWs (AgNWm) at concentrations of 0.5 and 1.0 wt%. The mechanical (flexural and impact strength) and antibiofilm properties against Candida albicans was investigated. AgNWm showed an enhancement in the dispersion and adhesion within the PMMA matrix, which were responsible for improvements in the mechanical properties. Results of flexural strength showed significant improvements for the sample with incorporation of 0.5 wt% of AgNWm and no significative changes for the sample with AgNWp. In addition, a reduction of about 50% in the biofilm formation by C. albicans was observed for the samples with 0.5 and 1.0 wt% of AgNWm. The incorporation of silanized-AgNWs into PMMA dental resins can combine improvements in antimicrobial activity and in the flexural strength, being a potential antimicrobial biomaterial for dental applications.

Keywords
dental acrylic resin, silanization, silver nanowires, γ-methacryloxypropyltrimethoxysilane
INTRODUCTION

The applications of Ag nanoparticles (AgNPs) have been largely studied due to their antimicrobial activity\(^1\) and the potential to be incorporated in several types of biomaterials. Due to the negative impacts of the infectious diseases and increasing occurrence of antimicrobial resistance, the search for innovative strategies is needed.\(^2\) Some of the limitations of the conventional antimicrobials might be overcome with the use of nanoparticles with antimicrobial activity, such as the AgNPs.\(^3\)

The antimicrobial effect of the AgNPs results from the damage in microbial cell membrane and sub-cellular structure. First, AgNPs adhere to the microbial cells, generating structural and functional alterations. Then, AgNPs penetrate inside the cell, releasing Ag\(^+\) ions and producing reactive oxygen species (ROS) and free-radicals, inactivating essential macromolecules.\(^1\) AgNPs can be found in several morphologies and configurations, depending on the synthesis method. The most common types of AgNPs are Ag nanowires (AgNW), Ag nanorods (AgNR), Ag nanocubes (AgNC), and Ag nanospheres (AgNS).

Among these AgNPs species, AgNWs have gained major attention for their high aspect ratio due to the one-dimensional structure, resulting in specific physicochemical properties. AgNWs have the potential to combine antibacterial activity with lower cytotoxicity to host cells compared to the others AgNPs species.\(^4\) These unique set of properties provides the possibility of using AgNW for biomedical applications, such as drug delivery, tissue regeneration, and antimicrobial material.\(^5\)–\(^7\)

Polymeric matrices used as restorative composites resins and dental prostheses, such as polymethylmethacrylate (PMMA), can take advantage of AgNWs to improve their properties and expand their applications. PMMA used as dental material presents a great number of limitations, such as low mechanical resistance, susceptibility to microbial colonization, water absorption, and surface imperfections.\(^8\) The incorporation of AgNWs in PMMA matrix can be an interesting alternative to overcome both physical and biomechanical properties. In order to optimize AgNWs properties, surface treatments by silanization can be performed, improving their dispersion state and adhesion with the proper matrix. Tetraethyl orthosilicate (TEOS) and γ-methacryloxypropyltrimethoxysilane (MPS) are important silane coupling agents, widely used as grafting agents to promote interfacial interactions between inorganic nanoparticles and polymeric matrix.\(^9\)–\(^10\)

Some studies have already reported improvements in the properties of PMMA for dental applications after the surface silanization of nanofillers. de Menezes et al. incorporated MPS-modified silver vanadate (AgVO\(_3\)) in PMMA and investigated the effect of AgVO\(_3\) dispersion and interaction in the mechanical properties of the final nanocomposite.\(^11\) The MPS silanization process improved the inorganic–organic phase interaction and AgVO\(_3\) dispersion in PMMA, resulting in higher Shore-D and impact strength values when compared do neat PMMA and PMMA/pristine AgVO\(_3\) nanocomposites. The study by de Menezes et al.\(^11\) showed the potential use of the silanization process to improve the dispersion and interaction of inorganic nanomaterials in organic matrices. The use of AgNWs can combine those properties with the potential antibiofilm activity of the silver compound.

In this way, this work reports the pioneer AgNWs surface modification through silanization reactions using TEOS and MPS. To our knowledge, the AgNWs have not been functionalized yet and has not been incorporated in PMMA for dental prosthetic production. A sequential silanization, first using TEOS and then, using MPS was performed. The morphology and surface characteristic of pristine and silanized AgNWs were analyzed and, then, the nanofillers were incorporated in PMMA in varying amounts (0.5 and 1.0 wt%). The resulting mechanical properties and antibiofilm effect on Candida albicans were verified. The results showed that the use of MPS-modified AgNWs in dental acrylic resins could lead to great improvements in the mechanical and biological properties of these nanocomposites.

MATERIALS AND METHODS

Silanization of AgNWs

AgNWs with a minimum purity of 99.9 wt% were supplied from Nanostructured & Amorphous Materials, Inc., USA. AgNWs were received as a suspension consisting of 1.0 wt% AgNWs in 99.0 wt% water, showing average diameter of 55–75 nm and average length of 20–40 μm (product #0475NW6W). Pristine AgNWs, labeled as AgNW\(_p\), were obtained through centrifugation (Solab, SL-701) of the AgNWs/water suspension, at -10 °C and 3500 rpm for 10 minutes. Then, the sedimented AgNW\(_p\) was dried in conventional oven (SPLABOR, SP 100) at 60 °C for 12 hours.

AgNWs silanization was performed in two steps. First, the AgNWs were modified using TEOS as an interface agent, with the purpose of increasing the density of hydroxyl (OH) groups on AgNWs surfaces.\(^12\) Then, the TEOS-modified AgNWs were silanized using γ-MPS. For the silanization using TEOS, 30 mL of AgNWs/water suspension were mixed with 30 mL of absolute ethanol (Synth, 99.8%) in ultrasonic bath (Tecnal, Eco-Sonics).
FIGURE 1  Silanization process of AgNWs using a two-route methodology: first using TEOS as interface agent and then, using MPS. The molecules of Si, O, C, and H are represented by the spheres in the colors green, red, gray, and white, respectively.

