

Article

Cu@Ag Nanoparticles Coating onto Polyethylene Terephthalate Films Functionalized with Amino Groups: Antimicrobial Activity

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Featured Application

This research focuses on the development of antimicrobial polymeric materials with biocidal properties by incorporating Cu@Ag nanoparticles. These innovative materials require rigorous experimental monitoring to ensure their safety and biocompatibility. Nevertheless, they show significant potential for a wide range of applications, including medical devices, water treatment, food packaging, and other sectors where antimicrobial functionality is essential.

Abstract

Poly(ethylene terephthalate) (PET) is widely used in various sectors due to its biocompatibility, mechanical strength, and chemical stability. However, its inert surface makes it challenging to functionalize and coat with antimicrobial agents to prevent microbial growth and biofilm formation. Therefore, in this work, antimicrobial activity was imparted to PET films using a Cu@Ag nanoparticle coating. The resulting materials were characterized by spectroscopic, thermal, and microscopic techniques, and their mechanical properties and antimicrobial efficacy against *S. aureus* and *E. coli* were evaluated. The results demonstrated significant antimicrobial activity and good retention of PET's mechanical and thermal properties, which are relevant for potential applications in the biomedical and packaging sectors, where infection prevention is crucial.

Keywords: nanoparticles; loading; coating; bimetallic nanoparticles; PET; silver; copper



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1. Introduction

Nanocoating with nanoparticles on polymeric materials has emerged as an advanced technique that involves applying a nanoscale layer to polymer surfaces to modify and improve their functional properties [1]. These nanolayers can be composed of coatings of other polymeric materials or of nanoparticles incorporated into the surface of the polymer matrix, generating a nanostructured composite with enhanced characteristics. This nanocoating confers unique properties to the materials, such as improved abrasion resistance, corrosion protection, antimicrobial properties, increased hydrophilicity or self-cleaning, and chemical resistance [2–5]. The nanoparticles used can be metal oxides (ZnO or TiO₂) or copper and silver [4,6,7], which are highly effective antimicrobial agents against Gram-positive and Gram-negative bacteria [4,8,9]. These nanoparticles not only provide antimicrobial activity

but also enhance mechanical strength, thermal stability, and protection against ultraviolet radiation, reducing degradation and extending the material's useful life [10,11].

This approach is applied in various sectors, including automotive manufacturing, innovative packaging, functional textiles, and flexible electronic devices, where the textile sector has explored diverse engineering strategies for PET modification, including physical coatings with natural brucites [12], bio-inspired Cu₂O immobilization using polydopamine [13], and carboxylation to anchor AgCl or silver nanoparticles onto chitosan grafts, polypropylene sutures or bioplastics [4,14–16], evidencing that nanocoatings require molecular engineering to ensure homogeneous nanoparticle distribution and strong adhesion between the nanostructured layer and the polymer matrix [17–20].

Nanocoating with core@shell type nanoparticles on PET polymers represents an innovative technique for improving the functional properties of this widely used material. Despite its widespread use, PET is limited in demanding environments by inherent vulnerabilities, including sensitivity to ultraviolet radiation, thermal degradation, and susceptibility to microbial proliferation in specific applications, where the core@shell bimetallic nanoparticles, where copper–silver combinations provide synergistic antimicrobial activity against Gram-positive bacteria, Gram-negative bacteria, and fungi, while offering reduced toxicity and cost-effectiveness [21].

Therefore, nanocoatings on the PET surface or the incorporation of nanoparticles into its matrix create a nanostructured composite that provides superior properties. In the case of PET, a common thermoplastic polymer in packaging and textile fibers, the inclusion of nanoparticles can provide significant improvements in thermal stability and protection against ultraviolet radiation, as well as conferring antimicrobial properties [4,17].

One challenge is achieving a homogeneous distribution of nanoparticles with strong adhesion to the polymer surface, thereby maximizing functional benefits without compromising the material's properties. Molecular engineering technologies and methods, such as plasma functionalization, chemical deposition, or successive immersion, can provide fine control over the nanometric layer [22–25]. Thus, nanocoating on PET opens a wide field of advanced applications, where the combination of light weight, durability, and functionality is key to developing new high-performance materials [26]. In summary, nanoparticle nanocoating represents a technological revolution in improving polymeric materials, combining nanotechnology with polymer science to create products with advanced functional properties that expand their use in high-performance applications.

Although the efficacy of these core@shell structures has been demonstrated in matrices like PVA, their synthesis and direct incorporation onto PET surfaces functionalized with amino groups via aminolysis remain unexplored. This work addresses the coating of PET films with Cu@Ag nanoparticles through surface functionalization with amino groups using an aminolysis reaction, followed by the reduction of copper and silver ions to form Cu@Ag nanoparticles. The materials were characterized using spectroscopic techniques, thermal analysis, mechanical tests, and evaluation of their antimicrobial activity against Gram-positive and Gram-negative microorganisms.

2. Materials and Methods

2.1. Materials

All reagents used were analytical grade and were used without further purification. Polyethylene terephthalate (PET) films, 100 µm thick, were purchased from Sigma-Aldrich (St. Louis, MO, USA). Deionized water, ethylenediamine (≥99%), copper sulfate pentahydrate (99%), silver nitrate (≥99%), and sodium borohydride (95%) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Sodium hydroxide, hydrochloric acid, methanol

(99.7%), and sodium orange II salt ($\geq 85\%$) were obtained from Meyer Reagents (Mexico City, Mexico).

