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Plasma surface treatment of bacterial cellulose to increase hydrophobicity

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Abstract Bacterial cellulose presents itself as an alternative to traditional textiles due to its versatility, aesthetics, mechanical similarity to leather and, most importantly, sustainability in production processes. However, its use depends on surface modifications that promote suitable performance in fashion products, due to its high hydrophilicity. A less polluting alternative is the plasma treatment, which does not involve effluents or solid or liquid waste. In this context, this study aims to use the cathodic cage plasma process, an environmentally friendly technique, to reduce the hydrophilic nature of bacterial cellulose for its application in the fashion industry. Samples were produced from kombucha and treated through a modified low-pressure cold plasma system, named

cathodic cage plasma. The influence of the gas mixture (Ar/acetylene and Ar/acetylene/H₂), treatment time and duty cycle was evaluated. The samples were characterized through wetting behavior (contact angle), FTIR, TG and dTG, XPS and FEG-SEM. The cultivated bacterial cellulose exhibited apparent flexibility, roughness, and some transparency. The plasma treatment was proven effective, forming a thin hydrocarbon film on the surface of the BC, sufficient to decrease the hydrophilicity and purify it without degradation. The bacterial cellulose could be made hydrophobic by using parameters such as a longer treatment time, a combination of gases without the addition of hydrogen, and a lower duty cycle (from the most to the least influential factor, respectively). Plasma treatment mitigated the common issues of hydrophilic bacterial cellulose without the need to introduce processes that generate effluents or waste while maintaining the material's biodegradability.

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Introduction

Bacterial cellulose (BC) is a homopolymer composed of repeating glucose units (C₆H₁₀O₅) (Rajwade et al. 2015), arranged in a porous three-dimensional structure with interconnected fibers (Fernandes et al. 2019b). It is produced through fermentation by

bacteria from the *Acetobacter*, *Gluconobacter*, *Zygosaccharomyces*, *Saccharomyces*, and *Schizosaccharomyces* families (Laavanya et al. 2021), and differs from plant cellulose due to its high degree of purity and nanoscale dimensions (Lee et al. 2014), as well as greater flexibility and higher hydrophilicity (Dima et al. 2017).

Bacterial cellulose presents itself as an alternative to traditional textiles in the fashion industry due to its versatility, aesthetics, mechanical similarity to leather and, most importantly, its sustainability in production processes (Yim et al. 2017). Currently, the fashion industry is focused on producing clothes and accessories with cheaper materials and shorter life spans aiming to increase consumption, which results in more manufacturing activities, disposal and environmental impact (Rathinamoorthy and Kiruba 2022). From the traditional textile life cycle, these impacts arise from the use of toxic chemicals and large amounts of water and energy (Mazzoto et al. 2021).

For these reasons, bacterial cellulose has been the subject of studies looking for new ways of producing clothes and accessories. Kamiński et al. 2020 studied a method to enhance properties of bacterial cellulose enabling its application on astronauts' clothes, for the purpose of recycling the used pieces (Gregory et al. 2021). Fernandes et al. 2019a did the same for the application in shoes, obtaining an appropriate material in terms of malleability and breathability. Fashion designer Suzanne Lee used bacterial cellulose textile to produce a jacket with cutting and sewing (da Silva et al. 2021), showing it's possible to manufacture bacterial cellulose clothes through conventional processes.

However, the use of bacterial cellulose depends on surface modifications that promote suitable performance in fashion products, since its high hydrophilicity, evidenced by its contact angle lower than 90.0° (Betlej et al. 2021), results in challenges related to product hygiene and even unsuitability for human skin contact (Wood 2019).

It is possible to reduce the hydrophilicity of bacterial cellulose through wet chemistry, such as surface functionalization through polymerization, as tested by Krishnamurthy et al. (2020); Sulaeva et al. 2019; Hettergger et al. 2015). There is also the possibility of creating composites with synthetic polymers, presented by Fernandes et al. (2019a). However, wet chemistry makes the process unsustainable due to

effluent production, and the association with synthetic polymers eliminates one of the key desired characteristics of bacterial cellulose: biodegradability.

One less polluting alternative is plasma treatment, which does not involve effluents, solid or liquid waste. Furthermore, surface modification with plasma is facilitated because plasma generates excited species (electronically and vibrationally) and radicals (especially through molecular dissociation), making the environment much more reactive (Zheng et al. 2010). Organic species, once activated by the plasma, tend to react with the surface and form thin films (Mourgues et al. 2005). The present paper uses a modified plasma system, namely cathodic cage plasma (Guintier et al. 2019; Correa et al. 2018; Gallo et al. 2017), which is characterized by the plasma being produced at the space outside the cage. Since the biofabric sample of bacterial cellulose (substrate) is placed inside the cage, its surface will not be bombarded by plasma energetic ions (generated outside the cage), therefore it will not suffer overheating and can be maintained close to room temperature. However, reactive species produced in the plasma (outside the cage), from the precursor gas (e. g. C_2H_2 , Ar and H_2), can reach the sample inside the cage. They work as active species to produce a polymer film on the substrate surface.

Studies have been published regarding the interaction of plasma with traditional fabrics. Vilaplana and Cabanes (2012), Yan et al. (2017) and Sohbatzadeh et al. (2019) successfully made the surface of cotton and polyester fabrics hydrophobic after plasma treatments using gases composed of molecules containing carbon and hydrogen. As to bacterial cellulose, surface modification using plasma has been associated with other potentially polluting processes, such as silanization (Leal et al. 2020). Silanization is a chemical surface coating process with silane molecules that, when combined with plasma, affects both the roughness and surface energy of bacterial cellulose to enhance the hydrophobic result, but the disposal of the involved chemical materials can lead to environmental issues.

Few studies demonstrate the reduction in hydrophilicity of bacterial cellulose surface through plasma treatment (Aditya et al. 2022; Kurniawan et al. 2012). Furthermore, the outcome of surface modifications after plasma treatment is linked to the chemical aspects of the gases involved, peculiarities of the treated material, and treatment

parameters, a matter for which there is no consensus in the literature regarding the operational mechanism (Zille et al. 2014). Therefore, there is a knowledge gap concerning the optimization of plasma treatment parameters to decrease the hydrophilicity of bacterial cellulose without degrading it, as achieved by established techniques using chemical agents.

In this context, the aim of this study is to use the cathodic cage plasma, an environmentally friendly technique, to reduce the hydrophilic nature of bacterial cellulose, targeting its application in the fashion industry.

Materials and methods

In order to study the hydrophilic nature of bacterial cellulose, samples were produced from kombucha and treated with low-pressure cold plasma. The influence of the gas mixture (Ar/acetylene and Ar/acetylene/H₂), treatment time and duty cycle was evaluated. The samples were characterized through wetting behavior (contact angle), FTIR (Fourier transform infrared spectroscopy), TG and dTG (Thermogravimetry–differential thermal analysis), XPS (X-ray photoelectron spectroscopy) and FEG-SEM (Field emission gun—Scanning electron microscopy).

Preparation of bacterial cellulose

Bacterial cellulose was produced using the cultivation technique proposed by designer Suzanne Lee and biologist David Hepworth, using kombucha for the cultivation of microorganisms in an aerobic and aqueous environment (Costa et al. 2017). The cultivation medium was prepared with water, granulated sugar, green tea, apple cider vinegar, and a SCOBY (Symbiotic Culture Of Bacteria and Yeast), according to Lima et al. (2021). The mixture remained at room temperature (below 20 °C) and, when bubbles appeared on the surface, fermentation began, forming a thin, transparent layer. This layer thickened over time and, at the end of the 28-day cultivation period (Fig. 1), it was removed from the container and washed with cold water and neutral detergent, then left to air dry at room temperature. The thickness of the obtained bacterial cellulose was measured using calipers and subsequently segmented into rectangular samples measuring 3.0 cm×2.0 cm. Before the plasma treatment, each sample was placed in a glass desiccator with silica gel for 30.0 min.

Plasma treatment

Plasma treatments were carried out in a cathodic cage plasma system, described in a previous work by Correa et al. (2018) and Guinter et al. (2019). In such

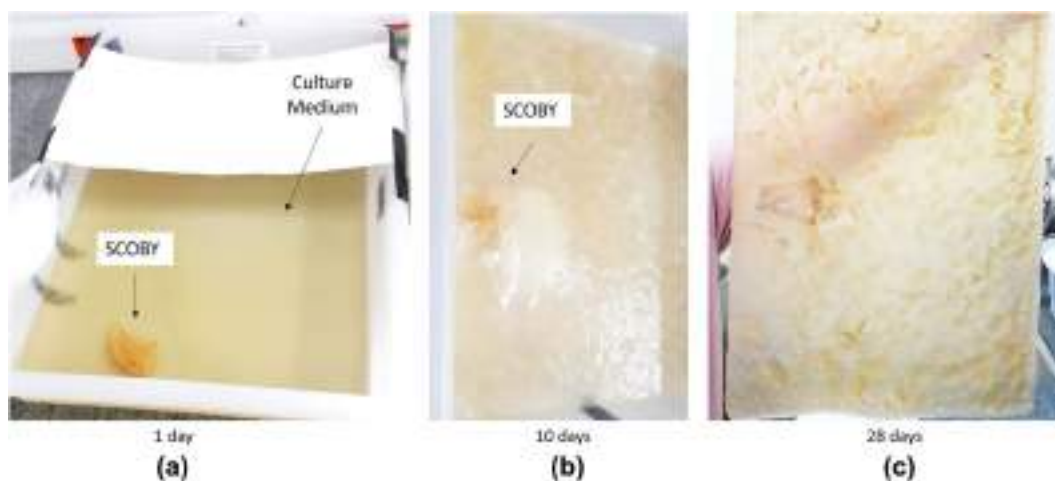
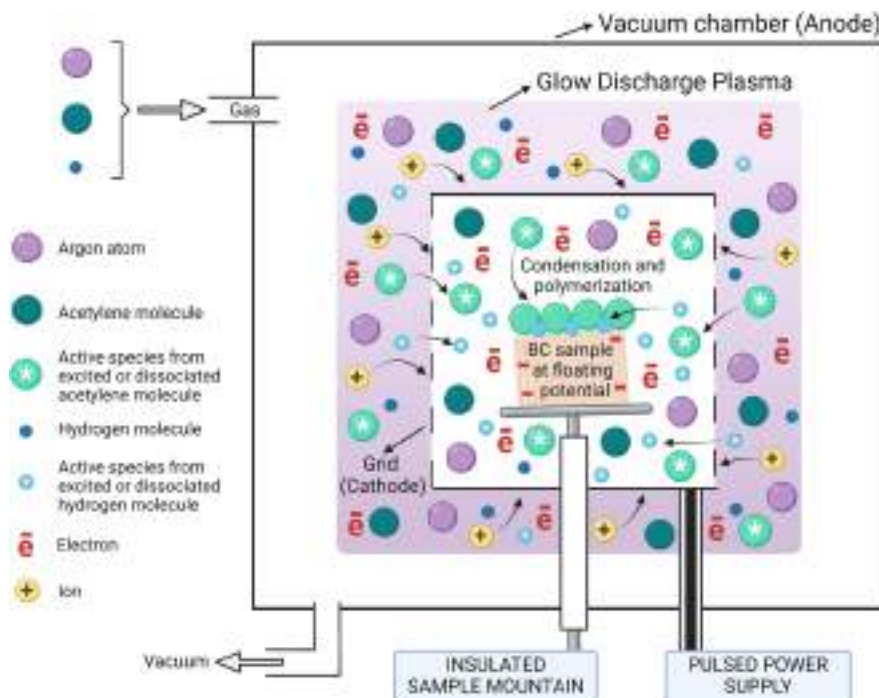


Fig. 1 Development of bacterial cellulose over time. **a** First day of cultivation; **b** After 10 days of cultivation; **c** After 28 days of cultivation

systems, the sample is placed on a substrate holder inside the cathodic cage, while the glow discharge plasma is kept outside the cage. The cathodic cage and the sample holder are placed inside the vacuum chamber, so gas composition and pressure can be controlled. This arrangement allows a lower energy transfer to the sample, avoiding surface damage, especially in thermally sensitive materials. Figure 2 shows a scheme of a Cathodic Cage Plasma setup. The cage was built from a stainless steel 18-gauge mesh with 1 mm openings. Similarly to a Faraday cage, the electric field is null inside and, consequently, the plasma glow discharge occurs only outside, once the anode is the chamber's walls. Ions from the glow discharge can be accelerated through the cathode sheath and bombard the mesh wires of the cathode, which are negatively biased (through pulsed bias) by an external power supply. However, considering the parameters used in the present paper, the ions do not have enough energy to pass through the openings of the cage and, therefore, do not reach the inner space. As the ions stay outside, there is no ionic bombardment on the substrate, which remains at a low temperature, enabling the condensation and polymerization of active species from the plasma, growing a film. Only the secondary electrons generated by the

ion bombardment on the surface of the mesh can enter the cage which, consequently, generates a high floating potential inside, close to the negative voltage applied to the cathode by the external power supply, in a way that the space inside is nearly equipotential and the electrical field is next to zero. However, neutral chemical species activated in the plasma, such as excited molecules and atoms, are not affected by the electrical field in the cathodic sheath and can move randomly. So, the neutral active species generated in the glow space plasma can pass through the grid's openings, without being affected by the electric field. Those chemically activated species can diffuse toward the inner space of the cage and react on the substrate's surface, producing a thin film (e. g. polymerization), as illustrated in Fig. 2. In the present paper, reactive species were generated in the glow plasma space from the precursor gas mixture $C_2H_2 / H_2 / Ar$. The argon is used as a dilution gas because it facilitates the discharge maintenance and the increase in ionization/dissociation rate in $C_xH_y/H_2/Ar$ gas mixtures (Denysenko et al. 2004). The acetylene can be involved in the plasma technology both as a product and as a precursor gas. According to Benedikt (2010), plasmas are relatively safe and environmentally friendly, the material content is usually very low,

Fig. 2 Schematic representation of the Cathodic Cage Plasma setup; the glow discharge plasma occurs outside the cage; active species generated in the plasma can diffuse towards the inner space; polymerization can occur on the surface of the sample by condensation of active species. Created with BioRender.com



reducing hazards for operating personnel and limiting the production of harmful products. In addition, the low-temperature plasma applications are considered a clean and environmentally sustainable method (Tatarova et al. 2014). Acetylene is a polymer precursor with a triple bond, which can form benzene structures, $3\text{HC}\equiv\text{CH}\rightarrow\text{C}_6\text{H}_6$ or it can polymerize via the triple bond: $n\text{HC}\equiv\text{CH}\rightarrow-(\text{HC}=\text{CH})_n-$. In addition, the use of H_2 in the gas mixture creates the possibility of a substitution reaction: $\text{HC}\equiv\text{CH}+\text{H}_2\rightarrow\text{H}_2\text{C}=\text{CH}_2$ (Friedrich 2011). Plasma polymerization using a $\text{C}_2\text{H}_2/\text{H}_2/\text{Ar}$ mixture as the precursor gas implies the production of several ions (H^+ , H_2^+ , H_3^+ , CH_3^+ , CH_4^+ , CH_5^+ , C_2H_2^+ , C_2H_4^+ , C_2H_5^+ and Ar^+) and neutral radicals (H , CH , CH_2 , CH_3 , C_2H_5) (Denysenko et al. 2004). So, the film deposition based on monomer fragmentation and recombination in plasma is determined by complex collisions and radiation emitted by the plasma, which produces active species which can react on the substrate's surface in the so-called plasma-polymerization process.

The discharge was maintained using a Pinnacle PlusTM pulsed DC power supply from Advanced Energy Inc. It operates at a constant average power of 50 W and a frequency of 100 kHz. The reverse time (time in which the cage is positively biased) was variable (2.0 μs and 4.0 μs) to achieve duty cycles of 80% and 60%, respectively. Changing the duty cycle parameter enables to achieve polymer films of different thicknesses (Gunter et al. 2019). The samples were treated for two different periods (5.0 min and 30.0 min) and in two different working atmospheres ($\text{Ar}+\text{C}_2\text{H}_2$ and $\text{Ar}+\text{C}_2\text{H}_2+\text{H}_2$). Using a Pirani gauge, the base pressure was established at 1.33×10^{-2} mBar and the working pressure at 2 mBar (N_2 equivalent pressure). For the $\text{Ar}+\text{C}_2\text{H}_2$ mixture, the N_2 equivalent pressure ratio was 1:1 and, for $\text{Ar}+\text{C}_2\text{H}_2+\text{H}_2$, it was 1:1:1. The 30-min treatment was set by Vilaplana and Cabanes (2012) for cotton and polyester, so the 5-min treatment was chosen as a counterpoint. Regarding the choice of the working gases, Ar is an inert gas that can promote physical modifications on the sample surface (Pascu et al. 2003), while the acetylene molecules can be dissociated in the plasma, and the fragments lead to the formation of a polymer film (Vilaplana and Cabanes 2012). On the other hand, hydrogen can generate active sites, facilitating the insertion of functional groups (Macedo et al. 2010), which can be beneficial

to the formation of the polymer film using acetylene as precursor gas.

To analyze the influence of treatment parameters on the wettability of the samples, a Taguchi L4 Orthogonal Arrange (2^3) (Montgomery 2013) with three factors (treatment time, working gas, and duty cycle) in two levels was developed (Table 1). For each experimental condition, a replica was produced.

Characterization

Bacterial cellulose was qualitatively characterized in terms of surface appearance using Field Emission Scanning Electron Microscopy (SEM-FEG) with a JSM-6701F JEOL electron microscope, operated at 1 kV and a working distance of 4.6 mm.

Sample wettability was determined through internal contact angle measurements conducted on a Ramé-hart Instruments 590 Goniometer, using 2 μL drops of deionized water. Each sample, 24 h after plasma treatment, had one drop deposited at 5 different non-collinear regions of its surface. For each drop, 50 static measurements were taken with a 0.01 s interval. The obtained values were calculated using DROPimage software from Ramé-Hart Instruments, based on static measurements through *circle fittings* (Akbari and Antonini 2021). The contact angle result was the average of the 5 tested regions on the sample, which were analyzed for mean and standard deviation.

In addition to bacterial cellulose analysis, contact angle testing was performed on a sample of polyurethane (PU) synthetic leather, taken from a fashion product after five years of use, with the intention of generating a wettability comparison data set. Statistical analysis was conducted on the contact angle data using Minitab Statistical Software.

Fourier Transform Infrared Spectroscopy (FTIR) analysis was carried out using a Bruker INVENIO-S

Table 1 Factors and levels of the factorial design for plasma treatment on bacterial cellulose

Factor	Levels	
Treatment time (min)	5.0	30.0
Working gas	$\text{Ar}+\text{C}_2\text{H}_2$	$\text{Ar}+\text{C}_2\text{H}_2+\text{H}_2$
Duty cycle (%)	80	60

FT-IR spectrophotometer. A total of 32 scans were performed in the spectral range from 4000 cm^{-1} to 400 cm^{-1} with a resolution of 4 cm^{-1} , under Attenuated Total Reflectance (ATR) transmission mode.

X-ray photoelectron spectroscopy (XPS) analyses were performed in a Thermo Scientific spectrometer (K-Alpha), operating at a base pressure below 10^{-7} mBar. In this system, the X-ray beam strikes the sample at 30° up from the surface. The Al-K α ($h\nu=1486.6\text{ eV}$) X-ray was used as the excitation source and, for the surveys, the pass energy was set to 200 000 eV, being the spectra an average of 10 scans, with 1 000 eV step size and a 10 ms dwell time. For high-resolution scans (C 1 s and O 1 s), the values were set to 20 000 eV pass energy, 10 scans, 0.025 eV step size, 10 ms dwell time. Data were analyzed in the Advantage software from Thermo Scientific. Atomic composition was calculated through the “Speciation” function available in Advantage. For the fittings, the spectra were charge corrected to C–C/C–H in 284.8 eV. The Shirley background was removed using the Smart routine of the software, and the peaks were fitted using the Voigtian function, a convolution of Gaussian (70%) and Lorentzian (30%) profiles. The C 1 s and O 1 s fitted spectra show the residual error, the chi-square and Abbe criterion values.

Results and discussion

The obtained bacterial cellulose was 2 mm thick immediately after cultivation. This result is lower than the expected 2 cm according to the procedure outlined by Lima et al. (2021). This difference indicates a lower amount of water in the obtained tissue, attributed to the slower action of microorganisms at lower room temperatures and, consequently, reduced water absorption during the process. According to Jayabalan et al. (2014), the ideal temperature for the action of kombucha SCOBY in the cultivation medium ranges between 18°C and 26°C . The appearance of bubbles indicating fermentation was expected after 5 days of cultivation in the ideal temperature range, but in the course of this work, conducted at room temperature between 13°C and 18°C , bubbles only appeared after 10 days. Nevertheless, after drying, the expected appearance and characteristics described in the literature for bacterial cellulose (Mehrotra et al. 2023; Morrow et al. 2023; Costa et al. 2017; Ng and

Wand 2015) could be achieved: flexible, rough, and slightly transparent.

Wettability

As expected, the untreated bacterial cellulose sample exhibited the lowest contact angle (33.4°), which indicates hydrophilic characteristics, as it is less than 90° (Fig. 3). The synthetic leather sample taken from a used fashion product also exhibited hydrophilic characteristics, with a contact angle of 78.6° . Bacterial cellulose exhibits hydrophilic characteristics due to its high free surface energy, which is associated with the abundant availability of free hydroxyl groups (Provin et al. 2021), resulting in hydrogen bonding between its nanofibers (Lee et al. 2011). Therefore, it displays varying contact angles depending on the cultivation conditions, typically around 40° , but always less than 90° (Table 2).

All plasma treatment conditions on bacterial cellulose resulted in an increased contact angle, indicating a reduction in hydrophilic characteristics. Depending on the plasma processing conditions, some contact angle results approached 100° , indicating hydrophobic characteristics (Latthe et al. 2014).

The literature points to various methods to reduce the hydrophilicity of bacterial cellulose, including the application of plasma, as shown in Table 2. This property can be diminished through changes in surface roughness or chemical surface modification aimed at decreasing its free energy (Mondal et al. 2018). Plasma treatments can induce both effects, increasing the roughness of bacterial cellulose with treatment duration (Aditya et al. 2022) and lowering the free surface energy by reorienting free groups (Pertile et al. 2010). In this study, the highly reactive environment of the plasma probably favored the reaction between the free hydroxyl groups and the functional groups generated in the plasma from the acetylene gas, forming a thin film and reducing the free surface energy. The treatment conditions (C1 to C4) align with results obtained from traditional wet chemical methods that increase the contact angle, achieving even greater angles when combined with the plasma treatment (Table 2).

The results of the plasma treatment were statistically analyzed according to fractional factorial design 2^{3-1} (or Taguchi L4) using the Analysis of Variance (ANOVA) method with a 95% confidence level. Data

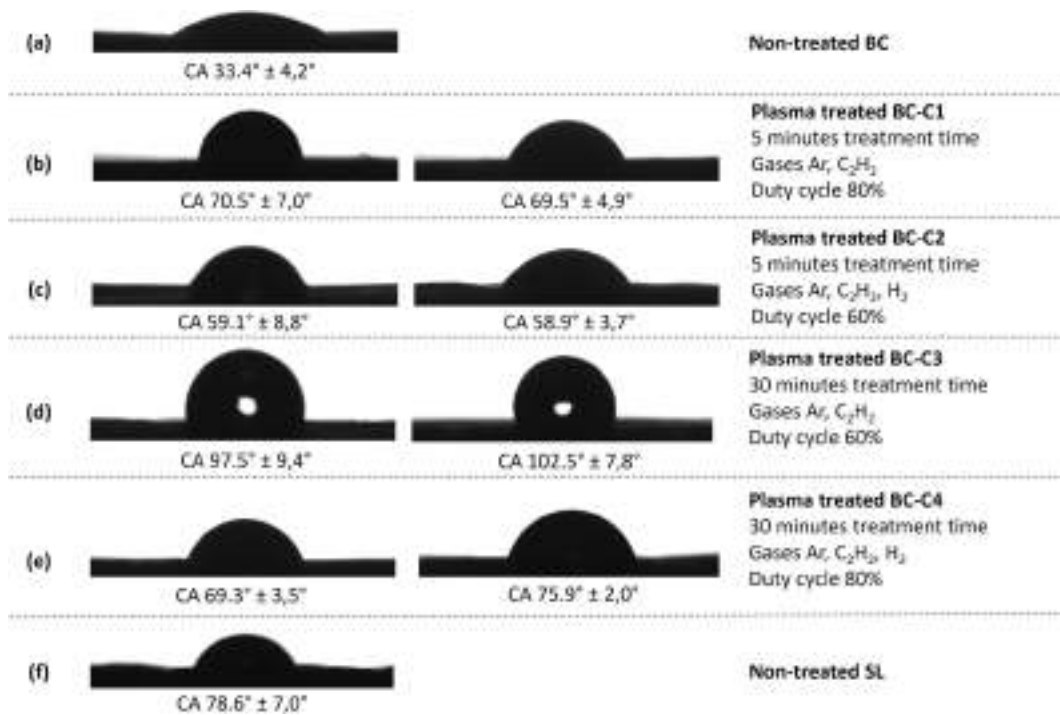


Fig. 3 Contact angle: **a** untreated bacterial cellulose (BC); **b, c, d, e** plasma-treated bacterial cellulose (BC-C1, C2, C3, C4); **f** synthetic leather (SL)

Table 2 Methods to increase the contact angle of bacterial cellulose

Author	Method	Non-treated BC contact angle ($^{\circ}$)	Treated BC maximum contact angle ($^{\circ}$)
Leal et al. (2020)*	Oxygen plasma deposition associated with silanization with trichloromethyl silane (TCMS)	24.9	132.6
Lv et al. (2016)*	Functionalization by magnetron sputtering and RF reactive sputtering with copper (Cu) and Al_2O_3	18.8	125.5
Fernandes et al. (2019a)	Development of BC based nanocomposites with hydrophobic polymers MS and Baygard EFN through exhaustion process	63.8	135.4
Song et al. (2019)	Polymerization: functionalization with poly(fluorophenol)	54.5	112.2
Krishnamurthy et al. (2020)	Functionalization of BC surface with click polymerization	34.5	102.1
Tomé et al. (2010)	Heterogeneous esterification with hexanoyl chloride	49.1	98.6
He et al. (2020)	Polycondensation using APTES to produce aminoalkyl-grafted BC membranes	47.6	84.3
Shao et al. (2017)	Functionalization of BC to produce aminoalkylsilane-grafted BC	48.3	86.4
Santos et al. (2015)	Alkaline treatment when the culture media contains ethanol and a thermal treatment if the media is free from ethanol	51.5	84.9
Wang et al. (2020)	Hypocrellin grafting to BC membrane (Hc-BC)	18.5	75.5

* Methods that combine traditional chemistry and plasma

analysis by ANOVA assumes independence of observations, normal data distribution, and homogeneity of variances (Kutner 2004). Each experiment was conducted with a single sample, and there was no simultaneous execution of experiments, ensuring the independence of observations. In Fig. 4a, the normality of the data is observed by the similarity between the distribution of residuals and the diagonal line, while Fig. 4b shows the homogeneity of variances, indicated by values close to 0 and the absence of trends in the distribution of residuals.

Three-factor ANOVA was conducted for the plasma treatment parameters: treatment time, gas, and duty cycle. If a parameter has influence on the contact angle response, the ANOVA result should have P-value less than 0.05 (Montgomery 2013), which was the case for all three parameters (Table 3). Another outcome of the analysis is the order of influence of the parameters, since a higher F-value

Table 3 ANOVA Three-factor results

Source	DF	SS	MS	F-value	P-value
Time of treatment	1	950.89	950.89	108.02	0.000
Gas	1	738.01	738.01	83.84	0.001
Duty cycle	1	135.20	135.20	15.36	0.017
Error	4	35.21	8.80		
Total	7	1859.32			

DF: degrees of freedom; SS: sum of squares; MS: mean squares; F-value: F statistics (means between two variances); P-value: probability of test significance

indicates greater influence (Montgomery 2013). Thus, the parameter with the strongest influence on the contact angle is treatment time, followed by gas and, lastly, duty cycle.

Figure 5 illustrates the change in contact angle based on the variation of each parameter and their interactions. It shows that the relationship between

Fig. 4 Residual distribution: **a** normal probability plot of the residuals; **b** residual vs. fitted plot

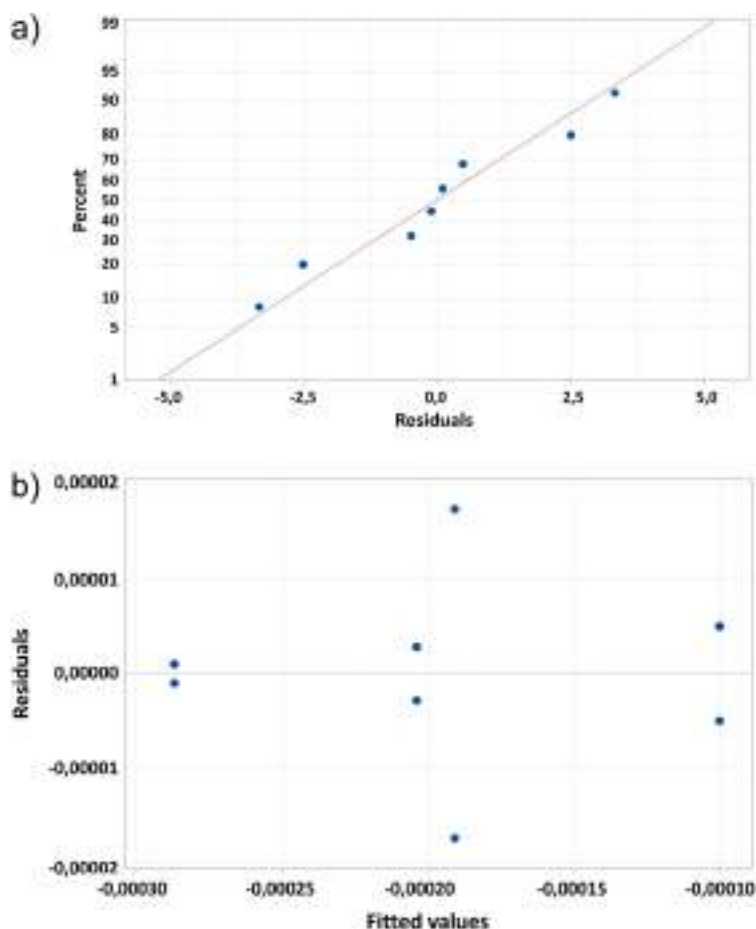
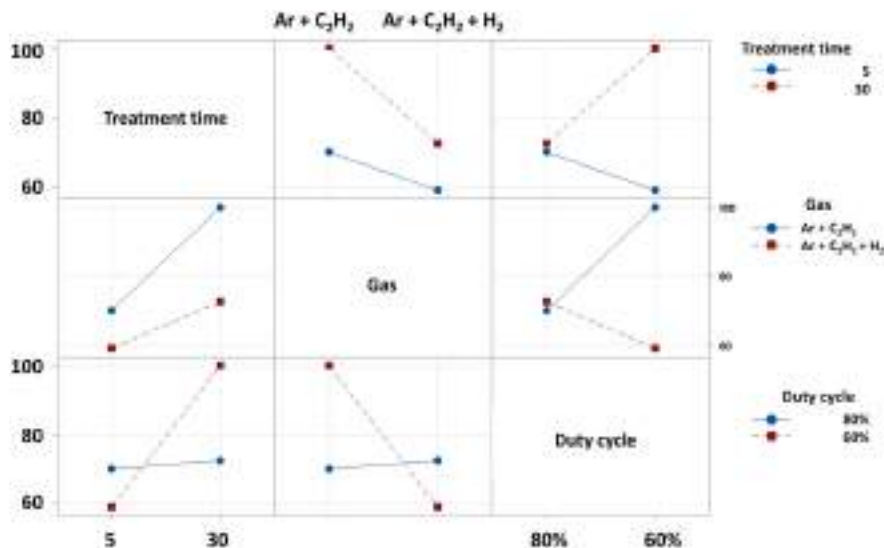


Fig. 5 Interaction plots between the analyzed factors for contact angle response



treatment time and contact angle depends on the gas (Fig. 5b). A treatment time of 30 min with Ar + C₂H₂ gases yields a contact angle close to 100°, while a 5 min treatment with the same gas results in a contact angle close to 70° (a difference of 30°). However, for Ar + C₂H₂ + H₂ gases, a 30-min treatment results in a contact angle close to 70° and, for 5 min, it's close to 60° (a difference of 10°). The varying differences confirm that the contact angle outcome depends both on treatment time and gas. Figure 5h shows such a strong interaction between the gas and duty cycle factors that there is even a change in behavior with their variation. For the 60% duty cycle, the highest contact angle is achieved with Ar + C₂H₂ gases, whereas for the 80% duty cycle, the gas producing the highest contact angle is the combination Ar + C₂H₂ + H₂.

For the studied parameters, the optimal contact angle (the highest) corresponds to treatment levels of 30.0 min, Ar + C₂H₂ gases, and a 60% duty cycle. This combination was repeated for treatment on a new sample (BC-C3), which underwent chemical characterization as described below.

Chemical characterization

Figure 6 presents the FTIR spectra for the non-treated and optimized samples. The Bacterial Cellulose spectrum (BC sample) presents the characteristic bands from 3495 cm⁻¹ to 3245 cm⁻¹ corresponding to O–H stretching. The absorption bands at 2920 cm⁻¹ and 1419 cm⁻¹ are assigned to the CH and CH₂ stretching,

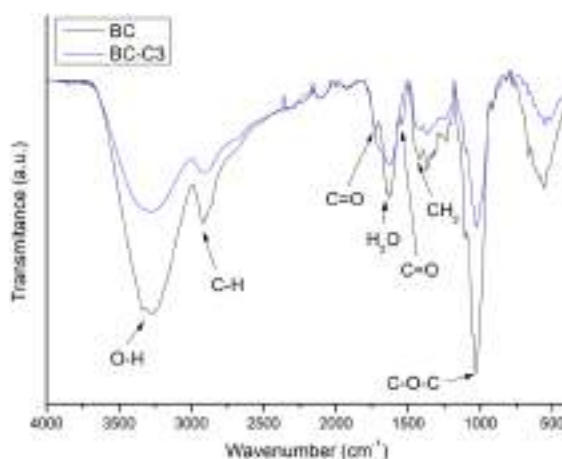


Fig. 6 FTIR spectra for BC (non-treated) and BC-C3 (30.0 min, Ar + C₂H₂ gases, and 60% duty cycle) samples

respectively, and the peak at 1034 cm⁻¹ to the vibrations of the glycosidic C–O–C bridges. The band at around 1635 cm⁻¹ is assigned to adsorbed water (Gea et al. 2011; Fernandes et al. 2019b; Zille et al. 2014).

After plasma treatment (BC-C3 sample), the bands' intensity decreased at 1720 cm⁻¹ and 1540 cm⁻¹, which is attributed to C=O from proteins, lipids, and Protein amide II absorption (Movasaghi et al. 2008), respectively. These two peaks may be associated with biological impurities (protein or residual biomass), possibly from bacteria or compounds in the culture medium bound to the cellulose (Santos et al. 2015). These alterations may

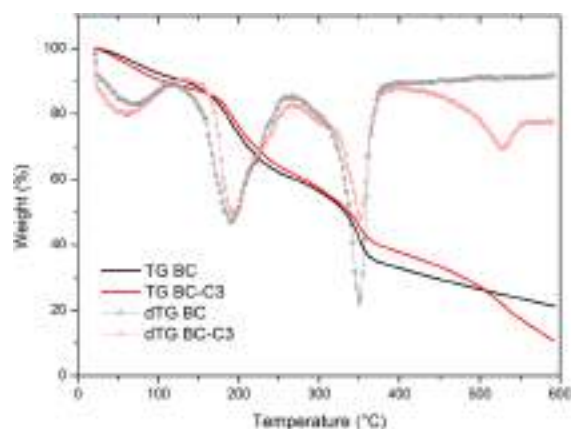


Fig. 7 TG and dTG spectra for BC (non-treated) and BC-C3 (30.0 min, Ar + C₂H₂ gases, and 60% duty cycle) samples

indicate that the plasma significantly reduced the bacteria, as observed by other authors (Zille et al. 2014; Gea et al. 2011).

Based on the TGA analysis, there is no significant difference in the degradation temperature for the untreated (BC) and plasma-treated (BC-C3) samples, as observed in Fig. 7. The first event is the evaporation of residual water from the drying process. The second phase event (250 °C to 400 °C) is related to the degradation of cellulose (dehydration and decomposition of glycosidic units). The third phase extends up to 500 °C and corresponds to the thermo-oxidative degradation of cellulose. Another degradation event (410 °C to 560 °C) is observed for the treated sample, which, although not well defined in the literature, can be explained by secondary reactions of carbon-containing residues (Burhenne et al. 2013). Both samples presented a considerable final residue (about 11% for BC-C3, and 21% for BC), which is not uncommon to bacterial cellulose (Amarasekara et al. 2020). According to Gea et al. (2011), this could be related to phosphorous compounds released by the green tea in the synthesis process (Chacko et al. 2010; Kluz et al. 2022), which can significantly increase char formation. The lower final residue for the treated sample corroborates the FTIR results, showing that the plasma treatment may purify the BC surface.

Figure 8 presents XPS survey data for the BC and BC-C3 samples. Both spectra show a major presence of carbon and oxygen, as expected for bacterial cellulose. Besides, the XPS survey indicates a slight increase in the C 1s contribution for the BC-C3

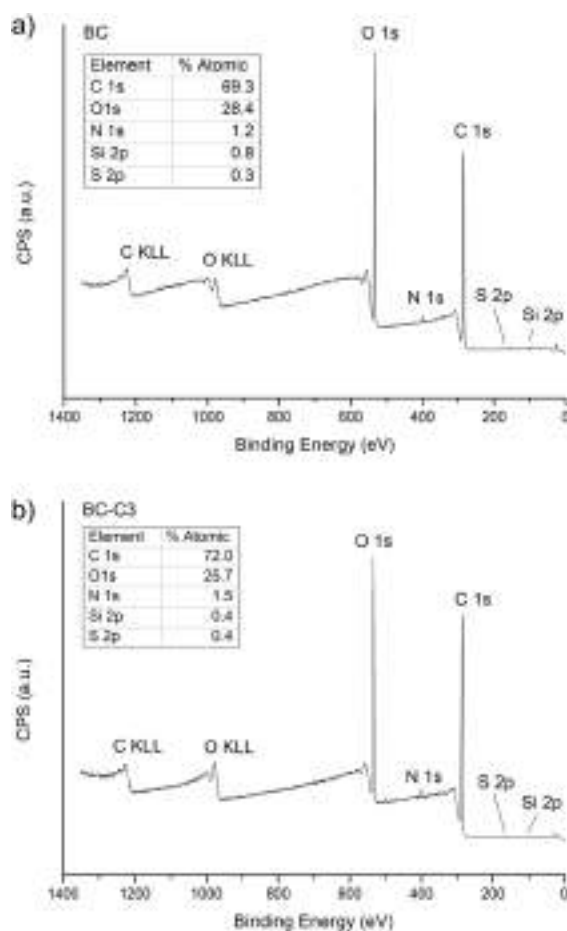


Fig. 8 XPS survey and chemical atomic composition for **a)** BC (non-treated) and **b)** BC-C3 (30.0 min, Ar + C₂H₂ gases, and 60% duty cycle) samples

sample, with a consequent reduction in O 1s atomic percent after the plasma treatment. Indeed, it is possible to establish the C/O ratio for each sample (2.4 for BC, and 2.8 for BC-C3), which clearly evidences that the carbon content was increased as a result of the plasma gas choice (Ražić et al. 2017). The results may indicate that the plasma does not chemically damage the samples and yet contributes by attaching carbon atoms provided by the acetylene gas onto the surface during the treatment. Survey spectra also show, in both samples, less than 3 at. % of contaminants (nitrogen, silicon, and sulfur), which can be originated from the bacterial cellulose synthesis and/or process steps in which the samples remained in desiccator and plasma reactor.

Figure 9 shows high-resolution XPS C 1s spectra. Fitting reveals the presence of C–C/C–H (284.7 ± 0.1 eV), C–O (286.4 ± 0.1 eV), C=O/O–C–O (287.8 ± 0.1 eV) and O–C=O (289.1 ± 0.1 eV) bonds, with the peaks' full width at half maximum varying from 1.2 to 1.5 (Briggs and Beamson 1992; Flynn et al. 2013; Pertile et al. 2010). Note that, according to some authors (Flynn et al. 2013; Pertile et al. 2010), C=O and O–C–O contributions were not separated due to very close binding energies. The results indicate that, after the plasma treatment, the C–C/C–H contribution increases, while the ones related to oxygen bonds decrease, agreeing with the FTIR results, which show a decrease in carbon–oxygen bonds, associated with biological impurities removal by the plasma. On the other hand, the increased carbon bonds' contribution

could indicate a thin film formation on the sample surface, formed through the acetylene gas feed in the plasma reactor. This corroborates the O 1s spectra (Fig. 10), in which the fitting indicates a decrease in C–O and/or O–H bonds from the cellulose after treatment (532.8 eV; FWHM=1.4) (Briggs and Beamson 1992; Flynn et al. 2013; Pertile et al. 2010), once again pointing out to the sample surface recovering with a carbon-based thin film. However, the presence of C–O/O–H and other oxygen bonds (C=O at 531.8 eV and O–C=O at 533.7 eV, both with FWHM equal to 1.4) (Briggs and Beamson 1992; Flynn et al. 2013; Pertile et al. 2010), leads to believe that the formed film does not cover the entire surface and/or is too thin. Another hypothesis to the presence of oxygen in

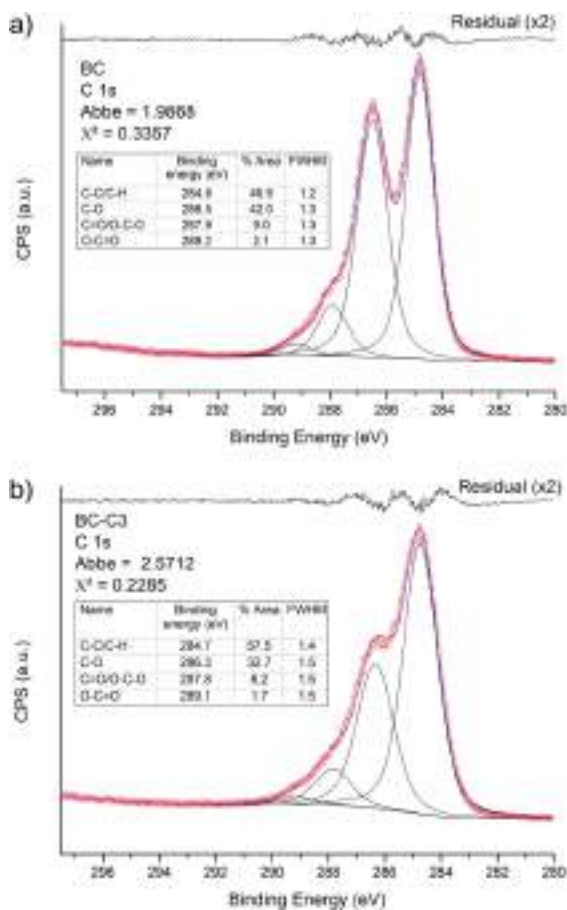


Fig. 9 High-resolution C 1s XPS spectra for **a)** BC (non-treated) and **b)** BC-C3 (30.0 min, Ar+C₂H₂ gases, and 60% duty cycle) samples

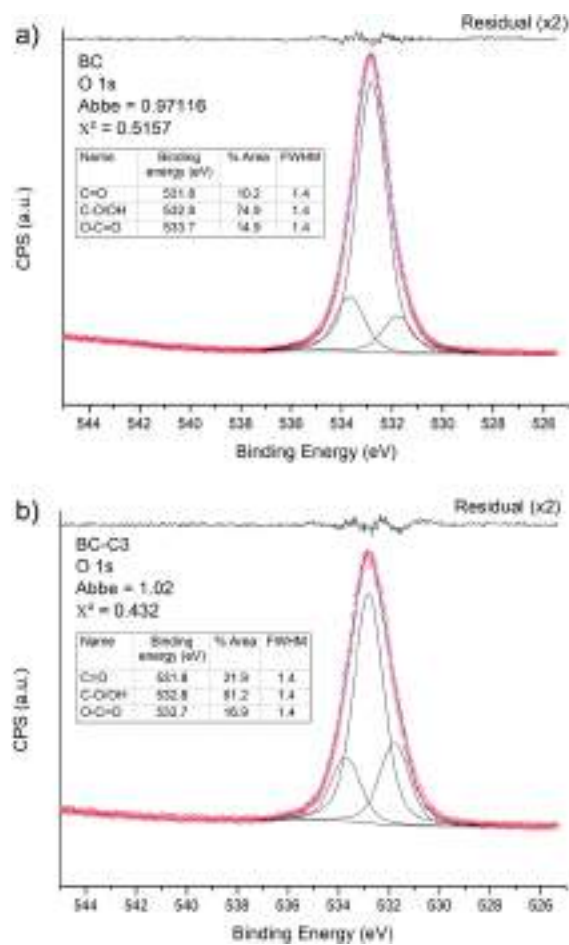


Fig. 10 High-resolution O 1s XPS spectra for **a)** BC (non-treated) and **b)** BC-C3 (30.0 min, Ar+C₂H₂ gases, and 60% duty cycle) samples

the polymer film is the reaction of the final coat with oxygen from the air, after the samples are removed from the vacuum chamber.

In fact, the film thickness can be estimated by data from the XPS results. Once cellulose is mainly composed of C-O and C-OH bonds, the C-O peak better characterizes the cellulose in the C 1 s spectra. So, the carbon layer deposited by plasma on the sample surface can be estimated through exponential attenuation (Walton et al. 2016) from the C-O signal in the C 1 s fitting due to the film presence, with the decreasing exponential probability of photoelectron escape. Equation 1 (Walton et al. 2016) shows it, where $I_{C-O(BC-C3)}$ is the intensity of the C-O signal from the C 1 s spectra of the BC-C3 sample; $I_{C-O(BC)}$ is the intensity of the C-O signal from the C 1 s spectra of the BC sample; z is the depth of photoelectron escape, whose value will indicate the thickness of the film; and λ_{C1s} is the photoelectron inelastic mean free path for the kinetic energy of the C 1 s orbital in the carbon matrix. Considering $\lambda_{C1s} = 3.0$ nm (Walton et al. 2016), and $I_{C-O(BC-C3)}$ and $I_{C-O(BC)}$ as 32.7 and 42.0, respectively, Eq. 1 leads to a film thickness of around 0.75 nm. This means four or five carbon atomic layers, which is considerably lower than the coating grown due to the plasma treatment. So, the small thickness obtained through Eq. 1 may be attributed to the formation of a thin film of oxide on the polymer film, after the samples were removed from the vacuum chamber due to the reaction of free radicals present in the polymer coating with oxygen from atmospheric air (Alvarez et al. 2019).

$$I_{C-O(BC-C3)} = I_{C-O(BC)} \cdot e^{\frac{-z}{\lambda_{C1s}}} \quad (1)$$

Surface characterization

The surface analysis of the untreated bacterial cellulose reveals the characteristic cellulose fibers of bacterial cellulose (Fig. 11a). The analysis of the plasma treated bacterial cellulose shows a smoothing of the surface due to the growth of a polymer coating (Fig. 11b). It also shows that the film is homogeneous and continuous, with no large defects on the topography, despite its thinness. This result shows that the plasma process used in present paper, namely the Cathodic Cage Plasma, is a good candidate to produce polymer films with superior homogeneity.

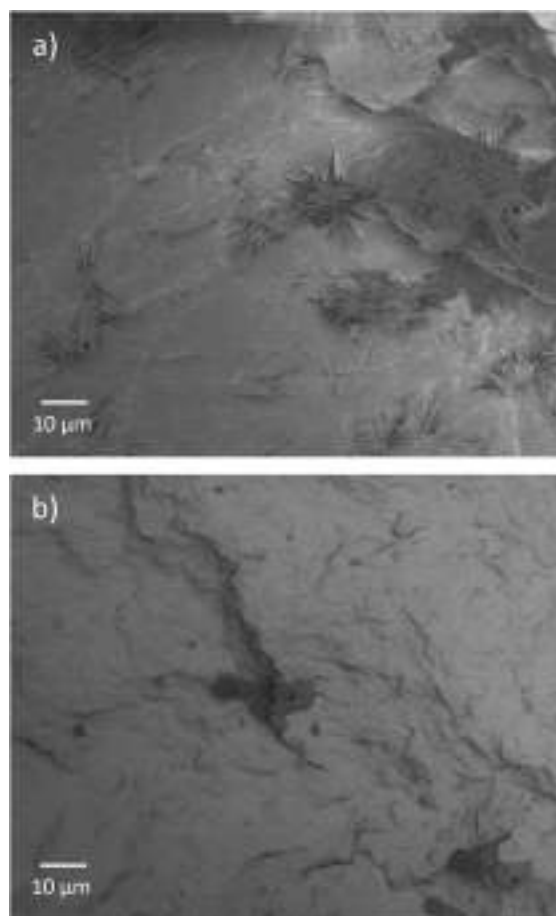


Fig. 11 Scanning Electron Microscope images for **a)** surface of BC (non-treated) and **b)** surface of BC-C3 (30.0 min, Ar+C₂H₂ gases, and 60% duty cycle)

Conclusions

In response to the need for more sustainable fabric alternatives for the fashion industry, this study cultivated bacterial cellulose and plasma-treated it to reduce its hydrophilicity. The biofabric surface treatment, through C₂H₂/Ar/H₂ plasma in a cathodic cage, was proven effective, forming a thin hydrocarbon film on the surface of the BC. Results show that the Cathodic Cage Plasma treatment turned the surface of the BC from hydrophilic to hydrophobic, as the static water drop contact angle changed from $\theta \approx 30^\circ$ to $\theta > 90^\circ$, besides purifying it without degradation. Bacterial cellulose can be made hydrophobic by using parameters such as a longer treatment time, a combination of gases without the addition of hydrogen, and

a lower duty cycle (from the most to the least influential factor, respectively).

Considering the effectiveness of plasma treatment in improving the hydrophobic behavior in bacterial cellulose, opportunities arise for its application in the fashion industry. This is particularly significant as fashion products come into contact with human skin, and the high hydrophilicity of bacterial cellulose poses challenges for hygiene and a greater susceptibility to microbial proliferation. The plasma treatment mitigates the common issues stemming from hydrophilic bacterial cellulose without the need to introduce processes that generate effluents or waste, while maintaining the material's biodegradability.

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Authors' contributions A.A.I.R., T.T.S., L.C.F. and D.Bond conceived and planned the experiments. A.A.I.R. and T.T.S. carried out the experiments. J.C.S. and D.Becker contributed to sample characterization. All authors contributed to the interpretation of the results. A.A.I.R., T.T.S. and D.Bond wrote the manuscript in consultation with J.C.S., L.R.L. and L.C.F. All authors provided critical feedback and helped shape the research, analysis, and manuscript.

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Declarations

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Competing interests Not applicable.

References

- Aditya T, Allain JP, Jaramillo C, Restrepo AM (2022) Surface Modification of Bacterial Cellulose for Biomedical Applications. *Int J Mol Sci* 23(2):610. <https://doi.org/10.3390/ijms23020610>
- Akbari R, Antonini C (2021) Contact angle measurements: From existing methods to an open-source tool. *Adv Colloid Interface Sci* 294:102470. <https://doi.org/10.1016/j.cis.2021.102470>
- Alvarez B, Sarmiento-Santos A, Vera-López E (2019) Acetylene polymerization in plasma of direct current. *J Phys Conf Ser* 1386:012044. <https://doi.org/10.1088/1742-6596/1386/1/012044>
- Amarasekara AS, Wang D, Grady TL (2020) A comparison of kombucha SCOBY bacterial cellulose purification methods. *SN Appl Sci* 2:240. <https://doi.org/10.1007/s42452-020-1982-2>
- Benedikt J (2010) Plasma-chemical reactions: low pressure acetylene plasmas. *J Phys D: Appl Phys* 43:043001. <https://doi.org/10.1088/0022-3727/43/4/043001>
- Betlej I, Salerno-Kochan R, Jankowska A, Krajewski K, Wilkowski J, Rybak K, Nowacka M, Boruszewski P (2021) The Impact of the Mechanical Modification of Bacterial Cellulose Films on Selected Quality Parameters. *Coatings* 11(11):1275. <https://doi.org/10.3390/coatings11111275>
- Briggs D, Beamson G (1992) High resolution XPS of Organic Polymers. The Scienta ESCA300 Database. Wiley, Chichester
- Burhenne L, Messmer J, Aicher T, Laborie MP (2013) The effect of the biomass components lignin, cellulose and hemicellulose on TGA and fixed bed pyrolysis. *J Anal Appl Pyrolysis* 101:177–184. <https://doi.org/10.1016/j.jaap.2013.01.012>
- Chacko SM, Thambi PT, Kuttan R, Nishigaki I (2010) Beneficial effects of green tea: A literature review. *Chin Med* 5:1–9. <https://doi.org/10.1186/1749-8546-5-13>
- Correa F, Becker D, Fontana LC (2018) Electron confinement in active screen plasma system and extreme floating potential into the cage. *Rev Bras Apl Vac* 37:59–64. <https://doi.org/10.17563/rbav.v37i2.1098>
- Costa AFS, Rocha MAV, Sarubbo LA (2017) Review - Bacterial Cellulose: An Ecofriendly Biotextile. *Int J Text Fash Technol* 7:11–26
- da Silva CJG, de Medeiros ADM, de Amorim JDP, do Nascimento HA, Converti A, Costa AFS, Sarubbo LA (2021) Bacterial cellulose biotextiles for the future of sustainable fashion: a review. *Environ Chem Lett* 19:2967–2980. <https://doi.org/10.1007/s10311-021-01214-x>
- Denysenko IB, Xu S, Long JD, Rutkevych PP, Azarenkov NA, Ostrikov K (2004) Inductively coupled Ar/CH₄/H₂ plasmas for low-temperature deposition of ordered carbon nanostructures. *J Appl Phys* 95:2713–2724. <https://doi.org/10.1063/1.1642762>
- Dima SO, Panaitescu DM, Orban C, Ghiurea M, Doncea SM, Fierascu RC, Nistor CL, Alexandrescu E, Nicolae CA, Trică B, Moraru A, Oancea F (2017) Bacterial Nanocellulose from Side-Streams of Kombucha Beverages Production: Preparation and Physical-Chemical Properties. *Polymers* 9(8):374. <https://doi.org/10.3390/polym9080374>
- Fernandes M, Gama M, Dourado F, Souto AP (2019) Development of novel bacterial cellulose composites for the textile and shoe industry. *Microb Biotechnol* 12(4):650–661. <https://doi.org/10.1111/1751-7915.13387>
- Fernandes M, Souto AP, Gama M, Dourado F (2019) Bacterial Cellulose and Emulsified AESO Biocomposites as an Ecological Alternative to Leather. *Nanomaterials* 9(12):1710. <https://doi.org/10.3390/nano9121710>
- Flynn CN, Byrne CP, Meenan BJ (2013) Surface modification of cellulose via atmospheric pressure plasma processing in air and ammonia–nitrogen gas. *Surf Coat Technol*

- 233:108–118. <https://doi.org/10.1016/j.surfcoat.2013.04.007>
- Friedrich J (2011) Mechanisms of Plasma Polymerization – Reviewed from a Chemical Point of View. *Plasma Process Polym* 8:783–802. <https://doi.org/10.1002/ppap.201100038>
- Gallo SC, Charitidis C, Dong H (2017) Surface functionalization of carbon fibers with active screen plasma. *J Vac Sci Technol* 35(2):021404. <https://doi.org/10.1116/1.4974913>
- Gea S, Reynolds CT, Roohpour N, Wirjosentono B, Soykeabkaew N, Bilotti E, Peijs T (2011) Investigation into the structural, morphological, mechanical and thermal behaviour of bacterial cellulose after a two-step purification process. *Bioresour Technol* 102(19):9105–9110. <https://doi.org/10.1016/j.biortech.2011.04.077>
- Gregory DA, Tripathi L, Fricker ATR, Asare E, Orlando I, Raghavendran V, Roy I (2021) Bacterial cellulose: A smart biomaterial with diverse applications. *Mater Sci Eng R Rep* 145:100623. <https://doi.org/10.1016/j.mser.2021.100623>
- Günter E, Fontana LC, Becker D (2019) Maleic anhydride film deposition through an active screen plasma system. *Bull Mater Sci* 42:23. <https://doi.org/10.1007/s12034-018-1706-z>
- He W, Zhang Z, Zheng Y, Qiao S, Xie Y, Sun Y, Qiao K, Feng Z, Wang X, Wang J (2020) Preparation of aminoalkyl-grafted bacterial cellulose membranes with improved antimicrobial properties for biomedical applications. *J Biomed Mater Res* 108:1086–1098. <https://doi.org/10.1002/jbm.a.36884>
- Hetegger H, Sumerskii I, Sortino A, Potthast A, Rosenau T (2015) Silane Meets Click Chemistry: Towards the Functionalization of Wet Bacterial Cellulose Sheets. *ChemSuschem* 8:680–687. <https://doi.org/10.1002/cssc.201402991>
- Jayabalan R, Malbaša RV, Lončar ES, Vitas JS, Sathishkumar M (2014) A Review on Kombucha Tea-Microbiology, Composition, Fermentation, Beneficial Effects, Toxicity, and Tea Fungus. *Compr Rev Food Sci Food Saf* 3(4):538–550. <https://doi.org/10.1111/1541-4337.12073>
- Kamiński K, Jarosz M, Grudzień J, Pawlik J, Zastawnik F, Pandya P, Kołodziejczyk AM (2020) Hydrogel bacterial cellulose: a path to improved materials for new eco-friendly textiles. *Cellulose* 27:5353–5365. <https://doi.org/10.1007/s10570-020-03128-3>
- Kluz MI, Pietrzyk K, Pastuszczyk M, Kacaniova M, Kita A, Kapusta I, Zagula G, Zagrobelna E, Struś K, Marciniak-Lukasiak K, Stanek-Tarkowska J, Timar AV, Puchalski C (2022) Microbiological and Physicochemical Composition of Various Types of Homemade Kombucha Beverages Using Alternative Kinds of Sugars. *Foods* 11:1523. <https://doi.org/10.3390/foods11101523>
- Krishnamurthy M, Lobo NP, Samanta D (2020) Improved Hydrophobicity of a Bacterial Cellulose Surface: Click Chemistry in Action. *ACS Biomater Sci Eng* 6(2):879–888. <https://doi.org/10.1021/acsbiomaterials.9b01571>
- Kurniawan H, Lai JT, Wang MJ (2012) Biofunctionalized bacterial cellulose membranes by cold plasmas. *Cellulose* 19:1975–1988. <https://doi.org/10.1007/s10570-012-9785-2>
- Kutner MH (2004) *Applied Linear Statistical Models*. McGraw-Hill, New York
- Laavanya D, Shirkole S, Balasubramanian P (2021) Current challenges, applications and future perspectives of SCOBY cellulose of Kombucha fermentation. *J Cleaner Prod* 295:126454. <https://doi.org/10.1016/j.jclepro.2021.126454>
- Latthe SS, Terashima C, Nakata K, Fujishima A (2014) Superhydrophobic Surfaces Developed by Mimicking Hierarchical Surface Morphology of Lotus Leaf. *Molecules* 19(4):4256–4283. <https://doi.org/10.3390/molecules19044256>
- Leal S, Cristelo C, Silvestre S, Fortunato E, Sousa A, Alves A, Correia DM, Lanceros-Mendez S, Gama M (2020) Hydrophobic modification of bacterial cellulose using oxygen plasma treatment and chemical vapor deposition. *Cellulose* 27:10733–10746. <https://doi.org/10.1007/s10570-020-03005-z>
- Lee KY, Quero F, Blaker JJ, Hill CAS, Eichhorn SJ, Bismarck A (2011) Surface only modification of bacterial cellulose nanofibres with organic acids. *Cellulose* 18:595–605. <https://doi.org/10.1007/s10570-011-9525-z>
- Lee KY, Buldum G, Mantalaris A, Bismarck A (2014) More Than Meets the Eye in Bacterial Cellulose: Biosynthesis, Bioprocessing, and Applications in Advanced Fiber Composites. *Macromol Biosci* 14:10–32. <https://doi.org/10.1002/mabi.201300298>
- Lima BL, Alves AS, Ferreira Martins GC (2021) Biofabricação: Cultivo de Celulose Bacteriana para a Área de Moda. *MIX Sustentável* 7(3):153–164. <https://doi.org/10.29183/2447-3073.MIX2021.v7.n3.153-164>
- Lv P, Xu W, Li D, Feng Q, Yao Y, Pang Z, Lucia LA, Wei Q (2016) Metal-based bacterial cellulose of sandwich nanomaterials for anti-oxidation electromagnetic interference shielding. *Mater Des* 112:374–382. <https://doi.org/10.1016/j.matdes.2016.09.100>
- Macedo MOC, Macedo HRA, Santos ZM, Pereira MR, Alves Junior C (2010) Avaliação da Modificação de Membranas de Quitosana Tratadas por Plasma de Hidrogênio para Aplicações Biomédicas. *Rev Bras Apl Vacuo* 29:31–36
- Mazotto AM, Silva JR, Brito LAA, Rocha NU, Soares AS (2021) How can microbiology help to improve sustainability in the fashion industry? *Environ Technol Innov* 23:101760. <https://doi.org/10.1016/j.eti.2021.101760>
- Mehrotra R, Sharma S, Shree N, Kaur K (2023) Bacterial Cellulose: An Ecological Alternative as a Biotextile. *Biosci Biotech Res Asia* 20(2):449–463. <https://doi.org/10.13005/bbra/3101>
- Mondal S, Pal S, Bal R, Maity J (2018) Fabrication of two sites hydrophobicity on cotton surface – a fluoropolymerization approach. *J Adhes Sci Technol* 32(18):1965–1974. <https://doi.org/10.1080/01694243.2018.1458407>
- Montgomery D (2013) *Design and Analysis of Experiments*. Wiley, New York
- Morrow R, Ribul M, Eastmond H, Lanot A, Baurley S (2023) Bio-producing bacterial cellulose filaments through co-designing with biological characteristics. *Materials* 16(14):4893. <https://doi.org/10.3390/ma16144893>
- Mourgues A, Sanchez J, Roualdès S, Durand J (2005) Modelling of gas permeability for membranes prepared by

- PECVD. *J Membr Sci* 262(1–2):42–48. <https://doi.org/10.1016/j.memsci.2005.03.045>
- Movasaghi Z, Rehman S, Rehman I (2008) Fourier transform infrared (FTIR) spectroscopy of biological tissues. *Appl Spectrosc Rev* 43:134–179. <https://doi.org/10.1080/05704920701829043>
- Ng MCF, Wang W (2015) A study of the receptivity to bacterial cellulosic pellicle for fashion. *RJTA* 19(4):65–69. <https://doi.org/10.1108/RJTA-19-04-2015-B007>
- Pascu M, Vasile C, Gheorghiu M (2003) Modification of polymer blend properties by argon plasma/electron beam treatment: surface properties. *Mater Chem Phys* 80(2):548–554. [https://doi.org/10.1016/S0254-0584\(03\)00092-0](https://doi.org/10.1016/S0254-0584(03)00092-0)
- Pertile RAN, Andrade FK, Alves C, Gama M (2010) Surface modification of bacterial cellulose by nitrogen-containing plasma for improved interaction with cells. *Carbohydr Polym* 82(3):692–698. <https://doi.org/10.1016/j.carbpol.2010.05.037>
- Provin AP, dos Reis VO, Hilesheim SE, Bianchet RT, Dutra ARA, Cubas ALV (2021) Use of bacterial cellulose in the textile industry and the wettability challenge—a review. *Cellulose* 28:8255–8274. <https://doi.org/10.1007/s10570-021-04059-3>
- Rajwade JM, Paknikar KM, Kumbhar JV (2015) Applications of bacterial cellulose and its composites in biomedicine. *Appl Microbiol Biotechnol* 99(6):2491–2511. <https://doi.org/10.1007/s00253-015-6426-3>
- Rathinamoorthy R, Kiruba T (2022) Bacterial cellulose-A potential material for sustainable eco-friendly fashion products. *J Nat Fibers* 19(9):3275–3287. <https://doi.org/10.1080/15440478.2020.1842841>
- Ražić SE, Čunko R, Bautista L, Bukošek V (2017) Plasma effect on the chemical structure of cellulose fabric for modification of some functional properties. *Procedia Eng* 200:333–340. <https://doi.org/10.1016/j.proeng.2017.07.047>
- Santos SM, Carbajo JM, Quintana E, Ibarra D, Gomez N, Ladero M, Eugenio ME, Villar JC (2015) Characterization of purified bacterial cellulose focused on its use on paper restoration. *Carbohydr Polym* 116:173–181. <https://doi.org/10.1016/j.carbpol.2014.03.064>
- Shao W, Wu J, Liu H, Ye S, Jiang L, Liu X (2017) Novel bio-active surface functionalization of bacterial cellulose membrane. *Carbohydr Polym* 178:270–276. <https://doi.org/10.1016/j.carbpol.2017.09.045>
- Sohbatzadeh F, Shakerinasab E, Eshghabadi M, Ghasemi M (2019) Characterization and performance of coupled atmospheric pressure argon plasma jet with n-hexane electrospray for hydrophobic layer coatings on cotton textile. *Diamond Relat Mater* 91:34–45. <https://doi.org/10.1016/j.diamond.2018.10.023>
- Song JE, Silva C, Cavaco-Paulo AM, Kim HR (2019) Functionalization of Bacterial Cellulose Nonwoven by Poly(fluorophenol) to Improve Its Hydrophobicity and Durability. *Front Bioeng Biotechnol* 7:332. <https://doi.org/10.3389/fbioe.2019.00332>
- Sulaeva I, Vejdovszky P, Beaumont M, Rusakov D, Rohrer C, Rosenau T, Potthast A (2019) Fast Approach to the Hydrophobization of Bacterial Cellulose via the Direct Polymerization of Ethyl 2-Cyanoacrylate. *Biomacromol* 20:3142–3146. <https://doi.org/10.1021/acs.biomac.9b00721>
- Tatarova E, Bundaleska N, Sarrette JPh, Ferreira CM (2014) Plasmas for environmental issues: from hydrogen production to 2D materials assembly. *Plasma Sources Sci Technol* 23:063002. <https://doi.org/10.1088/0963-0252/23/6/063002>
- Tomé LC, Brandão L, Mendes AM, Silvestre AJD, PascoalNeto C, Gandini A, Freire CSR, Marrucho IM (2010) Preparation and characterization of bacterial cellulose membranes with tailored surface and barrier properties. *Cellulose* 17:1203–1211. <https://doi.org/10.1007/s10570-010-9457-z>
- Vilaplana JF, Cabanes SG (2012) Aplicación de la Tecnología de Plasma Polimerización em Sustratos Textiles para Uso Técnico. *3C Tecnol* 1(2):6–21
- Walton J, Alexander MR, Fairley N, Roach P, Shard AG (2016) Film thickness measurement and contamination layer correction for quantitative XPS. *Surf Interface Anal* 48(3):164–172. <https://doi.org/10.1002/sia.5934>
- Wang T, Xu L, Shen H, Cao X, Wei Q, Ghiladi RA, Wang Q (2020) Photoinactivation of bacteria by hypocrellin-grafted bacterial cellulose. *Cellulose* 27:991–1007. <https://doi.org/10.1007/s10570-019-02852-9>
- Wood J (2019) Bioinspiration in Fashion—A Review. *Biomimetics* 4(1):16. <https://doi.org/10.3390/biomimetics4010016>
- Yan X, Li J, Yi L (2017) Fabrication of pH-responsive hydrophilic/hydrophobic Janus cotton fabric via plasma-induced graft polymerization. *Mater Lett* 208:46–49. <https://doi.org/10.1016/j.matlet.2017.05.029>
- Yim SM, Song JE, Kim HR (2017) Production and characterization of bacterial cellulose fabrics by nitrogen sources of tea and carbon sources of sugar. *Process Biochem* 59:26–36. <https://doi.org/10.1016/j.procbio.2016.07.001>
- Zheng J, Yang R, Xie L, Qu J, Liu Y, Li X (2010) Plasma-Assisted Approaches in Inorganic Nanostructure Fabrication. *Adv Mater* 22(13):1451–1473. <https://doi.org/10.1002/adma.200903147>
- Zille A, Oliveira FR, Souto AP (2014) Plasma Treatment in Textile Industry. *Plasma Processes Polym* 12(2):98–131. <https://doi.org/10.1002/ppap.201400052>

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The Effects of Graphene Oxide and Iron Oxide (II) Co-addition on Properties of a Polypropylene/high-density Polyethylene Blend

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This study investigated the impact of adding graphene oxide (GO) and iron oxide (II) (Fe_3O_4) nanoparticles individually and in combination on the morphology, thermo-mechanical, and dielectric properties of a Polypropylene/High-Density Polyethylene (PP/HDPE) blend. By adding these nanoparticles separately or as a mixture, we can determine if both mechanisms have a synergistic effect and how they impact the dielectric constant values of their nanocomposites. The nanoparticle mixture was prepared in both an alkaline and a neutral medium. The mixture in the alkaline medium contained lower quantities of iron nanoparticles than in the neutral medium, and they were localized on the surface of GO. The nanocomposites showed significant differences in dynamic-mechanical and dielectric properties. The system with Fe_3O_4 exhibited a higher storage modulus, while the system with GO had a higher dielectric constant. However, no synergistic effect was observed in the nanoparticle mixtures.

Keywords: Dielectric properties, nanocomposites, graphene oxide, iron oxide (II).

1. Introduction

Dielectric materials are used in capacitor fillings and have the function of isolating the capacitor's electrodes. This separator element must meet specific properties such as flexibility, resistance to electrolyte corrosion, and dielectric properties such as high ionic and low electrical conductivity in a wide operating range (avoiding short-circuit problems), all with a small thickness¹. The separators in standard capacitor systems are, in general, made of a blend of polypropylene (PP) and polyethylene (PE) due to some characteristic aspects besides the insulating characteristic, such as easy processing and recyclability, mechanical, thermal, and chemical stability². Although such desired properties, other factors should be improved in the PP/HDPE system, such as a high dielectric capacity, high resistivity, and low dielectric loss³.

Both graphene oxide (GO) and iron oxide (II) (Fe_3O_4) have similar properties in terms of enhancing dielectric properties since the carbon nanoparticles tend to add interfacial polarization mechanisms⁴, and the Fe_3O_4 introduces dipoles in the original polymer matrices⁵. As an example of such behavior change, studies in high frequencies show that these mechanisms can be combined when both nanoparticles are mixed to obtain Fe_3O_4 /GO nanocomposites⁶. The literature has shown that adding 1% of that mixture into polymer blends of polyvinyl alcohol (PVA) and poly(3,4-ethylenedioxythiophene) can produce a nanocomposite with potential properties of electronic compounds and electromagnetic shielding^{7,8}. A similar property enhancement was verified in the epoxy polymer matrix⁹ and in polyvinylidene fluoride (PVDF)¹⁰, to which mechanical properties, thermal stability, and the

dielectric constant improvements were observed. To this end, the nanoparticles can seemingly act by introducing new mechanisms of interfacial and dipole polarizations (depending on time and temperature) into the immiscible polymer matrix and changing the initially isolated properties of the polymer chain into a semiconductor state⁶. As a result, these nanocomposites have a wide range of applications, such as high-frequency or embedded capacitors⁴, heat transfer improvement in nanofluids¹¹, and high absorption devices⁸. To our knowledge, the influence of the simultaneous addition of graphene oxide and iron oxide in the PP/HDPE blend, especially in the dielectric properties, has not yet been studied.

So, this work aims to evaluate the influence of adding individually and mixed graphene oxide and iron oxide in the morphological, thermal, mechanical, and, especially, dielectric properties of a high-density polyethylene/polypropylene polymer blend. In order to understand the effect of polarization and dipole mechanisms brought by graphene oxide or iron oxide on the PP/HDPE matrix, these nanoparticles were added separately or as a mixture into the polymer blend. The results are compared to evaluate whether there is a synergic effect between both mechanisms and how they affect the dielectric constant values of their nanocomposites.

2. Experimental Procedures

2.1. Materials

Two polymers were chosen for this work, the heterophase copolymer of ethylene-propylene (PP) as the continuous phase and high-density polyethylene (HDPE) as the dispersed

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phase, both purchased from Braskem, with grades CP 741 and HC7260LS-L, respectively. The graphene was purchased as a powder from Chengdu Organic Chemistry (China) with purity above 99% and thickness from 4 nm to 20 nm. The iron oxide (II) was acquired as a powder from Sigma Aldrich, with a purity of 97%, size between 50 nm and 100 nm, and spherical geometry, according to the datasheet from the manufacturer. All materials were used as received, apart from the graphene that underwent an oxidation process.

2.2. Preparation of nanoparticles

Graphene oxide was prepared from the graphene through the modified Hummers’ Method¹². For this end, the graphene was initially put in a mixture of potassium permanganate, sulfuric acid, and phosphoric acid (6:9:1) and stirred for

12 h until the solution turned dark brown. After that, the resulting nanoparticle was filtered and dried at 60°C for 24 hours in an air circulation oven.

Two different methods were used to obtain the nanoparticle mixture between graphene oxide and iron oxide. The first method was based on another work¹¹ and called a mixture in alkaline medium (MAM): both nanoparticles, in the proportion of 1:1, were added in a recipient with ammonium hydroxide, heated at 70 °C for 30 min, sequentially, sonicated for another 30 min, and finally filtered. The second mixture method, namely mixture in neutral medium (MNM), was performed through simple water sonication for 30 min and subsequent filtration. Both mixtures were oven-dried for 1 hour at 60 °C. Figure 1a shows the procedure to obtain these mixtures.

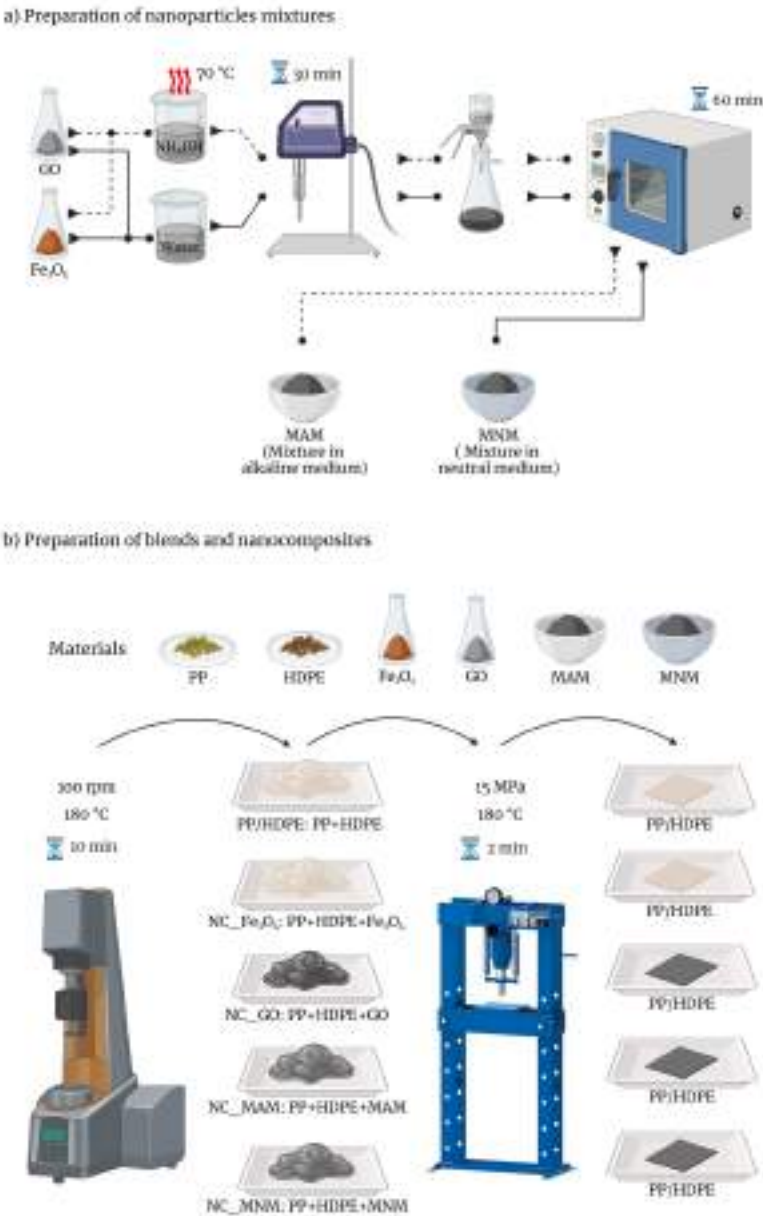


Figure 1. Schematic representation a) of the procedures conducted to obtain the mixtures between graphene oxide and iron oxide; and b) of the steps to obtain blend and nanocomposites samples. Created with BioRender.com

2.3. Processing of nanocomposites

The HDPE and the PP were previously dried at 100 °C in a circulating-air stove to eliminate all residual water before processing. The blend proportion was 90/10 (PP/HDPE), and a composition of 1% in mass of the nanoparticles, i.e., iron oxide (II), graphene oxide, bands (MAM) or mixture in neutral medium (MNM), was chosen to produce the nanocomposite samples. Both polymers were mixed using the torque rheometry technique (Thermo Scientific Haake Rheomix 600) at 180 °C, 100 rpm for 10 min, in which nanoparticles were added individually or as mixtures to the polymers. Films of the produced polymer nanocomposites were obtained through the hot-molding press (Bovenau P15 ST) at 180 °C and under 15 MPa for 2 min and cooled instantaneously to room temperature, which led to samples with an average thickness of 0.18 mm. That process is graphically represented in Figure 1b. Table 1 summarizes the sample names of each nanocomposite, having the PP/HDPE blend as a matrix.

2.4. Characterization

Graphene and Oxide graphene were characterized by Fourier Transform Infrared (FTIR), X-ray diffraction, and X-ray Photoelectron Spectroscopy (XPS). The nanoparticle mixtures were characterized by Transmission Electron Microscopy (TEM) and X-ray Photoelectron Spectroscopy (XPS). FTIR spectra were obtained with KBr using 12 scans in the range from 4000 cm⁻¹ to 550 cm⁻¹, with a resolution of 4 cm⁻¹, in a Spectrum One B Perkin-Elmer. The Shimadzu XRD 6000 equipment performed the x-ray diffraction test using monochromatic Cu radiation (0.154 nm). The measurements were performed from 5° to 70°, with a standard operating rate of 2°/min. XPS analyses were conducted in a Thermo Scientific XPS (Al-K α , $h\nu$ = 1486.6 eV). Survey spectra were collected from -10 eV to 1350 eV after ten scans, with a pass energy of 200.000 eV, a step size of 1.000 eV, and a dwell time of 10.000 ms. The base pressure was set to 10⁻⁸ mbar, and the X-ray spot was 400 μ m in diameter. A charge compensation gun (flood gun) was utilized during the analysis. Data were collected from three different surface points in each sample. The chemical composition was obtained through the “speciation” function available on the Advantage® software from Thermo Scientific. For the transmission electronic microscopy analysis, the nanoparticles were dispersed in acetone, sonicated for 2 min, and then characterized in a JEM 2100 JEOL microscope.

The blend morphology was studied through electronic scanning microscopy with field emission (FEG-SEM) using a JSM 6701F-JEOL at 10 kV. The samples were submerged

in N₂ for 5 minutes, and the cryo-fracture surfaces of the different samples were coated with a gold layer.

The dynamic-mechanical analysis (DMA) was carried out to observe how the nanoparticles affected the mechanical properties of the final nanocomposites through the analysis of the storage modulus (E') and the glass-transition temperature (T_g). The experiments were performed with a Netzsch DMA 242 E in the stress-strain mode under a nitrogen atmosphere, with a temperature range from -150 °C to 50 °C, considering a frequency of 1 Hz and a heating rate of 3 °C/min.

The effect of the samples' processing and composition on the crystallization temperature (T_c) and the crystallization degree (%) were analyzed using differential scanning calorimetry (DSC) on a Netzsch Maia-230. The samples were submitted to heating and cooling cycles under an N₂ atmosphere. Heating from 25 to 225 °C was applied at a 10°C min⁻¹ rate, keeping in isotherm for 2 min. Cooling was then carried out down to 25 °C at a 20 °C min⁻¹ rate, keeping in isotherm for 2 min, followed by a second heating of 10°C min⁻¹ up to 350 °C. The degree of crystallinity, X_c , was calculated from Equation 1, in which ΔH and $\phi \cdot \Delta H_0$ are, respectively, the enthalpy obtained through DSC and for the theoretical 100 % crystalline polymer, and indicates the fraction of each polymer in the blend. The values used for ΔH_0 were 287 J/g for HDPE and 207 J/g for PP¹³.

$$X_c = \left[\frac{\Delta H}{\phi \cdot \Delta H_0} \right] \cdot 100 \quad (1)$$

The electrochemical impedance spectroscopy (EIS) analysis was carried out to see how the dielectric constant was affected by the nanomaterials due to new polarization mechanisms brought to the polymer matrix of the nanocomposites. This study used a potentiostat/galvanostat coupled to a frequency analyzer module (Gamry 1010e) with the blocking electrode method. Tests were carried out at open circuit potential and room temperature, in which a thin film of each sample was sandwiched between two stainless steel electrodes, applying an AC potential of 10 mV (rms) in the frequency range between 10 kHz and 1 Hz. Dielectric constant data were calculated from impedance parameters using Equation 2, in which ϵ' indicates the real part of the electrical permittivity, and ϵ'' are, respectively, the real and imaginary impedances achieved through the analysis, ω is the frequency, and A and d express the geometric characteristics of area and thickness of the polymer film.

$$\epsilon' = \frac{-Z'}{2\pi f \epsilon_0 Z^2 \frac{A}{d}} \quad (2)$$

Table 1. Sample's name and indication of dispersed phase of the nanocomposites with PP/HDPE as matrix.