For the silanization using γ-MPS, an amount of 0.3 g of AgNW_T were dispersed in 30 mL of deionized water in ultrasonic bath for 30 minutes in room temperature. Then, 1.0 mL of γ-MPS (Sigma, 98%) were added to the suspension and mixed under magnetic stirring until homogenization. After that, 0.5 mL of acetic acid 1 M (Synth, 99.7%) were added dropwise. The mixture was maintained under magnetic stirring for 6 hours. Lastly, the product was centrifuged (Solab, SL-701) at −10°C and 3,500 rpm for 10 minutes, and washed with deionized water, and dried in conventional oven at 60°C for 12 hours. The AgNWs modified using MPS were labeled as AgNW_M.

The presence of functional groups on AgNWs after silanization was characterized by X-ray photoelectron spectroscopy (XPS) using a UNI-SPECS UHV spectrometer with monochromatized Al Kα irradiation (hν = 1254.6 eV) and pass energy set as 10 eV. The composition of the surface layer was determined from the ratio of the relative peak areas corrected by the Scofield sensitivity factors for the corresponding elements (Ag 3d, Si 2p, O 1s, and C 1s). The spectra were deconvoluted using a Voigt profile (70% Gaussian and 30% Lorentzian). The width at half maximum (FWHM) varied between 1.2 and 2.1 eV and the accuracy of the peak position was ±0.1.

2.2 Characterization of silanized AgNW

AgNW_P and AgNW_M were characterized to verify the chemical and morphological properties after the surface modification. The crystalline structure of the samples was identified by X-ray diffraction using a Philips X’Pert Equipment from PANalytical operating with Cu Kα radiation (λ = 1.54178 Å) at 45 kV and 40 mA. The data were collected in the 2θ range of 30° to 80°, with step size of 0.02° and 30 seconds per step.

The morphological changes were characterized by field emission gun scanning electron microscopy (FEG-SEM) using a Jeol JSM-5310 equipment, with detectors of secondary electrons mode (SE) and accelerating voltage of
30 kV. Energy dispersive X-ray spectroscopy (EDX) was also performed to analyze the chemical composition of the samples, using a Tescan Vega 3 SEM with accelerating voltage of 20 kV. AgNW\textsubscript{P} and AgNW\textsubscript{M} powders were fixed using carbon tapes on aluminum stubs. The samples were not covered with gold, since the silver is a conducting metal.

### 2.3 Preparation of PMMA/AgNW nanocomposites

Heat-polymerizable colorless acrylic resin provided by Clássico (Dental Articles, Brazil) was used to prepare the nanocomposites. Both AgNW\textsubscript{P} and AgNW\textsubscript{M} were used to produce samples at concentrations of 0.5 and 1.0 wt%. Initially, a proper amount of AgNWs (0.07 g for 0.5 wt% and 0.14 g for 1.0 wt%) were added to 7 mL of methyl methacrylate monomer and dispersed in handheld ultrasonic processor (Hielscher UP200Ht, Power: 10 W, Amplitude: 20%) for 20 minutes. Then, a proper amount of the polymer (13.93 g for 0.5 wt% and 13.86 g for 1.0 wt%) was added, and the mixture was manually manipulated. Neat PMMA specimens were also produced, following the same procedure. Additionally, 14 g of polymer were used to keep the same amount of powder for comparison. The samples were prepared following the manufacturer’s instructions, using the proportion of two-parts powder (14 g, polymer) to one-part liquid (7 mL, monomer). In the plastic phase, the resin was poured into holes prepared in metal muffles, which were gradually pressed in hydraulic press until 1.5 ton. The resin was polymerized according to the manufacturer’s recommendation. After the polymerization process, all samples were sanded and polished to standardize the surface characteristics. The samples were labeled as neat PMMA, PMMA/AgNW\textsubscript{P}-0.5, PMMA/AgNW\textsubscript{P}-1.0, PMMA/AgNW\textsubscript{M}-0.5, and PMMA/AgNW\textsubscript{M}-1.0.

### 2.4 Characterization of PMMA/AgNW nanocomposites

#### 2.4.1 Morphological, physical, and surface properties

The cross section (cryogenic fractured surfaces) of neat PMMA and PMMA/AgNW nanocomposites was analyzed by field emission gun scanning electron microscopy (FEG-SEM) using a Jeol JSM-5310 equipment, with detectors of secondary electrons mode (SE) and accelerating voltage of 5 kV. The samples were cryogenically fractured using liquid nitrogen, fixed on aluminum stubs and covered with gold.

The roughness of neat PMMA and PMMA/AgNW nanocomposites was quantified ($n = 10$) through profilometry using a mechanical profilometer KLA Tencor P-7. The contact angle using deionized water was also measured using a goniometer Ramé-Hart 500.

Degree of monomer conversion (DMC) was determined by Fourier-transformed infrared (FT-IR) spectrometry. The spectra were recorded in a Spectrum One, PerkinElmer, using attenuated total reflectance (ATR) method, in the region of 4000 to 400 cm$^{-1}$. All spectra were obtained from 16 scans at 4 cm$^{-1}$ of resolution. The DMC was obtained using the following equation (Equation 1):

$$DMC = 100 - \frac{A^P_{1638}}{A^P_{1730}} \times \frac{A^M_{1638}}{A^M_{1730}}$$

where $A^P_{1638}$ is the height of absorption peak of the C = C at 1638 cm$^{-1}$ for PMMA and nanocomposites, $A^P_{1730}$ is the height of absorption peak of the C = O at 1730 cm$^{-1}$ for PMMA and nanocomposites, $A^M_{1638}$ is the height of absorption peak of the C = C at 1638 cm$^{-1}$ for monomer (methyl methacrylate), and $A^M_{1730}$ is the height of absorption peak of the C = O at 1730 cm$^{-1}$ for monomer (methyl methacrylate).