2.2. Functionalization of PET Films with Amino Groups (PETNH)

The PET films (1.2×5 cm) were initially washed with water, followed by MeOH, and finally dried at 50°C for 15 min. The PET films were then immersed in 10 mL of ethylenediamine with constant stirring. The reaction was carried out at different reaction times and temperatures. The films were then thoroughly washed with deionized water and dried under vacuum at 50°C until a constant weight was achieved. The film degradation was then determined by measuring the weight loss of the PET film after the aminolysis reaction (Equation (1)).

$$\text{Weight loss (\%)} = 100((\text{PPET} - \text{PPETNH})/\text{PPET}) \quad (1)$$

where PPET is the weight of the unfunctionalized PET film, and PPETNH is the weight of the PET film functionalized with amino groups.

2.3. Detection and Quantification of Amino Groups

Amino group quantification was performed using a colorimetric method with orange II. PETNH films were immersed for 30 min at 40°C in 1 mL of an aqueous orange II solution (14 mg/mL) adjusted to pH 3 with 1 M HCl. After the reaction time, the samples were rinsed three times with an acidic aqueous solution (pH 3) and then dried. Subsequently, the orange II-treated films were immersed in 3 mL of an alkaline solution (a mixture of deionized water and 1 M NaOH adjusted to pH 12) to release the orange II. The resulting solution was adjusted to pH 3 with 1 M HCl. Finally, the absorbance was measured at 484 nm, and orange II was quantified using a calibration curve with a 1:1 stoichiometry for each amino group $-\text{NH}_2$ and orange II [27]. The calibration curve showed a linear relationship, described by the equation $[\text{NII}]_{\text{sol}} = 0.0293\text{Ab} - 0.0212$, with a correlation coefficient of 0.9976. The procedure was performed in triplicate.

The surface density of amino groups in the film ($[\text{NH}_2]_{\text{PET}}$) was determined by relating the total amount of desorbed dye to the exposed area of the sample:

$$[\text{NH}_2]_{\text{PET}} (\text{pmol/mm}^2) = ([\text{NII}]_{\text{sol}} \cdot V_{\text{sol}}) / A_{\text{film}}$$

where $[\text{NII}]_{\text{sol}}$ is the concentration of the desorbed orange II dye obtained with a 1:1 ratio with the amino groups present on the surface of the film, V_{sol} is the volume of the desorption solution (mL), and A_{film} is the area of the analyzed PET film (mm^2).

2.4. Synthesis and Loading of Copper Nanoparticles (PETNH-Cu)

Three PETNH films were placed in 20 mL of 0.02 M copper sulfate solution, and the air was removed by bubbling with argon for 10 min. Subsequently, 20 mL of 0.04 M sodium borohydride solution was added, and the reaction was allowed to continue for 10 min. Finally, the PETNH-Cu films were removed, washed with MeOH, and dried under vacuum at 50°C . Films with a dark orange color were stored in an argon atmosphere to prevent oxidation of the copper nanoparticles.

2.5. Synthesis of CU@Ag Nanoparticles (PETNH-Cu@Ag)

Three PETNH-Cu films were placed in 20 mL of a silver nitrate solution (0.3 M) for 5 min with constant stirring at room temperature. After this time, the films were removed from the medium and washed vigorously with deionized water. The PETNH-Cu@Ag films were stored under no special conditions until characterization.

2.6. Antimicrobial Tests

The ability of PETNH-Cu and PETNH-Cu@Ag films to inhibit bacterial growth against *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*) was evaluated. Petri dishes containing Mueller-Hinton agar were inoculated at a concentration of 1.2×10^9 CFU/mL for *S. aureus* and 3.4×10^9 CFU/mL for *E. coli* (where CFU is a colony-forming unit). PET and PETNH were used as controls, and PETNH-Cu and PETNH-Cu@Ag (0.6 cm in diameter) were tested to evaluate antimicrobial activity. The sample plates were incubated at 37 °C for 24 h. The zone of inhibition was measured using a scale. Antimicrobial activity was assessed in triplicate using a fresh sample.

2.7. Instrumental

Fourier Transform Infrared-Attenuated Total Reflection (FTIR-ATR) of dry samples was recorded using a Perkin-Elmer Spectrum 100 spectrometer (Norwalk, CT, USA) with 16 scans.

Scanning electron microscope (SEM) images were acquired by the Zeiss Evo LS15 instrument (Jena, Germany), and small pieces of 0.5 cm in length were cut and analyzed under a high vacuum with carbon and gold coating.

A GEEFUNTECH GF08 brightfield trilocular compound microscope with 40× magnification was used to obtain images of the samples placed directly onto a slide.

The TGA5000 Discovery Thermobalance from TA Instruments (New Castle, DE, USA) was used to perform the thermogravimetric study in a temperature range of 30 °C to 800 °C, using a heating rate of 20 °C/min and a nitrogen flow at 100 cm³/min.

The X-Ray Photoelectron spectroscopy (XPS) spectra of the samples were recorded using a Microprobe PHI 5000 Versa Probe II (Chanhassen, MN, USA), with an excitation source of Al K α monochromatic, energy 1486.6 eV, 100 μ m beam diameter, and with a Multi-Channel Detector (MCD). The energy scale was corrected using the C1s peak to 285.0 eV. Multipack v. 9.9.3. software was used analyze spectral data.

Mechanical properties of the films were studied by applying an uniaxial tension test, as described in ASTM D1708. All tests were carried out on an INSTRON 1125 (Instron Inc., Norwood, MA, USA) universal tensile testing machine at a crosshead speed of 10 mm/min, and all experiments were carried out in triplicate.

3. Results and Discussion

3.1. Surface Functionalization of PET with Amino Groups

The aminolysis reaction of PET films with ethylenediamine was carried out efficiently, showing a weight loss attributed to the rupture of the ester groups that comprise the polymer chains (Figure 1a). This degradation occurs as amino groups are incorporated through aminolysis reaction, and different reaction times and temperatures were studied to optimize functionalization and minimize the loss of the polymer's structural integrity. At 25 °C, the weight loss increased gradually with time, requiring longer reaction times for effective functionalization. However, at higher temperatures (40 and 50 °C), the weight loss was significantly greater over much shorter times, increasing from $1.0 \pm 0.05\%$ at 25 °C after 120 min to $11.3 \pm 1.51\%$ at 50 °C after 30 min. These results indicate that temperature accelerates aminolysis, decreasing the reaction time but increasing matrix degradation. In addition, crack formation was observed on the surface of the PET under high temperature and prolonged reaction times (Figure 2a,c).