Sample name	Dispersed phase
PP/HDPE	-
NC_Fe ₃ O ₄	Iron oxide II as purchased
NC_GO	Graphene oxide produced
NC_MAM	Mixture in alkaline medium
NC_MNM	Mixture in neutral medium

3. Results and Discussion

3.1. Characterization of graphene and graphene oxide

Figure 2 presents FTIR spectra for graphene and graphene oxide. The graphene spectrum has three characteristic bands,

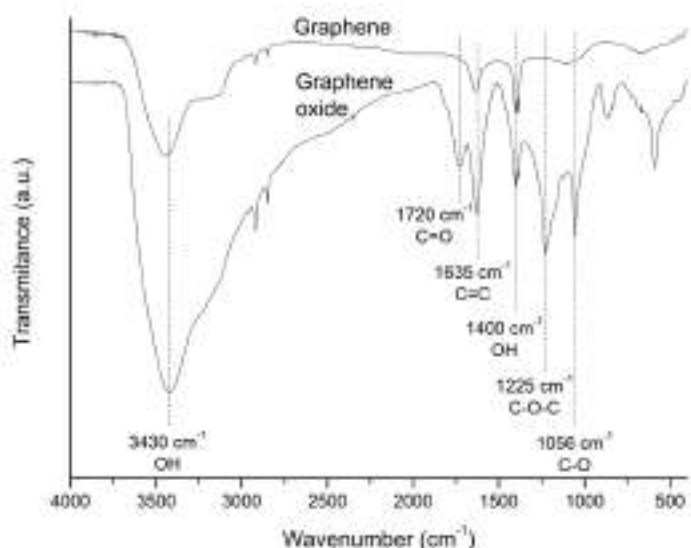


Figure 2. FTIR spectra for graphene and graphene oxide.

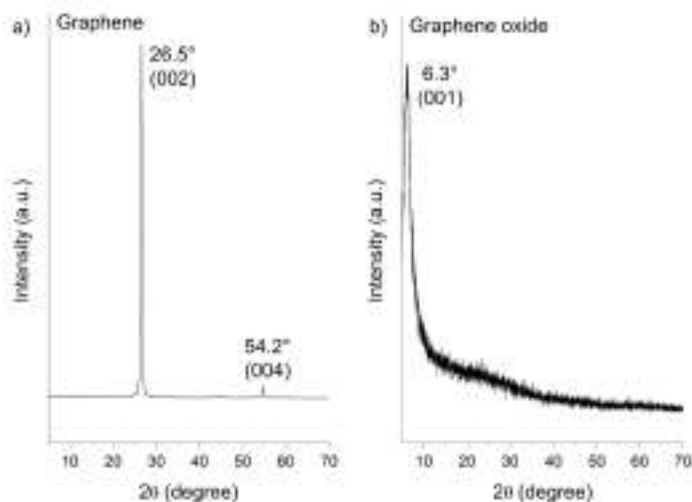


Figure 3. X-Ray diffraction spectra for a) graphene and b) graphene oxide samples.

at 3430 cm^{-1} , 1635 cm^{-1} , and 1400 cm^{-1} , assigned, respectively, to the stretching mode of O-H bonds, stretching vibrations of C=C, and deformation of hydroxyl groups¹². These same bands are present in the graphene oxide spectrum, and new ones that characterize this type of material appear as hydroxyl, carboxyl, and epoxide groups. At 1720 cm^{-1} , the peak is assigned to the stretching vibration of carbonyl groups (C=O); at 1225 cm^{-1} , it denotes C-O-C stretching, and the peak at 1056 cm^{-1} corresponds to the vibrational mode of the C-O group^{12,14,15}. All those bands' presence confirms Hummers' Method's efficacy in oxidizing the graphene.

Figure 3 shows the diffraction pattern for graphene (a) and graphene oxide (b) samples. The sharp peak at 26.5° (002) for the graphene sample indicates an interplanar distance of $3.4\text{ \AA}$, obtained through Bragg's Law. Despite this length being in accordance with the one referred to in the literature for graphene, the peak at 26.5° is not typical for graphene sheets but for graphite¹⁶, indicating that our

precursor material was in this form. For the graphene oxide sample, the peak on XRD appears at 6.3° , which leads to an interplanar distance of $14\text{ \AA}$, almost five times the distance for graphene and graphite. That increase relates to the presence of oxygen groups between sheets¹⁶⁻¹⁸, corroborating FTIR and confirming the oxidation of graphene (or graphite) by the Hummers' Method.

Table 2 presents the XPS results from the Survey. A significant increase in oxygen atomic percent for the graphene oxide sample indicates the graphene's oxidation. As a result, the carbon content decreases. Nitrogen and sulfur are also present, which could be related to sample contamination by the atmosphere and solvent used to oxidize the graphene. Moreover, the C 1s fitting (Figure 4) confirms that the increase in oxygen atomic percent for the GO sample is related to the oxidation of graphene once the area contribution related to C-O covalent bonds increases significantly.

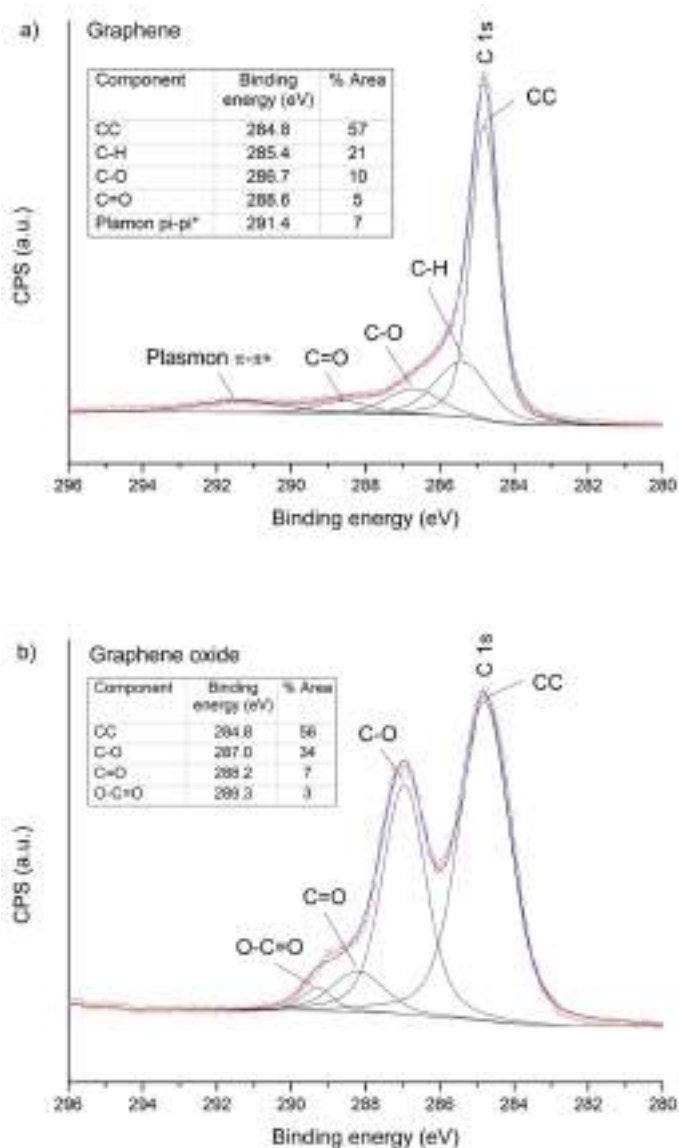


Figure 4. XPS C 1s fitting for a) graphene and b) graphene oxide samples, showing significant increase in C-O contribution after oxidation of graphene.

Table 2. XPS data for graphene and graphene oxide samples, obtained from Survey spectra.

	Atomic % (mean ± standard deviation)			
	C 1s	O 1s	N 1s	S 2p
Graphene	94.3 ± 0.4	3.6 ± 0.1	2.1 ± 0.3	-
Graphene oxide	65.3 ± 0.1	31.0 ± 0.5	1.4 ± 0.4	2.2 ± 0.1

3.2. Characterization of nanoparticle mixtures

Figure 5 presents XPS survey spectra for both alkaline medium (MAM) and neutral medium (MNM) mixtures between the GO and the iron oxide (II). Iron, carbon, nitrogen, and oxygen are the elements identified in the chemical composition of both samples. The MNM sample also detected sulfur on the surface, probably from contamination throughout the graphene oxidation process. The atomic percentage of each element for both samples is shown in Table 3. Significant

differences were observed for the carbon and iron values: carbon quantity (in atomic %) was doubled in the MAM, as was the iron in the MNM sample. The decrease in iron quantities in the MAM process could be related to the hydrolysis and dissolution/redeposition reactions that may occur with iron oxide in an alkaline solution^{19,20}, indicating its solubilization, probably in the FeOH_2 form, more stable at alkaline pH and with a solubility of 0.72g/100mL²⁰. Although the MNM mixture presented higher quantities of Fe(II), it is also stable in aerated neutral media in the insoluble FeOOH form.

In Figure 6, TEM images evidence that a significant number of smaller-sized Fe(II) nanoparticles cover the reduced graphene oxide sheet for the MAM sample (Figures 6a and b). However, this is not observed in samples obtained using a neutral medium (Figures 6c and d), where iron oxide nanoparticles

Table 3. XPS data for mixture in alkaline medium and mixture in neutral medium of graphene oxide and iron oxide.

	Atomic % (mean ± standard deviation)				
	C 1s	O 1s	N 1s	S 2p	Fe 2p
Mixture in alkaline medium	41.1 ± 1.0	45.5 ± 0.6	2.1 ± 0.2	-	11.3 ± 1.6
Mixture in neutral medium	25.5 ± 2.2	51.6 ± 2.3	1.3 ± 0.2	1.2 ± 0.5	20.4 ± 4.1

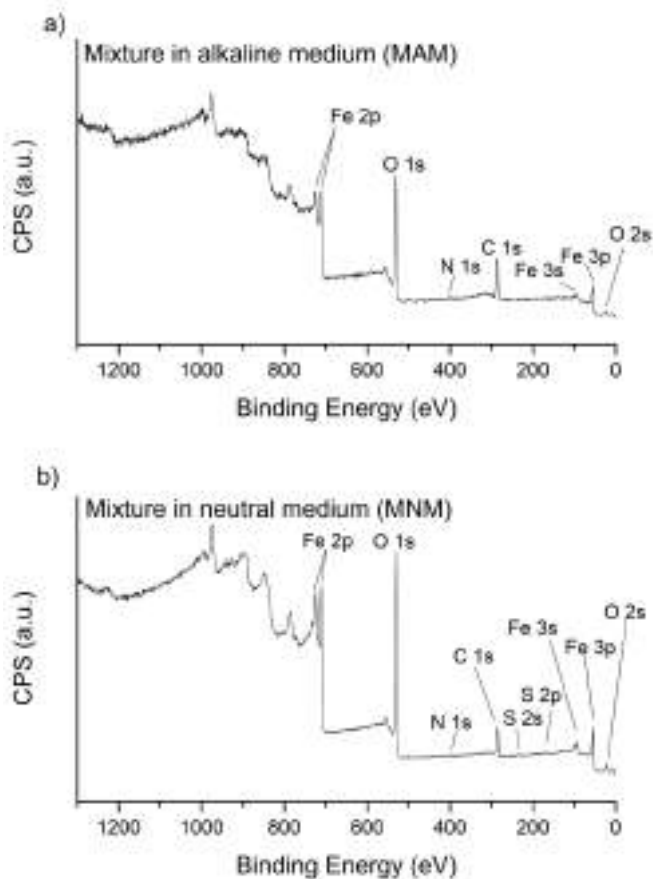


Figure 5. XPS Survey spectra of a) MAM and b) MNM samples, related to mixtures between graphene oxide and Fe₂O₃ (II) nanoparticles.

are agglomerated in regions close to the graphene oxide but not on its surface. This result suggests that an alkaline medium is necessary to guarantee that the iron nanoparticles are on the surface of the oxide graphene, even when the precursors are nanoparticles. Our method differs from the one used by Barai et al.¹¹, who synthesized iron oxide using FeCl₂·xH₂O and FeCl₃ as precursors in the presence of graphene oxide. Furthermore, Figures 6c and d showed Fe(II) agglomerates, possibly due to the hygroscopic FeOOH. At the same time, in the MAM mixture (Figure 6a and b), Fe(II) solubilization caused a good dispersion of the remaining iron oxide on the graphene sheets.

3.3. Characterization of nanocomposites

Figure 7 shows the FEG-SEM images for the PP/HDPE blend and its nanocomposites. It is not possible to observe the nanoparticles in the images, so only the fracture surface and the dispersed phase will be analyzed. The blend presents a matrix-dispersed particle structure, i.e., continuous PP and dispersed HDPE particles (indicated by arrows). These images also show adhesion between the phases since pullout

voids cannot be observed. This behavior may be related to the polypropylene used in this work, a heterophasic ethylene-propylene copolymer. No significant differences in the blend morphology are observed with nanoparticles, as observed in our previous paper²¹. Most of the system has no significant differences in the HDPE phase size, which may indicate that the nanoparticles are preferentially located in the matrix phase (PP)²² or in the interface.

The DSC analysis is shown in Figure 8, and Table 4 summarizes characteristic temperatures and the degrees of crystallinity for each sample. The data in Table 5 show that the crystallization temperature did not suffer any change for both the HDPE and the PP phases. On the other hand, the melting temperature and the degree of crystallinity were lowered mainly for the dispersed phase of the HDPE. It is well known that PP and the HDPE could interfere with each other's crystallization²³⁻²⁷, so the presence of the nanoparticles in the blend interface could increase this interference since nucleation at the interface between the two components has been observed by different authors^{26,27}.

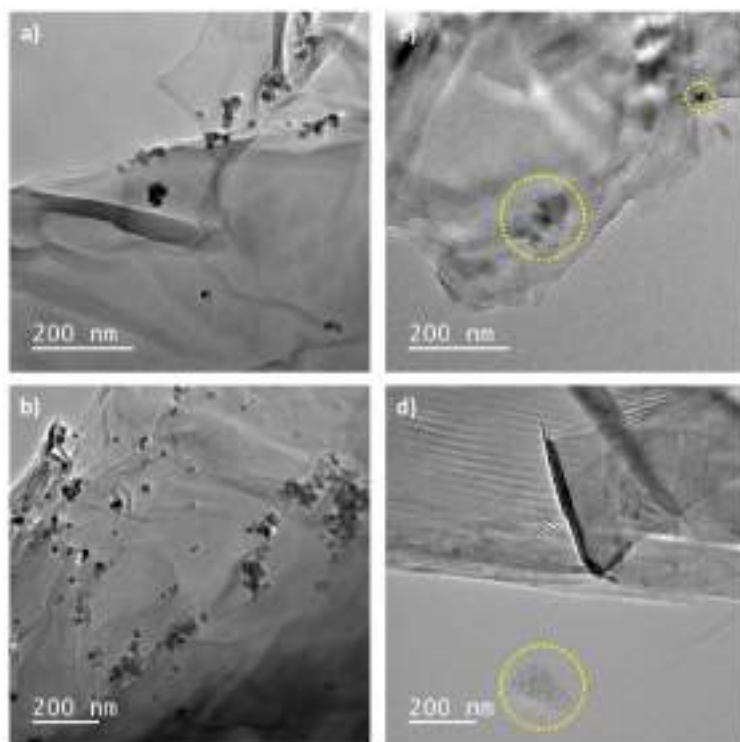


Figure 6. MET images for MAM (a and b) and MNM (c and d) samples, highlighting the Fe_3O_4 agglomerates for mixture conducted in neutral medium.

Table 4. Melting and crystallization temperatures, and degree of crystallinity for HDPE and PP phases in the PP/HDPE blend and nanocomposites.

System	T_c HDPE ($^{\circ}\text{C}$)	T_c PP ($^{\circ}\text{C}$)	T_m HDPE ($^{\circ}\text{C}$)	T_m PP ($^{\circ}\text{C}$)	X_c HDPE (%)	X_c PP (%)
PP/HDPE	119	162	149	182	48	27
NC_ Fe_3O_4	120	162	145	180	34	20
NC_GO	120	162	145	180	38	22
NC_MAM	119	161	146	182	37	26
NC_MNM	119	161	147	182	35	26

Table 5. Data summary of storage modulus and glass transition temperature for each sample. Values obtained through graphics from Figure 9.

Nanocomposite	E' (MPa) in -150°C	E' (MPa) in -75°C	E' (MPa) in 25°C	T_g ($^{\circ}\text{C}$) HDPE	T_g ($^{\circ}\text{C}$) PP
PP/HDPE	3,006	1,738	75	-127	-7.3
NC_ Fe_3O_4	10,800	62,59	205	-144	-0.5
NC_GO	4,063	2,045	80	-132	-2.3
NC_MAM	687	423	40	-134	-4.8
NC_MNM	2,285	1,253	68	-137	-7.3

The DMA results can be seen in Figure 9, and the data are summarized in Table 5. The glass transition temperature values decrease for the discontinuous phase of the HDPE and increase for the continuous phase in all configurations of the nanocomposites. When the nanoparticles were preferentially located in the interface, it was expected that the T_g should be the same as those of the neat polymers if there is no interaction between the phases or move closer to each other when the nanoparticle act as a compatibilizer, improving the miscibility between the polymer phases. In this case, the T_g moved further from each other, meaning

nanoparticles somehow immobilized the PP chains while creating more free volume in which the HDPE chains could move. The sharpest modification is observed for the system with Fe_3O_4 (NC_ Fe_3O_4 sample). This shows more attractive surfaces between the Fe_3O_4 and PP phases. This behavior corroborates the storage modulus result. The highest E' value is observed in the Fe_3O_4 ternary system. This also may indicate that there are Fe_3O_4 nanoparticles in the PP phase.

In quaternary systems, a decrease in the storage modulus is observed, which is more significant in the system with the addition of the mixture conducted in an alkaline medium

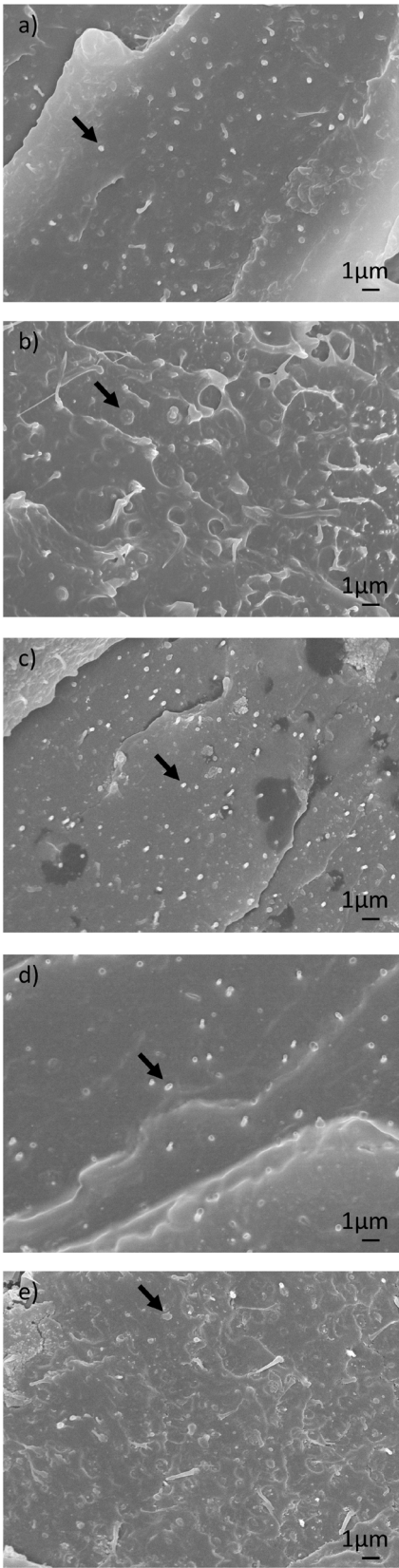


Figure 7. FEG-SEM images of a) PP/HDPE blend, and nanocomposites b) NC_Fe₃O₄; c) NC_GO; d) NC_MAM; and e) NC_MNM. Arrows pointed to HDPE dispersed phase.

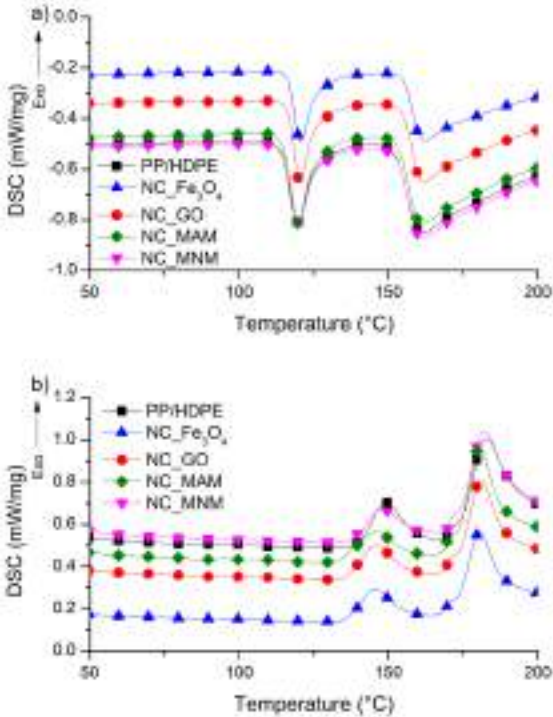


Figure 8. DSC curves of (a) heating and (b) cooling for the PP/HDPE blend and the nanocomposites.

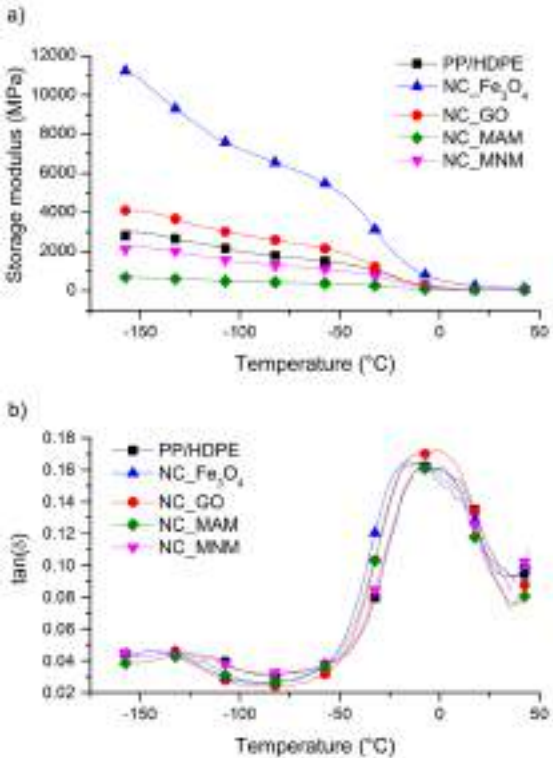


Figure 9. DMA results of the blend and nanocomposites: a) storage modulus (E') and b) $\tan\delta$ as a function of temperature.

(NC_MAM sample). The behavior of these systems can be linked to the amount of Fe₃O₄ in the mixture. According to the XPS results, the system with the highest amount of Fe₃O₄

nanoparticles (MNM sample) showed a minor reduction in the modulus. On the other hand, the NC_MAM sample, which has the highest amount of graphene oxide, showed the lowest E' value. Additionally, in the NC_MAM, the Fe_3O_4 nanoparticles were mainly on the oxide graphene surface, making it challenging to interact with the polymer. The results of the ternary systems show that Fe_3O_4 is more effective than graphene oxide in stress transfer and improves stiffness in PP/HDPE systems.

Figure 10 shows the variation of real permittivity (ϵ') with the frequency from the data obtained from the EIS analysis, and present the values obtained at 1 MHz, also known as the dielectric constant, for each sample.

Figure 10 show that higher dielectric constants were achieved after adding one nanoparticle: the dielectric constant almost doubled in the NC_ Fe_3O_4 (10.7) and tripled in the NC_GO sample (12.7). However, adding multiple nanoparticles does not positively affect the overall dielectric performance of the nanocomposite (NC_MAM, 6.8, and NC_MNM, 3.6, samples). This data was obtained in a frequency range characterized by the ionic polarization mechanism, which can be affected by carbon chains' stretching and elongation mechanism in polymeric blends³. Nanoparticles in the polymeric matrix add more polarization mechanisms than those already present in the carbon chains. So, it was expected that GO dispersion in the polymeric matrix had caused an increment in the capacity to store electrical energy by charge accumulation⁴. Similarly, iron oxide (II) adds more ionic polarization sites, improving charge accumulation through the material⁵. Comparing similar systems with the addition of graphene oxide²⁸ or iron oxide (II)²⁹ in PP blends a slight increase in the dielectric constant was observed: from 10 to 12.7 for NC_GO and from 5 to 10 for NC_ Fe_3O_4 samples. In both cases, the enhancement to dielectric constant values is explained by the polymeric matrix's high dispersion of the nanoparticles. This also promoted compatibilization and interfacial adhesion of different phases in the blend, observed by the microscopic analysis. This increment on interphase sites caused the insertion of new polarization mechanisms, which did not occur in the initial blend.

However, other effects should be considered when the quaternary composites are analyzed. Fe(II) in an aqueous solution may form metastable FeOH^+ and $\text{Fe}(\text{OH})_2$ phases according to Ph and aerated conditions. In this work, for the preparation of nanocomposite mixtures, Fe(II) was submitted to neutral or alkaline Ph in the presence of oxygen, which led to the formation of different Fe(II) species. In fact, XPS results showed different atomic ratios of Fe/C for the MAM and MNM mixtures. And, of course, all these aspects influence the dielectric properties of the final nanocomposites.

Although the presence of nanoparticles promotes the formation of polarization mechanisms that contribute to the real part of permittivity, hydrophilic nanoparticles contribute to dielectric loss since they form mechanisms for the dissipation of electromagnetic energy. This effect was also observed in nanocomposites with PP and silica, where nanocomposites with hydrophilic silica presented more significant dielectric losses, leading to the understanding that the presence of water and the greater state of agglomeration of the particles restrict the movement of the dipoles³⁰. So, in the quaternary nanocomposites, both effects are present.

In some cases, the atomic ratio of different elements in the nanocomposites was used to help explain some properties, such as hydrophilicity³¹; therefore, the same logic will be applied here to elucidate the differences observed for the dielectric constants. In NC_MAM and NC_MNM cases, the dielectric constant did not increase because of the amount of hydrolyzed iron oxide dispersed through the graphene oxide sheet. As observed in the XPS analysis, the proportion between iron and carbon was significantly different for MAM and MNM mixtures. The MAM sample, with a higher proportion of carbon atoms and well-dispersed iron nanoparticles, presented a higher dielectric constant than the MNM sample. On the other hand, in the MNM sample, the higher content of hydrolyzed iron nanoparticles has reduced the GO dispersion in the polymer matrix, creating agglomerates that are not effective in improving electrical (or dielectric) properties.

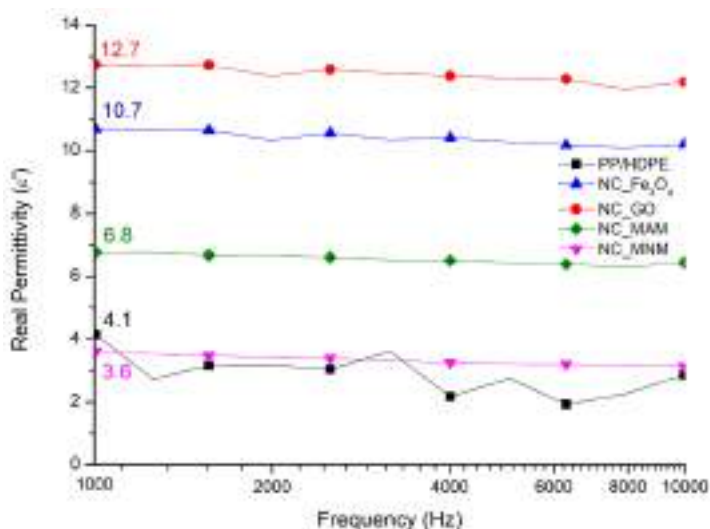


Figure 10. Dependence of real permittivity (ϵ') with the frequency calculated from EIS data, using Equation 2. Values inside the graph indicates ϵ' at 1 MHz.

4. Conclusions

The pH medium used to obtain mixtures of GO and Fe₃O₄ nanoparticles significantly impacts their chemical and morphological properties. The alkaline medium can promote hydrolysis and dissolution/redeposition reactions, decreasing the amount of iron nanoparticles in the final mixture. However, it is essential to use an alkaline medium to ensure the nanoparticle's dispersion and the iron nanoparticles remain on the surface of the GO.

In terms of nanocomposites, the addition of individual nanoparticles (ternary systems) yielded the best results. The Fe₃O₄ ternary system showed the highest storage modulus value, indicating that Fe₃O₄ is more effective than graphene oxide in stress transfer and improving stiffness in PP/HDPE systems. The dielectric constant almost doubled in the NC_Fe₃O₄ and tripled in the NC_GO sample. This increase in dielectric constant values may be related to the localization of nanoparticles in the polymeric matrix, which promotes compatibilization and interfacial adhesion of different phases in the blend. This, in turn, leads to the insertion of new polarization mechanisms that were not present in the initial blend.

In quaternary systems, the medium used also affects the nanocomposite properties. A decrease in the storage modulus was observed in both systems, but it was more significant when the mixture was added to an alkaline medium. This could be due to the iron nanoparticle quantities and their localization, which may delay stress transfer and improve stiffness in PP/HDPE systems. Nanoparticles in quaternary systems promote the formation of polarization mechanisms contributing to the real part of permittivity. Hydrophilic nanoparticles contribute to dielectric loss since they form mechanisms for the dissipation of electromagnetic energy. The presence of water and the greater state of agglomeration of the particles restrict the movement of the dipoles. The NC_MAM sample, with a higher proportion of carbon atoms and well-dispersed iron nanoparticles, showed a higher dielectric constant than the NC_MNM sample. On the other hand, in the NC_MNM sample, the higher content of hydrolyzed iron nanoparticles reduced the GO dispersion in the polymer matrix, creating agglomerates that are ineffective in improving electrical (or dielectric) properties.

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6. References

- Arora P, Zhang ZJ. Battery separators. *Chem Rev*. 2004;104(10):4419-62. <http://dx.doi.org/10.1021/cr020738u>.
- Chung TCM. Functional polyolefins for energy applications. *Macromolecules*. 2013;46(17):6671-98. <http://dx.doi.org/10.1021/ma401244t>.
- Dabbak SZA, Illias HA, Ang BC, Latiff NAA, Makmud MZH. Electrical properties of polyethylene/polypropylene compounds for high-voltage insulation. *Energies*. 2018;11(6):1448. <http://dx.doi.org/10.3390/en11061448>.
- Deshmukh K, Ahamed MB, Pasha SKK, Deshmukh RR, Bhagat PR. Highly dispersible graphene oxide reinforced polypyrrole/polyvinyl alcohol blend nanocomposites with high dielectric constant and low dielectric loss. *RSC Adv*. 2015;5(76):61933-45. <http://dx.doi.org/10.1039/C5RA11242G>.
- Radoń A, Łukowiec D, Kremzer M, Miśka J, Włodarczyk P. Electrical conduction mechanism and dielectric properties of spherical shaped Fe₃O₄ nanoparticles synthesized by co-precipitation method. *Materials*. 2018;11(5):735. <http://dx.doi.org/10.3390/ma11050735>.
- Mallesh S, Jang W, Kim KH. Facile synthesis of cube-like Fe₃O₄-graphene oxide nanocomposites with excellent microwave absorption performance. *Phys Lett A*. 2021;389:127069. <http://dx.doi.org/10.1016/j.physleta.2020.127069>.
- Arshad A, Iqbal J, Mansoor Q. Graphene/Fe₃O₄ nanocomposite: solar light driven Fenton like reaction for decontamination of water and inhibition of bacterial growth. *Appl Surf Sci*. 2019;474:57-65. <http://dx.doi.org/10.1016/j.apsusc.2018.05.046>.
- Hatel R, Goumri M, Ratier B, Baitoul M. Graphene derivatives/Fe₃O₄/polymer nanocomposite films: optical and electrical properties. *Mater Chem Phys*. 2017;193:156-63. <http://dx.doi.org/10.1016/j.matchemphys.2017.02.013>.
- Sharmila TKB, Antony JV, Jayakrishnan MP, Beegum PMS, Thachil ET. Mechanical, thermal and dielectric properties of hybrid composites of epoxy and reduced graphene oxide/iron oxide. *Mater Des*. 2016;90:66-75. <http://dx.doi.org/10.1016/j.matdes.2015.10.055>.
- Jayakumar OD, Abdelhamid EH, Kotari V, Mandal BP, Rao R, Jagannath J, et al. Fabrication of flexible and self-standing inorganic-organic three phase magneto-dielectric PVDF based multiferroic nanocomposite films through a small loading of graphene oxide (GO) and Fe₃O₄ nanoparticles. *Dalton Trans*. 2015;44(36):15872-81. <http://dx.doi.org/10.1039/C5DT01509J>.
- Barai DP, Bhavase BA, Saharan VK. Reduced graphene oxide-Fe₃O₄ nanocomposite based nanofluids: study on ultrasonic assisted synthesis, thermal conductivity, rheology, and convective heat transfer. *Ind Eng Chem Res*. 2019;58(19):8349-69. <http://dx.doi.org/10.1021/acs.iecr.8b05733>.
- Marcano DC, Kosynkin DV, Berlin JM, Sinitskii A, Sun Z, Slesarev A, et al. Improved synthesis of graphene oxide. *ACS Nano*. 2010;4(8):4806-14. <http://dx.doi.org/10.1021/nn1006368>.
- Jose S, Aprem AS, Francis B, Chandy MC, Werner P, Alstaedt V, et al. Phase morphology, crystallisation behaviour and mechanical properties of isotactic polypropylene/high density polyethylene blends. *Eur Polym J*. 2004;40(9):2105-15. <http://dx.doi.org/10.1016/j.eurpolymj.2004.02.026>.
- Zankana MM, Al-dalawy SM, Barzinjy AA. Synthesis and characterization of bio-nanocomposites: functionalization of graphene oxide with a biocompatible amino acid. *Hybrid Adv*. 2023;3:100070. <http://dx.doi.org/10.1016/j.hybadv.2023.100070>.
- Alkhouzaam A, Qiblawey H, Khraisheh M, Atieh M, Al-Ghouti M. Synthesis of graphene oxides particle of high oxidation degree using a modified Hummers method. *Ceram Int*. 2020;46(15):23997-4007. <http://dx.doi.org/10.1016/j.ceramint.2020.06.177>.
- Siburian R, Sihotang H, Raja SL, Supeno M, Simanjuntak C. New route to synthesize of graphene nano sheets. *Orient J Chem*. 2018;34(1):182-7. <http://dx.doi.org/10.13005/ojc/340120>.
- Johra FT, Lee JW, Jung WG. Facile and safe graphene preparation on solution based platform. *J Ind Eng Chem*. 2014;20(5):2883-7. <http://dx.doi.org/10.1016/j.jiec.2013.11.022>.
- Krishnamoorthy K, Veerapandian M, Yun K, Kim SJ. The chemical and structural analysis of graphene oxide with different degrees of oxidation. *Carbon*. 2013;53:38-49. <http://dx.doi.org/10.1016/j.carbon.2012.10.013>.

19. Lopes DV, Quina MJ, Frade JR, Kovalevsky AV. Prospects and challenges of the electrochemical reduction of iron oxides in alkaline media for steel production. *Front Mater.* 2022;9:1010156. <http://dx.doi.org/10.3389/fmats.2022.1010156>.
20. Duarte HA. Ferro: um elemento químico estratégico que permeia história, economia e sociedade. *Quim Nova.* 2019;42(10):1146-53. <http://dx.doi.org/10.21577/0100-4042.20170443>.
21. Carvalho D, Becker D, Dalmolin C. Effect of carbon nanotube location and dispersed phase on the dielectric properties of polypropylene/high-density polyethylene/carbon nanotube nanodielectrics. *J Appl Polym Sci.* 2022;139(29):e52656. <http://dx.doi.org/10.1002/app.52656>.
22. Zou H, Wang K, Zhang Q, Fu Q. A change of phase morphology in poly(p-phenylene sulfide)/polyamide 66 blends induced by adding multi-walled carbon nanotubes. *Polymer.* 2006;47(22):7821-6. <http://dx.doi.org/10.1016/j.polymer.2006.09.008>.
23. Mastalygina EE, Popov AA, Kolesnikova NN, Karpova S. Morphology, thermal behaviour and dynamic properties of the blends based on isotactic polypropylene and low-density polyethylene. *Int J Plast Technol.* 2015;19(1):68-83. <http://dx.doi.org/10.1007/s12588-015-9112-5>.
24. Villers D, Dosiére M, Paternostre L. New dynamical effects in spherulitic growth. *Polymer.* 1994;35(8):1586-92. [http://dx.doi.org/10.1016/0032-3861\(94\)90831-1](http://dx.doi.org/10.1016/0032-3861(94)90831-1).
25. Dong L, Olley RH, Bassett DC. On morphology and the competition between crystallization and phase separation in polypropylene–polyethylene blends. *J Mater Sci.* 1998;33(16):4043-8. <http://dx.doi.org/10.1023/A:1004474902723>.
26. Góra M, Coba-Daza S, Carmeli E, Tranchida D, Albrecht A, Müller AJ, et al. Surface-enhanced nucleation in immiscible polypropylene and polyethylene blends: the effect of polyethylene chain regularity. *Polymer.* 2023;282:126180. <http://dx.doi.org/10.1016/j.polymer.2023.126180>.
27. Huang DE, Kotula AP, Snyder CR, Migler KB. Crystallization kinetics in an immiscible polyolefin Blend. *Macromolecules.* 2022;55(24):10921-32. <http://dx.doi.org/10.1021/acs.macromol.2c01691>.
28. Wang D, Zhang X, Zha JW, Zhao J, Dang ZM, Hu G-H. Dielectric properties of reduced graphene oxide/polypropylene composites with ultralow percolation threshold. *Polymer.* 2013;54(7):1916-22. <http://dx.doi.org/10.1016/j.polymer.2013.02.012>.
29. Ahangaran F, Hassanzadeh A, Nouri S, Neisiany RE. Investigation of thermal and dielectric properties of Fe₃O₄/high-density polyethylene nanocomposites. *J Compos Mater.* 2017;51(28):3923-9. <http://dx.doi.org/10.1177/0021998317695419>.
30. Hui L, Schadler SL, Nelson JK. The influence of moisture on the electrical properties of crosslinked polyethylene/silica nanocomposites. *IEEE Trans Dielectr Electr Insul.* 2013;20(2):641-53.
31. Al-Gaashani R, Najjar A, Zakaria Y, Mansour S, Atieh MA. XPS and structural studies of high quality graphene oxide and reduced graphene oxide prepared by different chemical oxidation methods. *Ceram Int.* 2019;45(11):14439-48. <http://dx.doi.org/10.1016/j.ceramint.2019.04.165>.

Controlling Plasma-Functionalized Fillers for Enhanced Properties of PLA/ZnO Biocomposites: Effects of Excess L-Lactic Acid and Biomedical Implications

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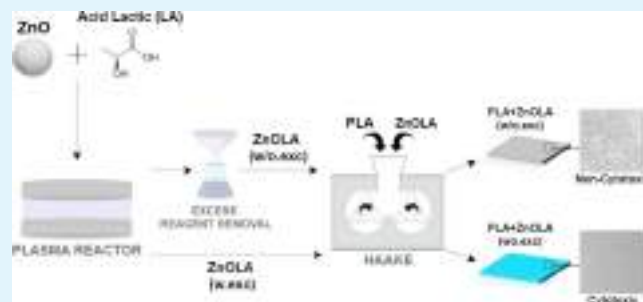
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ABSTRACT: Plasma surface treatment of ceramic particles has emerged as a promising approach for developing biocomposites intended for use in tissue engineering applications. Introducing functional groups on particle surfaces promotes changes in material surface properties, enhancing adhesion, biocompatibility, and reactivity. It can also mitigate degradation during the processing of polymer matrices in composite materials. Therefore, carefully choosing the functionalizing agent responsible for generating the functional groups and selecting appropriate functionalization parameters are significant steps in the plasma surface treatment process. However, in a tissue engineering context, an excess of the functionalizing agent can be harmful, increasing cell toxicity and inhibiting the stimulation of cell growth, consequently delaying or even hindering tissue regeneration. This article examines how the functionalizing agent excess of L-lactic acid (LA) applied in the plasma surface treatment of the filler affects the thermal, rheological, biological, and wettability properties of poly(lactic acid) (PLA) and zinc oxide (ZnO) biocomposites. The investigation reveals that the surface treatment effectively mitigated the catalytic effects of ZnO on PLA degradation during melt processing, regardless of the excess functionalizing agent. There was minimal impact on the material's rheological, thermal, and wettability characteristics, but the LA residue significantly influenced cell proliferation and the biological response. These findings show the importance of removing excess functionalizing agents to obtain biocomposites suitable for tissue engineering applications.

KEYWORDS: poly(lactic acid), zinc oxide, biocomposites, plasma surface treatment, excess functionalizing agent, washing, material properties



INTRODUCTION

Biomaterials are of considerable interest and play a key role in various biomedical applications, including regenerative medicine and tissue engineering (TE).¹ Within this field of research, living cells are grown in specific structures to create functional substitutes for damaged tissues or organs.^{1,2} Substantial advancements have been achieved in TE and contemporary medical practices, focusing on biomaterials tailored to integrate seamlessly with the body.³ Ensuring that the properties of implanted biomaterials remain stable during the treatment period is fundamental to guaranteeing continued function and tissue regeneration.⁴ In this context, the challenge is to develop functional biomaterials with adequate biological properties and a favorable structure capable of stimulating cell adhesion, growth, and the formation of new tissues.⁵

Biocomposites consisting of a biodegradable polymer matrix and bioceramics have proven effective in various biomedical applications.⁶ The biocompatibility and osteoconductivity of

bioceramics, combined with the relatively high mechanical properties of polymers, make them ideal for the development of implantable structures.⁷ Therefore, poly(lactic acid) and zinc oxide (PLA/ZnO) biocomposites are highly promising formulations. PLA is an ideal polymer matrix for medical devices and diverse other applications due to its excellent processability and unique properties, such as biocompatibility and biosorption.^{3,8} Furthermore, it is the most widely used biodegradable polymer, offering superior mechanical strength and elastic modulus compared to other biodegradable polymers, and it is generally recognized as safe (GRAS) by

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the FDA.⁹ Its biodegradation behavior is a critical attribute that underscores its suitability for medical and industrial applications, making it particularly attractive for the development of sustainable biomedical materials.^{9,10} Incorporating ZnO fillers further enhances the properties of the polymer matrix, giving it antibacterial properties and bioactivity capable of promoting the regeneration process of various types of cells and tissues.^{11,12} Due to these advantages, PLA/ZnO biocomposites have been targeted for different applications, especially in the biomedical field. Studies highlight their effectiveness in wound healing, bone regeneration, drug release, and implant coatings.¹² For instance, Radwan-Pragłowska et al. demonstrated that hybrid nanofibrous scaffolds, consisting of PLA doped with ZnO nanoparticles and acylated chitosan, support wound healing by ensuring adequate water vapor permeability and biodegradability, key factors for skin tissue engineering. The study also revealed that the improved conductivity imparted by ZnO enhanced cell proliferation during electrical stimulation.^{13,14} Harb et al. investigated PLA-based scaffolds with ZnO and tricalcium phosphate (TCP), finding that the addition of ZnO significantly increased surface roughness, which in turn enhanced protein adsorption by up to 85%. This improvement facilitated mesenchymal stem cell proliferation and promoted osteogenic differentiation, as evidenced by elevated alkaline phosphatase activity.¹⁵ These findings underscore the versatility and potential of PLA/ZnO biocomposites in diverse biomedical fields.

While PLA/ZnO biocomposites offer significant advantages, certain challenges still hinder their widespread application. For example, in TE, achieving an optimized ratio between the inorganic filler and the polymer matrix and its availability is essential for bone formation and regeneration, as its contact with cells and fluids can be hindered, and the degradation rate must be tailored with tissue restoration and healing.^{15,16} Therefore, material stability during processing and when implanted, is a critical factor in controlling the degradation of PLA/ZnO biocomposites.¹⁷ Recent studies have reported significant degradation of the PLA polymer matrix, particularly when in the molten state, driven by multiple mechanisms catalyzed by ZnO. Qu et al. demonstrated that incorporating ZnO nanoparticles can catalyze the hydrolytic degradation of PLA even at temperatures below its glass transition temperature (T_g). According to the authors, the activation energy for the hydrolysis of PLA favored by ZnO is around 38% lower than the hydrolysis of neat PLA.¹⁸ Hydrolytic degradation of PLA is facilitated by the carboxyl end groups generated after the cleavage of the ester bond, leading to the formation of acidic products that can further accelerate the deterioration of the polymer.¹⁹ Simultaneously with hydrolytic degradation, PLA degradation occurs through the release of Zn^{2+} ions, which reduce the activation energy of the process, especially under conditions of high shear rates and temperature.²⁰ Lizundia et al. propose that, under these conditions, intermolecular depolymerization and transesterification reactions are triggered, resulting in a severe reduction in the molar mass, thermal stability, and physical properties of PLA.²¹ Similar results were already observed by our group when melt compounding PLA with Biosilicate, which also, during processing, can release significant cations (Ca^{2+}) and results in considerable thermoregulation.¹⁷

One promising strategy to reduce the autocatalytic degradation of PLA in biocomposites with ZnO is to modify

the surface of the particles. This approach, particularly when using plasma surface treatment, has emerged as an effective alternative for biomedical applications as it avoids the need for potentially toxic solvents.¹⁹ Plasma surface is a versatile treatment that allows the introduction of specific groups, such as carbonyls, amines, and hydroxyls, onto the surface of the particles.^{22,23} This provides a protective effect that can control the release of degradation catalyst ions, thereby increasing the stability of the fillers and their interaction with the polymer.¹⁷ The incorporation of functional groups generally occurs through the dynamic balance between the material's surface conditioning and active species in the plasma activation medium. When these activated species reach the surface of the substrate, the breaking of the molecular chain can result in the formation of new functional groups. Therefore, the recombination of atoms to activate the surface depends on the functionalizing agent, the selection of which must consider the desired properties of the particles and the process conditions.^{24,25}

Incorporating carboxylic acid functional groups, derived from L-lactic acid and acrylic acid, for example, is an attractive alternative for biomedical applications due to their known ability to promote cell adhesion, proliferation, and differentiation.²⁵ Previous studies have revealed that acrylic acid plasma-derived polymers can sustain high levels of cell attachment, both of cell lines and primary cells.²⁶ Furthermore, research highlights the potential of these functional groups to reduce degradation effects in PLA polymer matrices when combined with high-bioactive particulate biocomposites. Specifically, incorporating carboxylic groups can decrease water absorption on particle surfaces and prevent the release of ions that catalyze degradation reactions under process conditions.^{17–20} However, the literature indicates that the main difficulty in functionalizing plasma with these agents lies in the stability of the treated material in aqueous environments, such as in implant conditions.²⁷ When carboxylic groups are deposited under inadequate operating conditions, the rate of incorporation of functional groups is reduced, and the medium is also acidified. This acidification is of particular concern in biomedical applications due to its adverse effects on cell viability and proliferation.^{27,28} Therefore, the central question is how the excess of functionalizing agents affects the rheological, thermal, wettability, and biological properties of the biocomposite with plasma-functionalized fillers. Plasma functionalization is a nonequilibrium reaction that may not entirely consume all the initially added reagents, resulting in an excess of these substances after the process. Additionally, it is essential to control the byproducts that promote acidity in the medium to develop biomaterials suitable for biomedical applications.

Given these considerations, this study aims to provide experimental evidence on the influence of residual L-lactic acid (LA), resulting from the plasma surface modification process in the absence of a washing step, on the properties of PLA/ZnO biocomposites and its impact on the material's applications. For this purpose, two types of PLA/ZnO biocomposites with plasma-functionalized fillers were produced: one with an excess of LA in the formulation, present in a form not chemically bound to ZnO, and one without an excess. Both formulations and the control samples (PLA and nonfunctionalized PLA/ZnO) were characterized to compare the biocomposites' rheological, thermal, and wettability properties. Additionally, biological analyses were conducted to assess the cytotoxicity

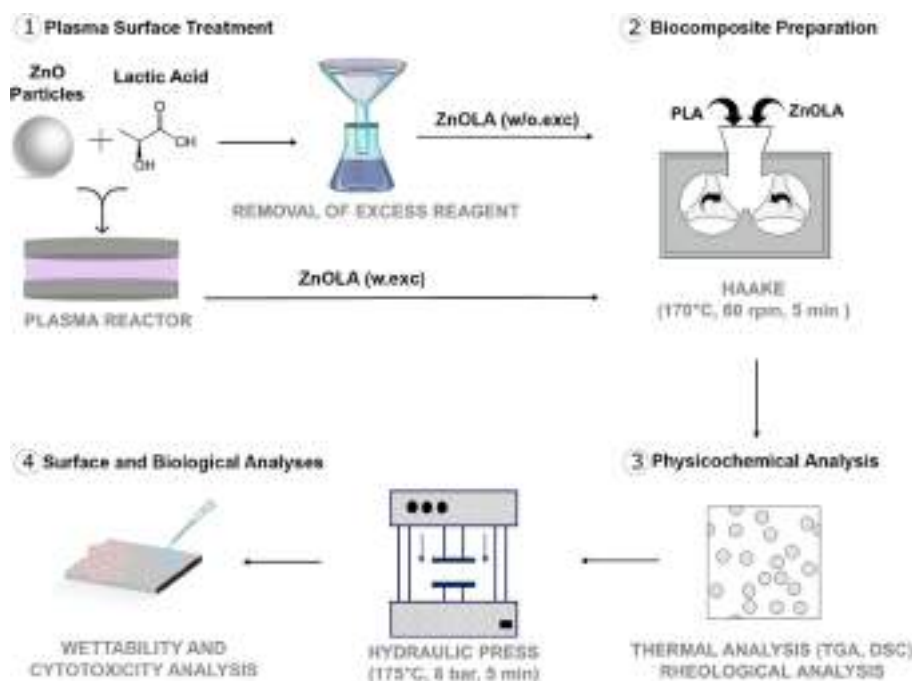


Figure 1. Schematic representation of the experimental procedure: (1) Plasma treatment of ZnO with L-lactic acid (LA), followed by washing (for samples without excess LA). (2) Incorporation into the PLA matrix. (3) Physicochemical analysis. (4) Surface and biological analyses of biocomposites.

and cell proliferation of the biocomposites with and without excess, considering their potential application in biomedical contexts.

EXPERIMENTAL SECTION

Materials. The Poly(L-lactic acid) (PLA, Biopolymer, 2003D) used in this study was supplied by NatureWorks (Ingeo). According to the manufacturer's specifications, it has a density of 1.24 g cm^{-3} , a glass transition temperature (T_g) between 55 and 60°C , and a melting temperature (T_f) of between 145 and 160°C .²⁹ Additionally, gel permeation chromatography (GPC) analysis performed by Backes et al. reported a number-average molecular weight (M_n) of 118,600 g/mol and a weight-average molecular weight (M_w) of 168,000 g/mol for PLA of the same grade (2003D) and manufacturer.¹⁷

The zinc oxide (ZnO) used as the bioceramic filler was supplied by Interprise with a purity of 99% and an average particle size of $44 \mu\text{m}$. L-lactic acid (LA) with 85% purity (Aldrich Chemistry) was used as the functionalizing agent for ZnO surface modification through plasma treatment.

Methods. The experimental procedure involved a multistep process to prepare and characterize PLA/ZnO biocomposites (Figure 1). To mitigate the catalytic degradation of PLA induced by ZnO during melt processing, the ZnO particles were plasma-treated using LA as a functionalizing agent. To evaluate the effect of excess LA on the biocomposites' properties, the samples were divided into two groups: one was washed to remove excess LA, while the other remained unwashed. The treated ZnO particles were subsequently incorporated into a PLA matrix via melt mixing. The resulting biocomposites underwent further processing, including hot pressing to obtain the final samples. A comprehensive characterization encompassed physicochemical analyses, as well as biological evaluations such as wettability and cytotoxicity assays.

Plasma Surface Treatment. A solid mixture of zinc oxide and L-lactic acid (ZnOLA) in a 30/70 mass proportion was manually mixed in a beaker using a spatula until no visual segregation was observed. This mixture was then dried at room temperature (RT) for 24 h. To achieve optimal homogeneity, ZnO was incrementally incorporated into LA. The resulting mixture exhibited consistency resembling a relatively thick paste. After drying at room temperature (RT), the

mixture was ground using a mortar and pestle for 2 min to ensure a finer particle size and enhance material homogeneity. Then, the mixture was inserted into a homemade capacitively coupled plasma (CCP) reactor to functionalize the zinc oxide. At a base pressure of 2×10^{-1} Torr, argon gas was introduced at a flow rate of 36.5 sccm, reaching a working pressure of 9×10^{-1} Torr, measured by a Pirani gauge coupled to the reactor. The argon flow was maintained for 15 min to purge the chamber before starting the plasma discharge. Then, the RF plasma power of 35 W was chosen based on previous work, and the treatment was carried out for 5 min.²³

After functionalization, the plasma-treated sample was divided into two groups. One group was subjected to vacuum filtration to remove excess LA from the particles. This group was then stirred in distilled water for 12 h to remove residual LA further, followed by additional vacuum filtration and washing with distilled water. The washed samples were then dried at 70°C for 1 h before being stored in a desiccator. The second group, which retained excess functionalizing agent, was immediately placed into the desiccator after plasma treatment.

Characterization of ZnO Filler. The ZnO was characterized by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) to confirm the functionalization of the ZnOLA particles. XPS analyses were performed using a UNI-SPECS UHV system and a Thermo Fisher Scientific (K-Alpha) spectrometer, operating at a base pressure below 5×10^{-7} Pa. As the excitation source, the X-ray Al K_α ($h\nu = 1486.6 \text{ eV}$) was used with the pass energy set to 200 eV for survey and 20 eV for high-resolution scans. The inelastic noise of the high-resolution C 1s, O 1s, and Zn 2p_{3/2} spectra was subtracted using the Shirley method. A flood gun was employed for charge shift correction, using the C 1s hydrocarbon component (C=C/C-CH) at 284.8 eV as a reference. The composition was determined by the relative proportions of peak areas, which were corrected using Scofield atomic sensitivity factors, with an accuracy of $\pm 5\%$. The spectra were deconvoluted using a Voigtian-type function, with Gaussian (70%) and Lorentzian (30%) combinations. The full width at half-maximum was varied between 1.2 and 2.2 eV, and as a criterion for assigning the fitted components, a chemical shift $>0.5 \text{ eV}$, relative to the C-CH (284.8 eV) and ZnO (1022.1 eV) references, was used.

FTIR spectra of samples in potassium bromide (KBr) tablets were obtained using a Bruker device (INVENIO-S). 32 scans were performed in the 4000–400 cm^{-1} region, with a resolution of 4 cm^{-1} .

Thermogravimetric analysis (TGA) was performed using a NETZSCH STA 449C analyzer. The technique identifies the functional groups bonded to the material's surface by analyzing mass changes as a function of temperature. The analysis was conducted at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ from 25 to 1000 $^{\circ}\text{C}$ under a synthetic air flow.

Biocomposites Preparations. The PLA/ZnO composite formulations were processed using an internal mixer coupled to a Thermo Scientific Rheomix 600p HAAKE torque rheometer. This equipment is equipped with counter-rotating and semi-interpenetrating roller-type rotors, which homogenized the compositions at a temperature of 175 $^{\circ}\text{C}$ for 5 min at a speed of 60 rpm. Four samples were processed, distinguished by the type of surface treatment applied to the ZnO load and the post-treatment wash. Table 1 presents the samples

Table 1. Sample Descriptions and Identifications

Description	Sample
Pure PLA	PLA
ZnO without LA excess	ZnOLA
PLA with 2.5% untreated ZnO	PLA + 2.5% ZnO
PLA with 2.5% ZnO with LA excess	PLA + 2.5% ZnOLA (w.exc)
PLA with 2.5% ZnO without LA excess	PLA + 2.5% ZnOLA (w/o.exc)

processed along with their corresponding descriptions. After processing in the internal mixer, the samples were divided into two portions. One was subjected to thermal and rheological analysis, while the other underwent compression molding to produce test specimens. A hydraulic press model (Marconi, MA098/A) was used for

compression molding, maintaining a constant temperature of 175 $^{\circ}\text{C}$ and applying a pressure of 8 bar for 5 min, then cooling until RT. The specimens obtained from this process were used in the contact angle tests and biological analyses.

The processed samples were subjected to thermal, rheological, morphological analysis, wettability, and biological characterizations to assess the influence of excess functionalizing agents on the materials' properties.

Physicochemical Analysis. Thermal Analyses. TGA of the biocomposite samples was performed using a TGA 4000 analyzer from PerkinElmer. Approximately 10 mg of each sample was analyzed, with the temperature increasing from room temperature to 800 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C min}^{-1}$, under a nitrogen atmosphere.

For the Differential Scanning Calorimetry (DSC) analysis, a TA Instruments Q2000 calorimeter was used, with a continuous nitrogen flow of 50 mL/min. The procedure consisted of two heating stages, ranging from 0 to 200 $^{\circ}\text{C}$, at a heating rate of 10 $^{\circ}\text{C min}^{-1}$. The transition temperatures and enthalpy data of the biocomposites were determined from the results of the second heating. The degree of crystallinity was calculated during the second heating cycle using eq 1, where ΔH_m is the enthalpy of crystalline fusion, ΔH_c is the enthalpy of cold crystallization, ΔH_{m0} is the theoretical enthalpy of crystalline fusion for 100% crystalline PLA (93 J g^{-1}),³⁰ and x is the mass fraction of biofillers incorporated into the polymer matrix.

$$X_c(\%) = \frac{(\Delta H_m - \Delta H_c)}{\Delta H_{m0}(1 - x)} \times 100\% \quad (1)$$

Rheological Analysis. The steady-state rheological properties of the samples were assessed through parallel plate rheometry. The objective of the analysis was to compare the viscosity levels of the materials under low shear rates (ranging from 0.01 to 100 s^{-1}). For this purpose, a TA Instruments AR G2 controlled stress rheometer

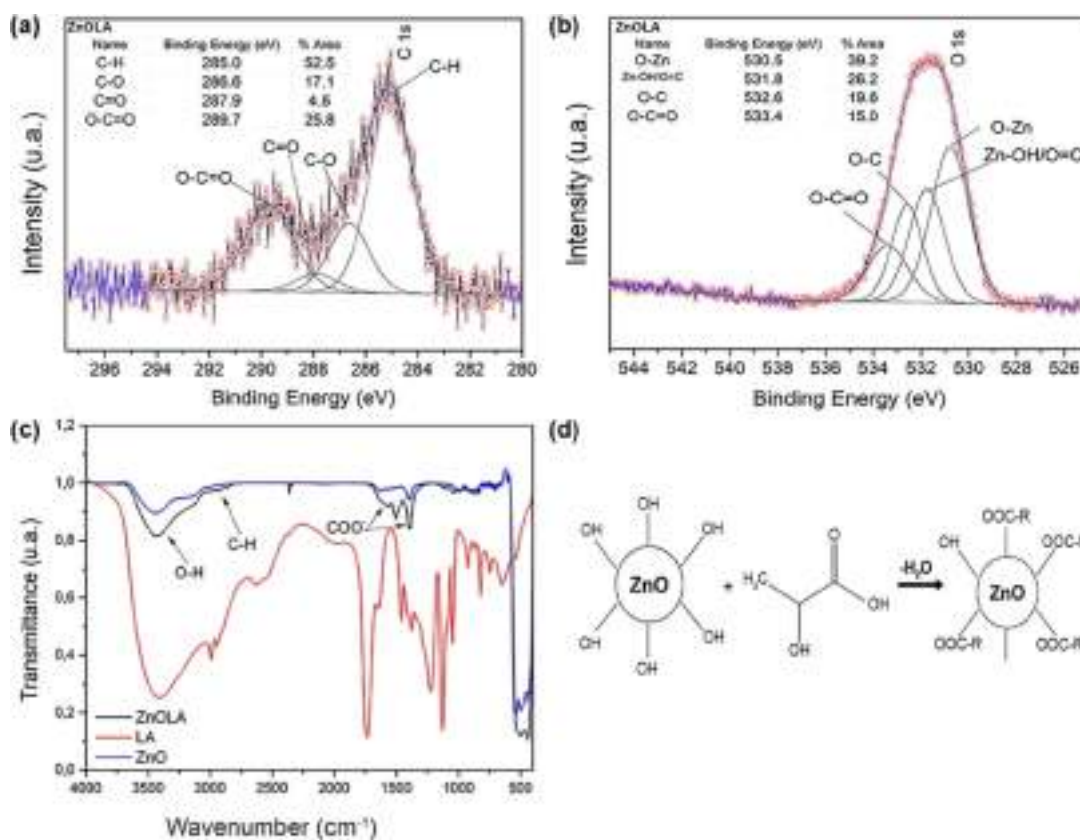


Figure 2. Characterization of ZnO Functionalization: (a) C 1s: 4.6% increase in carbonyl (C=O) from lactic acid (LA). (b) O 1s: increased O content (53%) and O–Zn bonds. (c) FTIR spectra. (d) Scheme of ZnO–LA preferential complexation. Figure 2d was adapted from the reference by Tang et al.³⁸

was used, equipped with plates with a diameter of 25 mm and a distance between the plates of 1 mm, operating under an inert atmosphere of nitrogen (N₂) at a temperature of 165 °C.

Morphological Analysis. Scanning electron microscopy (SEM) was performed to evaluate the dispersion and distribution of ZnO and ZnOLA particles within the PLA matrix. The analysis utilized a Tescan Mira SEM, equipped with a Field Emission Gun (FEG), operated at an acceleration voltage of 5 kV. Initially, the samples were compressed using a hydraulic press (model MA098/A, Marconi) at 175 °C under a pressure of 7 bar for 5 min. Subsequently, the samples were cryogenically fractured along the cross-section to expose the internal structure, facilitating direct observation of the fracture surface for detailed morphological characterization.

Surface and Biological Analyses. Wettability Analysis. Contact angles were measured on films prepared by pressing the samples using a hydraulic press (Marconi MA098/A) at 175 °C under 9 bar for 5 min. Wettability measurements of the films were conducted using a Biolin Scientific optical tensiometer (Attension TF3000-PLUS) with 7 µL drops of distilled water, and the angles were analyzed using OneAttension software.

Cytotoxicity Analysis. Preosteoblastic mouse cells MC3T3 were cultured in a medium containing 89% v/v α-MEM (Gibco) supplemented with 10% fetal bovine serum (FBS, Vitrocell) and 1% antibiotic-antimycotic (Vitrocell) in an incubator (Series II 3110, Thermo Fisher Scientific) at 37 °C, humidified and containing 5% CO₂.

Prior to biological tests, the PLA and biocomposites were sterilized by immersing them in 70% alcohol under UV light on both sides for 15 min each; following, they were rinsed with phosphate-buffered saline (PBS) to remove the alcohol. After sterilization, the samples were placed in a 48-well plate and left in contact with 500 µL of culture medium for 24 h in an incubator at 37 °C and 5% CO₂. After this time, the samples were transferred to a new culture plate, and 500 µL of an osteoblastic cell solution with 50,000 cells was added to each well, and the plates were incubated for 1, 7, and 14 days. The medium was changed every 2–3 days. A working solution was prepared for cell proliferation assay by diluting resazurin solution (#R7017, Millipore-Sigma) in a culture medium (1:9 dilution). After each time point, the medium was removed, 500 µL of the working solution was added to each well, and the plate was incubated at 37 °C for 4 h in the dark. Subsequently, 100 µL of the solution from all samples was transferred to a black plate where the fluorescence end point (560 nm/590 nm) was measured using a microplate reader (SpectraMax M5). Three samples of each composition were analyzed, along with three negative controls containing a cell-free resazurin solution. An autoclaved resazurin solution was used as a positive control to estimate cell viability. The results are presented in reduction percentage (%) which represents the relationship between the end point fluorescence measured in the samples (with cells) and the fluorescence of the cell-free resazurin solution (blank) and the autoclaved resazurin solution (positive control).

The cells' characteristics on the samples' surfaces after 14 days were assessed by scanning electron microscopy (SEM). A sample of each was removed to a new plate and washed with PBS solution. Then, 1 mL of 10% aqueous paraformaldehyde solution was added to each sample and kept for 30 min for cell fixation. Subsequently, the samples were washed with PBS and underwent a dehydration series using 50, 70, 90, and 100% ethanol concentrations. As a final step, the specimens were dried at room temperature, transferred to a stub, coated with a thin layer of gold, and analyzed using a Philips SEM model XL-30 FEG, operating at an acceleration voltage of 5 kV.

RESULTS AND DISCUSSION

ZnO Functionalization. XPS analyses were carried out for ZnO and the plasma-treated ZnOLA sample without excess LA to verify the effectiveness of the filler's functionalization. Figure 2 and Table 2 summarizes the results obtained. The main components present in ZnO are the elements O 1s and Zn 2p, in addition to a contribution of the element C 1s, common in the literature, from impurities and

Table 2. Atomic Percentage of Carbon (C 1s), Oxygen (O 1s) and Zinc (Zn 2p); and Peak Area Percentage of Functional Groups Related to C 1s and O 1s^a

Sample	Concentration (at. %)		Peak area percentage of functional groups (area %)						
	Zn 2p	O 1s	C 1s	C-H (C 1s)	C-O (C 1s)	C=O (C 1s)	O-C=O (C 1s)	O-Zn (O 1s)	Zn-OH/O=C (O 1s)
ZnO	41	46	13	54.0	25.8	4.6	20.2	57.4	21.6
ZnOLA	30	53	17	52.5	17.1		25.8	39.2	26.2
^a Error: ±5%.									
									O-C≡O (O 1s)
									16.8
									19.6
									4.2
									15.0

surface contamination by hydrocarbons.^{31–33} After plasma treatment, an increase in the atomic percentage of oxygen relative to zinc was observed in the ZnOLA sample, with an O/Zn ratio of 1.8 against 1.1 for the ZnO sample. In our other work,³² the same behavior was observed and attributed to a sign of the particles' functionalization. In addition, there is an increase in carbon contribution. Both changes indicate functionalization through oxygen and carbon elements in different bonds through different functional groups.^{23,33}

The high-resolution C 1s spectrum for the treated sample (Figure 2a) indicates 4.6% of carbonyl groups that were nonexistent in ZnO, which comes from the functionalizing agent lactic acid. Furthermore, as the presence of oxygen atoms increases by 7 at. % in the plasma-treated sample (53 at. % against 46 at. %), the percentage of the O–Zn bond from high-resolution O 1s spectrum, as Figure 2b decreases from 57.4% (ZnO sample) to 39.2% (ZnOLA), which indicates the involvement of oxygen atoms forming bonds with other elements after treatment. In this regard, the significant increase related to functional groups from O 1s is assigned to the O–C=O group, which almost triples the original value, increasing from 4.2 to 15.0 in area percentage.

The FTIR spectra of the treated sample, shown in Figure 2c, exhibit the characteristic band of ZnO in the region below 650 cm^{-1} (Zn–O bond). C–H bonds are observed around 3000 cm^{-1} , and significant peaks between 1600 and 1500 cm^{-1} and between 1400 and 1300 cm^{-1} are attributed to the asymmetric and symmetric stretching of the carboxylic acid salt functional group (COO^-), respectively.³⁴ Carboxylic acids form stable covalent bonds with metal oxide particles, mainly through carboxylate groups, and experiments indicate that the COO^- group is a suitable anchor for binding to ZnO.³⁵ Therefore, this result suggests that LA binding to ZnO occurs preferentially by forming surface bonds through the COOH group. The mechanism probably involved with the formation of chemical bonds between ZnO and LA is a dehydration reaction between the carboxyl group of lactic acid and hydroxyl groups on the surface of ZnO particles.³⁶ The C=O bands (carboxylic groups) at 1733 cm^{-1} and C–O (elongation) between 1300 and 1000 cm^{-1} , characteristic of LA, are not present, indicating both that the COOH group is in its deprotonated form and that the predominance of insertion in this plasma functionalization process is of C–H and carboxylate (COO^-) functional groups.³⁶ This result agrees with the literature, which reports that when salt comes from a carboxylic acid, it is expected that the carboxylic group bands C=O, C–O, and O–H, will be replaced by two other carbon–oxygen bands, identified as carboxylic acid salts.³⁷

The displacement of the carboxylate bands in the spectra is evidence for forming metal complexes to the Zn^{2+} cation, which concludes that coordination complexes were formed.³⁷ Thus, based on the results obtained by XPS and FTIR analyses, it was possible to propose a hypothesis of a preferential mechanism through which ZnO particles interact with LA. Hydroxyl groups present on the surface of particles due to the impact of moisture or water interact with the carboxylate ions coming from the functionalizing agent LA and form a complex with the Zn^{2+} ions present on the ZnO surface due to the oxygen vacancies generated in the particle by the plasma treatment.^{18,38} The functional groups are grafted onto the particle surface through several points, schematically illustrated in Figure 2d.

Figure 3 presents the TGA curve for both functionalized and nonfunctionalized ZnO samples. According to Barrak et al., the mass loss observed in TGA can be used to assess the quantity of functionalizing agents attached to modified particles.³³ No mass loss was detected for the pure ZnO sample, confirming its thermal stability. In contrast, the washed ZnOLA sample (without excess) exhibited a thermal decomposition event between 200 and $300\text{ }^\circ\text{C}$, as indicated by the derivative thermogravimetry (DTG) curve. Unlu et al. reported that mass losses in metal oxides typically occur only above $500\text{ }^\circ\text{C}$.³⁹ This suggests that the decomposition event observed in the washed ZnOLA sample is due to the functional groups of LA adhered to the ZnO surface. Based on this analysis, the LA content attached to the surface of the particles is estimated to be approximately 2%. Since the functionalization process was conducted with a 70:30 ZnO/LA

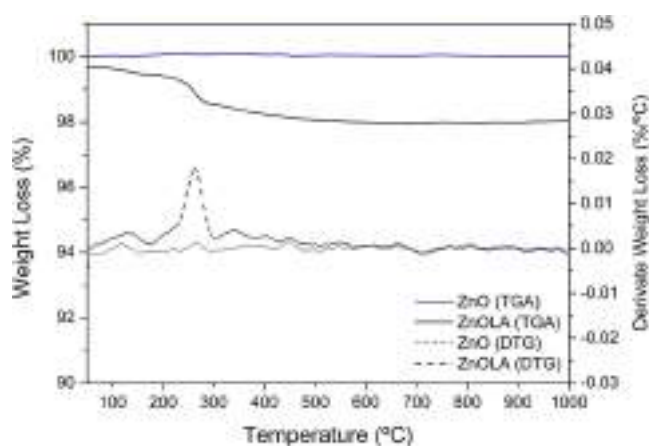


Figure 3. Thermogravimetry analysis (TGA) of nonfunctionalized and functionalized ZnO.

mass ratio, the nonwashed ZnOLA sample is expected to contain approximately 30% LA. This total amount consists of two fractions: 2% of LA bound to the ZnO particles and the excess LA not removed during the washing process.

Processing and Rheological Analysis of Biocomposites.

Torque rheometry was utilized to process the biocomposite formulations and to provide an initial evaluation of the impact of bioceramic fillers on the rheological behavior of the PLA polymer matrix. Figure 4a illustrates torque curves (N_m) versus time (minutes) for the biocomposites processed. According to the results, PLA has an equilibrium torque of approximately 4 N m after 5 min. In contrast, the non-surface-modified PLA/ZnO biocomposites (PLA + 2.5% ZnO) exhibited the lowest equilibrium torque, registering a value close to 0.5 N m at the end of the mixture process, signifying an 87.5% reduction compared to the unfilled PLA. The biocomposites containing plasma-functionalized ZnO (PLA + 2.5% ZnOLA (w/o.exc) and PLA + 2.5% ZnOLA (w.exc)) showed a less significant torque reduction than the composite with unfunctionalized ZnO.

The results confirm that incorporating plasma surface-modified ZnO allows the production of biocomposites that yield a higher torque after complete melting when contrasted with biocomposites featuring untreated filler. Quantitatively, PLA/ZnO biocomposites with plasma-functionalized filler, both with and without excess LA, showed an increase in equilibrium torque of 81% and 86%, respectively, compared to the composite without treated filler. Considering the correlation between material viscosity during processing in the internal mixer and torque on the rotors during the shear interval, the observed decrease in torque in samples with incorporated ZnO, whether surface-modified or not, suggests potential degradation in the polymer matrix during the process. Previous studies have also observed a reduction in torque values during the mixing of PLA/ZnO biocomposites. For instance, Harb et al. reported that ZnO in PLA at high processing temperatures can cause significant polymer degradation through catalyzed depolymerization, substantially decreasing thermal and mechanical properties.^{15–40} Such results highlight the need to understand how various filler treatments impact the overall material integrity during processing.

The samples' rheological behavior was investigated using parallel plate rheometry under steady-state conditions to assess viscosity changes linked to PLA degradation. This analysis allowed for a better understanding of the influence of bioceramic fillers on the degradation process during melt processing. Figure 4b presents viscosity curves relative to a shear rate ranging from 0.01 to 100 s^{-1} . All biocomposites exhibited nearly Newtonian fluid behavior between 0.01 and 10 s^{-1} , with viscosity remaining constant as the shear rate increased. However, viscosity values differed among the biocomposites in this plateau region.

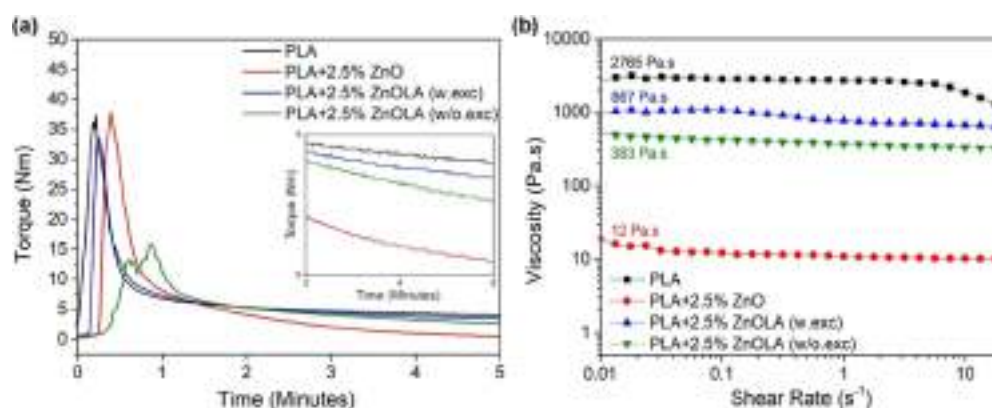


Figure 4. Rheological analysis: (a) torque versus time for the samples. (b) Viscosity versus shear rate from parallel plate rheometry.

PLA exhibited the highest viscosity in the Newtonian regime at the low shear rate (η_0), approximately 2765 Pa s. The composite PLA + 2.5% ZnO showed the lowest viscosity in the Newtonian plateau (12 Pa s), representing a 99% reduction compared to the polymer. Intermediate η_0 values were observed for biocomposites with plasma-treated particles. Specifically, the viscosity for biocomposites PLA + 2.5% ZnOLA (w/o.exc) and PLA + 2.5% ZnOLA (w.exc) were 867 and 393 Pa s, respectively, indicating a reduction in η_0 of 68% and 85% compared to PLA. These results indicate that the untreated ZnO composite samples degraded considerably. In contrast, plasma treatment, regardless of the excess functionalizing agent, resulted in lower polymer degradation. These results, observed in parallel plate rheometry, were further corroborated by the rheological behavior obtained from torque rheometry.

Shojaeiarani et al. investigated the rheological behavior of PLA/ZnO biocomposites, analyzing the complex viscosity as a function of angular frequency. They observed that as the ZnO concentration increased (from 0.5% to 1.5%), the biocomposite's viscosity decreased in the Newtonian plateau region compared to pure PLA. The authors suggested that the higher viscosity of the sample with the lower ZnO content indicates a more efficient interaction between the nanoparticles and PLA, which could affect particle dispersion or aggregation, influencing the shear modulus. Shojaeiarani et al. also noted that at high angular frequencies (high shear rates), the viscosities of the different formulations tended to overlap, with the composite containing a higher percentage of ZnO showing a lower viscosity.⁴¹ In the present study, it is expected that under processing conditions, such as high shear rates, the viscosities of the biocomposites will tend to converge. However, biocomposites with plasma-treated fillers are expected to exhibit slightly higher viscosity, which could provide greater stability and control during processing. In contrast, biocomposites with untreated fillers tend to be more brittle, which may compromise their mechanical properties, highlighting the importance of functionalization for improved stability and performance of the material.

The presence of excess LA had a significant influence on the viscosity of PLA + 2.5% ZnOLA biocomposites: the composite with excess LA (PLA + ZnOLA (w.exc)) had a η_0 of 867 Pa s. In comparison, the one without excess LA (PLA + ZnOLA (w/o.exc)) had a η_0 of 393 Pa s, representing a reduction of approximately 55%. This phenomenon occurs because large, poorly dispersed filler agglomerates can obstruct polymer flow, increasing flow resistance. The matrix–charge interaction in biocomposites is significantly influenced by the polymer matrix's structure and the filler surface's characteristics, such as area, roughness, and chemical state.^{42,43} The surface treatment of the filler affects its dispersion and tendency to agglomerate, factors that primarily govern the filler–matrix interaction.⁴² In the case of the biocomposites analyzed, it was found that the excess of LA significantly influenced the poor dispersion and distribution of the particles. Figure 5 shows SEM micrographs of the surface fracture of the biocomposites analyzed, where the PLA + 2.5% ZnOLA (w.exc) sample exhibited poor particle

dispersion and the presence of agglomerates. These morphological observations are consistent with the particle size distribution analysis, also shown in Figure 5. The histogram analysis revealed differences in the dispersion of ZnO particles in the PLA samples. The PLA + 2.5% ZnO sample showed the best homogeneity, with a good incorporation of the particles into the polymer matrix. In contrast, the PLA + 2.5% ZnOLA (w/o.exc) sample exhibited a slight tendency to form agglomerates, which can be observed by the higher incidence of particles with diameters greater than 10 μm . The PLA + 2.5% ZnOLA (w.exc) sample demonstrated less efficient dispersion, with larger and more agglomerated particles, showing a more pronounced shift in the distribution toward higher values, with agglomerates reaching sizes of up to 60 μm . These results suggest that the washing process to remove excess LA improves the dispersion and distribution of the particles, as it helps prevent agglomeration and enhances the overall homogeneity of the biocomposite.

Thermal Analyses. The thermal stability of the samples was evaluated by TGA under a nitrogen atmosphere, generating the curves shown in Figure 6a (TG) and Figure 6b (DTG). The PLA sample exhibited a single thermal degradation event with an onset temperature (T_{onset}) of 312 °C and a peak temperature (T_{peak}) of 340 °C. This is attributed to its simple chemical structure, mainly consisting of LA monomers in concordance with previously reported results.⁴⁴ However, the decomposition temperatures (T_{onset} and T_{peak}) decreased with the addition of untreated and treated ZnO, indicating the acceleration of PLA degradation with the incorporation of fillers. Comparing PLA with PLA + 2.5% ZnO, PLA + 2.5% ZnOLA (w.exc), and PLA + 2.5% ZnOLA (w/o.exc) samples revealed decreases of 46, 57, and 38 °C in T_{onset} temperatures, respectively. This trend of decreased thermal stability is also evident when comparing the T_{peak} temperatures in the DTG analysis. The reduction in thermal stability correlated with the observed weight loss attributed to the breakdown of fragile chemical bonds within the molecular chains of the composite due to the degradative processes occurring within the composite mixture.⁴⁵

Another critical point that characterizes thermal behavior is the pattern of the TGA curve, which describes the overall degradation mechanism. In the biocomposites, weight loss occurs in two stages: the first between 250 and 270 °C and the second around 380–400 °C. In the first thermal event, the expected decomposition of the samples is evidenced by the reduction in mass as the temperature increases. In the second thermal event, there is a further decrease in the mass of the biocomposites, albeit smaller. This behavior was also observed in TGA analyses of similar formulations in previous research.^{40–46} This behavior is probably due to the decomposition and desorption of anchored groups, such as those from the functionalizing agent on the ZnO surface or the adsorption of PLA molecules on the filler.¹⁸

The comparison between the PLA + 2.5% ZnOLA (w/o.exc) and PLA + 2.5% ZnOLA (w.exc) reveals that the biocomposite without excess LA exhibits higher thermal stability, with a T_{onset} of 273 °C and T_{peak} of 307 °C, compared to 255 and 298 °C for PLA + 2.5% ZnOLA

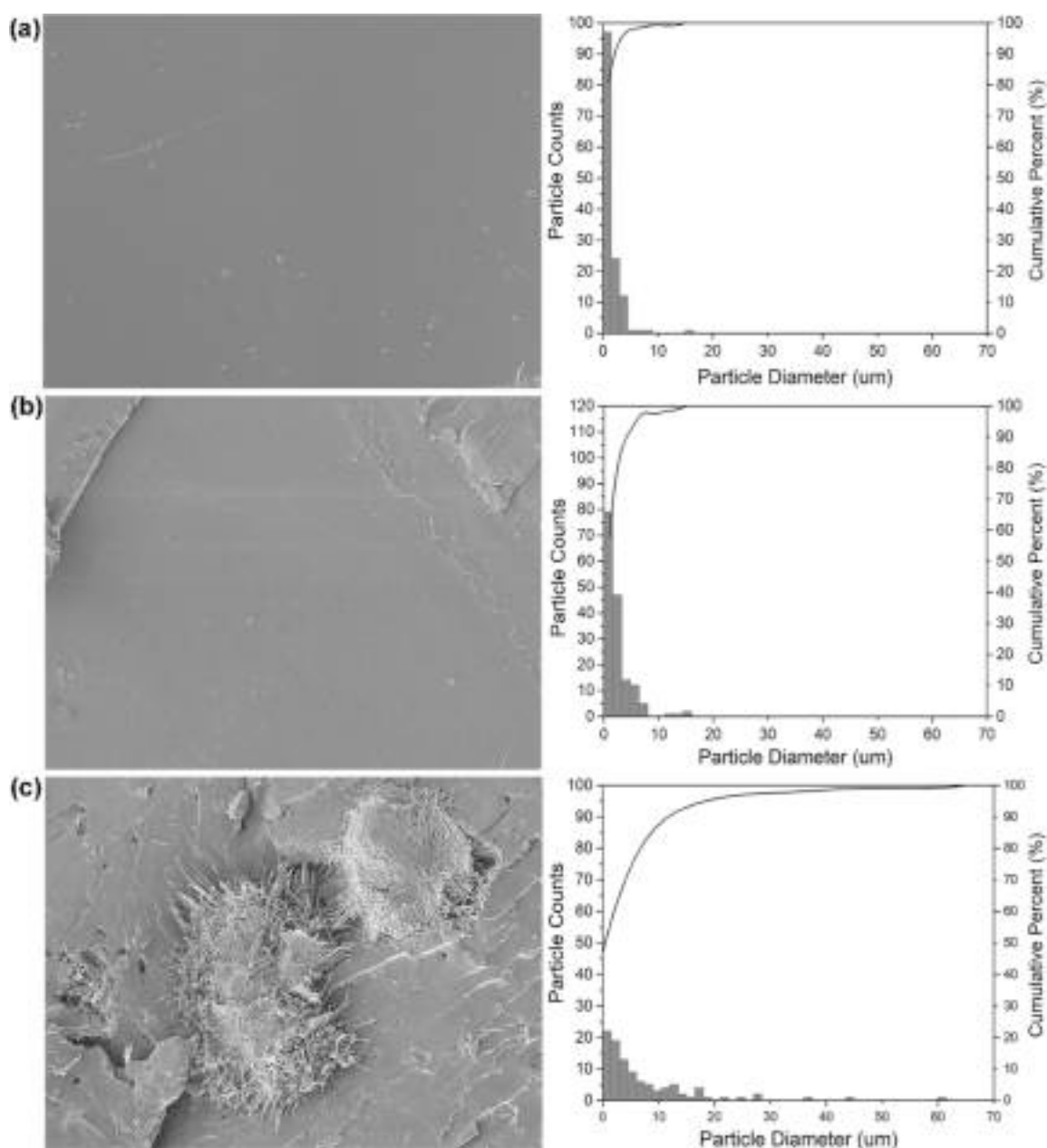


Figure 5. Scanning electron microscopy (SEM) micrographs and particle size distribution curves of the biocomposites: (a) PLA + 2.5% ZnO (particle size predominantly $<10\ \mu\text{m}$). (b) PLA + 2.5% ZnOLA (w.exc) (agglomerates up to $60\ \mu\text{m}$). (c) PLA + 2.5% ZnOLA (w/o.exc) (particles $>10\ \mu\text{m}$).