#### 2.4.2 Mechanical properties

For mechanical testing, 10 specimens were used for each group. The three-point flexural strength test was performed according to ISO 20795-1:2008 using a universal testing machine MTS Landmark at speed of 5 mm min$^{-1}$ and load of 100 kgf. The dimensions of the specimens were 30 mm $\times$ 10 mm $\times$ 3 mm. The flexural strength was calculated in MPa according to the following equation (Equation 2):

$$s = \frac{3FD}{2BH^2}$$

were $F$ is the maximum load (N), $D$ is the distance between the supports (20 mm), $B$ is the width of the specimens (mm), and $H$ is height of the specimens (mm).

Notched Izod impact strength test was conducted using a CEAST Instron Impactor 905 according to ASTM D256-06. Standard Izod-type hammer with impact loading of 1.0 J was used. The specimens, with dimensions of 65 mm $\times$ 10 mm $\times$ 3 mm, were positioned vertically and the hammer reached the upper free end. Statistical analysis (one-way analysis of variance and Tukey’s multiple comparison) of flexural and impact strength results were performed using GraphPad Prism 6.
2.4.3 Antibiofilm properties

Standardized specimens of neat PMMA and PMMA/AgNWs nanocomposites \( (n = 12) \) were prepared with 2 mm of height \( \times \) 9 mm of diameter. After, they were sterilized by UV radiation for 10 minutes per side.

*\textit{C. albicans* ATCC 18804} was included in the experiments. *\textit{C. albicans*} was cultivated in Sabouraud dextrose agar for 24 hours at 37 \(^\circ\)C, under aerobiciosis. Fungal inoculum was obtained in sterile saline solution (NaCl 0.9%) and adjusted spectrophotometrically (AJX-1600, AJMicronal) to \( 10^6 \) cells mL\(^{-1}\) \((\lambda = 530 \text{ nm, OD} = 0.138)\). Aliquots of 200 \( \mu \text{L} \) of the fungal inoculum were added to 2 mL of culture medium RPMI supplemented with 2% glucose in a 24-well plate.

Under aseptic conditions, the specimens were transferred to the microplates and completely immersed in the culture medium. Plates were incubated at 37 \(^\circ\)C under agitation (75 rpm) for 90 minutes for pre-adherence phase. Then, the specimens were washed with saline solution and 2 mL of RPMI supplemented with 2% glucose were added in each well. Plates were incubated for 24 hours at 37 \(^\circ\)C. After 24 hours, the biofilm formed on the specimens were gently washed with sterile saline solution, transferred to tubes containing 1 mL of sterile saline solution, after sonicated in an ultrasonic processor (Vibra Cell, Sonics, Power: 15 W, Amplitude: 40%) for 30 seconds (2 pulses of 15 seconds), and the suspension were mixed with vortex for 30 seconds.

Final suspensions were serially diluted in sterile saline solution and plated on Sabouraud dextrose agar. Petri dishes were incubated at 37 \(^\circ\)C for 24 hours and, after, the values of colony forming units per specimen (CFU/specimen) were calculated. Fungal growth control and culture medium sterility controls were prepared following the same procedure. For fungal growth control, no specimens were included and for the culture medium sterility control, no specimens and no inoculum were added to the well. Sterility tests were performed for all the samples. For that, neat PMMA and the nanocomposites were seeded in Petri dishes with Sabouraud dextrose agar without the fungal suspension. The Petri dishes were incubated for 24 hours, under aerobiosis. The sample sterility was determined visually by the identification of microbial growth. Data were compared by one-way ANOVA Tukey’s multiple comparison, by using GraphPad Prism 6. The level of significance was set at 5%.

2.4.4 Morphological analysis of the biofilms

The morphology of *\textit{C. albicans*} biofilms formed on neat PMMA and PMMA/AgNWs nanocomposites after the incubation for 24 hours was analyzed by SEM. Prior to observations, biofilm specimens were fixed using 2.5% glutaraldehyde (Sigma, 25%) in 0.1 M phosphate buffer pH 7.4 for 24 hours. Then, the specimens were exposed to an ethanol dehydration series of 30, 50, 70, 80, 90, and 2 \( \times \) 100% (v/v) ethanol (Synth, 99.8%), for 10 minutes in each concentration.[15] All specimens were, then, dried for 1 day and coated with gold thin film. SEM analysis were performed in Tescan Vega 3 microscope with accelerating voltage of 10 kV and magnification of 1.0 and 3.0 kx.

3 RESULTS

3.1 Characterization of silanized AgNW

Figure 2A shows the XRD diffractograms of AgNW\(_P\) and AgNW\(_M\). As noted, both samples exhibited the characteristic peaks of crystalline face-centered-cubic silver, with Joint Committee on Power Diffraction Standards (JCPDS) 01-087-0718.[16,17] The diffraction peaks are at around \( \theta = 38.2\,^\circ\), 44.4\,^\circ\), 64.6\,^\circ\), and 77.6\,^\circ\), corresponding to the (111), (200), (220), and (311) planes, respectively. The position of these peaks remains substantially unchanged after the silanization processes, indicating that the addition of functional groups on the nanowires surfaces does not affect the basic crystalline structure of AgNWs.