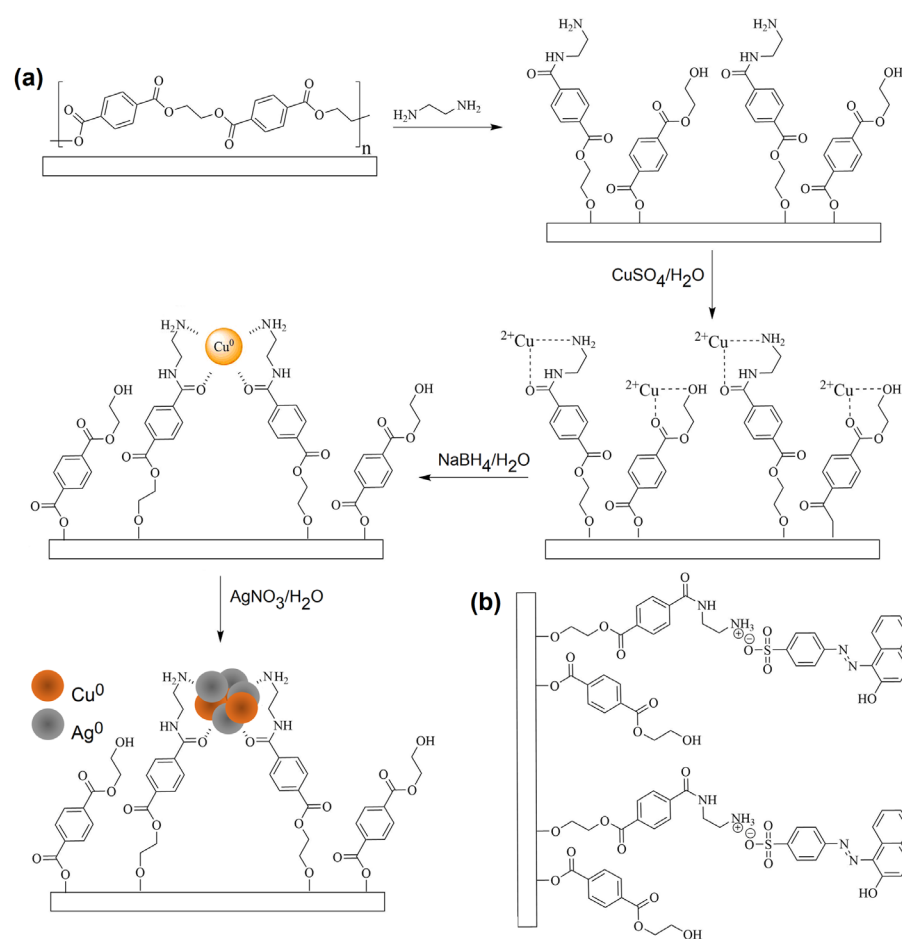


Figure 1. (a) Schematic of the aminolysis reaction with ethylenediamine and synthesis and loading of Cu@Ag nanoparticles, (b) interactions of orange II with primary amino groups in the colorimetric quantification method.

The quantification of amino groups in PET films was performed using a colorimetric method employing orange II (Figure 1b), and this analysis indicated that increasing the temperature and reaction time favors the incorporation of amino groups to the surface of the polymer, despite some degradation of the material. Films treated at 50°C showed the highest concentration of amino groups, reaching $276.13 \pm 23.65 \text{ pmol/mm}^2$ in short reaction times, while longer reaction times were required at 25°C and 40°C to achieve lower concentrations, with $130.02 \pm 12.93 \text{ pmol/mm}^2$ and $134.89 \pm 4.83 \text{ pmol/mm}^2$, respectively (Figure 2b,d). Based on these results, PET-NH films obtained at 50°C for 15 min were selected for subsequent loading with Cu@Ag nanoparticles, thereby optimizing the surface functionalization process to enhance nanoparticle binding and stabilization.

3.2. FTIR-ATR Analysis

Figure 3 presents the FTIR spectra of pristine PET and chemically functionalized samples during nanoparticle incorporation. The unmodified PET film spectrum shows a characteristic band at 1714 cm^{-1} , corresponding to the carbonyl stretching vibration (sv $\text{C}=\text{O}$), and another at 1242 cm^{-1} , attributed to the ester stretching vibration (sv $\text{C}-\text{O}-\text{C}$). Signals in the $2098\text{--}2967 \text{ cm}^{-1}$ range correspond to C-H stretching vibrations (sv C-H), while a band at 3030 cm^{-1} is assigned to aromatic $\text{C}=\text{C}-\text{H}$ stretching (sv $\text{C}=\text{C}-\text{H}$). Additionally, overtone bands from aromatic ring stretching (sv $\text{C}=\text{C}$) appear between 1950 and 2000 cm^{-1} .