(w.exc), resulting in a difference of $18\ ^\circ\text{C}$ for T_{onset} and $9\ ^\circ\text{C}$ for T_{peak} . This increased thermal stability of PLA + 2.5% ZnOLA (w/o.exc) can be attributed to the more efficient dispersion of the ZnOLA particles, which promotes better interaction between the matrix and the filler. This improvement is evident in the SEM micrographs (Figure 5), which show a more homogeneous morphology and fewer agglomerates. The literature suggests that proper particle distribution enhances the matrix and filler interaction, improving heat transfer and delaying thermal degradation.⁴⁷ On the other hand, a higher concentration of agglomerates can create thermal stress points, acting as initial foci for degradation, thereby compromising the thermal stability of the biocomposite.^{48,49}

Rheological analyses (Figure 4), particularly viscosity measurements (Figure 4b), showed that the PLA + 2.5% ZnOLA (w.exc) samples exhibited higher viscosity, which can be attributed to flow restrictions caused by the agglomeration of particles. However, this sample demonstrated lower thermal stability than PLA + 2.5%

ZnOLA (w/o.exc). These findings emphasize the importance of the particle-washing process in optimizing the interaction between the matrix and the filler. Washing enhances the dispersion and homogenization of the biocomposite, thereby increasing its thermal stability, although it results in lower viscosity at low shear rates.

The enhanced thermal stability observed in PLA + 2.5% ZnOLA (w/o.exc) suggests potential advantages for biomedical applications, especially in scenarios requiring sterilization to ensure material safety. Conventional methods, such as autoclaving, which involve high temperatures ($120\text{--}130\ ^\circ\text{C}$), are unsuitable for PLA due to its heat sensitivity and susceptibility to structural degradation.^{50,51} Alternative methods, such as gamma irradiation and ethylene oxide (EtO), are more compatible with PLA-based materials but present challenges, including polymer chain scission, molecular weight reduction, and structural alterations. The improved thermal stability in biocomposites with washed, plasma-functionalized ZnO fillers indicates increased resistance to thermally induced degradation and structural

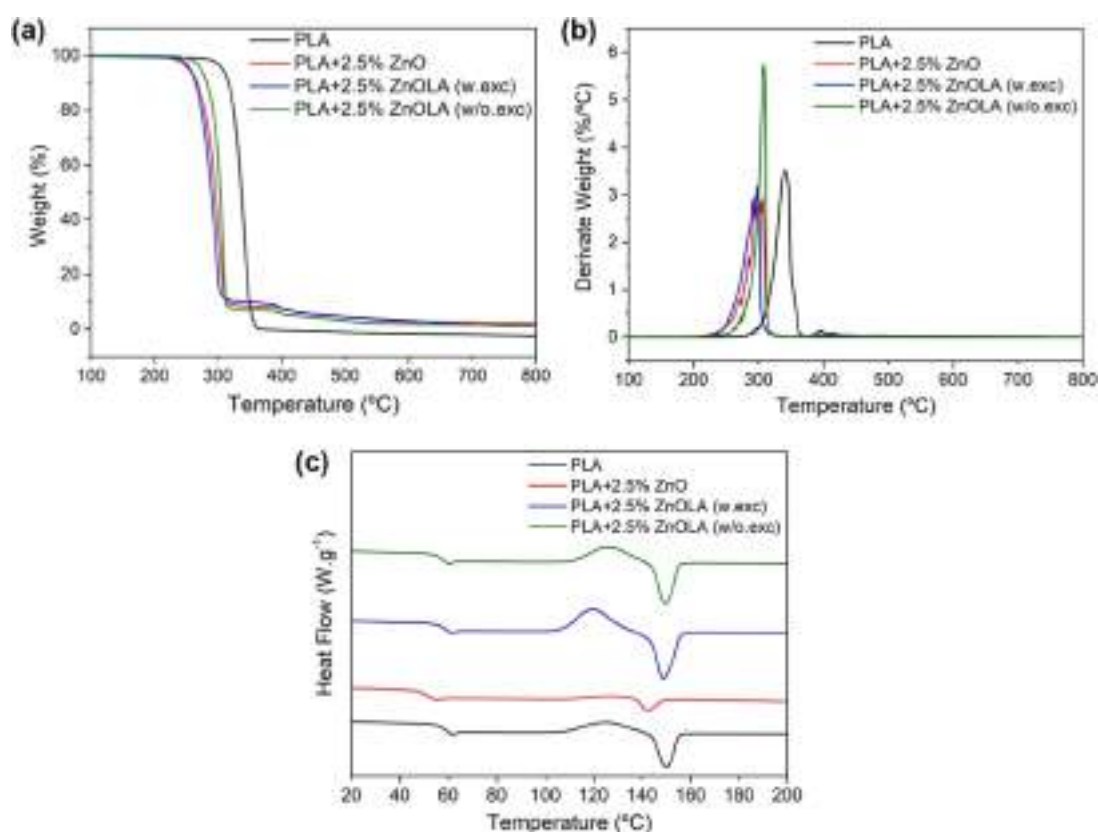


Figure 6. Thermal analysis of PLA and biocomposites: (a) TGA. (b) DTG. (c) DSC (curves from the second heating).

Table 3. Thermal Characteristics of Pure PLA and PLA/ZnO Biocomposites for Second Heating.

Samples	T_g (°C)	T_c (°C)	ΔH_c (J g ⁻¹)	T_m (°C)	ΔH_m (J g ⁻¹)	X_c (%)
PLA	59.5	125	14.9	150	15.6	0.84
PLA + 2.5% ZnO	52.2	127	138	142	4.40	0.21
PLA + 2.5% ZnOLA (w.exc)	58.2	126	144	149	19.0	0.40
PLA + 2.5% ZnOLA (w/o.exc)	59.3	120	143	149	24.2	0.55

disruption, potentially mitigating the effects of sterilization processes and preserving the material's mechanical and functional properties. These findings highlight the importance of optimizing filler functionalization to develop PLA-based biocomposites that can meet the demands of biomedical applications.

The thermal behavior of the formulations was also investigated using differential scanning calorimetry (DSC). The curves corresponding to the second heating are shown in Figure 6c. The thermal characteristics of the samples are summarized in Table 3.

The DSC curves revealed that the PLA + 2.5% ZnO biocomposite significantly reduced the glass transition temperature (T_g), indicating greater mobility of the polymer chains as a result of degradation during processing. This finding aligns with previous research,⁴¹ which suggested that the introduction of filler interferes with the intermolecular interactions of PLA macromolecules, probably by reducing the length of the chain, increasing chain mobility, and reducing T_g . However, the formulations with plasma-functionalized ZnO (PLA + 2.5% ZnO (w.exc) and PLA + 2.5% ZnO (w/o.exc)) showed a less pronounced decrease in T_g , suggesting a more efficient interaction between the ZnO particles and the polymer matrix, possibly due to the functional groups on the surface of the particles.

During the second heating, it was observed that PLA exhibited a cold crystallization temperature peak (T_c), an intrinsic characteristic of this polymer due to its low crystallization rate when cooled rapidly from the molten state.⁴⁶ In contrast, the PLA + 2.5% ZnO biocomposite did not show this phenomenon, suggesting that ZnO acts as a nucleating agent during cooling. Previous studies⁵²

corroborate this observation by attributing the absence of cold crystallization to the induction of crystallization by the ZnO in the composite. Analysis of the DSC curves of the PLA + 2.5% ZnOLA (w.exc) and PLA + 2.5% ZnOLA (w/o.exc) biocomposites reveals the presence of a cold crystallization peak, indicating that the surface treatment of the filler modifies the interaction between the PLA and the ZnO particles, affecting nucleation efficiency and resulting in cold crystallization during heating. Studies such as that by Bussiere et al. investigated the effects of adding silane-treated ZnO nanoparticles to the PLA matrix, observing that these particles hindered the crystallization of the polymer by acting as antinucleating agents due to the strong interaction between the organic groups on the surface of the ZnO and the carboxylic groups of the PLA.⁵³

In summary, the DSC results indicate that the PLA + 2.5% ZnOLA samples (with and without excess) showed similar thermal behavior to PLA, as evidenced by the proximity in the T_g , T_c , and T_m values. These findings highlight the effectiveness of the functionalization of the fillers in preserving the thermal transitions and stability of the polymer matrix, suggesting that functionalization improves the interaction between the ZnO particles and PLA, resulting in a more thermally stable material.

Wettability Analysis. The contact angle of the water droplets on the sample's films was measured to investigate variations in hydrophobicity and assess the impact of excess LA on the wettability of the surfaces. As Figure 7 illustrates, PLA demonstrated hydrophilic properties, with an average contact angle of approximately 81° slightly below the 90° limit.⁵⁴ Adding untreated ZnO to PLA reduced the

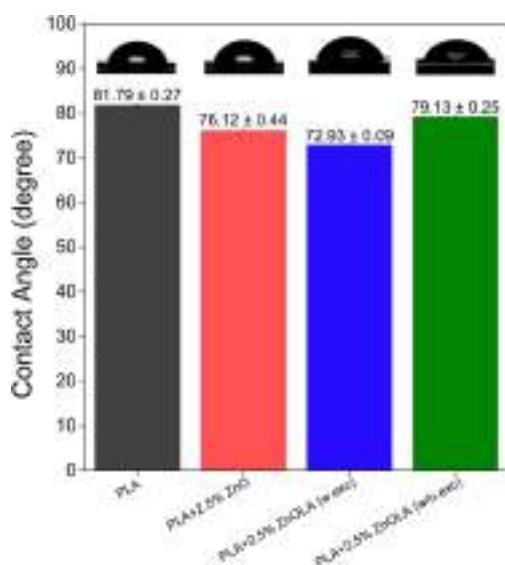


Figure 7. Contact angle values for PLA and PLA/ZnO biocomposites were obtained with drop deposition on the film samples.

contact angle to approximately 76° ($76.12^\circ \pm 0.44^\circ$) for the PLA + 2.5% ZnO composite, suggesting an increase in surface hydrophilicity, probably due to ZnO's intrinsically hydrophilic nature. This trend was most evident in the PLA + 2.5% ZnO (w.exc) sample, which recorded the lowest contact angle ($72.9^\circ \pm 0.09^\circ$), possibly due to residual LA, which contains highly hydrophilic carboxyl and hydroxyl groups.⁵⁵ The influence of washing the functionalized ZnO fillers can be seen in the approximately 6° increase in the contact angle of the PLA + 2.5% ZnO (w/o.exc) sample ($79.13^\circ \pm 0.25^\circ$) compared to the PLA + 2.5% ZnO (w.exc) sample. These observations align with the findings of Guo, Xiang, and Dong (2014), who utilized citric acid to modify PLLA surfaces, reducing the contact angle from 80 to 57° and enhancing material hydrophilicity. The authors attributed this effect to the formation of hydroxyl and carboxyl polar groups and an increase in surface roughness.⁵⁶

Cytotoxicity Analysis. Cytotoxicity assay was carried out over 1 to 14 days of cell culture in the samples to investigate the effect of ZnO without treatment and with treatment (with and without excess LA); the results are illustrated in Figure 8. On the first day of testing, it was found that the PLA composite with treated filler and excess LA (PLA + 2.5% ZnOLA (w.exc)) showed no percentage increase in resazurin reduction, indicating cytotoxicity from the start of the analysis. Therefore, this was the only sample showing a significant difference from the PLA sample ($p < 0.0001$). During this same period, the other biocomposites (PLA + 2.5% ZnO and PLA + 2.5% ZnOLA (w/o.exc)) exhibited a percentage increase in resazurin reduction of 10 to 15%, showing no statistical difference from PLA. On the seventh day, the PLA, PLA + 2.5% ZnO, and PLA + 2.5% ZnOLA (w/o.exc) samples showed a substantial increase in the percentage of reduction compared to the first day, attributed to a higher number of osteoblasts metabolizing resazurin into resorufin. The highest percentage increase in resazurin occurred for the PLA + 2.5% ZnOLA (w/o.exc) composite, indicating a higher cellular response in this sample than the others. Conversely, the cellular response for the PLA + 2.5% ZnOLA (w.exc) composite remained constant after the seventh and 14th day, with no percentage increase in reduction observed throughout all assay periods. This is corroborated by the statistically significant difference observed between the percentages of resazurin reduction in PLA and the PLA + 2.5% ZnOLA (w.exc) composite ($p < 0.0001$). On the 14th day, there was an increase in the percentage of resazurin reduction for PLA and the PLA + 2.5% ZnOLA (w/o.exc) composite, indicating that the cellular response was maintained for a prolonged period of the test.

For the biocomposite with nonfunctionalized filler (PLA + ZnO), there was initially an increase in the percentage of resazurin reduction,

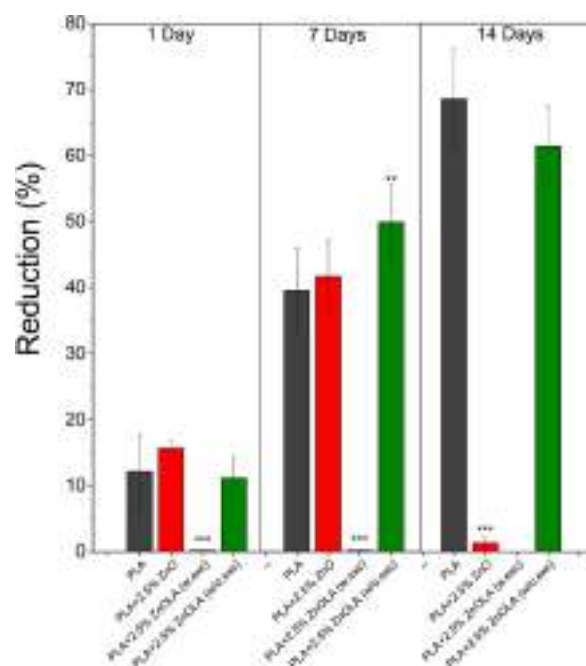


Figure 8. Cytotoxicity assay for PLA, PLA + 2.5% ZnO, PLA + 2.5% ZnOLA (w/o.exc), and PLA + 2.5% ZnOLA (w.exc) samples after 1 to 14 days of osteoblast culture (MC3T3-E1). Turkey's statistical analysis was carried out about PLA: *** for $p < 0.0001$; ** for $p < 0.01$; and * for $p < 0.05$ ($n = 6$).

suggesting cell proliferation in the first 7 days. However, on the 14th day of analysis, this percentage was substantially decreased.

For the central purpose of this research, the difference in the percentage of resazurin between the PLA + 2.5% ZnOLA (w/o.exc) and PLA + 2.5% ZnOLA (w.exc) samples was revealed. As observed, there was no cellular response for the PLA + 2.5% ZnOLA (w.exc) biocomposite throughout the entire assay period. In contrast, for the PLA + 2.5% ZnOLA (w/o.exc) biocomposite, an average increase of up to 60% in percentage reduction was recorded. Notably, the PLA + 2.5% ZnOLA (w/o.exc) sample demonstrated cell proliferation after 14 days of culture, suggesting that the functionalization and washing process enabled a favorable cellular environment. He et al. observed that above a concentration of 20 mmol L^{-1} , LA promotes cell viability and osteogenic differentiation by distinct mechanisms, causing death mainly by acidification of the medium, i.e., pH reduction, as well as oxidative stress or interference in metabolic processes.⁶⁰ In the present study, the excess of LA present in the PLA + 2.5% ZnOLA (w.exc) samples may have caused cell death through these mechanisms, as well as by the direct action of zinc ions in high concentration, given that the literature suggests that ZnO particles are sensitive to pH, which is evidenced by the increased release of Zn^{2+} ions at lower pH values.^{61,62} Therefore, if the zinc oxide particles are not washed after plasma functionalization, the excess LA may remain in the composition, potentially reducing the culture medium pH. This reduction in pH would increase the dissociation of Zn^{2+} ions, resulting in cell death over the incubation period.^{57–59} Trujillo et al. describe that cell proliferation is favored when the concentration of Zn^{2+} ions in the culture medium is between 25 and $50 \mu\text{M}$, and above this concentration range, the material can be cytotoxic.⁶³ These results reinforce the importance of properly controlling composite properties, including postfunctionalization washing, to ensure an adequate cellular response to tissue regeneration and repair.

Figure 9 shows the SEM images, which was used to assess the attachment of the MC3T3-E1 osteoblastic cells to the surface of the samples. The SEM images corroborate the results obtained in the cell culture test (Figure 8), showing that the osteoblastic cells are completely adhered to the surface of the PLA (Figure 9a) and PLA + 2.5% ZnOLA (w/o.exc) (Figure 9d) samples, demonstrating a high

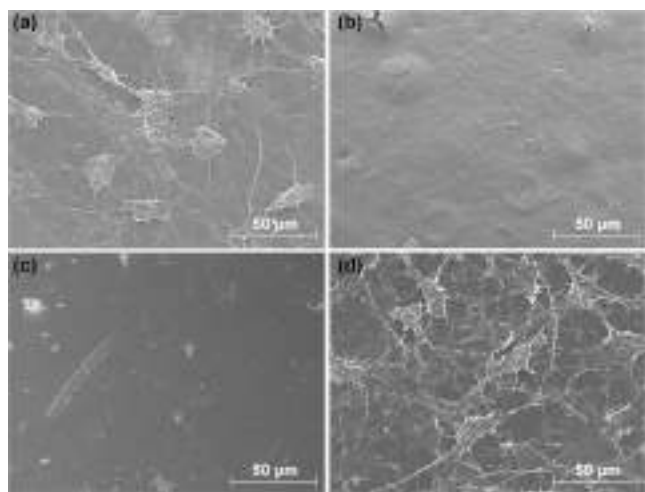


Figure 9. SEM images of the attachment of MC3T3-E1 osteoblastic cells to the surface of the samples: (a) PLA. (b) PLA + 2.5% ZnO. (c) PLA + 2.5% ZnOLA (w.exc). (d) PLA + 2.5% ZnOLA (w/o.exc).

affinity for these materials. The adhered osteoblastic cells had a planar arrangement, extending evenly over the surface and showing distinct filopodia.

In contrast, a negligible number of cells were observed on the surface of PLA + 2.5% ZnO (Figure 9b) and PLA + 2.5% ZnOLA (w.exc) (Figure 9c) biocomposites. In the samples with untreated filler (PLA + 2.5% ZnO), the presence of degradation spots on almost the entire surface was noteworthy, while they were significantly absent in the other samples studied.

CONCLUSIONS

This study investigated the functionalization of ZnO particles by plasma treatment, emphasizing the influence of excess L-lactic acid (LA) as a functionalizing agent on the thermal, rheological, wettability, and biological properties of PLA-based biocomposites. XPS and FTIR analyses confirmed the effectiveness of the functionalization, showing the formation of carboxylate groups (COO[−]) on the surface of the particles as a result of the interaction between the LA and the hydroxyl groups present in the ZnO. The biocomposites with plasma-treated ZnO exhibited reduced PLA degradation during processing, as evidenced by the increased equilibrium torque and the lower viscosity compared to biocomposites containing untreated ZnO. Specifically, the absence of excess LA resulted in a 55% reduction in viscosity, highlighting the significant impact of the functionalizing agent on the dispersion of ZnO particles. Furthermore, thermal analysis indicated that functionalization of ZnO, particularly after removing excess LA, helped maintain the thermal stability of the biocomposites, with a less pronounced decrease in PLA degradation temperatures. The increased viscosity observed in samples with excess LA is likely due to the restriction of chain mobility caused by the agglomeration of ZnO particles. This highlights the importance of particle dispersion quality in influencing the rheological properties and stability of PLA-based biocomposites.

However, biological analysis revealed that excess residual LA in the samples inhibited cell proliferation, underscoring the need to remove this excess for biomedical applications. This finding highlights the importance of washing the particles after functionalization, particularly when the biocomposite is intended for biological contact applications, to ensure the

material's biocompatibility. On the other hand, for applications where cell proliferation is not a key factor, washing the particles may be unnecessary, as the thermal, rheological, and wettability properties of the samples with and without excess LA remain comparable.

In conclusion, this study demonstrates that plasma functionalization of ZnO, followed by washing to remove excess LA, can mitigate PLA degradation and reduce the material's toxicity. The introduction of functional groups onto the ZnO surface appears to aid in controlling the release of Zn²⁺ ions, which, in turn, may support cell proliferation over 14 days, as shown in cytotoxicity assays. These findings emphasize the role of the washing process in removing excess contaminants, potentially extending cell proliferation time, which is advantageous for biomedical applications requiring controlled cell growth. For other applications where biocompatibility is not a critical requirement, washing can be omitted, simplifying the preparation of the biocomposite without compromising its rheological, thermal, and miscibility properties. These results open new possibilities for utilizing PLA biocomposites in various contexts, from advanced biomedical applications to industrial uses, provided that the postfunctionalization treatment is appropriately tailored to the final application of the material. This flexibility in processing could significantly advance the practical applications of PLA-based biocomposites.

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REFERENCES

- (1) Todros, S.; Todesco, M.; Bagno, A. Biomaterials and Their Biomedical Applications: From Replacement to Regeneration. *Processes* **2021**, *9* (11), 1949.
- (2) Bellani, C. F.; Pollet, E.; Hebraud, A.; Pereira, F. V.; Schlatter, G.; Avérous, L.; Bretas, R. E. S.; Branciforti, M. C. Morphological, Thermal, and Mechanical Properties of Poly(ϵ -Caprolactone)/Poly(ϵ -Caprolactone)-Grafted-Cellulose Nanocrystals Mats Produced by Electrospinning. *J. Appl. Polym. Sci.* **2016**, *133* (21), 43445.
- (3) Liu, S.; Qin, S.; He, M.; Zhou, D.; Qin, Q.; Wang, H. Current Applications of Poly(Lactic Acid) Composites in Tissue Engineering and Drug Delivery. *Composites, Part B* **2020**, *199*, 108238.
- (4) Echeverria Molina, M. I.; Malollari, K. G.; Komvopoulos, K. Design Challenges in Polymeric Scaffolds for Tissue Engineering. *Front. Bioeng. Biotechnol.* **2021**, *9*, 617141.
- (5) Mohamad Yunos, D.; Bretcanu, O.; Boccaccini, A. R. Polymer-Bioceramic Composites for Tissue Engineering Scaffolds. *J. Mater. Sci.* **2008**, *43* (13), 4433–4442.
- (6) Ramakrishna, S.; Mayer, J.; Wintermantel, E.; Leong, K. W. Biomedical Applications of Polymer-Composite Materials: A Review. *Compos. Sci. Technol.* **2001**, *61* (9), 1189–1224.
- (7) Pina, S.; Kwon, I. K.; Reis, R. L.; Oliveira, J. M. Biocomposites and Bioceramics in Tissue Engineering: Beyond the Next Decade. In *Innovative Bioceramics in Translational Medicine I: Fundamental Research*; Choi, A. H., Ben-Nissan, B., Eds.; Springer: Singapore, 2022; pp 319–350.
- (8) Chen, Y.; Geever, L. M.; Killion, J. A.; Lyons, J. G.; Higginbotham, C. L.; Devine, D. M. Review of Multifarious Applications of Poly (Lactic Acid). *Polym.-Plast. Technol. Eng.* **2016**, *55* (10), 1057–1075.
- (9) Lee, H.; Shin, D. Y.; Bang, S.-J.; Han, G.; Na, Y.; Kang, H. S.; Oh, S.; Yoon, C.-B.; Vijayavenkataraman, S.; Song, J.; Kim, H.-E.; Jung, H.-D.; Kang, M.-H. A Strategy for Enhancing Bioactivity and Osseointegration with Antibacterial Effect by Incorporating Magnesium in Polylactic Acid Based Biodegradable Orthopedic Implant. *Int. J. Biol. Macromol.* **2024**, *254*, 127797.
- (10) Lee, H.; Shin, D. Y.; Na, Y.; Han, G.; Kim, J.; Kim, N.; Bang, S.-J.; Kang, H. S.; Oh, S.; Yoon, C.-B.; Park, J.; Kim, H.-E.; Jung, H.-D.; Kang, M.-H. Antibacterial PLA/Mg Composite with Enhanced Mechanical and Biological Performance for Biodegradable Orthopedic Implants. *Biomater. Adv.* **2023**, *152*, 213523.
- (11) Anžlovar, A.; Kržan, A.; Žagar, E. Degradation of PLA/ZnO and PHBV/ZnO Composites Prepared by Melt Processing. *Arabian J. Chem.* **2018**, *11* (3), 343–352.
- (12) Chong, W. J.; Shen, S.; Li, Y.; Trinch, A.; Pejak Simunec, D.; Kyratzis, I. L.; Sola, A.; Wen, C. Biodegradable PLA-ZnO Nanocomposite Biomaterials with Antibacterial Properties, Tissue Engineering Viability, and Enhanced Biocompatibility. *Smart Mater. Manuf.* **2023**, *1*, 100004.
- (13) Chong, W. J.; Shen, S.; Li, Y.; Trinch, A.; Pejak, D.; Louis Kyratzis, I.; Sola, A.; Wen, C. Additive Manufacturing of Antibacterial PLA-ZnO Nanocomposites: Benefits, Limitations and Open Challenges. *J. Mater. Sci. Technol.* **2022**, *111*, 120–151.
- (14) Radwan-Pragłowska, J.; Janus, E.; Piątkowski, M.; Bogdał, D.; Matýsek, D. Hybrid Bilayer PLA/Chitosan Nanofibrous Scaffolds Doped with ZnO, Fe₃O₄, and Au Nanoparticles with Bioactive Properties for Skin Tissue Engineering. *Polymers* **2020**, *12* (1), 159.
- (15) Harb, S. V.; Kolanthai, E.; Pinto, L. A.; Beatrice, C. A. G.; Bezerra, E. d. O. T.; Backes, E. H.; Costa, L. C.; Seal, S.; Pessan, L. A. Additive Manufacturing of Bioactive and Biodegradable Poly (Lactic Acid)-Tricalcium Phosphate Scaffolds Modified with Zinc Oxide for Guided Bone Tissue Repair. *Biomed. Mater.* **2024**, *19* (5), 055018.
- (16) Collins, M. N.; Ren, G.; Young, K.; Pina, S.; Reis, R. L.; Oliveira, J. M. Scaffold Fabrication Technologies and Structure/Function Properties in Bone Tissue Engineering. *Adv. Funct. Mater.* **2021**, *31* (21), 2010609.
- (17) Backes, E. H.; Pires, L. de N.; Costa, L. C.; Passador, F. R.; Pessan, L. A. Analysis of the Degradation During Melt Processing of PLA/Biosilicate® Composites. *J. Compos. Sci.* **2019**, *3* (2), 52.
- (18) Qu, M.; Tu, H.; Amarante, M.; Song, Y.-Q.; Zhu, S. S. Zinc Oxide Nanoparticles Catalyze Rapid Hydrolysis of Poly(Lactic Acid) at Low Temperatures. *J. Appl. Polym. Sci.* **2014**, *131* (11), 40287.
- (19) Benali, S.; Aouadi, S.; Dechief, A.-L.; Murariu, M.; Dubois, P. Key Factors for Tuning Hydrolytic Degradation of Polylactide/Zinc Oxide Nanocomposites. *Nanocomposites* **2015**, *1* (1), 51–61.
- (20) Larrañaga, A.; Petisco, S.; Sarasua, J. R. Improvement of Thermal Stability and Mechanical Properties of Medical Polyester Composites by Plasma Surface Modification of the Bioactive Glass Particles. *Polym. Degrad. Stab.* **2013**, *98* (9), 1717–1723.
- (21) Lizundia, E.; Ruiz-Rubio, L.; Vilas, J. L.; León, L. M. Towards the Development of Eco-Friendly Disposable Polymers: ZnO-Initiated Thermal and Hydrolytic Degradation in Poly(L-Lactide)/ZnO Nanocomposites. *RSC Adv.* **2016**, *6* (19), 15660–15669.
- (22) Rolim, A. A. I.; Steffen, T. T.; Becker, D.; Leite, L. R.; Sagás, J. C.; Fontana, L. C.; Bond, D. Plasma Surface Treatment of Bacterial Cellulose to Increase Hydrophobicity. *Cellulose* **2024**, *31* (8), 4817–4831.
- (23) Klok, L. A.; Steffen, T. T.; Sabedra, H. R.; Fontana, L. C.; Hammer, P.; Marega, F. M.; Costa, L. C.; Pessan, L. A.; Becker, D. ZnO Surface Modification with Maleic Anhydride Using Plasma Treatment. *Plasma Processes Polym.* **2024**, *21* (5), 2300165.
- (24) Jordá-Vilaplana, A.; Fombuena, V.; García-García, D.; Samper, M. D.; Sánchez-Nácher, L. Surface Modification of Polylactic Acid (PLA) by Air Atmospheric Plasma Treatment. *Eur. Polym. J.* **2014**, *58*, 23–33.

- (25) Bitar, R.; Cools, P.; De Geyter, N.; Morent, R. Acrylic Acid Plasma Polymerization for Biomedical Use. *Appl. Surf. Sci.* **2018**, *448*, 168–185.
- (26) Colley, H. E.; Mishra, G.; Scutt, A. M.; McArthur, S. L. Plasma Polymer Coatings to Support Mesenchymal Stem Cell Adhesion, Growth and Differentiation on Variable Stiffness Silicone Elastomers. *Plasma Processes Polym.* **2009**, *6* (12), 831–839.
- (27) Cools, P.; Declercq, H.; De Geyter, N.; Morent, R. A Stability Study of Plasma Polymerized Acrylic Acid Films. *Appl. Surf. Sci.* **2018**, *432*, 214–223.
- (28) He, L.; Liu, X.; Rudd, C. Additive-Manufactured Gyroid Scaffolds of Magnesium Oxide, Phosphate Glass Fiber and Poly(lactic Acid) Composite for Bone Tissue Engineering. *Polymers* **2021**, *13* (2), 270.
- (29) NatureWorks *Safety Datasheet*; Datasheet Ingeo Biopolymer PLA 2003D; NatureWorks: Plymouth, 2022. <https://www.natureworkslc.com/resources> (accessed 02 19, 2024).
- (30) Fischer, E. W.; Sterzel, H. J.; Wegner, G. Investigation of the Structure of Solution Grown Crystals of Lactide Copolymers by Means of Chemical Reactions. *Kolloid-Z. Z. Polym.* **1973**, *251* (11), 980–990.
- (31) Rodwihok, C.; Charoensri, K.; Wongrataphisan, D.; Choi, W. M.; Hur, S. H.; Park, H. J.; Chung, J. S. Improved Photocatalytic Activity of Surface Charge Functionalized ZnO Nanoparticles Using Aniline. *J. Mater. Sci. Technol.* **2021**, *76*, 1–10.
- (32) Mathioudaki, S.; Barthélémy, B.; Detriche, S.; Vandenaabeele, C.; Delhalle, J.; Mekhalif, Z.; Lucas, S. Plasma Treatment of Metal Oxide Nanoparticles: Development of Core–Shell Structures for a Better and Similar Dispersibility. *ACS Appl. Nano Mater.* **2018**, *1* (7), 3464–3473.
- (33) Barrak, H.; Saied, T.; Chevallier, P.; Laroche, G.; M'nif, A.; Hamzaoui, A. H. Synthesis, Characterization, and Functionalization of ZnO Nanoparticles by N-(Trimethoxysilylpropyl) Ethylenediamine Triacetic Acid (TMSEDTA): Investigation of the Interactions between Phloroglucinol and ZnO@TMSEDTA. *Arabian J. Chem.* **2019**, *12* (8), 4340–4347.
- (34) Simonelli, G.; Arancibia, E. L. Effects of Size and Surface Functionalization of Zinc Oxide (ZnO) Particles on Interactions with Bovine Serum Albumin (BSA). *J. Mol. Liq.* **2015**, *211*, 742–746.
- (35) Taratula, O.; Galoppini, E.; Wang, D.; Chu, D.; Zhang, Z.; Chen, H.; Saraf, G.; Lu, Y. Binding Studies of Molecular Linkers to ZnO and MgZnO Nanotip Films. *J. Phys. Chem. B* **2006**, *110* (13), 6506–6515.
- (36) Ghaffari, S.-B.; Sarrafzadeh, M.-H.; Fakhrouiean, Z.; Shahriari, S.; Khorramizadeh, M. R. Functionalization of ZnO Nanoparticles by 3-Mercaptopropionic Acid for Aqueous Curcumin Delivery: Synthesis, Characterization, and Anticancer Assessment. *Mater. Sci. Eng. C* **2017**, *79*, 465–472.
- (37) Salas Fernández, P.; Alvino De La Sota, N.; Galli Rigo-Righi, C. Síntesis de Nuevos Complejos de Oxovanadio (IV) de Potencial Actividad Insulinomimética Con Ligandos Cumarina-3-Ácido Carboxílico y Derivados Sustituidos. *Rev. Soc. Quím. Peru* **2013**, *79* (3), 243–255.
- (38) Tang, E.; Cheng, G.; Ma, X.; Pang, X.; Zhao, Q. Surface Modification of Zinc Oxide Nanoparticle by PMAA and Its Dispersion in Aqueous System. *Appl. Surf. Sci.* **2006**, *252* (14), 5227–5232.
- (39) Unlu, I.; Soares, J. W.; Steeves, D. M.; Pang, R.; Welsh, E. A.; Whitten, J. E. Multifunctional Metal Oxide Nanoparticle Decorated Polypropylene Knitted Swatches. *J. Mater. Sci.* **2018**, *53* (2), 1514–1526.
- (40) Murariu, M.; Benali, S.; Paint, Y.; Dechief, A.-L.; Murariu, O.; Raquez, J.-M.; Dubois, P. Adding Value in Production of Multifunctional Polylactide (PLA)–ZnO Nanocomposite Films through Alternative Manufacturing Methods. *Molecules* **2021**, *26* (7), 2043.
- (41) Shojaeiarani, J.; Bajwa, D.; Jiang, L.; Liaw, J.; Hartman, K. Insight on the Influence of Nano Zinc Oxide on the Thermal, Dynamic Mechanical, and Flow Characteristics of Poly(Lactic Acid)–Zinc Oxide Composites. *Polym. Eng. Sci.* **2019**, *59* (6), 1242–1249.
- (42) Pandey, A. K.; Pal, T.; Sharma, R.; Kar, K. K. Study of Matrix–Filler Interaction through Correlations between Structural and Viscoelastic Properties of Carbonous-Filler/Polymer-Matrix Composites. *J. Appl. Polym. Sci.* **2020**, *137* (27), 48660.
- (43) Feng, J.; Venna, S. R.; Hopkinson, D. P. Interactions at the Interface of Polymer Matrix-Filler Particle Composites. *Polymer* **2016**, *103*, 189–195.
- (44) Herrera-Kao, W. A.; Loria-Bastarrachea, M. I.; Pérez-Padilla, Y.; Cauch-Rodríguez, J. V.; Vázquez-Torres, H.; Cervantes-Uc, J. M. Thermal Degradation of Poly(Caprolactone), Poly(Lactic Acid), and Poly(Hydroxybutyrate) Studied by TGA/FTIR and Other Analytical Techniques. *Polym. Bull.* **2018**, *75* (9), 4191–4205.
- (45) Lv, S.; Zhang, Y.; Tan, H. Thermal and Thermo-Oxidative Degradation Kinetics and Characteristics of Poly (Lactic Acid) and Its Composites. *Waste Manage.* **2019**, *87*, 335–344.
- (46) da Cruz Faria, E.; Dias, M. L.; Ferreira, L. M.; Tavares, M. I. B. Crystallization Behavior of Zinc Oxide/Poly(Lactic Acid) Nanocomposites. *J. Therm. Anal. Calorim.* **2021**, *146* (4), 1483–1490.
- (47) Rakmae, S.; Ruksakulpiwat, Y.; Sutapun, W.; Suppakarn, N. Physical Properties and Cytotoxicity of Surface-Modified Bovine Bone-Based Hydroxyapatite/Poly(Lactic Acid) Composites. *J. Compos. Mater.* **2011**, *45* (12), 1259–1269.
- (48) Tazibt, N.; Kaci, M.; Dehouche, N.; Ragoubi, M.; Atanase, L. I. Effect of Filler Content on the Morphology and Physical Properties of Poly(Lactic Acid)-Hydroxyapatite Composites. *Materials* **2023**, *16* (2), 809.
- (49) Zheng, Y.; Fu, G.; Wang, B.; Pang, C.; Hall, P.; Sharmin, N. Physico-Chemical, Thermal, and Mechanical Properties of PLA-nHA Nanocomposites: Effect of Glass Fiber Reinforcement. *J. Appl. Polym. Sci.* **2020**, *137* (42), 49286.
- (50) Dai, Z.; Ronholm, J.; Tian, Y.; Sethi, B.; Cao, X. Sterilization Techniques for Biodegradable Scaffolds in Tissue Engineering Applications. *J. Tissue Eng.* **2016**, *7*, 2041731416648810.
- (51) Pérez Davila, S.; González Rodríguez, L.; Chiussi, S.; Serra, J.; González, P. How to Sterilize Poly(lactic Acid) Based Medical Devices? *Polymers* **2021**, *13* (13), 2115.
- (52) Nonato, R. C.; Mei, L. H. I.; Bonse, B. C.; Chinaglia, E. F.; Morales, A. R. Nanocomposites of PLA Containing ZnO Nanofibers Made by Solvent Cast 3D Printing: Production and Characterization. *Eur. Polym. J.* **2019**, *114*, 271–278.
- (53) Bussiere, P. O.; Therias, S.; Gardette, J.-L.; Murariu, M.; Dubois, P.; Baba, M. Effect of ZnO Nanofillers Treated with Triethoxy Caprylsilane on the Isothermal and Non-Isothermal Crystallization of Poly(Lactic Acid). *Phys. Chem. Chem. Phys.* **2012**, *14* (35), 12301–12308.
- (54) Popa, A.; Stan, G.; Husanu, M.; Mercioniu, I.; Santos, L.; Fernandes, H.; Ferreira, J. Bioglass Implant-Coating Interactions in Synthetic Physiological Fluids with Varying Degrees of Biomimicry. *Int. J. Nanomed.* **2017**, *12*, 683–707.
- (55) Khorasani, M. T.; Mirzadeh, H.; Irani, S. Plasma Surface Modification of Poly (L-Lactic Acid) and Poly (Lactic-Co-Glycolic Acid) Films for Improvement of Nerve Cells Adhesion. *Radiat. Phys. Chem.* **2008**, *77* (3), 280–287.
- (56) Guo, C.; Xiang, M.; Dong, Y. Surface Modification of Poly (Lactic Acid) with an Improved Alkali-Acid Hydrolysis Method. *Mater. Lett.* **2015**, *140*, 144–147.
- (57) Singh, S. Zinc Oxide Nanoparticles Impacts: Cytotoxicity, Genotoxicity, Developmental Toxicity, and Neurotoxicity. *Toxicol. Methods* **2019**, *29* (4), 300–311.
- (58) Liu, J.; Kang, Y.; Zheng, W.; Song, B.; Wei, L.; Chen, L.; Shao, L. From the Cover: Ion-Shedding Zinc Oxide Nanoparticles Induce Microglial BV2 Cell Proliferation via the ERK and Akt Signaling Pathways. *Toxicol. Sci.* **2017**, *156* (1), 167–178.
- (59) Wu, P.; Cui, P.; Du, H.; Alves, M. E.; Liu, C.; Zhou, D.; Wang, Y. Dissolution and Transformation of ZnO Nano- and Microparticles in Soil Mineral Suspensions. *ACS Earth Space Chem.* **2019**, *3* (4), 495–502.

- (60) He, Y.; Wang, W.; Ding, J. Effects of L-Lactic Acid and D,L-Lactic Acid on Viability and Osteogenic Differentiation of Mesenchymal Stem Cells. *Chin. Sci. Bull.* **2013**, *58* (20), 2404–2411.
- (61) Perera, W. P. T. D.; Dissanayake, R. K.; Ranatunga, U. I.; Hettiarachchi, N. M.; Perera, K. D. C.; Unagolla, J. M.; De Silva, R. T.; Pahalagedara, L. R. Curcumin Loaded Zinc Oxide Nanoparticles for Activity-Enhanced Antibacterial and Anticancer Applications. *RSC Adv.* **2020**, *10* (51), 30785–30795.
- (62) Cai, X.; Luo, Y.; Zhang, W.; Du, D.; Lin, Y. pH-Sensitive ZnO Quantum Dots–Doxorubicin Nanoparticles for Lung Cancer Targeted Drug Delivery. *ACS Appl. Mater. Interfaces* **2016**, *8* (34), 22442–22450.
- (63) Trujillo, S.; Lizundia, E.; Vilas, J. L.; Salmeron-Sanchez, M. PLLA/ZnO Nanocomposites: Dynamic Surfaces to Harness Cell Differentiation. *Colloids Surf., B* **2016**, *144*, 152–160.



Full Length Article

Amine functionalization of carbon nanotubes with solid urea using different plasma treatments

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ABSTRACT

Carbon nanotubes (CNTs) were amine-functionalized through treatments in inductively coupled post-discharge, capacitively coupled micro spark and pulsed micro arc/glow discharge plasma regions, using urea in solid state as functionalization agent. In each plasma mode, the CNT functionalization yield was evaluated according to the variation of the plasma power and treatment time. For that, the samples were characterized through Fourier-transform infrared spectroscopy, Raman spectroscopy, transmission electron microscopy and X-ray photoelectron spectroscopy. The results show that, while preserving the integrity of the CNTs, an 80 % increase in oxygen content and up to 1.2 at.% of nitrogen was achieved using an asymmetric bipolar plasma power supply (ABIPPS). The adsorbed water can be completely removed from the CNTs through both a high-plasma-density treatment and a methanol washing procedure, conducted before sample characterization to remove any unreacted urea.

1. Introduction

To expand the number of applications of carbon nanotubes (CNTs) it is crucial to properly modify their surface. CNT treatment include cleaning, dispersion, activation and/or functionalization, conducted as to achieve the surface energy, surface area and polarity required for a specific application [1]. Since the modification of CNTs is not the focus in the development and production of novel materials, but only a process step, it is essential to use a process that is fast, clean, environmentally friendly, and does not generate waste products. Considering these challenges, plasma treatment appears as a viable route that meets the mentioned requirements [2], as it allows for a wide range of chemical surface modifications of nanoparticles through the adjustment of well-defined experimental parameters [1,3].

Indeed, several authors successfully performed the functionalization of carbon nanostructures through plasma treatment with reactive gases [3–8] or organic compounds in vapor phase [9–12]. Plasma treatment also proved to be effective in CNT functionalization when the functionalization agent is inserted into the chamber in the solid state, as proposed in a previous work [13]. Performing the experiment this way offers the advantages of eliminating the need for a heating system to promote the organic compound sublimation; avoiding reactor contamination by condensation of organic compounds in reactor chamber's

walls; and not needing the use of mass-flow controllers to regulate the flux into the plasma chamber.

Amine-functionalized carbon materials can be used in several applications, as in the fabrication of nanocomposites [14] and lithium-air battery cathodes [15], in the adsorption of CO₂ molecules [16] and in organic wastewater purification processes [17,18]. However, since the triple bond in N₂ is extremely strong [19], N₂ gas activation is troublesome under mild conditions [20], hindering the plasma amination of the CNTs through nitrogen gases. In addition, there is another drawback on CNTs direct treatment through gases, namely the difficulty in obtaining homogeneous modifications on a large scale. Homogeneous treatment through low pressure plasma requires the use of reactors with suitable system for stirring the nanoparticles, for example, a fluidized bed reactor [21]. As an alternative, a solid mixture composed by CNT and functionalization agent, could be a new option for CNT functionalization [13]. The electrical discharge through the mixture load, could provide evaporation and activation of molecules into the load volume. In this way, present paper uses a solid mixture composed by urea (functionalization agent) and CNT as the mixture load. Urea molecules contains oxygen and nitrogen arranged in one carbonyl and two amine groups, is highly reactive [22] and can be used as a source of nitrogen to be attached to the carbon nanotubes' surface, i.e., to promote the amine functionalization of the CNTs [23]. In fact, some papers report CNT

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functionalization with urea [24–26], but mostly conducting the experiments via wet chemistry, leaving the CNT plasma treatment approach poorly explored.

More than that, some studies have shown that, in the wet chemical route, the nitrogen insertion works better with oxygen-functionalized CNTs, which requires a previous treatment step with acids [27,28]. Therefore, multi-step processes are commonly used to achieve amino functionalization of CNTs [17,29–30], which include oxygen functionalization, chloride functionalization and, finally, nitrogen functionalization [31,32], taking up to 48 h. Plasma functionalization makes skipping those multiple steps possible, as it enables a process that simultaneously attaches oxygen and nitrogen to the CNT surface.

Plasma functionalization of nanoparticles is influenced by several factors, namely plasma parameters, reactor geometry, treatment time and input power [1], which all work together and must have their cumulative effects considered, once the quantity and type of functional groups inserted onto the nanoparticles' surface is defined through a combination of such factors influencing each other [3]. Therefore, plasma parameters are adjusted according to the nanoparticles to be functionalized.

Considering the advantages of plasma treatment and the wide range of plasma parameters influencing the CNT amination process, this work aims to explore different plasma conditions and configurations to achieve functionalization from the solid phase. Using urea as a functionalization agent, different plasma parameters and configurations were employed, including inductively coupled plasma (ICP) and capacitively coupled plasma (CCP) in the direct current (DC) and radio frequency (RF) modes, with CNTs being treated in the post-discharge, micro spark or micro arc/glow discharge plasma regions. The samples were characterized using different spectroscopic and microscopic techniques.

2. Experimental procedure

2.1. Materials

Multi-walled carbon nanotubes from Chengdu Organic Chemicals Co. Ltd (TNIM4) were used in this work, with a purity of 95 %, 10 μm to 30 μm in length, from 10 nm to 30 nm in external diameter and from 5 nm to 10 nm in internal diameter. The urea, with a purity of approximately 99 %, was purchased from Dinâmica Química Contemporânea Ltda. The plasma discharge used ultrapure Argon gas (>99.999 %).

2.2. Plasma functionalization process

Two plasma reactor configurations were used to treat the samples: a home-made inductively coupled plasma (ICP) reactor working with an RF power supply as reported by Steffen et al. [13] and schematically shown in Fig. 1a, and a capacitively coupled plasma (CCP) reactor (Fig. 1b). In the case of the treatment conducted in the ICP reactor, which is described in detail by Steffen et al. [13], the samples were positioned under the coil, in a post discharge region (Fig. 1a). On the other hand,

the CCP reactor is composed of a cylindrical quartz tube with a length of 240 mm, an internal diameter of 11 mm and electrodes 1.5 cm apart. The stainless-steel cathode is coated with a 0.2 μm thick TiO_2 film, which favors the spark channels spreading on the electrode surface and prevents arcing during high-frequency voltage biasing [33]. In addition, the TiO_2 coating has a high chemical/thermal stability [34], so it can minimize the reciprocal contamination of both the electrode surface and the CNT load. In the CCP reactor, the samples were positioned between the electrodes, filling the entire cylindrical tube volume in this region (Fig. 1b).

The treated material was a powder mixture of CNT and urea, mixed with mortar and pestle in a mass proportion of 90:10. Before plasma functionalization, the reaction chamber was pumped down from atmospheric pressure to 1.3 Pa, using a mechanical pump. The chamber volume was cleaned during 15 min with argon gas in a flowing rate of 12.2 sccm. Then, using the same Ar flow, a working pressure of 1.3×10^2 Pa and a 13.56 MHz RF plasma power in both plasma modes (ICP and CCP) of 35 W or 100 W, functionalized CNT samples were produced varying the treatment time. This set of plasma parameters were selected based on previous work [13]. Table 1 summarizes the sample names and plasma conditions used, where the letters I, C and the numbers (30 and 1) refer to ICP, CCP and treatment time, respectively. The last number, followed by the letter W, indicates the RF power, in Watts. CNT.C-30. ABiPPS was the only sample not treated by RF discharge but with an Asymmetric Bipolar Plasma Power Supply (ABiPPS), a plasma source developed by Scholtz et al. [35], operating as a pulsed power supply. In this case, 5 positive 600 V pulses, interspersed by negative pulses of 200 V, with approximately 1 μs per pulse, were applied, followed by a 100 μs off time, as indicated in the graphs in Fig. 2. The parameters for plasma generation through ABiPPS power supply, used in this work, were based on a previous work [35]. The selected parameters provide high plasma stability and increase the secondary electrons emission from electrodes. So that, the generated plasma can produce micro-spark discharge and controlled micro-arc during a short period ($T < 1 \mu\text{s}$).

Before the characterization, the samples were washed with methanol

Table 1
Sample nomenclature and plasma parameters.

SAMPLE	Plasma mode and source	Treatment region	Treatment time (min)
CNT/pristine	–	–	–
CNT.I-30.35 W	ICP-RF	Post discharge	30
CNT.I-30.100 W	ICP-RF	Post discharge	30
CNT.C-30.35 W	CCP-RF	Micro Spark Plasma	30
CNT.C-1.100 W	CCP-RF	Micro Spark Plasma	1
CNT.C-30. ABiPPS	CCP-ABiPPS	Micro arc plasma and Glow discharge	30

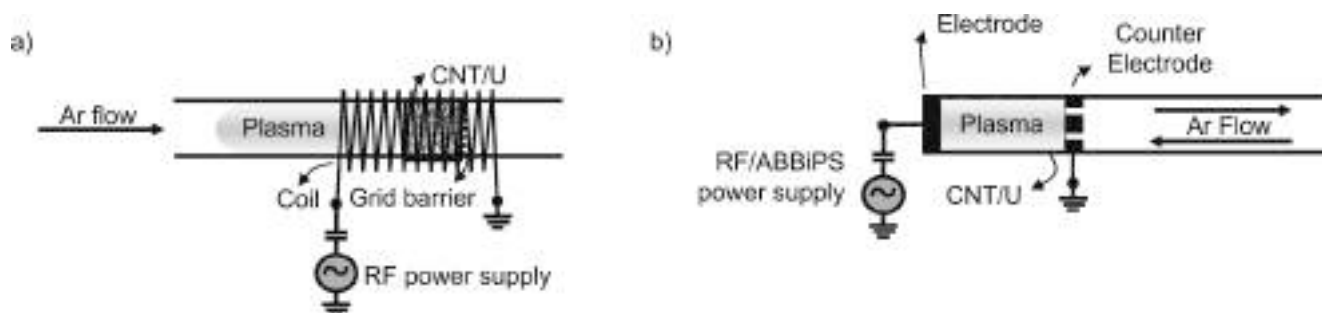


Fig. 1. Schematic representation of the a) ICP plasma reactor in which samples were treated in post-discharge with an RF supply, and the b) CCP plasma reactor, in which CNT samples were treated with both an RF supply and an ABiPPS (see text).

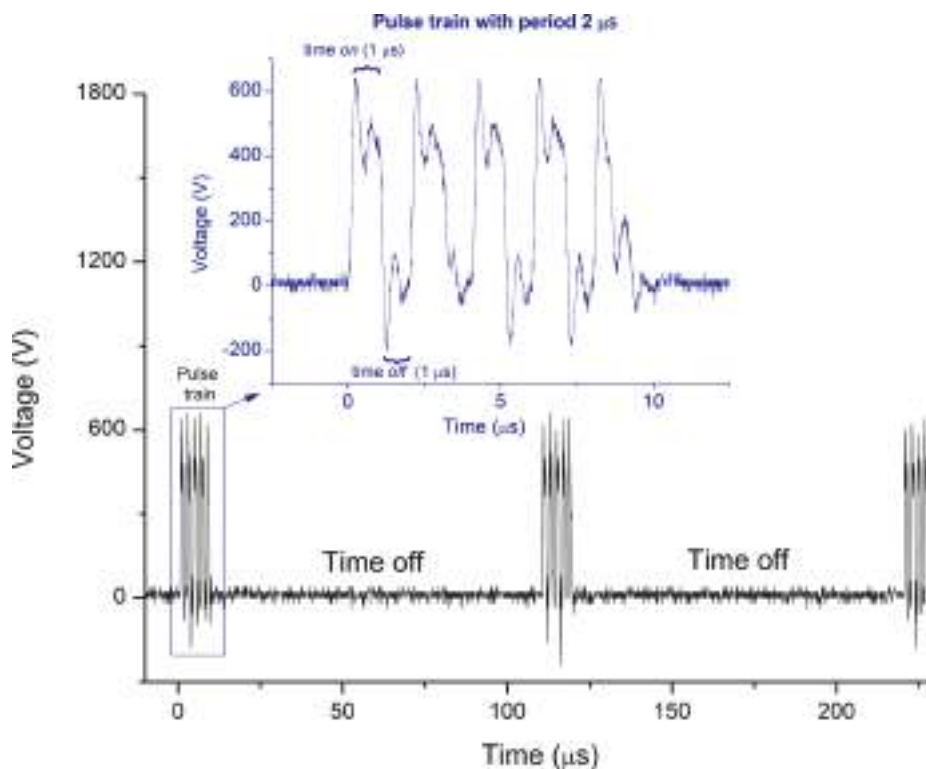


Fig. 2. Waveform established with ABiPPS in treatment of CNT.C-30.ABiPPS sample.

to remove any unreacted urea, following a process employed in our previous work [13]. Throughout this text, samples referred to as “CNT samples” imply a carbon nanotubes/urea mixture.

2.3. Characterization techniques

Fourier Transform Infrared (FTIR) spectra of samples in form of KBr tablets were obtained using a Bruker device (INVENIO-S). For each sample, 32 scans were conducted in the 4000 to 400 cm^{-1} region, with a resolution of 4 cm^{-1} . Raman spectra were recorded using a Micro-

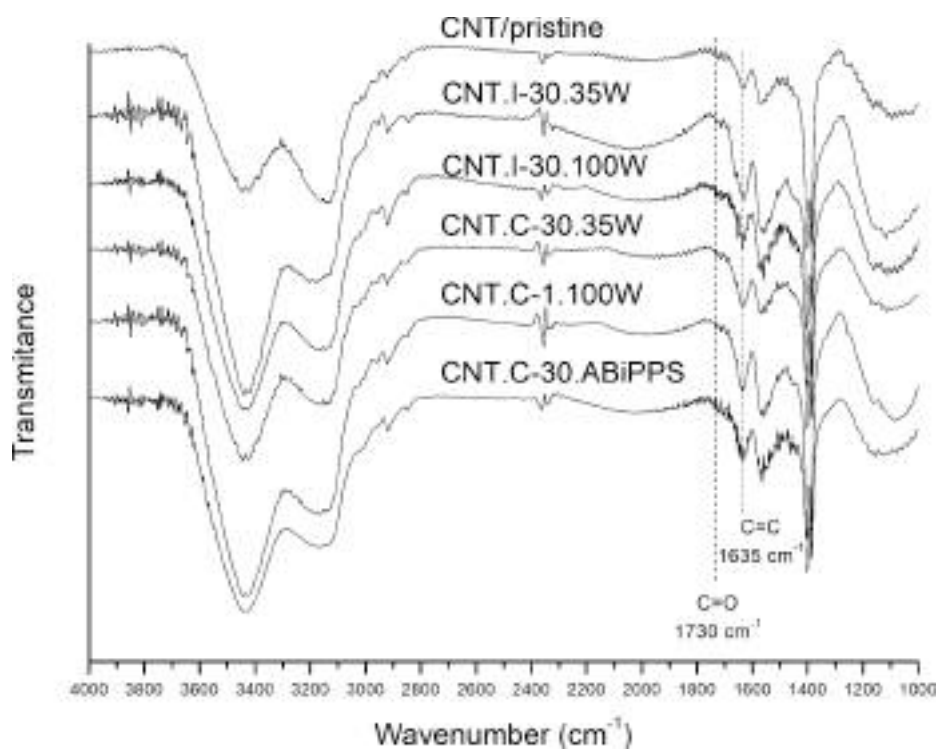


Fig. 3. FTIR spectra for CNT/pristine and all the samples treated with plasma.

Raman system (Horiba LabRAM HR Evolution 2000), using a laser wavelength of 514.5 nm (Ar) and 10 mW of power. The data were collected with a resolution of 4 cm^{-1} in the range of 940 to 2230 cm^{-1} . Samples analyzed in a JEOL (JEM 2100) Transmission Electronic Microscope (TEM) were previously dispersed in acetone and sonicated for 2 min. X-ray photoelectron spectroscopy (XPS) analyses were performed in a Thermo Scientific spectrometer (K-Alpha), operating at a base pressure below 10^{-7} mBar. The X-ray Al-K α ($h\nu = 1486.6$ eV) was used as the excitation source and the pass energy was set to 200 eV for survey and 50 eV for high-resolution scans. Spectra deconvolutions were performed using the Voigtian function, a combination of Gaussian (70 %) and Lorentzian (30 %) profiles. Surface characterization of the titanium-dioxide-coated stainless-steel electrode was performed using field emission scanning electron microscopy (FE-SEM), using a JEOL JSM 6701F instrument.

3. Results and discussions

Fig. 3 shows the FTIR spectra of pristine and plasma-treated multi-walled carbon nanotubes. A characteristic CNT peak appears at 1635 cm^{-1} , associated with C=C stretching vibration of sp^2 hybridized carbon [36]. In the region between 3150 cm^{-1} and 3500 cm^{-1} , the broad bands are associated to C-H and hydroxyl stretching vibrations, respectively [36,37]. Strong bands also appear at 1400 cm^{-1} and 1385 cm^{-1} , respectively associated to O-H in-plane deformation [37,38] and CH_2 bending [39]. In the 1100 to 1200 cm^{-1} region, the bands are related to C-O stretching vibrations [38,40]. After plasma treatment, it was expected to observe a peak or shoulder formation trend at 1730 cm^{-1} , related to C=O stretching vibration, indicating the carbon nanotubes functionalization [41]. Probably due to the slightly increase in oxygen contribution after functionalization, the peak is not clearly visible in FTIR spectrum, however, the increase in C=O bonding contribution, for treated samples, is confirmed by data provided by deconvolution of the XPS C 1 s spectra (Table 2). Peaks related to the nitrogen contribution from the urea could be overlapping the cited bands related to carbon and oxygen, once NH_2 bending vibration may appears at around 1635 cm^{-1} [42], symmetric and asymmetric NH_2 urea stretching modes in the 3000 to 3500 cm^{-1} region [42,43], and N-H in-plane bending vibrations at 1400 cm^{-1} [43]. Hence, due to the overlapping bands, C-N bonding is not evident from the FTIR spectra, however, confirmed by the XPS analysis.

Raman results are commonly used to evaluate carbon nanotube functionalization and integrity [44]. The I_D/I_G ratio relates the intensity of D and G bands, located at 1350 cm^{-1} and 1580 cm^{-1} , respectively. The D band is associated to sp^3 hybridized carbons, indicative of CNT defects and/or impurities, and the G band is related to the hexagonal planes of sp^2 hybridized carbon [44,45]. Fig. 4 shows the normalized (G band) spectra of pristine and plasma-treated samples, including the I_D/I_G ratio obtained after integrating the peak areas. The essentially unchanged I_D/I_G values indicate the preservation of the CNT structural integrity after plasma treatment. As FTIR results indicate CNT functionalization and Raman results show similar I_D/I_G values, a possible

interpretation is a preferential attachment of the functional groups to pre-existing CNT defects, rather than the creation of new active sites, i. e., defects formed during the plasma process. The preservation of the CNT structural integrity was confirmed through TEM analysis.

Fig. 5 presents TEM images of all CNT samples for two magnification levels. The low-magnification images (Fig. 5a-f) indicate that there was no significant change in CNT morphology after plasma functionalization, preserving their integrity. Some CNT with open tips are observed for plasma treated samples, as indicated by the black arrows (Fig. 5c and d). The tip opening was also reported by Deng et al. [46] after plasma treatment of CNT. High magnification image for non-treated CNT samples (Fig. 5g) show well-defined walls, while treated samples (Fig. 5h-l) show blurred surface, pointed by white arrows. Moreover, Fig. 5h-l indicate the presence of an amorphous region on the CNT walls of treated samples, not observed for the CNT/pristine sample. According to other studies [47–48], the presence of such a layered structure on CNT walls after plasma functionalization may be attributed to the deposition of a thin polymeric film. Fig. 5l shows that this deposit is not covering the entire but only some regions of the CNT surface.

The CNT functionalization after plasma treatment was confirmed through quantitative XPS analysis (Table 2 and Figure S1) and deconvoluted high-resolution C 1 s, N 1 s and O 1 s spectra, shown in Figure S2–S4. For the fitting of the sub-peak of aromatic carbon (C-C sp^2 at 284.4 eV) of the C 1 s spectra an asymmetric Doniach-Sunjc function was used to account for the intra-band transitions due to the elevated density of states of multiwall carbon nanotubes at the Fermi level ($\pi \rightarrow \pi^*$ transitions) [49] (Fig. S2). The weaker intensity at 284.8 eV is related to adventitious carbon (C-H) and sp^3 C-C bonds, followed by C-N and C-O groups at 296.2 eV [50]. Although it is well known that the C-N bonds in aromatic structure are located about 0.5 eV below C-O (ether/alcohol) groups, both components were not separated due to the variability of converging solutions using the Levenberg-Marquardt fitting algorithm leading to variable intensities of C-O and C-N sub-peaks [50–52]. Components at higher binding energy are related to carbonyl (287.8 eV) and carboxylic groups (289.2 eV) which overlap with O=C-N₂ bonds (288.7 eV) [50]. Again, the small separation, between both environments makes the introduction of an additional sub-peak problematic. The intensities at 291.1 eV and 293.2 eV are associated with $\pi \rightarrow \pi^*$ satellites due to π electron transitions at the Fermi level [51]. The noisy N 1 s spectra were fitted with only one component at about 399.5 eV, associated with N-C bonds in pyrrole and amine groups [50,52] (Fig. S3). It is known that insertion of nitrogen into the aromatic structure gives rise to the formation of five-membered rings [53]. The O 1 s spectra were fitted with components related to oxygenated carbon groups of O=C (531.3 eV), O-C (532.6 eV) and O-C=O (533.7 eV), already identified by the analysis in the C 1 s spectra [50,52]. The high binding energy component, observed at about 536 eV, is related to small contribution of water molecules, often observed in the CNT structure [52] (Fig. S4).

Table 2 shows that nitrogen insertion into the CNTs was more efficient (0.2 at.% to 0.5 at.%) when increasing the power (35 W to 100 W) and using a CCP discharge. This can be related to the higher power

Table 2

Atomic percent composition of carbon (C 1 s), oxygen (O 1 s) and nitrogen (N 1 s); Peak area percentage of the deconvoluted C 1 s spectra; Sum of the peak area of CO and CN functional groups (C 1 s); and O 1 s peak area percentage of H_2O ; of all the CNT samples. *Error: $\pm 5\%$. The error of nitrogen atomic concentration is a: $\pm 0.04\%$, b: $\pm 0.03\%$ and c: $\pm 0.01\%$.

SAMPLE	Concentration (at.%) ^a			Peak area percentage of functional groups (%)						
	C 1 s	O 1 s	N 1 s	CC sp^2 (C 1 s)	C-H (C 1 s)	C-O/C-N (C 1 s)	C=O (C 1 s)	O-C=O/O=CN ₂ (C 1 s)	Sum of CO, CN bonds	H ₂ O (O 1 s)
CNT/pristine	98.0	2.0	–	78.06	5.17	5.10	1.73	2.25	9.08	7.74
CNT.I-30.35 W	97.9	1.9	0.2 ^a	74.39	4.48	6.66	2.17	2.98	11.81	6.08
CNT.I-30.100 W	97.8	1.8	0.4 ^b	74.94	4.42	6.38	2.18	2.94	11.50	6.86
CNT.C-30.35 W	97.7	1.9	0.4 ^a	69.47	8.70	6.35	3.60	2.33	12.28	0.00
CNT.C-1.100 W	96.7	2.8	0.5 ^b	69.59	9.24	7.19	2.93	2.50	12.62	0.00
CNT.C-30.ABiPPS	95.2	3.6	1.2 ^c	64.30	13.05	8.64	2.24	3.98	14.86	0.00

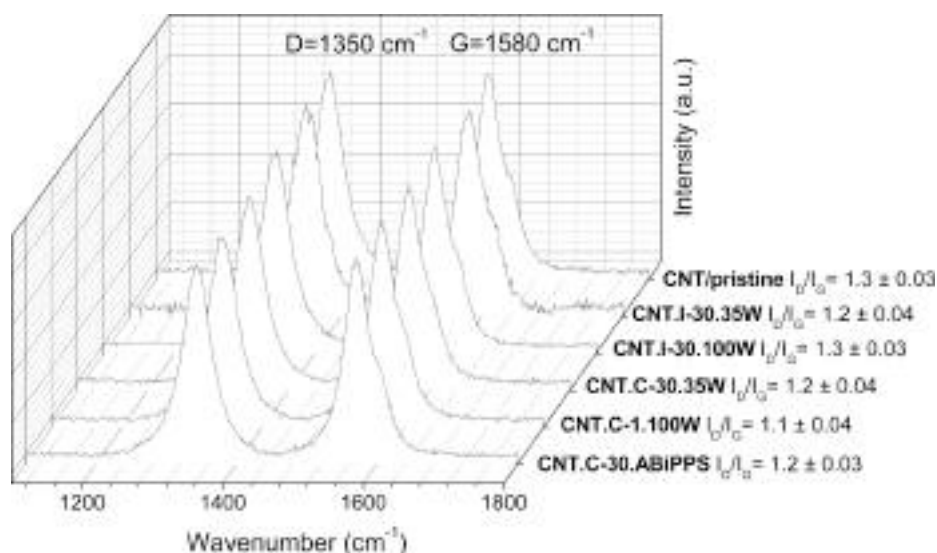


Fig. 4. Raman spectra and I_D/I_G ratio for CNT/pristine and all the functionalized samples, suggesting that CNT structure is preserved after plasma treatment.

density that generates a higher number of ionic species that form urea radicals [54]. As expected, a further nitrogen increase was achieved using the ABiPPS 600 V pulse mode. Compared with the pristine CNTs, the CNT.C-30.ABiPPS sample presented a nitrogen content of 1.2 at.% and the oxygen concentration increased by 1.6 at.%.

Although the oxygen concentration only increased significantly for sample treated capacitively at 100 W and for that using ABiPPS, the increase in the nitrogen content contributed to higher intensities of the C-O/C-N (286.5 ± 0.2 eV) and O-C=O/O=CN₂ (289.2 ± 0.2 eV) functional groups [50], as shown in the fitted high-resolution C 1 s spectra of Figure S2. The presence of N-C bonds was evidenced through fitting the N 1 s spectra (Figure S3) with a single component at a binding energy of 399.9 eV, which is somewhat higher than that reported of urea (399.5 ± 0.2 eV). The presence of O=C (531.4 ± 0.2 eV), C-O (532.5 ± 0.2 eV) and O-C=O (533.7 ± 0.2 eV) was confirmed through the deconvolution of the O 1 s spectra [50], shown in Figure S4.

To further evaluate the feasibility of the CCP method, two electrode polarization modes were applied: RF and pulsed voltage bias. The RF discharge in the CCP configuration is shown in Fig. 6a, which displays the generation of a spark discharge in spaces between the electrode and the CNT load. The spark channels alternate rapidly and branch throughout the TiO₂ coated electrode. The spark discharge occurs in the gaps between the dielectric cathode and neighboring powder particles. Consequently, a plasma discharge takes place in the spark region between the CNT nanoparticles, configuring a micro spark plasma [55]. Due to the high temperature in the vicinity of the micro spark region, a local low-gas-density volume may be formed, which, in turn, favors the electron energy gain due to the increase in the mean free path. Therefore, the ionization and/or excitation of atoms and molecules sublimed from the CNT/urea load may be increased. On the other hand, along with the ionization process, the potential across the micro-spark drops below a critical plasma-maintenance voltage, ceasing that localized discharge. In this way, successive micro spark spots are created and extinct on the electrode surface. Fig. 6b illustrates a schematic representation of an instantaneous RF discharge at the electrode/load interface.

Since the 100 W CCP-RF mode generates plasma between the particles and the electrode (i.e., micro spark plasma discharge), which enhances the interaction between ionic species and the CNT sample, the short plasma process (1 min) leads to a significant increase in the oxygen content (40 %) of the CNT.C-1.100 W sample, compared to that of the pristine CNT. Moreover, for this sample, a higher nitrogen concentration (0.5 at.%) was reached than for the CNT.I-30.100 W, treated for 30 min

with ICP-RF plasma (Table 2). The applied 100 W power supplied the necessary dissociation energy for the oxygen and nitrogen, the latter being significantly higher (9.8 eV) than the former (5.1 eV) [56,57].

The ABiPPS-generated discharge provides high peak voltages (600 V) during five 1 μ s pulses, which implies that the provided pulse width (1 μ s) is tens of times longer than that provided by the RF power supply (approximately 37 ns). The voltage pulse intensity provided by the ABiPPS was sufficiently high to generate micro-arc discharges that created micrometric holes on the TiO₂ coated cathode. Fig. 6c illustrates the micro-hole formation due to local overheating of the TiO₂ and Fig. 7 shows the micro-holes generated after a 30 min discharge on the electrode and the molten metal surrounding them. Once the micro-holes are created, they expose the metallic electrode, leading to a dense discharge in the micro-hole region, similarly to a micro hollow cathode plasma, as illustrated in Fig. 6c. As the periods of individual pulses are shorter than 1 μ s, and the pulse trains are interrupted by 100 μ s (voltage off), the overheating produced by micro-arcs is localized at micro-holes and their proximities. Their area and density may increase with the electrode usage time. Therefore, the electrode can suffer aging, which needs to be examined in future studies.

Results presented in Table 2 for the CNT.C-30.ABiPPS sample show a remarkable effect of the ABiPPS plasma in terms of CNT functionalization, presenting the highest amounts of inserted oxygen and nitrogen of 3.6 at.% and 1.2 at.%, respectively. In fact, besides the formation of a micro arc plasma, the presence of the load in the glow discharge region may be an additional reason for the higher oxygen content, since, in this region, the oxygen dissociation rate is significantly higher [57] than in the afterglow zone used in the ICP-RF treatment. In the case of the nitrogen, the higher plasma density within the micro-arc discharge may have contributed to an enhanced functionalization of the carbon nanotubes [57]. The plasma functionalization efficiency in the ABiPPS mode is evident not only from the results of the quantitative elemental XPS analysis, but also from the intensity increase in fitted components associated with oxygenated and nitrogenated functional groups (Table 2). However, as the high-voltage pulses were applied only for a few microseconds, followed by a long off time (100 μ s), the CNT integrity was preserved, as verified through Raman results and TEM images.

When comparing XPS C 1 s fitting results of plasma-treated samples with those of pristine CNTs, the amount of oxygen and nitrogen containing functional groups (Total in Table 2) increased up to 64 % (Fig. 8). An increase in those groups occurs even when the oxygen atomic percent remains almost constant (CNT.I-30.35W, CNT.I-

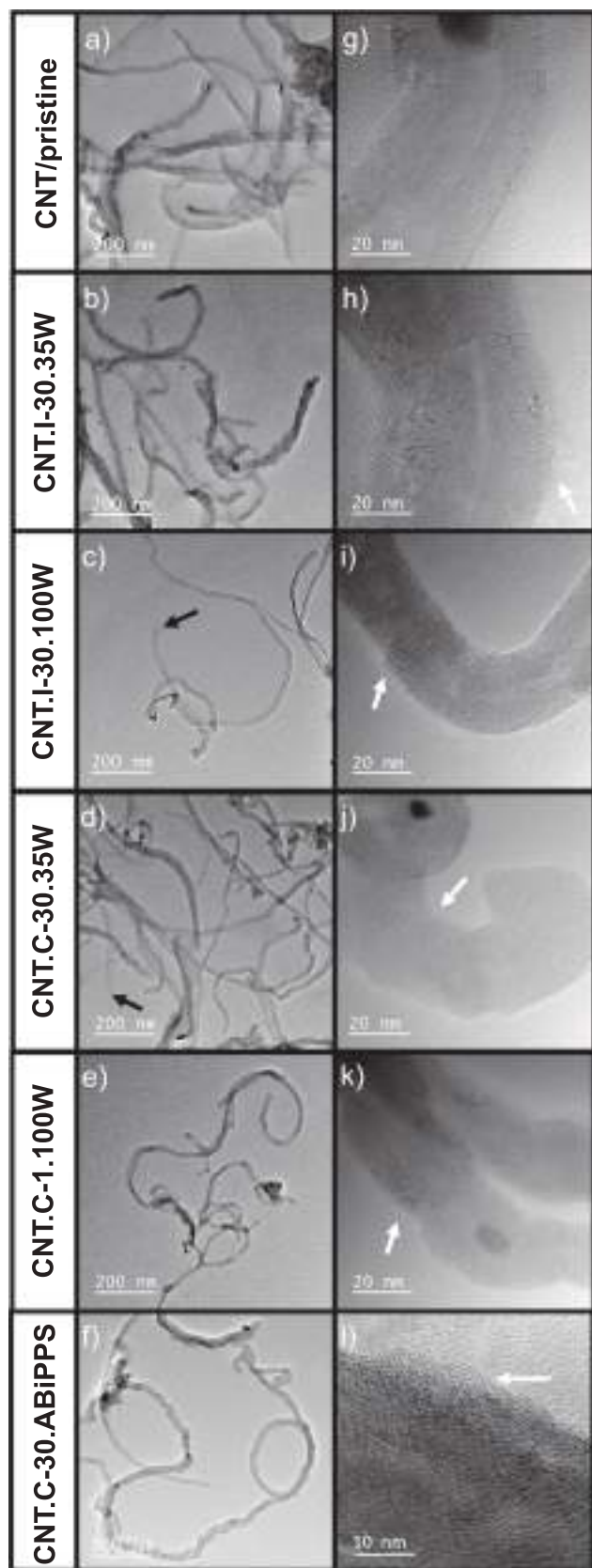


Fig. 5. TEM images of low (a to f) and high magnification (g to l). Black arrows (c, d) indicate CNTs with open tips, white arrows point to CNT blurred surfaces (h to k) and an amorphous region (l) on the CNT walls.

30.100W and CNT.C-30.35W), indicating the contribution of the nitrogen functionalization. This might be related to a partial substitution of oxygen with nitrogen atoms, as proposed by Liu et al. [27]. Furthermore, the increase in those groups, but also in sp^3 C-H bonds (~ 285.0 eV), observed at higher plasma energies is accompanied by a reduction in the intensity of aromatic sp^2 CC bonds, which implies the efficiency of the plasma process in breaking chemical bonds and creating defects that favor the functionalization process. The reached nitrogen level for the urea-treated samples are comparable to those reported for wet chemical routes, in the range from 0.28 at% to 1.9 at.%, involving several hours of treatment [28,39,58–59]. Consequently, the plasma route using a solid-state precursor has proven to be an attractive alternative to the nitrogen functionalization of CNTs, providing advantages of short treatment times in a clean and solvent-free process, using urea in the solid form.

Another interesting aspect of CNT functionalization, rarely discussed in the literature, is related to its water content. By deconvoluting the high-resolution XPS O 1 s spectra of samples treated in post-discharge with ICP-RF plasma, a small reduction of the sub-peak area at about 536 eV was observed (Table 2, Fig. 9 and Figure S4b-c). For samples treated with CCP-RF plasma, this contribution disappeared after the methanol washing procedure (Figure S4d-f), used to remove any unreacted species. This phenomenon, already observed in a previous work [13], was attributed by Tian et al. [60] to the capability of alcohols to fully replace water molecules inside the CNTs. According to these authors, this can be explained by an energetic approach: when penetrating CNTs, alcohol molecules gain in Van der Waals energy overcompensating the loss in electrostatic energy. On the other hand, despite the water molecules present similar tendencies, the energy gain is not high enough to reach overcompensation. This results in a preferential interaction between the CNTs and the solvent, rather than with water. Indeed, Winarto et al. [61] showed by simulations that the variation of internal energy (ΔU) is 63.18 kJ/mol for water-CNT interaction, while -179.02 kJ/mol for methanol-CNT, which explains the alcohol preference to fill the CNT and replace the water. To evaluate whether this phenomenon is also a consequence of the plasma treatment or only the washing procedure applied before sample characterization, the pristine CNT sample was analyzed after washing, resulting in an essentially unchanged contribution of the H_2O sub-peak area of about 8 % (Figure S5). This indicates that the methanol washing reduces the water content in the CNTs only in combination with the plasma treatment, i.e. in case of functionalized CNT. This could be related to the fact that during the plasma treatment urea molecules behave like alcohol in CNT, replacing water molecules due to energy balance previously mentioned [62]. This was shown through simulation by Xiu et al. [62], suggesting that the water desorption from CNT is due to a stronger dispersion interaction of urea than water with the nanoparticles. Therefore, already during plasma treatment, a process of CNT drying may occur. In addition, the functional groups attached to CNT could also play a role in this process: the correlation between functionalization degree and water removal seems to be a trend by analyzing Table 2. As the sum (Total) of functional groups increases, the H_2O sub-peak area decreases to zero (Fig. 9). Winarto et al. [63] showed that, in a water-methanol solution, the density of methanol molecules at CNT tips is higher than water molecules, due to stronger Van der Waals interactions between methanol and CNT. Therefore, once the functionalization increases the CNT reactivity [64], their interaction with molecules of the solvent during the washing procedure may further increase the methanol concentration at CNT tips, consequently, replacing the water in CNT. Further in-depth analysis is needed to better understand this behavior. Moreover, the increase of the power density of the CCP-RF plasma significantly reduces the H_2O content (~ 4 % peak area), which reaches zero after ABiPPS high-plasma-density treatment (Figure S6). The water removal at high power densities clearly correlates with the increasing presence of C-H groups, as Fig. 9 shows. Therefore, the plasma-induced water splitting might be the source of hydrogen that contributes to C-H bond formation, possibly at the nanotube extremities.