The surface’s changes of AgNWs after the silanization process were investigated using XPS analysis. Figure 2B shows the survey spectra obtained for AgNW\(_P\) and AgNW\(_M\). Sample AgNW\(_P\) showed photoelectric peaks for Ag 3d and Ag 3p in the range of 367–375 eV and 571–603 eV, respectively, related to the silver components, as metallic silver.[18] In addition, peaks related to O 1s, at around 531 eV, and C 1s, at around 285 eV were also observed. C 1s peak results from hydrocarbon contaminants adsorbed onto samples surfaces due to the laboratory environment.[19] After the silanization process, new peaks related to Si 2p clearly appears at binding energy in the range of 104–155 eV.[20] Also, the intensity of O 1s peak was enhanced while the intensity of Ag 3d was decreased. Those changes are associated to the functional groups inserted on AgNW\(_M\) surfaces, which are composed mostly by silicon, oxygen, and carbon elements. XPS analysis is a surface technique able to evaluate about 2–5 nm from the top of the sample.[21] In this way, for AgNW\(_M\), XPS detected mostly silanols and methacryloxy groups, reducing the detection of silver.

Table 1 shows the atomic percentage (at%) quantification of the surface species (Ag, O, Si) on AgNW\(_P\) and AgNW\(_M\). The percentage of carbon was not included in the table and in the discussion, since it can be associated both to the sample and to hydrocarbon contaminants. In
this way, the percentage of silver, oxygen, and silicon were normalized. Sample AgNW$_P$ is mostly composed of silver (54.8 at%) and oxygen (45.2 at%). This result indicates the presence of metallic silver and silver oxide (Ag$_2$O) in the nanowires. The Ag$_2$O phase is produced in the AgNWs surfaces when in contact with the humidity in the air, as a passivation coating. Since XPS analysis evaluate about 2–5 nm from the top of the sample, great amount of Ag$_2$O was quantified while the signal of metallic silver was reduced. After the silanization process, about 23.2 at% of silicon were identified. Also, the amount of oxygen was increased by 36%, suggesting the attachment of silanol and methacryloxy groups on AgNW$_M$ surfaces.

FE-SEM with EDX was used to evaluate the morphological changes produced by the silanization processes. Figure 2D shows the FEG-SEM images of AgNW$_P$ and AgNW$_M$ with the respective EDX spectrum. Sample AgNW$_P$ showed nanowires with relatively smooth and homogeneous surfaces, being mostly parallel to each other, with a close contact. AgNW$_P$ diameters were measured from the FEG-SEM images, being around 30–35 nm. After silanization, some morphological modifications were identified. Sample AgNW$_M$ maintained the original wire-like structure, but the nanowires surfaces become rougher. The diameter increased to about 37–52 nm. The surface roughness and increase in diameter values can be attributed to the formation of an outer layer of silanols and methacryloxy groups attached to the surface of the nanowires. The silanol and methacryloxy coating on AgNWs occurs by
the hydrolysis of ethoxy groups of TEOS (Equation 3) and methoxy groups of MPS (Equation 4) into hydroxyl groups.[23]

\[
\text{Si(OC}_2\text{H}_5)_4 + \text{excess H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4\text{C}_2\text{H}_5\text{OH} \quad (3)
\]

\[
\begin{align*}
\text{C}_7\text{O}_2\text{H}_{11} - \text{Si(OC}_2\text{H}_5)_3 + \text{excess H}_2\text{O} & \rightarrow \\
\text{C}_7\text{O}_2\text{H}_{11} - \text{Si(OH)}_3 + 3\text{C}_2\text{H}_5\text{OH}
\end{align*}
\]

The hydroxyl groups react to other hydroxyl groups, producing a crosslink between the silanol molecules during condensation on AgNW surfaces, growing the desired coating.[24,25] The hydroxyl-hydroxyl reaction will initially occur between the hydroxyl groups of TEOS and hydroxyl groups of MPS (Equation 5). Then, reactions with other nucleophiles can also occur, and the condensation will take place between the hydroxyl groups of MPS molecules (Equation 6).[23]

\[
\begin{align*}
\text{C}_7\text{O}_2\text{H}_{11} - \text{Si(OH)}_3 + \text{Si(OH)}_4 & \leftrightarrow \\
\text{C}_7\text{O}_2\text{H}_{11} - \text{Si(OH)}_2 - \text{O} - \text{Si(OH)}_3 + \text{H}_2\text{O}
\end{align*}
\]

\[
\begin{align*}
2\text{C}_7\text{O}_2\text{H}_{11} - \text{Si(OH)}_3 & \leftrightarrow \\
\text{C}_7\text{O}_2\text{H}_{11} - \text{Si} - \text{O} - \text{Si} - \text{C}_7\text{O}_2\text{H}_{11} + \text{H}_2\text{O}
\end{align*}
\]

According to the FEG-SEM images, almost every AgNWs were covered densely and uniformly with a great quantity of silanol and methacryloxy groups, indicating that the silanization process using TEOS and MPS is reproducible.

Regarding the EDX spectrum (Figure 2C), AgNW_P presented strong signal peaks for silver in the range of 2.6–3.2 keV.[26] Also, a small peak at around 0.3 keV, related to carbon, was observed. This carbon peak is majorly attributed to the carbon tape used in the EDX-SEM analysis. After the silanization process, two new peaks were observed. The peak at around 1.7 keV belongs to silicon[27] and the peak at around 0.5 keV is attributed to oxygen.[28] Silicon and oxygen peaks indicate the presence of silanols and methacryloxy groups on AgNWs surfaces after the silanization reactions. The inserted table in EDX spectra presents the atomic percentage (at%) quantification of the elements in the samples. The percentage of carbon was not included in the table and in the discussion, since it can be associated both to the sample and to carbon tape used in the SEM analysis. In this way, the percentages of silver, oxygen, and silicon were normalized. According to Figure 2C, AgNW_P is majorly constituted of silver, as expected. After silanization, 10.0 at% of silicon was verified for samples AgNW_M. Also, a great amount of oxygen (45.0 at%) was observed due to silanol groups on AgNW_M surfaces. Consequently, the atomic percentage of silver was reduced, since new elements were inserted in the sample. The increase in the quantification of silicon and oxygen is related to the reaction of methacryloxy groups with the previously inserted silanol groups on AgNW_T surfaces (Figure 1). EDX-SEM observations show some differences on atomic percentage when compared to XPS results. EDX-SEM analyses the whole materials instead of only the surface (like XPS). The depth of analysis for EDX-SEM is about 60–160 nm from the top of surface, depending on the electron beam voltage, while for XPS analysis is only 2–5 nm.[29] Even with this difference from the type of technique, both XPS and EDX-SEM proved that the silanization reactions had successfully occurred.