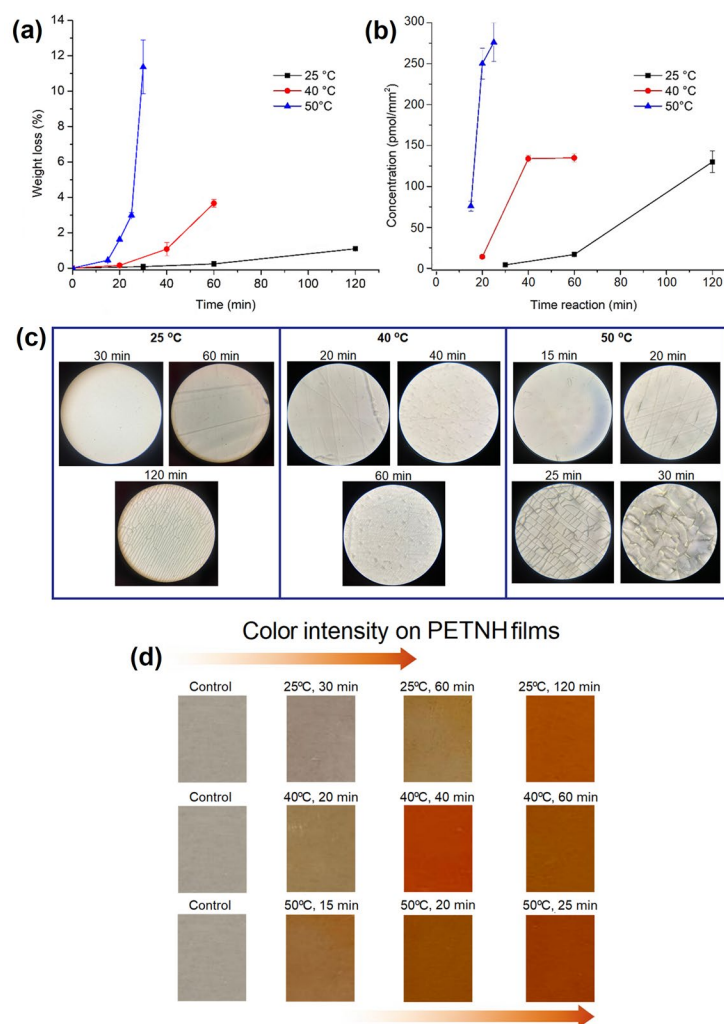


Figure 2. (a) Effect of the aminolysis reaction on the degradation of the PET film as a function of reaction time and temperature, (b) amount of primary amino groups determined by colorimetric method on the surface of the film as a function of reaction time and temperature, (c) photos of the effect of the aminolysis reaction on the surface of the PET films, and (d) photos of PETNH films treated with orange II show that the color intensity increases depending on the reaction conditions, evidencing the increase in primary amino groups present on the surface of the matrix.

In the PET-NH sample, a broad band centered around 3350 cm^{-1} indicates overlapping O-H and N-H stretching vibrations (sv O-H and sv N-H), accompanied by a new band at 1656 cm^{-1} assigned to amide carbonyl stretching (sv C=O, amide), confirming successful PET surface functionalization with amino groups via aminolysis using ethylenediamine [28]. The PETNH-Cu@Ag spectrum, although very similar to that of the aminofunctionalized film, shows a higher intensity at approximately 3350 cm^{-1} . This is likely due to residual OH groups from $\text{Cu}(\text{OH})_2$, a byproduct of the reduction reaction, and to N-H groups. The band at 1681 cm^{-1} , corresponding to the amide carbonyl group, also shows higher intensity and a higher wavenumber. These variations in the N-H and carbonyl bands suggest interactions with the nanoparticles, a finding also observed by XPS analysis [4]. Additionally, narrowing of this band suggests stronger interactions between amino and amido groups after chemical functionalization, evidencing effective nanoparticle stabilization on the modified PET surface.

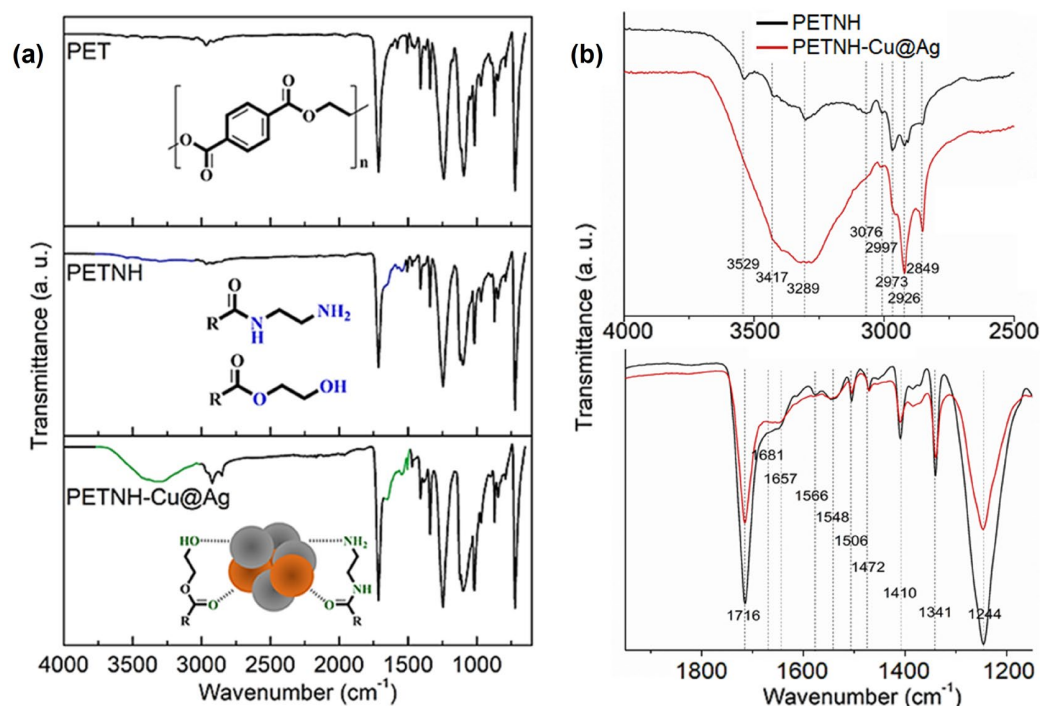


Figure 3. (a) FTIR-ATR spectra of the PET film in the process of functionalization with amino groups at 50 °C and 15 min, and loading of Cu@Ag nanoparticles and (b) expansion of the areas that showed significant differences in the Cu@Ag nanoparticle load.