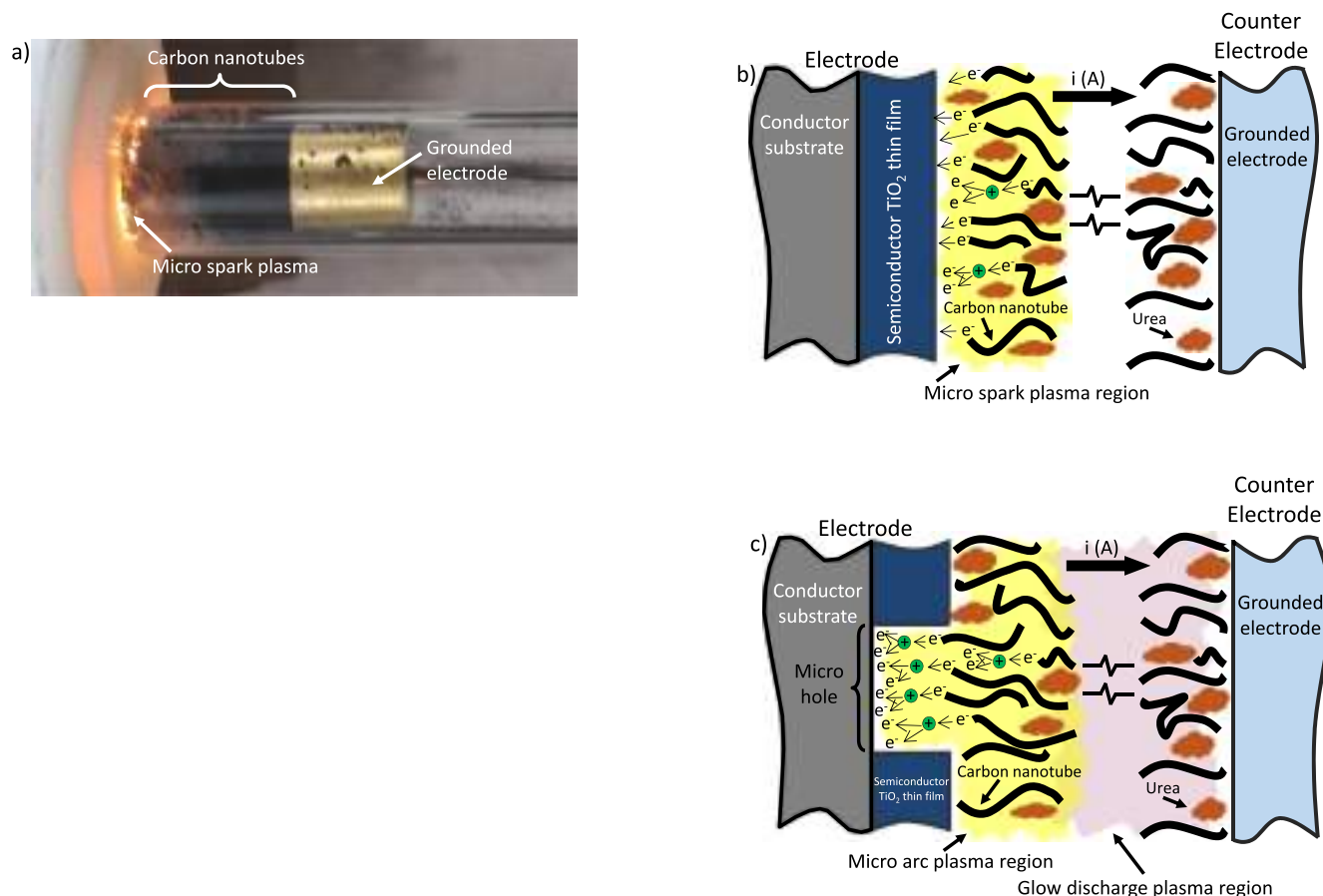


Fig. 6. a) Photo evidencing micro spark plasma discharge during the treatment of CNT.C-30.35W sample; b) a schematic representation of micro spark plasma occurring in RF discharge during a positive voltage peak; c) a schematic representation of micro-arc plasma being favored by micro hole through the semiconductor TiO_2 thin film and reaching the conductor substrate, after high power pulse voltage provided by the ABiPPS.

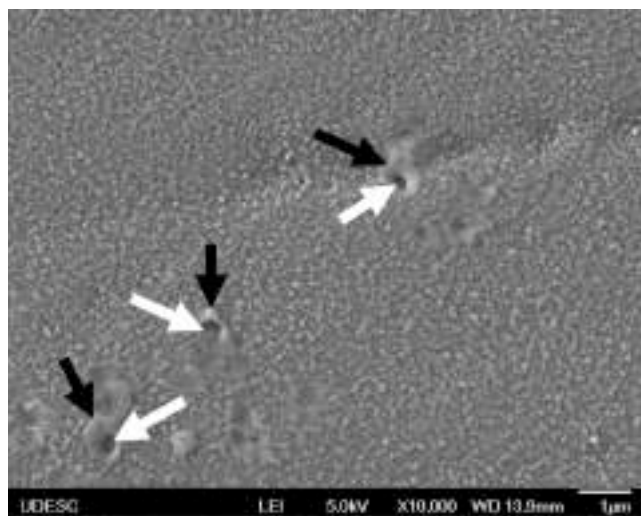


Fig. 7. SEM image of the electrode coated with a TiO_2 thin film, after a 30 min discharge powered by the ABiPPS. The white arrows indicate the micro holes found at the thin film surface and the black arrows point to the molten metal from the electrode that surrounds the micro holes.

4. Conclusions

Functionalization of multi-walled carbon nanotubes using urea in solid state was conducted through different plasma configurations,

including inductively coupled, capacitively coupled and pulsed plasma. In all sets of parameters, CNT functionalization was verified through the increase in oxygen and nitrogen contents in the samples. The capacitively coupled RF-plasma at 100 W stands out as an efficient functionalization method, allowing, in a short time interval (1 min), for a significant concentration increase in oxygen (0.8 at.%) and nitrogen (0.5 at.%). A further increase in nitrogenated functional groups was achieved using an asymmetric bipolar plasma power supply (ABiPPS), reaching, after 30 min, a nitrogen insertion of up to 1.2 at.%. TEM and Raman spectroscopy results showed that the structural integrity of CNT was preserved after the plasma treatment, indicating a preferential insertion of oxygenated and nitrogenated functional groups at the tips of the CNTs and pre-existing defects. The CCP-RF and ABiPPS modes also proved to be efficient in removing residual water adsorbed on the CNT walls. For both methods, the high plasma energy, available in the micro spark and micro arc/glow discharge regions, provided the best conditions to promote water dissociation and the effective attachment of functional groups to the carbon nanotubes.

CRediT authorship contribution statement

Teresa Tromm Steffen: Conceptualization, Investigation, Formal analysis, Writing – original draft, Visualization. **Luis César Fontana:** Conceptualization, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Peter Hammer:** Formal analysis, Writing – review & editing. **Daniela Becker:** Conceptualization, Writing – review & editing, Supervision, Project administration.

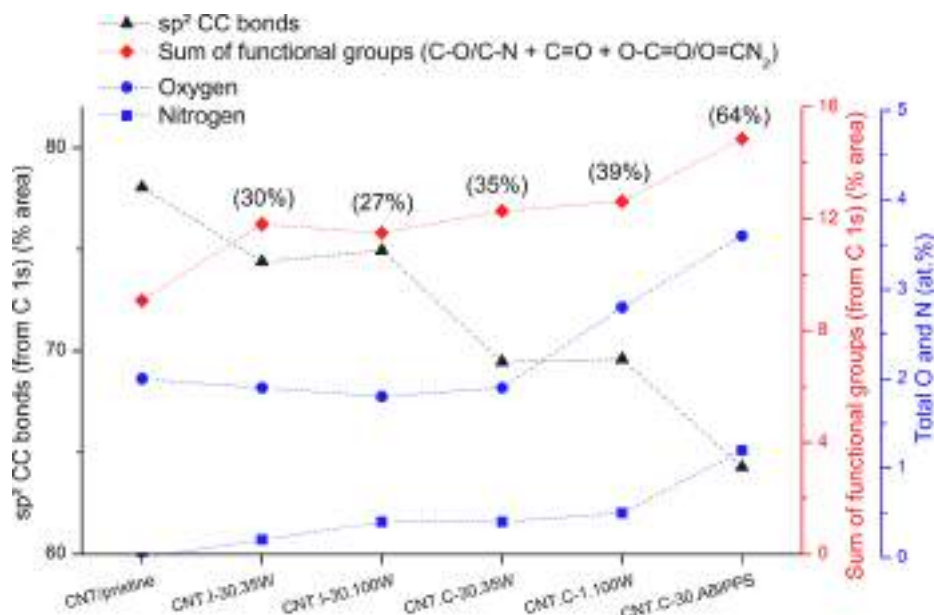


Fig. 8. Atomic percent of oxygen and nitrogen (blue), and percent related to area (from C 1 s) of sp^2 CC bonds (black) and oxygen/nitrogen functional groups (red). Numbers in parentheses indicate the percent increase regarding the CNT/pristine sample. The lines are just a visual aid.

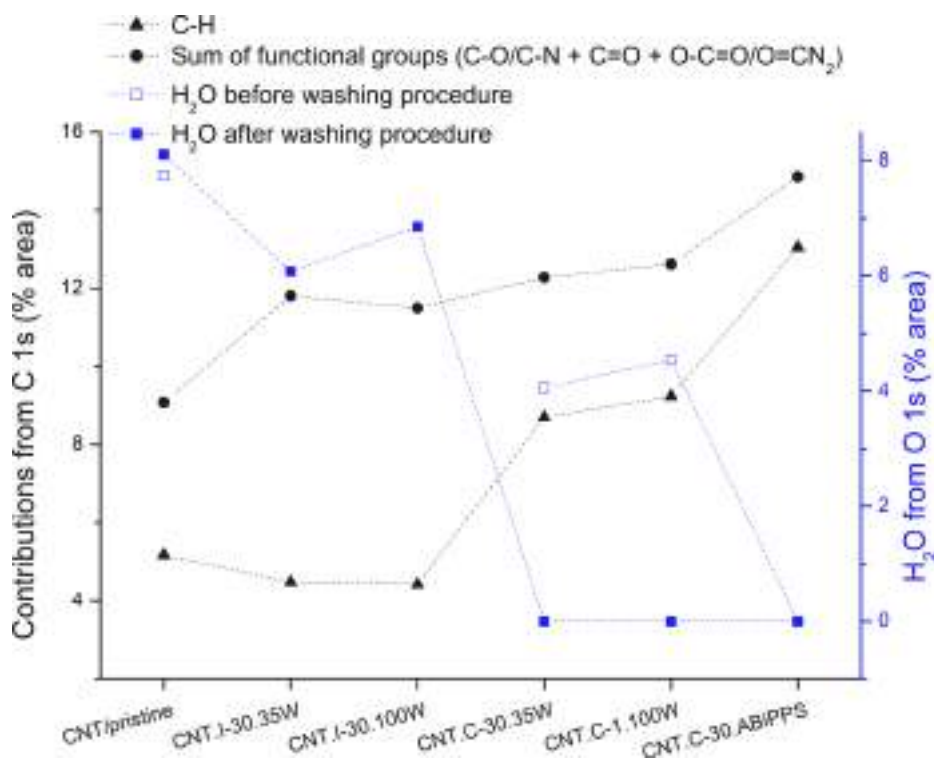


Fig. 9. Percent related to sum (Total) of functional groups and C-H bonds (black) related to water content (blue) in samples before (open square) and after (closed square) methanol washing procedure. The lines are just a visual aid.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apsusc.2022.152493>.

References

- [1] C.R. Vandenabeele, S. Lucas, Technological challenges and progress in nanomaterials plasma surface modification – A review, *Mat Sci Eng R*. 139 (2020) 100521, <https://doi.org/10.1016/j.mser.2019.100521>.
- [2] B. Ouyang, Y. Zhang, X. Xia, R.S. Rawat, H.J. Fan, A brief review on plasma for synthesis and processing of electrode materials, *Mater Today*. 3 (2018) 28–47, <https://doi.org/10.1016/j.mtnano.2018.11.002>.
- [3] A. Felten, C. Bittencourt, J.J. Pireaux, G. Van Lier, J.C. Charlier, Radio-frequency plasma functionalization of carbon nanotubes surface O₂, NH₃, and CF₄ treatments, *J Appl Phys*. 98 (7) (2005) 074308, <https://doi.org/10.1063/1.2071455>.
- [4] C. Chen, B.o. Liang, A. Ogino, X. Wang, M. Nagatsu, Oxygen Functionalization of Multiwall Carbon Nanotubes by Microwave-Excited Surface-Wave Plasma Treatment, *J. Phys. Chem. C*. 113 (18) (2009) 7659–7665, <https://doi.org/10.1021/jp9012015>.
- [5] S. Hussain, R. Amade, E. Jover, E. Bertran, Nitrogen plasma functionalization of carbon nanotubes for supercapacitor applications, *J Mater Sci*. 48 (21) (2013) 7620–7628, <https://doi.org/10.1007/s10853-013-7579-z>.
- [6] L.G. Nair, A.S. Mahapatra, N. Gomathi, K. Joseph, S. Neogi, C.P.R. Nair, Radio frequency plasma mediated dry functionalization of multiwall carbon nanotube, *Appl Surf Sci*. 340 (2015) 64–71, <https://doi.org/10.1016/j.apsusc.2015.02.036>.
- [7] T.T. Steffen, L.C. Fontana, J. Nahorny, D. Becker, Role of nitrogen–oxygen plasma functionalization of carbon nanotubes in epoxy nanocomposites, *Polym Composite*. 40 (S2) (2019) E1162–E1171, <https://doi.org/10.1002/pc.24921>.
- [8] P.K. Adusei, S. Gbordzoe, S.N. Kanakaraj, Y. Hsieh, N.T. Alvarez, Y. Fang, K. Johnson, C. McConnell, V. Shanov, Fabrication and study of supercapacitor electrodes based on oxygen plasma functionalized carbon nanotube fibers, *J Energy Chem*. 40 (2020) 120–131, <https://doi.org/10.1016/j.ijechem.2019.03.005>.
- [9] A. Manakhov, M. Michlíček, D. Nečas, J. Polčák, E. Makhneva, M. Eliáš, L. Zajíčková, Carboxyl-rich coatings deposited by atmospheric plasma copolymerization of maleic anhydride and acetylene, *Surf Coat Technol*. 295 (2016) 37–45, <https://doi.org/10.1016/j.surfcoat.2015.11.039>.
- [10] J. Moosburger-Will, M. Bauer, F. Schubert, C. Kunzmann, E. Lachner, H. Zeininger, M. Maleika, B. Hönisch, J. Küpfer, N. Zschoerper, S. Horn, Methyltrimethoxysilane plasma polymerization coating of carbon fiber surfaces, *Surf Coat Technol*. 311 (2017) 223–230, <https://doi.org/10.1016/j.surfcoat.2017.01.017>.
- [11] L. Zajíčková, P. Jelínek, A. Obrušník, J. Vodák, D. Nečas, Plasma-enhanced CVD of functional coatings in Ar/maleic anhydride/C₂H₂ homogeneous dielectric barrier discharges at atmospheric pressure, *Plasma Phys Contr F*. 59 (2017) 34003–34016, <https://doi.org/10.1088/1361-6587/aa52e7>.
- [12] S. Kocaman, M. Gursoy, M. Karaman, G. Ahmetli, Synthesis and plasma surface functionalization of carbon nanotubes for using in advanced epoxy-based nanocomposites, *Surf Coat Technol*. 399 (2020) 126144, <https://doi.org/10.1016/j.surfcoat.2020.126144>.
- [13] T.T. Steffen, L.C. Fontana, P. Hammer, D. Becker, Carbon nanotube plasma functionalization: The role of carbon nanotube/maleic anhydride solid premix, *Appl Surf Sci*. 491 (2019) 405–410, <https://doi.org/10.1016/j.apsusc.2019.06.176>.
- [14] F.V. Ferreira, W. Franceschi, B.R.C. Menezes, F.S. Brito, K. Lozano, A.R. Coutinho, L.S. Cividanes, G.P. Thim, Dodecylamine functionalization of carbon nanotubes to improve dispersion, thermal and mechanical properties of polyethylene based nanocomposites, *Appl Surf Sci*. 410 (2017) 267–277, <https://doi.org/10.1016/j.apsusc.2017.03.098>.
- [15] M.I. Ionescu, A. Laforgue, Synthesis of nitrogen-doped carbon nanotubes directly on metallic foams as cathode material with high mass load for lithium-air batteries, *Thin Solid Films*. 709 (2020) 138211, <https://doi.org/10.1016/j.tsf.2020.138211>.
- [16] M.A.O. Lourenço, M. Fontana, P. Jagdale, C.F. Pirri, S. Bocchini, Improved CO₂ adsorption properties through amine functionalization of multi-walled carbon nanotubes, *Chem Eng J*. 414 (2021) 128763, <https://doi.org/10.1016/j.cej.2021.128763>.
- [17] X. Zhang, Q. Huang, M. Liu, J. Tian, G. Zeng, Z. Li, K. Wang, Q. Zhang, Q. Wan, F. Deng, Y. Wei, Preparation of amine functionalized carbon nanotubes via a bioinspired strategy and their application in Cu²⁺ removal, *Appl Surf Sci*. 343 (2015) 19–27, <https://doi.org/10.1016/j.apsusc.2015.03.081>.
- [18] G. Yang, Y. Li, S. Yang, J. Liao, X. Cai, Q. Gao, Y. Fang, F. Peng, S. Zhang, Surface oxidized nano-cobalt wrapped by nitrogen-doped carbon nanotubes for efficient purification of organic wastewater, *Sep Purif Technol*. 259 (2021) 118098, <https://doi.org/10.1016/j.seppur.2020.118098>.
- [19] C. Geng, J. Li, T. Weiske, H. Schwarz, Complete cleavage of the N≡N triple bond by Ta₂N⁺ via degenerate ligand exchange at ambient temperature: A perfect catalytic cycle, *PNAS*. 116 (43) (2019) 21416–21420, <https://doi.org/10.1073/pnas.1913664116>.
- [20] S. Shen, Y. Chai, Q. Shen, Y. Jiang, X. Fang, Y. Pan, Gas-phase amination of aromatic hydrocarbons by corona discharge-assisted nitrogen fixation, *Sci Rep-UK*. 11 (2021) 2841, <https://doi.org/10.1038/s41598-021-82190-8>.
- [21] M.G. Trulli, E. Sardella, F. Palumbo, G. Palazzo, L.C. Giannossa, A. Mangone, R. Comporelli, S. Musso, P. Favia, Towards highly stable aqueous dispersions of multi-walled carbon nanotubes: the effect of oxygen plasma functionalization, *J Colloid Interf Sci*. 491 (2017) 255–264, <https://doi.org/10.1016/j.jcis.2016.12.039>.
- [22] B. Sajjadi, J.W. Broome, W.Y. Chen, D.L. Mattern, N.O. Egiebor, N. Hammer, C. L. Smith, Urea functionalization of ultrasound-treated biochar: A feasible strategy for enhancing heavy metal adsorption capacity, *Ultrason Sonochemistry*. 51 (2019) 20–30, <https://doi.org/10.1016/j.ultsonch.2018.09.015>.
- [23] W.E. Ford, A. Jung, A. Hirsch, R. Graupner, F. Scholz, A. Yasuda, J.M. Wessels, Urea-Melt Solubilization of Single-Walled Carbon Nanotubes, *Adv Mater*. 18 (9) (2006) 1193–1197, <https://doi.org/10.1002/adma.200502257>.
- [24] A. Gomathi, M. Ramya Harika, C.N.R. Rao, Urea route to coat inorganic nanowires, carbon fibers and nanotubes by boron nitride, *Mat Sci Eng A-Struct*. 476 (1–2) (2008) 29–33, <https://doi.org/10.1016/j.msea.2007.04.057>.
- [25] C.D. Doyle, J.M. Tour, Environmentally friendly functionalization of single walled carbon nanotubes in molten urea, *Carbon*. 47 (14) (2009) 3215–3218, <https://doi.org/10.1016/j.carbon.2009.07.035>.
- [26] N. Omidfar, A. Mohamadizadeh, S.H. Mousavi, Carbon dioxide adsorption by modified carbon nanotubes, *Asia-Pac J Chem Eng*. 10 (6) (2015) 885–892, <https://doi.org/10.1002/apj.1925>.
- [27] R. Liu, R. Liu, X. Ma, B.H. Davis, Z. Li, Efficient diesel production over the iron-based Fischer-Tropsch catalyst supported on CNTs treated by urea/NaOH, *Fuel*. 211 (2018) 827–836, <https://doi.org/10.1016/j.fuel.2017.09.114>.
- [28] N. Mohamad Yatim, A. Shaaban, M.F. Dimin, F. Yusof, J. Abd Razak, Effect of Functionalised and Non-Functionalised Carbon Nanotubes-Urea Fertilizer on the Growth of Paddy, *Trop. Life Sci. Res*. 29 (1) (2018) 17–35.
- [29] Z. Zhao, Z. Yang, Y. Hu, J. Li, X. Fan, Multiple functionalization of multi-walled carbon nanotubes with carboxyl and amino groups, *Appl Surf Sci*. 276 (2013) 476–481, <https://doi.org/10.1016/j.apsusc.2013.03.119>.
- [30] A. Alam, C. Wan, T. McNally, Surface amination of carbon nanoparticles for modification of epoxy resins: plasma-treatment vs. wet-chemistry approach, *Eur Polym J*. 87 (2017) 422–448, <https://doi.org/10.1016/j.eurpolymj.2016.10.004>.
- [31] G.-X. Chen, H.-S. Kim, B.H. Park, J.-S. Yoon, Multi-walled carbon nanotubes reinforced nylon 6 composites, *Polym*. 47 (13) (2006) 4760–4767, <https://doi.org/10.1016/j.polymer.2006.04.020>.
- [32] Y.N. Yue, W.J. Meng, L. Liu, Q.L. Hu, H. Wang, J.X. Lu, Amino acid-functionalized multi-walled carbon nanotubes: A metal free chiral catalyst for the asymmetric electroreduction of aromatic ketones, *Electrochim Acta*. 260 (2018) 606–613, <https://doi.org/10.1016/j.electacta.2017.12.058>.
- [33] Y. Yin, M.M.M. Bilek, D.R. McKenzie, R.W. Boswell, C. Charles, Micro-arcing in radio frequency plasmas, *J Phys D Appl Phys*. 37 (20) (2004) 2871–2875, <https://doi.org/10.1088/0022-3727/37/20/014>.
- [34] U. Diebold, The surface science of titanium dioxide, *Surf Sci Rep*. 48 (5–8) (2003) 53–229, [https://doi.org/10.1016/S0167-5729\(02\)00100-0](https://doi.org/10.1016/S0167-5729(02)00100-0).
- [35] J.S. Scholtz, L.C. Fontana, M. Mezaroba, Asymmetric Bipolar Plasma Power Supply to Increase the Secondary Electrons Emission in Capacitive Coupling Plasmas, *Ieee T Plasma Sci*. 46 (8) (2018) 2999–3007, <https://doi.org/10.1109/TPS.2018.2851071>.
- [36] M. Varga, T. Izak, V. Vretenar, H. Kozak, J. Holovsky, A. Artemenko, M. Hulman, V. Skakalova, D.S. Lee, A. Kromka, Diamond/carbon nanotube composites: Raman, FTIR and XPS spectroscopic studies, *Carbon*. 111 (2017) 54–61, <https://doi.org/10.1016/j.carbon.2016.09.064>.
- [37] L. Stobinski, B. Lesiak, L. Kövér, J. Tóth, S. Biniak, G. Trykowski, J. Judek, Multiwall carbon nanotubes purification and oxidation by nitric acid studied by the FTIR and electron spectroscopy methods, *J Alloy Compd*. 501 (1) (2010) 77–84, <https://doi.org/10.1016/j.jallcom.2010.04.032>.
- [38] M. Lavorgna, V. Romeo, A. Martone, M. Zarelli, M. Giordano, G.G. Buonocore, M. Z. Qu, G.X. Fei, H.S. Xia, Silanization and silica enrichment of multiwalled carbon nanotubes: Synergistic effects on the thermal-mechanical properties of epoxy nanocomposites, *Eur Polym J*. 49 (2) (2013) 428–438, <https://doi.org/10.1016/j.eurpolymj.2012.10.003>.
- [39] N.M. Yatim, A. Shaaban, M.F. Dimin, N. Mohamad, F. Yusof, Urea functionalized multiwalled carbon nanotubes as efficient nitrogen delivery system for rice, *Adv Nat Sci-Nanosci*. 10 (1) (2019) 015011, <https://doi.org/10.1088/2043-6254/ab0881>.
- [40] L. Vanyorek, Á. Prekob, V. Hajdu, G. Muránszky, B. Fiser, E. Sikora, F. Kristály, B. Viskolcz, Ultrasonic cavitation assisted deposition of catalytically active metals on nitrogen-doped and non-doped carbon nanotubes - A comparative study, *J Mater Res Technol*. 9 (3) (2020) 4283–4291, <https://doi.org/10.1016/j.jmrt.2020.02.054>.
- [41] H. Kong, C. Gao, D. Yan, Functionalization of Multiwalled Carbon Nanotubes by Atom Transfer Radical Polymerization and Defunctionalization of the Products, *Macromolecules*. 37 (11) (2004) 4022–4030, <https://doi.org/10.1021/ma049694c>.
- [42] R. Mahani, S.D. Mekky, B.A. El Sayed, G.S. EL-Bahy, A. Ward, Structural and AC electrical properties study of solid metal urea complexes, *J Adv Dielectr*. 08 (02) (2018) 1850013, <https://doi.org/10.1142/S2010135X18500133>.
- [43] M. Eichelbaum, A.B. Siemer, R.J. Farrauto, M.J. Castaldi, The impact of urea on the performance of metal-exchanged zeolites for the selective catalytic reduction of NO_x – Part II Catalytic, FTIR and NMR studies, *Appl Catal B-Environ*. 97 (1–2) (2010) 98–107, <https://doi.org/10.1016/j.apcatb.2010.03.028>.
- [44] S. Osswald, M. Havel, Y. Gogotsi, Monitoring oxidation of multiwalled carbon nanotubes by Raman spectroscopy, *J Raman Spectrosc*. 38 (6) (2007) 728–736, <https://doi.org/10.1002/jrs.1686>.
- [45] R. Gupta, B. Singh, Chemical modification of carboxylated MWCNTs for enhanced electrical conducting and magnetic properties, *Mater Sci Eng B*. 262 (2020) 114730, <https://doi.org/10.1016/j.mseb.2020.114730>.
- [46] J.H. Deng, L. Cheng, F.J. Wang, B. Yu, G.Z. Li, D.J. Li, G.A. Cheng, Ultralow field emission from thinned, open-ended, and defected carbon nanotubes by using microwave hydrogen plasma processing, *Appl Surf Sci*. 324 (2015) 293–299, <https://doi.org/10.1016/j.apsusc.2014.10.137>.
- [47] P. He, Y. Gao, J. Lian, L. Wang, D. Qian, J. Zhao, W. Wang, M.J. Schulz, X.P. Zhou, D. Shi, Surface modification and ultrasonication effect on the mechanical

- properties of carbon nanofiber/polycarbonate composites, *Compos Part A-Appl S.* 37 (9) (2006) 1270–1275.
- [48] J. Li, Z. Wu, C. Huang, Z. Chen, R. Huang, L. Li, Plasma functionalization for improving dispersion and interfacial bonding of multi-wall carbon nanotubes in cyanate ester/epoxy nanocomposites, *Colloid Surface A.* 433 (2013) 173–180, <https://doi.org/10.1016/j.colsurfa.2013.04.057>.
- [49] L. Fedrizzi, F.J. Rodriguez, S. Rossi, F. Deflorian, R. Di Maggio, The use of electrochemical techniques to study the corrosion behaviour of organic coatings on steel pretreated with sol–gel zirconia films, *Electrochim Acta* 46 (24–25) (2001) 3715–3724, [https://doi.org/10.1016/S0013-4686\(01\)00653-3](https://doi.org/10.1016/S0013-4686(01)00653-3).
- [50] A.V. Naumkin, A. Kraut-Vass, S.W. Gaarenstroom, C.J. Powell, NIST X-ray Photoelectron Spectroscopy Database 20, v4.1, 2012. <https://doi.org/10.17632/xwj98nb39r.1>.
- [51] A. Theodosiou, B.F. Spencer, J. Counsell, A.N. Jones, An XPS/UPS study of the surface/near-surface bonding in nuclear grade graphites: A comparison of monatomic and cluster depth-profiling techniques, *Appl Surf Sci.* 508 (2020) 144764, <https://doi.org/10.1016/j.apsusc.2019.144764>.
- [52] M. Ayiania, M. Smith, A.J.R. Hensley, L. Scudiero, J. McEwen, M. Garcia-Perez, Deconvoluting the XPS spectra for nitrogen-doped chars: An analysis from first principles, *Carbon.* 162 (2020) 528–544, <https://doi.org/10.1016/j.carbon.2020.02.065>.
- [53] R. Droppa, P. Hammer, A.C.M. Carvalho, M.C. dos Santos, F. Alvarez, Incorporation of nitrogen in carbon nanotubes, *J Non-Cryst Solids.* 299–302 (2002) 874–879, [https://doi.org/10.1016/S0022-3093\(01\)01114-0](https://doi.org/10.1016/S0022-3093(01)01114-0).
- [54] X. Fan, J. Li, D. Qiu, T. Zhu, Production of ammonia from plasma-catalytic decomposition of urea: Effects of carrier gas composition, *J Environ Sci.* 66 (2018) 94–103, <https://doi.org/10.1016/j.jes.2017.05.033>.
- [55] N. Sharma, S.N. Alam, B.C. Ray, Fundamentals of Spark Plasma Sintering (SPS): An Ideal Processing Technique for Fabrication of Metal Matrix Nanocomposites, *Spark Plasma Sintering of Materials.* (2019) 21–59, https://doi.org/10.1007/978-3-030-05327-7_2.
- [56] J.A. Dean, *Lange's Handbook of Chemistry*, fifteenth ed., McGraw-Hill Inc, New York, 1998.
- [57] M. Mozetič, A. Vesel, G. Primc, R. Zaplotnik, Chapter 2 - Introduction to Plasma and Plasma Diagnostics, in: S. Thomas, M. Mozetič, U. Cvelbar, P. Spatenka, K. M. Praveen (Eds.), *Non-Thermal Plasma Technology for Polymeric Materials - Applications in Composites, Nanostructured Materials and Biomedical Fields*, Elsevier, Slovenia, 2019, pp. 23–65, <https://doi.org/10.1016/B978-0-12-813152-7.00002-0>.
- [58] N.M. Yatim, A. Shaaban, M.F. Dimin, F. Yusof, Statistical Evaluation of the Production of Urea Fertilizer Multiwalled Carbon Nanotubes using Plackett Burman Experimental Design, *Procedia Soc Behav Sci.* 195 (2015) 315–323, <https://doi.org/10.1016/j.sbspro.2015.06.358>.
- [59] Y. Wei, X. Zhang, Z. Luo, D. Tang, C. Chen, T. Zhang, Z. Xie, Nitrogen-Doped Carbon Nanotube-Supported Pd Catalyst for Improved Electrocatalytic Performance toward Ethanol Electrooxidation, *Nano-Micro Lett.* 9 (2017) 28, <https://doi.org/10.1007/s40820-017-0129-5>.
- [60] X. Tian, Z. Yang, B.o. Zhou, P. Xiu, Y. Tu, Alcohol-induced drying of carbon nanotubes and its implications for alcohol/water separation: A molecular dynamics study, *J. Chem. Phys.* 138 (20) (2013) 204711, <https://doi.org/10.1063/1.4807484>.
- [61] W. Winarto, D. Takaiwa, E. Yamamoto, K. Yasuoka, Yasuoka, Separation of water–ethanol solutions with carbon nanotubes and electric fields, *Phys Chem Chem Phys.* 18 (48) (2016) 33310–33319.
- [62] P. Xiu, Z. Yang, B.o. Zhou, P. Das, H. Fang, R. Zhou, Urea-Induced Drying of Hydrophobic Nanotubes: Comparison of Different Urea Models, *J Phys Chem B.* 115 (12) (2011) 2988–2994, <https://doi.org/10.1021/jp108303q>.
- [63] W. Winarto, D. Takaiwa, E. Yamamoto, K. Yasuoka, Yasuoka, Water–methanol separation with carbon nanotubes and electric fields, *Nanoscale.* 7 (29) (2015) 12659–12665.
- [64] R. Dubey, D. Dutta, A. Sarkar, P. Chattopadhyay, Functionalized carbon nanotubes: synthesis, properties and applications in water purification, drug delivery, and material and biomedical sciences, *Nanoscale Adv.* 3 (20) (2021) 5722–5744.

Development of surface-treated poly(lactic acid)/zinc oxide biocomposites for 3D printing in bone tissue engineering

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Abstract

The increase in bone fractures has been driving the development of materials for bone repair with better mechanical and biological properties. This work reports the development of poly (lactic acid) (PLA)-zinc oxide (ZnO) biocomposites for 3D printing of scaffolds to be applied in bone tissue engineering. The ZnO surface was functionalized with maleic anhydride (ZnOMA) by applying radio frequency plasma treatment as an alternative to control the catalytic effects of ZnO on the degradation of the PLA during the molten state processing. PLA and ZnOMA powders were processed using a heated internal mixer and the resulted biocomposites were used to manufacture scaffolds by 3D printing. The scaffolds were characterized by their rheological, thermal, microstructural, mechanical, and biological properties. Compositions containing ZnOMA presented higher viscosities, evidencing the control of degradation by surface functionalization, and achieved an elastic modulus near 1 GPa, suitable for bone applications, unlike the untreated samples. In relation to cell functions, PLA-ZnOMA scaffolds exhibited cell viabilities at 160%, compared to 50% for untreated samples and stimulated mesenchymal stem cells toward osteoblast. Therefore, ZnO's negative thermal degradation effect on PLA was successfully overcome using plasma functionalization, enabling the 3D printing of bioactive scaffolds with great potential for application in tissue engineering.

1 | INTRODUCTION

The aging of the population has promoted an increase in the incidence of bone fractures and tumors, which are treated using grafts.¹ However, due to scarcity, high rejection rates, and high costs, tissue engineering has been

involved in developing synthetic substitute scaffolds with properties closer to those of living tissue.^{2–4} Bone tissue is structured with cells like osteocytes, osteoblasts, and osteoclasts and an extracellular matrix rich in type I collagen and hydroxyapatite. This composition provides flexibility, and structural strength, enabling bones to withstand

impacts while supporting the body, facilitating hematopoiesis, and regulating minerals. Building upon this, bone tissue scaffolds mimic this hierarchical structure, enhancing osteoconductivity and osteoinduction.⁵ They provide necessary compression resistance and porosity for vascularization and metabolic waste transport. Effective scaffolds feature an interconnected pore network with diameters between 250 and 500 μm to optimize cell and nutrient mobility and prevent cell proliferation issues.^{6,7} Recent advances in materials, such as the combination of biodegradable polymers and ceramic materials like hydroxyapatite and bioactive glass, have been crucial in achieving the chemical composition of natural bone.⁸ The combination of poly(lactic acid) (PLA) with zinc oxide (ZnO) shows promise in achieving these objectives; however, the degradation of the polymeric matrix in the presence of these particles remains a challenge, as it reduces the molecular weight, the mechanical properties and generates acidic products, making it impractical for use as a scaffold.^{9–11}

PLA is a semi-crystalline polymer that has been extensively studied and applied in the biomedical field due to its excellent biocompatibility and the relationship between biodegradation rate and mechanical properties, with the biodegradation rate being very close to the rate of bone regeneration.^{12,13} However, for application in bone tissue, this polymer does not present itself as an osteoinductive material, an indispensable property for stimulating bone regeneration.¹⁴ As a result, the incorporation of ceramic particles (MgO , SiO_2) has proven successful in imparting this characteristic to the polymeric matrix.¹⁵

ZnO is an inorganic particle that is osteoinductive, mainly due to the release of Zn^{2+} ions that stimulate mesenchymal stem cells to differentiate into osteoblasts through the upregulation of the gene expression of RUNX-2 (transcription factor), BMP-2 (morphogenetic protein), and osteocalcin (protein), thus primarily acting in the mineralization phase of the extracellular matrix.^{16–18} In addition, ZnO has bactericidal properties, reducing the risk of implant rejection due to infections.¹⁹

The major challenge in combining these two materials is the catalytic effect of Zn^{2+} ions released by ZnO on the thermal degradation reactions of PLA during melt.^{20,21} Lizundia et al.²² observed the catalytic effect of ZnO on the unzipping, and transesterification reactions of PLA, reducing the thermal stability of the composite. To enhance the stability of ZnO in polymer applications, modifying the surface to regulate ion release could be effective. Although the literature often cites wet chemical functionalization of zinc oxide, this approach has limitations due to its reliance on solvents and extended processing times.²³ For medical applications, plasma

functionalization is a viable alternative that avoids the use of predominantly cell-toxic organic solvents, thus offering a safer and potentially quicker solution.^{24,25} Then, plasma surface treatment represents a promising strategy in tissue engineering, aiming to create reactive sites and introduce functional groups to achieve a delicate balance between hydrophilicity and hydrophobicity. Various studies highlight the biological efficacy of functionalizing particles with substances such as carboxylic acids, amines, thiols, and alcohols. However, when it comes to metal oxide particles like zinc oxide, the challenge lies in minimizing degradative effects on the polymeric matrix without compromising biological interactions.^{26,27}

Scaffolds are typically manufactured using conventional techniques such as solvent-casting, particulate leaching, electrospinning, and gas foaming. While these methods are widely employed, they exhibit several drawbacks, including limited control over the shape, size, distribution, and architecture of the pores, as well as the composition and use of toxic solvents.^{28,29} In contrast, 3D printing emerges as a promising alternative in scaffold development. It enables the precise control of pore size and shape and facilitates the creation of complex geometries tailored to specific clinical cases, all without the need for toxic solvents.⁷

Therefore, the present work aims to develop and assess the efficacy of surface-treated poly (lactic acid)/zinc oxide (PLA/ZnOMA) scaffolds for bone tissue engineering. Utilizing 3D printing technology, we aim to explore the potential of maleic anhydride plasma-treated zinc oxide particles (ZnOMA) in enhancing the structural integrity of PLA. This treatment is hypothesized to mitigate the catalyzed degradation by ZnO typically observed in PLA during the processing phase. By stabilizing the scaffold's degradation, we seek to preserve the mechanical and biological properties essential for its application as a viable bone substitute. The significance of this research lies in its potential to advance bone regeneration technologies, offering improved solutions for bone repair and replacement.

2 | EXPERIMENTAL

2.1 | Materials

The PLA Biopolymer 2003D (PLA 2003D) was supplied by NatureWorks, Ingeo™ with a specific mass of 1.24 g cm^{-3} , a melt flow index of $6.0 \text{ g.10 min}^{-1}$ (210°C , 2.16 kg), tensile Strength of 53 MPa, tensile modulus of 3.5GPa and contains 4.3% (m.m^{-1}) of the D-isomer, as detailed in the product's datasheet.³⁰ The micrometer-sized ZnO (99% purity and 325 mesh) was

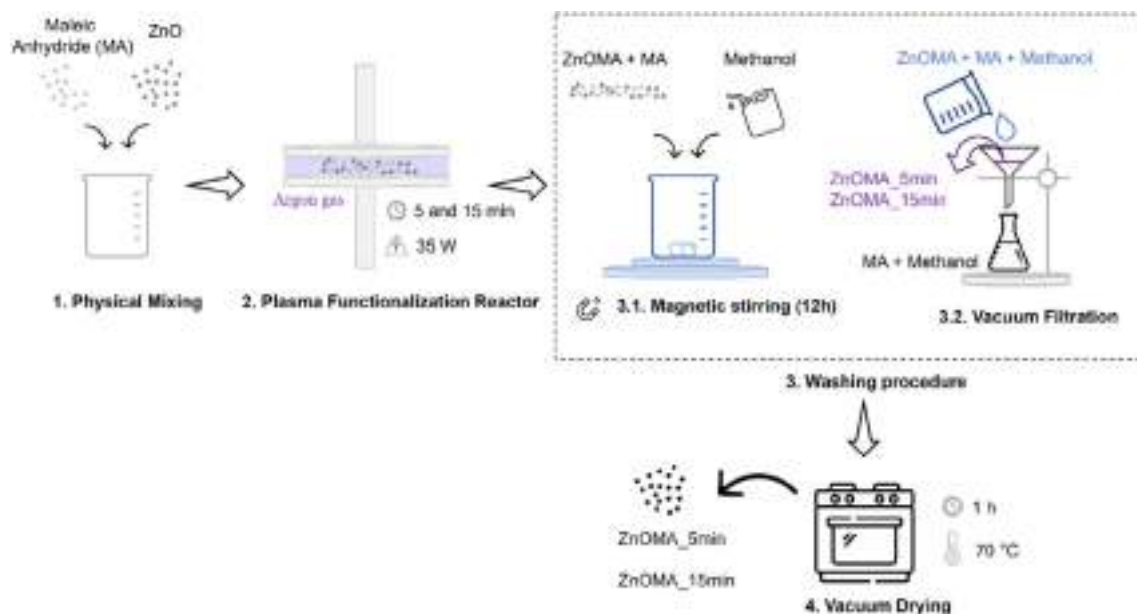


FIGURE 1 Process representation of customized plasma functionalization of zinc oxide with MA. MA, maleic anhydride. [Color figure can be viewed at wileyonlinelibrary.com]

obtained from Alfa Aesar and treated by plasma using maleic anhydride (99% purity) purchased from Sigma-Aldrich Chemistry.

2.2 | In-situ plasma functionalization

The plasma surface treatment process was carried out according to the methodology represented in Figure 1.^{27,31} This methodology has been extensively described and discussed in our previous work.²⁷ The Capacitive Coupled Plasma reactor employed for functionalizing zinc oxide was homemade, based on the experience assembling previous reactors.^{27,31,32} The combination of zinc oxide and maleic anhydride (ZnOMA) was carried out in a mass proportion of 90/10, mixed for 2 min using mortar and pestle. Starting with a base pressure of 2×10^{-1} Torr, argon gas was introduced at a rate of 36.5 sccm, achieving a working pressure of 9×10^{-1} Torr. The argon flow, without plasma discharge, was maintained for 15 min to facilitate cleaning the discharge environment. Subsequently, plasma treatment was executed at a power of 35 W for 5 and 15 min. Following functionalization, a washing procedure was implemented to eliminate any potential non-reacted molecules of the functionalizing agent. This involved leaving the samples under magnetic stirring for 12 h and then passing them through a vacuum filtration process to separate solid and liquid phases. Finally, the samples were placed in an oven at 70 °C for 1 h. More detailed information about the experimental procedure and plasma

surface treatment results can be accessed in our previous work.²⁷

2.3 | Characterization of zinc oxide's surface

Fourier-transform infrared spectroscopy (FTIR) was performed to evaluate how the plasma treatment modified the surface of zinc oxide. The experiment was conducted using a Thermo Nicolet 6700 FT-IR Spectrometer, scanning the spectral region from 4000 to 400 cm^{-1} , with a resolution of 4 cm^{-1} , at transmittance mode using KBr pellets.

2.4 | Manufacturing of scaffolds

The processing was carried out in a mixing chamber coupled to a Haake torque rheometer, model Rheomix 600p, with counter-rotating and semi-interpenetrating roller-type rotors at 175 °C. Mixing occurred for 5 min at 60 rpm. The processed material was hot pressed (Marconi®, MA098/A) at a temperature of 175 °C and 7 bar for 5 min, chopped, and taken to the 3D printer to manufacture the scaffolds, as described in Figure 2. The printed scaffolds were designed using Prusa Slicer® software with a 0–90° cylindrical geometry, composed of 10 layers of 300 μm thickness, with 400 μm pores (Figure 2) and printed using an extrusion-based 3D printer (3D Biotechnology Solutions). The chopped

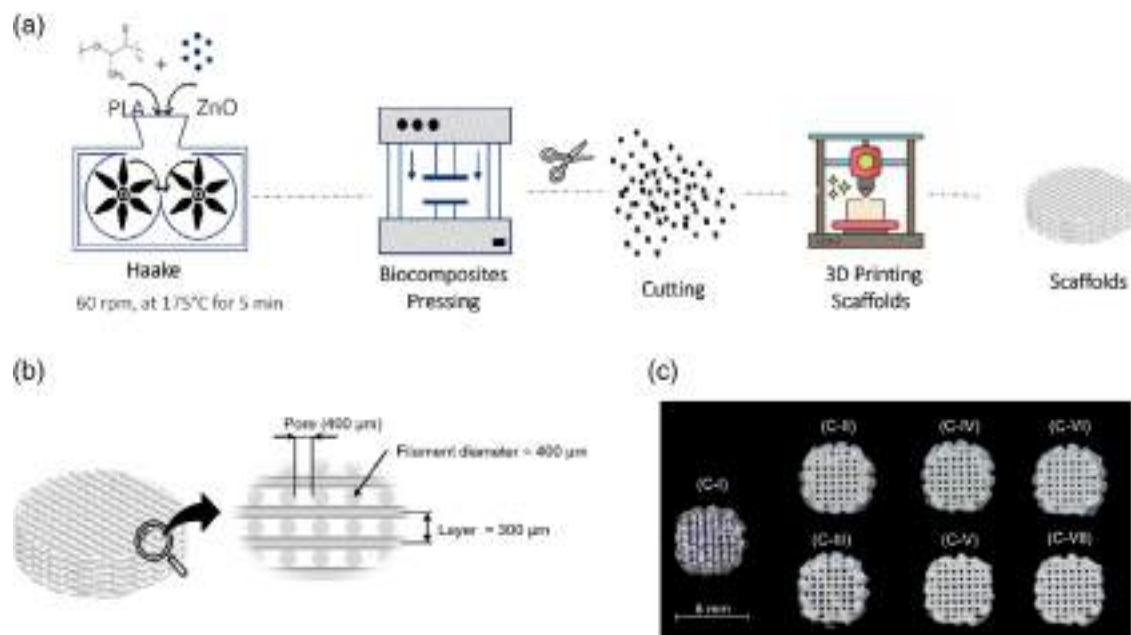


FIGURE 2 (a) Experimental procedure for composites fabrication using melting processing, and subsequently scaffold manufacture using 3D printing. (b) Concept of the designed scaffold, with the dimensions; (c) Photo of the printed scaffolds: (C-I) PLA; (C-II) PLA + 5% ZnO; (C-III) PLA + 10%ZnO; (C-IV) PLA + 5%zinc oxide and maleic anhydride (ZnOMA)_5 min; (C-VI) PLA + 10%ZnOMA_5 min; (C-VI) PLA + 5%ZnOMA_15 min; (C-VII) PLA + 15%ZnOMA_15 min. [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Printing parameters of the scaffolds.

Sample	Printing temperature (°C)	Printing speed (mm/s)	Infill (%)
PLA PELLET	175	300	42
PLA PURE			
PLA + 5%ZnO	155		
PLA + 10%ZnO			
PLA + 5%ZnOMA_5 min	165		
PLA + 10%ZnOMA_5 min			
PLA + 5%ZnOMA_15 min			
PLA + 10%ZnOMA_15 min			

Abbreviation: PLA, poly(lactic acid).

materials were placed in a heated metal syringe and deposited layer by layer to form the scaffold. The parameters used for 3D printing scaffolds of each composition are listed in Table 1.

2.5 | Rheology

To characterize the rheological behavior, essential for the printing process, the steady-state rheological behavior of PLA and PLA/ZnO biocomposites was evaluated after processing in Haake, using a controlled-stress parallel plate rheometer (AR G2 model from TA Instruments)

with a 25 mm diameter and 0.6 mm distance between plates. The shear rate was scanned between 0.01 and 100 s⁻¹, under an inert N₂ atmosphere at the printing temperature of each composition. The oscillatory regime was performed under the same equipment and conditions but in a range of angular frequency from 0.02 to 500 rad s⁻¹, with a deformation of 1%.

2.6 | Scanning electron microscope

Morphological analysis was performed using scanning electron microscopy on a Quanta 400 FEI scanning

electron microscope, operating at an acceleration voltage of 15 kV. The samples were prepared by cryofracture of the scaffolds in the cross-sectional portion, which were then fixed on stubs and coated with a thin layer of gold.

2.7 | Thermogravimetric analysis

To evaluate the thermal stability of the composites, the thermogravimetric analysis technique was performed on the scaffolds using a TGA 4000 instrument (PerkinElmer) at a heating rate of 10°C/min, from room temperature to 800°C, under a N₂ atmosphere.

2.8 | Differential scanning calorimetry

The differential scanning calorimetry technique was performed to evaluate the crystallinity of composites using the TA Instruments model Q2000 instrument with continuous nitrogen flow at 50 mLmin⁻¹. The thermal program consisted of two heating cycles from 0 to 200°C at a rate of 10°Cmin⁻¹, separated by a cooling cycle at the same rate and isotherms at the maximum and minimum temperatures for 5 min. The T_g and T_m temperatures, as well as the thermodynamic parameters of enthalpy, were obtained from the second heating cycle. The degree of crystallinity was calculated using Equation (1).

$$X_c = \frac{(\Delta H_m - \Delta H_c)}{\Delta H_m^o (201 - m)} \quad (1)$$

where X_c is the degree of crystallinity, ΔH_m and ΔH_m^o are, respectively, the enthalpy of crystalline fusion of the sample and the theoretical enthalpy of crystalline fusion of 100% crystalline PLA (93 J.g⁻¹), ΔH_{cc} is the enthalpy of cold crystallization if it occurs, and m is the mass fraction of ZnO present in the PLA matrix.

2.9 | Mechanical characterization

The mechanical characterization of the scaffolds was specifically focused on evaluating Young's modulus, performed in uniaxial compression mode using an Instron universal testing machine, model 5569. A load cell of 500 N was selected to enhance the precision of the measurements. Testing was conducted at a crosshead speed of 1.3 mm/min, with six specimens measured for each composition.

2.10 | Hydrophilicity

The Biolin Scientific optical tensiometer, Attension TF3000-Plus, was applied to obtain the contact angle between the samples and water. Drops of distilled water with a volume of 10 µL were dispensed, and after 10 s, the contact angle was measured using the OneAttension software. The analysis used six measurements for each composition, the mean and standard deviation of which were calculated.

2.11 | Cell viability

Prior to biological assays, the printed scaffolds were sterilized by immersion in 70% ethanol for 5 min, followed by UV irradiation for 60 min. The cytotoxicity of the scaffolds was evaluated after 1 and 7 days in contact with mesenchymal stem cells derived from bone marrow (MSCs, ATCC PCS-500-012™). The composition of the cell culture medium was 89% modified Eagle's medium-Dulbecco (DMEM, high glucose with L-glutamine), 10% fetal bovine serum (FBS), and 1% penicillin/streptomycin. For WST-1 and live/dead assays, the scaffolds were placed in a 48-well plate, and MSCs (0.4 mL) solution was added to the wells. The plate was kept in an incubator at 37°C, humidified, and containing 5% CO₂. The medium was changed every 2–3 days. Cell viability was evaluated using the WST-1 assay kit (ab65475, Abcam) and analyzed by measuring absorbance at 440 nm using a microplate reader. The live/dead assay (LIVE/DEAD™ viability/cytotoxicity kit for mammalian cells, Thermo Fisher Scientific) stains live cells with green dye and dead cells with red dye. The images were captured in a fluorescent microscope (Nikon TS2-LS).

2.12 | Mineralization (alizarin red)

To evaluate the calcium deposition, the MSCs were cultured in an osteogenic medium composed of StemPro™ medium (100 mL), StemPro™ osteogenic supplement (10 mL), and 55 µL 1% penicillin/streptomycin (StemPro™ Osteogenesis Differentiation Kit-Gibco™, Thermo Fisher Scientific). After 28 days of cell culture on the scaffolds, the cells were fixed with 4% formaldehyde, and alizarin red staining and quantification was performed. After fixing, the scaffolds were washed with PBS, stained with 2% alizarin red S (Sigma Aldrich), washed with deionized water and imaged. For ARS quantification, 0.5 N HCl containing 5% sodium dodecyl sulphate (SDS) solution was used to solubilize the staining and the absorbance was measured at 415 nm using a microplate reader (FLUOstar® Omega, BMG LABTECH).

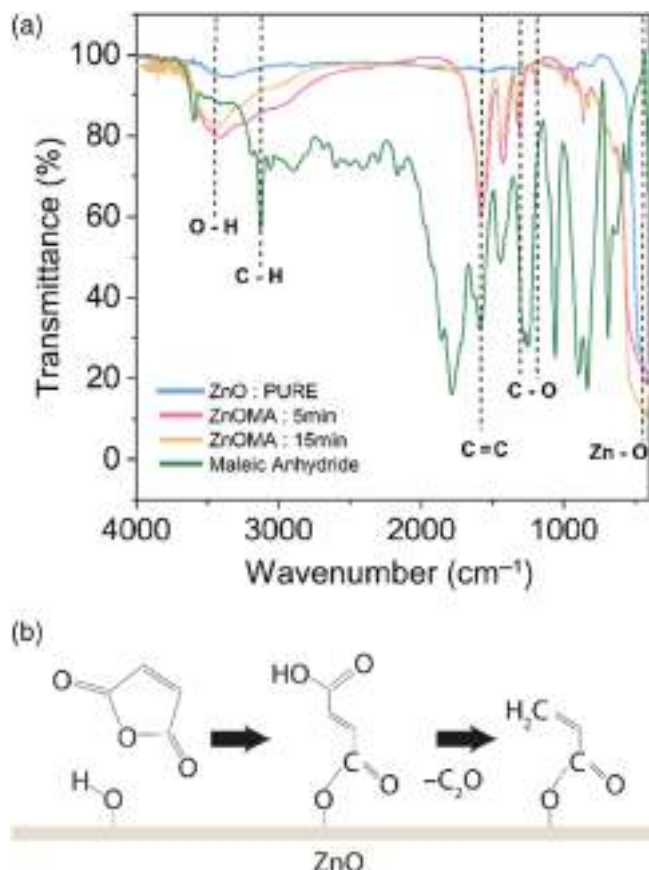


FIGURE 3 (a) Fourier-transform infrared spectra for PURE ZnO, ZnO_AM_5 min, ZnO_AM_15 min and maleic anhydride samples. (b) Representation of the functionalization mechanism of ZnO with maleic anhydride. [Color figure can be viewed at wileyonlinelibrary.com]

2.13 | Data analyses

The statistical analysis of the data was performed using one-way ANOVA followed by the Tukey multiple comparison test, considering significant variation for $p < 0.05$.

3 | RESULTS AND DISCUSSION

3.1 | Zinc Oxide's surface characterization

Figure 3a shows the FTIR spectra for the ZnOMA_5 min and ZnOMA 15 min samples compared to pure ZnO and maleic anhydride. In the spectrum of zinc oxide, there are absorption bands at 530, 3434 and 1300–1600 cm^{-1} , which respectively represent the stretching vibration of the Zn–O bond, hydroxyls present on the surface of the oxide zinc, and carboxylate impurities.³³ On the other hand, in the spectrum of maleic anhydride, it was possible to observe bands at 980–1310 cm^{-1} (C–O–C bond

stretch), 1290 and 1242 cm^{-1} (C–O asymmetric stretch), 1635 and 1590 cm^{-1} (C=C bond stretch of the ring of the anhydride), 1835 and 1738 cm^{-1} (asymmetric and symmetric stretching of the C=O bond of the cyclic anhydride), 3130 cm^{-1} (stretching of the C–H bond) and 3420 cm^{-1} (possible presence of water in the sample).³⁴ The spectra for the superficially treated zinc oxide present bands characteristics of maleic anhydride that are not present in the pure zinc oxide spectra: the band at 1585 cm^{-1} refers to the elongation of the C=C double bond, and the bands between 1309 and 1187 cm^{-1} , the elongation of the C–O bond. Therefore, indicating the functionalization of the ZnO through plasma. Furthermore, there are no significant differences in the spectra between the treated samples at different times (5 and 15 min), indicating that the functionalization occurred in both conditions, probably due to the mechanism described in Figure 3b. Initially, the ring opening is initiated through the action of hydroxyl groups present on the particle surface. The sequence progresses to encompass decarboxylation and decarboxylation reactions, resulting in the formation of stable surface species.^{26,35} These reactions align with the observed augmentation in C–O and C=C functional groups at the FTIR spectrum.

3.2 | Rheological characterization

The mixing of PLA and ZnO particles was performed using HAAKE torque rheometry to analyze the torque of the mixture under high temperatures. The results presented in Figure 4a indicate that after 5 min of mixing, the torque for the biocomposites was lower than that of pure PLA, particularly in samples without surface treatment. This observation suggests that ZnO may catalyze degradation reactions in PLA, leading to a more pronounced effect on torque reduction. In steady-state rheological analysis, Figure 4b, the viscosity curves by shear rate show that between 0.01 and 10 s^{-1} , all materials exhibit nearly Newtonian fluid behavior. Nevertheless, as the concentration of ZnO increases, the reduction of the viscosity plateau concerning pure PLA becomes more pronounced. Furthermore, samples with ZnOMA presented a greater viscosity than untreated ones. In Figure 4c, it is observed that the depolymerization and intermolecular transesterification reactions of PLA are catalyzed by the release of Zn^{2+} ions, which act to reduce the activation energy of degradation, mainly during processing in which the material is in an environment thermomechanical of high shear rates and temperature. Thus, the reduction in the viscosity of the Newtonian plateau (η_0) in the presence of ZnO is an indication of the occurrence of these reactions, given that by reducing

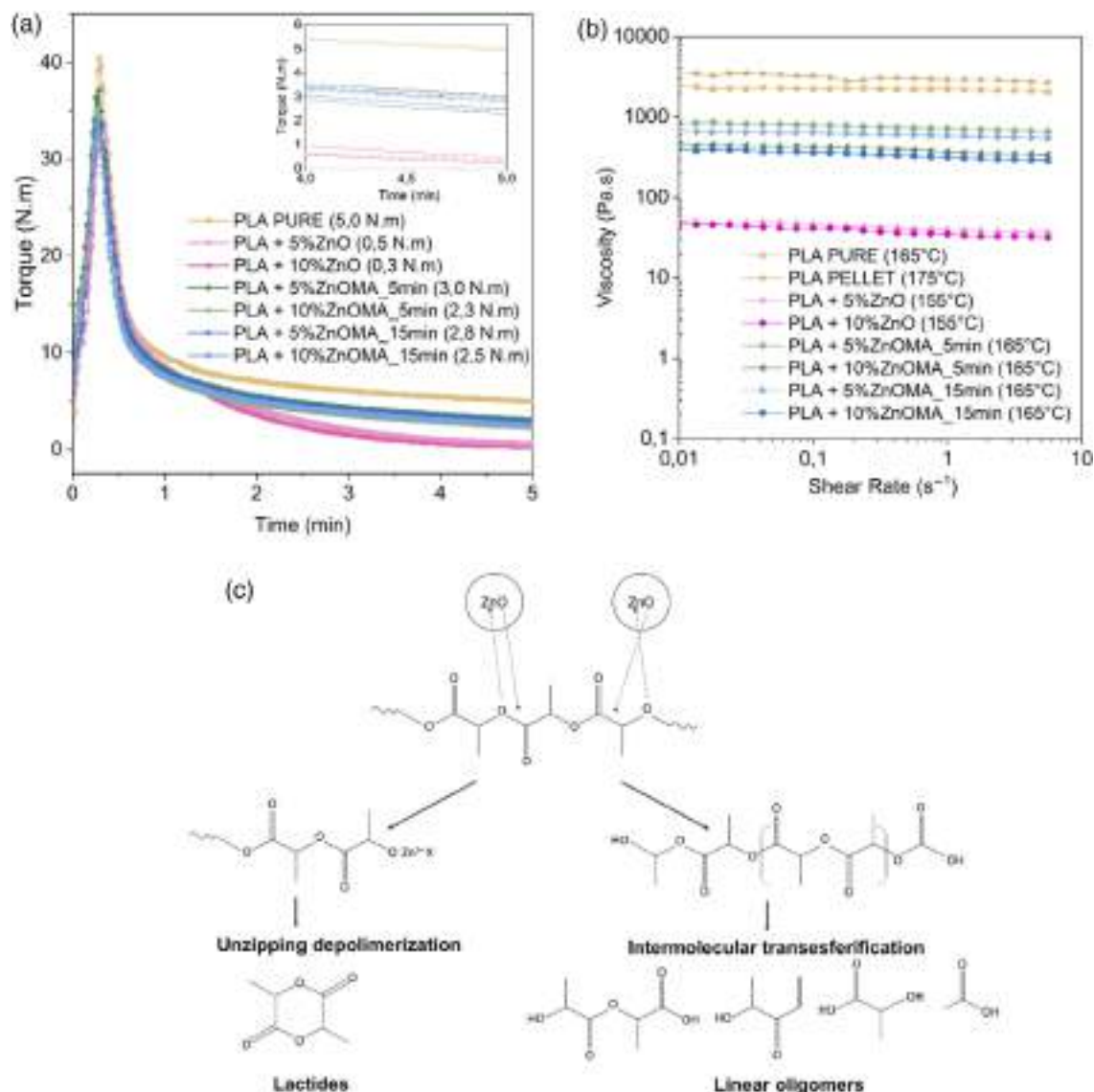


FIGURE 4 (a) Torque variation curves as a function of time for mixing PLA and biocomposites during processing in a Haake; (b) Viscosity versus shear rate curves for PLA, PLA/ZnO and PLA/ZnOMA biocomposites at the printing temperature of each sample; (c) Catalyst mechanism of PLA degradation reactions by ZnO. [Color figure can be viewed at wileyonlinelibrary.com]

the molecular mass, it reduces the average size of the chains, which results in a lower probability of entanglement density between macromolecules, promoting fewer flow restrictions that lead to a decrease in the viscosity level.³⁶ Thus, the functionalization of the ZnO surface acted to reduce the PLA degradation rate, providing higher viscosity values than samples with untreated ZnO.

The oscillatory state analysis is an important technique for investigating the relationship between the elastic and viscous behavior of the material. For 3D printing of scaffolds, it is recommended that the material present enough elasticity (storage modulus G') to maintain the deposited shape after the polymer's relaxation; therefore, for good printability, the material must have a storage modulus (G') higher than or at least close enough to the

loss modulus (G''). Figure 5a,b exhibit, respectively, the curves of G' and G'' as a function of oscillatory frequency (ω). All biocomposites exhibit predominantly viscous behavior ($G'' > G'$) within the range of 0.02 to 500 rad s⁻¹. In contrast, pure PLA shows a transition point at 88 rad/s, where, for higher frequencies, elastic behavior becomes predominant ($G' > G''$). This suggests that samples containing ZnO particles experience lower molecular interaction due to degradation during processing, leading to a reduced molecular weight of the PLA matrix. Consequently, this reduction in entanglement density increases the predominance of viscous behavior over elastic behavior.

The observed behavior under both test conditions suggests that the presence of functionalization resulted in

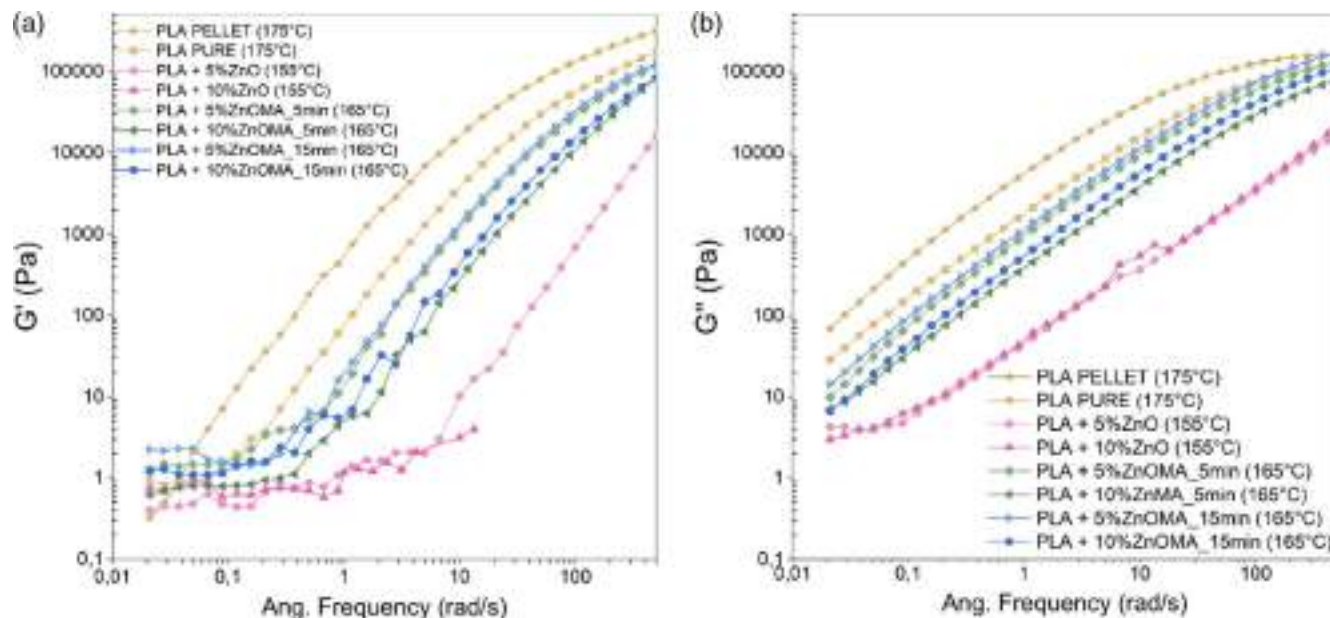


FIGURE 5 G'' and G' curves versus angular frequency for PLA and biocomposites of PLA/ZnO and PLA/ZnOMA at their respective printing temperatures. [Color figure can be viewed at wileyonlinelibrary.com]

fewer variations in rheological properties compared to pure PLA. This effect is particularly noticeable when compared to untreated samples. It is probably linked to the decrease in degradation during processing. Degradation typically leads to a reduction in molecular weight, and chain size, diminishing the probability of entanglements. As a result, this decrease in entanglements eases the flow restriction, leading to lower viscosity values and a predominance of viscous behavior over elastic behavior. Surface functionalization, by inserting C=C and C—O groups, acted as a protection for the ZnO surface, reducing its reactivity and the release of ions, therefore reducing the role of this particle as a catalyst for PLA degradation reactions under melt processing conditions.

3.3 | Thermal analysis

A thermogravimetric test was carried out to analyze the effects of ZnO and ZnOMA on the thermal stability of each composition (Figure 6a,b). From the TG and DTG curves, along with the data described in Table 2, it can be concluded that the presence of ZnO reduces the thermal stability of the PLA matrix, as evidenced by the premature onset of the degradation event. In the ZnO sample, the T_{onset} was 64°C lower than that of pure PLA, while for samples with ZnOMA, it was 42°C lower. Through this result, we can evaluate the affectivity of the surface treatment in controlling the catalytic action of zinc oxide on the PLA, showing that plasma functionalization with maleic anhydride reduces the

reactivity of the ZnO, decreasing the catalyzation of the matrix.

The presence of a secondary peak in mass variation can be linked to the process of molecule desorption, possible PLA molecules absorbed during processing. Qu et al.³⁷ also observed the occurrence of this second peak and, through an FTIR analysis of particles isolated from the polymer matrix using dissolution in toluene, associated this thermal event with the desorption of PLA molecules adsorbed on the surface of ZnO during processing, given that the spectrum of these particles indicated the presence of carboxyl group stretching bands (1761 cm^{-1}). The residue observed at 800°C validates the composition and regularity of the samples, showing that in samples with treated particles, the maleic anhydride groups inserted were decomposed during heating.

It is known that PLA 2003D, due to the presence of 4.3% of the D isomer, exhibits slow crystallization kinetics, manifesting in an amorphous form. Therefore, a DSC test was conducted to analyze whether the presence of ZnO interferes with the crystallization of the matrix. The cooling curves did not show exothermic crystallization peak for any of the sample; however, the second heating curves revealed different behaviors for the samples (Figure 6c). Pure PLA and PLA + ZnOMA, unlike the pellets, exhibited cold crystallization and fusion peaks that may be associated with smaller chain sizes that, due to greater mobility, allow for adequate crystallization conformation and acting as nucleation points. The presence of a double melting peak in biocomposites with ZnOMA may be attributed to the coexistence of different

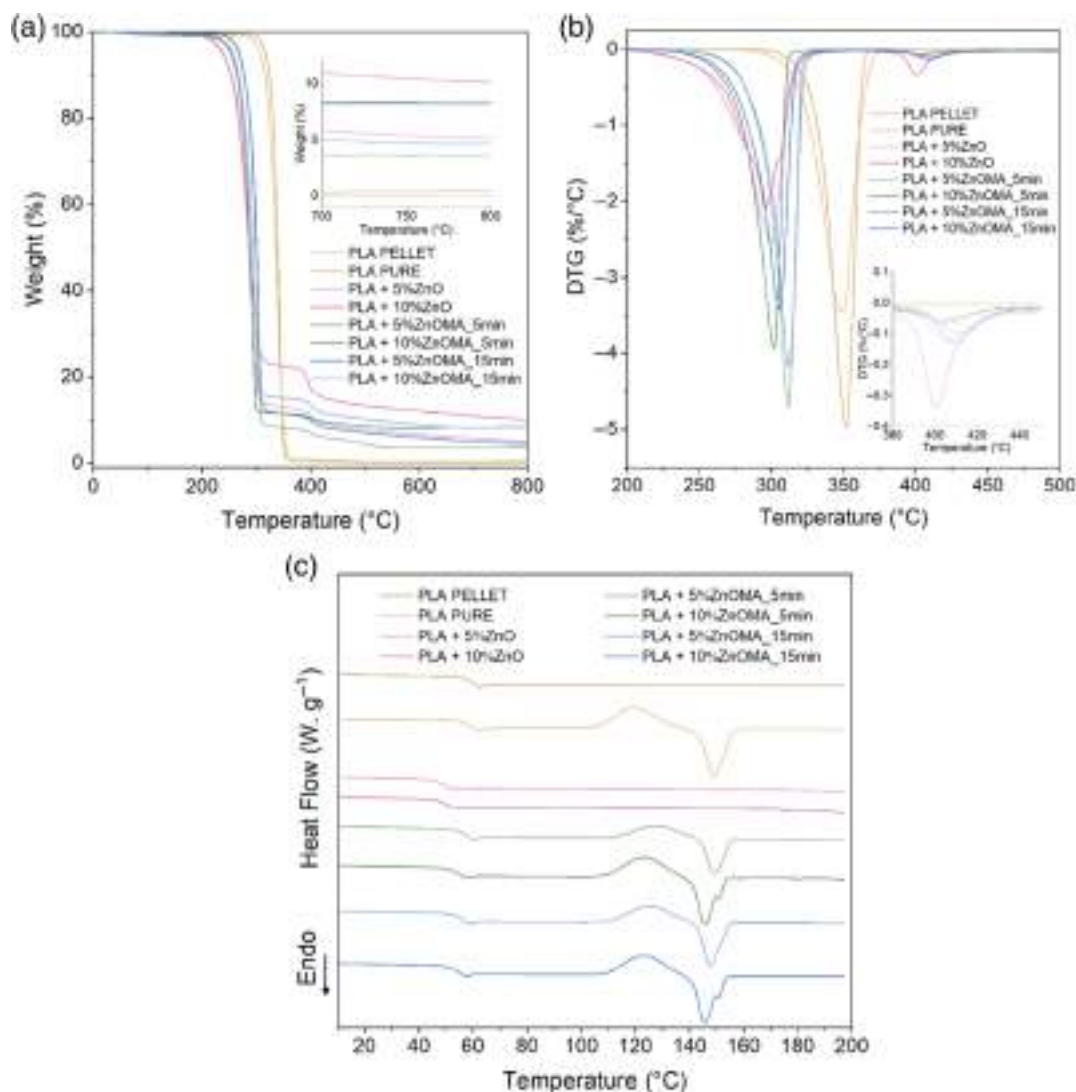


FIGURE 6 (a) TG curves of the biocomposites. (b) DTG curves of the biocomposites. (c) Differential scanning calorimetry curves for the second heating of scaffold samples. [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2 TGA results for samples of PLA and biocomposites scaffolds.

Sample	1° peak			2° peak			Residue (800°C) (%)
	T_{onset} (°C)	T_{peak} (°C)	Δm (%)	T_{onset} (°C)	T_{peak} (°C)	Δm (%)	
PLA PELLET	319.7	351.8	98.9	-	-	-	0.0
PLA PURE	313.1	348.2	99.1	-	-	-	0.0
PLA + 5%ZnO	256.6	299.2	86.3	391.6	406.6	5.3	5.1
PLA + 10%ZnO	255.7	294.7	76.8	287.6	400.1	9.1	10.0
PLA + 5%ZnOMA_5 min	277.1	311.3	91.4	391.6	405.5	3.7	3.6
PLA + 10%ZnOMA_5 min	263.1	301.4	87.6	386.6	403.3	2.7	8.4
PLA + 5%ZnOMA_15 min	280.8	311.8	88.4	395.0	412.5	3.9	4.6
PLA + 10%ZnOMA_15 min	272.8	305.4	84.3	396.3	409.8	4.5	8.2

Abbreviations: PLA, poly(lactic acid); TGA, thermogravimetric analysis.

TABLE 3 Differential scanning calorimetry results for samples of PLA and biocomposites scaffolds.

Sample	T_g (°C)	T_{cc}			T_m			X_c (%)
		T_{onset} (°C)	T_{peak} (°C)	ΔH_{cc} (J/g)	T_{onset} (°C)	T_{peak} (°C)	ΔH_m (J.g ⁻¹)	
PLA PELLET	59.9	-	-	-	-	-	-	-
PLA PURE	59.8	106.7	120.2	24.9	143.3	149.3	25.1	0.3
PLA + 5%ZnO	50.2	-	-	-	-	-	-	-
PLA + 10%ZnO	50.5	-	-	-	-	-	-	-
PLA + 5%ZnOMA_5 min	57.8	112.9	128.9	14.8	140.6	149.5	15.0	0.2
PLA + 10%ZnOMA_5 min	55.5	109.6	124.0	21.3	140.9	145.9	21.5	0.2
PLA + 5%ZnOMA_15 min	56.9	110.8	126.4	18.9	143.2	147.7	19.1	0.2
PLA + 10%ZnOMA_15 min	57.3	111.7	125.3	20.2	141.9	146.2	20.5	0.2

Abbreviation: PLA, poly(lactic acid).

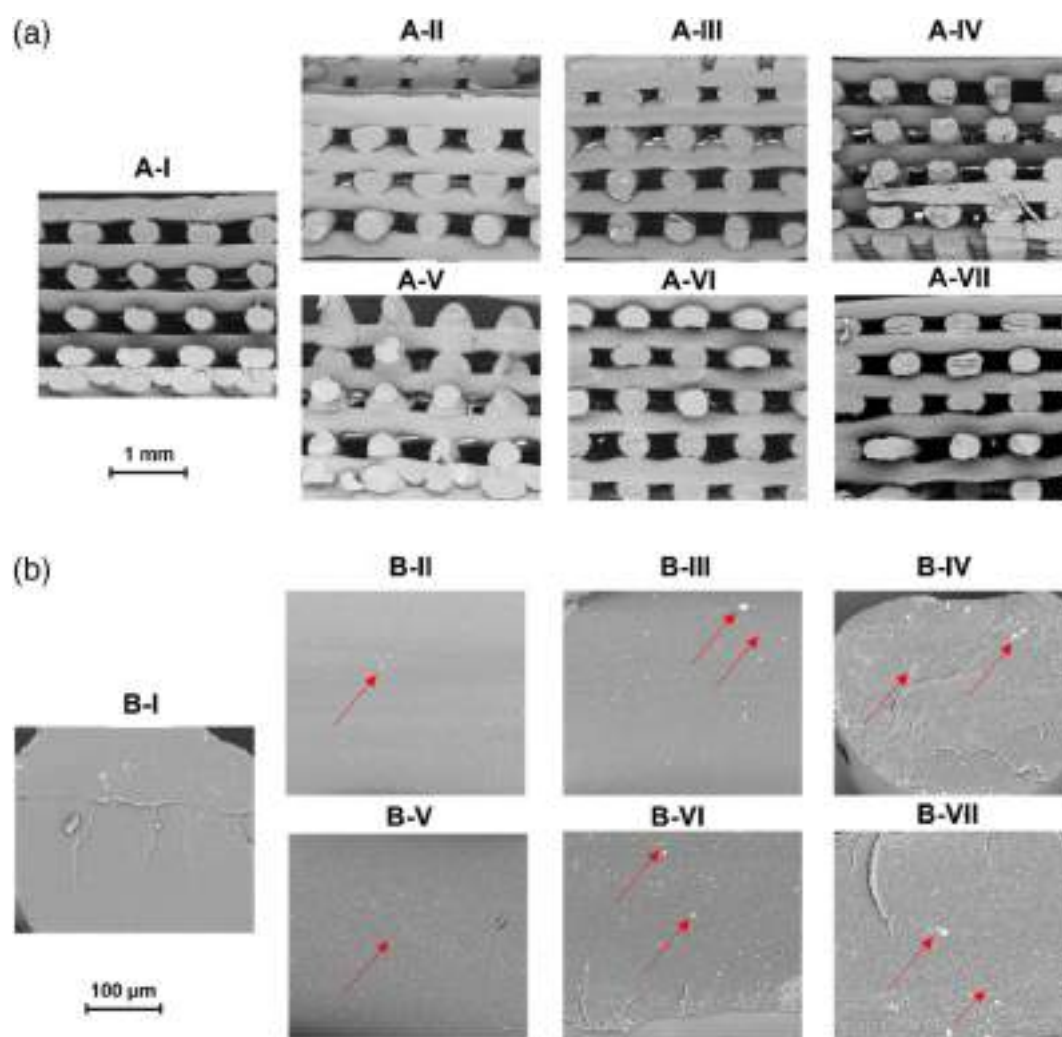


FIGURE 7 (a) Micrographs obtained using SEM for the cross-sectional view of the PLA scaffolds and biocomposites. (A-I) PLA; (A-II) PLA + 5%ZnO; (A-III) PLA + 10%ZnO; (A-IV) PLA + 5%ZnOMA_5 min; (A-VI) PLA + 10%ZnOMA_5 min; (A-VI) PLA + 5% ZnOMA_15 min; (A-II) PLA + 10%ZnOMA_15 min; (b): Micrographs obtained using of SEM for the cross-sectional view of PLA scaffolds and biocomposites. The red arrows indicate points of ZnO clusters. (B-I) PLA; (B-II) PLA + 5%ZnO; (B-III) PLA + 10%ZnO; (B-IV) PLA + 5%ZnOMA_5 min; (B-V) PLA + 10%ZnOMA_5 min; (B-VI) PLA + 5%ZnOMA_15 min; (B-VII) PLA + 10%ZnOMA_15 min. PLA, poly(lactic acid); SEM, scanning electron microscope. [Color figure can be viewed at wileyonlinelibrary.com]

crystalline structures or lamellar situations with varying degrees of perfection. These variations may have arisen during cold crystallization due to the presence of chains degraded by different mechanisms or clusters. Therefore, the lower temperature peak is attributed to less perfect crystals, which are manifested in the α' crystalline phase, exhibiting a metastable pseudo-orthorhombic structure. In contrast, the higher temperature peak is attributed to more perfect crystals of the α' phase, characterized by a more stable orthorhombic crystalline structure. The metastable α' phase features thinner lamellae than the α phase, and at high temperatures, it can undergo conversion into the more stable phase through the thermal annealing process.^{38,39} For the ZnO samples, the absence of cold crystallization followed by fusion may be associated with a high degree of degradation that severely reduces particle size, decreasing the entanglement density and making it difficult to pack.⁴⁰

The decrease in Tg (Table 3) for all compositions with ZnO indicates degradation, as the greater mobility of smaller chains reduces molecular restriction, thus lowering the Tg. Finally, it was found that the presence of ZnO particles, with and without treatment, although they act to modify the thermal behavior of the PLA matrix, does not alter the degree of total crystallinity of the polymer, maintaining it practically amorphous.

3.4 | Structural characterization of the 3D printed scaffolds

Figure 7a shows scanning electron microscopy images with low magnification, where a greater deformation of the filaments can be observed in samples with untreated ZnO, probably due to the lower viscosity and the predominance of viscous character. These characteristics harm the maintenance of the shape during and after deposition. Additionally, in compositions with ZnOMA, particle agglomerates are visible, which becomes more explicit in the images of Figure 7b with higher magnification. Therefore, indicating that the method used does not have the energy necessary to provide dispersion of the particles is a factor that may have contributed to a lower degradation of the matrix because agglomerates decrease the total surface area of the particles, reducing the reactivity and release of Zn ions. Thus, the reduction in degradation observed in ZnO-treated samples stems from a synergistic effect. This effect arises from the surface treatment through plasma, introducing groups onto the ZnO surface and decreasing its reactivity, subsequently curbing ion release. Simultaneously, the presence of agglomerates decreases particle surface area, minimizing

interaction with the environment and, consequently, decreasing ion release during processing.

To analyze the pore size of the scaffolds after printing, it was measured the minimum distance of two adjacent struts using the ImageJ[®] software. The scaffolds were designed to present pores and a strut width of 400 μm , while the strut height was 300 μm in size. The PLA samples with untreated ZnO did not maintain the cylindrical shape after deposited, probably due to the lower viscosity and predominance of the viscous behavior character as observed in the rheological tests. Therefore, the PLA-ZnO composites presented the smallest pore sizes (Table 4), a consequence of the different rheological behavior induced by the greater degradation of the matrix in the presence of untreated ZnO. However, similar to the other samples, they were within the pore size required range for bone tissue engineering of 100–500 μm , in which cell proliferation, vascularization and development of new tissue occurs.⁴¹ Theoretical porosity was determined using the Prusa Slicer[®] software, with the samples designed to have a fill density of 42%, which corresponds to their porosity.

Contact angle measurements were performed to characterize the wettability of the scaffolds. The results presented in Figure 8 show that the incorporation of ZnO and ZnOMA did not promote a statistically significant difference compared to pure PLA, staying close to 90°, which seems to be good for tissue engineering applications to ensure good wettability of the scaffolds, allowing for cellular interactions and nutrient exchange.⁴²

3.5 | Mechanical characterization of the 3D printed scaffolds

The mechanical property was evaluated by compression measurements. Young's modulus was extracted from the initial linear region of the stress x strain curves (Figure S1). The results shown in Figure 9 demonstrate that particle functionalization was important for preserving the mechanical properties of the PLA matrix. In the absence of treatment, the samples had a significantly lower Young's modulus compared to pure PLA, and during compression load, they could not withstand the mechanical stress, and consequently, they fractured, making them unsuitable for bone tissue applications. The compositions with ZnOMA did not show statistically significant variations compared to pure PLA or among themselves. Notably, the PLA-ZnOMA scaffolds achieved an elastic modulus within the range of 0.5 to 10 GPa, aligning with the requirements for trabecular bone substitutes, thereby confirming their potential application in bone grafts.^{3,43}

Sample	Strut width (μm)	Strut height(μm)	Pore size (μm)
PLA PURE	295 $\pm$ 10	299 $\pm$ 11	425 $\pm$ 11
PLA + 5%ZnO	442 $\pm$ 18	359 $\pm$ 30	287 $\pm$ 11
PLA + 10%ZnO	373 $\pm$ 44	301 $\pm$ 29	291 $\pm$ 41
PLA + 5%ZnOMA_5 min	384 $\pm$ 20	329 $\pm$ 25	403 $\pm$ 14
PLA + 10%ZnOMA_5 min	400 $\pm$ 8	343 $\pm$ 22	379 $\pm$ 16
PLA + 5%ZnOMA_15 min	357 $\pm$ 8	293 $\pm$ 6	429 $\pm$ 16

TABLE 4 Measurement of scaffolds structural parameters using ImageJ[®] software.