3.2 | PMMA/AgNW nanocomposites surface characteristic

The cryogenic fracture surfaces of neat PMMA and PMMA/AgNW nanocomposites were analyzed by FEG-SEM to evaluate the dispersion and adhesion of AgNW to the PMMA matrix. Figure 3A-E shows the cryogenic fracture surface micrographs of the samples. Fracture surface of neat PMMA (Figure 3A) is smooth, homogeneous and without major deformations. Agglomerates of AgNW_P can be clearly identified in the area marked with a white square in the images of PMMA/AgNWP-0.5 (Figure 3B) and PMMA/AgNW_P-1.0 (Figure 3C) nanocomposites. These agglomerates indicate a poor dispersion of the nanowires in PMMA matrix, increasing the size of agglomerates by increasing the content of AgNW_P inserted in PMMA matrix. Also, the addition of AgNW_P resulted in a weak adhesion between the nanowires and PMMA, since the AgNW_P agglomerates were pulled-out from the matrix. PMMA/AgNW_M-0.5 (Figure 3D) and PMMA/AgNW_M-1.0 (Figure 3E) nanocomposites showed the dispersion of AgNW agglomerates and their fracture inside the polymeric matrix, being the gray points identified with white arrows. Even the sample with higher concentration of AgNW_M showed improved dispersion of the modified nanowires. This behavior is related to the higher interfacial compatibility among the silanized nanowires and the polymer, since the AgNW_M fractured along with the PMMA, instead of being pulled-out.

Water contact angle test (Figure 3F) using deionized water showed no significant difference between the neat PMMA and the nanocomposites. The samples showed water contact angle varying between 56 and 64°, similar to the values found in the literature for neat PMMA,[30] indicating a hydrophilic behavior. The contact angle remained unchanged because in a polymer nanocomposite, the fillers are mostly embedded by the matrix.[31] The surface
roughness ($R_a$) was also evaluated (Figure 3G), showing no significant difference between the neat PMMA and the nanocomposites. This result was expected since the surface of all specimens were polished to reduce roughness influence in the microbial adhesion.

The DMC for neat PMMA and the nanocomposites was determined by Equation (1), based on the intensities of the bands at 1638 cm$^{-1}$, related to $C = C$ bond, and the band at 1730 cm$^{-1}$, corresponding to $C = O$ bond. The results are presented in Figure 3H. Neat PMMA showed DMC equal to 90.1%, which is in accordance to DMC values found in the literature.$^{[32,33]}$ The incorporation of AgNWs in PMMA decreased the DMC value, especially for the nanocomposites with AgNW$_M$. The samples PMMA/AgNW$_P$-0.5 and PMMA/AgNW$_P$-1.0 showed a reduction on DMC of about 6%, while the samples PMMA/AgNW$_M$-0.5 and PMMA/AgNW$_M$-1.0 showed a reduction of about 17%. 

FIGURE 3 A-E, FEG-SEM micrographs of cryogenic fracture cross section, (F) water contact angle, (G) surface roughness, and (H) degree of monomer conversion for: neat PMMA, PMMA/AgNW$_P$-0.5, PMMA/AgNW$_P$-1.0, PMMA/AgNW$_M$-0.5, and PMMA/AgNW$_M$-1.0. Asterisks (*) indicate statistical significance compared to neat PMMA (***$p < 0.001$, ****$p < 0.0001$)
3.3 PMMA/AgNW nanocomposites mechanical properties

Figure 4A shows the average results and standard deviation obtained for Izod impact strength test. The impact strength of neat PMMA, which was 134.2 J m⁻¹, practically did not change after the incorporation of AgNW_p. A slight increase to 140.6 and 141.9 J m⁻¹ was observed for the samples PMMA/AgNW_p-0.5 and PMMA/AgNW_p-1.0, respectively. The incorporation of AgNW_M showed improved impact strength value, when compared to AgNW_p. Samples PMMA/AgNW_M-0.5 and PMMA/AgNW_M-1.0 showed impact strength of 151.2 and 154.9 J m⁻¹, with an increase of about 13% and 15%, respectively, compared to neat PMMA. For all samples, no statistical difference was observed, when compared to neat PMMA, indicating that the incorporation of AgNW_p and AgNW_M had no statistical effect in PMMA impact strength (p ≥ 0.05).

The flexural strength of neat PMMA and the nanocomposites was evaluated, and the average results and standard deviation are shown in Figure 4B. Neat PMMA showed a flexural strength equal to 102.2 MPa, in accordance to flexural strength for denture base polymers defined by ISO 20795-1:2008. The incorporation of AgNW_p at concentration of 0.5 and 1.0 wt%, and AgNW_M at concentration of 1.0 wt%, did not result in significant changes in the flexural strength values, when compared to neat PMMA. Only the addition of AgNW_M at 0.5 wt% resulted in statistically significant increase in the flexural strength value (about 10%), when compared to neat PMMA (p ≤ 0.05).