3.3. Thermal Analysis

Thermogravimetric analysis (TGA) under a nitrogen atmosphere (Figure 4a) showed that the films exhibited similar thermal decomposition temperatures, with onset between 457.1 and 460.3 °C and a 10 wt% loss between 390.4 and 424.8 °C. These results indicate that chemical functionalization has a minimal impact on the thermal stability of the PET matrix, likely because the modifications are limited to the film surface. The thermogram of the PETNH film showed the lowest temperature for a 10% loss, indicating a higher concentration of volatile compounds, such as occluded water, attributed to the greater hydrophilicity generated by the amino groups on the surface. Furthermore, the residual mass after decomposition was comparable in most samples, except for the PETNH film, which showed a reduced residual yield. Taken together, these results suggest that surface functionalization and nanoparticle incorporation do not significantly compromise PET's inherent thermal properties.

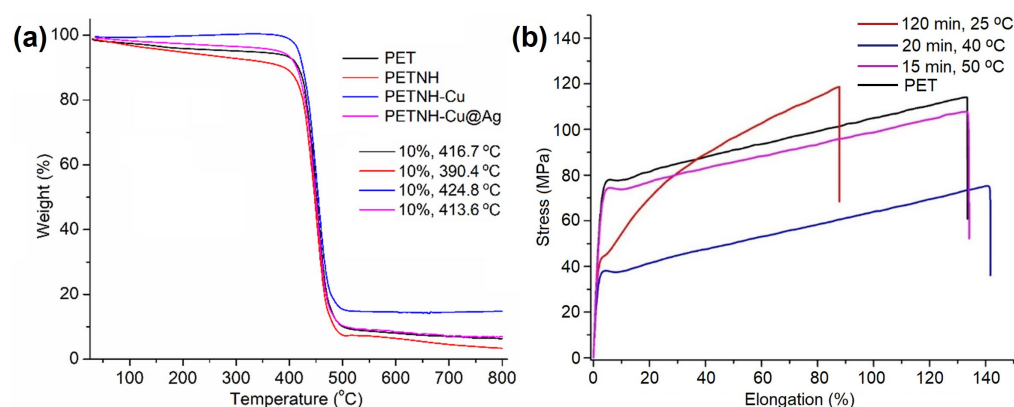


Figure 4. (a) Thermogram of the PET films in the functionalization process with amino groups at 50 °C and 15 min and their subsequent loading of Cu@Ag nanoparticles, the TGA was carried out at 20 °C/min in a nitrogen atmosphere with a flow of 100 cm³/min, (b) Mechanical properties of the PET films subjected to different reaction conditions by uniaxial stress.

3.4. Mechanical Properties

The mechanical properties of PET functionalized by aminolysis allowed for the evaluation of the impact of this reaction on the films. Key parameters, including maximum tensile strength, strain at break, Young's modulus, and energy absorbed, were measured via uniaxial tensile testing; the results are summarized in Figure 4b and Table 1.

Table 1. Mechanical properties of PET and PETNH under different conditions of amyolysis reaction.

Sample and Reaction Conditions	Tensile Strength/Maximum Load	Tensile Strength/Yield Strength	Tensile/Yield Deformation	Tensile Strength/Breaking	Tensile Deformation (Extension)/Break	Young's Modulus	Energy/Breakdown
	(MPa)	(MPa)	(%)	(MPa)	(%)	(MPa)	(J)
PET	114.44	114.44	132.87	114.16	133.43	2929.8	5.69
PETNH, 120 min. 25 °C	119.08	119.08	87.77	68.58	87.8	1517.07	9.72
PETNH, 20 min. 40 °C	75.48	75.48	140.6	64.37	141.67	1251.08	10.47
PETNH, 15 min. 50 °C	108.79	108.79	134.02	94.71	134.04	2893.14	15.4

Unmodified PET exhibited a maximum tensile strength of 114.44 MPa, an elongation of 132.87%, and a high Young's modulus (2929.8 MPa), demonstrating its high strength and ductility. Samples subjected to aminolysis at 25 °C for 120 min showed a slightly higher maximum tensile strength (119.08 MPa) but a significant decrease in strain to 87.8%, indicating increased brittleness associated with surface microcracks observed under microscopy.

On the other hand, films treated at 40 °C for 20 min exhibited a notable reduction in maximum stress (75.48 MPa) but high elongation (141.6%), suggesting a less strong but more ductile material, consistent with surface irregularities and intermediate weight loss (Table 1). Finally, the sample processed at 50 °C for 15 min maintained mechanical properties similar to pristine PET with a maximum stress of 108.79 MPa and an elongation of 134.02%, confirming that functionalization under these conditions does not significantly compromise mechanical performance.

These results demonstrate that aminolysis conditions critically affect the balance between functionalization and structural stability: lower temperatures preserve strength but increase brittleness; intermediate temperatures reduce strength but improve ductility, reflecting different types of damage to the polymer network.

3.5. SEM-EDS Analysis

The SEM studies (Figure 5) illustrate the morphological changes on the film surfaces induced by chemical reactions. The pristine PET film exhibits a smooth surface with minimal roughness and no visible cracks. Following the aminolysis modification, the surface developed elongated, layered structures resembling increased roughness with evident microcracks. In the PETNH-Cu@Ag samples, SEM images reveal well-dispersed nanoparticles firmly anchored on the amino-functionalized PET surface. These observations confirm that chemical functionalization and nanoparticle incorporation significantly alter the surface morphology, potentially enhancing the material's antimicrobial properties.