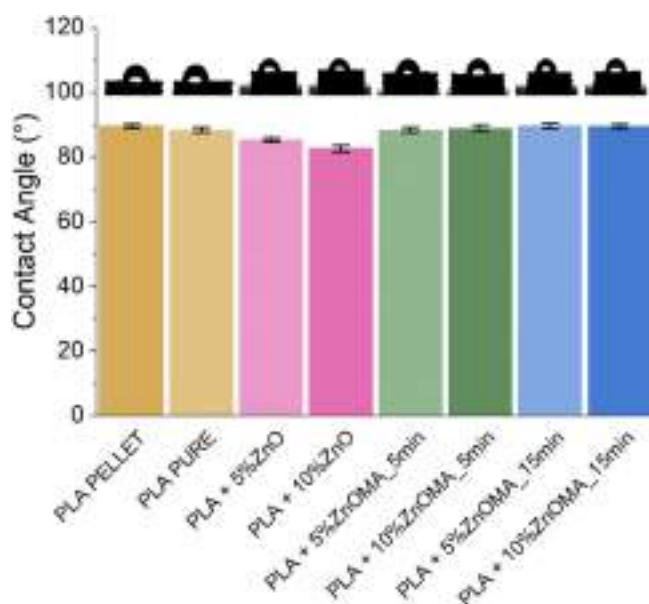


FIGURE 8 Contact angle test results for PLA, PLA/ZnO and PLA/ZnOMA scaffolds. The statistical analysis was expressed relative to the PLA scaffold ($N = 6$; $*p < 0.05$; $**p < 0.01$; $***p < 0.005$). [Color figure can be viewed at wileyonlinelibrary.com]

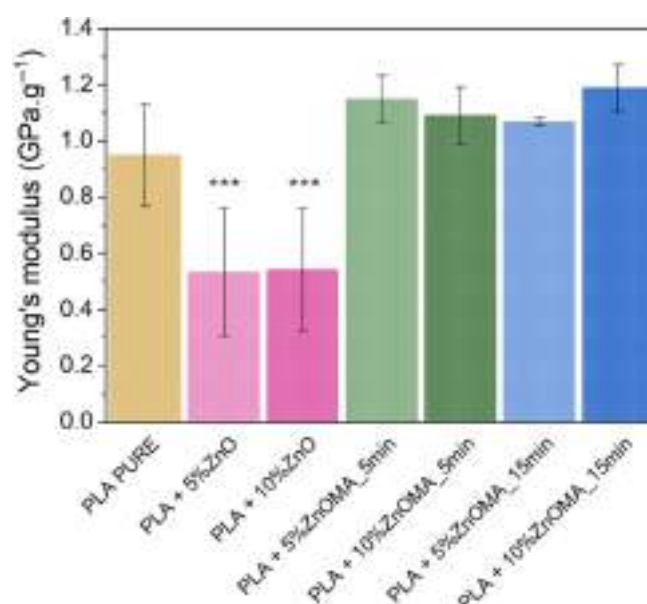


FIGURE 9 Young's modulus obtained by compression testing for all compositions. The statistical analysis was expressed relative to the PLA scaffold ($N = 6$; $*p < 0.05$; $**p < 0.01$; $***p < 0.005$). [Color figure can be viewed at wileyonlinelibrary.com]

3.6 | Biological characterization of the 3D printed scaffolds

The cytocompatibility of the biocomposites was evaluated after 1 and 7 days of mesenchymal stem cell culture on the scaffolds. As shown in Figure 10a, after the first day, all PLA-ZnOMA scaffolds displayed cell viability statistically similar to pure PLA, which is a well-known cytocompatible material and has been approved by the Food and Drug Administration (FDA) for implantation in humans. As expected, the samples containing non-functionalized ZnO (PLA + 5%ZnO and PLA + 10%ZnO) were cytotoxic ($<70\%$) due to the acid degradation of the PLA that harmed cell viability. After 7 days of MSCs culture, an increase in cell viability was observed for all samples compared to the first day, which indicates that the cells are proliferation as function of time. The sample with 10% of nonfunctionalized ZnO remained cytotoxic,

while the other compositions did not present toxicity. This effect can also be observed in the fluorescence microscopy images of Figure 10b, which show the amount of live and dead cells at each time point.

Calcium deposition is a marker of mineralization of the bone matrix. It can be associated with the differentiation of mesenchymal stem cells into osteoblasts due to the rich calcium content in the extracellular matrix of osteoblast cells. Figure 11a,b show the results of Alizarin Red staining and quantification after 28 days of MSCs culture. Unlike the viability results, the samples with ZnO showed the highest calcium deposition, indicating a greater differentiation potential. Both results may be associated with the degree of degradation of each composition.²³ As observed in previous analyses, surface functionalization promoted a reduction in PLA degradation. Therefore, untreated compositions that undergo a significant reduction in molar mass are more susceptible to

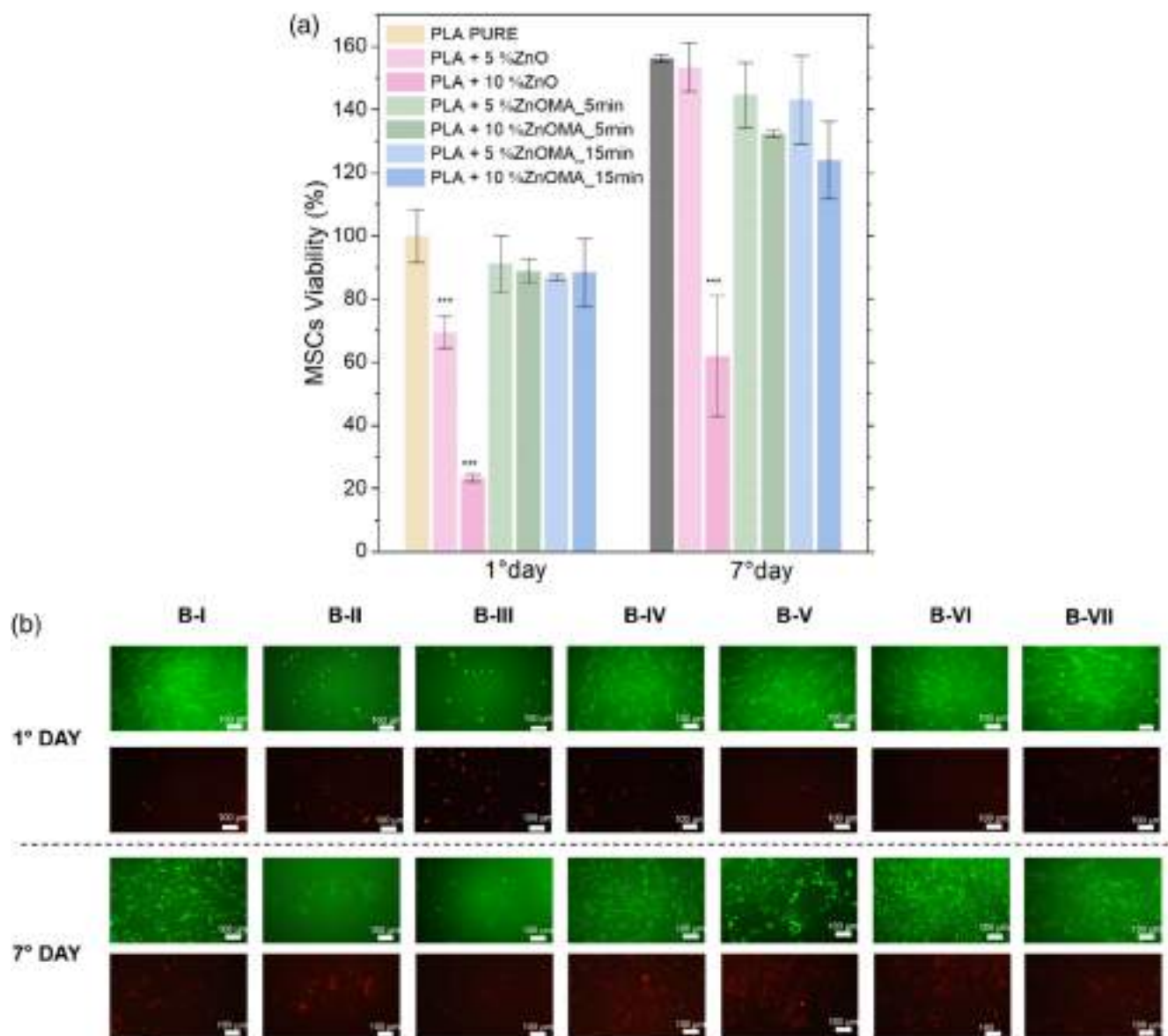


FIGURE 10 (a) Results of the cell viability assay for analysis on the first and seventh day of incubation of the scaffolds in culture medium. The statistical analysis was expressed relative to the PLA scaffold ($N = 3$; $*p < 0.05$; $**p < 0.01$; $***p < 0.005$); (b) Fluorescence microscopy of the Live/Dead test. The green signal indicates live cells, and the red signal indicates dead cells. (B-I) PLA; (B-II) PLA + 5% ZnO; (B-III) PLA + 10%ZnO; (B-IV) PLA + 5%ZnOMA_5 min; (B-V) PLA + 10%ZnOMA_5 min; (B-VI) PLA + 5%ZnOMA_15 min; (B-VII) PLA + 10%ZnOMA_15 min. [Color figure can be viewed at wileyonlinelibrary.com]

degradation in the culture medium, releasing higher concentrations of acidic products that promote a decrease in pH in cellular environments, killing cells.^{23,30} On the other hand, according to the literature, it is suggested that more degraded compositions may lead to a higher release of Zn^{2+} ions into the medium, which stimulates the expression of bone-related genes and, consequently, the maturation of the extracellular matrix.⁴⁴ Felice et al.¹⁷ observed the same relationship between cell viability and calcium deposition in Polycaprolactone (PCL) scaffolds with 1.3% and 6% ZnO (% w/w) produced by electrospinning, indicating that the release of acidic

products and Zn^{2+} ions were responsible for altering the pH, promoting a decrease in cell viability, but also inducing a greater stem cell differentiation. Samples with 10% ZnOMA showed higher mineralization values compared to pure PLA, suggesting that particle functionalization may potentially enhance cytocompatibility and could play a role in controlling Zn^{2+} release. This, in turn, might stimulate differentiation into osteoblasts and contribute to the mineralization of the matrix. Different times of plasma treatment (5 and 15 min) did not promote significant variation in cell functions; both times seem to be efficient in surface functionalization.

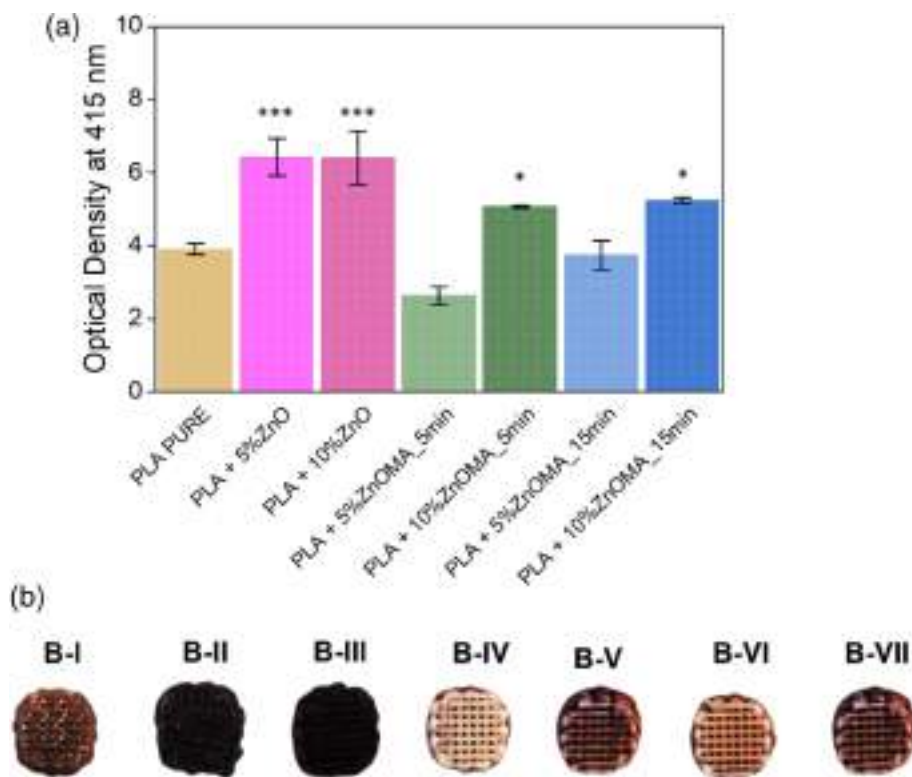


FIGURE 11 Calcium deposition (a) staining and (b) quantification on scaffolds after 28 days of MSCs culture in osteogenic culture medium. The statistical analysis was expressed relative to the PLA scaffold ($N = 3$; $*p < 0.05$; $**p < 0.01$; $***p < 0.005$). (B-I) PLA; (B-II) PLA + 5%ZnO; (B-III) PLA + 10% ZnO; (B-IV) PLA + 5%ZnOMA_5 min; (B-V) PLA + 10%ZnOMA_5 min; (B-VI) PLA + 5%ZnOMA_15 min; (B-VII) PLA + 10%ZnOMA_15 min. [Color figure can be viewed at wileyonlinelibrary.com]

4 | CONCLUSIONS

This study aimed to develop PLA/ZnO biocomposites for use in 3D-printed scaffolds for bone tissue engineering. The surface treatment of ZnO with maleic anhydride using plasma was evaluated as a viable alternative for controlling PLA degradation in the presence of the particle. The effective functionalization of the ZnO reduced PLA degradation and produced biocomposites with greater thermal stability. 3D-printed porous scaffolds exhibited elastic modulus close to that of biological bone tissue, ideal for application as a bone substitute. The PLA-ZnOMA biocomposites were not Fc cytotoxic to mesenchymal stem cells and stimulated their differentiation into osteoblasts, promoting mineralization of the bone matrix. Throughout the analysis, it was observed that longer plasma exposure times did not significantly affect the results, but the ZnO concentration significantly influenced all evaluated properties; the samples containing 10%ZnOMA exhibited a more favorable correlation between cellular mineralization and cell viability, making them particularly promising for biomedical applications. Therefore, we demonstrated that ZnO plasma functionalization with maleic anhydride has excellent potential for controlling PLA degradation, enabling melt processing of these promising biocomposite for bone tissue engineering applications. Future endeavors must address multiple challenges to facilitate the transition of PLA/ZnO

biocomposites from experimental research to clinical practice. These challenges include ensuring the scalability and consistent quality of plasma-treated ZnO, navigating the regulatory landscape, and conducting exhaustive biocompatibility assessments. Subsequent research should concentrate on refining the plasma treatment techniques to optimize ZnO functionalization, exploring additional synergistic biodegradable polymers, and cultivating collaborative engagements with biomedical firms and regulatory agencies to satisfy clinical standards and expedite clinical trials.

AUTHOR CONTRIBUTIONS

Felippe Migliato Marega: Conceptualization (lead); data curation (lead); formal analysis (lead); investigation (lead); methodology (lead); validation (lead); visualization (lead); writing – original draft (lead). **Larissa Aline Klok:** Investigation (equal); methodology (equal); writing – review and editing (supporting). **Daniel A. L. V. Cunha:** Investigation (supporting); methodology (supporting). **Teresa Tromm Steffen:** Methodology (supporting); writing – review and editing (supporting). **Samarah V. Harb:** Investigation (equal); methodology (equal); supervision (equal); writing – review and editing (equal). **Elayaraja Kolanthai:** Supervision (equal); writing – review and editing (supporting). **Sudipta Seal:** Funding acquisition (equal); resources (supporting). **Daniela Becker:** Funding acquisition (lead); project

administration (lead); supervision (lead); writing – review and editing (supporting). **Luiz Antonio Pessan:** Funding acquisition (lead); project administration (lead); supervision (lead); writing – review and editing (supporting). **Lidiane Cristina Costa:** Funding acquisition (lead); methodology (lead); project administration (lead); supervision (lead); validation (equal); writing – review and editing (equal).

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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REFERENCES

- [1] M. A. Clynes, N. C. Harvey, E. M. Curtis, N. R. Fuggle, E. M. Dennison, C. Cooper, *Br. Med. Bull.* **2020**, *113*, 105.
- [2] F. Shang, Y. Yu, S. Liu, L. Ming, Y. Zhang, Z. Zhou, J. Zhao, Y. Jin, *Bioact. Mater.* **2020**, *6*, 666.
- [3] D. W. Hutmacher, J. T. Schantz, C. X. F. Lam, K. C. Tan, T. C. Lim, *J. Tissue Eng. Regen. Med.* **2007**, *1*, 245.
- [4] F. J. O'Brien, *Mater. Today* **2011**, *14*, 88.
- [5] G. Yuqui, Y. Yue, G. Ling, Z. Shengchang, C. Jiatian, Y. Junyuan, H. Zhou, J. Li, *Bionic Syst.* **2023**, *4*, 58.
- [6] S. S. V. Dorozhkin, *Biomaterials* **2010**, *31*, 1465.
- [7] S. Liu, S. Qin, M. He, D. Zhou, Q. Qin, H. Wang, *Composites, Part B* **2020**, *199*, 108238.
- [8] E. Saeid, A. A. Hossein, M. Mehdi, S. S. Saeed, H. M. Amir, B. Mohammad, S. Erfan, K. Amirsalar, *Eur. J. Orthop. Surg. Traumatol* **2020**, *30*, 123.
- [9] M. Oliveira, E. Santos, A. Araújo, G. J. M. Fechine, A. V. Machado, G. Botelho, *Polym. Test.* **2016**, *51*, 109.
- [10] A. W. White, S. M. Best, *Appl. Ceram. Technol.* **2007**, *4*, 1.
- [11] J. Ivanovic, K. Rezwan, S. Kroll, *J. Appl. Polym. Sci.* **2017**, *135*, 45824.
- [12] V. H. Sangeetha, H. Deka, T. O. Varghese, S. K. Nayak, *Polym. Compos.* **2018**, *39*, 81.
- [13] A. P. Gupta, V. Kumar, *Eur. Polym. J.* **2007**, *43*, 4053.
- [14] J. M. Raquez, Y. Habibi, M. Murariu, P. Dubois, *Prog. Polym. Sci.* **2013**, *38*, 1504.
- [15] S. V. Harb, E. Kolanthai, E. H. Backes, C. A. G. Beatrice, L. A. Pinto, A. C. C. Nunes, H. S. Selistre-de-Araújo, L. C. Costa, S. Seal, L. A. Pessan, *Tissue Eng. Regen. Med.* **2023**, *21*, 223.
- [16] S. Trujillo, E. Lizundia, J. L. Vilas, M. Salmeron-Sanchez, *Colloids Surf., B* **2016**, *144*, 152.
- [17] S. Nilawar, M. Uddin, K. Chatterjee, *Mater. Adv.* **2021**, *2*, 7820.
- [18] B. Felice, M. A. Sánchez, M. C. Socci, L. D. Sappia, M. I. Gómez, M. K. Cruz, C. J. Felice, M. Martí, M. I. Pividori, G. Simonelli, A. P. Rodríguez, *Mater. Sci. Eng., C* **2018**, *93*, 724.
- [19] E. A. S. Dimapilis, C.-S. Hsu, R. M. O. Mendoza, M. C. Lu, *Sustainable Environ. Res.* **2018**, *28*, 47.
- [20] J. R. Pragłowska, Ł. Janus, M. Piątkowski, D. Bogdał, D. Matysek, *Polymer* **2020**, *12*, 1.
- [21] E. Lizundia, L. Lizundia, J. L. Vilas, L. M. León, *RSC Adv.* **2016**, *6*, 15660.
- [22] E. Lizundia, P. Mateos, J. P. Vilas, *Mater. Sci. Eng., C* **2017**, *75*, 714.
- [23] R. Chatchai, C. Korakot, W. Duangmanee, M. C. Won, H. H. Seung, J. P. Hyun, S. C. Jin, *J. Mater. Sci. Technol.* **2012**, *76*, 1.
- [24] R. A. Kolodziejczak, T. Jesionowski, *Materials* **2014**, *7*, 2833.
- [25] T. Dutta, D. Bagchi, A. Bera, S. Das, T. Adhikari, S. K. Pal, *ACS Sustainable Chem. Eng.* **2019**, *7*, 10920.
- [26] G. Moku, V. R. Gopalsamuthiram, T. R. Hoyer, J. Panyam, *Surface Modification of Nanoparticles: Methods and Applications*, Surface Modification of Polymers, *Em* **2019**, p. 317.
- [27] L. A. Klok, T. T. Steffen, H. R. Sabedra, L. C. Fontana, P. Hammer, F. M. Marega, L. C. Costa, L. A. Pessan, D. Becker, *Plasma. Process Polym.* **2023**, *21*, e2300165.
- [28] X. Yuanhang, Z. Feiyang, Z. Weijie, C. Shujie, L. Jinghua, W. Yi Wang, *Polymer* **2022**, *14*, 566.
- [29] U. A. Zia, Y. K. Muhammad, N. Reza, S. Ali, J. Meisam, H. Mokarram, *J. Biol. Macromol.* **2022**, *218*, 930.
- [30] NatureWorks, PLA, 2003D Datasheet. https://www.natureworkslc.com/~media/TechnicalResources/Technical_Data_Sheets/TechnicalDataSheet_2003D_FFP-FSW.pdf, accessed: April, 2024
- [31] T. T. Steffen, L. C. Fontana, P. Hammer, D. Becker, *Appl. Surf. Sci.* **2022**, *583*, 152493.

- [32] T. T. Steffen, L. C. Fontana, P. Hammer, D. Becker, *Appl. Surf. Sci.* **2019**, 491, 405.
- [33] N. Khurana, P. Arora, A. S. Pente, K. C. Pancholi, V. Kumar, C. P. Kaushik, S. Rattan, *Inorg. Chem. Commun.* **2021**, 124, 108347.
- [34] G. Mishra, S. L. McArthur, *J. Surfaces Colloids.* **2010**, 26, 9645.
- [35] S. G. Girol, T. Strunskus, M. Muhler, C. Wöll, *J. Phys. Chem. B* **2004**, 108, 13736.
- [36] H. A. Barnes, *A Handbook of Elementary Rheology*, University of Wales, Aberystwyth **2000**.
- [37] M. Qu, H. Tu, M. Amarante, Y.-Q. Song, S. S. Zhu, *J. Appl. Polym. Sci.* **2014**, 131, 40287.
- [38] É. Da Cruz Faria, M. L. Dias, L. M. Ferreira, M. I. B. Tavares, *Nanocomposites. J. Therm. Anal. Calorim.* **2021**, 146, 1483.
- [39] A. A. Cuadri, J. E. Martín-Alfonso, *Polym. Degrad. Stab.* **2018**, 150, 37.
- [40] J. Ahmed, J. X. Zhang, Z. Song, S. K. Varshney, *J. Therm. Anal. Calorim.* **2009**, 95, 957.
- [41] V. Karageorgiou, D. Kaplan, *Biomaterials* **2005**, 26, 5474.
- [42] A. C. Popa, G. Stan, M. A. Husanu, I. Mercioniu, L. Santos, H. Fernandes, J. Ferreira, *Int. J. Nanomed.* **2017**, 12, 683.
- [43] C. F. Guimarães, L. Gasperini, A. P. Marques, R. L. Reis, *Nat. Rev. Mater.* **2020**, 5, 351.
- [44] K. Yusa, O. Yamamoto, M. Fukuda, S. Koyota, Y. Koizumi, T. Sugiyama, *Biochem. Biophys. Res. Commun.* **2011**, 412, 273.

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Effect of maleic anhydride and oxygen functionalized carbon nanotube on polyamide 6 and polypropylene blend properties

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Abstract

This work aims to investigate how adding functionalized carbon nanotubes (CNTs) to a Polyamide 6/polypropylene blend influences its properties. CNT functionalization was carried on through plasma with oxygen (CNT_O₂) or maleic anhydride (CNT_MA). CNT_O₂ presented the highest amount of oxygen, but, as the treatment time in plasma was twice as long as that of the CNT_MA sample, the oxygenated groups, for the most part, tended to form lactones. On the other hand, plasma treatment with maleic anhydride was more efficient to insert carboxylic groups onto the CNT surface. Adding non-functionalized CNT in the blend, an elongation of PP phase was observed. In the functionalized CNT nanocomposites, a significant decrease in phase size was observed. No improvement in adhesion between phases was observed. Crystallinity degree decreased when non-functionalized CNT was added and increased with functionalized CNT. Despite the greater interaction between amorphous and crystalline regions observed in nanocomposites with CNT_O₂, the highest values of storage module came from CNT_MA nanocomposite. The COOH groups on the CNT surface reacted with the polyamide, improving tension transfer between phases and leading to a better performance in blend mechanical properties.

Keywords Carbon nanotube · Functionalization · Plasma · Maleic anhydride · Polyamide

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Introduction

Polyamide 6/polypropylene (PA6/PP) blends have been catching attention in the last few years since they combine the PA6 thermomechanical properties with the PP easy processing [1, 2]. Due to its low cost and good mechanical resistance, the PA6/PP blend is indicated as an alternative in packaging and automotive parts production [3]. However, being an immiscible blend, compatibilizing agents are needed to improve properties and performance. Polypropylene grafted with maleic anhydride (MA) is the most studied compatibilizing agent, improving phase adhesion and blend properties [1, 4, 5]. Compatibilization based in MA is often used as compatibilizers in blends with polyamide (PA) because of the high probability of chemical reaction between MA functional unities and the amine end groups of PA during melt blending [6, 7].

More than compatibilizing agents, nanoparticles can also be used as a third component in a polymeric blend, changing the immiscible polymer phase morphology [8]. Indeed, there are studies showing that adding nanoparticles to blend systems has similar results to those of adding compatibilizing agents, modifying the immiscible polymer interfacial properties. Nanoparticles used to this purpose include titanium dioxide [9] and organophilic clay [10] in poly(lactic acid) (PLA)/poly(ϵ -caprolactone) (PCL) blend and carbon nanotubes in copolyamide 6/12 (PA6/12) blend [11], in polypropylene (PP)/polycaprolactone (PCL) and polyamide 12 (PA12)/PCL blends [12] and poly(styrene acrylonitrile) (SAN)/polycarbonate (PC) blend [13].

Carbon nanotubes are promising nanoparticles that have been widely used for several applications, since they have excellent mechanical, electrical and thermal properties [14]. Before being added to the blend, carbon nanotubes (CNTs) can be functionalized, increasing their surface energy and improving dispersion stability, phase compatibility, interaction and miscibility with the polymer matrix [15]. Madhukar et al. [16] observed that CNTs functionalized with carboxylic groups act as compatibilizing agents in PA6/poly (methyl methacrylate) blends. The same was observed by Cheng et al. [17] in blends with polyamide 6 and liquid crystal polymer. Researchers studying CNT addition to PA6/PP blends also employ compatibilizing agents based on maleic anhydride [18–20]. The authors observed a synergistic effect in the blend mechanical properties due to the CNT and compatibilizing agent addition.

Once MA is an important compatibilizing agent, different carbon nanotube functionalization methods were studied in the past [21–27]. Some authors add the functionalized CNT to different polymeric matrices, as poly (methyl methacrylate) [28] and epoxy [24, 25], observing better dispersion, mechanical properties improvement and electrical percolation threshold reduction.

In previous works [27, 29], plasma efficiency in inserting different chemical groups to CNT surface was evaluated. Steffen et al. [29] treated CNT with plasma with different gas mixtures (Ar/O_2 and $\text{Ar/O}_2/\text{N}_2$) for further synthesis of epoxy nanocomposites. Besides the CNT oxidation, they observed an improvement in the nanocomposite mechanical properties. In another work [27], plasma

functionalization was conducted in a CNT/MA solid premix. In fact, the plasma tool is an efficient alternative to CNT functionalization, with the advantages of being fast, free of solvents and contaminants, and allowing inserting a great variety of chemical modifications, even under relatively mild conditions, which enables to maintain the CNT integrity [30].

Therefore, this work aims to investigate the effects of different functionalized CNT (by O₂ and MA) in the properties of a PA6/PP blend. For this purpose, blend morphology was characterized through transmission and scanning electron microscopy, and thermal properties were evaluated through DSC and DMA.

Experimental

Materials

Multi-walled carbon nanotubes (>95% purity) with 10–30 µm of length, 10–30 nm of external diameter and 5–10 nm of internal diameter were purchased from Chengdu Organic Chemicals Co. Ltd. (TNIM4). Maleic anhydride (>98.5% purity) was purchased from Sigma-Aldrich in briquettes form. Argon and oxygen gases, used for plasma discharge, had purity above 99,999%. PA6 (Radilon S32E) and PP (CP741) were supplied by Radici Group and Braskem, respectively.

CNT plasma functionalization

The sample named CNT_O₂ was treated in a homemade RF-generated capacitive coupled plasma (CCP) reactor, according to experimental procedures detailed by Steffen et al. [29]. Plasma treatment was conducted at 40 W power input, with argon and oxygen gases, for 60 min. The CNT_MA sample corresponds to a solid mixture of CNT and maleic anhydride (90:10 mass proportion, mixed using mortar and pestle assistance), treated for 30 min in a homemade RF-generated ICP (inductive coupled plasma) reactor, with argon gas and a 35 W power input. Both treatments are conducted at a pressure of 1.33×10^2 Pa. The methods to produce the premix and to run the plasma treatment are extensively described by Steffen et al. [27].

Nanocomposites preparation method

Before processing, the PA6 was dried in an oven with 100 °C air circulation for 12 h. The ternary systems were prepared with a PA6/PP mixing ratio of 80/20% wt/wt and the CNT added with a concentration of 0.5% wt/wt. The mixtures were processed in an internal chamber mixer coupled with a torque rheometer (Thermo Scientific Haake Rheomix 600), with roller-type mixing rotors, operating at 220 °C, at a rotation of 100 rpm for 10 min. The CNTs, whether functionalized or not, were added after 2 min of mixture. The DMA samples were compression molded at 220 °C for 8 min under a 15 MPa pressure.

Characterization techniques

To evaluate the CNT integrity and functionalization, Raman and XPS analyses were conducted. Raman spectra were collected in a Renishaw 2000 Micro-Raman, with a 10 mW 514.5 nm laser (Ar), in the range from 1000 to 2000 cm^{-1} , with a resolution of 4 cm^{-1} . X-ray photoelectron spectroscopy (XPS) analyses were performed using a KAlpha Thermo Scientific spectrometer (Al-K α $h\nu = 1486.6$ eV), pressure below 10^{-7} mBar, 200 eV pass energy for Survey and 50 eV for high-resolution Scans. The spectra deconvolution was performed using Shirley background and Voigtian function [Gaussian (70%) and Lorentzian (30%) combinations].

To analyze the dispersed phase morphology, the samples microtome surface was analyzed through field emission scanning electron microscopy (FE-SEM) in a Jeol JSM 6701F equipment. To determine the size of the dispersed phases, the Image J software was used. The CNT dispersion was observed in a JEM 2100 transmission electron microscope (TEM). The samples were cut into thin sections with a nominal thickness of 30 nm in an RCM Power Tome X ultramicrotome, with a sample temperature of -70 °C. The analyses voltage was 200 kV. The samples were stained with ruthenium tetroxide (RuO_4) for 30 min.

Differential scanning calorimetry (DSC) thermal analyses were performed on a Maia-230 NETZSCH. The samples were submitted to heating and cooling cycles under N_2 atmosphere. Heating from 25 °C to 280 °C was applied at a 10 °C min^{-1} rate, keeping in isotherm for 2 min. Cooling was then carried out down to 0 °C at a 10 °C min^{-1} rate, keeping in isotherm for 2 min, followed by a second heating of 10 °C min^{-1} up to 280 °C. The values for the glass transition temperature (T_g), melting temperature (T_m) and cold crystallization temperature (T_c) were measured during the second heating cycle. The PA6 and PP crystallinity degree (X_c) was calculated from the melting and the crystallization enthalpy, using Eq. (1).

$$\%X_c = \frac{\Delta H_1}{\Phi \times \Delta H_0} \times 100 \quad (1)$$

ΔH_1 is the enthalpy of the melting peak (T_m), Φ is the mass fraction of the polymer (PA6 or PP) in the sample, and ΔH_0 is the melting enthalpy of the 100% crystalline PP: 207 J.g^{-1} [31], and 100% crystalline PA6: 230 J.g^{-1} [32].

Dynamic mechanical analysis (DMA) was performed in a DMA 242 E NETZSCH, under a nitrogen atmosphere in stress-strain mode. For the analysis, rectangular samples of $6 \times 20 \times 0.250$ mm were heated from -50 °C to 190 °C at a frequency of 1 Hz with a heating rate of 3 °C/min.

OriginPro 8.5 was used to generate all the graphs present in the article.

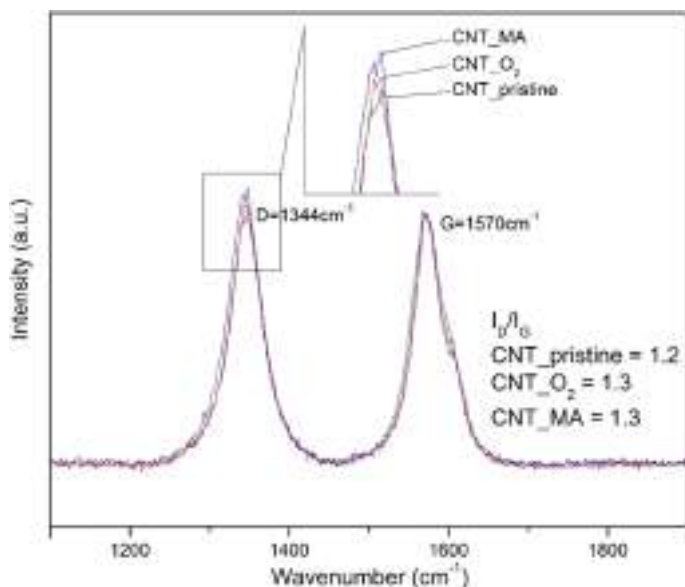


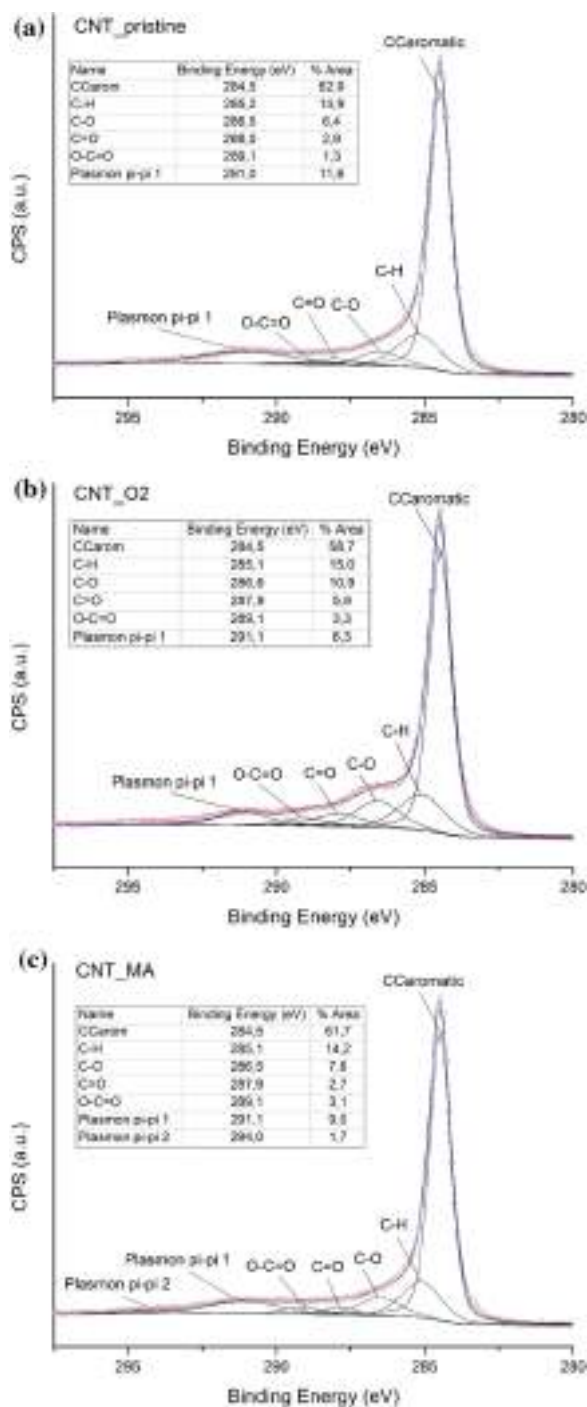
Fig. 1 Raman spectra and I_D/I_G ratio for pristine carbon nanotube and samples treated by plasma. Zoom box shows the increase in the D band after plasma treatment

Results and discussion

Figure 1 shows the Raman spectra, normalized by the G band, for pristine CNT and for samples treated with maleic anhydride and oxygen plasma. The D band is a second-order Raman scattering process, dependent on CNT defects, while the G band is a first-order Raman scattering process unrelated to the D band. Due to these features, it is common to normalize the curves by the G band and use both the D and the G bands intensity to evaluate CNT defects content [33]. Compared to the CNT pristine sample, the treated samples present an increase in the D band, as the zoom box shows in Fig. 1, which indicates the CNT surface chemical modification, once this band is associated with the presence of defects and functional groups bonded to the CNT [34]. Indeed, the presence of carboxylate groups on CNT surface, which is further supported by XPS results showing increase for treated samples, collaborates to increase D band intensity [35]. The shift in the D band also yields an increase of the I_D/I_G ratio for functionalized samples. However, the I_D/I_G values are close, which indicates that the CNT integrity remains in good shape even after the nanoparticles were submitted to the plasma chemical conditions [27, 36].

XPS results obtained from the survey spectra indicate an increase in oxygen atomic percentage in samples treated with plasma. For the CNT_O₂ sample, it was 8.6 O at %, 4 times higher than that of the CNT pristine (2.2 O at %), and the solid-state functionalized CNT_MA had an increase of 40% (3.1 O at %) compared to the pristine samples. This oxygen insertion pointed by XPS is in

Fig. 2 Deconvoluted C 1 s XPS spectra for **a** CNT_pristine, **b** CNT_O₂ and **c** CNT_MA samples



accordance with the D band increase for samples treated by plasma, observed by Raman spectra, once the oxygen atoms configure a defect in the carbon structure of CNT.

With the intent to analyze the functional groups formed on the CNT surface, the C 1 s XPS spectra were deconvoluted and are presented in Fig. 2. All the samples presented the CNT characteristic bands [27, 37]: aromatic carbon (284.5 eV), C–H (285.2 eV), carbon–oxygen bonds C–O, C=O and O–C=O (respectively, 286.5, 288.0 and 289.1) and the Plasmon peaks (~ 291 and ~ 294 eV) related to collective electronic excitations of π orbitals.

Figure 3 presents the atomic percent related to oxygen groups obtained from C 1 s XPS deconvolution. Compared to pristine CNT, the CNT_MA sample presented an increase in atomic percentage contribution of C–O (18%) and O–C=O (143%) bonds, while the C=O bond contribution dropped 7%. That means the plasma treatment with maleic anhydride was more efficient in promoting the insertion of carboxylic groups into CNT surfaces. This is in accordance with other works that proposed plasma functionalization of CNT with maleic anhydride and observed both oxygen insertion in CNT and a significant increase in O–C=O bonds, attributed to functional groups provided by MA [26, 38]. Indeed, other authors noticed that, in MA plasma functionalization, the MA ring is easily opened, according to plasma ambient conditions, leading to a preferential formation of carboxylic groups [39, 40]. On the other hand, for the CNT_O₂ sample, there was a significant increase in the contribution of all oxygen groups, with increments of 70, 104 and 157% of C–O, C=O and O–C=O bonds, respectively, in comparison with the values from the CNT pristine sample. The fact that oxygen was inserted as a gas, it may have left the oxygen atoms more free to bond.

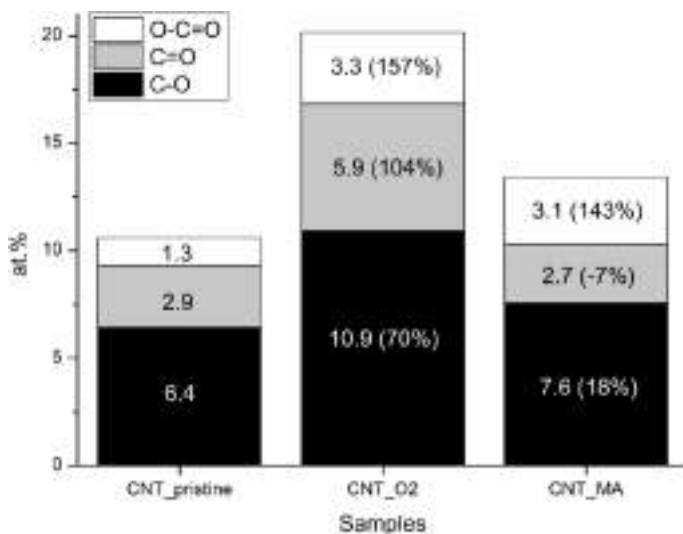
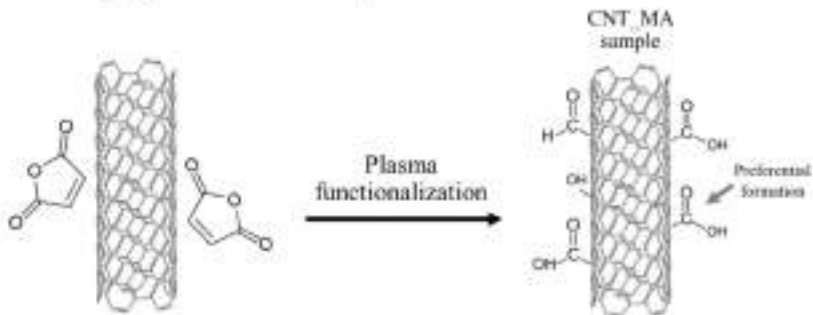


Fig. 3 Oxygen functional groups atomic percentage, obtained from C 1 s XPS deconvolution, for pristine CNT and for plasma-treated samples treated. Numbers in parentheses represent the percentual increase of bond contribution compared to CNT_pristine sample

Chen et al. [41] observed the reaction mechanisms for the formation of these three groups (C–O, C=O and O–C=O) in Ar/O₂ plasma treatment. Once C=C bonds are active, they are more susceptible to be attacked by plasma-active species. Therefore, radicals are first formed on the dissociated π bonds of the C=C atoms on the CNT surface. These active sites react with oxygen, forming C–O and then C–OH bonds, through stabilization by the hydrogen available in the chains. C=O bonds can be formed through the intramolecular reorganization of C–C bonds, and O–C=O bonds are formed through the reaction of plasma-generated radicals with C=O and active oxygen in plasma ambient. Besides that, according to the functionalization type and plasma conditions, the formed bonds can be assigned to different functional groups, both acid, like carboxyl, lactones, phenol and lactol groups, or basic, like chromene structures, diketone or quinone groups, and pyrone-like groups [42]. Figure 4 shows a schematic representation of oxygen groups attached to CNT surface after plasma functionalization. For MA functionalization, there is a preferential formation of O–C=O bonds providing by MA

(a) Functionalizing agent: solid maleic anhydride



(b) Functionalizing agent: gaseous oxygen

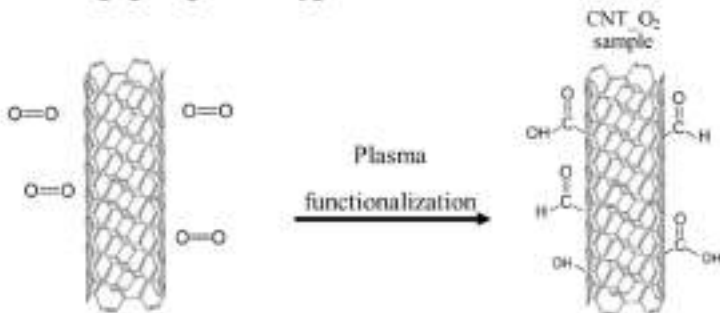


Fig. 4 Schematic representation of oxygen functional groups attached to CNT surface after plasma functionalization. For **a** CNT_MA sample, there is a preferential formation of O–C=O groups, while for **b** CNT_O₂ sample all the oxygen functional groups are formed in significant amounts. These schematic figures do not intend to represent oxygen groups in correct percent amount, but only to illustrate the functionalization process

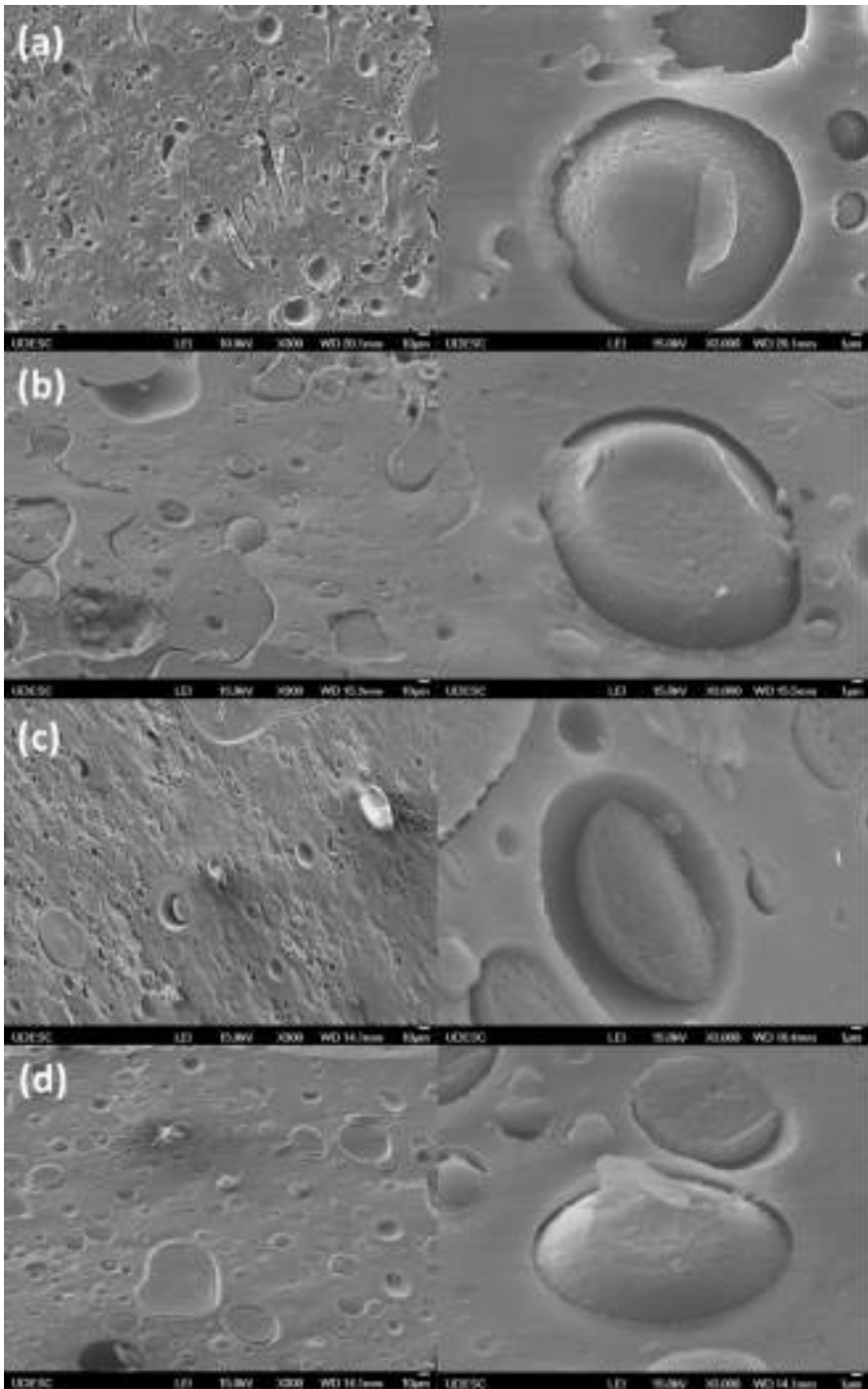


Fig. 5 FEG images of blend **a** PA6/PP and nanocomposites **b** PA6/PP/CNT_pristine, **c** PA6/PP/CNT_O₂ and **d** PA6/PP/CNT_MA

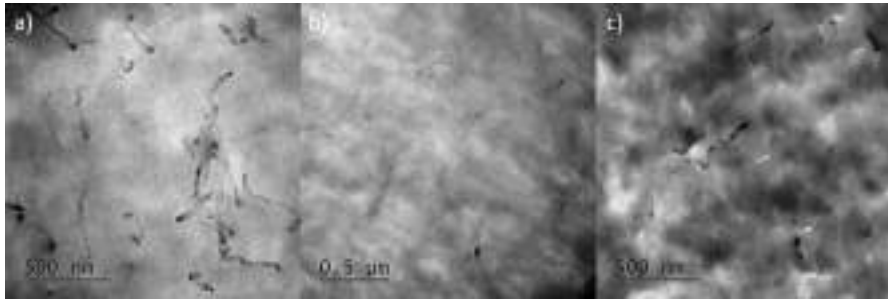


Fig. 6 TEM images for nanocomposite samples **a** PA6/PP/CNT_pristine, **b** PA6/PP/CNT_O₂; and **c** PA6/PP/CNT_MA

opening ring, while for O₂ functionalization, all groups are formed in significant amounts due to the plasma chemistry, as explained before (Fig. 5).

Figure 6 presents FEG-SEM micrographs for all studied systems. The CNTs are hard to observe in the FEG-SEM images due to the low magnification. Figure 6a shows the typical sea-island morphology for the PA6/PP blend in which the PP phase is dispersed in nearly-spherical domains in the PA6 matrix, with an average particle diameter of $17.05 \pm 9.67 \mu\text{m}$. No adhesion between phases was observed, showing poor interfacial adhesion and compatibility between PA6 and PP, which was also observed by other authors [4, 43, 44]. The addition of non-functionalized CNT does not alter significantly the dispersed phase size ($18.72 \pm 19.75 \mu\text{m}$); however, dispersed phases tend to elongate, as also observed in the increase in the standard deviation. Adding the functionalized CNT, on the other hand, a decrease in the phase size was observed (PA6/PP/CNT_O₂— $7.76 \pm 4.6 \mu\text{m}$ and PA6/PP/CNT_MA— $12.64 \pm 7.76 \mu\text{m}$). There is no improvement in the adhesion between phases as well. Figure 6 shows that most functionalized CNTs are individually distributed, that is, they are more locally distributed than in nanocomposites with non-functionalized CNT. However, it is not possible, with this analysis, affirm that they are better globally distributed or about their dispersion. Although the blend phases cannot be identified in the MET image, the CNT distribution and dispersion throughout the sample indicate that they are preferentially localized in the PA6 matrix in all studied cases. Several studies [18, 19, 45] show that carbon nanotubes tend to be localized in the PA6 phase, since the CNTs have more affinity with polar materials such as the PA6 itself. However, small amounts of CNT cannot be stopped from localizing in the PP phase. Wang et al. [19] studied the CNT influence in the PA6/PP and PA6/PP/PP-MA systems. They also observed that the nanoparticles were preferentially localized in the PA6, and found an elongation in the PP phase when the CNT was added to a 70/30 wt/wt blend, reaching an elongated co-continuous structure with the addition of 4% CNT in the systems without PP-MA. In the compatible nanocomposite, smaller sizes of the dispersed phase were observed and only in those with a high CNT concentration was a change in the dispersed phase format observed. No improvement in the phase adhesion could be observed in all studied systems as well. The CNT was observed to induce interfacial slip, thereby reducing the dispersed

Table 1 Thermal properties of PA6/PP blend and the nanocomposites

Sample	T_g (°C)	PA 6			PP		
		T_m	T_c	% X_c	T_m	T_c	% X_c
PA6/PP	24	220	190	17	165	115	17
PA6/PP/CNT_pristine	27	220	192	14	165	120	23
PA6/PP/CNT_O ₂	24	220	192	20	165	117	18
PA6/PP/CNT_MA	24	220	190	18	165	120	23

phase deformation rate. When PP-MA was added, tension transfer improved, thus reducing the interfacial slip and accelerating the dispersed phase deformation. Considering the observations made in this work, the CNT functionalization may have improved the tension transfer between the CNT and the PA6 [46, 47] and, thereby, suppressed the interfacial slip, consequently reducing the dispersed phase size.

Table 1 shows the DSC-obtained thermal properties of the nanocomposites. The PA6 Crystallinity degree decreased with the non-functionalized CNT and increased with the functionalized ones. Two main effects on crystallization are observed after adding CNT: heterogeneous crystal nucleation and physical chain impediment. As there is no change in the PA6 melting (T_m) and crystallization temperature (T_c), the predominant effect may be the physical impediment that slows down the PA6 chains and molecular interaction, reducing the nanocomposite crystallinity degree (X_c), which was also observed by other authors [46, 48]. Adding functionalized CNT led to an increase in the crystallinity degree when compared to the system with non-functionalized CNT. Liu et al. [48] observed the same behavior and related the increase to the better dispersion and CNT-polyamide interaction due to functionalization, thus decreasing the physical molecular movement impediment effect. Ying et al. [49] investigated the effects of surface functionalization of carbon nanotubes (CNTs) on their nucleation ability for poly (lactide acid) during isothermal and non-isothermal crystallization. There are 2 main effect polarities of the functional group and steric effect. The polarity of the functional CNTs gives rise to varied interactions with PLA chains. The strong interfacial interaction arising from the polarity of functional groups was beneficial to the adsorption of PLA chains on CNTs. Because of the steric effect of functional groups, it could act as blocking sites, constraining the mobility of polymer chains. The authors observed, in general, an increase in the crystallinity of PLA. So, they conclude that the functional groups played a counteraction or competition on nucleation efficiency of functional CNTs attributing to the interfacial interaction and the steric effect.

For the PP phase, an increase is observed both in the crystallization temperature and in the crystallinity degree when CNT pristine functionalized with MA was added. The pristine CNT and the CNT_MA have the lowest oxygen concentration, as seen in the XPS results, thus being able to migrate to the PP phase, as they have less hydrophilic character. The CNTs function as nucleating agents, promoting faster crystal growth and heterogeneous nucleation [50].

The blend without CNT showed a characteristic Tan δ peak with its maximum close to 69 °C (Table 2), as found by other authors [51]. When adding carbon nanotubes,

Table 2 Tan δ and elastic modulus for PA6/PP blend and nanocomposites

Sample	$\tan \delta$ ($^{\circ}\text{C}$ em α)	$\tan \delta$ ($^{\circ}\text{C}$ em β)	E' (Gpa) at 25 $^{\circ}\text{C}$
PA6/PP	69		1.26
PA6/PP/CNT_pristine	22	84	1.46
PA6/PP/CNT_O ₂	34	87	1.35
PA6/PP/CNT_MA	25	77	1.79

2 characteristic peaks are observed, one between 20 $^{\circ}\text{C}$ and 30 $^{\circ}\text{C}$ and the other 77 $^{\circ}\text{C}$ –87 $^{\circ}\text{C}$ (Table 2), respectively, corresponding to α - and γ -crystallites of the polymer [52]. The T_g of α -crystals occurs at lower temperatures than that of γ -crystals, although γ is thermodynamically less stable. In the γ -crystalline, there is a 3D hydrogen bonding network that can more closely interact with neighboring amorphous segments. The hydrogen bond in the α -crystalline phase is confined within the fold planes and, therefore, a weaker interaction with the amorphous regions was observed [53]. The amount of oxygen in the CNT significantly changes the $\tan \delta$ temperature values, as well as the peak intensity (Fig. 7a). CNT_O₂ showed the highest temperatures and the highest peak intensity for γ conformation. According to Rotter and Ishida [53], the appearance of the high shoulder peak in the γ crystalline material can, therefore, be explained by the crystallization nature of each material, in which amorphous regions more restricted by the neighboring γ -crystalline zones can be expected to have a higher glass transition. Therefore, the greater presence of oxygen verified by the XPS results can facilitate the hydrogen-bonding interaction between the amorphous segments of the polyamide.

Despite the greater interaction between the amorphous and crystalline regions observed in the nanocomposites with CNT_O₂, the highest values of storage module were observed for the nanocomposite with CNT_MA (Table 2 and Fig. 7b). An increase of 42% was observed in relation to the pure blend and 22% to the nanocomposite with CNT pristine. For the CNT_O₂ sample, whose treatment time in plasma was twice as long as the CNT_MA sample, the oxygenated groups, for the most part, may have formed lactones. This would agree with Kondratowicz et al. [54], who pointed out that, after a certain period of treatment in plasma, carboxyl groups that are placed in the vicinity of hydroxyl groups can merge and create lactone groups. In the CNT functionalization with maleic anhydride, the ring opening is observed, and COOH groups are preferably formed on the CNT surface [39, 40]. The reaction between the COOH groups and the polyamide is well known in the literature [5, 16, 55, 56]. This bond could improve the tension transfer between the phases, allowing an improvement in the mechanical behavior of the material.

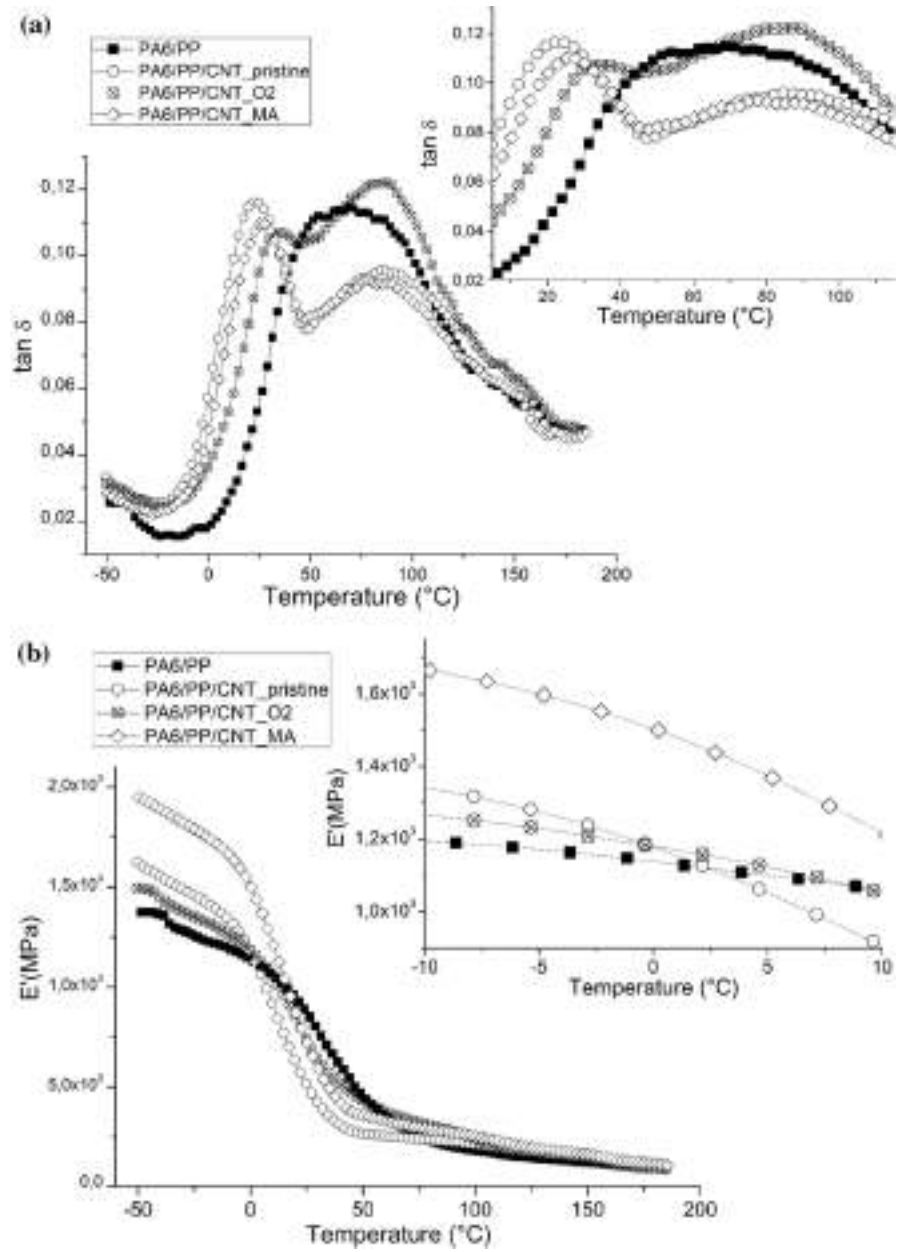


Fig. 7 DMA curves **a** $\tan \delta$ versus temperature and **b** storage modulus (E') versus temperature of PP/PA6 nanocomposites

Conclusion

The oxygen atomic percentage is 4 times higher for the CNT functionalized with O₂ (8.6 O at %), and the CNT_MA sample had a 40% increase (3.1 O at %) compared to the pristine sample (2.2 O at %). Besides the oxygen quantity, the chemical group's contribution was also different between both cases. The plasma treatment with maleic anhydride was more efficient in promoting the insertion of carboxylic groups into CNT surfaces. On the other hand, for the CNT_O₂ sample, there was a significant increase in the contribution of all oxygen groups and, since the time in this plasma treatment was twice as long as the CNT_MA sample, the oxygenated groups, for the most part, may have formed lactones.

Adding non-functionalized CNT led to an elongation of dispersed phase. Regarding to functionalized CNT addition, a significant reduction in phase size was observed. There is also no improvement in adhesion between phases. The interaction between the functionalized CNT and the PA6 may have suppressed the interfacial slip and, consequently, reduced the dispersed phase size. The crystallinity degree decreased with non-functionalized CNT and increased with the functionalized ones. The predominant effect may be the physical impediment that slows down the PA6 chains movement and molecular interaction, reducing the nanocomposites crystallinity degree (X_c). The better dispersion and CNT-polyamide interaction due to functionalization may reduce the molecular movement physical impediment effect. The presence of oxygen may facilitate hydrogen-bonding interaction between the amorphous segments of the polyamide.

Despite the greater interaction between the amorphous and crystalline regions observed in the nanocomposites with CNT_O₂, the highest values of storage modulus were observed for the nanocomposite with CNT_MA. A 42% increase in relation to the pure blend and 22% to the nanocomposite with CNT pristine was observed. The COOH groups on the CNT surface may react with the polyamide, improving tension transfer between phases and leading to a better performance in the blend's mechanical properties.

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Compliance with ethical standards

Conflicts of interest No conflict of interest exists.

References

1. Chow WS, Ishiaku US, Ishak ZAM et al (2003) Polyamide/Polypropylene/Organoclay nanocomposites: influence of organoclay and compatibiliser on the morphological and tensile properties. *J Teknol* 39:45–54. <https://doi.org/10.11113/jt.v39.440>
2. Tang Y, Hu Y, Zhang R et al (2004) Investigation on polypropylene and polyamide-6 alloys/montmorillonite nanocomposites. *Polymer* 45:5317–5326. <https://doi.org/10.1016/j.polymer.2004.03.090>
3. Afshari M, Kotek R, Kish MH et al (2002) Effect of blend ratio on bulk properties and matrix-fibril morphology of polypropylene/nylon-6 polyblend fibers. *Polymer* 43:1331–1341. [https://doi.org/10.1016/S0032-3861\(01\)00689-9](https://doi.org/10.1016/S0032-3861(01)00689-9)
4. La Mantia FP, Capizzi L (2001) Recycling of compatibilized and uncompatibilized nylon/polypropylene blends. *Polym Degrad Stab* 71:285–291. [https://doi.org/10.1016/S0141-3910\(00\)00177-4](https://doi.org/10.1016/S0141-3910(00)00177-4)
5. Agrawal P, Rodrigues AWB, Araújo EM et al (2010) Influence of reactive compatibilizers on the rheometrical and mechanical properties of PA6/LDPE and PA6/HDPE blends. *J Mater Sci* 45:496–502. <https://doi.org/10.1007/s10853-009-3967-9>
6. Misra A, Sawhney G, Kumar RA (1993) Structure and properties of compatibilized blends of polyamide-6 and ABS. *J Appl Polym Sci* 50:1179–1186. <https://doi.org/10.1002/app.1993.070500708>
7. Becker D, Hage E Jr, Pessan LA (2007) Synthesis and characterization of poly(methyl methacrylate-co-maleic anhydride) copolymers and its potential as a compatibilizer for amorphous polyamide blends. *J Appl Polym Sci* 106:3248–3252. <https://doi.org/10.1002/app.26836>
8. Taguet A, Cassagnau P, Lopez-Cuesta J-M (2014) Structuration, selective dispersion and compatibilizing effect of (nano) fillers in polymeric blends. *Prog Polym Sci* 39:1526–1563. <https://doi.org/10.1016/j.progpolymsci.2014.04.002>
9. Mofokeng JP, Luyt AS (2015) Morphology and thermal degradation studies of melt-mixed poly(lactic acid) (PLA)/poly(ϵ -caprolactone) (PCL) biodegradable polymer blend nanocomposites with TiO₂ as filler. *Polym Test* 45:93–100. <https://doi.org/10.1016/j.polymertesting.2015.05.007>
10. Wu D, Lin D, Zhang J et al (2011) Selective localization of nanofillers: effect on morphology and crystallization of PLA/PCL Blends. *Macromol Chem Phys* 212:613–626. <https://doi.org/10.1002/macp.201000579>
11. Baudouin A-C, Bailly C, Devaux J (2010) Interface localization of carbon nanotubes in blends of two copolymers. *Polym Degrad Stab* 95:389–398. <https://doi.org/10.1016/j.polymdegradstab.2009.11.007>
12. Cayla A, Campagne C, Rochery M et al (2011) Electrical, rheological properties and morphologies of biphasic blends filled with carbon nanotubes in one of the two phases. *Synth Met* 161:1034–1042. <https://doi.org/10.1016/j.synthmet.2011.03.012>
13. Gödel A, Marmur A, Kasaliwal GR et al (2011) Shape-dependent localization of carbon nanotubes and carbon black in an immiscible polymer blend during melt mixing. *Macromolecules* 44:6094–6102. <https://doi.org/10.1021/ma200793a>
14. Muhulet A, Miculescu F, Voicu SI et al (2018) Fundamentals and scopes of doped carbon nanotubes towards energy and biosensing applications. *Mater Today Energy* 9:154–186. <https://doi.org/10.1016/j.mtener.2018.05.002>
15. Kim SW, Kim T, Kim YS et al (2012) Surface modifications for the effective dispersion of carbon nanotubes in solvents and polymers. *Carbon* 50:3–33. <https://doi.org/10.1016/j.carbon.2011.08.011>
16. Madhukar K, Sainath AVS, Rao BS et al (2012) Role of carboxylic acid functionalized single walled carbon nanotubes in polyamide 6/poly(methyl methacrylate) blend. *Polym Eng Sci*. <https://doi.org/10.1002/pen.23272>
17. Cheng HKF, Sahoo NG, Khin TH et al (2010) The role of functionalized carbon nanotubes in a PA6/LCP blend. *J Nanosci Nanotechnol* 10:5242–5251. <https://doi.org/10.1166/jnn.2010.2415>
18. Zhang L, Wan C, Zhang Y (2009) Investigation on the multiwalled carbon nanotubes reinforced polyamide 6/polypropylene composites. *Polym Eng Sci* 49:1909–1917. <https://doi.org/10.1002/pen.21428>
19. Wang L, Guo Z-X, Yu J (2014) Effects of carbon nanotubes on the morphology and properties of uncompatibilized and maleic anhydride-grafted polypropylene-compatible polyamide 6/polypropylene blends. *J Macromol Sci Part B* 53:1205–1221. <https://doi.org/10.1080/00222348.2014.891170>

20. Anjali S, Aishwaryalakshmi S, Ashwin V et al (2018) Effect of compatibilizer and carbon nanotubes on blends of polypropylene and nylon 6. *Mater Today Proc* 5:25524–25533. <https://doi.org/10.1016/j.matpr.2018.10.359>
21. Wu H-L, Wang C-H, Ma C-CM et al (2007) Preparations and properties of maleic acid and maleic anhydride functionalized multiwall carbon nanotube/poly(urea urethane) nanocomposites. *Compos Sci Technol* 67:1854–1860. <https://doi.org/10.1016/j.compscitech.2006.10.028>
22. Araújo RF, Proença MF, Silva CJ et al (2014) The solvent effect on the sidewall functionalization of multi-walled carbon nanotubes with maleic anhydride. *Carbon* 78:401–414. <https://doi.org/10.1016/j.carbon.2014.07.019>
23. Le CMQ, Cao XT, Lim KT (2017) Ultrasound-promoted direct functionalization of multi-walled carbon nanotubes in water via Diels-Alder “click chemistry”. *Ultrason Sonochem* 39:321–329. <https://doi.org/10.1016/j.ultsonch.2017.04.042>
24. Yao H, Zhou G, Wang W et al (2018) Effect of polymer-grafted carbon nanofibers and nanotubes on the interlaminar shear strength and flexural strength of carbon fiber/epoxy multiscale composites. *Compos Struct* 195:288–296. <https://doi.org/10.1016/j.compstruct.2018.04.082>
25. Tseng C-H, Wang C-C, Chen C-Y (2007) Functionalizing carbon nanotubes by plasma modification for the preparation of covalent-integrated epoxy composites. *Chem Mater* 19:308–315. <https://doi.org/10.1021/cm062277p>
26. Lu Y-Y, Li H, Liu H-Z (2010) Maleic anhydride functionalization of multi-walled carbon nanotubes by the electron beam irradiation in the liquid media. *Phys E Low Dimens Syst Nanostruct* 43:510–514. <https://doi.org/10.1016/j.physe.2010.09.004>
27. Steffen TT, Fontana LC, Hammer P et al (2019) Carbon nanotube plasma functionalization: the role of carbon nanotube/maleic anhydride solid premix. *Appl Surf Sci* 491:405–410. <https://doi.org/10.1016/j.apsusc.2019.06.176>
28. Huang YL, Ma C-CM, Yuen S-M et al (2011) Effect of maleic anhydride modified MWCNTs on the morphology and dynamic mechanical properties of its PMMA composites. *Mater Chem Phys* 129:1214–1220. <https://doi.org/10.1016/j.matchemphys.2011.06.020>
29. Steffen TT, Fontana LC, Nahorny J et al (2019) Role of nitrogen–oxygen plasma functionalization of carbon nanotubes in epoxy nanocomposites. *Polym Compos* 40:E1162–E1171. <https://doi.org/10.1002/pc.24921>
30. Loos MR, Nahorny J, Fontana LC (2013) Plasma modification of carbon nanotubes. *Curr Org Chem* 17:1880–1893. <https://doi.org/10.2174/13852728113179990089>
31. Karger-Kocsis J (1995) Polypropylene structure, blends and composites England 1995, vol 1. Chapman and Hall England, London
32. Wang H, Huang R, Wu D et al (2013) Effects of thermal oxygen aging on the crystallization behavior and properties of nylon 6. *Polym Mater Sci Eng* 29:88–92
33. Lee S, Liu YC, Chen CH (2012) Raman study of the temperature-dependence of plasma induced defect formation rates in carbon nanotubes. *Carbon* 50:5210–5216. <https://doi.org/10.1016/j.carbon.2012.07.004>
34. Mercier G, Gleize J, Ghanbaja J et al (2013) Soft oxidation of single-walled carbon nanotube samples. *J Phys Chem C* 117:8522–8529. <https://doi.org/10.1021/jp400890n>
35. Talla J, Zhang D, Kandadai M et al (2010) A resonance Raman study of carboxyl induced defects in single-walled carbon nanotubes. *Phys B* 405:4570–4573. <https://doi.org/10.1016/j.physb.2010.08.041>
36. Hoa LETM (2018) Characterization of multi-walled carbon nanotubes functionalized by a mixture of HNO₃/H₂SO₄. *Diam Relat Mater* 89:43–51. <https://doi.org/10.1016/j.diamond.2018.08.008>
37. Harb SV, Pulcinelli SH, Santilli CV et al (2016) A comparative study on graphene oxide and carbon nanotube reinforcement of PMMA-siloxane-silica anticorrosive coatings. *Appl Mater Inter* 8:16339–16350. <https://doi.org/10.1021/acsami.6b04780>
38. Chiang CL, Wang CC, Chen CY (2018) Carbon nanotubes functionalized with maleic anhydride chelated silver nanoparticles as conductive additives for polyanion-based lithium-ion batteries. *Mater Sci Eng B* 238–239:42–49. <https://doi.org/10.1016/j.mseb.2018.12.013>
39. Mishra G, McArthur SL (2010) Plasma polymerization of maleic anhydride: just what are the right deposition conditions? *Langmuir* 26:9645–9658. <https://doi.org/10.1021/la100236c>
40. Ma J, Wang W, Huang J et al (2009) Surface structure and hydrophilicity of polypropylene porous membranes modified by maleic anhydride plasma polymerization. *Polym Mater Sci Eng* 25:16–18

41. Chen C, Liang B, Ogino A et al (2009) Oxygen functionalization of multiwall carbon nanotubes by microwave-excited surface-wave plasma treatment. *J Phys Chem C* 113:7659–7665. <https://doi.org/10.1021/jp9012015>
42. Saka C (2018) Overview on the surface functionalization mechanism and determination of surface functional groups of plasma treated carbon nanotubes. *Crit Rev Anal Chem* 2:1–14. <https://doi.org/10.1080/10408347.2017.1356699>
43. Huber T, Misra M, Mohanty AK (2014) Mechanical properties of compatibilized nylon 6/polypropylene blends; studies of the interfacial behavior through an emulsion model. *J Appl Polym Sci*. <https://doi.org/10.1002/app.40792>
44. Shin BY, Ha MH, Han DH (2016) Morphological, rheological, and mechanical properties of polyamide 6/polypropylene blends compatibilized by electron-beam irradiation in the presence of a reactive agent. *Materials*. <https://doi.org/10.3390/ma9050342>
45. Moud AA, Javadi A, Nazockdast H et al (2014) Effect of dispersion and selective localization of carbon nanotubes on rheology and electrical conductivity of polyamide 6 (PA 6), Polypropylene (PP), and PA 6/PP nanocomposites. *J Polym Sci Polym Phys* 53:368–378. <https://doi.org/10.1002/polb.23638>
46. Zeng H, Gao C, Wang Y et al (2006) In situ polymerization approach to multiwalled carbon nanotube-reinforced nylon 1010 composites: mechanical properties and crystallization behavior. *Polymer* 47:113–122. <https://doi.org/10.1016/j.polymer.2005.11.009>
47. Scaffaro R, Maio A, Agnello S et al (2012) Plasma Functionalization of Multiwalled Carbon Nanotubes and Their Use in the Preparation of Nylon 6-Based Nanohybrids. *Plasma Process Polym* 9:503–512. <https://doi.org/10.1002/ppap.201100140>
48. Liu H, Wang X, Fang P et al (2010) Functionalization of multi-walled carbon nanotubes grafted with self-generated functional groups and their polyamide 6 composites. *Carbon* 48:721–729. <https://doi.org/10.1016/j.carbon.2009.10.018>
49. Ying LY, Zhuang XJ, Yang LX et al (2013) Role of surface chemical groups on carbon nanotubes in nucleation for polymer crystallization: Interfacial interaction and steric effect. *Polymer* 54:6479–6488. <https://doi.org/10.1016/j.polymer.2013.09.027>
50. Bikiaris D, Vassiliou A, Chrissafis K et al (2008) Effect of acid treated multi-walled carbon nanotubes on the mechanical, permeability, thermal properties and thermo-oxidative stability of isotactic polypropylene. *Polym Degrad Stab* 93:952–967. <https://doi.org/10.1016/j.polymdegradstab.2008.01.033>
51. Stankowski M, Kropidowska A, Gazda M et al (2008) Properties of polyamide 6 and thermoplastic polyurethane blends containing modified montmorillonites. *J Therm Anal Calorim* 94:817–823. <https://doi.org/10.1007/s10973-007-8886-x>
52. Zwane RDS, Sadiku ER, Ray SS et al (2019) Thermal and rheological properties of polyamide 6/layered double hydroxide clay composites. *Polym Polym Compos* 27:567–581. <https://doi.org/10.1177/0967391119853969>
53. Rotter G, Ishida H (1992) Dynamic mechanical analysis of the glass transition: curve resolving applied to polymers. *Macromolecules* 25:2170–2176. <https://doi.org/10.1021/ma00034a017>
54. Kondratowicz I et al (2018) Tailoring properties of reduced graphene oxide by oxygen plasma treatment. *Appl Surf Sci* 440:651–659. <https://doi.org/10.1016/j.apsusc.2018.01.168>
55. Filippi S, Chiono V, Polacco G et al (2002) Reactive compatibilizer precursors for LDPE/PA6 blends, 1 Ethylene/acrylic acid copolymers. *Macromol Chem Phys* 203:1512–1525. [https://doi.org/10.1002/1521-3935\(200207\)203:10/11<1512:AID-MACP1512>3.0.CO;2-G](https://doi.org/10.1002/1521-3935(200207)203:10/11<1512:AID-MACP1512>3.0.CO;2-G)
56. La Mantia FP, Ceraulo M, Mistretta MC et al (2019) Compatibilization of Polypropylene/Polyamide 6 Blend Fibers Using Photo-Oxidized Polypropylene. *Materials*. <https://doi.org/10.3390/ma12010081>



Enhancing the corrosion protection of Ti-6Al-4V alloy through reactive sputtering niobium oxide thin films

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ABSTRACT

Here, a set of polycrystalline niobium oxide thin films were produced by using reactive sputtering technique on the Ti-6Al-4V alloy surfaces and characterized by OM, SEM/EDX, AFM, DRX/Rietveld refinement, and XPS techniques. CPDP and SVET tests were performed on the coated and uncoated material considering an aggressive medium (NaF and Hank's solution). The results demonstrated the technique used in the present survey was advantageous to produce thin films on the Ti-6Al-4V surfaces. XPS analysis demonstrated that the niobium oxide thin films were composed by Nb₂O₅/NbO₂. Measured and Rietveld refined X-ray diffraction patterns for the Nb-oxide thin film demonstrated the presence of the Nb₂O₅, NbO₂, and NbO crystalline phases. The thin film acts as a barrier layer, suggesting a better corrosion performance when compared to the bare alloy ($E_{\text{corr}} = -111 \text{ mV}_{\text{SCE}}$ vs $-290 \text{ mV}_{\text{SCE}}$). The CPDP results demonstrated the current density of the coated Ti-6Al-4V specimen, at the same potential, was lower when compared to the bare alloy. SVET results revealed the coated material displayed low values of current density ($\sim 100 \mu\text{A}/\text{cm}^2$ for 15 h of immersion time), whilst the bare material (in the range $700\text{--}2200 \mu\text{A}/\text{cm}^2$ for 1 h of immersion time), suggesting the niobium oxide thin films act as an effective protective barrier against corrosion process evolution over time.

1. Introduction

The demand for the development and use of biomaterials, especially orthopedic, traumatological or dental implants has been increasing daily. Among metallic biomaterials, titanium (Ti) and its alloys are given preference to use as orthopedic implants. Ti alloys display good mechanical strength, good resistance to corrosion process in an aggressive medium, low density (4.43 g cm^{-3}), relatively low Young's modulus ($101\text{--}120 \text{ MPa}$) as well as good biocompatibility [1–3].

Considering all production of Ti alloy about 50% is related to the Ti-6Al-4V. The Ti-6Al-4V alloy is used as reference material for the development and improving other alloys [4–7]. Despite the range of attractive properties mentioned above, Ti-6Al-4V alloy exhibits low hardness, poor resistance to wear and corrosion processes [8,9] in a medium containing fluoride aggressive ion [10,11]. In fact, when the Ti-6Al-4V alloy is exposed to an aggressive media, the TiO₂ thin films produced spontaneously on the alloy surface are broken, leading the material to global and localised corrosion processes [12]. In this sense,

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considering the most diverse applications of the Ti-6Al-4V alloy, it is crucial to improve its surface properties.

As reported by the literature [13–15], several surface modifications may be used to improve the mechanical and corrosive properties of this kind of material such as nitriding [16,17], thermal treatments [18], solid carburization [19], anodization [20], laser cladding [21,22], sol-gel dip-coating [23], grafting [24], plasma electrolytic oxidation (PEO) [25], chemical vapor deposition (CVD) [26,27], and physical vapor deposition (PVD) [28–32]. The PVD technique appears as a powerful tool for the coating of metallic materials, providing the formation of homogeneous thin films, with good parameters of purity, density and adhesion [33].

In reactive sputtering, the thin films of oxides, nitrides and others are deposited on the substrates from metallic targets. For this purpose, a reactive gas mixed with an inert working gas is used [34]. The reactive sputtering technique has been employed in numerous industrial applications forming a wide variety of compound coating used in technological devices such as zinc sulfide [35], aluminium nitride [36], tantalum oxide [37], and chromium oxide [38]. Several experimental parameters can affect the film composition and the deposition rate such as the gas composition, partial pressure and supply rate, the current ion, the sputtering yield, substrate position and others [39]. In addition, these parameters should be carefully established in order to produce thin films with good adhesion and quality [40].