3.4 PMMA/AgNW nanocomposites antibiofilm activity

Figure 5 shows C. albicans biofilm formation (after 24 hours) expressed by the colony-forming units per specimen (CFU/specimen) for neat PMMA and the test nanocomposites. According to the results, the incorporation of functionalized AgNW (AgNW_M) reduced the biofilm formation, when compared to neat PMMA. On the other hand, the addition of non-functionalized AgNW (AgNW_p) showed no statistical difference when compared to neat PMMA.

The addition of AgNW_M reduced significantly the number of CFU/specimen in relation to neat PMMA (p < 0.01). For both PMMA/AgNW_M-0.5 and PMMA/AgNW_M-1.0 the reduction in the biofilm formation was about 50% compared to neat PMMA, indicating an effective antifungal activity against C. albicans for these samples. Although the results for both samples were similar, PMMA/AgNW_M-0.5 showed increased variability when compared to PMMA/AgNW_M-1.0.
Figure 6 shows the SEM images of *C. albicans* 24 hours biofilm on neat PMMA and nanocomposites. In neat PMMA a mature *Candida* biofilm covering almost all the surface of the sample was observed. This biofilm was composed by yeasts and pseudohyphae/hyphae, surrounded by extracellular matrix. SEM analysis also evidenced a substantial decrease in the biofilm formation on the nanocomposites when compared to neat PMMA. The images evidenced the notable antibiofilm effect of the composites with incorporation of AgNW_M, as detected in viable cells analysis. The reduction of about 50% in the biofilm formation is clearly observed for the nanocomposites with incorporation of AgNW_M. Also, samples incorporated with AgNW_M showed a clear morphological change in the biofilm, with a marked decrease in *C. albicans* filamentous structures.

### 4 DISCUSSION

The present study incorporated MPS-silanized AgNWs in PMMA to improve the mechanical properties of impact and flexural strength, and induce anti *C. albicans* biofilm effects. The silanization treatment of AgNWs using MPS was successfully performed, as showed by XPS, FEG-SEM, and EDX-SEM results. These analyses demonstrated that silanol and methacryloxy groups were inserted on AgNWs surfaces through non-covalent reactions. In this way, no network perturbations occurred, as showed by XRD diffractograms. The inserted functional groups, specially the methacryloxy one, are expected to improve the dispersion and interaction of the AgNWs in the PMMA matrix. Both PMMA and MPS have methacrylate group on their structures, as showed by Figure 7. The
similarities in the molecular structures of PMMA and MPS favors their interaction, since the reactive methacryloxy groups on the AgNWs surfaces can efficiently conjugate to PMMA.\textsuperscript{35} According to some studies, the C – C bond in MPS methacrylate group can copolymerize with the C – C bond of methyl methacrylate, during the polymerization reactions of PMMA.\textsuperscript{36}

SEM images showed that the incorporation of AgNW\textsubscript{P} resulted in the formation of agglomerates with weak interaction with the polymer. The weak PMMA-AgNW\textsubscript{P} adhesion is probably related to the poor interaction between metallic fillers with organic matrix.\textsuperscript{37} The poor dispersion associated with the weak PMMA-AgNW\textsubscript{P} interface can harm the load transfer of matrix to nanowires, reducing the mechanical properties of the nanocomposites.\textsuperscript{21,38} On the other hand, after the surface silanization, AgNW\textsubscript{M} showed improved dispersion and interaction with PMMA. The good dispersion and superior PMMA-AgNW\textsubscript{M} interfacial adhesion may be related to non-covalent bonds between the functional groups attached to AgNW\textsubscript{M} surfaces (i.e., methacryloxy groups) and the acrylic molecular chain of PMMA. The rougher surface of AgNW\textsubscript{M} (Figure 2D) is another important aspect that may have contributed to enhanced PMMA-AgNW\textsubscript{M} adhesion.\textsuperscript{38}

Jiangkongkho et al.\textsuperscript{39} showed similar relation between nanofiller silanization and dispersion/interaction with the polymeric matrix. The authors studied the relation between nanosilica (NP) silanization with MPS with the dispersion and interaction with PMMA. SEM micrographs of PMMA reinforced with 1% unsilanized NP showed agglomerated and uncovered NP, indicating no chemical bonds between the inorganic NP and the organic PMMA matrix. On the other hand, the addition of 1% of NP silanized with MPS in PMMA resulted in more dispersed nanofiller and increased PMMA-NP chemical interactions. SEM results were related to the toughening of the nanocomposites with silanized NP. The authors concluded that silanized NP act as obstacles for cracks, deviating and branching the crack front. As demonstrated by the previously cited works, improved dispersion and interaction between AgNW\textsubscript{M} and PMMA will probably allow more efficient load transfer of the matrix to the nanofiller, enhancing the mechanical performance.\textsuperscript{31}

DMC is another important factor that can affect the mechanical response, since the lower percentage of monomer conversion is associated with the loss in the mechanical properties.\textsuperscript{40,41} The results showed a great reduction in DMC values for the nanocomposites with AgNW\textsubscript{M} when compared to neat PMMA and nanocomposites with AgNW\textsubscript{P}. The incorporation of fillers in a polymeric matrix impairs the mobility of the radical chain ends, interfering in the polymerization kinetic. In this way, AgNWs will act as a barrier, limiting the interaction between reactive groups.\textsuperscript{42} The greater reduction in DMC for the nanocomposites with AgNW\textsubscript{M} can be attributed to better dispersion of the nanowires in the polymeric matrix, increasing the number of barriers for polymerization. On the other hand, the addition of AgNW\textsubscript{P} did not produce a large number of barriers as AgNW\textsubscript{M}, since the nanowires were organized as clusters inside the PMMA.