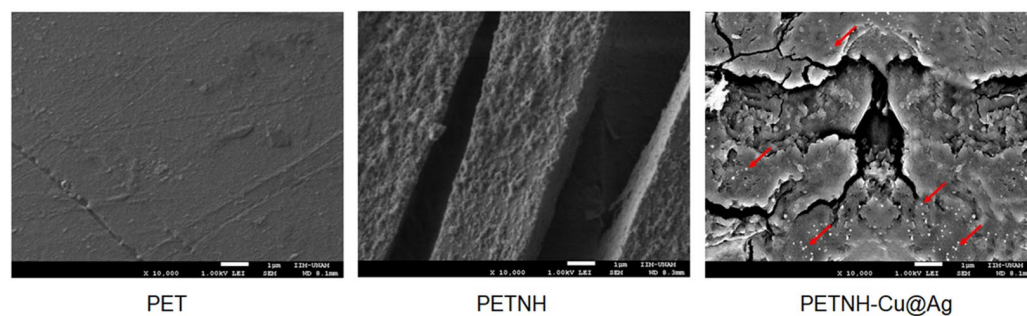


Figure 5. SEM images of PET and PETNH films obtained under reaction conditions of 50 °C and 15 min, showing the surface changes in the PET films during the functionalization process with Cu@Ag nanoparticles. The Cu@Ag nanoparticles are indicated with red arrows in the PETNH-Cu@Ag image.

Furthermore, SEM-EDS mapping and spectra (Figure 6) revealed the presence of carbon and oxygen atoms in the PET film, while a uniform distribution of nitrogen was observed in PETNH, consistent with previous spectroscopic studies. Copper and silver atoms were identified in the PETNH-Cu@Ag films, confirming the presence of Cu@Ag nanoparticles. A lower concentration of copper atoms was also observed, suggesting the presence of bimetallic Cu@Ag nanoparticles as well as the possible presence of Cu^{2+} residues from the silver reduction reaction on the copper nanoparticles. The mapping and spectroscopy results are fully consistent with infrared and XPS studies, confirming that the chemical modification with amino groups on the PET surface allowed for the successful integration of bimetallic nanoparticles.

3.6. XPS Analysis

The wide-scan XPS spectra shown in Figure 7a provide an overview of the elemental compositions of PET, PETNH, PETNH-Cu, and PETNH-Cu@Ag films, showing characteristic peaks for carbon (C1s at 284.8 eV) and oxygen (O1s at 532.8 eV) in the PET films. Additionally, a peak corresponding to nitrogen (N1s at 399.8 eV) was observed in the PETNH films, while the PETNH-Cu and PETNH-Cu@Ag films, their corresponding doublet to copper ($\text{Cu}2p_{3/2}$ 934.70 and $\text{Cu}2p_{1/2}$ 953.06 eV) silver (368.0 eV ($\text{Ag } 3d_{5/2}$) and 374.0 eV ($\text{Ag } 3d_{3/2}$)) were also observed, suggesting the presence of copper and silver in the form of Cu@Ag nanoparticles as it was confirmed by the SEM images (Figure 5) [29,30].

The atomic composition of the films was determined by integrating the XPS peaks and applying appropriate sensitivity factors. The atomic composition of the carbon and oxygen in the films is listed in Figure 7a, which is consistent with that of PET. The results indicated a decrease in the proportion of O1s due to the presence of N1s assigned to the covalent coating of amino groups on the PETNH films. Furthermore, the results of the PETNH-Cu@Ag showed that the atomic composition of the PETNH surface for O1s and C1s was altered by the presence of the Cu@Ag nanoparticles. In addition, the atomic percentage of Cu (0.10%) decreased after the formation of Cu@Ag nanoparticles, due to oxidation of the Cu, releasing copper ions into the reaction medium, and possibly covering the Cu nanoparticle with Ag atoms to form the Cu@Ag nanoparticles.

Figure 7b details the high-resolution XPS analysis of PET, PETNH, PETNH-Cu, and PETNH-Cu@Ag samples, presenting the deconvolution of the C1s, O1s, N1s, Cu2p, and Ag3d core-level spectra. This analysis reveals the chemical evolution of the polymeric surface (PET) after functionalization. In the high-resolution C 1s spectra PET is characterized by a dominant C–C/C–H component at 284.67 eV, associated with the polymer backbone, together with contributions at 286.85 eV and 288.54 eV assigned to C–O/C–OH and O–C=O groups of the ester functionalities (Table 2). After aminolysis, the C 1s envelope broadens and new components appear at 286.26 eV, attributed to overlapping C–O/C–N species

indicating successful surface functionalization. Additionally, the emergence of a component at 287.91 eV, assigned to N–C=O (amide) groups, confirms the partial conversion of ester moieties into amide functionalities. The π – π^* shake-up satellite observed at ~291 eV, typically associated with aromatic PET, its absence in PET and PETNH suggests that, in the metal-containing samples, this peak is primarily influenced by electronic interactions with the Cu and Ag nanoparticles or surface plasmon effects.