Recently, our research group demonstrated the advantageous to produce corrosion protective niobium oxide thin films on the surface of different materials by using the reactive sputtering technique. In the first study, we improved the corrosion protection of the 2524-T3 aluminium alloy used as aircraft material, considering the localised and global electrochemical tests in 0.05 and 0.6 mol L⁻¹ NaCl corrosive solution. Moreto et al. [41] mentioned that the reactive sputtering technique was shown advantageous for producing niobium oxide thin film on the aluminium surfaces. In addition, the coating improved the corrosion resistance of the 2524-T3 aluminium alloy and the wear resistance.

Another work that deserves to be mentioned was also published by Moreto et al. [42] in which were exhibited new insights of niobium oxide thin films coated on the 316L stainless steel (316L SS) to be used in the dentistry field as brackets. Besides, the coating improved the biological responses of the 316L SS and promoted a less toxic and less inflammation in gingival cells (fibroblast cell-line HGF-1). Regarding the Ti-6Al-4V alloy, in a previous work [43], we performed cytotoxicity and biocompatibility tests by using VERO-CCL-8 cell line as a detailed study concerning inflammatory responses with Human blood leukocyte cells on the specimens coated with niobium oxide films. Our results demonstrated a higher level of the anti-inflammatory cytokine was found for the functionalized surface.

Although we have published several studies demonstrating the benefits of the functionalized surface with niobium oxide thin films for biomedical applications, there is still no work in the literature that considers the global and localised corrosion processes of the Ti-6Al-4V alloy containing the technology developed in this study. For this purpose, here we present an innovative and applied work, considering the effect of the niobium oxide coating on the global and localised corrosion process of the Ti-6Al-4V alloy.

2. Experimental

2.1. Material

In the present investigation, specimens of Ti-6Al-4V were used as-received conditions. All samples were sanded using silicon carbide (SiC) sandpapers in the sequence range of 600, 800, 1200, 2400, and 4000#. After the sanded process, the samples were cleaned with distilled water and isopropyl alcohol for a period of 15 min at room temperature. The specimens were kept in appropriate holders until the deposition process by using the reactive sputtering technique. More

information about the specimen's preparation is available at reference [43].

2.2. Coating preparation

The polycrystalline niobium oxide thin films were deposited on the Ti-6Al-4V alloy surface by using a reactive sputtering technique at the Thin Films and Plasma Processes Laboratory at Federal University of Triângulo Mineiro, UFTM, Brazil. The DC magnetron sputtering design technique used to produce the films over Ti-6Al-4V alloy may be found at Machuno et al. [44].

Fig. 1 exhibits a schematic drawing of the reactive sputtering system used herein. It is very important to mention this drawing was adapted from Machuno et al. [44] and based on the system published for the authors elsewhere [43]. The same procedure adopted by Bino et al. [43], Moreto et al. [41], and Moreto et al. [42] to produce niobium oxide thin films was used in the present work.

To obtain polycrystalline thin films, at first the pressure in the chamber was set to 0.005 mTorr, using a rotating and turbo molecular vacuum pump. After, Argon (99.999% White Martins) was introduced in the chamber until reaching 5.0 mTorr. Finally, oxygen (99.999% White Martins) was added up to 5.5 mTorr. The coated-Ti-6Al-4V were obtained after 45 min of deposition using a current of 140 mA and voltage about 440 V, resulting in a homogeneous compact layer in the range 300 to 450 nm of thickness. The Niobium target (99.9%) used in the present work was donated by the Companhia Brasileira de Metalurgia e Mineração (CBMM), Araxá, Minas Gerais, Brazil.

2.3. Morphological characterization

The morphological characterization of the coated and uncoated Ti-6Al-4V alloy was assessed by SEM, using a FEG-SEM JEOL-JSM7001F model in the Chemistry Department of the Federal University of Uberlândia, Uberlândia, Minas Gerais, Brazil. The AFM and OM analysis were performed at the Federal University of Triângulo Mineiro, Minas Gerais, Brazil. For this purpose, a Shimadzu SPM9700 microscopy in a dynamic mode and cantilevers purchase from NT-MDT Co was used. In the present work, the *imageJ* software was used to improve the contrast and brightness of the BSE images obtained via SEM. The image treatment allowed a better visualization of the α and β phases, respectively.

2.4. Structural characterization

The thin film was also characterized by XPS technique, using a K-Alpha Thermo Scientific spectrometer equipped with a monochromatic Al-K α X-ray source (1486.6 eV), at a pressure below 10⁻⁷ mBar. Survey spectra were collected at pass energy of 200 eV for survey and whilst high-resolution spectra were recorded at 50 eV. The spectra deconvolution was performed using the Voigtian function, with Gaussian (70%) and Lorentzian (30%) combinations. The XPS measurements have been performed at the Technological Science Centre, State University of Santa Catarina, UDESC, Santa Catarina, Brazil.

DRX diffractograms were obtained by a PANalytical model X'Pert PRO MPD diffractometer, under CuK α radiation. Measurements were carried out by the grazing incidence X-ray diffraction technique (GID) on the incident angle fixed at 6°. A high-resolution PIXcel 1D semiconductor radiation detector scanned the diffracted radiation rotating between 5 and 80° (2 θ), under the angular step of 0.0263°, and 80 s of counting time per point. The voltage and current used were 40 kV and 30 mA, respectively. The crystallographic plane of the Si substrate surface was identified by X-ray diffraction taken in the Bragg-Brentano θ -2 θ configuration. The X'Pert High Score Plus (XPHSP) software was employed for Rietveld refinements to determine the relative weight of each crystalline phase present in the film material. PDF files (pattern diffraction files) and CIF (crystallographic information files) of niobium oxides were used in the refinement procedures. The refinement quality

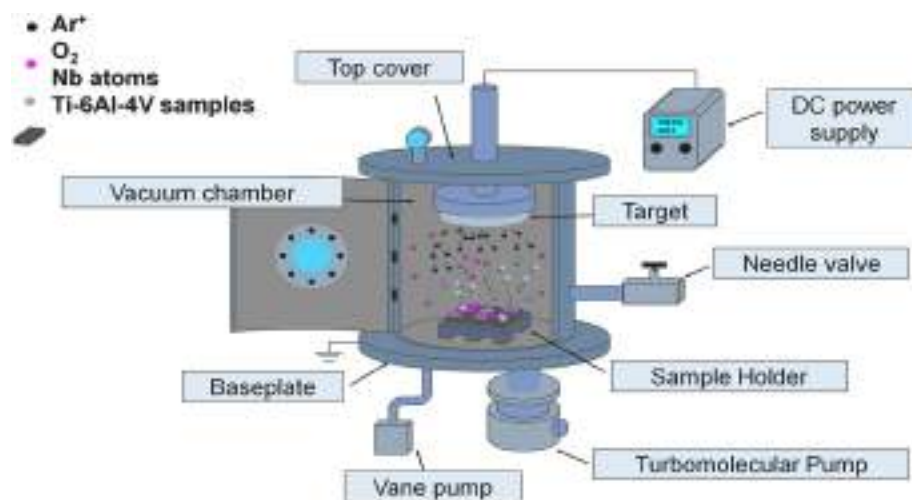


Fig. 1. An overview of the schematic drawing of the reactive sputtering system used in the present work.

was evaluated by the two factors, the goodness of fit χ^2 , and the weighted profile residual, Rwp.

The measurements were performed at the X-ray Diffraction Laboratory (Lab DRX) of the X-Ray Analysis Laboratory (Lab LARX), which in turn belongs to the Multi-User Research Laboratory Central of UEL's Research Laboratories (CMLP-UEL). The niobium oxide thin films were deposited on Si substrates for the DRX measurements.

2.5. Contact angle characterization

The contact angle (θ) measurements were performed in order to determine the wettability of the coated and uncoated specimens in Hank's solution at room temperature [45]. This evaluation was conducted using the sessile drop method from an apparatus developed by the Corrosion Research Laboratory (LAPEC) at the Federal University of Rio Grande do Sul (Porto Alegre, Brazil) [46].

2.6. Corrosion susceptibility tests

The corrosion susceptibility of the coated and uncoated samples was evaluated by using cyclic potentiodynamic polarization (CPDP) tests in a Hank's solution, which simulates body fluid (1000 mL of solution were used) [45]. The tests were performed in an Autolab PGSTAT302N potentiostat/galvanostat using a three-electrode electrochemical cell consisting of a platinum counter electrode, a saturated calomel reference electrode (SCE) and the evaluated sample as working electrode (exposed area: 0.503 cm^2).

Prior to test, the samples were washed in an ultrasonic bath in the sequence: acetone, alcohol and deionized water and then dried with a jet of cold air. The measurements were carried out at $37 \pm 1^\circ\text{C}$ and $\text{pH} = 7.4$ in a de-aerated medium. The open circuit potential (OCP) was monitored for 1 h before CPDP tests, which was performed from $-100 \text{ mV}_{\text{OCP}}$ to $+2000 \text{ mV}_{\text{SCE}}$, with a scan rate of 1 mVs^{-1} . OM analysis was performed before and after the electrochemical tests. For this purpose, a Zeiss Axio Lab.A1 microscope was used using the ZEN 2.6 software (blue edition).

2.7. Scanning vibrating electrode technique (SVET) analysis

The equipment used was the Applicable Electronics Inc. with the ASET-Sciencewares software. The maps were generated by QuikGrid version 5.4 software. The SVET measurements were performed by using a vibration frequency of 124 Hz. The microelectrode used was a platinum/iridium vibrating probe from MicroProbes with $10 \mu\text{m}$ diameter of platinum deposit and two semi-reference electrodes of platinum. The

distance between probe and sample surface was $100 \mu\text{m}$. The tests were performed using a solution of 0.01 mol L^{-1} NaF at pH 2, with sample exposed area delimited with bee wax. SVET scans were performed during 15 h.

3. Results & discussion

3.1. Morphological and structural analysis

3.1.1. Scanning electron microscopy (SEM)

Fig. 2 (a–d) displays SEM micrograph images of the bare and coated Ti-6Al-4V alloy, in 1.0, 10.0 and 30.0 kx magnifications. As well known, SEM is a technique that provides images of a sample by scanning the surface with a focused beam of electrons. The interaction of electrons with the atoms of the sample produces signals, which contain information about the composition as well as the surface topography of the specimen. Secondary electron (SE) images for uncoated and coated material are displayed in Fig. 2 (a, c, d), providing information of the topography. An overview of the Ti-6Al-4V alloy surface is presented in Fig. 2 (a), demonstrating a presence of grooves, probably, caused during the mechanical polishing process. The backscattered electrons (BSE) image of the uncoated material with 10.0 kx magnification may be observed in Fig. 2 (b), providing a characteristic image of composition. It can be observed in Fig. 2 (b), the microstructure of the as-received Ti-6Al-4V alloy is formed by two phases (α and β). As mentioned in the Experimental section, the *software imageJ* was used to improve the contrast and brightness of the BSE image. The energy-dispersive X-ray spectroscopy (EDX) analysis performed in a previous work [43], demonstrated the dark region displays a higher concentration of aluminium (Al), whilst the predominant element in the light region is vanadium (V). A homogeneous thin film was deposited by using reactive sputtering technique on the Ti-6Al-4V alloy surface (see Fig. 2 (c)), and the yellow arrow on the SE image (Fig. 2 (d)) revealed a depleted region in niobium oxide.

As reported by Amigó-Borrás [47], $\alpha + \beta$ alloys containing both α and β phases stabilizer elements. In addition, the mechanical and corrosive properties of the Ti-6Al-4V alloy exhibit a strong dependence on the microstructure. Furthermore, the Ti-6Al-4V alloy is widely used in several sectors due to its low density, high resistance at elevated temperature, high creep as well as corrosion resistance in an aggressive medium. It is important to mention, the resistance to corrosion process is due to the formation of a spontaneous TiO_2 thin films on the alloy surface.

The surface morphology of the uncoated material revealed some scratching due to the mechanical polishing process [43,48]. With

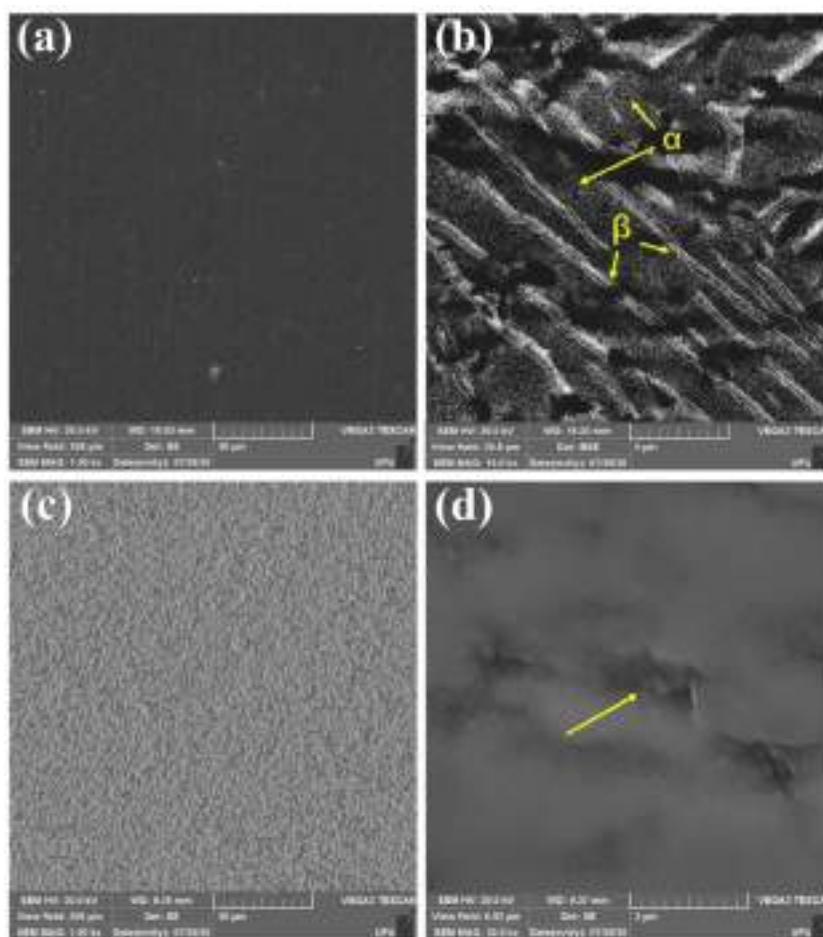


Fig. 2. (a, b) SEM images obtained for the uncoated material and (c, d) coated material.

respect to coated material, the niobium oxide films deposited on the Ti-6Al-4V alloy surface were free of cracks, and relatively more homogeneous when compared to the substrate. Our results provided a formation of a dense coating with good adhesion and any detachment (not shown here). As highlighted in Fig. 2 (d) there was a formation of spherical particle aggregates, forming protrusions on the coating. There was a good agreement between SEM and AFM results, which will be discussed in the next section.

3.1.2. Atomic force microscopy

Fig. 3 illustrates the representative surface topography as well as the 3D AFM images of the uncoated (a–f) and coated-Ti-6Al-4V alloy (g–i). Regarding the bare material, it was noticed the presence of different phases, which interfered more prominently in the phase angle as displayed on the Fig. 3 (b) and (e), respectively. As well known, the reactive sputtering technique promotes the formation of granules, which may be related to the nucleation of the thin films in the different deposition stages. In addition, the presence of scratches has been confirmed on the alloy surfaces, which are more evident in the phase mode, and probably is due to the polishing process.

The phase mode image of the Nb oxide coating shown in Fig. 3 (h), displays the most homogeneous surface among all others, i.e., the cantilever phase change was the lowest for this sample among all others.

Fig. 4 displays the Ti-6Al-4V substrate over sputtering sample holder Fig. 4 (a) before and Fig. 4 (b) after the deposition process. Fig. 4 (c) shows details of the sample used on the AFM investigations. Fig. 4 (d) and (e) present the AFM mapping for pink and green regions, respectively. The profile measurement in three places of the samples may be observed in Fig. 4 (f) and (g).

Since our reactive sputtering is a custom design equipment, the magnetron allows using target of 2 in. diameter, in order to optimize the deposition time the substrate holder is positioning closer to the niobium target, generating a thickness variation as can be seen in Fig. 4 (b) and (c). Our results demonstrate the thickness estimation in pink and green regions were about 400 and 450 nm (see Fig. 4 (f) and (g)).

In a previously published work [43], it was demonstrated by Raman spectroscopy an increase in the band intensity associated with the Nb-O-Nb. In fact, we observed a greater thickness in the green region when compared to the pink region. In this sense, considering the equipment assembly used in the present work and the sample position in the sputtering chamber, the thickness variation observed (400–450 nm) is not significant and in this way, the reactive sputtering process was considered appropriate to produce niobium oxide thin films over Ti-6Al-4V alloy.

3.2. X-ray photoelectron spectroscopy

Survey XPS spectrum shows a surface chemical composition of the thin film as 32.5 at.% of carbon, 49.8 at.% of oxygen and 17.7 at.% of niobium. The niobium Nb 3d high resolution spectrum clearly present the doublet assigned to Nb₂O₅ (Nb 3d_{5/2} at 207.0 eV and Nb 3d_{3/2} at 209.8 eV) and also the doublet related to NbO₂ state (Nb 3d_{5/2} at 205.7 eV and Nb 3d_{3/2} at 208.5 eV) [49,50]. It indicates a thin film formation with a major contribution (peak area percentage: 96.6%) of Nb₂O₅ chemical state, and a slightly (peak area percentage: 3.4%) contribution of NbO₂. In agreement, O 1 s spectrum indicates 82.6% of oxygen as Nb₂O₅/NbO₂ oxidation state (530.0 eV) and 17.4% regarding to the contribution of oxygen bonds with carbon and/or hydrogen (531.6 eV).

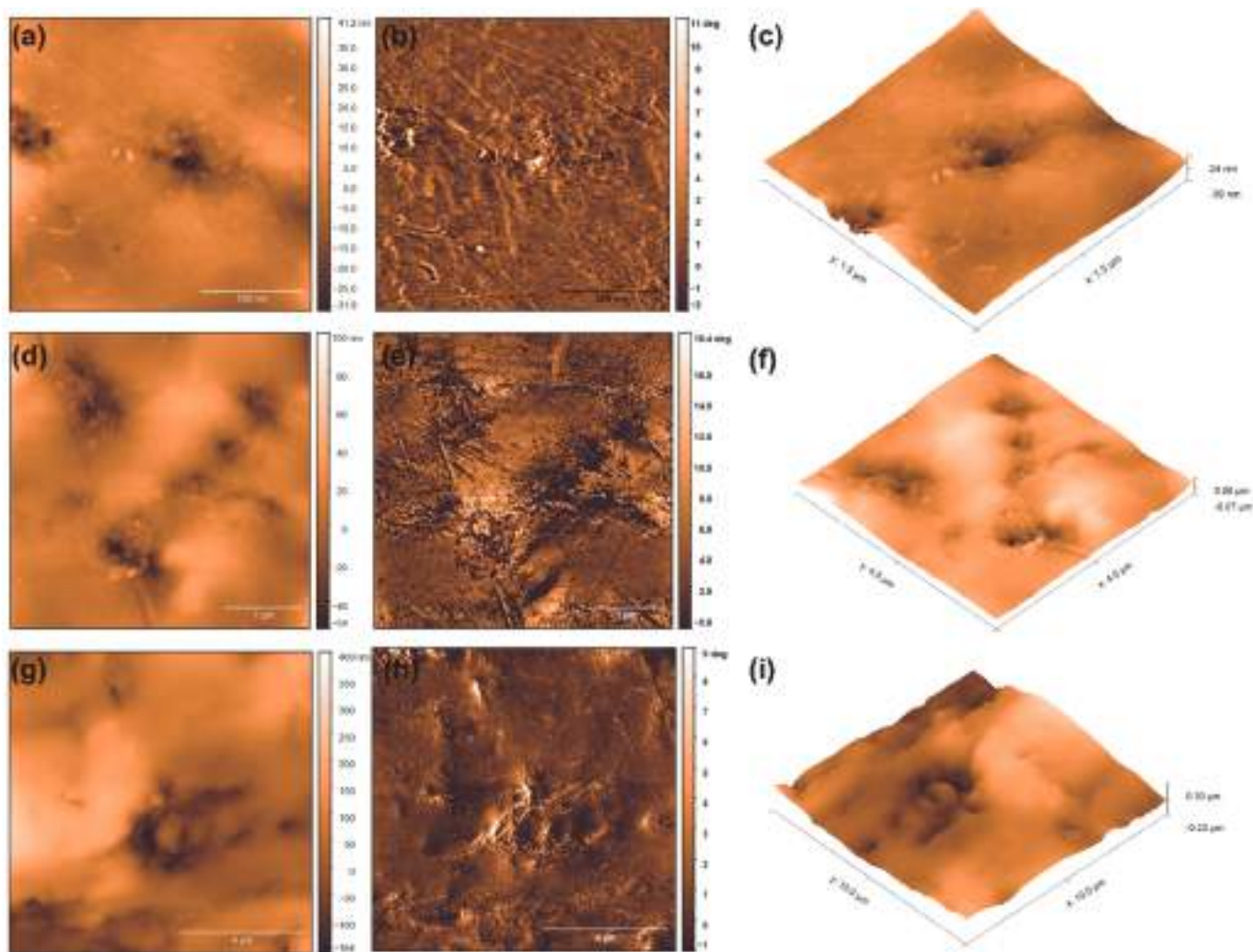


Fig. 3. Surface topography of the uncoated (a–f) and coated (h–i) obtained by AFM.

[51]. Fig. 5 shows the XPS survey spectrum of the Ti-6Al-4V alloy surface containing polycrystalline niobium oxide thin films.

3.3. X-ray diffraction patterns refined by Rietveld method

The measured and Rietveld refined X-ray diffraction patterns for the Nb thin films obtained in the present work by the reactive sputtering technique are presented in Fig. 6. The black dots represent the experimental data, and thin colored lines describe the crystalline phases for the simulated diffractograms. The analysis of XRD patterns and diffraction peaks revealed the presence of three possible oxides NbO, NbO₂, and Nb₂O₅. The oxide compositions were identified using the crystallographic data files PDF 01-089-6902 for NbO, PDF 01-076-1095 for NbO₂, and PDF 01-080-2493 for Nb₂O₅. Monocrystalline Si was employed as the standard to correct the instrumental errors, particularly significant in calculation size and microdeformation of crystallites.

In Fig. 6, the red color line represents the sum of the NbO, NbO₂, and Nb₂O₅ individual refined structures. The fitting between the experimental and simulated diffractogram was improved considering a preferential growth of the (3 1 -1) planes of Nb₂O₅, at the 28.6° diffraction angle and of the (002) planes of NbO, at 42.5°. Fig. 7 displays the X-ray diffractogram of the Si substrate plate showing its surface was cut-oriented in the [211] direction.

The relative weight concentrations of the Nb oxide phases obtained from the Rietveld refinement are presented in Table 1. The deposited

film is composed of 89(1), 9(1), and 2.1(1) weight% of Nb₂O₅, NbO₂, and NbO, respectively. The number in parentheses after each weight value gives the error on the last digit in calculating the relative weights.

In addition, crystallites size was estimated by the Williamson-Hall, Size-Strain Plot (SSP), and Scherrer techniques for the three Nb oxides [52]. As shown in Table 2, regardless of the method used, there is a good agreement between the results obtained for the crystallite sizes, resulting in about 26 Å for the NbO₂ and Nb₂O₅ oxides and 55 Å for the NbO oxide. A large number of studies have evidenced the effect of the grain and crystallite sizes on the corrosion of a wide range of materials [53,54]. In general, small crystallite size contributes positively to corrosion resistance. In this sense, the very small crystallite size obtained for the niobium oxide film is an indication that it will offer a barrier against the corrosion of the Ti-6Al-4V alloy surface, as follow.

3.4. Corrosion susceptibility

The open circuit potential (OCP) was monitored during 1 h before CPDP tests. Aiming to understand the coating behaviour, niobium sample was evaluated under the same conditions of Ti-6Al-4V and Ti-6Al-4V coated samples. Fig. 8 (a) shows that the coated sample presented stability at more positive potential (~-111 mV_{SCE}) than the sample Ti-6Al-4V (~-290 mV_{SCE}) and the niobium sample (~-471 mV_{SCE}), what suggests a better corrosion resistance of the coated sample [55]. It is worth mentioning that the abrupt OCP variations is related to

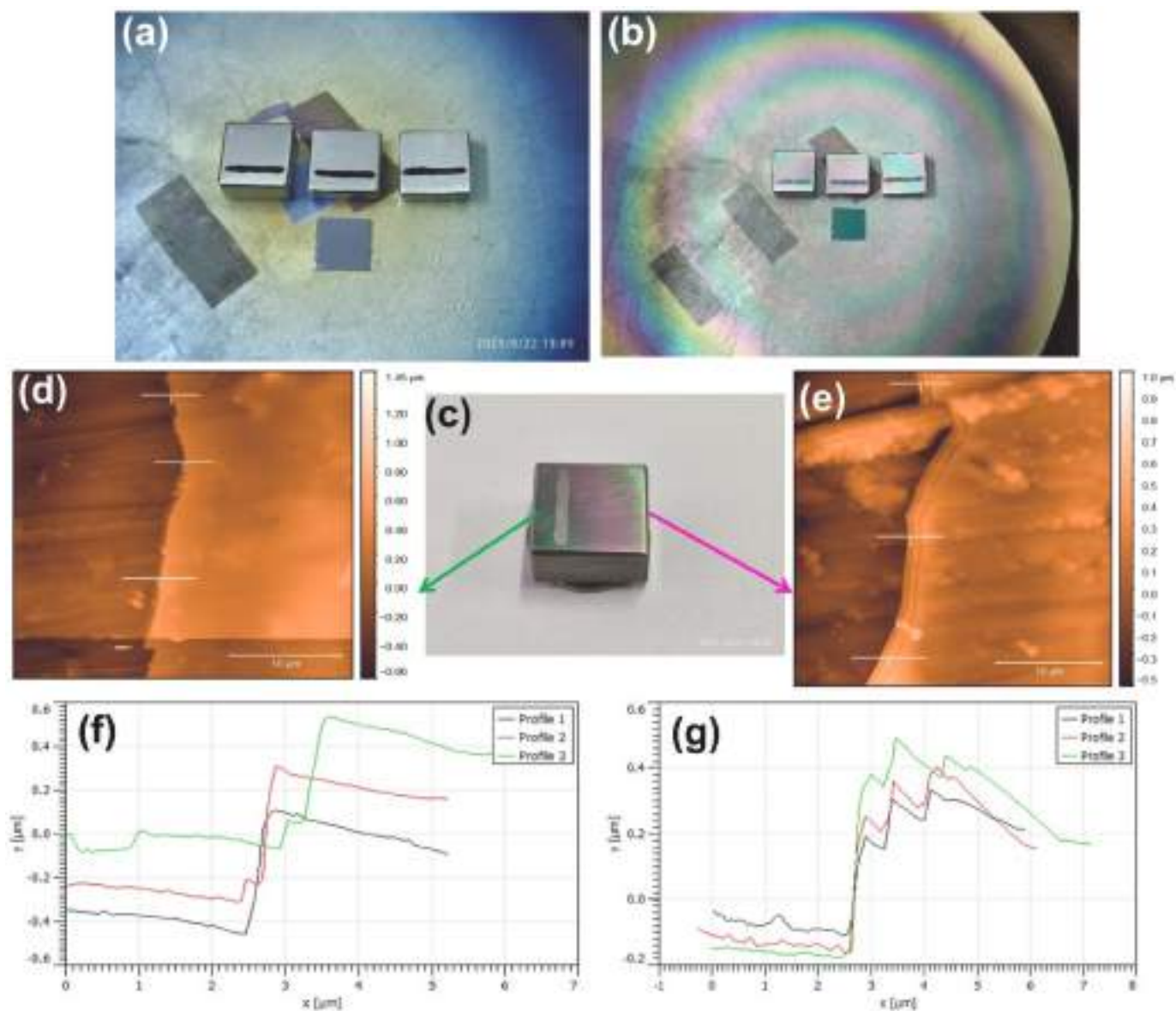


Fig. 4. Ti-6Al-4V substrate over sputtering sample holder, (a) before and (b) after the deposition process, (c) details of the sample used on the AFM investigations, (d, e) AFM mapping for pink and green regions, (f, g) represent the profile measurement in three places of the samples.

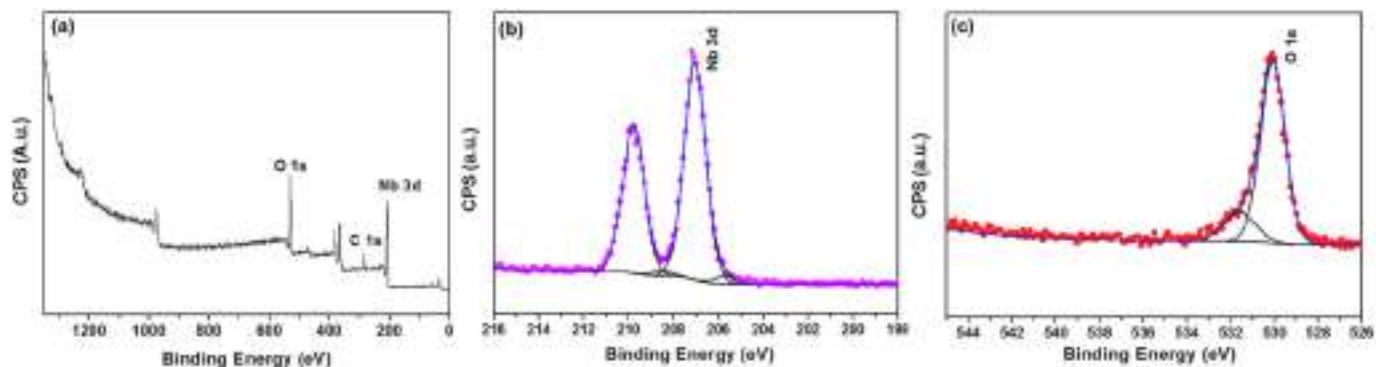


Fig. 5. XPS survey spectrum of the Ti-6Al-4V alloy surface containing polycrystalline niobium oxide thin film (a) chemical composition, (b) Nb 3d, and (c) O1s levels.

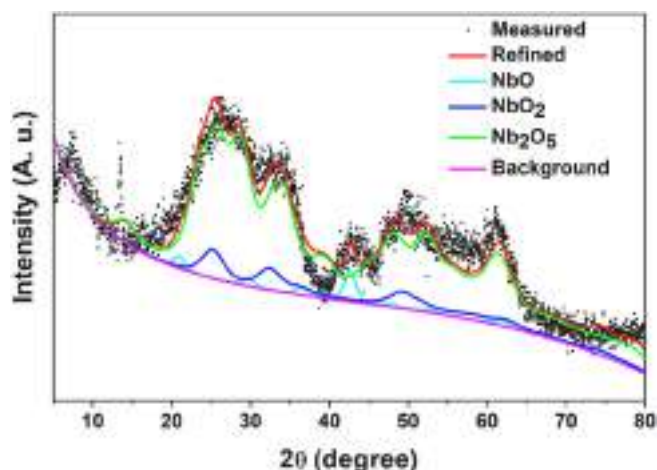


Fig. 6. Measured and Rietveld refined X-ray diffraction patterns for the Nb-oxide thin film composed of the Nb₂O₅, NbO₂, and NbO crystalline phases.

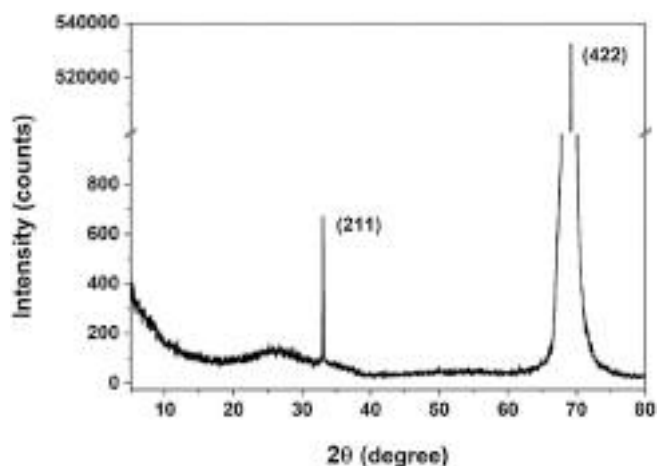


Fig. 7. X-ray diffractogram of Si substrate, with surface oriented in the [211] crystallographic direction.

Table 1

The relative concentration in weight of Nb₂O₅, NbO₂, and NbO thin films grown over the Si substrates and the χ^2 and R_{wp} refinement quality parameters.

Compound	(wt%)	χ^2	R_{wp}
Nb ₂ O ₅	89(1)	2.69	8.06
NbO ₂	9(1)		
NbO	2(1)		

Table 2

Average Nb_xO_y crystallite size estimated by Williamson-Hall, Size-Strain Plot (SSP), and Scherrer methods.

Oxides	Williamson-Hall	SSP	Scherrer
	Crystallite (Å)	Crystallite (Å)	Crystallite (Å)
Nb ₂ O ₅	26.32	27.03	26.35
NbO ₂	26.12	26.71	26.26
NbO	54.91	55.62	54.05

the pH adjustment during the experiments.

The Fig. 8 (b) and (c) show the CPDP curves. It is possible to observe, for all analysed samples, with the potential reduction toward negative potentials, that the current density in the reverse scan was lower than the current density in the forward scan (negative hysteresis). This behaviour evidence a protective effect of passive layer obtained, indicating that the analysed samples are susceptible to passive and restore the damaged oxide film, additionally, they are not susceptible to pitting corrosion. The corrosion potential (E_{corr}) in the reverse scan is more noble than the corrosion potential in the forward scan (see Table 3), probably due to the increase in the thickness of the passive film for Ti-6Al-4V and Nb samples [56].

This behaviour, for titanium and its alloys (Fig. 8 (b)) was found by several authors, in different electrolytes, and it has been associated to a modification of the film in its thickness, and its structural characteristics [57,58]. An increase in current is registered during the initial phases of the anodic scan, which can be attributed to the nucleation of Ti oxides on the surface of the alloy.

This is observed from 0.0 to 1500 mV_{SCE}, followed by the formation of a small peak at 1820 mV_{SCE}. This peak may be associated to the transpassive condition of the Ti-6Al-4V alloy, the nucleation of a new phase or evolution of oxygen [59]. Chaves-Diaz et al. [60] performed tests with Ti-6Al-4V in Hank's solution. The results obtained by these authors were like those found in this study. According to these authors, an increase in oxide thickness is expected as the potential becomes more positive. The results of Assis et al. [61] of Ti-6Al-4V in Hank's solution also confirmed that Ti oxide is passive in this electrolyte.

The CPDP results of the coated sample (Fig. 8 (b)) indicated a higher corrosion resistance compared to Ti-6Al-4V and Nb samples. The current density of the Ti-6Al-4V-coated sample, at the same potential, was lower than current density found in both uncoated samples. This behaviour can be observed in forward and reverse scan and corrosion potentials in both scanning directions (Table 3) were also higher than those found in the bare Ti-6Al-4V and Nb. The coating composition, determined by XPS and DRX can explain this behaviour once, a higher concentration of Nb₂O₅ was detected. Nb₂O₅ is an insulating oxide and with greater thermodynamic stability [62,63], which can contribute to the greater resistance to corrosion of the Ti-6Al-4V-coated sample. Moreover, in the reverse scan, there was a significant decrease in the current density.

The growth of the protective film on the Nb substrate (Fig. 8 (c)) generated the passive region between the potentials of −250 mV_{SCE} to 1000 mV_{SCE}. However, this behaviour was not observed for Ti-6Al-4V-coated sample (Fig. 8 (c)). The current density of coated sample increased continuously to values close to 2000 mV_{SCE}. Therefore, in the reverse scan the current densities develop by the system was lower compared to the current densities developed in the forward scan, as mentioned above.

Furthermore, Metikoš-Huković, Kwokal and Piljac [56] demonstrated that the oxide film grows from the increase in current density at potentials close to 2000 mV_{SCE}. Structural change of the oxide film and oxygen evolution may occur at values close to this potential. This can be explained by the additional crystallization process of amorphous oxide that was present in the coating before carrying out the CPDP tests. In addition, as the thickness of the oxide increases, the electronic conductivity decreases, leading to a decrease in currents in the reverse scan and an improvement in corrosion resistance. Fig. 9 shows the surface of the uncoated and coated Ti-6Al-4V alloy after the CPDP tests. No aspects of localised corrosion were observed in the coated sample after the CPDP tests. As observed by Bino et al. [43] by using Raman spectroscopy technique, specimens of Ti-6Al-4V alloy coated with niobium oxide thin film display one large band at 700 cm^{−1} and that was assigned to the symmetric and antisymmetric stretching mode of the Nb-O-Nb linkage.

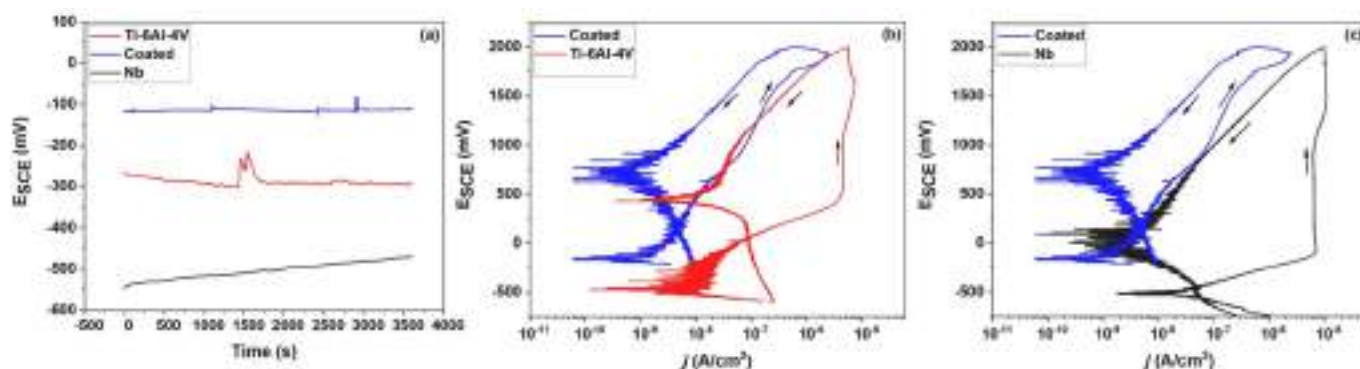


Fig. 8. Electrochemical tests in Hank's solution at 37 ± 1 °C and pH = 7.4. (a) Open circuit potential; (b) CPDP – coated-Ti-6Al-4V and Ti-6Al-4V; (c) CPDP – coated Ti-6Al-4V and Nb.

Table 3

E_{corr} obtained by Cyclic Potentiodynamic Polarization tests.

Sample	Scanning potential direction	E_{corr} (mV _{SCE})
Ti-6Al-4V alloy	Anodic direction (forward scan)	−494
	Cathodic direction (reverse scan)	+444
Niobium	Anodic direction (forward scan)	−500
	Cathodic direction (reverse scan)	0
Coated Ti-6Al-4V alloy	Anodic direction (forward scan)	−342
	Cathodic direction (reverse scan)	+401

As well known, the Nb_2O_5 thin film is transparent and the greenish region observed in Fig. 9 (b) is due to the light reflection phenomenon. Besides, the dark regions in both samples come from the surface preparation processes of the Ti-6Al-4V substrate (sanding process).

3.5. Contact angle characterization

In the present work, contact angle measurements were performed on the coated and uncoated specimens before and after the CPDP tests. As shown in Table 4, it was not observed an important difference between the samples studied herein, considering the Hank's solution. All contact angles are less than 90°, suggesting that the surface of the materials has a hydrophilic behaviour.

In fact, considering a previously work [43], the presence of niobium oxide thin film does not make the Ti-6Al-4V alloy surfaces hydrophobic, when distilled water, formamide, and α -bromonaphthalene were considered. In addition, the total free energy of interaction was related as $-60.046 \text{ mJ m}^{-2}$ for the uncoated material, and 2.851 mJ m^{-2} for the coated Ti-6Al-4V alloy.

In a recent study [64], it was demonstrated the influence of surface free energy of interaction on the biological responses of the Ti-6Al-4V alloy coated by a:C-H thin film. Here, it was verified the coated Ti-6Al-4V alloy display a less negative value of surface free energy ($-22.156 \text{ mJ m}^{-2}$ vs $-60.046 \text{ mJ m}^{-2}$ for uncoated sample), which demonstrated the reduction of the inflammatory process. In this sense, the results shown here only reinforce the good properties of the niobium oxide thin film, demonstrating that even after an aggressive corrosion test, the coated Ti-6Al-4V surfaces still present a hydrophilic behaviour that is extremely important for biological applications.

3.6. Scanning electrode vibrating technique (SVET)

Fig. 10 shows the SVET ionic current maps obtained during 15 h of sample immersion in 0.01 mol L^{-1} NaF solution at pH 2. We have tried to obtain the SVET ionic currents maps in 0.05 mol L^{-1} NaCl solution, but no activity has been detected because this solution is not aggressive to titanium. A solution containing fluoride ions at acidic pH can act as an aggressive agent to titanium. Regarding the uncoated titanium sample,

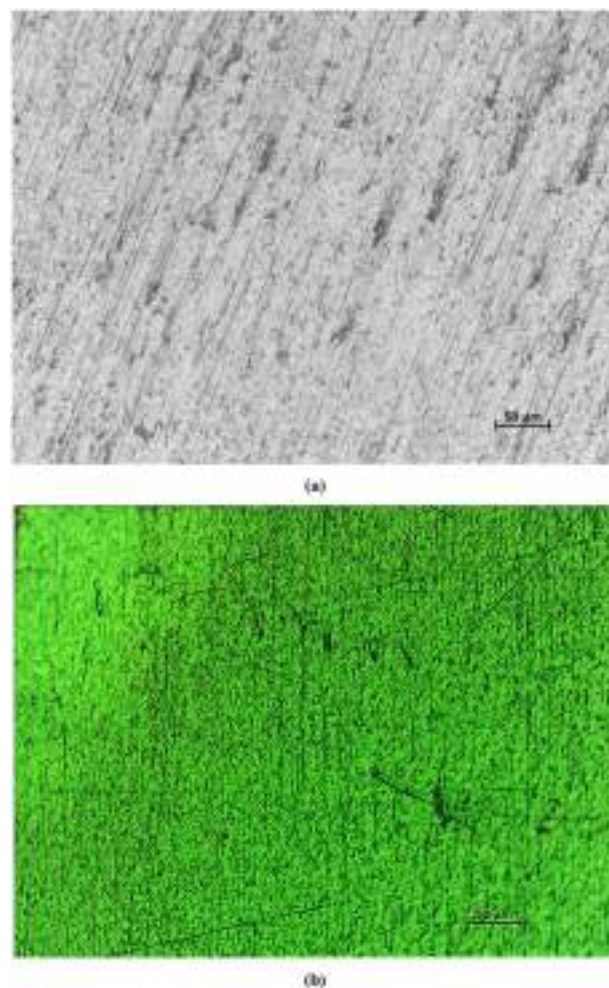


Fig. 9. (a) Ti-6Al-4V alloy after the CPDP tests and (b) coated Ti-6Al-4V alloy after the CPDP tests in Hank's solution at 37 ± 1 °C and pH = 7.4.

Table 4

Contact angle values of the Ti-6Al-4V and Ti-6Al-4V-coated sample in a presence of Hank's solution.

Sample		Contact angle	Standard deviation
Ti-6Al-4V	Before CPDP test	59.00°	±3.41
	After CPDP test	54.77°	±4.93
Ti-6Al-4V-coated	Before CPDP test	55.00°	±3.56
	After CPDP test	50.03°	±1.71

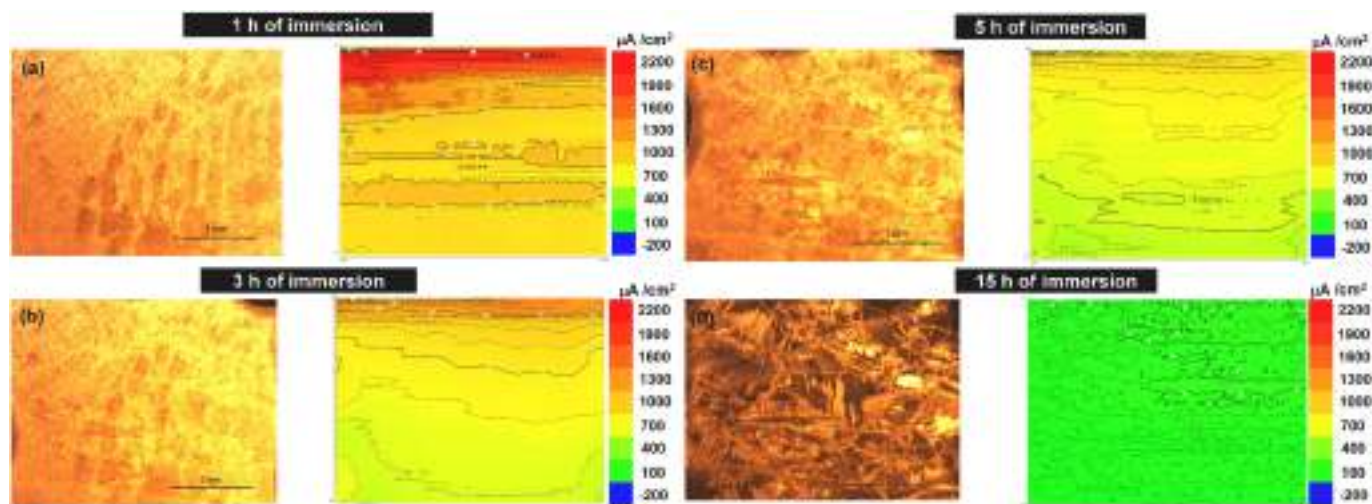


Fig. 10. Current density distributions of uncoated Ti-6Al-4V alloy after (a) 1 h, (b) 3 h, (c) 5 h, (d) 15 h and OM images at each immersion time in the presence of F^- aggressive ions.

it was possible to state that, at beginning (1 h of immersion) high anodic ionic current density values were obtained, characterized by red and yellow colours in the map, showing great activity sites suggesting that general corrosion process was taken place on sample surface. In the following hours (3 h and 5 h), the anodic ionic current density values keep high, but with a slightly decrease in its intensity. After 15 h of immersion, a huge quantity of corrosion products is seen on the sample surface and a decrease in ionic current density maps was observed, due to a physical barrier generated by corrosion products.

Concerning coated Ti-6Al-4V sample, it is possible to conclude that for all immersion times (from 1 h to 15 h) the ionic current density presented lower values, almost negligible, which means that the film was an effective protective barrier against corrosion process evolution over time. According to SVET results, coating layer formed on Ti-6Al-4V was homogeneous and no cracks or micro-cracks were found on the coating surface. In this way, probably, a percentage of residual metallic Nb did not become oxide during coating formation as it was observed in previous work [41] and the permeation of the electrolyte in the coating during the increase in potential on the CPDP test (Section 3.4)

contributed to a passive and active behaviour, generated by the formation of oxide from the retained metallic Nb in the coating. Figs. 10 and 11 present the SVET maps of the uncoated and coated Ti-6Al-4V alloys as well as the respective optical microscopy images at each time of immersion in the presence of F^- aggressive ions.

Finally, we demonstrated in the present work the benefits of the functionalized surface of the Ti-6Al-4V alloy containing niobium oxide thin films. The corrosion susceptibility of the coated and uncoated specimens was evaluated by using global and localised electrochemical techniques, demonstrating the coatings increased the corrosion resistance of the Ti-6Al-4V alloy, i.e., lower current density values were obtained for the coated specimens when compared to the bare material. The results for both electrochemical techniques are in close agreement. In addition, it was evidenced the effect of the crystallite sizes of the niobium-based films on the corrosion behaviour. This study is the starting point for the development of robust studies in biomedical area by using niobium oxide thin films as a protective barrier against corrosion process.

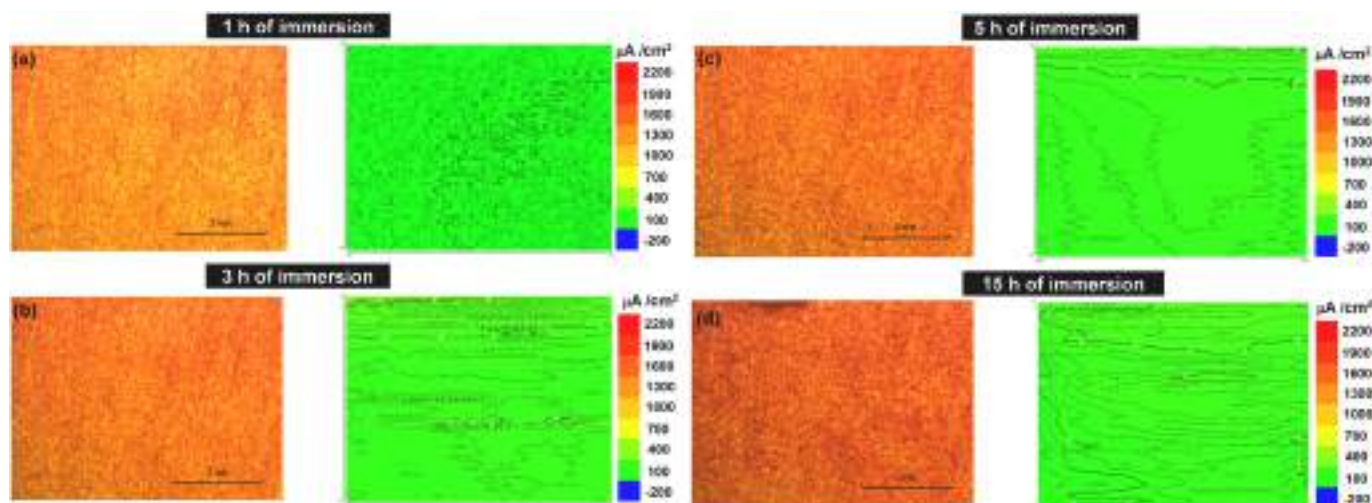


Fig. 11. Current density distributions of coated Ti-6Al-4V alloy after (a) 1 h, (b) 3 h, (c) 5 h, (d) 15 h and OM at each immersion time in the presence of F^- aggressive ions.

4. Conclusions

In the present investigation, we produced niobium oxide thin films on the Ti-6Al-4V alloy surface by using reactive sputtering technique in order to improve the corrosion protection of the biomaterial when exposed to an aggressive medium. The main conclusions resulting of this investigation are:

- § The deposition method was able to produce homogeneous thin films on the Ti alloy surfaces with thickness in the range of 300–450 nm;
- § The DRX and XPS results demonstrated the niobium oxide thin films produced on the Ti alloy surfaces are composed, mostly, by Nb₂O₅.
- § The coating obtained by reactive sputtering technique on Ti-6Al-4 shifted the corrosion potential (E_{corr}) to less negative values (−111 mV_{SCE} vs −290 mV_{SCE} for the bare material), suggesting better corrosion performance in Hank's solution;
- § CPDP tests revealed that the niobium oxide thin film increased the corrosion resistance of the Ti-6Al-4V alloy, presenting lower current density values when compared to bare material as well as pure Nb in Hank's solution;
- § SVET results revealed the coated material displayed low values of current density (~100 µA/cm² for 15 h of immersion time), whilst the bare material (in the range 700–2200 µA/cm² for 1 h of immersion time), demonstrating the powerful effect of the thin film produced herein as surface corrosion protection.

Data availability

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

Code availability

Not applicable.

CRediT authorship contribution statement

The authors' contributions are:

J.P.L do Nascimento – Resources, Formal analysis, Writing - Review & Editing
 M.O.A Ferreira – Resources, Formal analysis, Writing - Review & Editing
 R.V. Gelamo – Investigation, Formal analysis, Writing - Original Draft, Writing - Review & Editing
 T.T. Steffen – Resources, Formal analysis, Writing - Review & Editing
 B.P. da Silva – Resources, Formal analysis, Writing - Review & Editing
 I.V. Aoki – Investigation, Formal analysis, Writing - Original Draft, Writing - Review & Editing
 A. G. Santos Jr. – Resources, Formal analysis, Writing - Review & Editing
 V. V. de Castro – Resources, Formal analysis, Writing - Review & Editing
 C.F. Malfatti – Investigation, Formal analysis, Writing - Original Draft, Writing - Review & Editing
 J. Scarmínio – Resources, Formal analysis, Writing - Review & Editing
 J.A. Moreto – Conceptualization, Investigation, Formal analysis, Writing - Original Draft, Writing - Review & Editing

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] J.T. Philip, J. Mathew, B. Kuriachen, Tribology of Ti6Al4V: a review, *Friction* 7 (2019) 497–536, <https://doi.org/10.1007/s40544-019-0338-7>.
- [2] F. Gao, W. Li, B. Meng, M. Wan, X. Zhang, X. Han, Rheological law and constitutive model for superplastic deformation of ti-6Al-4V, *J. Alloys Compd.* 701 (2017) 177–185, <https://doi.org/10.1016/j.jallcom.2017.01.096>.
- [3] J.N. Oliver, Y. Su, X. Lu, P.H. Kuo, J. Du, D. Zhu, Bioactive glass coatings on metallic implants for biomedical applications, *Bioact. Mater.* 4 (2019) 261–270, <https://doi.org/10.1016/j.bioactmat.2019.09.002>.
- [4] S.H. Kim, H. Kim, N.J. Kim, Brittle intermetallic compound makes ultrastrong low-density steel with large ductility, *Nature* 518 (2015) 77–79, <https://doi.org/10.1038/nature14144>.
- [5] L.Y. Chen, J.Q. Xu, H. Choi, M. Pozuelo, X. Ma, S. Bhowmick, J.M. Yang, S. Mathaudhu, X.C. Li, Processing and properties of magnesium containing a dense uniform dispersion of nanoparticles, *Nature* 528 (2015) 539–543, <https://doi.org/10.1038/nature16445>.
- [6] X. Yang, C.R. Hutchinson, Corrosion-wear of β-Ti alloy TMZF (Ti-12Mo-6Zr-2Fe) in simulated body fluid, *Acta Biomater.* 42 (2016) 429–439, <https://doi.org/10.1016/j.actbio.2016.07.008>.
- [7] P.J. Arrazola, A. Garay, M. Armendia, S. Marya, in: *Machinability of titanium alloys (Ti6Al4V and Ti555.3)* 9, 2008, pp. 2223–2230, <https://doi.org/10.1016/j.jmatprotec.2008.06.020>.
- [8] H. Dong, T. Bell, Designer surfaces for titanium components, *Ind. Lubr. Tribol.* 50 (1998) 282–289, <https://doi.org/10.1108/00368799810245891>.
- [9] K. Aniolek, M. Kupka, Surface characterization of thermally oxidized ti-6Al-7Nb alloy, *Mater. Chem. Phys.* 171 (2016) 374–378, <https://doi.org/10.1016/j.matchemphys.2016.01.031>.
- [10] A. Robin, J.P. Meirelis, Influence of fluoride concentration and pH on corrosion behavior of ti-6Al-4V and ti-23Ta alloys in artificial saliva, *Mater. Corros.* 58 (2007) 173–180, <https://doi.org/10.1002/maco.200604004>.
- [11] J.C.M. Souza, S.L. Barbosa, E.A. Ariza, M. Henriques, W. Teughels, P. Ponthiaux, J. P. Celis, L.A. Rocha, How do titanium and Ti6Al4V corrode in fluoridated medium as found in the oral cavity? An in vitro study 47 (2015) 384–393, <https://doi.org/10.1016/j.jmsec.2014.11.055>.
- [12] O.S. Adesina, B.A. Obadele, G.A. Farotade, D.A. Isadore, A.A. Adediran, P. P. Ikubanni, Influence of phase composition and microstructure on corrosion behavior of laser based Ti-Co-Ni ternary coatings on Ti-6Al-4V alloy, *J. Alloys Compd.* 827 (2020), 154245, <https://doi.org/10.1016/j.jallcom.2020.154245>.
- [13] S. Kaur, G. Ghadirinejad, R.H. Oskoue, An overview on the tribological performance of titanium alloys with surface modifications for biomedical applications, *Lubricants* 7 (2019), <https://doi.org/10.3390/lubricants7080065>.
- [14] J. Quinn, R. Mcfadden, C. Chan, L. Carson, iScience II titanium for orthopedic applications: an overview of surface modification to improve biocompatibility and prevent bacterial biofilm formation, *iScience* 23 (2020), 101745, <https://doi.org/10.1016/j.isci.2020.101745>.
- [15] Q. Chen, G.A. Thouas, Metallic implant biomaterials 87 (2015) 1–57, <https://doi.org/10.1016/j.msar.2014.10.001>.
- [16] V. Bonu, M. Jeevitha, V. Praveen Kumar, G. Srinivas, H.C. Barshilia Siju, Solid particle erosion and corrosion resistance performance of nanolayered multilayered Ti/TiN and TiAl/TiAlN coatings deposited on Ti6Al4V substrates, *Surf. Coat. Technol.* 387 (2020), 125531, <https://doi.org/10.1016/j.surfcoat.2020.125531>.
- [17] T.M. Manhabosco, S.M. Tamborim, C.B. dos Santos, I.L. Müller, Tribological, electrochemical and tribo-electrochemical characterization of bare and nitrided Ti6Al4V in simulated body fluid solution, *Corros. Sci.* 53 (2011) 1786–1793, <https://doi.org/10.1016/j.corsci.2011.01.057>.
- [18] P. Patel, N.I. Jamnapara, A. Zala, S.D. Kahar, Investigation of hot-dip aluminized Ti6Al4V alloy processed by different thermal treatments in an oxidizing atmosphere, *Surf. Coat. Technol.* 385 (2020), 125323, <https://doi.org/10.1016/j.surfcoat.2019.125323>.
- [19] K. Cheng, N. Pagan, D. Bijukumar, M.T. Mathew, M. McNallan, Carburized titanium as a solid lubricant on hip implants: corrosion, tribocorrosion and biocompatibility aspects, *Thin Solid Films* 665 (2018) 148–158, <https://doi.org/10.1016/j.tsf.2018.08.048>.

- [20] S.K. Saha, Y.J. Park, S.O. Cho, Fabrication of highly ordered nanoporous oxide layer on Ti6Al4V surfaces for improved corrosion resistance property, *J. Mol. Struct.* 1223 (2021), 129244, <https://doi.org/10.1016/j.molstruc.2020.129244>.
- [21] A.P.I. Popoola, L. Phume, S. Pityana, V.S. Aigbodion, In-situ formation of laser Ti6Al4V-TiB composite coatings on Ti6Al4V alloy for biomedical application, *Surf. Coat. Technol.* 285 (2016) 161–170, <https://doi.org/10.1016/j.surfcoat.2015.10.079>.
- [22] A.M. Murmu, S. Kumar, S.K. Parida, A.K. Das, Evaluation of hardness and wear behavior of laser cladding zirconia-alumina-titania ceramic top coating on pure Ti6Al4V, *Mater. Today Proc.* 26 (2019) 1103–1107, <https://doi.org/10.1016/j.matpr.2020.02.221>.
- [23] F.R. García-Galván, M.A. Mezour, G.J. Hickman, I.E. Soliman, A. Jiménez-Morales, V. Barranco, J.C. Galván, C.C. Perry, A.A. el hadad, organic-inorganic hybrid coatings containing phosphorus precursors prepared by sol-gel on ti6al4v alloy: electrochemical and in-vitro biocompatibility evaluation 148 (2020) 105834, <https://doi.org/10.1016/j.porgcoat.2020.105834>.
- [24] W. Ge, Z. Chang, A. Siddique, B. Shi, C. Liu, Large-area fabrication of TiN thin films with photothermal effect via PECVD, *Ceram. Int.* 46 (2020) 7355–7361, <https://doi.org/10.1016/j.ceramint.2019.11.231>.
- [25] E. Matykina, R. Arrabal, B. Mingo, M. Mohedano, A. Pardo, M.C. Merino, In vitro corrosion performance of PEO coated ti and Ti6Al4V used for dental and orthopaedic implants, *Surf. Coat. Technol.* 307 (2016) 1255–1264, <https://doi.org/10.1016/j.surfcoat.2016.08.018>.
- [26] W.A. Eurídice, N.B. Leite, R.V. Gelamo, P.A. de Almeida Buranello, M.V. da Silva, C.J.F. de Oliveira, R.F.V. Lopez, C.N. Lemos, A. de Siervo, J.A. Moreto, a-C, H films produced by PECVD technique onto substrate of Ti6Al4V alloy: chemical and biological responses, *Appl. Surf. Sci.* 503 (2020), <https://doi.org/10.1016/j.apsusc.2019.144084>.
- [27] M. Kazemi, S. Ahangarani, M. Esmailian, A. Shanaghi, Investigation on the corrosion behavior and biocompatibility of ti-6Al-4V implant coated with HA/TiN dual layer for medical applications, *Surf. Coat. Technol.* 397 (2020), 126044, <https://doi.org/10.1016/j.surfcoat.2020.126044>.
- [28] H.H. Huang, D.K. Shiau, C.S. Chen, J.H. Chang, S. Wang, H. Pan, M.F. Wu, Nitrogen plasma immersion ion implantation treatment to enhance corrosion resistance, bone cell growth, and antibacterial adhesion of ti-6Al-4V alloy in dental applications, *Surf. Coat. Technol.* 365 (2019) 179–188, <https://doi.org/10.1016/j.surfcoat.2018.06.023>.
- [29] A.M. Oje, A.A. Ogwu, A.I. Oje, N. Tsendzughul, S. Ur Rahman, A comparative study of the corrosion and ion release behaviour of chromium oxide coatings exposed to saline, Ringer's and Hank's physiological solutions, *Corros. Sci.* 167 (2020), 108533, <https://doi.org/10.1016/j.corsci.2020.108533>.
- [30] A. Oluyinka, A. Esther, O. Philip, Examination of electrochemical corrosion properties of titanium carbide thin film grown by RF magnetron sputtering, *Mater. Today Proc.* (2020), <https://doi.org/10.1016/j.matpr.2020.11.170>.
- [31] B. Rahmati, A.A.D. Sarhan, W.J. Basirun, W.A.B.W. Abas, Ceramic tantalum oxide thin film coating to enhance the corrosion and wear characteristics of ti-6Al-4V alloy, *J. Alloys Compd.* 676 (2016) 369–376, <https://doi.org/10.1016/j.jallcom.2016.03.188>.
- [32] S. Datta, M. Das, V.K. Balla, S. Bodhak, V.K. Murugesan, Mechanical, wear, corrosion and biological properties of arc deposited titanium nitride coatings, *Surf. Coat. Technol.* 344 (2018) 214–222, <https://doi.org/10.1016/j.surfcoat.2018.03.019>.
- [33] A.M. Al-Baradi, M.M. El-Nahass, A.M. Hassanien, A.A. Atta, M.S. Alqahtani, A. O. Aldawsari, Influence of RF sputtering power on structural and optical properties of Nb2O5 thin films, *Optik* 168 (2018) 853–863, <https://doi.org/10.1016/j.ijleo.2018.05.020>.
- [34] M. Ohring, Plasma and ion beam processing of thin films, in: *Materials Science of Thin Films*, 2nd ed., Elsevier, New Jersey, 2002, pp. 203–275, <https://doi.org/10.1016/b978-012524975-1/50008-2>.
- [35] L.X. Shao, K.H. Chang, H.L. Hwang, Zinc sulfide thin films deposited by RF reactive sputtering for photovoltaic applications, *Appl. Surf. Sci.* 212–213 (2003) 305–310, [https://doi.org/10.1016/S0169-4332\(03\)00085-0](https://doi.org/10.1016/S0169-4332(03)00085-0).
- [36] A. Iqbal, F. Mohd-Yasin, Reactive sputtering of aluminum nitride (002) thin films for piezoelectric applications: a review, *Sensors* 18 (2018) 1797, <https://doi.org/10.3390/S18061797>.
- [37] J.E. Stevens, A.J. Lohn, S.A. Decker, B.L. Doyle, P.R. Mickel, M.J. Marinella, Reactive sputtering of substoichiometric Ta2Ox for resistive memory applications, *J. Vac. Sci. Technol. A* 32 (2013), 021501, <https://doi.org/10.1116/1.4828701>.
- [38] Y. Yin, Y. Pan, L.X. Hang, D.R. McKenzie, M.M.M. Bilek, Direct current reactive sputtering Cr-Cr2O3 cermet solar selective surfaces for solar hot water applications, *Thin Solid Films* 517 (2009) 1601–1606, <https://doi.org/10.1016/j.tsf.2008.09.082>.
- [39] S. Berg, T. Nyberg, Fundamental understanding and modeling of reactive sputtering processes, *Thin Solid Films* 476 (2005) 215–230, <https://doi.org/10.1016/j.tsf.2004.10.051>.
- [40] W.D. Sproul, D.J. Christie, D.C. Carter, Control of reactive sputtering processes, *Thin Solid Films* 491 (2005) 1–17, <https://doi.org/10.1016/J.TSF.2005.05.022>.
- [41] J.A. Moreto, R.V. Gelamo, J.P.L. Nascimento, M. Taryba, J.C.S. Fernandes, Improving the corrosion protection of 2524-T3-Al alloy through reactive sputtering Nb2O5 coatings, *Appl. Surf. Sci.* 556 (2021), 149750, <https://doi.org/10.1016/j.apsusc.2021.149750>.
- [42] J.A. Moreto, R.V. Gelamo, M.V. Silva, T.T. Steffen, C.J.F. Oliveira, M.R. Pinto, P.A. de A. Buranello, New insights of Nb2O5 -based coatings on the 316L SS surfaces: enhanced biological responses, *J. Mater. Sci. Mater. Med.* (2021) 2–7, <https://doi.org/10.1007/s10856-021-06498-7>.
- [43] M.C.A. Bino, W.A. Eurídice, R.V. Gelamo, N.B. Leite, M.V. da Silva, A. de Siervo, M. R. Pinto, P.A. de Almeida Buranello, J.A. Moreto, Structural and morphological characterization of Ti6Al4V alloy surface functionalization based on Nb2O5 thin film for biomedical applications, *Appl. Surf. Sci.* 557 (2021), 149739, <https://doi.org/10.1016/j.apsusc.2021.149739>.
- [44] L.G.B. Machuno, A.B. Lima, R.R. Buso, R.M.F. Abdanur, E.C. Rangel, R.V. Gelamo, Desenvolvimento e avaliação de uma fonte DC de Alta tensão Para utilização em sistema de deposição de filmes finos por pulverização catódica, *Matéria (Rio de Janeiro)* 21 (2016) 492–500, <https://doi.org/10.1590/S1517-707620160002.0046>.
- [45] ASTM International, in: F2129 19a Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements to Determine the Corrosion Susceptibility of, i, 2009, pp. 1–8 (accessed July 21, 2021), <https://webstore.ansi.org/Standards/astm/astmF212994>.
- [46] P.B. Santos, E.K. Baldin, D.A. Krieger, V. Velho De Castro, C. Aguzzoli, J. C. Fonseca, M. Rodrigues, M.A. Lopes, C.F. Malfatti, Wear performance and osteogenic differentiation behavior of plasma electrolytic oxidation coatings on ti-6Al-4V alloys: potential application for bone tissue repairs, *Surf. Coat. Technol.* 417 (2021), 127179, <https://doi.org/10.1016/j.surfcoat.2021.127179>.
- [47] V. Amigó-Borrás, J. Lario-Femenía, A. Amigó-Mata, Á. Vicente-Escuder, Titanium, titanium alloys and composites, in: *Reference Module in Materials Science and Materials Engineering*, Elsevier, 2020, <https://doi.org/10.1016/b978-0-12-819726-4.00044-2>.
- [48] P. Amaravathy, S. Sowndarya, S. Sathyanarayanan, N. Rajendran, Novel sol gel coating of Nb2O5 on magnesium alloy for biomedical applications, *Surf. Coat. Technol.* 244 (2014) 131–141, <https://doi.org/10.1016/j.surfcoat.2014.01.050>.
- [49] V.I. Chukwuike, K. Rajalakshmi, R.C. Barik, Surface and electrochemical corrosion analysis of niobium oxide film formed in various wet media, *Appl. Surf. Sci. Adv.* 4 (2021), 100079, <https://doi.org/10.1016/j.apsadv.2021.100079>.
- [50] M. Aufray, S. Menuel, Y. Fort, J. Eschbach, D. Rouxel, B. Vincent, New synthesis of nanosized niobium oxides and lithium niobate particles and their characterization by XPS analysis, *J. Nanosci. Nanotechnol.* 9 (2009) 4780–4785, <https://doi.org/10.1166/jnn.2009.1087>.
- [51] D. Bekermann, D. Barreca, A. Gasparotto, H.W. Becker, R.A. Fischer, A. Devi, Investigation of niobium nitride and oxy-nitride films grown by MOCVD, *Surf. Coat. Technol.* 204 (2009) 404–409, <https://doi.org/10.1016/j.surfcoat.2009.07.029>.
- [52] Y.T. Prabhu, K.V. Rao, V.S.S. Kumar, B.S. Kumari, X-ray analysis by Williamson-hall and size-strain plot methods of ZnO nanoparticles with fuel variation, *World J. Nano Sci. Eng.* 4 (2014) 21–28, <https://doi.org/10.4236/wjnse.2014.41004>.
- [53] A. Aliyu, C. Srivastava, Correlation between growth texture, crystallite size, lattice strain and corrosion behavior of copper-carbon nanotube composite coatings, *Surf. Coat. Technol.* 405 (2021), 126596, <https://doi.org/10.1016/j.surfcoat.2020.126596>.
- [54] K.D. Ralston, N. Birbilis, Effect of grain size on corrosion: a review, *Corrosion* 66 (2010), <https://doi.org/10.5006/1.3462912> (075005-075005-13).
- [55] K. Shi, Y. Zhang, J. Zhang, Z. Xie, Electrochemical properties of niobium coating for biomedical application, *Coatings* 9 (2019) 546, <https://doi.org/10.3390/coatings9090546>.
- [56] M. Metiko, A. Kwokal, J. Piljac, S. Hukovi, The influence of niobium and vanadium on passivity of titanium-based implants in physiological solution, *Biomaterials* 24 (2003) 3765–3775, [https://doi.org/10.1016/S0142-9612\(03\)00252-7](https://doi.org/10.1016/S0142-9612(03)00252-7).
- [57] L.C. Noronha, V.V. de Castro, G.A. Ludwig, R.M. Schroeder, C.F. Malfatti, Ti-Cp: Electrochemical Behaviour Under Slurry Erosion, *Wear* 7 (2021.), <https://doi.org/10.1007/s40735-020-00442-y>.
- [58] C.E.B. Marino, E.M. de Oliveira, R.C. Rocha-Filho, S.R. Biaggio, On the stability of thin-anodic-oxide films of titanium in acid phosphoric media, *Corros. Sci.* 43 (2001) 1465–1476, [https://doi.org/10.1016/S0010-938X\(00\)00162-1](https://doi.org/10.1016/S0010-938X(00)00162-1).
- [59] P. Bocchetta, L.-Y. Chen, J.D.C. Tardelli, A.C. dos Reis, F. Almeraya-Calderón, P. Leo, Passive layers and corrosion resistance of biomedical Ti-6Al-4V and β -Ti alloys, *Coatings* 11 (2021) 487, <https://doi.org/10.3390/coatings11050487>.
- [60] M.P. Chávez-Díaz, R.M. Luna-Sánchez, J. Vazquez-Arenas, L. Lartundo-Rojas, J. M. Hallen, R. Cabrera-Sierra, XPS and EIS studies to account for the passive behavior of the alloy Ti-6Al-4V in Hank's solution, *J. Solid State Electrochem.* 23 (11) (2019) 3187–3196, <https://doi.org/10.1007/S10008-019-04368-5>.
- [61] S.L. Assis, S. Wolynec, I. Costa, Corrosion characterization of titanium alloys by electrochemical techniques, *Electrochim. Acta* 51 (2006) 1815–1819, <https://doi.org/10.1016/j.electacta.2005.02.121>.
- [62] S.-H. Lee, J.-D. Kwon, J.-H. Ahn, J.-S. Park, Compositional and electrical modulation of niobium oxide thin films deposited by plasma-enhanced atomic layer deposition, 2017, <https://doi.org/10.1016/j.ceramint.2017.02.089>.
- [63] N. Usha, R. Sivakumar, C. Sanjeeviraja, M. Arivanandhan, Niobium pentoxide (Nb2O5) thin films: rf power and substrate temperature induced changes in physical properties, *Optik* 126 (2015) 1945–1950, <https://doi.org/10.1016/j.ijleo.2015.05.036>.
- [64] J.P.L. do Nascimento, L.R. Freitas, C.N. Lemos, R.V. Gelamo, J.A. Moreto, A new view of a:C-H-coated Ti-6Al-4V alloy to be used as orthopedic implants: influence of surface free-energy of interaction on the biological responses, *Orbital: Electron. J. Chem.* 13 (3) (2021) 264–268, <https://doi.org/10.17807/orbital.v13i3.1622>.



Rapid Communication

New insights of Nb₂O₅-based coatings on the 316L SS surfaces: enhanced biological responses

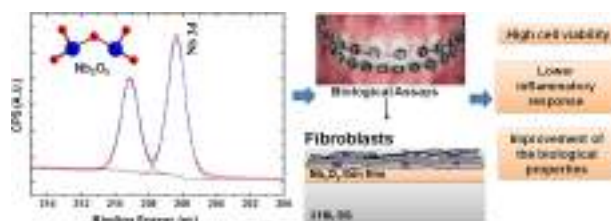
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Abstract

This communication aims to propose new insights of Nb₂O₅-based coatings on the 316L SS surface with great prospects to be used in the dentistry field as brackets. The Nb₂O₅ thin film was incorporated into the 316L SS by using PVD method. For this purpose, the studied system was characterized structurally and morphologically by using AFM, FTIR-IRRAS, Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). Biological assays were performed using human gingival fibroblast cell-line HGF-1. In agreement with FTIR and Raman results, the XPS technique indicates that Nb is present in an oxidation state assigned to Nb₂O₅. Furthermore, the coatings produced by PVD technique are less toxic and induces less inflammation in gingival cells (cell-line HGF-1), suggesting the strategy of use Nb₂O₅ thin film to cover the 316L SS promoted since its protection of the physiological environment to its biocompatibility improvement.

Graphical Abstract



Highlights

- PVD method was shown advantageous for producing Nb₂O₅ thin film on the 316L SS.
- 316L SS coated with Nb₂O₅ film to be used in biomedical devices.
- Nb₂O₅ coating improved biological response of the 316L SS.
- Nb₂O₅ thin film are less toxic and induces less inflammation in gingival cells.

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1 Introduction

The development of new biomaterials has been growing in recent decades and among the requirements for its use one can cite, good resistance to the wear process, good corrosion resistance in media containing aggressive ions and biocompatibility [1]. Many methods of surface treatments can be used to obtain biomaterials with a wide variety of applications, such as anodizing [2], chemical conversion coating [3], electrodeposition [4], plasma enhanced chemical vapor deposition [5] and physical vapor deposition (PVD) [6]. Although conventional materials such as 316L stainless steels (SS), titanium alloys containing hydroxyapatite doped with rare earth elements [7], titanium alloys coated with diamond-like carbon thin films [8], Co–Cr alloys and magnesium alloys have been used for a long time as biomaterial, there are still several limitations to their use [9]. Improving the biological responses of 316L SS is a long-standing and active area of biomedical research [10]. However, most studies on corrosion processes in aggressive media found in the literature do not associate them with biological effects such as cytotoxicity and biocompatibility. The biomaterials to be used in clinical practice need to fulfill many requirements once it needs to ensure the safety and effectiveness to the patient [10]. Among these requirements, we may mention the absence of cytotoxic activity, irritation and induction of the immune and inflammatory response by the biomaterial. Here, we provide new insights of Nb₂O₅-based coatings on the 316L SS surface, validating its applicability potential in dentistry field to be used as brackets.

2 Material and methods

Specimens of 316L SS were ground with SiC abrasive paper from 600# to 4000#. Prior the deposition, the samples were immersed in neutral detergent during 1 h, rinsed with distilled water, dried and cleaned with 70% (v/v) alcohol. The Nb₂O₅ thin films were deposited using argon (99.99%) and oxygen (99.99%) at 5.0 and 0.5 mTorr in a DC-magnetron sputtering [11]. Over a Niobium (99.99%) 2-in. diameter target was applied 440 V and 140 mA resulting film of 300 nm thick.

The topography of the films was investigated by using AFM (Shimadzu SPM 9700 Microscope equipment) in tapping mode. The structural characterization of the 316L SS containing Nb₂O₅ coatings was performed by FTIR technique. The spectra were collected 64 scan s⁻¹ using an Agilent Cary 640 spectrometer in the range of 4000–500 cm⁻¹. An IRRAS (Infrared reflection-absorption spectroscopy) apparatus from Pike Veemax incidence at 70° was used. Raman spectroscopy was performed with a

Horiba LabRAM HR Evolution instrument equipped with a confocal microscope. Spectra were collected using a 532 nm Ar⁺ laser source, 50 mW power, 100× objective in the range 80–4000 cm⁻¹. The thin film was also characterized by X-ray Photoelectron Spectroscopy (XPS), using a K-Alpha Thermo Scientific spectrometer (X-ray Al-K α , $h\nu = 1486.6$ eV), at a pressure below 10⁻⁷ mBar. Pass energy applied to obtain the spectra was 200 eV for survey and 50 eV for high-resolution scans. The spectra deconvolution was performed using the Voigtian function, with Gaussian (70%) and Lorentzian (30%) combinations.

Biological assays were performed using human gingival fibroblast cell-line HGF-1. Gingival fibroblasts HGF-1 (CRL-2014, ATCC) were cultured in T-25 culture vessels (Nunc), temperature of 37 °C, in an atmosphere of 5% CO₂, with Dulbecco's Modified Eagle's Medium (DMEM) enriched with 10% FBS (Sigma-Aldrich, USA). DMEM medium was renewal 2 to 3 times per week until HGF-1 cells reach an 80–90% confluence. After, cells were removed using 0.25% trypsin, 0.53 mM EDTA solution and seeded at 1 × 10⁵ cells/mL on the uncoated and coated 316L SS with Nb₂O₅ thin film. After 24 h of incubation at 37 °C, 5% CO₂, cells were mechanically removed and evaluated for viability by flow cytometry using Annexin-V plus 7-ADD staining, performed as manufacturer's instructions (BD Biosciences, USA). Cell supernatants were used for quantification of TNF- α , IL-10, IL-17, IL-6, IFN- γ , and IL-4 cytokines by immunoenzymatic assay—ELISA, performed as manufacturer's instructions (BD Biosciences, USA).

3 Results and discussion

The topography of 316L SS coated and uncoated obtained by AFM are displayed at Fig. 1 and presents 2D and 3D images of the specimens studied here. The second-phase particles from the steel making process, which was marked with red circles are presented in Fig. 1A. The nucleation process in the vapor phase promoted the formation of a thin film that accompanies the risks arising from the sanding process (see Fig. 1B). The root means square surface roughness values obtained were 2.94 and 2.40 nm for the coated and uncoated 316L SS, respectively.

FTIR spectra of the Nb₂O₅ thin film in range of 1400–600 cm⁻¹ is presented in Fig. 2A. The spectrum resulted in an intense band between 1100 and 700 cm⁻¹. The deconvolution of this large band resulted in two other bands centered at ~940 and ~844 cm⁻¹ attributed to Nb=O and Nb–O–Nb stretching [12, 13], respectively. The inset in Fig. 2A displays the whole IR spectra of Nb₂O₅ film herein studied indicating no additional bands related to the niobium oxide film. The major Raman band appears

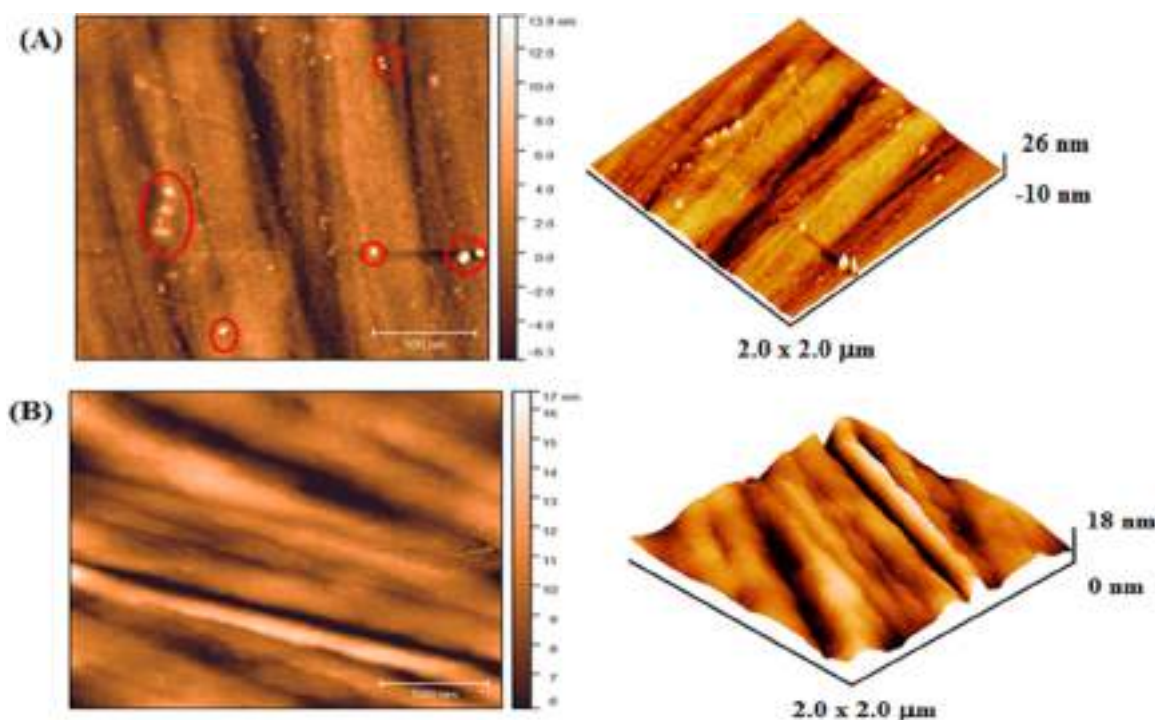


Fig. 1 2D and 3D images of **A** 316L SS substrate, scale $2.0 \times 2.0 \mu\text{m}$ and **B** 316L SS containing the Nb_2O_5 thin film, scale $3.0 \times 3.0 \mu\text{m}$

at $\sim 655 \text{ cm}^{-1}$ as well as another band presenting a lower intensity around 206 cm^{-1} attributed to Nb_2O_5 [14] (see Fig. 2B).