Similar results were found by Shaaban et al.\textsuperscript{33} The authors reported a decrement of DMC for PMMA after the incorporation of hydrophobically modified silica aerogel nanoparticles (H-SiANp). According to the results, by increasing the H-SiANp content, lower DMC was obtained. For 3 wt% H-SiANp incorporation, the DMC value decreased from 92% to 74%. The negative effect of the H-SiANp on PMMA polymerization was attributed to restriction in the radical mobility. The authors concluded that higher concentrations of H-SiANp results in more restrictions. Then, lower values of DMC were obtained.

The incorporation of higher concentrations of AgNW\textsubscript{P} or AgNW\textsubscript{M} did not affect the DMC values when compared to lower concentrations, unlike the work reported by Shaaban et al.\textsuperscript{33} A slight reduction was observed, by comparing the samples with 0.5% and 1.0% of nanofiller. In this case, the degree of AgNW dispersion interfered more in the DMC values than the AgNW concentration. The DMC of the nanocomposites were adversely affect by the addition of AgNWs, especially AgNW\textsubscript{M}. The reduction in the DMC values indicates an increase in the residual monomer, which act as a plasticizer. The combination of lower values of DMC and higher residual monomer amount might cause a loss in the mechanical properties, limiting the application as dental materials.\textsuperscript{40,41}

Izod impact and flexural strength tests were performed to predict the behavior of these nanocomposites when exposed to forces similar to the oral cavity. Impact strength, in the case of dental resins, can be associated with forces arising from accidental falls, stress concentration areas, and repeated masticatory forces.\textsuperscript{34} The addition of AgNW\textsubscript{P} and AgNW\textsubscript{M} did not cause any statistically significant change in the PMMA matrix, although the average impact strength was increased. For the samples PMMA/AgNW\textsubscript{P}-0.5 and PMMA/AgNW\textsubscript{P}-1.0 the increase was about 5%, while for the samples PMMA/AgNW\textsubscript{M}-0.5 and AgNW\textsubscript{M}-1.0 the increase was about 15%, when compared to neat PMMA.

Glassy polymers, as PMMA, show fragile nature and limited ductility, which reduces their impact strength. This behavior is usually associated to their relatively low entanglement density, when compared to crystalline polymers, favoring the break of the polymeric chains at
relatively low tensions. These breaks commonly occur through craze formation, propagation, and breakdown.\cite{43}
Some theoretical and experimental works have shown that the incorporation of filler nanoparticles reduces even more the entanglement density of amorphous polymers due to the confinement effect.\cite{44-47} The confinement effect creates some distortion in the polymer chain, reducing even more the number of interchain entanglements for PMMA.\cite{48} As a result, a reduction in the impact strength response can be observed.

Chladek et al.\cite{49} incorporated unmodified silver-releasing filler into PMMA at concentrations of 0.25, 0.5, 1.0, 2.0, 4.0, and 8.0 wt% and analyzed the impact strength using the Charpy methodology. The results showed a significant reduction in impact strength values after the addition of the silver-releasing fillers, especially for the nanocomposites with higher concentrations of fillers. This result attributed the reduction in the impact strength to the inhomogeneous dispersion of the fillers, producing agglomerates regions. In addition, the low chemical interaction between the filler and the polymeric matrix was also associated to the reduction in the impact strength values. According to the authors, these two factors make the nanofillers act as structural defects, leading to stress concentration.

Although the addition of filler in PMMA usually leads to the reduction in the impact strength, in this work this effect was not observed. The impact strength was not changed after the addition of the AgNWs. For PMMA/AgNW$_M$-0.5 and AgNW$_M$-1.0, the hypothesis is that the incorporation of AgNW$_M$ is able to develop the confinement effect, without harming the entanglement density. Probably, the better dispersion of AgNW$_M$ led just to a hindrance on the interchain motion due to AgNW$_M$ effect as crosslinking agent.\cite{45} In addition, one-dimension nanofillers, as AgNWs, are able to redistribute the stress load on the polymeric matrix and stop crack propagation.\cite{50}

Flexural strength is some of the most important mechanical properties for dental resins prosthesis due to the stress caused by repetitive chewing movement.\cite{34} The results showed that only the addition of AgNW$_M$ at 0.5 wt% resulted in statistically significant increase in the flexural strength value (about 10%), when compared to neat PMMA ($p \leq 0.05$). The nanocomposites with addition of AgNW$_P$ or AgNW$_M$ at concentration of 1.0 wt% did not result in significant changes in the flexural strength value. This result is associated with the better dispersion and interaction of the AgNW$_M$ with the matrix. Stronger adhesion between the nanofillers and the polymeric matrix results in greater strengthening effect. On the other side, nanofillers with low interaction with the matrix and formation of agglomerates can act as voids, with little load transferred between the filler and the matrix.\cite{51}

The nanocomposite PMMA/AgNW$_M$-1.0 showed similar values of flexural strength than neat PMMA. Only the addition of 0.5 wt% of AgNW$_M$ resulted in improved values. Probably, the addition of increased amount of nanofillers in a polymeric matrix results in some negative effects, that impairs the flexural strength improvements. This behavior was also observed by Al-Harbi et al.\cite{52} The authors added different concentrations (0.5, 1.0, and 1.5 wt%) of nanodiamond on PMMA acrylic resins and verified their influence on the flexural strength. The results showed significant higher flexural strength for the sample with 0.5 wt% of nanodiamond, when compared to neat PMMA. On the other side, the composite with addition of 1.0 wt% of nanodiamond showed similar flexural strength than neat PMMA, and the composite with 1.5 wt% showed decreased values of flexural strength.