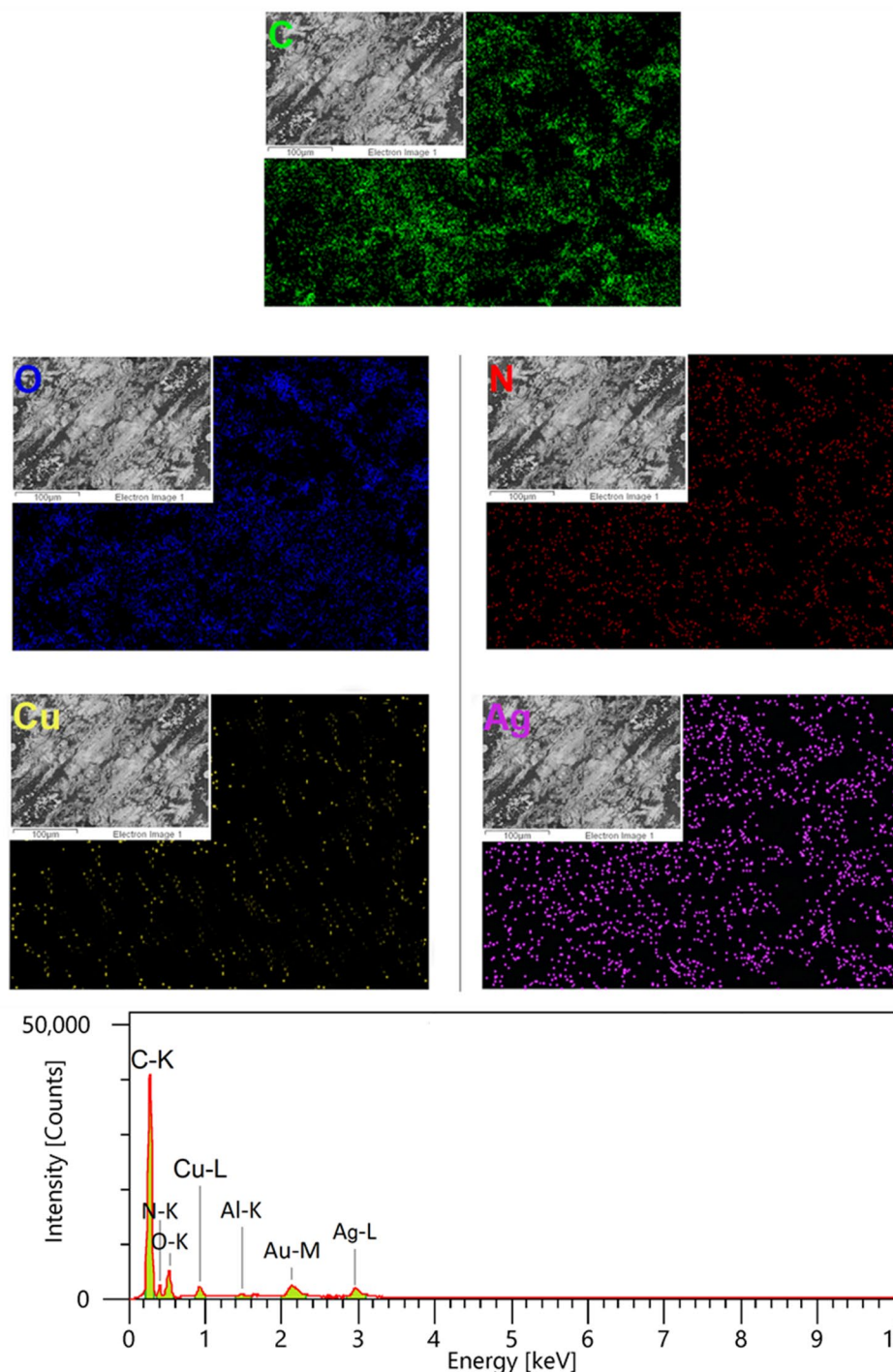


Figure 6. Scanning electron microscopy (SEM) images, energy-dispersive X-ray spectroscopy (EDS) spectra, and elemental mapping of C, O, N, Cu, and Ag. Results are presented using PET films functionalized under aminolysis reaction conditions of 50 °C/15 min (PETNH) and subsequent loading of Cu@Ag nanoparticles (PETNH-Cu@Ag). The peak Al-K is an artifact and Au-M is caused by the coating to endow the conductivity and avoid the overcharge of the sample.