Survey XPS indicates the film chemical composition as 53 at.% of oxygen, 27 at.% of carbon and 20 at.% of niobium. The chemical states of niobium and oxygen were determined by high-resolution scans deconvolution, showed in Fig. 2C, D. Nb 3d deconvolution shows doublets for Nb $3d_{5/2}$ and Nb $3d_{3/2}$, at 206.4 eV and 209.1 eV, respectively. In agreement with FTIR and Raman results, it indicates that Nb is present in an oxidation state assigned to Nb_2O_5 [15, 16]. Also, O 1s deconvolution presents a major contribution (83 at.%) of the peak at 529.5 eV, assigned to Nb_2O_5 [16]. The other peak, at 531.1 eV, is related to $-\text{OH}$ groups and/or oxidized carbon species [17]. These results confirm the thin film formation preferentially composed by niobium in Nb_2O_5 oxidation state.

The biological results presented that the 316L SS containing the Nb_2O_5 thin film induces significantly less cell death, as demonstrated by total apoptosis (Annexin-V + cells, $p = 0.02$), early apoptosis (Annexin-V + 7-ADD—cells, $p = 0.02$) and late apoptosis (Annexin-V + 7-ADD + cells, $p = 0.04$) evaluation. Figure 3 displays the HGF-1 cell-line cultured on the coated and uncoated 316L SS substrates. As can be seen, the total (A), early (B) and late apoptosis (C) are demonstrated. The results showed the Nb_2O_5 thin film improved the biocompatibility of the 316L SS substrate.

Probably, the increase of the biocompatibility may be related to the surface properties, particularly the surface energy and surface wettability as related by Hao and Lawrence [18]. Niobium coatings are biocompatible to fibroblast cells that assumed the elongated fibroblastic appearance typical of osteoblast-like cells. The results obtained in the present work are in accordance to Eisenbarth et al. [19], which attributes the increase viability, proliferation, mitochondrial and osteogenic activity of titanium implants to the niobium-based films on the substrate surfaces.

In addition to improving cell compatibility by reducing cell toxicity of tested surfaces, it is desirable that bio-materials do not induce harmful inflammation after cell contact. In this context, the 316L SS containing the Nb_2O_5 thin film induces significantly less TNF- α production, a huge pro-inflammatory cytokine involved in a diversity of inflammatory and autoimmune diseases ($p = 0.02$), and similar levels of IL-10, a classical anti-inflammatory cytokine (see Fig. 4A, B). Besides, the 316L SS containing Nb_2O_5 film induced less production of IL-17 ($p = 0.001$), other cytokine deeply involved in inducing and mediating pro-inflammatory responses (Fig. 4C). We also observed a similar production of IL-6, besides a trend to lower levels in 316L SS coated with Nb_2O_5 ($p = 0.06$). Like TNF- α and IL-17, IFN- γ , and IL-4 are important inflammatory cytokines, however, these molecules were not changed in the culture with all the films tested (Fig. 4D–F).

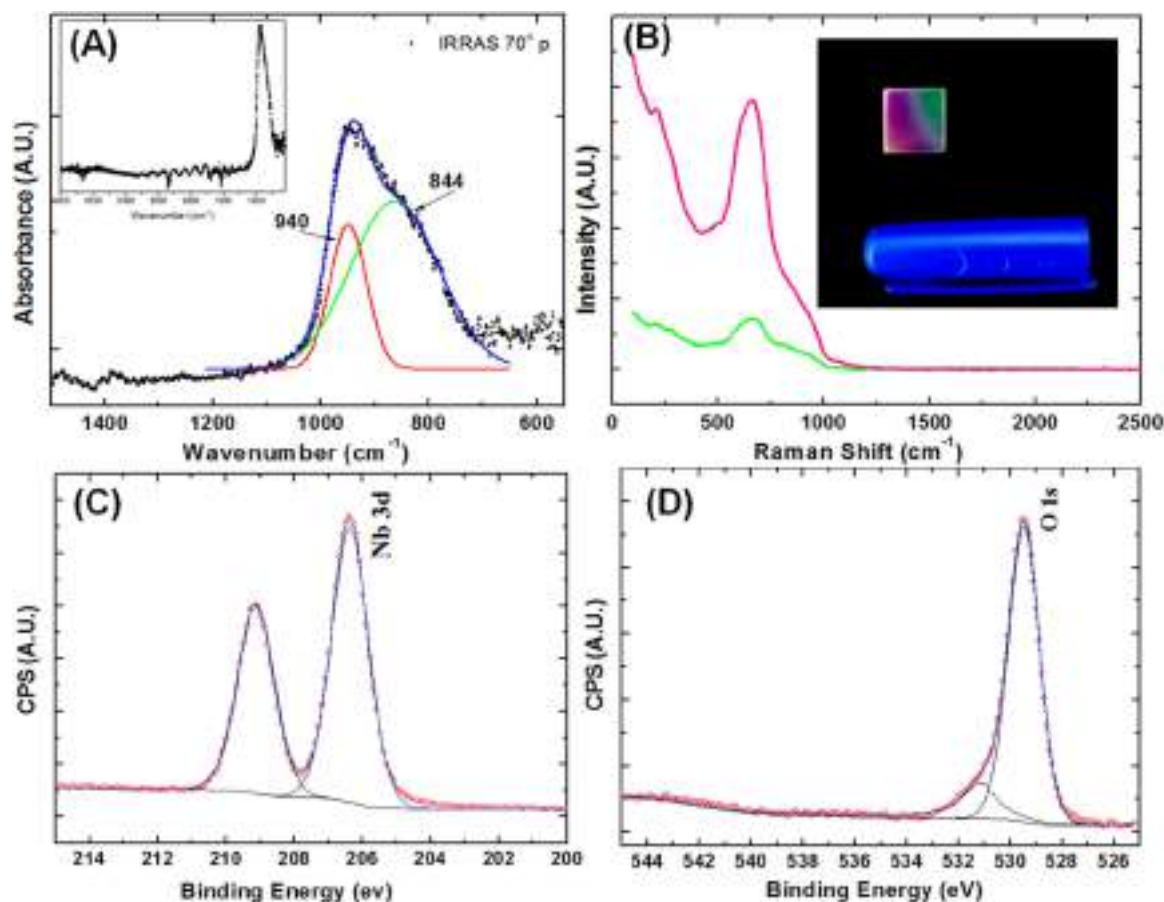


Fig. 2 A FTIR-IRRAS spectrum obtained at 70° p-polarized for Nb₂O₅ thin film showing the bands centered at 844 and 940 cm⁻¹ (inset displays the FTIR spectra in the range 4000 to 500 cm⁻¹). B Raman spectra

for the 316L SS containing Nb₂O₅ film (inset displays the different regions of the film and its spectra). C Nb 3d levels and D O 1s XPS deconvolution spectra

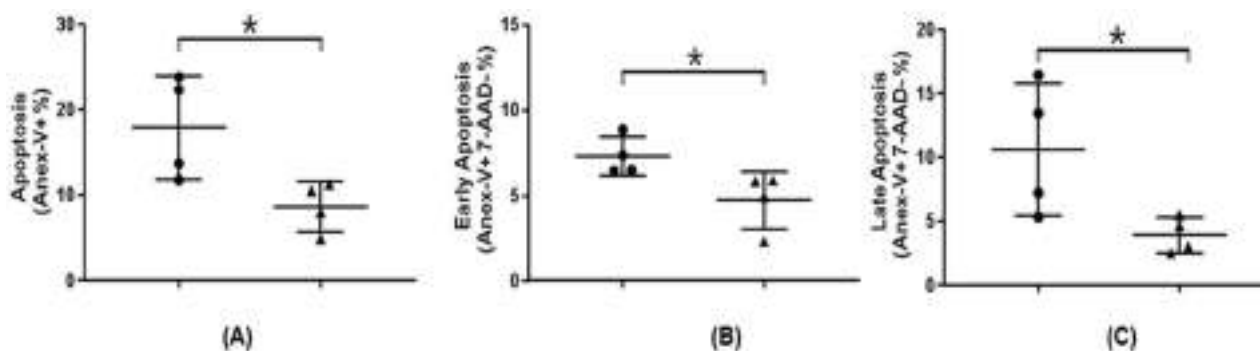


Fig. 3 HGF-1 cell-line cultured on the coated and uncoated 316L SS substrates, A total, B early, and C late apoptosis. Points represent each independent culture and lines the mean $\pm$ standard deviation. * $P < 0.05$. (●) 316L SS and (▲) 316L SS coated Nb₂O₅

TNF- α is directly involved in inflammation maintenance and activation of osteoblasts, inducing bone desorption, and films that act inducing lower concentrations are more bio-compatible in a long term [20], such as demonstrated by lower levels of TNF- α production by murine macrophage

cells cultured with niobium-covered surfaces [21]. In a similar way, IL-17 is a huge pro-inflammatory cytokine associated with chronic inflammation [22], osteoclastogenesis [22] and that can amplify inflammatory responses by inducing TNF- α secretion by macrophages [23].

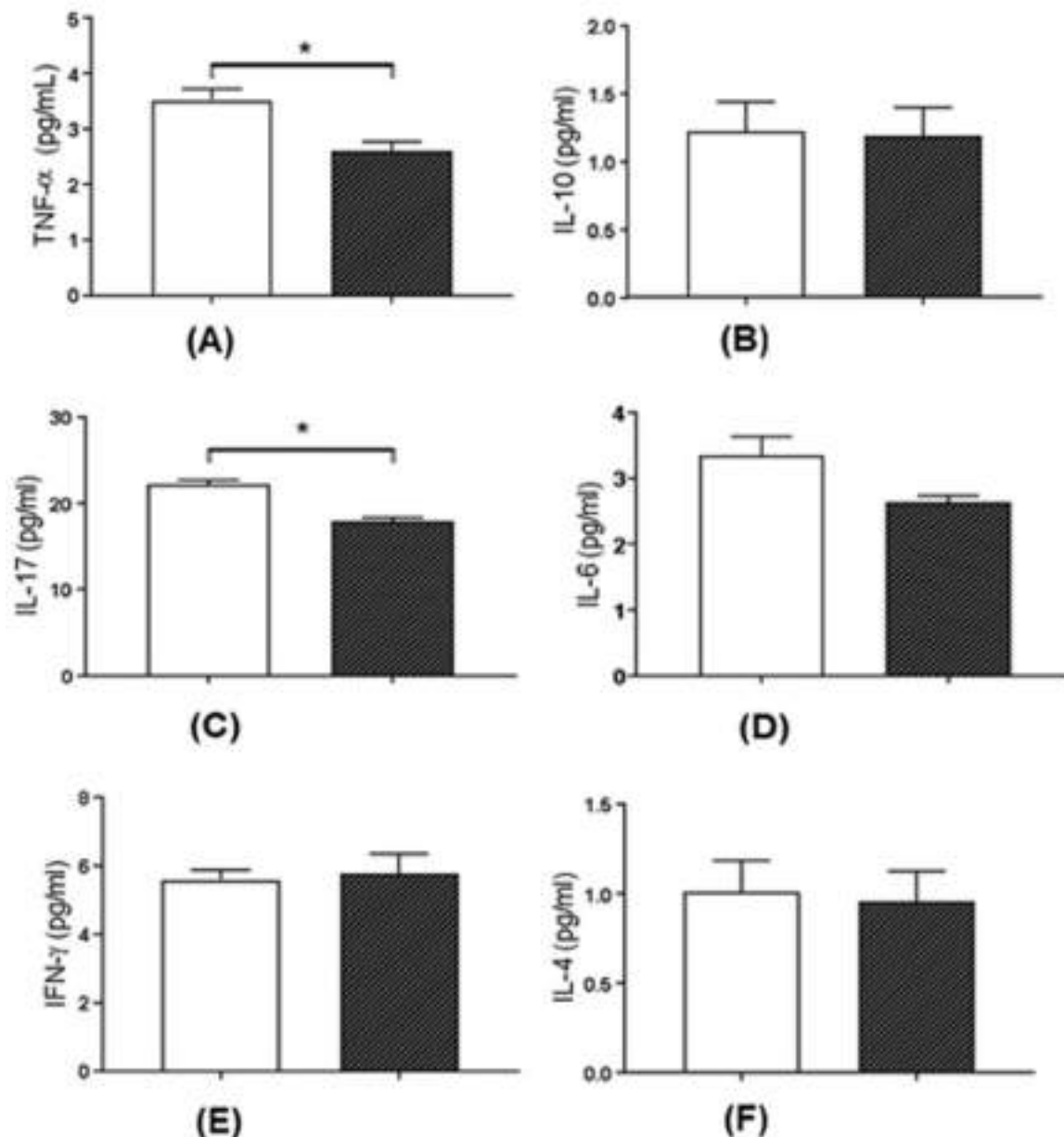


Fig. 4 Effect of 316L SS coated and uncoated in cytokine production of HGF-1. The cells were cultured for 24 h on both specimens. After 24 h of culture supernatant was collected and TNF- α (A), IL-10 (B), IL-17 (C), IL-6 (D), IFN- γ (E) and IL-4 (F) were analyzed by

cytometric bead array (CBA). Bars represent the mean $\pm$ standard deviation of cytokine production from quadruplicate samples. * $P < 0.05$. (□) 316 L SS and (■) 316L SS coated Nb₂O₅

4 Conclusion

The PVD method was shown advantageous for producing Nb₂O₅ thin film on the 316L SS surface. The coatings produced are less toxic and induces less inflammation than 316L SS in gingival cells (cell-line HGF-1) with high prospects to be used in the dentistry field as orthodontic brackets. The biological results suggest that the strategy of use Nb₂O₅ thin film to cover the 316L SS promoted since its protection of the physiological environment to its biocompatibility improvement. Furthermore, this study is the starting point for

the development of robust studies in biomedical area by using Nb₂O₅ thin film as a protective barrier against corrosion process and enhanced biological responses.

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Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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References

1. Rajan ST, Bendavid A, Subramanian B. Cytocompatibility assessment of Ti-Nb-Zr-Si thin film metallic glasses with enhanced osteoblast differentiation for biomedical applications. *Coll Surf B: Biointerfaces*. 2018. <https://doi.org/10.1016/j.colsurfb.2018.09.041>.
2. Qianyu Z, Li X. High rate capability of Nd-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as an effective anode material for lithium-ion battery. *Int J Electrochem Sci*. 2013;8:7816–7824.
3. Caiwen O, Wei L, Zaili Z, Ping H, Pengfei Y, Biao Y, Minsheng C. Effect of Ca and P ion concentrations on the structural and corrosion properties of biomimetic Ca-P coatings on ZK60 magnesium alloy. *Int J Electrochem Sci*. 2013. <https://doi.org/10.1016/j.msec.2016.11.132>
4. Zhong C, Liu F, Wu YT, Le JJ, Liu L, He MF, Zhu JC, Hu WB. Protective diffusion coatings on magnesium alloys: a review of recent developments. *J Alloy Compd*. 2012. <https://doi.org/10.1016/j.jallcom.2011.12.124>
5. Aisenberg S, Chabot R. Ion-beam deposition of thin films of diamond-like carbon. *J Appl Phys J Appl Phys*. 1971. <https://doi.org/10.1063/1.1660654>
6. Rausch M, Golizadeh M, Kreiml P, Cordill MJ, Winkler J, Mitterer C. Sputter deposition of NiW films from a rotatable target. *Appl Surf Sci*. 2020. <https://doi.org/10.1016/j.apsusc.2020.145616>.
7. Deng Z, Wang L, Zhang D, Liu J, Liu C, Ma J. *Med Sci Monit*. 2014; <https://doi.org/10.12659/MSM.889894>.
8. Kobayashi S, Ohgoe Y, Ozeki K, Sato K, Sumiya T, Hirakuri KK, Aoki H. *Diam Relat Mater*. 2005. <https://doi.org/10.1016/j.diamond.2004.11.036>.
9. Eliaz N. Corrosion of metallic biomaterials: a review. *Materials*. 2019. <https://doi.org/10.3390/ma12030407>.
10. Eurídice WA, Bueno Leite N, Gelamo RV, Buranello PAA, da Silva VM, Oliveira CJF, et al. a-C:H films produced by PECVD technique onto substrate of Ti6Al4V alloy: chemical and biological responses. *Appl Surf Sci*. 2020; <https://doi.org/10.1016/j.apsusc.2019.144084>.
11. Machuno LGB, Lima AB, Buso RR, Abdanur RMF, Rangel EC, Gelamo RV. Desenvolvimento e avaliação de uma fonte DC de alta tensão para utilização em sistema de deposição de filmes finos por pulverização catódica. *Rev Matér*. 2016. <https://doi.org/10.1590/S1517-707620160002.0046>.
12. Orel B, Maček M, Grdadolnik J, Meden A. In situ UV-Vis and ex situ IR spectroelectrochemical investigations of amorphous and crystalline electrochromic Nb₂O₅ films in charged/discharged states. *J Solid State Electrochem*. 1998. <https://doi.org/10.1007/s100080050092>.
13. Burcham LJ, Datka J, Wachs IE. In situ vibrational spectroscopy studies of supported niobium oxide catalysts. *J. Phys. Chem. B*. 1999; <https://doi.org/10.1021/jp990289a>.
14. Jehng JM, Wachs IE. Structural chemistry and Raman spectra of niobium oxides. *Chem Mater*. 1991. <https://doi.org/10.1021/cm00013a025>.
15. Pillis MF, de Oliveira MCL, Antunes RA. Surface chemistry and the corrosion behavior of magnetron sputtered niobium oxide films in sulfuric acid solution. *Appl Surf Sci*. 2018. <https://doi.org/10.1016/j.apsusc.2018.08.123>.
16. Yang Z, Lu X, Tan W, Zhao J, Yang D, Yang Y, He Y, Zhou K. XPS studies of nitrogen doping niobium used for accelerator applications. *Appl Surf Sci*. 2018. <https://doi.org/10.1016/j.apsusc.2017.12.214>.
17. Bekermann D, Barreca D, Gasparotto A, Becker HW, Fischer RA, Devi A. Investigation of niobium nitride and oxy-nitride films grown by MOCVD. *Surf Coat Technol*. 2009. <https://doi.org/10.1016/j.surfcoat.2009.07.029>.
18. Hao L, Lawrence J. Effects of CO₂ laser irradiation on the wettability and human skin fibroblast cell response of magnesia partially stabilised zirconia. *Mater Sci Eng C*. 2003. [https://doi.org/10.1016/S0928-4931\(03\)00056-0](https://doi.org/10.1016/S0928-4931(03)00056-0).
19. Eisenbarth E, Velten D, Müller M, Thull R, Breme J. Biocompatibility of beta-stabilizing elements of titanium alloys. *Biomaterials*. 2004; <https://doi.org/10.1016/j.biomaterials.2004.01.021>.
20. Lin T, Tamaki Y, Pajarinen J, Rogan H, Woo D, Yao Z, Goodman S. Chronic inflammation in biomaterial-induced periprosthetic osteolysis: NF- κ B as a therapeutic target. *Acta Biomater*. 2013. <https://doi.org/10.1016/j.actbio.2013.09.034>.
21. Vandrovicova M, Jirka I, Novotna K, Lisa V, Frank O, Kolska Z, Stary V, Bacakova L. Interaction of human osteoblast-like Saos-2 and MG-63 cells with thermally oxidized surfaces of a titanium-niobium alloy. *PLoS ONE*. 2014; <https://doi.org/10.1371/journal.pone.0100475>.
22. Kuwabara T, Ishikawa F, Kondo M, Kakiuchi T. The Role of IL-17 and related cytokines in inflammatory autoimmune diseases. *Mediators Inflamm*. 2017; <https://doi.org/10.1155/2017/3908061>
23. Miossec P, Kolls JK Targeting IL-17 and TH17 cells in chronic inflammation. *Nat Rev Drug Discov*. 2012; <https://doi.org/10.1038/nrd3794>.

RESEARCH ARTICLE

PLASMA PROCESSES
AND POLYMERS

ZnO surface modification with maleic anhydride using plasma treatment

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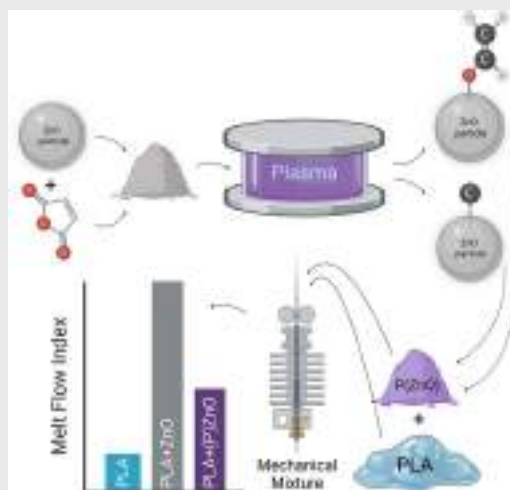
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Abstract

Zinc oxide (ZnO) was surface treated using argon plasma at 5 and 15 min, using maleic anhydride (MA) in solid state as the functionalizing agent. The samples were characterized by X-ray photoelectron spectroscopy, Fourier-transform infrared spectroscopy, and thermogravimetric analysis. The results indicate that ZnO surface modification occurs through two main routes: the decomposition of MA and the plasma-induced formation of C–Zn bonds, with 15 min being the most favorable time span. Poly(lactic acid) (PLA) and ZnO were processed in an internal chamber mixer, which was coupled with a torque rheometer and characterized by the Melt Flow Index. Composites containing treated ZnO present fluidity indices closer to those of pure PLA, indicating the functionalization contribution to control the degradation of the polymer matrix.



KEYWORDS

maleic anhydride, PLA degradation, plasma treatment, surface modification, zinc oxide

1 | INTRODUCTION

Poly(lactic acid) (PLA)/zinc oxide (ZnO) composites represent a promising class of materials for bone regeneration scaffolds, considering that they combine the flexibility, formability, and bioabsorption/bio-compatibility of the polymer with the stiffness, mechanical strength, bioactivity, and antibacterial properties of

the particle.^[1] However, one of the main challenges in developing PLA and ZnO composites is the catalytic behavior of ZnO in polymeric matrix degradation reactions, mainly in the molten state. The study by Qu et al.^[2] regarding ZnO particles indicates that water partially dissociates and forms hydroxylated structures on the surface of the particles, which catalyzes rapid hydrolysis of PLA. In addition to degradation by

hydrolysis, studies indicate the influence of metal compounds/ions such as Sn, Mg, and Zn on the degradation of PLA. Metal compounds can come from residual components or functional fillers of the polymer synthesis process added to the PLA matrix. Abe et al.^[3] studied the thermal decomposition process of PLA in the presence of residual zinc from the polymer synthesis process. They reported that residual zinc compounds catalyze the degradative processes that occur in PLA at processing temperatures. The study pointed out that degradation is governed by the formation of lactides as a product of depolymerization and/or intermolecular transesterification reactions, catalyzed by metal ions.

One way to slow down this process would be to modify the surface of this filler to control the release of ions from the surface of the particles, which cause the scission of polymer chains. In addition, surface functionalization has also proven to be efficient in promoting better dispersion of fillers in the polymer matrix, which improves polymer/particle adhesion and, consequently, the mechanical properties of the composite.^[1] Doumbia et al.^[4] studied the production of PLA/ZnO filaments with minimum degradation of thermal and mechanical properties. The filaments were produced by extrusion with ZnO coated with triethoxycaprylsilane for optimal antibacterial properties. The results showed that treated ZnO was better dispersed in PLA and had low degradation rates through depolymerization, with a decomposition temperature increase of up to 36°C, unlike that for untreated ZnO. Also, better antibacterial activity was achieved with PLA/3% treated ZnO (instead of 1% filler), thanks to the good dispersion of the treated fillers into PLA.

Several studies are found in the literature that describe different compounds used for functionalization/compatibilization in PLA systems. The functionalizing agent maleic anhydride (MA), in addition to being widely used in applications with PLA due to its low toxicity and good chemical reactivity with the polymer, is an option to improve dispersion of fillers as it increases the interfacial adhesion between PLA and the particles and reduces water absorption of the composite.^[5–8]

Wet chemical functionalization of zinc oxide is discussed in the literature; however, it uses solvents and is time consuming.^[9–11] On the other hand, some works explore zinc oxide functionalization through the plasma technique.^[12–15] Plasma functionalization is an alternative to the traditional chemical methods, with several advantages. First, it is attractive from an environmental perspective since it is a dry, contaminant-free process. Second, it is controllable and reproducible, fast, and efficient even in moderate conditions, as it enables high energy levels, requires reasonable power, and maintains the sample close to room temperature, preventing the degradation of particles.^[13,16–18]

Studies in the literature promote the functionalization of ZnO through plasmas using molecular gases.^[12–13,15] Ciolan et al.^[12] discussed the effects of the gas mixture ratio of argon to ammonia during surface amination of ZnO nanoparticles. Argon facilitates the dissociation of ammonia and the production of ionic species, responsible for introducing amine groups. They observed the creation of NH₂ radicals, which are directly related to the introduction of the amine groups, and the creation of hydrogen radicals, which act mainly as the etchant. Ciolan et al.^[13] studied the surface functionalization of ZnO thin films by low-pressure Ar/NH₃ mixture plasmas. The mixture ratio of 70%/30% Ar/NH₃ obtained the maximum amine group functionalization over the ZnO, which greatly influences the crystalline properties of the ZnO thin films. Meena et al.^[15] investigated the influence of O₂ plasma treatments on ZnO films and confirmed changes in the electrical properties of the ZnO caused by the oxygen ions reacting with residual hydrocarbons and the production of excess oxygen vacancies near the Zn atoms. In other cases, organic compounds are used as functionalizing agents,^[14] bringing the advantage to allow the formation of more diversified functional groups. Mathioudaki et al.^[14] discussed low-pressure plasma polymerization of cyclopropylamine to functionalize ZnO nanoparticles. X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared (FTIR) analyses revealed the incorporation of reactive functional groups such as amines and imines, while transmission electron microscopy micrographs showed that a plasma polymer film of approximately 5 nm was deposited onto the nanoparticles' surface. Beyond that, in our other works, plasma treatment of carbon nanotubes (CNT) using urea as a functionalizing agent promotes the formation of C–N and O=CN₂ groups attached to CNT,^[17] while the treatment with O₂ and N₂ gases only formed C–N bonds.^[16] Besides, our previous work has shown that maleic anhydride functionalization of CNT plasma results in better outcomes for produce nanocomposites with a blend of polyamide 6 and polypropylene, as compared to oxygen gas CNT functionalization.^[19] Although the plasma polymerization of MA has been studied for several years,^[20] most of the studies introduced the organic compounds in gaseous forms, which could reduce the available monomers when condensation occurs in the reactor chamber's piping and walls. Alternatively, before the plasma treatment, the organic compound that acts as a functionalizing agent can be premixed with the particle in solid form to be functionalized. It both prevents the necessity of a sublimation apparatus and the reactor's contamination. Our previous work originally proposed this technique, whose efficiency was proven in functionalizing carbon

nanotubes with MA using argon plasmas.^[16] This study provided an increase of 43% in attached covalent O–C=O groups in the functionalized sample relative to the pristine CNT.

Given the motivations and problems presented, this work proposes using a method based on a mixture of MA and ZnO powder particles to be treated using radio-frequency (RF) plasma. Samples of ZnO/MA solid mixtures were treated through a capacitive coupled plasma (CCP) in an argon atmosphere. The ZnO plasma surface modification efficiency was evaluated using different characterization techniques. The functionalization effect on the PLA degradation was also evaluated by mixing the treated ZnO with PLA and then assessing the composite's Melt Flow Index (MFI).

2 | EXPERIMENTAL SETUP

2.1 | Materials

This work used zinc oxide from Alfa-Aesar, American Chemical Society (ACS), with a purity of 99%. MA was purchased from Aldrich Chemistry with an approximate purity of 99%. The plasma discharge used ultrapure argon gas (purity above 99.999%). Methanol, used in the filtration washing process, was obtained from Dinâmica Química Contemporânea Ltda (99.8% pure). The membranes used in the filtration were manufactured by Filtrilo, in PVDF 0.45 μm 47 mm.

2.2 | Plasma functionalization process

The CCP reactor used to functionalize the zinc oxide was homemade, based on the experience in assembling

previous reactors.^[16,17] The reactor is basically composed of stainless steel electrodes inside a cylindrical glass chamber, as presented in Figure 1. The sample holder has a diameter of 58 mm, which is placed in the reactor chamber with a volume of 56.5 cm³. The other parts of the chamber, shown in Figure 1, consist of entries for a pressure gauge, vacuum pump, and gas feed.

Initially, a solid mixture of zinc oxide and maleic anhydride (ZnOMA) with a 90/10 mass proportion was placed in a mortar, mixed for 2 min, and then inserted in the reactor. A RF plasma power of 35 W was chosen based on a previous work.^[17] At a base pressure of 2×10^{-1} Torr, argon gas was introduced at a flow rate of 36.5 sccm, reaching a working pressure of 9×10^{-1} Torr, measured by a Pirani gauge coupled to the reactor. The argon flow was maintained for 15 min to help to purge the chamber before starting the plasma process. Finally, the glow discharge plasma treatment was carried out with a power of 35 W for 5 and 15 min.

After functionalization, a washing procedure was conducted to remove possible non-reacted molecules of the functionalizing agent, following these steps: the samples were left for 12 h in methanol solution under magnetic stirring, submitted to an ultrasound tip at 16 000 J and, then, passed through the vacuum filtration process promoting the separation of solid and liquid phases. Finally, the samples were placed in an oven at 70°C for 1 h. All the samples, except ZnO and MA references, went through this washing procedure.

2.3 | Characterization techniques

Table 1 presents the samples characterized in this work for easy access and understanding during the interpretation and discussion of the proposed analyses.

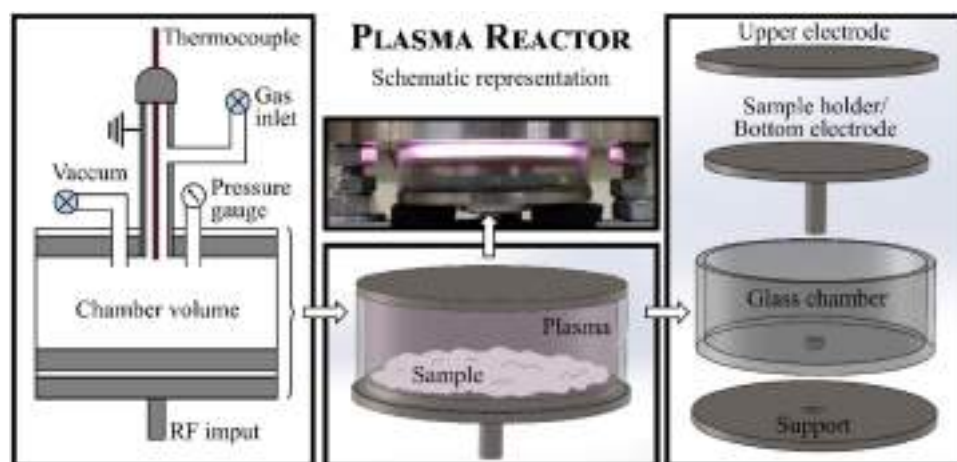


FIGURE 1 Photo and schematic representation of the reactor used to treat the samples.

TABLE 1 Summary of the analyzed samples.

Sample	Description
ZnO	Zinc oxide as received
MA	Maleic anhydride
ZnOMA_mixture	Mixture of ZnO and MA (not plasma treated)
ZnOMA_5 min	ZnO and MA samples were treated in plasma for 5 min and subsequently washed
ZnOMA_15 min	ZnO and MA samples were treated in plasma for 15 min and subsequently washed

XPS analyses were performed in two different spectrometers: a UNI-SPECS UHV and a Thermo Fisher Scientific (K-Alpha), operating at a base pressure below 5×10^{-7} Pa. As the excitation source, the X-ray Al-K α ($h\nu = 1486.6$ eV) was used with the pass energy set to 200 eV for survey and 20 eV for high-resolution scans. The inelastic noise of the high-resolution C 1s, O 1s, and Zn 2p $_{3/2}$ spectra was subtracted using the Shirley method. For charge shift correction, a flood gun was employed, using the C 1s hydrocarbon component (CC-H) at 284.8 eV as a reference. The composition was determined by the relative proportions of peak areas corrected by Scofield atomic sensitivity factors with an accuracy of $\pm 5\%$. The spectra were deconvoluted using a Voigtian-type function, with Gaussian (70%) and Lorentzian (30%) combinations. The full width at half maximum was varied between 1.2 and 2.2 eV, and as a criterium for assigning the fitted components, a chemical shift > 0.5 eV, relative to the CC-H (284.8 eV) and ZnO (1022.1 eV) references, was used. FTIR spectra of samples in the form of KBr tablets were obtained using a Bruker device (INVENIO-S). A total of 32 scans were conducted in the 4000 to 400 cm^{-1} region, with a resolution of 4 cm^{-1} . Thermogravimetric (TG) analyses were performed using a NETZSCH STA 449C, with a heating rate of 10°C/min and temperature from 25°C to 1000°C, with synthetic airflow.

The PLA/ZnO composites were processed in a mixing chamber coupled to a Rheomix 600p Haake torque rheometer with roller-type counter-rotating semi-interpenetrating rotors at 175°C. Mixing took place for 5 min at 60 rpm with 50 g of material in total. The balance torque was evaluated for 5 min. Seven samples were processed, varying the particle percentage from 0% to 5% and 10% for ZnO, namely ZnOMA_5 min and ZnOMA_15 min, respectively. Previously, all materials were dried for 12 h at 40°C in a vacuum oven to eliminate moisture. A physical and manual mixture of PLA and ZnO was performed for the composites before insertion into the mixer.

The MFI analyses were carried out using a GÖTT-FERT MI2 at 155°C and with 1050 g of material. Thus, the flow rate was determined by measuring the mass of the material drained for 10 min.

3 | RESULTS AND DISCUSSIONS

The composition of the plasma-modified ZnO/MA samples and the relative proportions of the bonding environments of C, O, and Zn, obtained by deconvoluting the XPS spectra, are shown in Table 2. The main components in the ZnO sample are the elements O 1s and Zn 2p. From the atomic percentage contribution of oxygen and zinc obtained from the survey spectra, the O:Zn ratios were calculated for all samples and used to identify the introduction of functional groups, indicated by their increase. The O:Zn ratio for the ZnO sample is 1.1, as indicated in the survey spectrum in the supplementary information section (Supporting Information S1: Figure S1a). An O:Zn ratio of 1.0 is expected for the ZnO sample,^[21] which agrees with the 1:1 chemical balance characteristic of the zinc oxide ionic compound. The percentage of oxygen may be slightly higher than that of zinc due to the presence of contamination and hydroxyls adsorbed on the surface.^[22] The survey also shows a contribution from C 1s, which was not expected in theory in ZnO. However, the presence of carbon in ZnO samples is quite common from impurities and surface contamination by hydrocarbons.^[11,14,23]

The samples ZnOMA_5 min and ZnOMA_15 min presented an O:Zn of 2.2 and 2.7, respectively, indicating the effective functionalization by the plasma treatment. Besides, the carbon contribution to the samples' chemical composition obtained from the survey (Supporting Information S1: Figure S1) increased from 13.1 at. % in the ZnO sample to 43.5 at. % (ZnOMA_5min) and 49.3 at. % (ZnOMA_15min). This carbon contribution is no longer only attributed to hydrocarbon contamination but to oxygen-carbon functional groups provided by MA molecules.

The C 1s high-resolution spectrum for the ZnO sample (Supporting Information S1: Figure S2a) indicates a contribution of C-H (285.2 eV), related to hydrocarbon contamination, C-O (286.8 eV), and O=C-O (289.2 eV).^[14] The O 1s high-resolution spectrum (Supporting Information S1: Figure S2b) for that same sample shows a contribution of zinc and oxygen's ionic bond (530.4 eV), besides other chemical bonds related to contamination or pre-existing defects: hydroxylic and carbonylic groups (531.2 eV), C-O (532.4 eV), and O=C=O (533.1 eV) bonds.^[24]

TABLE 2 Atomic percentage of carbon (C 1s), oxygen (O 1s), and zinc (Zn 2p) and peak area percentage of functional groups (error: $\pm 5\%$).

Sample	Concentration (at.%)			Peak area percentage of functional groups (%)											
	Zn 2p	O 1s	C 1s	C-Zn (C 1s)	C=C/C-CH (C 1s)	O-C (C 1s)	C=O (C 1s)	O-C=O (C 1s)	O-Zn (O 1s)	OH/O=C (O 1s)	O-C (O 1s)	O-C=O (O 1s)	ZnO (Zn 2p)	Zn-C (Zn 2p)	
ZnO	41	46	13	-	54.0	25.8	-	20.2	57.4	21.6	16.8	4.2	100.0	-	
MA	-	38	62	-	62.5	6.0	-	31.5	-	42.7	14.6	42.7	-	-	
ZnOMA_5 min	18	39	43	14.9	57.0	6.8	8.0	13.3	42.4	18.8	30.9	1.7	86.9	13.1	
ZnOMA_15 min	14	37	49	27.8	37.9	9.0	18.1	7.2	35.5	19.7	28.5	2.4	41.8	58.2	
ZnOMA_mixture	36	44	20	-	59.4	2.7	-	37.9	48.7	18.7	32.0	0.6	100.0	-	

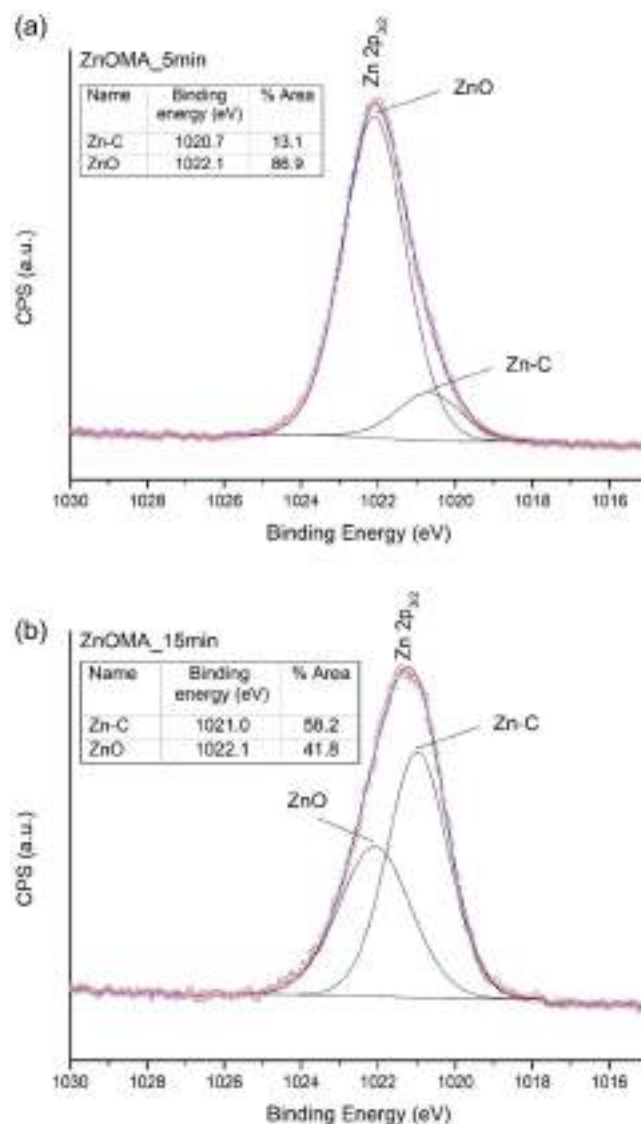


FIGURE 2 High-resolution X-ray photoelectron spectroscopy (XPS) Zn 2p spectra for ZnOMA_5 min (a) and ZnOMA_15 min (b).

Comparing the C 1s high-resolution spectra of the ZnO sample with those of the treated ones (Supporting Information S1: Figures S2a, S3a, and S4a) shows the appearance of a C–Zn bond at 283.9 eV for samples ZnOMA_5 min (14.9%) and ZnOMA_15 min (27.8%). The presence of this bond is confirmed by the Zn 2p high-resolution spectrum in Figure 2, indicating that the samples were functionalized by MA. The C–Zn bond can be established by carbon atoms allocating in interstitial sites of a wurtzite ZnO crystalline structure or by replacing oxygen vacancies.^[25] Indeed, oxygen vacancies are easily created in oxides, including zinc oxide, by plasma surface treatments.^[15,26]

Regarding the O 1s high-resolution spectrum (Supporting Information S1: Figures S2b, S3b, and S4b), results indicate an increase in the O–C content for the

treated samples (30.9% for ZnOMA_5 min and 28.5% for ZnOMA_15 min) if compared to the ZnO sample (16.8%), indicating the insertion of oxygen functional groups onto the zinc oxide surface. Besides, in plasma-treated samples, the presence of $\text{O}-\text{C}=\text{O}$ bonds decreases (1.7% for ZnOMA_5 min and 2.4% for ZnOMA_15 min, against 4.2% for the ZnO sample), which could indicate the opening of MA rings due to the plasma discharge.

The O 1s spectrum indicates an O-Zn contribution reduction reaction for treated samples, and so does the

Zn 2p spectrum (Table 2), which occurs due to the appearance of Zn-C bonds. For ZnOMA_5min, the Zn-C contribution in the Zn 2p spectrum is 13.0% (with consequent 87.0% of Zn-O bonds), and for ZnOMA_15 min, this value is 58.2% (with 41.8% of Zn-O contribution), indicating that the plasma treatment was more efficient in functionalizing zinc oxide in the 15-min treatment.

The ZnOMA_mixture sample was also analyzed through FTIR and TG, as shown in Figures 3 and 4, to

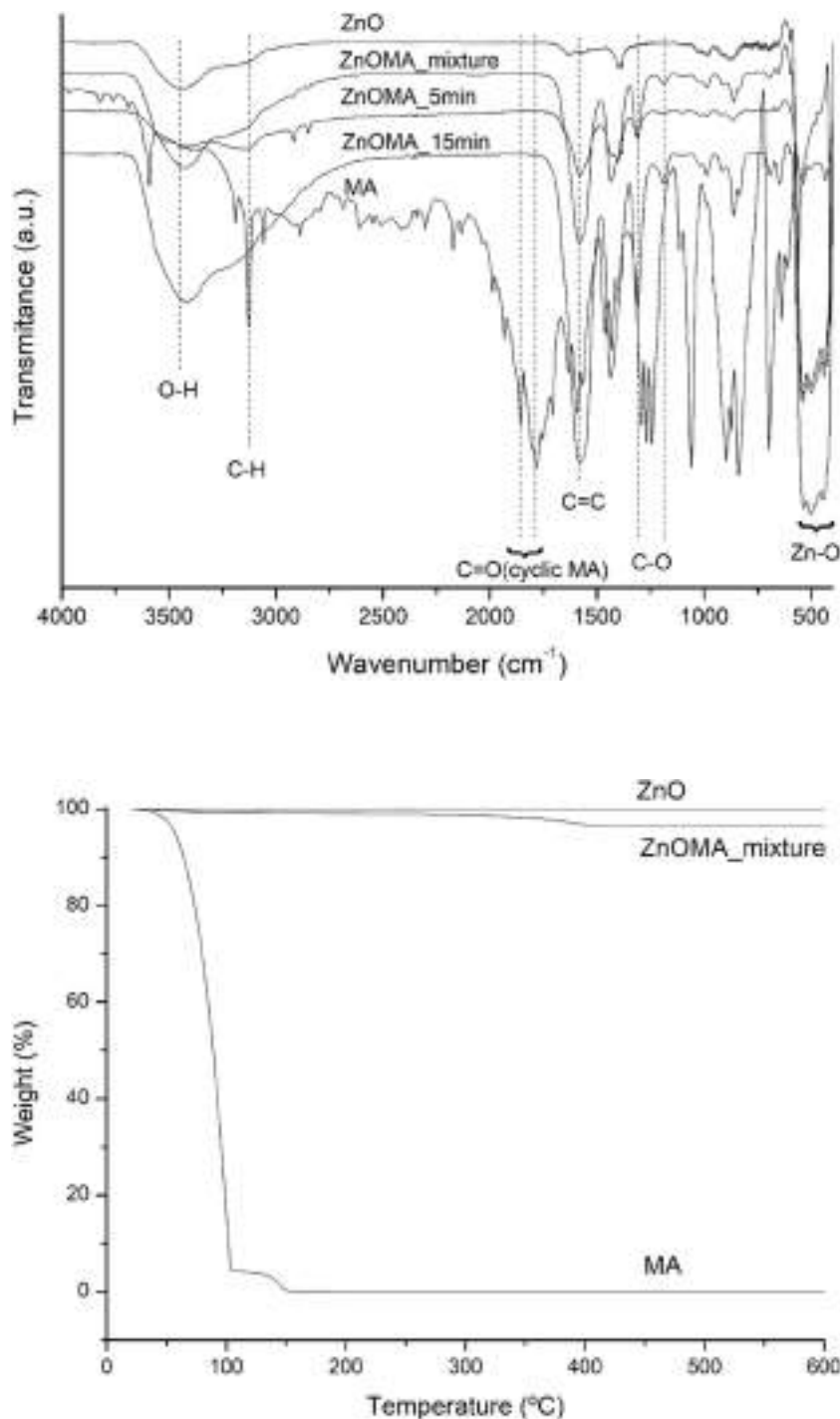


FIGURE 3 Fourier transform infrared (FTIR) spectra for ZnO, MA, ZnOMA_mixture, ZnOMA_5 min, and ZnOMA_15 min samples.

FIGURE 4 Thermogravimetric curves for zinc oxide (ZnO), maleic anhydride (MA), and ZnOMA_mixture, under synthetic airflow.

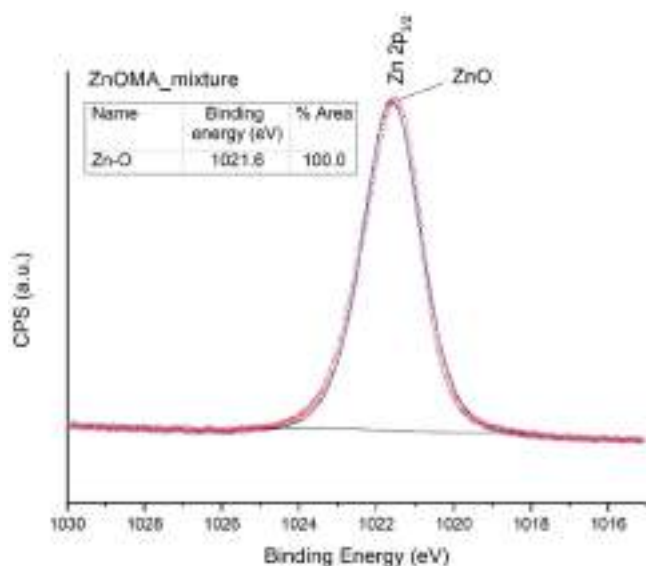


FIGURE 5 High-resolution X-ray photoelectron spectroscopy (XPS) Zn 2p_{3/2} spectrum for the ZnOMA_mixture.

evaluate if the washing procedure had any influence on the sample's functionalization. Both techniques indicated that the washing procedure did not completely remove the unreacted MA from the mixture; once, if that was the case, both the FTIR and TG curves of the ZnOMA_mixture would be very similar to those of the ZnO sample. From that, to ensure that the formation of the C–Zn bonds comes from the plasma treatment, the ZnOMA_mixture sample was analyzed by XPS, and the high-resolution Zn 2p is shown in Figure 5. Results provided by surveys (Supporting Information S1: Figure S5) and high-resolution scans are presented in Table 2, along with all other samples. The O:Zn ratio presented a slight increase (1.2) related to the ZnO sample, supporting FTIR results that indicate the presence of some residual MA molecules. The results also indicate the MA decomposition during the washing procedure, once both O–C (from O 1s) and C=C/C–C (from C 1s) bonds increased from 16.8% and 54.0%, respectively, in the ZnO sample, to 32.0% and 59.4% in the ZnOMA_mixture sample (Supporting Information S1: Figure S6). However, the most important conclusion refers to the C–Zn bond formation: no sign of this bond is found in the fitting of the C 1s and Zn 2p spectra of the ZnOMA_mixture sample (Figure 5), which confirms that the bond established between carbon and zinc is a result of the plasma treatment.

The FTIR spectra for both plasma-treated samples, as shown in Figure 2, show characteristic MA bands in addition to zinc oxide bands. The band at 1585 cm^{−1} refers to the elongation of the C=C double bond. As for the oxygenated groups, compared to the ZnO (Figure 3), new bands appear between 1309 and 1187 cm^{−1}, associated with the elongation of the C–O bond for

treated samples. These observations indicate the effective functionalization of the ZnO through plasma. Finally, the spectra of the treated samples also indicate the absence of bands at 1858 and 1790 cm^{−1}, which points to the opening of the MA rings during the plasma functionalization process, corroborating the XPS results.

In addition to the formation of the Zn–C bonds, there may be another mechanism involved in the functionalization of the ZnO with MA in the present study, considering the functional groups C=C, C–H, and C–O observed from the XPS and FTIR analyses in the treated samples. MA molecules in contact with the ZnO surface can undergo decomposition, according to the scheme in Figure 6. First, the opening of the ring occurs, promoted by the hydroxyl groups found on the surface of the particles. The process moves to decarboxylation and decarbonylation reactions, yielding stable surface species.^[21] These reactions agree with the increase in C–O and C=C functional groups observed through XPS and the absence of infrared bands referring to carbonyl species (Figure 3).

The TG analysis (Figure 7) was carried out to study the thermal behavior of the particles after the surface treatment with plasma. For both samples treated with MA, it presents two main decomposition events, that is, two stages of mass loss, which can be better visualized from the derivative thermogravimetry (DTG) curves (derivative of TG, shown as dashed line), as illustrated in Figure 7. The temperature ranges and percentages of weight loss for each sample are described in Table 3.

According to Barrak et al.,^[23] the content of the functionalizing agent grafted into the modified particles can be evaluated by the weight loss in the TG analysis. The first decomposition event occurs due to the elimination of water and residual solvent. Unlu et al.^[27] report that mass losses of metal oxides only occur after 500°C, which may indicate that the second event can be attributed to the decomposition and desorption of the MA anchored to the particles.^[28] Castillo et al.^[28] observed that, in their TG analyses, peaks related to the appearance and adsorption of MA on the TiO₂ particles' surface for a temperature ranging from 200°C to 580°C, values that agree with what was obtained in that study. Thus, the MA content grafted on the surface of the particles would be 5.2% for 5 min and 8.7% for 15 min of treatment. The results obtained through the TG analysis are in consonance with the XPS results, indicating the highest degree of functionalization for the 15-min treatment.

Figure 8 presents the MFI for PLA and PLA/ZnO composites, with treated and untreated ZnO. All compositions presented a higher MFI than that of the pure polymer, those with ZnO without functionalization being the most divergent. Comparing different

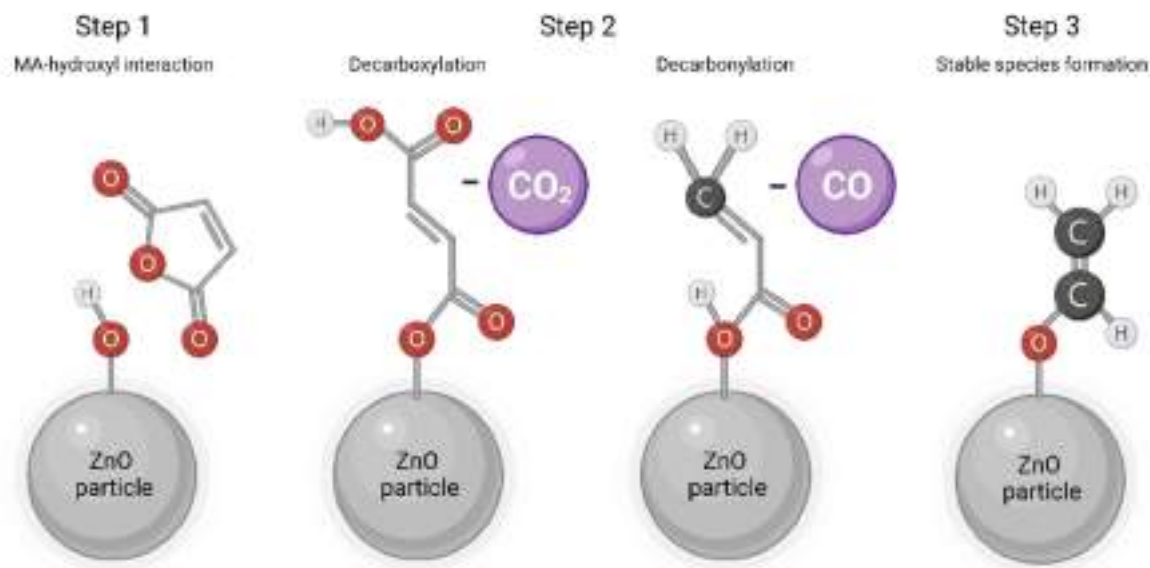


FIGURE 6 Scheme of maleic anhydride (MA) decomposition on the surface of zinc oxide (ZnO) particles. *Source:* Adapted from Girol et al.^[21] (Created with BioRender.com).

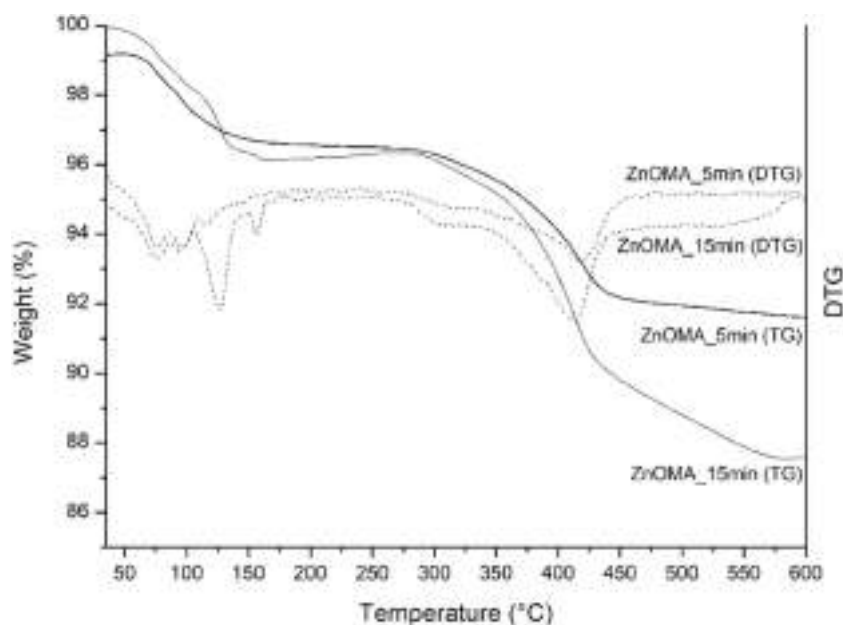


FIGURE 7 Thermogravimetric (TG) and DTG curves of plasma treated samples, under synthetic airflow.

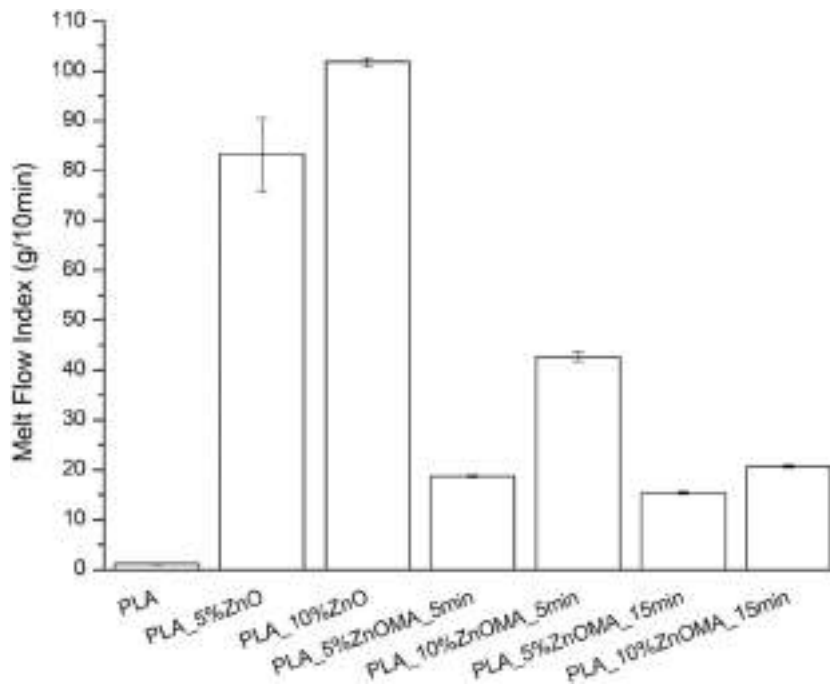
Decomposition	ZnOMA_5 min Temperature (°C)	Weight %	ZnOMA_15 min Temperature (°C)	Weight %
1° stage	50–175	3.6	25–175	3.9
2° stage	250–475	4.5	250–590	8.6

TABLE 3 Thermal behavior of ZnOMA_5 min and ZnOMA_15 min treated samples.

functionalization lengths, 15 min of treatment yielded a lower MFI than 5 min. Furthermore, the increase in particle concentration can be measured to promote higher MFIs, both for compositions with surface

treatment and for untreated ZnO. The fluidity index is known to be inversely proportional to the viscosity of the material, so the increase in the MFI in the presence of a ceramic filler may be associated with catalyzed

FIGURE 8 Melt flow index results obtained for poly(lactic acid) (PLA) and PLA/ZnO composites.



degradation reactions during processing. This degradation causes the molar mass to decrease, reducing the probability of entanglement between macromolecules, generating less flow restriction and reducing viscosity and an increased fluidity index.^[29] Therefore, the particle functionalization may have contributed to control matrix degradation by reducing the liberation of Zn^{+2} ions, maintaining the fluidity index at levels closer to that of the pure polymer, with 15 min of functionalization (ZnOMA_15 min) being the most effective treatment length.

4 | CONCLUSIONS

The results of this work evidence the plasma functionalization of zinc oxide particles using the organic compound MA. The plasma treatment on the ZnO molecule generates oxygen vacancies, which induce the formation of chemical bonds between MA and the oxide. XPS spectra revealed the presence of Zn-C bonds on the surface of the treated oxide: 14.9% (C 1s) for ZnOMA_5min and 27.8% (C 1s) for ZnOMA_15min, revealing the ability of carbon to fill in oxygen vacancies. Furthermore, based on XPS data, a decomposition mechanism for MA with the insertion of functional groups such as C–O, C=C, and C–H was established. The TG analysis revealed a 5.2% content of functional groups grafted onto the surface of the particles for 5 min of treatment and 8.7% for 15 min. From the processing of the PLA/ZnO composites and the MFI assay, it was possible to

conclude that the functionalization reduces the degradation of the polymer matrix, presenting better results for the 15 min of plasma treatment.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

- [1] I. Armentano, M. Dottori, E. Fortunati, S. Mattioli, J. M. Kenny, *Polym. Degrad. Stab.* **2010**, 95, 2126. <https://doi.org/10.1016/j.polymdegradstab.2010.06.007>
- [2] M. Qu, H. Tu, M. Amarante, Y. Q. Song, S. S. Zhu, *J. Appl. Polym. Sci.* **2014**, 131, 40287. <https://doi.org/10.1002/app.40287>
- [3] H. Abe, N. Takahashi, K. J. Kim, M. Mochizuki, Y. Doi, *Biomacromolecules* **2004**, 5, 1606. <https://doi.org/10.1021/bm0497872>
- [4] A. S. Doumbia, H. Vezin, M. Ferreira, C. Campagne, E. Devaux, *J. Appl. Polym. Sci.* **2015**, 132, 41776. <https://doi.org/10.1002/app.41776>

- [5] A. Birnin-Yauri, N. Ibrahim, N. Zainuddin, K. Abdan, Y. Then, B. Chieng, *Polymers* **2017**, 9, 165. <https://doi.org/10.3390/polym9050165>
- [6] A. Gregorova, M. Hrabalova, R. Kovalcik, R. Wimmer, *Polym. Eng. Sci.* **2010**, 51, 143. <https://doi.org/10.1002/pen.21799>
- [7] S. Detyothin, S. E. M. Selke, R. Narayan, M. Rubino, R. Auras, *Polym. Degrad. Stab.* **2013**, 98, 2697. <https://doi.org/10.1016/j.polymdegradstab.2013.10.001>
- [8] L. Zhou, H. He, M. Li, S. Huang, C. Mei, Q. Wu, *Ind. Crops Prod.* **2018**, 112, 449. <https://doi.org/10.1016/j.indcrop.2017.12.044>
- [9] E. Tang, G. Cheng, X. Ma, X. Pang, Q. Zhao, *Appl. Surf. Sci.* **2006**, 252, 5227. <https://doi.org/10.1016/j.apsusc.2005.08.004>
- [10] C. G. Allen, D. J. Baker, J. M. Albin, H. E. Oertli, D. T. Gillaspie, D. C. Olson, T. E. Furtak, R. T. Collins, *Langmuir* **2008**, 24, 13393. <https://doi.org/10.1021/la802621n>
- [11] C. Rodwihok, K. Charoensri, D. Wongrataphisan, W. M. Choi, S. H. Hur, H. J. Park, J. S. Chung, *J. Mater. Sci. Technol.* **2012**, 76, 1. <https://doi.org/10.1016/j.jmst.2020.09.041>
- [12] M. A. Ciolan, I. Motrescu, D. Luca, M. Nagatsu, *Jpn. J. Appl. Phys.* **2013**, 53, 010207. <https://doi.org/10.7567/jjap.53.010207>
- [13] M. A. Ciolan, I. Motrescu, K. Sugiura, D. Luca, M. Nagatsu, *Langmuir* **2018**, 34, 11253. <https://doi.org/10.1021/acs.langmuir.8b01183>
- [14] S. Mathioudaki, B. Barthélémy, S. Dettriche, C. Vandenabeele, J. Delhalle, Z. Mekhalif, S. Lucas, *ACS Appl. Nano Mater.* **2018**, 1, 3464. <https://doi.org/10.1021/acsanm.8b00645>
- [15] J. S. Meena, M. C. Chu, Y. C. Chang, H. C. You, R. Singh, P. T. Liu, H. P. D. Shieh, F. C. Chang, F. H. Ko, *J. Mater. Chem. C* **2013**, 1, 6613. <https://doi.org/10.1039/c3tc31320d>
- [16] T. T. Steffen, L. C. Fontana, P. Hammer, D. Becker, *Appl. Surf. Sci.* **2019**, 491, 405. <https://doi.org/10.1016/j.apsusc.2019.06.176>
- [17] T. Tromm Steffen, L. César Fontana, P. Hammer, D. Becker, *Appl. Surf. Sci.* **2022**, 583, 152493. <https://doi.org/10.1016/j.apsusc.2022.152493>
- [18] B. Ouyang, Y. Zhang, X. Xia, R. S. Rawat, H. J. Fan, *Mater. Today Nano* **2018**, 3, 28. <https://doi.org/10.1016/j.mtnano.2018.11.002>
- [19] J. A. Rocha, T. T. Steffen, L. C. Fontana, D. Becker, *Polym. Bull.* **2020**, 78, 5623. <https://doi.org/10.1007/s00289-020-03394-y>
- [20] M. E. Ryan, A. M. Hynes, J. P. S. Badyal, *Chem. Mater.* **1996**, 8, 37. <https://doi.org/10.1021/cm9503691>
- [21] S. Gil Girol, T. Strunskus, M. Muhler, C. Wöll, *J. Phys. Chem. B* **2004**, 108, 13736. <https://doi.org/10.1021/jp048386d>
- [22] S. B. Ghaffari, M. H. Sarrafzadeh, Z. Fakhroueian, S. Shahriari, M. R. Khorramizadeh, *Mater. Sci. Eng. C* **2017**, 79, 465. <https://doi.org/10.1016/j.msec.2017.05.065>
- [23] H. Barrak, T. Saied, P. Chevallier, G. Laroche, A. M'nif, A. H. Hamzaoui, *Arab. J. Chem.* **2019**, 12, 4340. <https://doi.org/10.1016/j.arabjc.2016.04.019>
- [24] N. C. Rissi, P. Hammer, L. A. Chiavacci, *Mater. Res. Express* **2017**, 4, 015027. <https://doi.org/10.1088/2053-1591/aa58fc>
- [25] N. D. Dung, C. T. Son, P. V. Loc, N. H. Cuong, P. T. Kien, P. T. Huy, N. N. Ha, *J. Alloys Compd.* **2016**, 668, 87. <https://doi.org/10.1016/j.jallcom.2016.01.208>
- [26] H. Akazawa, *Appl. Phys. Express* **2009**, 2, 081601. <https://doi.org/10.1143/apex.2.081601>
- [27] I. Unlu, J. W. Soares, D. M. Steeves, R. Pang, E. A. Welsh, J. E. Whitten, *J. Mater. Sci.* **2017**, 53, 1514. <https://doi.org/10.1007/s10853-017-1577-5>
- [28] P. C. H. Castillo, S. R. Manuel, F. Ruiz, V. R. González, *Sustain. Environ. Res.* **2022**, 32, 1. <https://doi.org/10.1186/s42834-022-00116-z>
- [29] O. Mysiukiewicz, M. Barczewski, K. Skórczewska, D. Matykievicz, *Polymers* **2020**, 12, 1333. <https://doi.org/10.3390/polym12061333>

SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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Comparative performance of carbon nanotube and nanoclay on thermal properties and flammability behavior of amorphous polyamide/SEBS blend

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Abstract

Multiwall carbon nanotubes (CNT) or montmorillonite clay (MMT-30B) were added to a poly(hexamethylene isophthalamide-co-terephthalamine) (an amorphous polyamide - aPA) and styrene-ethylene/butylene-styrene graphitized with maleic anhydride (SEBS) blend, in different concentrations, in order to investigate the morphology, thermal properties and flammability behavior. Different nanoparticle localizations in the phase blend were observed through transmission electronic microscopy. CNT nanoparticles are localized in SEBS phase, and MMT-30B nanoparticles in aPA phase. No significant changes were observed on transition temperatures and thermal stability with both nanoparticle additions. However, a slight increase on storage modulus for clay nanocomposites and a slight reduction for carbon nanotube nanocomposites were observed, due to their different phase localizations. Regarding flammability, CNT nanocomposites showed better performance as a flame retardant when compared to samples with MMT-30B. Although the MMT-30B nanocomposites could not be classified according to the UL-94 criteria, no dripped flaming particles were observed, due to the a char barrier formation on the polymer surface. The CNT nanocomposites were classified according to the UL-94 criteria as V-2. The CNT's selective localization on the SEBS phase decreases its heat-release rate, but no interconnected network structure was formed in the matrix to suppress the dripping flaming particles.

KEYWORDS

blends, carbon nanotube, clay, flammability, polyamide, SEBS, thermal properties

1 | INTRODUCTION

Amorphous polyamides (aPA) have a lower processing temperature and moisture absorption and a better chemical resistance and thermal stability when compared to semi-crystalline polyamides.^{1,2} However, they present a low resistance to crack propagation. Huang et al.³ and Yoo et al.⁴ studied the toughening of amorphous polyamides with different rubbers and compatibilizing agents.

Huang et al.³ pointed out that the SEBS-g-AM showed better toughening in amorphous polyamide than in polyamides 6 and 6.6. Nevertheless, Wu et al.⁵ observed that toughening flame-retardant polyamides using blends with elastomers is difficult without harming the flame-retardant performance. SEBS-g-AM, for example, has an approximately 50% higher heat-release rate than polyamide. In their work, the authors observed that, by adding 20 wt% of flame retardant to polyamide, the flame

spontaneously and almost immediately extinguishes after the burner is removed from the sample, thus obtaining a V-0 rating. By adding 20 wt% of SEBS-g-AM, although there were no problems with dripping, the flame tended to persist longer, thus achieving a V-1 rating on UL-94. The authors concluded that adding the elastomer beyond a certain threshold can harm the blend's flammability properties.

Polymer nanocomposites are gaining prominence as materials that can have flame retardation and self-extinguishing properties in place of conventional halogenated compounds to avoid environmental concerns. Halogenated additives are great flame retardants, however, toxic acids are produced during combustion, restricting their applications.⁶ Carbon nanotubes (CNT) are, then, a promising alternative. By adding a small amount of carbon nanotubes, flame retardation has been reported to be increased over a wide range of polymers, such as polypropylene,⁷ polyethylene, ethylene vinyl acetate and polystyrene,⁸ poly(lactic acid),⁹ poly(methyl methacrylate),¹⁰ polyamides,¹¹ polycarbonate,¹² poly(ether-ether-ketone)¹³, and epoxy.¹⁴ The carbon nanotubes' effectiveness as flame retardants can be attributed to an interconnected protective layer formed during burning.¹⁵ Clays can also be used as flame retardants, but they predominantly act in the continuous phase, creating a carbonaceous layer that prevents heat and mass transfer.⁵ Araujo et al.¹⁶ observed a burning-rate reduction of a polyethylene-MMT nanocomposite by adding 3% of clay, without losing mechanical properties. Kaynak and Sipahioglu¹⁷ studied the nanoclay addition effects on polystyrene (PS) with triphenylphosphate retardant (TFF) via ultrasound intercalation, achieving a significant increase in flame retardancy with 5% of clay. Other polymer materials were tested, such as polymethyl methacrylate (PMMA),¹⁸ acrylonitrile butadiene styrene (ABS)¹⁹ and polyurethane (PU),²⁰ and promising results were found.

However, in a ternary system (two polymers and one particle), property improvement is closely connected to the nanoparticles' localization. The factors responsible for the nanoparticles' selective localization in polymer blends are thermodynamic, rheological and kinetic aspects,²¹ as well the nanoparticles' geometry.²² Nanoparticles in immiscible polymer blends are known to be localized in the matrix, in the dispersed phase, or at the interface.²³ In the specific case of polymer blends that tend to adopt the dispersed phase morphology, different mechanisms that influence blend morphology depending on the nanoparticles' selective localization can be verified.²⁴ When the nanoparticles are localized in the continuous phase, the dispersed phase domain diameter is often reduced due to an increase in the matrix viscosity caused

by them. That is an interesting reduction for matrix toughening, as a size reduction in the rubber phase is a key issue for toughening in thermoplastic matrices.²⁵ The nanoparticles' interfacial localization also yields a reduction in the dispersed phase size, due to a barrier that prevents the dispersed phase's coalescence. When the nanoparticles are homogeneously dispersed at the interface, they have the ability to increase adhesion between phases by reducing the interfacial tension between blending components.²⁶

With that scope, this work evaluates the effects of adding modified nanoclay or carbon nanotubes and their selective localization on the morphology, thermal properties and flammability behavior of aPA/SEBS nanocomposites.

2 | EXPERIMENTAL

2.1 | Material

The polyamide employed in this work was poly(hexamethylene isophthalamide co-terephthalamide) (PA6I-6T), Grivory G 21, from EMS-Chemie Holding AG, hereinafter simply called amorphous polyamide (aPA), and maleic anhydride graft styrene-ethylene-butylene-styrene (SEBS), RP6670, from Kraton. The nanoparticles were the multiple-wall carbon nanotubes purchased from Chengdu Organic Chemical with a diameter range of 10 to 30 nm and purity above 90%, and montmorillonite nanoclay Cloisite 30B, supplied by Southern Clay, called MMT-30B.

2.2 | Preparation method

Before processing, the aPA, the CNT, and the MMT-30B were dried in an oven with air circulation at 100°C for 8 hours, and the SEBS-g-MA was dried at 60°C for 6 hours in a similar equipment. The mixing of the aPA with the SEBS was performed manually, with a ratio (wt/wt) of 80% aPA and 20% SEBS. The carbon nanotubes and the MMT-30B were also manually added in different proportions, according to Table 1.

The nanocomposites were obtained from melt mixing in a twin-screw extruder with an $L/D = 40$ from AX Plastico. Processing temperatures ranged from 210°C to 250°C over nine zones, the screw speed was 100 rpm and the feeder speed was 10 rpm.

The approximately 0.30-mm-thick films were molded on a P15 ST Bovenau hydraulic press at a 15.27 MPa pressure, at 210°C for 2 minutes, and were used for DMA and TG analysis. The rectangular specimens were molded at

TABLE 1 Formulations with respective nanocomposite nomenclature

Nomenclature	aPA (%wt/wt)	SEBS (%wt/wt)	CNT (%wt/wt)	MMT-30B (%wt/wt)
aPA/SEBS	80	20	-	-
aPA/SEBS/0.25% CNT	80	20	0.25	-
aPA/SEBS/1.0% CNT	80	20	1.0	-
aPA/SEBS/0.25% MMT	80	20	-	0.25
aPA/SEBS/1.0% MMT	80	20	-	1.0

15.27 MPa, 270°C for 8 minutes, following the UL-94 dimensions for flammability testing, and were used for chemical and morphological analysis, conducted respectively through X-Ray photoelectron spectroscopy and transmission electron microscopy.

2.3 | Characterization

In order to evaluate the blend and nanocomposites' phase morphology, as well as the dispersion and nanoparticles' localization, transmission electron microscopy (TEM) analyses were performed on a Jeol JEM-2100. Ultrathin 30 nm sections were cut from the compression molded samples with a diamond knife at −70°C, using an RCM Power Tome X Ultramicrotome. They were collected on the surface of a water-dimethylsulfoxide (60/40 vol/vol) bath cooled to −85°C. The samples were stained with Ruthenium tetroxide for 1 hour and 30 minutes. To determine the dispersed phase size, Image J software was used. The dispersed phase average size was determined by measuring the rubbery phases' area, which was chosen due to the deformation of non-spherical domains when adding the nanoparticles for some nanocomposite. The particles were selected one by one, drawn and the software calculated the area. Approximately 60 domains were measured, and the SD was calculated.

Dynamic mechanical analysis (DMA) was performed in a DMA 242 E NETZSCH, under a nitrogen atmosphere in tensile mode. For the analysis, rectangular samples of 5 × 30 × 0.250 mm were heated from room temperature to 190°C at a frequency of 1 Hz and an amplitude of 10 μm, with a heating rate of 3°C/min.

Thermogravimetric analysis (TG) was performed using a NETZSCH 449C. A heating rate of 10°C/min was used under a nitrogen atmosphere, starting at room temperature (~ 25°C) up to 600°C.

The nanocomposites' flammability was evaluated according to the UL-94—*Standard for Tests for Flammability of Plastic Materials for Parts in Devices and Appliances*, on the vertical burn test mode. The test consists of applying a standard flame for 10 seconds twice,

measuring the sample combustion time until it self-extinguishes. The specimen is positioned vertically relative to the flame. A piece of cotton is placed at the bottom to verify any dripping of melted polymer material. The three ratings, V-2, V-1, and V-0 (best) indicate that the material was tested in a vertical position and self-extinguished within a specified period after the ignition source was removed. Those ratings also indicate whether the test specimen dripped flaming particles that ignited the cotton indicator mentioned above. Five specimens of each formulation with dimensions of 100 × 65 × 3.5 mm were used. The burned surface morphology was analyzed by field emission electron microscopy (FEG-SEM) in a JSM 6701F-JEOL microscope at a 10 kV voltage.

The carbon bonds on the tip of the burned specimens were identified through X-ray photoelectron spectroscopy (XPS). The analyses were performed using a K-Alpha Thermo Scientific spectrometer, at a pressure below 10^{−7} mBar. The XPS parameters were: X-ray Al-Kα ($h\nu = 1486.6$ eV) excitation, 50 eV pass energy for survey and 10 eV for high-resolution scans. The spectra deconvolution was performed using the Voigtian function, with Gaussian (70%) and Lorentzian (30%) combinations, and the full width at half maximum ranged from 1.0 to 2.0 eV.

3 | RESULTS AND DISCUSSION

Figure 1A shows the aPA/SEBS blend morphology, the SEBS rubbery phase is notably regularly dispersed in the aPA matrix and has a predominantly spherical geometry, with an average size of $48.8 \pm 27.6 \mu\text{m}^2$. In the ternary system with CNT, Figure 1B,C, the CNT's selective localization is in the SEBS phase. Such selective localization behaves as predicted by the thermodynamic analysis using the harmonic method to determine the interfacial tension and the wettability parameter shown in Table 2.²⁹ The rheological factor is also satisfied, since the SEBS has a lower viscosity than the aPA (for a shear strength rate of 500 seconds^{−1} at 245°C, the aPA and the SEBS viscosities are 254.8 and 143.2 Pa s, respectively).³⁰

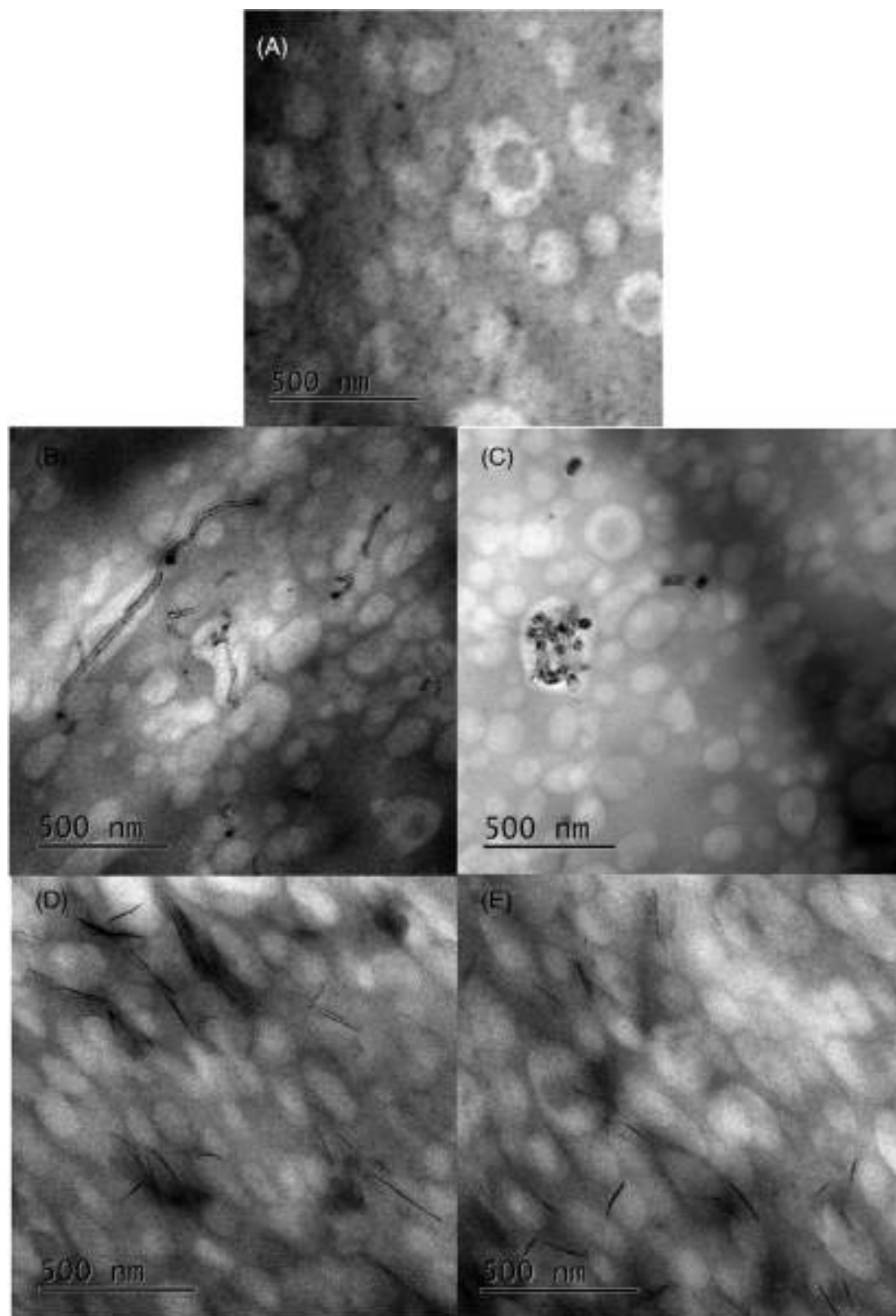


FIGURE 1 TEM micrograph for aPA/SEBS (A), aPA/SEBS/1.0% CNT (B and C), and aPA/SEBS/1.0% MMT-30B (D and E)

Some deformation is observed in the SEBS domains, changing the spherical geometry (pure system) into elongated or ellipsoidal forms, consequently yielding an area

increase in relation to the pure system. The increase was of 54% ($73.7 \pm 53.04 \mu\text{m}^2$) for 0.25% CNT samples and 140% for 1.0% CNT samples ($150.0 \pm 71.2 \mu\text{m}^2$). Such an

increment can be explained by the fact that the CNT are localized within the rubbery phase, so that phase's chains are adsorbed onto the nanoparticles' surface, causing a significant difference in dimension.^{27,31}

Figure 1D,E shows that, in the ternary system with MMT-30B, the SEBS domains also suffered a geometry deformation, becoming ellipsoidal, as well as, the fact that the MMT-30B is well distributed and intercalated with the exfoliated clay regions. Samples with 0.25% MMT-30B increased the rubbery phase area by 37% ($65.6 \pm 38.5 \mu\text{m}^2$), and samples with 1.0% MMT-30B presented a 48% increase ($71.1 \pm 42.5 \mu\text{m}^2$). Farahani and Ramazani³² suggest that introducing the organoclay alters the viscosity ratio between the two polymers, thus reducing the SEBS-g-MA dispersibility in the polyamide matrix, resulting in larger rubbery phases. Unlike the CNT nanocomposites, the MMT-30B was preferably localized in the aPA phase. That selective localization disagrees with the thermodynamic prediction made by calculating the wettability coefficient with a value under 1 (Table 2),²⁹ and also with the rheological prediction that relates the preferred localization to the different viscosities. In this case, a combination of two other factors, the nanoparticle geometry and the polarity of the nanoparticle may enhance the interaction with the

matrix and contribute to the unexpected result. According to Gödel et al.,²² nanoplatelets cannot easily diffuse through a polymeric matrix because of their aspect ratio. Attari et al.³³ suggest that polarity should provide a good affinity between polyamides and clay. Thus, combining the inherent movement difficulty from nanoparticle geometry with the affinity between the aPA and the MMT-30B, contrary to the thermodynamic, rheological and kinetic factors, the MMT-30B was preferentially localized in the aPA matrix. Other researchers studied similar systems and

TABLE 2 Interfacial tension (mN m^{-1}) and wetting parameter of polymer-polymer and polymer-nanoparticle systems

Components	Interfacial tension (mJ m^{-2})	Wetting parameter (ω)
aPA/SEBS	0.7	-
aPA/CNT	14.9	-
SEBS/CNT	11.2	-
aPA/MMT	6.4	-
SEBS/MMT	3.1	-
aPA/SEBS/ CNT	-	-5.3
aPA/SEBS/ MMT	-	-4.7

Note: Measured through contact angle and calculated as reported in References 27 and 28.