The hypothesis is that the flexural strength of acrylic resins is able to increase to a certain limit until the resin chains become insufficient to interact with the reinforcement material. In this way, as the concentration of nanofiller increases, the flexural strength decreases. Another important factor that can impair the mechanical properties enhancement is the DMC values. Unreacted monomers and lack of homogeneity in the resin matrix conversion leads to poor mechanical properties. In this work, the composites with incorporation of AgNW$_M$ showed lower values of DMC, when compared to neat PMMA. However, even with this negative effect, PMMA/AgNW$_M$-0.5 showed improved mechanical properties than neat PMMA and the nanocomposites with AgNW$_P$. Probably, the confinement effect created by AgNW$_M$ was more effective to improve the mechanical properties than the negative effect caused by the reduced DMC value. According to Izod impact and flexural strength results, the reinforcement effect is directly related to the amount and the surface properties of the nanofiller inserted on the PMMA matrix.

Regarding the antibiofilm activity of neat PMMA and the nanocomposites, a substantial reduction of 50% was observed after the incorporation of AgNW$_M$ (0.5 and 1.0 wt%) in the matrix. These alterations may influence the pathogenicity of C. albicans since its virulence is highly related to ability to form mature biofilm and express increased resistance patterns.\cite{53} Several factors can interfere in the C. albicans adhesion and biofilm formation, such as surface roughness, hydrophobicity, porosity, and surface energy.\cite{54} All these factors are directly related with the surface properties of the material. Usually, low-energy hydrophobic surfaces are more prone to the biofilm formation, as well as rough surfaces that provides larger area for adhesion and proliferation of C. albicans.\cite{55} In this work, all samples showed hydrophilic behavior with similar contact angle. MPS has a hydrophilic character; so, the
silanization of AgNWs using this type of molecule makes the nanowires more hydrophilic and more compatible with the polar PMMA.\[56,57\] So, no difference in the contact angle is expected by adding hydrophilic nanofillers into hydrophilic matrix. Also, the roughness did not change after the incorporation of the AgNWs since all samples had their surface roughness standardized before the mechanical and antibiofilm assays. In this way, the explanation for the reduction in the formation of \textit{C. albicans} biofilm can be associated to the presence of silver. The antimicrobial properties of silver have been explored since ancient times, being related to the release of Ag\(^+\) ions. Ag\(^+\) ions can interfere in the microbial cell through two different mechanisms: (i) Ag\(^+\) ions interact with the sulfur-containing proteins of the cell membrane, causing membrane damaging and/or (ii) Ag\(^+\) ions interact with respiratory chain proteins inside the cell, preventing DNA replication.\[38\] Also, prior study showed that silver nanoparticles can affect the cell integrity of \textit{C. albicans} by damaging the cell wall and cytoplasmic membrane.\[59\]

Since the antimicrobial property is directly related with the release of Ag\(^+\) ions, silver nanostructures with increased surface area present substantial improvements in the antimicrobial activity.\[60\] Figure 5 showed that only the nanocomposites with addition of AgNW\(_M\) decreased the \textit{C. albicans} biofilm formation with statistical significance \((p < 0.01)\). As showed by SEM images of cryogenic fracture cross section (Figure 3), the silanization process led to better dispersion of AgNW\(_M\) into PMMA matrix. Probably, in the case of PMMA/AgNW\(_P\)-0.5 and PMMA/AgNW\(_P\)-1.0, the nanowires are so agglomerated that no significant antimicrobial effect can be detected. On the other hand, for PMMA/AgNW\(_M\)-0.5 and PMMA/AgNW\(_M\)-1.0, the improved dispersion of AgNW\(_M\), provided by the silanization process, resulted in more nanowires in the surface of the sample able to release Ag\(^+\) ions and more interaction with \textit{C. albicans} biofilm. The SEM images of \textit{C. albicans} biofilm formation evidenced these findings (Figure 6). Both AgNW\(_P\) and AgNW\(_M\) showed the reduction of the biofilm formation; however, the addition of AgNW\(_M\) lead to more expressive reduction.

The relation between antibiofilm activity and dispersion of silver nanoparticles was also studied by Ogawa et al.\[61\] The authors incorporated silver nanoparticles in organic coatings for cooling pipe systems at concentration of 0.1 and 5.0 mol\% and studied the biofilm formation of several microorganism in the seawater. Antibiofilm results showed that the addition of silver at concentration of 0.1 mol\% inhibited the biofilm formation, while the concentration of 5.0 mol\% was not effective to prevent the biofilm formation. According to the results, increased concentrations of silver resulted in nanoparticles aggregated to each other, reducing the homogeneity of the coating. In this way, the authors concluded that the proper dispersion of silver in coating is a potential methodology to prevent biofilm formation.

5 | CONCLUSIONS

The hypothesis of this study regarding the potential effect of silanized-AgNWs into PMMA resins was proved. This study is the first to perform the surface modification of AgNWs, showing that MPS-silanization treatment improved the dispersion and interaction of the AgNWs with the PMMA resin. As result, improvements in the flexural strength due to the load transfer mechanism between the filler and the polymer. Also, the addition of AgNW\(_M\) resulted in an expressive reduction of the \textit{C. albicans} biofilm formation, due to the higher liberation of Ag\(^+\) ions showed by the dispersed AgNW\(_M\). The PMMA nanocomposites containing 0.5 wt\% of AgNW\(_M\) showed the optimal combination of mechanical properties and antibiofilm activity. For this sample, a reduction of 50\% in the \textit{C. albicans} biofilm formation \((p < 0.01)\) and an increase of about 10\% in the flexural strength \((p \leq 0.05)\) were observed. These results suggest that PMMA/AgNW\(_M\) nanocomposites, especially for the incorporation of 0.5 wt\% of AgNW\(_M\), exhibited mechanical and antibiofilm properties compatible with the application as dental materials, especially for denture base applications.

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CONFLICTS OF INTEREST

The authors declare that they have no conflict of interest.

DATA AVAILABILITY STATEMENT

Research data are not shared.
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