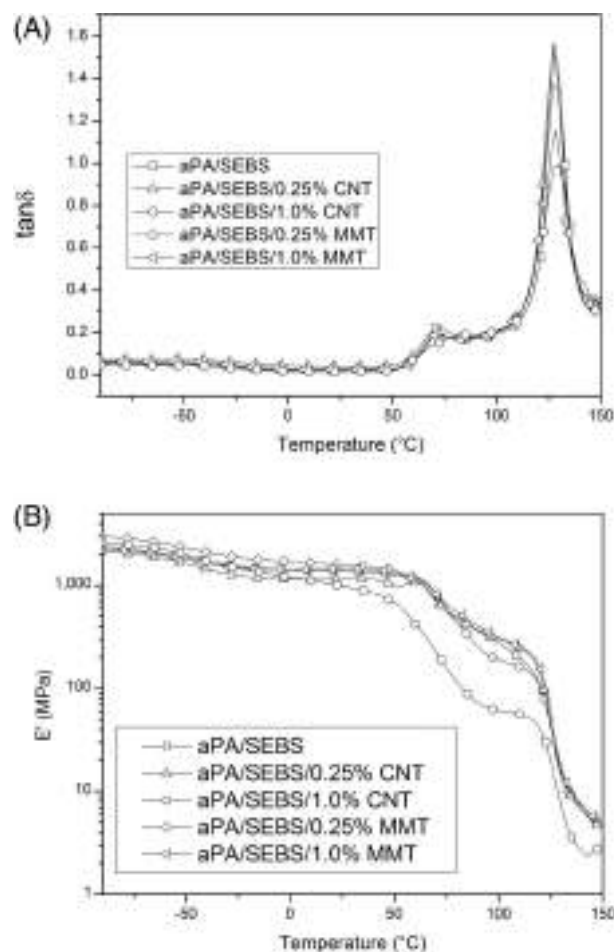


FIGURE 2 DMA curves (A) $\text{Tan}\delta$ vs temperature and (B) Storage Modulus (E') vs temperature of aPA/SEBS nanocomposites with CNT or MMT-30B

TABLE 3 Pure blend and nanocomposite thermal properties obtained by DMA and TG

Sample	T_g^1 ($^{\circ}\text{C}$)	T_g^2 ($^{\circ}\text{C}$)	E' at 25°C (MPa)	T_{onset} ($^{\circ}\text{C}$)	T_{peak} ($^{\circ}\text{C}$)
aPA/SEBS	-44	128	1375	425	456
aPA/SEBS/0.25% CNT	-43	127	1158	415	451
aPA/SEBS/1.0% CNT	-42	130	985	423	452
aPA/SEBS/0.25% MMT	-45	127	1588	422	457
aPA/SEBS/1.0% MMT	-42	128	1449	428	457

obtained the same results, such as Attari et al.,³³ with PA6/SEBS-g-AM/MMT-30B and Chow et al.,³⁴ with PA6/PP-g-AM/MMT.

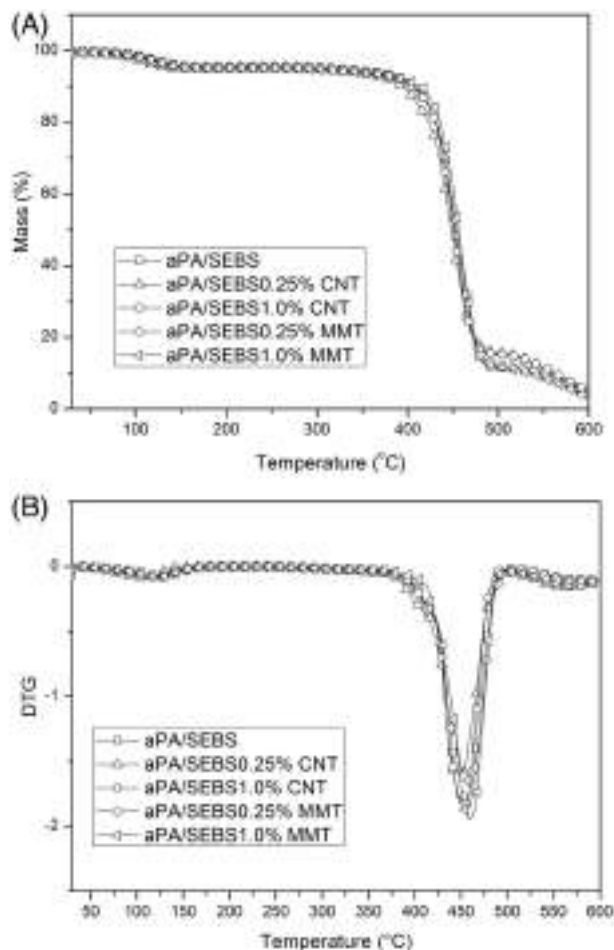


FIGURE 3 (A) TG and (B) DTG curves of aPA/SEBS nanocomposites with CNT or MMT-30B

Table 3 shows the glass transition temperature values obtained from $\text{Tan}\delta$ (Figure 2A) for the pure blend and its nanocomposites. Analyzing the glass transition region of the pure sample (aPA/SEBS), a T_g is observed at 128°C. Regarding nanocomposites, a small shift in T_g , within the equipment error ($\pm 2^\circ\text{C}$), is noticed in all cases. A small peak can be observed just below T_g , at around 74°C, which could be related to secondary chain segment relaxations in the aPA, due to the fact that the aPA is a copolymer and, possibly, a block copolymer.³⁵ According to the literature,^{36,37} SEBS has a T_g at around -50°C , which, in the analyzed samples, appeared at approximately -44°C . That value is in accordance with the one found by Muller et al.³⁸

Figure 2B shows the storage modulus curve as a function of temperature while Table 3 shows the value of E' for a temperature of 25°C. It shows that the Storage Modulus slightly increases for clay nanocomposites and has a slight reduction for carbon nanotube ones. Such behavior can be related to the nanoparticle nature and its location in the polymer blend. The clays are preferably localized in the amorphous polyamide phase and, due to their affinity with the matrix, stress transfer is facilitated. On the other hand, the CNT were localized in the rubbery phase, leading to a significant increase in the dispersed phase size beyond its form, which might have induced the storage modulus reduction.

Figure 3 presents the TG and DTG curves of aPA/SEBS nanocomposites, and Table 3 presents the T_{onset} and T_{peak} values. A small weight loss can be seen close to 100°C, which can be attributed to the release of adsorbed water, since polyamides easily absorb water. The nanocomposites with CNT present a slight T_{onset} and T_{peak} reduction, which can be related to the selective localization in SEBS phase.

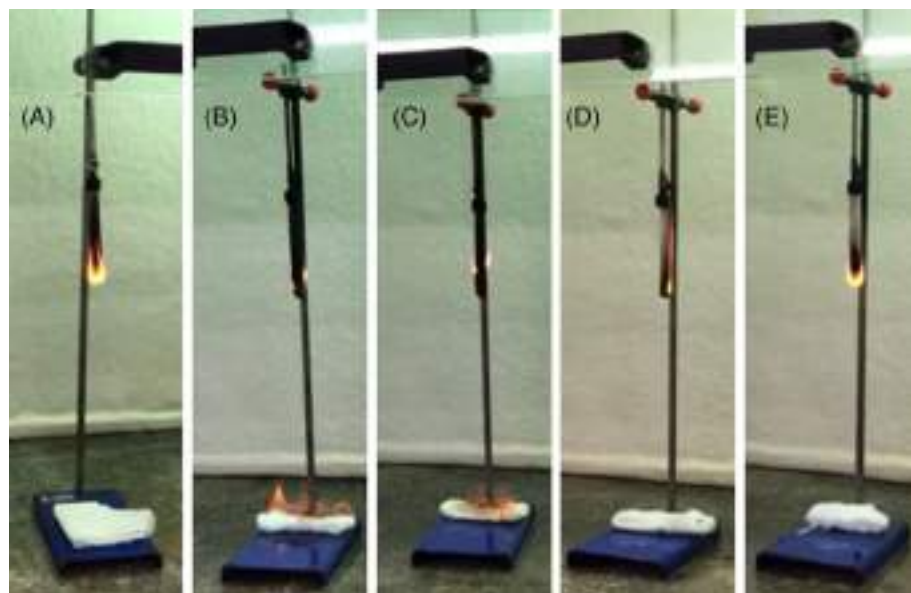


FIGURE 4 Flammability test images after a 28 seconds flame of (A) aPA/SEBS, (B) aPA/SEBS/0.25% CNT, (C) aPA/SEBS/1.0% CNT, (D) aPA/SEBS/0.25% MMT, and (E) aPA/SEBS/1.0% MMT [Color figure can be viewed at wileyonlinelibrary.com]

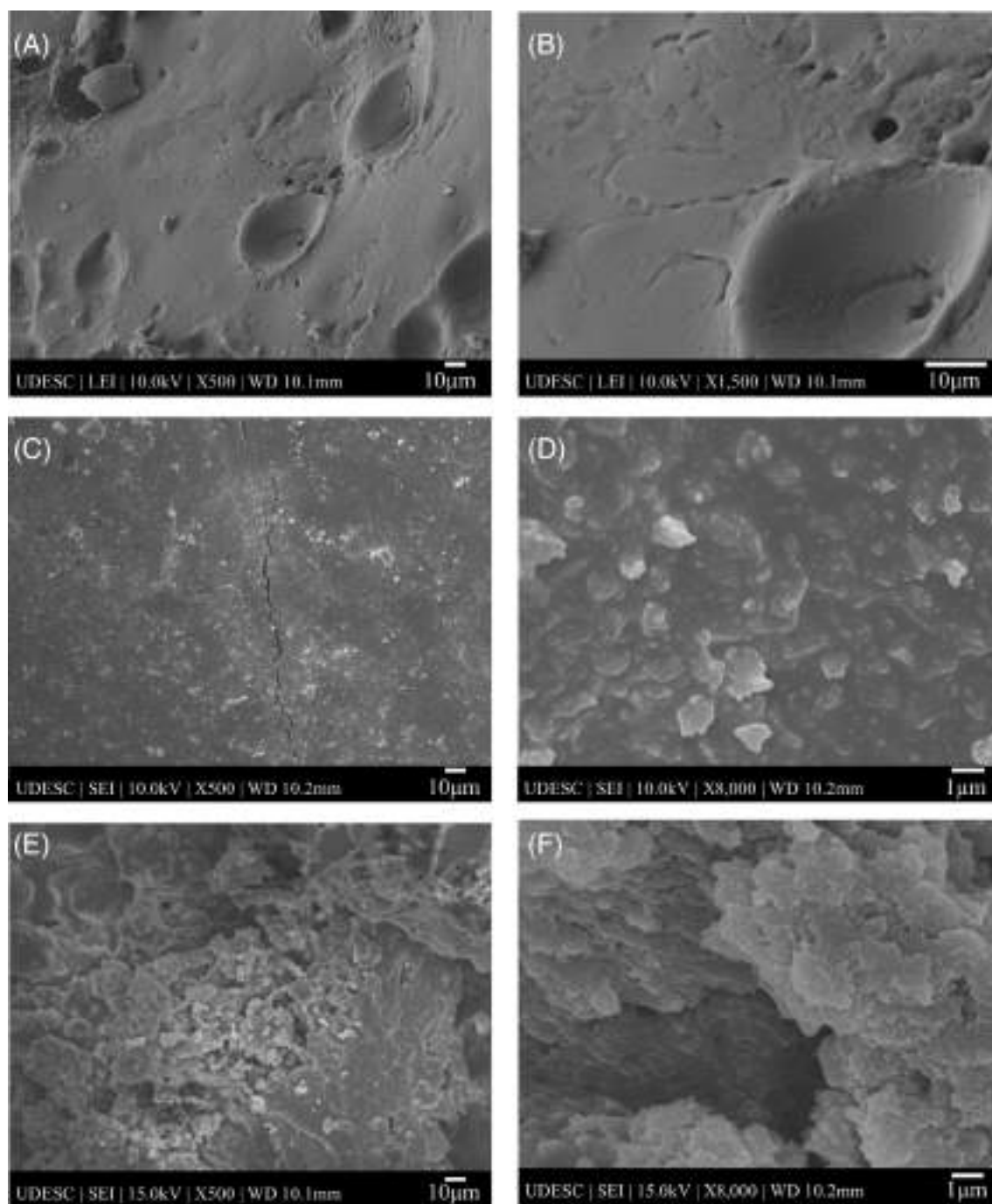


FIGURE 5 Burned surface FEG images of (A and B) aPA/SEBS, (C and D) aPA/SEBS/1.0% CNT, and (E and F) aPA/SEBS/1.0% MMT-30B

TABLE 4 C 1s XPS data for samples before (b) and after (a) burn, in atomic percent

Sample	C—C	C—N	C—O	C=O	N/C	O/C
aPA/SEBS ^b	90.71	7.82	0.33	1.13	0.086	0.016
aPA/SEBS ^a	92.07	5.43	1.38	1.11	0.059	0.027
aPA/SEBS/1.0% CNT ^b	91.51	8.24	0.24	-	0.090	0.003
aPA/SEBS/1.0% CNT ^a	94.22	5.72	0.06	-	0.061	0.001
aPA/SEBS/1.0% MMT ^b	90.39	8.23	0.56	0.82	0.091	0.015
aPA/SEBS/1.0% MMT ^a	85.42	10.53	1.48	2.56	0.123	0.047

Carbon nanotubes were preferably localized in the SEBS phase, which may have hindered energy dissipation and facilitated the onset of degradation in specific regions of the sample, causing such reduction. Other authors^{39,40} also observed a similar thermal stability reduction in polyamide with carbon nanotubes and nanoclay. Sheng et al.³⁹ affirmed that carbon nanoparticles, for example, may hinder the thermo-oxidation of PA6 in earlier degradation stages, thus increasing the composites' thermal stability, but that effect is not obvious under a nitrogen atmosphere, due to the lack of oxygen.

Regarding flammability tests, not all samples can be classified as UL94 standard compliant since, for most of them, t_1 could not be determined. The first flame extended all the way up to the fastener, requiring intervention to manually extinguish the fire, as shown in Figure 4. In summary, the pure blend continuously burned up to the fastener, which leads to the conclusion that there is little/no flame resistance, an already expected

result due to the blend's nature. In Figure 5A,B, voids from the SEBS phase can be observed, which could indicate that the SEBS is consumed first because of its high flammability. As for the samples with MMT-30B, in general, there was no significant improvement in flammability if compared to the pure blend. However, for the 1% MMT-30B nanocomposites, no dripped flaming particles were observed on the cotton. Such effect is mainly attributed to the formation of a char barrier on the polymer's surface, which insulates the underlying materials and slows down the mass-loss rate of decomposition products during pyrolysis and combustion, as observed in Figure 5E,F. In fact, as the XPS results show in Table 4, the N/C ratio, obtained from C 1s deconvolution (Figure 6), is higher for 1% MMT-30B nanocomposites, which can be associated with those barriers that inhibit the release of NH_3 , thus more N is available for char formation.⁴¹ However, clays have failed to act as stand-alone flame retardants due to only having minor effects in reducing the total heat release, since nanocomposites do not self-extinguish even after a protective char is formed, until most of the fuel has burned out.⁴² According to the literature, higher MMT concentrations are needed to improve flame resistance, as Nemati et al.⁴³ added 5 wt% MMT to polystyrene and Monti et al.⁴⁴ used 2% of MMT in polyamide 6.

When the samples with CNT (Table 5) are analyzed, the t_1 and t_2 sum, according to the UL-94 criteria, could be classified as V-1. However, as all samples presented dripping and cotton burning, the rating fell to V-2. For the samples in which the parameter $t_1 + t_2$ was higher than the threshold established by the evaluation criteria (Table 5), the classification could not be performed and they were labeled "NC" (not classified).

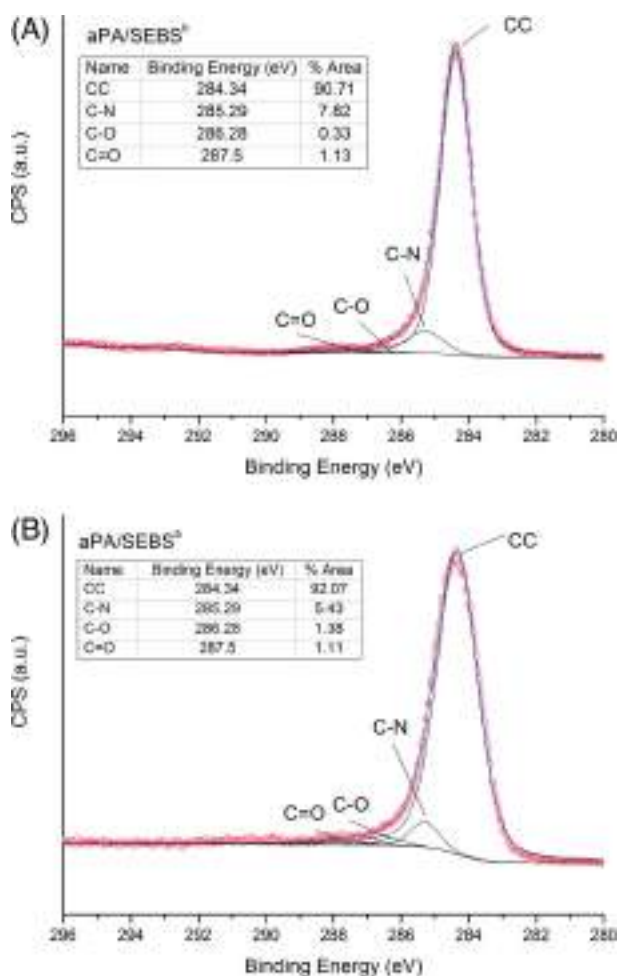


FIGURE 6 XPS C 1s deconvolution for samples (A) aPA/SEBSb, (B) aPA/SEBSa. For C 1s deconvolution of all other samples (see Supporting Information). b, before burned; a, after burned [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 5 Nanocomposite classification according to UL-94

Nomenclature	$t_1 + t_2$ (s)	Dripped flaming particles on the cotton	UL-94 Classification
aPA/SEBS	-	Yes	NC
aPA/SEBS/0.25% CNT	136	Yes	V-2
aPA/SEBS/1.0% CNT	169	Yes	V-2
aPA/SEBS/0.25% MMT	-	Yes	NC
aPA/SEBS/1.0% MMT	-	No	NC

Abbreviation: NC, not classified.

Qualitatively speaking, in general, samples with CNT performed better than the other two groups (pure and MMT-30B), even though small amounts of nanoparticles were used in their compositions. Such positive results are in accordance with the literature,¹⁵ which predicts good flame retardancy in smaller CNT quantities than usually applied in conventional additives. Indeed, among all analyzed samples, the CNT nanocomposite was the only one to improve flame retardancy. Table 4 presents the oxygen/carbon ratio obtained from XPS, which is in accordance with that observation, once the O/C only reduced when burning for the aPA/SEBS/1.0% CNT sample. For the other samples, aPA/SEBS and aPA/SEBS/1.0% MMT-30B, the O/C increased after the flame test, indicating that oxygen was able to reach the blend and sustain the fire. In Figure 5C,D, no char or voids can be observed on the surface of the polymer, as observed in nanocomposites with clay and the pure blend. Schartel et al.¹¹ observed dripping suppression on PA6/CNT nanocomposites, which they attributed to the interconnected network structure of the CNT causing the fixing of the melt. In that case, no char layer and no interconnected network structure was formed in the matrix, and the aPA molten material flowed down due to its localization in SEBS phase. However, the CNT's selective localization on the SEBS phase decreases its heat release rate,¹⁵ and a typical UL classification for polyamides was obtained.^{5,11,39}

4 | CONCLUSION

In this study, the aPA/SEBS blend and nanocomposites with CNT or MMT-30B were prepared in a co-rotating twin-screw extruder and morphology, thermal properties and flammability behavior were evaluated. TEM showed that nanoparticles were in different localizations in the phase blend: CNT nanoparticles were localized in the SEBS phase and MMT-30B nanoparticles in the aPA phase, due to the affinity between the nanoparticles and the polymers. No significant changes were observed on transition temperatures and thermal stability with both nanoparticle additions. However, a slight increase on storage modulus for clay nanocomposites and a slight reduction for carbon nanotube nanocomposites were observed, due to their different phase localization.

Nanocomposites with CNT present a better flame-retarding performance and could be classified according to the UL-94 criteria as V-2. The CNT selective localization on the SEBS phase reduces the heat release rate, but no interconnected network structures were formed in the matrix to suppress the dripping of flaming particles. XPS results also show a reduction in the O/C rate for those nanocomposites, which can indicate that the CNT

prevent the oxygen from reaching the blend, so less oxygen is available to sustain the burning. However, for nanocomposites with 1.0% MMT-30B, no dripping flaming particles were observed on the cotton. This effect is mainly attributed to the formation of a char barrier on the surface of the polymer, which could be observed by FEG-SEM. XPS results presented a higher N/C ratio for these nanocomposites, which can be associated to such barrier that inhibits the release of NH₃, thus more N is available for char formation.

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REFERENCES

- [1] J. Canales, M. Fernandez, J. J. Pena, M. E. Munoz, A. Santamaria, *Polym. Eng. Sci.* **2015**, 55, 1142.
- [2] T. Cousin, J. Galy, J. Dupuy, *Polymer* **2012**, 53, 3203.
- [3] J. J. Huang, H. Keskkula, D. R. Paul, *Polymer* **2006**, 47(2), 639.
- [4] Y. Yoo, R. R. Tiwari, Y. T. Yoo, D. R. Paul, *Polymer* **2010**, 51(21), 4907.
- [5] H. Wu, M. Krifa, J. H. Koo, *Fiber Polym.* **2018**, 19(7), 1500.
- [6] S. Lee, H. M. Kim, D. G. Seong, D. Lee, *Carbon* **2019**, 143, 650.
- [7] T. Kashiwaga, E. Grulkeb, J. Hilding, et al., *Polymer* **2004**, 45(12), 4227.
- [8] M. C. Costache, M. J. Heidecker, E. Manias, et al., *Polymer* **2007**, 48(22), 6532.
- [9] T. D. Hapuarachchi, T. Peijs, *Compos. A Appl. S* **2010**, 41(8), 954.
- [10] T. Kashiwagi, M. Mu, K. Winey, et al., *Polymer* **2008**, 49(20), 4358.
- [11] B. Schartel, P. Pötschke, U. Knoll, M. Abdel-Goad, *Eur. Polym. J.* **2005**, 41(5), 1061.
- [12] B. Schartel, U. Braun, U. Knoll, et al., *Polym. Eng. Sci.* **2007**, 48(1), 149.
- [13] P. Patel, A. A. Stec, T. H. Hull, et al., *Polym. Degrad. Stab.* **2012**, 97(12), 2492.
- [14] S. S. Rahatekar, M. Zammarano, S. Matko, et al., *Polym. Degrad. Stab.* **2010**, 95(5), 870.
- [15] X. Wang, E. N. Kalali, J. T. Wana, D. Y. Wang, *Prog. Polym. Sci.* **2017**, 69, 22.
- [16] E. M. Araujo, E. Hage Jr., *Polímeros* **2003**, 13(3), 205.
- [17] C. Kaynak, B. M. Sipahioglu, *J. Fire Sci.* **2013**, 31(4), 339.
- [18] A. Laachachia, E. Leroyb, M. Cocheza, M. Ferriola, J. M. L. Cuesta, *Polym. Degrad. Stab.* **2005**, 89(2), 344.
- [19] S. Wang, Y. Hua, R. Zonga, Y. Tanga, Z. Chenb, W. Fana, *Appl. Clay Sci.* **2004**, 25, 49.
- [20] G. Huang, J. Gao, Y. Li, L. Han, X. Wang, *Polym. Degrad. Stab.* **2010**, 95(2), 245.

- [21] D. Wu, D. Lin, J. Zhang, et al., *Macromol. Chem. Phys.* **2011**, 212(6), 613.
- [22] A. Göldel, A. Marmur, G. R. Kasaliwal, P. Pötschke, G. Heinrich, *Macromolecules* **2011**, 44(15), 6094.
- [23] M. Sumita, K. Sakata, S. Asai, K. Miyasaka, H. Nakagawa, *Polym. Bull.* **1992**, 25(2), 265.
- [24] R. R. Tiwari, D. L. Hunter, D. R. Paul, *J. Polym. Sci. Pol. Phys.* **2012**, 50(22), 1577.
- [25] Y. C. Ahn, D. R. Paul, *Polymer* **2006**, 47(8), 2830.
- [26] J. P. Mofokeng, A. S. Luyt, *Polym. Test.* **2015**, 45, 93.
- [27] J. Aguiar, M. Decol, W. M. Pachekoski, D. Becker, *Polym. Eng. Sci.* **2019**, 59(2), 323.
- [28] M. Decol, W. M. Pachekoski, D. Becker, *J. Appl. Polym. Sci.* **2018**, 135(6), 44849.
- [29] F. Fenouillot, P. Cassagnau, J. C. Majesté, *Polymer* **2009**, 50(6), 1333.
- [30] J. Feng, C. M. Chan, J. X. Li, *Polym. Eng. Sci.* **2003**, 43(5), 1058.
- [31] H. Zou, K. Wang, Q. Zhang, Q. Fu, *Polymer* **2006**, 47(22), 7821.
- [32] R. D. Farahani, A. Ramazani, *Mater. Design.* **2008**, 29(1), 105.
- [33] M. Attari, A. Arefazar, G. Bakhshandeh, *Polym. Eng. Sci.* **2014**, 55(1), 29.
- [34] W. S. Chow, Z. A. M. Ishak, J. K. Kocsis, *Macromol. Mater. Eng.* **2005**, 290(2), 122.
- [35] M. R. R. Hamester, C. Dalmolin, D. Becker, *J. Appl. Polym. Sci.* **2019**, 136(45), 48195.
- [36] M. Sahnoune, A. Taguet, B. Otazaghine, M. Kaci, J. M. L. Cuesta, *Eur. Polym. J.* **2017**, 90, 418.
- [37] D. Tomacheski, M. Pittol, C. E. Ermel, D. N. Simões, V. F. Ribeiro, R. M. C. Santana, *Polym. Bull.* **2017**, 74(12), 4841.
- [38] D. Muller, M. Garcia, G. V. Salmoria, A. T. N. Pires, R. Paniago, G. M. O. Barra, *J. Appl. Polym. Sci.* **2010**, 120(1), 351.
- [39] Z. Sheng, G. Jia, S. Yongyuan, et al., *Polym. Compos.* **2019**, 40, E1884.
- [40] W. Hea, J. Gaoa, S. Liaoc, X. Wangc, S. Qinc, P. Song, *Compos. Commun.* **2019**, 13, 143.
- [41] B. Yuan, A. Fan, M. Yang, et al., *Polym. Degrad. Stab.* **2017**, 143, 42.
- [42] W. T. He, S. T. Liao, Y. S. Xiang, L. J. Long, S. H. Qin, J. Yu, *Polymer* **2018**, 10(3), 312.
- [43] M. Nemati, H. K. Eslam, M. Talaeipour, B. Bazayr, A. Samariha, *BioResources* **2016**, 11(1), 748.
- [44] M. Monti, S. A. Tsampas, S. P. Fernberg, et al., *Polym. Degrad. Stab.* **2015**, 121, 1.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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RESEARCH ARTICLE

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The effects of nanoclay and carbon nanotube co-addition on properties of an amorphous polyamide/maleated styrene-ethylene-co-butylene-styrene blend

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2020TR716; CNPq; CAPES**Abstract**

This work studied the individual and combined addition of natural (MMT-Na) and modified (MMT-30B) nanoclays, and carbon nanotubes (CNTs) to a poly (hexamethylene isophthalamide co-terephthalamide) (aPA)/styrene-ethylene/butylene-styrene (SEBS) blend grafted with maleic anhydride. Their effects on the blend's morphology, thermo-mechanical properties, and flammability were evaluated. Morphological analysis showed that both clays were located in the aPA matrix, with the MMT-Na as agglomerates and the MMT-30B intercalated with exfoliated regions. The CNTs were dispersed and randomly oriented in the aPA matrix. Data obtained through dynamic-mechanical analysis (DMA) showed that adding 1.0% MMT-30B and 1.0% CNT increased the storage modulus (E') by 26% and 27%, respectively, while adding both 0.5% MMT-30B and 0.5% CNT increased E' by 38%, suggesting synergy between the nanoparticles related to mechanical properties. Regarding flammability, since the first burn timing (t_1) could not be obtained, none of the samples could be classified according to the UL94 standard. However, qualitatively, a better flammability performance was noticed for the nanocomposites than for the pure blend.

KEYWORDS

carbon Nanotube, clay, dynamic-mechanical properties, flammability, polyamide, SEBS

1 | INTRODUCTION

Adding nanoparticles to immiscible polymer blends can affect the resulting material's properties in several ways, improving mechanical, thermal, electrical, barrier, and flame retardancy characteristics, among others.^[1–5] When nanoparticles are added to an immiscible polymer blend, they can be in one of the polymer phases, at the interface, or in both phases. The particles' location is an important parameter that can directly affect the material's final properties and depends on thermodynamic, rheological, and kinetic factors, their geometry and their aspect ratio. In general, a hybrid system's final properties

are related to the individual properties of their constituents, the dispersion and nanoparticle location in the mixture, and the phase morphology formed in the processing.^[1–4]

Quaternary hybrid systems of polymer composites draw the interest of many researchers, as they offer a range of properties that cannot be achieved with a single type of particle. In those systems, two different particles can be used, which produce the so-called hybrid structures, in which properties of different components are combined. To prepare high-performance hybrid compounds, the particles' dispersion and their interfacial interaction with the matrix are considered a major

subject. Recent works^[6–11] have shown that those polymer nanocomposites exhibited superior properties to those obtained by adding individual particles, due to the existence of potential synergy between them. The main particles used in those studies are carbon nanoparticles and nanoclays, the former due to their improvement in mechanical, electrical, and thermal properties in relatively low loads, and the latter due to their leading to easily processability and better barrier properties, besides being economically and industrially viable.^[12] Bouakaz et al.^[6] observed a synergistic effect between organomodified montmorillonite nanoparticles (MMT-30B and MMT-15A) and graphene in a PLA/PCL blend, yielding an increased thermal resistance and water vapor permeability in the quaternary nanocomposite. A better MMT exfoliation and intercalation and an improved graphene nanoparticle dispersion were also observed. Adrar et al.^[11] studied the synergistic effect of graphene and organomodified montmorillonites (MMT-30B and MMT-15A) in a PLA and poly(butylene adipate-co-terephthalate) (PBAT) blend. They observed that graphene/MMT interactions affected the nanoparticle dispersion, leading to synergy in the quaternary nanocomposite, increasing complex viscosity, and storage modulus. In the work of Sivanjineyulu et al.,^[10] 0.5% to 3.0% (m/m) of carbon nanotubes and 1.0% of MMT-15A clay were added to a polypropylene (PP) and poly(butylene succinate) (PBS) blend. The authors observed an increase in thermal stability and in Young's modulus, and a reduction in the toughness of the quaternary mixtures. Sanusi et al.^[12] also presented several works in which carbon nanotubes and montmorillonite were used to produce polymeric nanocomposites, resulting in remarkable rheological, morphological, and thermal properties, as well as an improvement in tribology, mechanical and electrical properties.

Nanoparticles have been attracting attention as materials with flame retardancy properties, replacing conventional halogenated compounds, which are considered environmentally unsafe due to the potential toxicity of their decomposition products. Besides, they also replace non-halogenated flame retardant compounds that, despite not being toxic, are needed in very large amounts to produce flame retardancy, consequently degrading the mechanical properties of the material, also restricting its applications.^[13,14] According to Nemati et al.,^[15] one advantage of using nanoclays in nanocomposites is the reduction in the ignition rate, which depends on the proportion in which they are added to the polymer. When a nanocomposite is heated, the polymer melts and generates volatile compounds, which will lead to structural deterioration and the formation of smaller intercalation spaces between the silicate or the clay layers. A carbonaceous layer is formed

on the surface of the material during firing, creating a protective barrier to heat and mass transfer. This structure quickly forms under pyrolysis and remains stable even after its completion.^[15,16] According to Wang et al.,^[17] carbon nanotubes act in the condensed phase of the polymer. Its effectiveness can be attributed to the formation of a network-structured protective layer covering the sample surface during burning, acting as an insulating barrier, reducing the emission of volatile compounds, and decreasing the mass-loss rate.

Regarding the matrix, despite all the advantages, polyamides have low resistance to crack propagation and, when there are defects, they break easily.^[18] Polymer toughening has been a recurring topic in academic research and industry to circumvent this problem. An example of an elastomer used for this purpose in blends with polyamides is styrene-ethylene/butylene-styrene (SEBS). Compatibilizing agents, such as maleic anhydride, which reacts with the terminal amine groups of polyamides, are used to improve the adhesion between the elastomer and the polyamide.^[19] Huang et al.,^[20] in their research, varied the amount of SEBS/SEBS-g-AM from 5% to 20% (w/w) in different polyamides, which were polyamide 6, 6.6, and an amorphous polyamide, obtaining good results in the impact test. Besides, the blends of SEBS-g-AM with aPA showed better toughening than those with polyamides 6 and 6.6.

Elastomers are known to be highly flammable. Studies show that SEBS-g-AM has an approximately 50% higher heat-release rate than polyamide. Furthermore, when polyamide is burned, it generates large amounts of smoke and dripping.^[14,21] Thus, PA/SEBS-g-AM blends are a difficult system to achieve good flammability properties, even when using conventional flame retardants, which require high concentrations, affecting the mechanical properties and reducing the effects of material toughening.^[21] The addition of nanoparticles, such as nanoclays and carbon nanotubes, which are added in small amounts, is, therefore, a promising alternative to the use of flame retardants in a such system.

This work studies the influence of individually and simultaneously adding natural (MMT-Na) and/or modified (MMT-30B) montmorillonite clay and carbon nanotubes (CNTs) on the dispersion and nanoparticles' location, and on the properties of amorphous polyamide (aPA) and styrene-ethylene/butylene-styrene blend grafted with maleic anhydride (SEBS-g-AM). The nanoparticles' dispersion and location were evaluated using transmission electron microscopy (TEM), the thermo-mechanical properties using dynamic-mechanical analysis (DMA) and flammability was evaluated through the UL94 vertical burn test mode and X-ray photoelectron spectroscopy (XPS) results.

2 | EXPERIMENTAL PROCEDURE

2.1 | Materials

An amorphous polyamide, poly (hexamethylene isophthalamide co-terephthalamide) (aPA), (MFI [275°C, 5 kg], 23.6 g/10 min) Grivory G 21, from EMS-Chemie Holding AG, and maleic anhydride grafted styrene-ethylene-butylene-styrene (SEBS), (MFI [230°C, 5 kg], 22 g/10 min, rubber/styrene ratio 70/30) FG1901G, from Kraton, were used. The carbon nanotubes (CNTs) used are multi-walled obtained from Chengdu Organic Chemical, with diameters ranging from 10 to 30 nm, an average length of 10–30 μm , and purity above 90%. The montmorillonite nanoclays Cloisite® Na + and Cloisite® 30B, referred to in this work as MMT-Na, and MMT-30B, respectively, were supplied by Southern Clay.

2.2 | Nanocomposite preparation

The blend used in this work was prepared with a ratio of 80% aPA and 20% SEBS (wt/wt). In our previous work,^[22] the best results for flammability behavior were with 1.0% of nanoparticles, so we used this concentration. We started this research by studying differences in nanoparticles proportion (1:1, 1:2, and 2:1). The preliminary results did not show significant differences, so we opted to continue the study only with the 1:1 ratio. Before processing, the aPA, MMT-Na and MMT-30B were dried in an air-circulating oven at 100°C for 8 h, and the SEBS-g-MA was similarly dried at 60°C. The nanocomposites were obtained from melt-mixing all the components at the same time (without pre-blending) in a twin-screw extruder with an L/D = 40, from AX Plastico. Processing temperatures ranged from 210°C to 250°C over nine zones, the screw speed was 100 rpm and the feeder rate was 1.4 kg/h. The approximately 0.20-mm-thick films were molded on a P15 ST Bovenau hydraulic press at 15 MPa, at 210°C for 2 min, and were used for the DMA analysis. The rectangular specimens were molded at 15 MPa, 270°C for 8 min, following the UL-94 dimensions for flammability testing, and were used for chemical and morphological analyses, conducted respectively through X-ray photoelectron spectroscopy and scanning and transmission electron microscopy.

2.3 | Nanocomposite characterization

The phase morphology and nanoparticle location were evaluated using transmission electron microscopy (JEOL JEM – 2100 TEM). The samples were cut into 30-nm-thick thin sections in an RCM Power Tome X ultramicrotome

equipped with a diamond knife at –70°C. The samples were stained with ruthenium tetroxide for 1.5 h. Emission scanning electron microscopy (FE - SEM) in a Jeol JSM 6701F was also used to analyze the dispersed phase size. The specimens were subjected to cryogenic fracture after being submerged in liquid nitrogen. Then, the fractured surfaces were submerged in xylene for six days to extract the rubbery phase (SEBS), as performed by Hoor et al.^[23] and by Babaei and Arefazar.^[24] To determine the size of the dispersed phases, the Image J software was used. Approximately 300 domains were measured, and the standard deviation was calculated.

Dynamic mechanical analysis (DMA) was performed in a NETZSCH DMA 242 E, under a nitrogen atmosphere in tensile mode at a frequency of 1 Hz. For the analysis, rectangular samples of 5 mm $\times$ 30 mm $\times$ 0.250 mm were heated from room temperature to 190° with a heating rate of 3°C/min.

The nanocomposites' flammability was evaluated according to the UL-94 - *Standard for Tests for Flammability of Plastic Materials for Parts in Devices and Appliances*, using the vertical burn test mode, which consists of applying a standard flame for 10 s twice, measuring the sample combustion time and its self-extinguishment from the fire. The specimen is positioned vertically relative to the flame. Other parameters recorded for each test are whether the flame reaches the top of the sample and whether the cotton under the specimen is ignited by drops of the burning sample. Five specimens of each formulation with dimensions of 100 mm $\times$ 65 mm $\times$ 3.5 mm were used.

X-ray photoelectron spectroscopy (XPS) analyses, before and after flammability testing, were conducted in a Thermo Scientific spectrometer (K-Alpha), operating at 10^{-7} mBar base pressure. An Al-K α X-ray ($h\nu = 1486.6$ eV) was used as the excitation source and the pass energy was set to 200 eV for a survey and 20 eV for high-resolution scans. Spectrum deconvolutions were performed using the Voigtian function, a combination of Gaussian (70%) and Lorentzian (30%) profiles.

3 | RESULTS AND DISCUSSIONS

Figure 1 shows TEM micrographs of the aPA/SEBS nanocomposites. The rubber phase of SEBS (light region) is observed dispersed in the aPA matrix (dark region), adopting a spherical geometry with approximately homogeneous dimensions. The addition of nanoparticles did not cause changes in the blends' morphology. This is confirmed through FEG-SEM images (Figure 2) with the SEBS phase extraction: the average phase size is about 0.15 ± 0.05 μm (Table 1). The blend also presents a good adhesion between phases due to the maleic anhydride found in the SEBS phase.

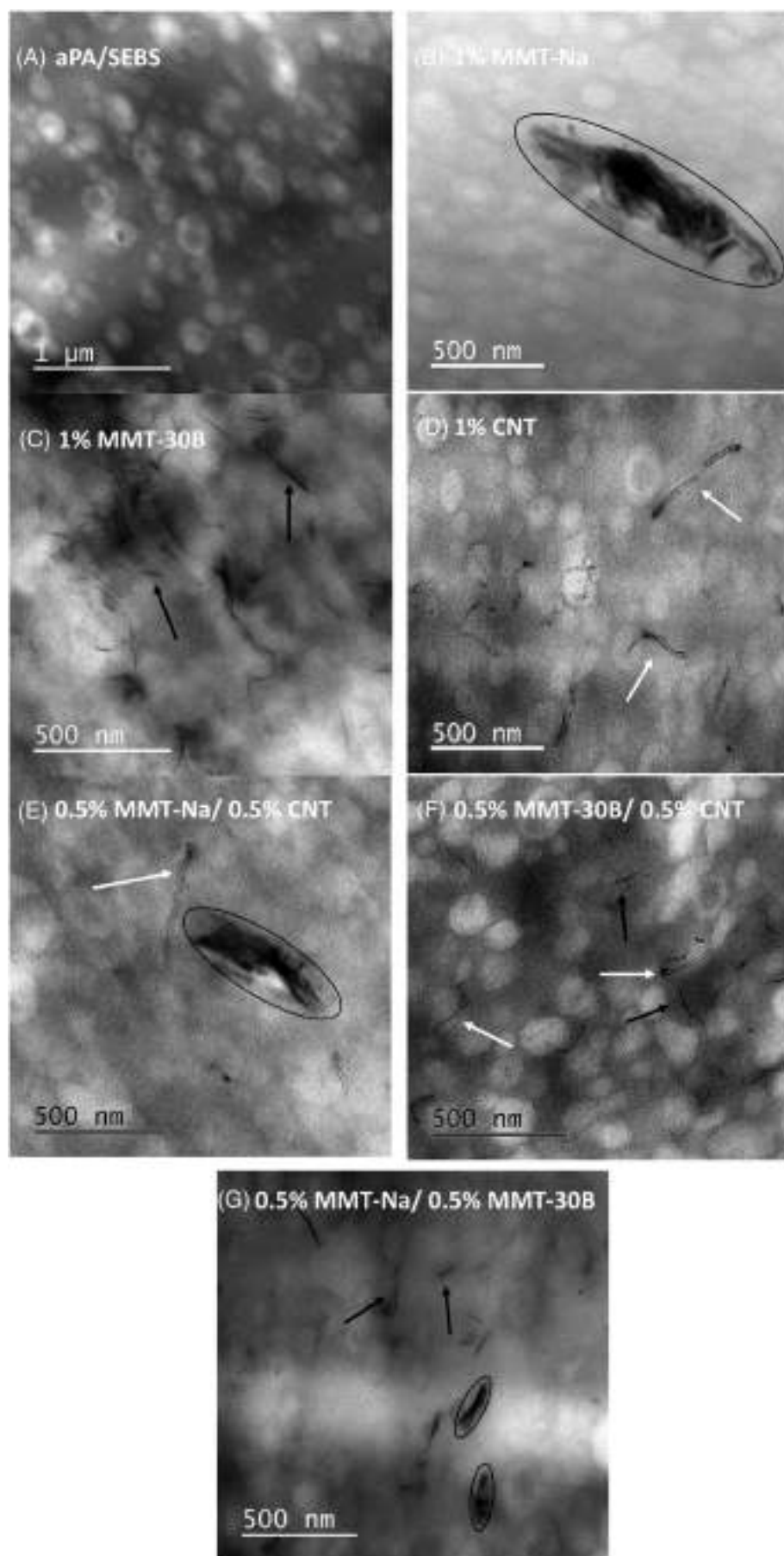


FIGURE 1 TEM Images obtained from the pure blend (A) aPA/SEBS and its nanocomposites: (B) 1% MMT-Na; (C) 1% MMT-30B; (D) 1% CNT; (E) 0.5% MMT-Na/0.5% CNT; (F) 0.5% MMT-30B/0.5% CNT; (G) 0.5% MMT-Na/0.5% MMT-30B. MMT-Na is highlighted by ellipses, MMT-30B by black arrows and CNTs by white arrows

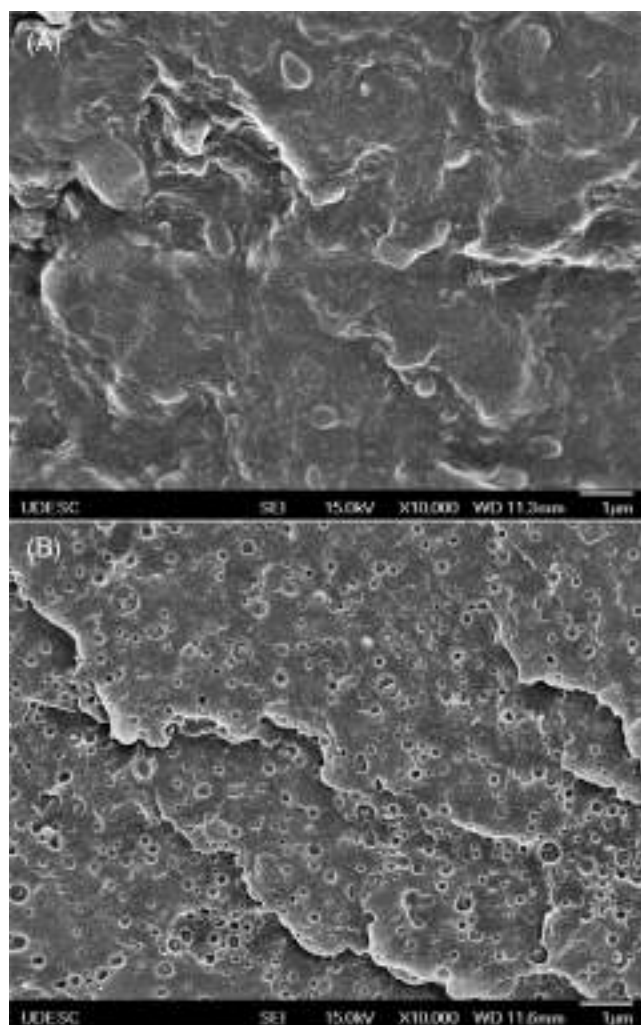


FIGURE 2 FEG-SEM images of aPA/SEBS blend (A) before and (B) after SEBS phase extraction performed with xylol

TABLE 1 Area (μm^2) and mean diameter (μm), with the corresponding standard deviation, of the dispersed SEBS phase

Sample	Area (μm^2)	Diameter (μm)
aPA/SEBS	18.87 ± 12.76	0.15 ± 0.05
1% MMT-Na	12.10 ± 7.12	0.12 ± 0.03
1% MMT-30B	14.99 ± 8.82	0.13 ± 0.04
1% CNT	12.50 ± 7.26	0.12 ± 0.03
0.5% MMT-Na/0.5% CNT	15.55 ± 10.17	0.14 ± 0.04
0.5% MMT-30B/0.5% CNT	13.06 ± 7.23	0.12 ± 0.03
0.5% MMT-Na/0.5% MMT-30B	12.63 ± 8.31	0.12 ± 0.04

Adding the nanoparticles led to a slight reduction in the SEBS dispersed phase area and diameter. According to Tiwari et al.,^[25] when the nanoparticles are in the continuous phase, the dispersed phase domain's diameter is commonly reduced. The nanoparticles present in the continuous phase

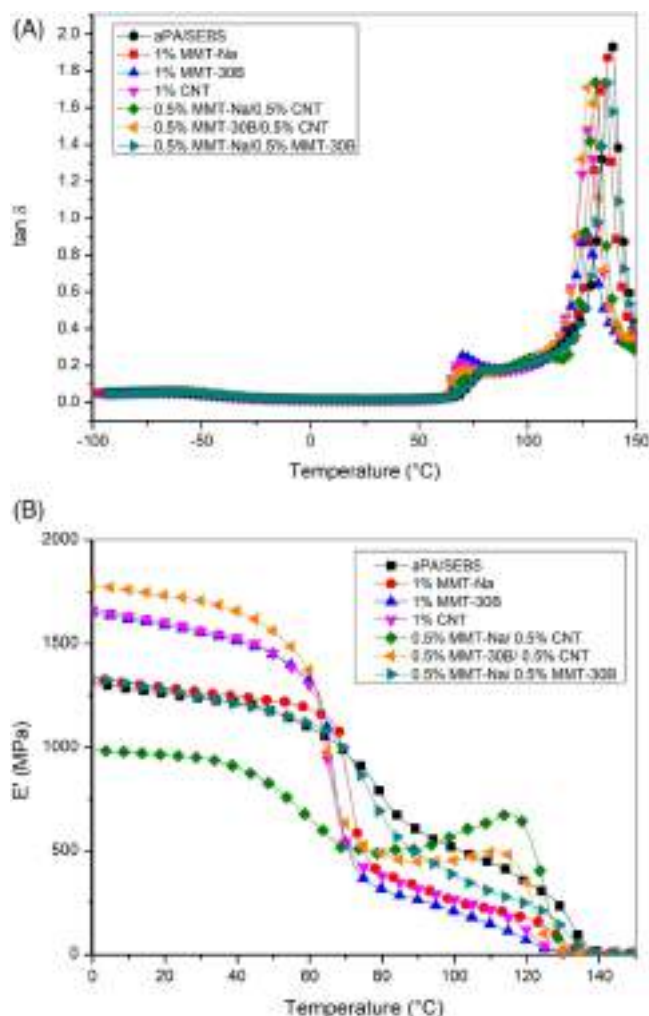


FIGURE 3 DMA Results of the blend and nanocomposites: (A) $\tan\delta$ and (B) storage modulus (E') as a function of temperature

act as physical barriers preventing the coalescence of the dispersed domains, resulting in smaller diameters of the dispersed phase. The selective location of nanoparticles in the polymer matrix may also cause an increase in the continuous phase viscosity, which can also yield a reduction in the diameter of the dispersed domains.^[26–28]

Both montmorillonite clays were located in the aPA matrix (Figure 1). In samples containing MMT-Na, agglomerates were observed, whereas in samples with MMT-30B, the nanoclay is well distributed and intercalated with some exfoliated regions. The nanoclay location in the PA matrix was influenced by the nanoparticle's geometry and the presence of surfactants in the MMT-30B clay.^[29] According to Gödel et al.,^[4] the particles' aspect ratio and dispersion state are important aspects of the location behavior. Even if the MMT is in the exfoliated state, the nanosheets present high interfacial stability and slow transfer through the interface. Besides, according to other authors,^[26,30] modified clay is located

TABLE 2 DMA Results of PA/SEBS blend and the nanocomposites

Sample	Tan δ peak height	Tan δ FWHM	Tg ($^{\circ}$ C) ^a	E' (MPa) (25 $^{\circ}$ C)
aPA/SEBS	1.9	10.0	138	1.255
1% MMT-Na	1.7	10.9	135	1.285
1% MMT-30B	0.9	11.6	127	1.585
1% CNT	1.4	10.8	127	1.600
0.5% MMT-Na/0.5% CNT	1.7	9.2	131	0.960
0.5% MMT-30B/0.5% CNT	1.7	10.1	127	1.730
0.5% MMT-Na/0.5% MMT-30B	1.7	10.3	136	1.280

^aStandard deviation (σ): 2 $^{\circ}$ C.

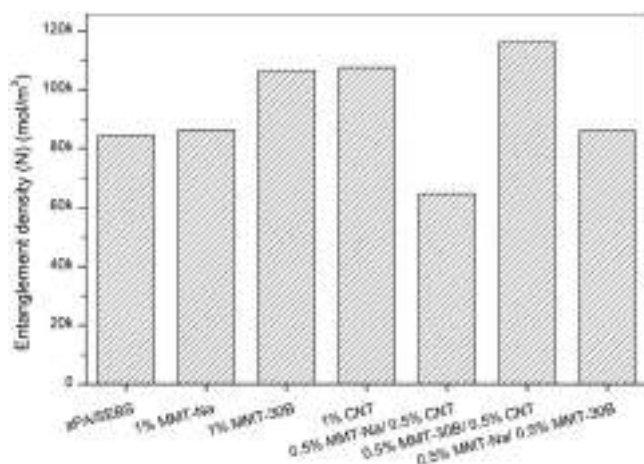


FIGURE 4 Entanglement density at 25 $^{\circ}$ C of aPA/SEBS and its nanocomposites

preferentially in the polyamide matrix, due to the polarity that provides good affinity between the modified MMT and the polyamide. Thus, considering the inherent diffusion difficulty of both clays due to the dispersion state, in the case of the MMT-30B, combined with the affinity with the aPA, the two montmorillonite clays were located preferentially in the aPA matrix, as also observed by other authors.^[26,31]

Most of the CNTs are dispersed and randomly oriented in the aPA matrix, with some observable CNT agglomerates and some CNTs in the SEBS rubber phase, also observed by González et al.^[26] The carbon nanotubes' preferential location in the aPA matrix may be related to the aPA's two benzene rings in the middle of its main chain, which could favor interactions with the CNTs, with the possibility of π - π interactions between aromatic rings and carbon nanotubes, providing a better dispersion and distribution in the polymeric matrix.^[32] When two nanoparticles were added simultaneously to the aPA/SEBS blend, there were no significant changes in the nanoparticles' location and dispersion (Figure 1E–G).



FIGURE 5 Flammability test photos for the blend (A) and nanocomposites with MMT-30B and CNT (B)–(D)

The pure blend's Tg was 138 $^{\circ}$ C, as in Figure 3A and Table 2, which is close to the temperature range observed by other authors for the aPA, between 128 $^{\circ}$ C^[33] and 136 $^{\circ}$ C.^[34] Regarding the nanocomposites, a reduction in Tg is noted for all samples (Table 2). Other authors studying nanocomposites with a polyamide matrix also observed this behavior.^[35–37] According to Aranburu and Eguiazabal,^[5] this can be attributed to the nanoparticles' interference in the interactions between the polymer chains, leading to a greater free volume and, consequently, a lower Tg. All samples presented a smaller peak between 70 $^{\circ}$ C and 76 $^{\circ}$ C, which could be related to secondary chain segment relaxations in the aPA, since it is a copolymer and, possibly, a block copolymer.^[38] Also, according to Tiggemann,^[39] the peak in this temperature range could also be related to the relaxations of the styrene found in the SEBS copolymer. Those two peaks could, then, be superimposed in the DMA analysis. The SEBS glass transition

FIGURE 6 Photos of sample surfaces after flammability test, for the blend (A) and the nanocomposites with MMT-30B and CNT (B)–(D)

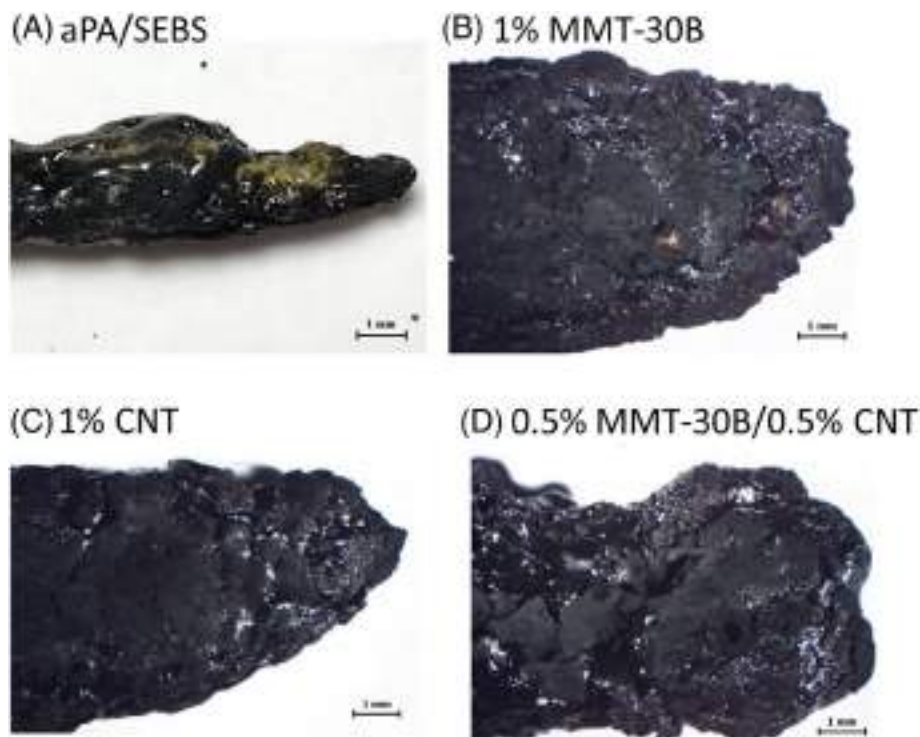
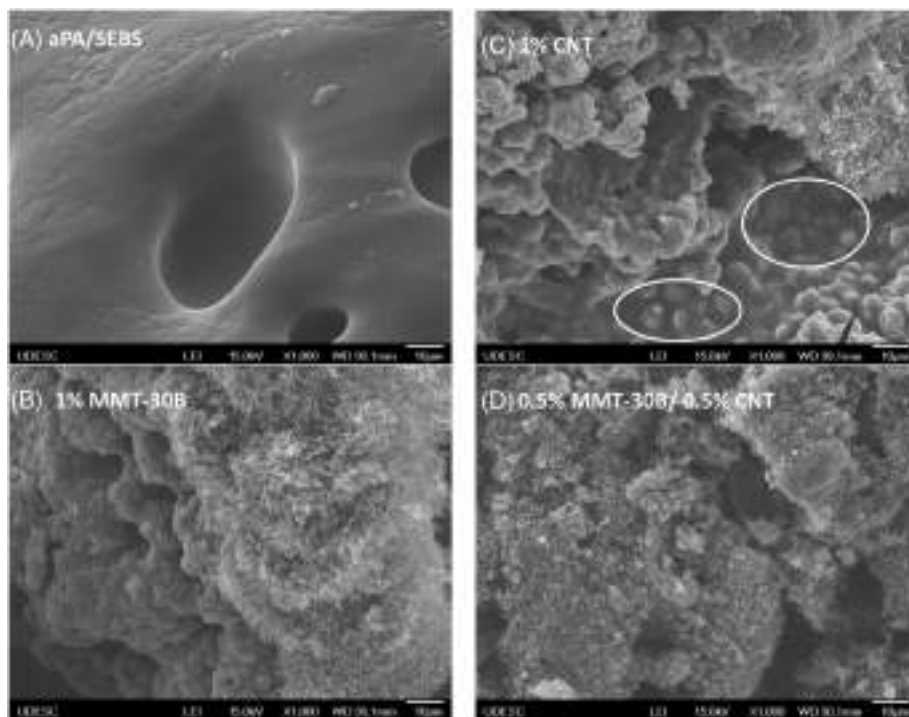


FIGURE 7 SEM Images of burned surface of aPA/SEBS (A) and nanocomposites with MMT-30B and CNT (B)–(D). Ellipses in 1.0% CNT sample evidence the CNT presence



temperature of around -50°C , is mentioned in the manufacturer's data sheet (Kraton) and in the literature.^[40] A subtle elevation around -60°C , attributed to the SEBS glass transition, was detected in all samples. No significant difference was observed with the addition of the nanoparticles, suggesting no nanoparticles existed in the SEBS phase.

In Figure 3B and Table 2, at a temperature of 25°C , samples containing 1.0% MMT-Na and 0.5% MMT-Na/0.5% MMT-30B present E' values similar to the pure blend's, exhibiting only a slight increase in the storage module. This is probably due to natural clay agglomerates and their lower interaction with the aPA matrix.^[41] A reduction of 23% in E' is observed in the sample with

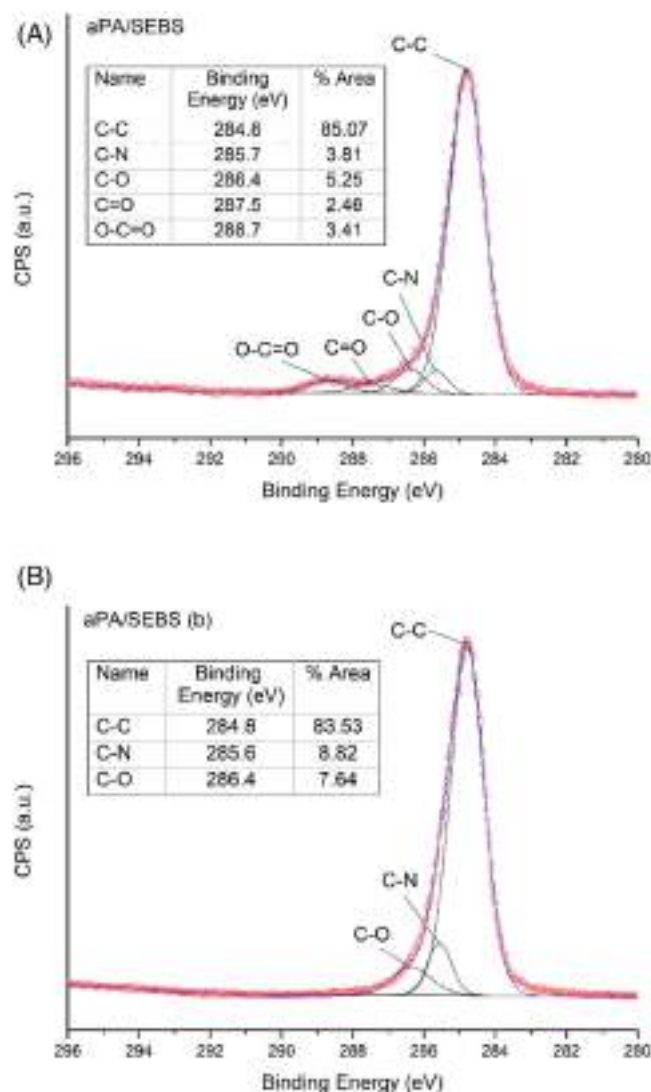


FIGURE 8 XPS C 1s deconvolution for aPA/SEBS sample before (A) and after (B) burning, evidencing the extinction of MA-characteristic C=O and O-C=O contributions, which indicates the preferable consumption of SEBS when burning the blend

0.5% MMT-Na/0.5% CNT. Thus, simultaneously adding natural clay and CNTs had a negative effect on the sample's storage modulus at room temperature. According to Zare,^[42] the formation of larger nanoparticle agglomerates directly affects the storage modulus of the nanocomposites, as it hinders interfacial adhesion and favors crack propagation. Besides, $\tan \delta$ full width at half maximum indicates the degree of homogeneity of a system. A wider distribution (larger peak width) reflects greater difference in the relaxation times of the chain segments.^[43] According to the results in Table 2, this parameter was increased in all samples after the incorporation of the nanoparticles, except for the sample containing 0.5% MMT-Na/0.5% CNT, which presented the lowest value.

Also considering 25°C, for the nanocomposites containing 1.0% MMT-30B and 1.0% CNT, an increase of 26% and 27% is observed for the modulus, respectively, compared to the aPA/SEBS blend. This increase is related to the mechanical properties of the CNTs, the rigidity of the clay layers and the combined effect of the high aspect ratio and nanoparticle dispersion.^[37,44] It is possible to observe that the sample containing 1.0% MMT-30B and 1.0% CNT have lower $\tan \delta$ peak height than the others. The $\tan \delta$ intensity drop may be related to less energy dissipation, indicating greater mobility restriction and possibly greater interfacial adhesion.^[43] An even greater increase in E' is observed in the sample with 0.5% MMT-30B/0.5% CNT, which presents an increase of about 38% in the storage modulus when compared to the pure blend, suggesting synergy between the two nanoparticles related to mechanical properties.

The two quaternary nanocomposites containing clay and CNTs present a different storage modulus versus temperature profile than the other samples. While all other samples show a drop in E' at approximately 70°C, these two samples show a drop followed by an increase in E' at near 120°C, when an abrupt reduction in the storage modulus is noticed. As the temperature increases, the storage modulus reaches the rubbery plateau region. This behavior of E' is related to changes in such regions. When heating the material in the T_g region, the polymer chains gain enough mobility to reorganize, which causes an increase in the modulus.^[45]

The dynamic-mechanical analysis is also used to study the interaction between the polymer matrix and the nanoparticles by analyzing the entanglement density of the molecules (N), which can be calculated according to Equation (1), in which E' is the storage modulus in the glassy region plateau, R is the gas constant, and T is the absolute temperature (K).^[46,47]

$$N = \frac{E'}{6RT} \quad (1)$$

Figure 4 shows the entanglement density of the molecules (N) at 25°C of aPA/SEBS and its nanocomposites. Regarding entanglement density, higher values indicate higher dispersion and higher levels of interactions between the nanoparticles and the matrix. When N is reduced, there usually is an increase in nanoparticle agglomerates.^[47,48] The results from Figure 4A show that, at 25°C, the nanocomposite with 0.5% MMT-30B/0.5% CNT has the highest N , about 38% higher than the pure blend. Samples containing 1.0% MMT-30B and 1.0% CNT also showed a large increase in N , which corroborated the better nanoparticle dispersion observed in these three samples in the TEM images (Figure 1C,D,F) and corroborates

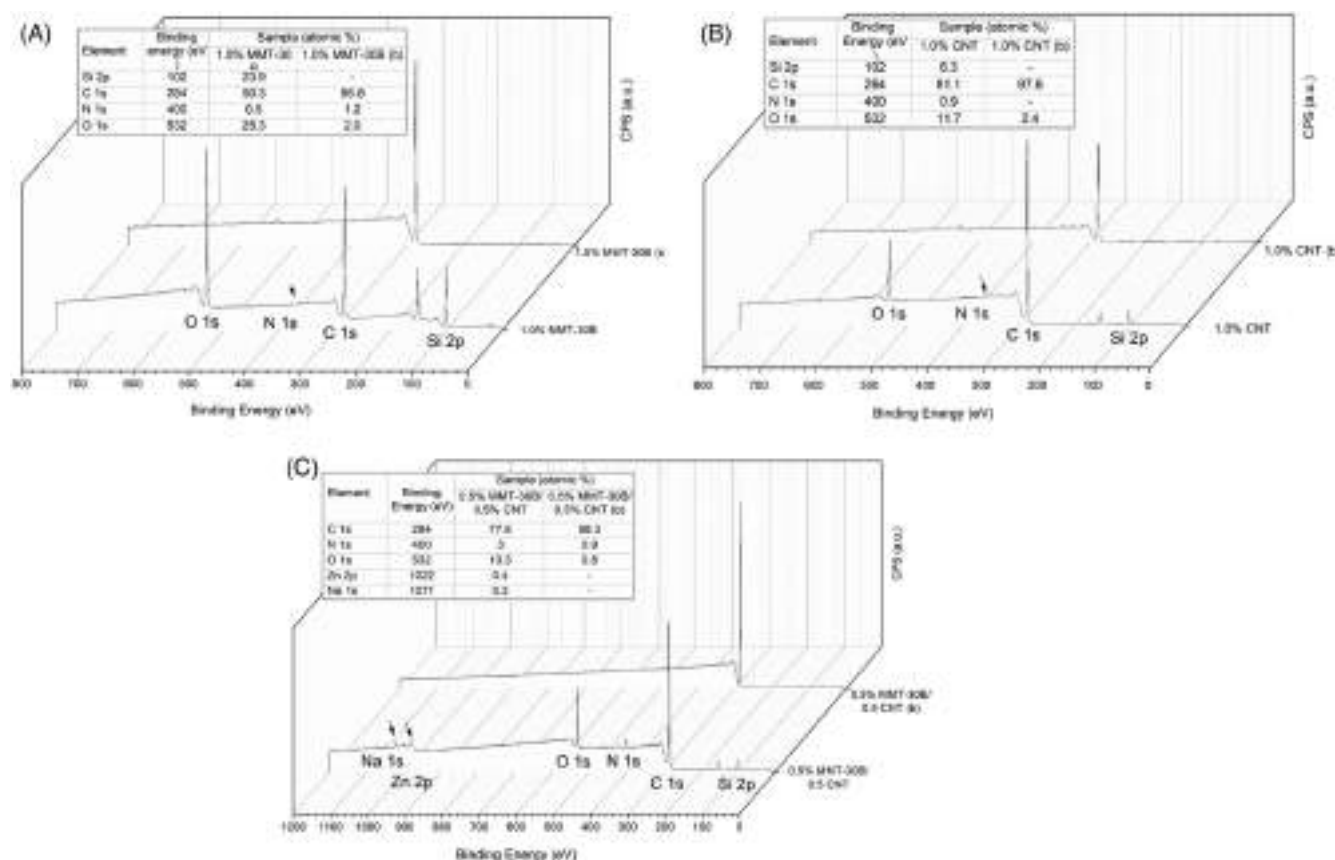


FIGURE 9 XPS Survey spectra for (A) 1% MMT-30B, (B) 1% CNT and (C) 0.5% MMT-30B/0.5% CNT samples, before and after (B) burning

the behavior of E' . On the other hand, in the sample with 0.5% MMT-Na/0.5% CNT, a considerable drop in the entanglement density can be observed, possibly due to the presence of nanoparticle agglomerates.

Regarding flammability, since the first burn timing (t_1) could not be obtained, none of the samples could be classified according to the UL94 standard. However, qualitatively, a better flammability performance of nanocomposites was noticed in comparison to the blend. The aPA/SEBS samples did not self-extinguish: the specimens burned to the fastener and flammable material started to drip from 10 to 16 s after the test began (Figure 5A). Therefore, most of the sample was consumed by the flame, as Figure 6A shows. Besides, burning the pure blend released a lot of smoke and a strong smell, which were hardly noticeable to the nanocomposites. Those observations led to the conclusion that aPA/SEBS samples have no flame resistance, which was a predictable behavior since both the polymers have a flammable characteristic, especially SEBS. Indeed, Figure 7A shows the SEBS void in the aPA matrix, indicating the initial consumption of the SEBS during burning. This corroborates the XPS C 1 s deconvolution for the aPA/SEBS burned sample (Figure 8B), in which the SEBS maleic anhydride (MA)-characteristic C=O and O-C=O

bonds contribution is extinguished, in comparison to the sample before burning (Figure 8A).

On the other hand, for the nanocomposites, as Figure 6 shows, the mass consumption was lower, probably due to the formation of a char layer that insulates the pure blend, slowing down the pyrolysis rate. Such layer also acts as a physical barrier preventing volatile gases and flammable pyrolyzed products from interacting with oxygen.^[49] For the 1% MMT-30B sample, despite the flame reaching the fastener, there was no dripping during the test (Figure 5B). Similar behavior was observed for the other sample containing MMT-30B (0.5% MMT-30B/0.5% CNT sample, Figure 5D). The ability to prevent or retard the dripping is related to the char formation, as already mentioned. Figure 7B,D evidences the char formed on burned surfaces, which is also indicated in XPS survey spectra, once the contribution of carbon atomic percentage greatly increases (Figure 9). As more char forms, less of the bulk material is really burned,^[17] which is macroscopically observed in Figure 6.

However, MMT-30B was not efficient in reducing heat release, once its nanocomposites had no flame auto extinguishing, despite the char formation at the sample surface. Figure 9 shows that there is no silicon on the

nanocomposite samples' burned surfaces, which indicates the absence of carbonaceous silicate char, a layer that could improve barrier properties for heat and volatiles, once it is an inorganic-rich ceramic-like char.^[16] A higher MMT-30B concentration on the nanocomposites is necessary to form such a silicate char layer. Indeed, other authors observed considerable improvement in flammability behavior for nanocomposites with more concentrated MMT-30B.^[15,50,51]

For the 1% CNT sample, only one specimen self-extinguished twice. According to Wang et al.,^[17] the flame retardancy action of carbon nanotubes involves the condensed phase, in which a protective layer that acts as a barrier to the flame is created, preventing volatiles from escaping. A three-dimensional CNT network structure promotes the formation of a continuous char layer, without any holes or cracks, not allowing heat and mass transfer from the flame to the polymers. However, for the 1% CNT sample, neither a CNT network structure nor a continuous char layer was observed, only some CNTs along the burned specimen (Figure 7C). Besides, the char formed on the 1% CNT sample surface is quite different from that in the samples containing MMT-30B (Figure 7). In a previous work,^[22] even without the formation of a CNT network structure, a V-2 classification was obtained for nanocomposites of aPA/SEBS and 0.5% and 1.0% of nanoparticles. The difference between the results obtained there and the ones in the present study can be related to the CNT location on the polymeric blend. In the work of Paes et al.,^[22] the CNTs were preferentially located in the SEBS phase, which burns first and rapidly. However, in this work, the CNTs were located in the aPA phase (Figure 1D–F).

Regarding the sample containing both MMT-30B and CNT (0.5% MMT-30B/0.5% CNT), there was an increase in the time to burn all the way to the fastener, approximately 25% longer. Like the 1% CNT sample, only two samples had no dripping. That behavior, which evidences the nanocomposites' inability to promote an anti-dripping effect, can be related to the lower clay content in the sample. The silicon content was reduced from 23.9 at. % (in the 1% MMT-30B sample) to 5.4 at. % (in the 0.5% MMT-30B/0.5% CNT sample) (Figure 9A,C), reducing the ability to form the char (Figure 7). Therefore, there was no synergy between the MMT-30B and the carbon nanotubes to improve the nanocomposite's flammability behavior.

4 | CONCLUSIONS

The SEBS's rubber phase is dispersed in the aPA matrix, taking a spherical shape with an approximately homogeneous dimension. Adding the nanoparticles did not cause any changes to the blend's morphology. All the nanoparticles

were preferentially located in the aPA matrix. The nanoclay location was influenced by the nanoparticles' geometry and the affinity between the MMT-30B and the polyamide matrix. The CNTs were preferentially located in the aPA matrix due to mutual interactions. When two nanoparticles were added simultaneously, no significant changes were observed in their location and dispersion. At a temperature of 25°C, samples with 1.0% MMT-30B and 1.0% CNT exhibited a 26% and 27% increase in E' , respectively, and the quaternary nanocomposite with 0.5% MMT-30B/0.5% CNT showed a 38% increase in the storage modulus, suggesting synergy between the two nanoparticles. Regarding flammability, the nanocomposites performed better than the pure blend. No synergy was observed between the nanoparticles in the flammability of the quaternary nanocomposites. The samples' behavior during the flammability test showed that the nanoparticles' quantity and location influenced the flammability behavior and the char formation on the samples' surface.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author, D. Becker, upon reasonable request.

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REFERENCES

- [1] A. Cayla, C. Campagne, M. Rochery, E. Devaux, *Synt. Metals*. **2011**, 161, 1034.
- [2] L. F. A. Bernardo, A. P. B. M. Amaro, D. G. Pinto, S. M. R. Lopes, *Comput. Mater. Sci*. **2016**, 118, 32.
- [3] D. Wu, D. Lin, J. Zhang, W. Zhou, M. Zhang, Y. Zhang, D. Wang, B. Lin, *Macromol. Chem. Phys*. **2011**, 212, 613.
- [4] A. Gödel, A. Marmur, G. R. Kasaliwal, P. Pötschke, G. Heinrich, *Macromolecules* **2011**, 44, 6094.
- [5] N. Aranburu, J. I. Eguiazabal, *J. Appl. Polym. Sci*. **2014**, 127, 5007.
- [6] B. S. Bouakaz, A. Habi, Y. Grohens, I. Pillin, *Appl. Clay Sci*. **2017**, 139, 81.
- [7] J. Cao, J. Zhao, X. Zhao, F. You, H. Yu, G. Hu, Z. M. Dang, *Compos. Sci. Technol*. **2013**, 89, 142.
- [8] J. Chen, H. Lu, J. Yang, Y. Wang, X. Zheng, C. Zhang, G. Yuan, *Compos. Sci. Technol*. **2014**, 94, 30.
- [9] M. Decol, W. M. Pachekoski, D. Becker, *Polym. Eng. Sci*. **2020**, 10, 2439.

- [10] V. Sivanjineyulu, Y. Chang, F. Chiu, *J. Polym. Res.* **2017**, 24, 130.
- [11] S. Adrar, A. Habi, A. Ajji, Y. Grohens, *Appl. Clay Sci.* **2018**, 157, 65.
- [12] O. M. Sanusi, A. Benelfellah, N. A. Hocine, *Appl. Clay Sci.* **2020**, 185, 105408.
- [13] E. S. Goda, K. R. Yoon, S. H. El-sayed, S. E. Hong, *Thermochim. Acta* **2018**, 669, 173.
- [14] W. He, J. Gao, S. Liao, X. Wang, S. Qin, P. Song, *Compos. Commun.* **2019**, 13, 143.
- [15] M. Nemati, H. K. Eslam, M. Talaeipour, B. Bazyar, A. Samariha, *Bioresources* **2016**, 11, 748.
- [16] H. Qin, S. Zhang, C. Zhao, G. Hu, M. Yang, *Polymer* **2005**, 46, 8386.
- [17] X. Wang, E. N. Kalali, J. Wan, D. Wang, *Prog. Polym. Sci.* **2017**, 69, 22.
- [18] G. P. Karayannidis, D. N. Bikiaris, G. Z. Papageorgiou, V. Bakirtzis, *Adv. Polym. Technol.* **2002**, 21, 153.
- [19] A. P. A. Carvalho, A. S. Sirqueira, *Polimeros* **2016**, 26, 2.
- [20] J. J. Huang, H. Keskkula, D. R. Paul, *Polymer* **2004**, 45, 4203.
- [21] H. Wu, M. Krifa, J. H. Koo, *Polym-Plast. Technol.* **2018**, 57, 727.
- [22] L. H. G. Paes, T. T. Steffen, D. Becker, *Polym. Eng. Sci.* **2020**, 60, 1333.
- [23] F. A. Hoor, J. Morshedean, S. Ahmadi, M. Rakhshanfar, A. Bahramzadeh, *J. Chem.* **2015**, 2015, 819580.
- [24] A. Babaei, A. Arefazar, *J. Macromol. Sci. B* **2014**, 53, 1406.
- [25] R. R. Tiwari, D. L. Hunter, D. R. Paul, *J. Polym. Sci. Polym. Phys.* **2012**, 50, 1577.
- [26] I. González, J. I. Eguiazábal, J. Nazábal, *Eur. Polym. J.* **2008**, 44, 287.
- [27] I. González, J. I. Eguiazábal, J. Nazábal, *Compos. Part A-Appl. S.* **2012**, 43, 1482.
- [28] L. Wang, Z. X. Guo, J. Yu, *J. Macromol. Sci. B* **2014**, 53, 1205.
- [29] X. Zhang, L. S. Loo, *J. Polym. Sci. B Polym. Phys.* **2008**, 48, 2605.
- [30] M. Attari, A. Arefazar, G. Bakhshandeh, *Polym. Eng. Sci.* **2014**, 55, 29.
- [31] A. Dasari, Z. Yu, M. Yang, Q. Zhang, X. Xie, Y. Mai, *Compos. Sci. Technol.* **2006**, 66, 3097.
- [32] M. R. R. Hamester, C. Dalmolin, D. Becker, *J. Appl. Polym. Sci.* **2019**, 136, 48195.
- [33] M. Vannini, *Polym. Eng. Sci.* **2014**, 57, 1475.
- [34] J. Canales, M. Fernández, J. J. Peña, M. E. Muñoz, A. Santamaría, *Polym. Eng. Sci.* **2014**, 55, 1142.
- [35] H. Meng, G. X. Sui, P. F. Fang, R. Yang, *Polymer* **2008**, 49, 610.
- [36] N. Aranburu, J. I. Eguiazábal, *Polym. Compos.* **2013**, 35, 587.
- [37] K. Kelar, B. Jurkowski, *J. Appl. Polym. Sci.* **2007**, 104, 3010.
- [38] S. N. Cassu, M. I. Felisberti, *Quim Nova* **2005**, 28, 255.
- [39] H. M. Tiggemann, *Propriedades de materiais híbridos com matriz de elastômeros termoplásticos à base de SEBS*. Doctoral dissertation, Federal University of Rio Grande do Sul, Brazil **2017**.
- [40] M. Sahnoune, A. Taguet, B. Otazaghine, M. Kaci, J. Lopez-Cuesta, *Polym. J.* **2017**, 90, 418.
- [41] A. N. Wilkinson, Z. Man, J. L. Stanford, P. Matikainen, M. L. Clemens, G. C. Lees, C. M. Liauw, *Macromol. Mater. Eng.* **2006**, 291, 917.
- [42] Y. Zare, *J. Adhes.* **2016**, 93, 1109.
- [43] V. Pistor, F. G. Ornaghi, H. L. Ornaghi, A. J. Zattera, *Mat. Sci. Eng A-Struct.* **2012**, 532, 339.
- [44] Z. A. Kusmono, M. Ishak, W. S. Chow, T. Takeichi, Rochmadi, *Polym. Compos.* **2010**, 31, 1156.
- [45] K. P. Menard, *Dynamic Mechanical Analysis: A Practical Introduction*, CRC Press, New York, USA **1999**.
- [46] J. Andrzejewski, M. Misra, A. K. Mohanty, *J. Appl. Polym. Sci.* **2018**, 135, 1.
- [47] S. Sharma, A. K. Pathak, V. N. Singh, S. Teotia, S. R. Dhakate, B. P. Singh, *Carbon* **2018**, 137, 104.
- [48] J. Jyoti, B. P. Singh, A. K. Arya, S. R. Dhakate, *RSC Adv.* **2016**, 6, 3997.
- [49] S. Araby, B. Philips, Q. Meng, J. Ma, T. Laoui, C. H. Wang, *Compos. Part B-Eng.* **2021**, 212, 108675.
- [50] S. V. Oliveira, E. M. Araújo, C. M. C. Pereira, A. M. D. Leite, *Polimeros* **2017**, 27, 91.
- [51] M. Monti, S. A. Tsampas, S. P. Fernberg, P. Blomqvist, F. Cuttica, A. Fina, G. Camino, *Polym. Degrad. Stab.* **2015**, 121, 1.

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