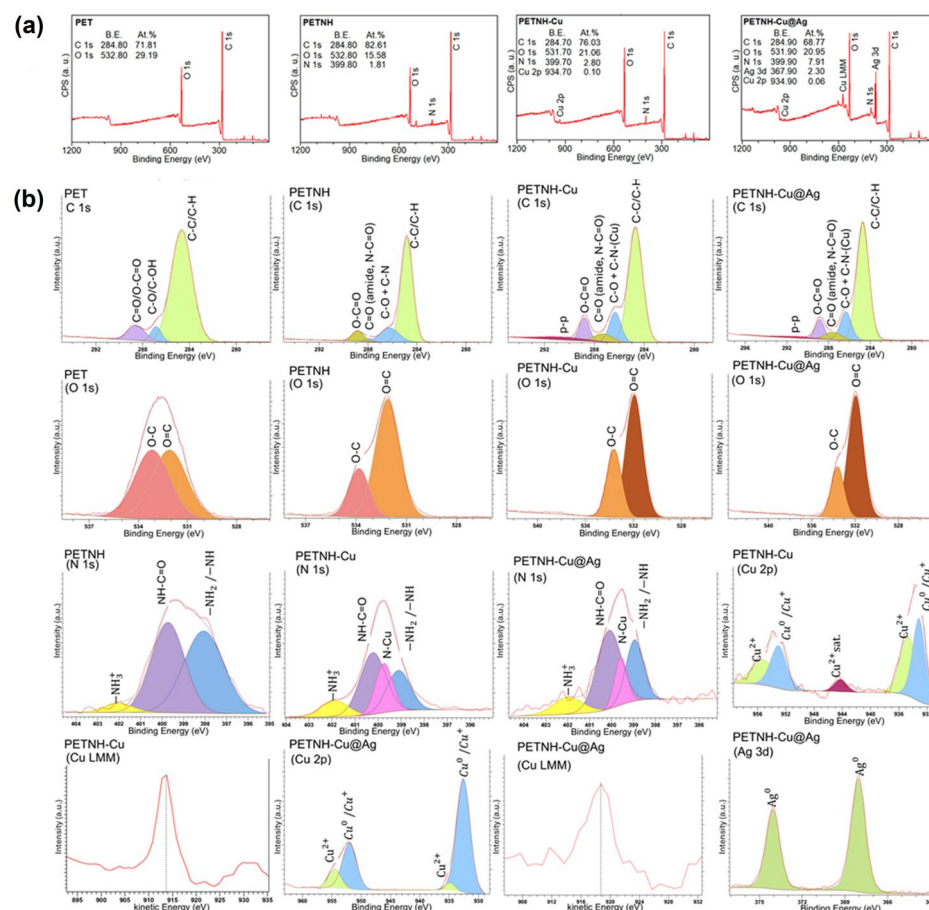


Figure 7. (a) XPS spectra of PET films in the process of functionalization with nanoparticles, the conditions of the aminolysis reaction in the PETNH film were 50 °C, and 15 min and its subsequent loading of Cu and Cu@Ag nanoparticles and (b) deconvolution of XPS spectra corresponding C1s, O1s, N1s, Cu2p, and Ag3d.

The O 1s spectra (Figure 7b) further corroborate these modifications. PET exhibits two main components at 532.10 eV (O=C) and 533.17 eV (O–C) (Table 2). Upon aminolysis and subsequent metal incorporation, a redistribution of these contributions is observed, with an increased relative intensity of the O=C component, consistent with the formation of amide groups and coordination interactions with copper species.

Nitrogen incorporation is evidenced in the N 1s region (Figure 7b). The PETNH sample exhibits components at 398.06 and 399.73 eV corresponding to $\text{–NH}_2/\text{–NH–}$ and amide (–CONH–) groups, along with a minor contribution at 402.02 eV attributed to protonated amines (–NH_3^+) (Table 2). After copper incorporation (PETNH–Cu), an additional component centered at 399.74 eV emerges and is assigned to N–Cu coordination, indicating strong interactions between copper species and surface nitrogen functionalities. This coordinated nitrogen contribution remains after silver coating (PETNH–Cu@Ag), demonstrating the stability of the Cu–N interfacial interactions.

The chemical state of copper was evaluated using the Cu 2p core-level spectra and the Cu LMM Auger transition (Figure 7b). In the Cu 2p spectrum of PETNH–Cu, the coexistence of Cu^0/Cu^+ and Cu^{2+} species is observed, as evidenced by the main peaks at 933.16 eV and 934.66 eV and by the presence of characteristic shake-up satellites associated with Cu^{2+} (Table 2). The occurrence of Cu^{2+} species can be attributed, at least partially, to surface oxidation processes promoted by exposure to ambient conditions during sample handling. In this context, the detected Cu^{2+} species are consistent with a superficial oxidized layer, while the underlying copper remains predominantly in a reduced state. This

interpretation is further supported by the Cu LMM Auger analysis, which shows a dominant contribution at 913.81 eV for PETNH–Cu, indicative of oxidized copper species. After silver coating (PETNH–Cu@Ag), the Cu 2p spectrum exhibits a pronounced increase in the Cu^0/Cu^+ contribution accompanied by a substantial decrease in Cu^{2+} species (Table 2). This observation is attributed to the protective effect of the metallic silver layer, which prevents further surface oxidation of the underlying copper. The Cu LMM Auger peak shifts to higher kinetic energy (918.71 eV), consistent with the presence of metallic or monovalent copper beneath the Ag layer. These results indicate that silver effectively stabilizes the copper nanoparticles against environmental oxidation, preserving the initial Cu^0/Cu^+ and Cu^{2+} distribution established after in situ synthesis.

Table 2. Binding energies (B.E., eV), kinetic energies (K.E., eV), and relative area percentages (%Area) obtained from XPS analysis.

Region	Component	PET		PETNH		PETNH–Cu			PETNH–Cu@Ag		
		B.E. (eV)	%Area (%)	B.E. (eV)	%Area (%)	B.E. (eV)	K.E. (eV)	%Area (%)	B.E. (eV)	K.E. (eV)	%Area (%)
C 1s	C–C/C–H	284.67	84.98	284.83	75.17	284.70	—	69.26	284.71	—	70.39
	C–O/C–OH	286.85	5.47	—	—	—	—	—	—	—	—
	C=O/O–C=O	288.54	9.55	—	—	—	—	—	—	—	—
	C–O + C–N	—	—	286.26	16.02	286.33	—	14.53	286.34	—	15.08
	N–C=O	—	—	287.91	1.43	287.32	—	6.28	287.57	—	5.94
	O–C=O	—	—	288.85	7.38	288.81	—	9.93	288.84	—	8.59
	P–P	—	—	—	—	290.59	—	—	291.20	—	—
O 1s	O=C	532.10	50.00	532.12	74.49	531.94	—	67.64	531.94	—	74.29
	O–C	533.17	50.00	533.82	25.51	533.61	—	32.36	533.62	—	25.71
N 1s	–NH ₂ /–NH–	—	—	398.06	50.06	399.12	—	24.79	398.95	—	26.43
	N–Cu	—	—	—	—	399.74	—	22.18	399.57	—	14.33
	–CONH–	—	—	399.73	45.85	400.23	—	41.43	400.11	—	46.94
	–NH ₃ ⁺	—	—	402.02	4.09	401.89	—	11.63	401.98	—	12.30
Cu 2p	Cu^0/Cu^+	—	—	—	—	933.16	—	51.13	932.59	—	95.52
	Cu^{2+}	—	—	—	—	934.66	—	48.86	934.88	—	4.47
	Cu LMM	—	—	—	—	—	913.81	—	—	918.71	—
Ag 3d	Ag ⁰	—	—	—	—	—	—	—	368.06	—	100

Finally, in PETNH–Cu@Ag, the Ag3d spectrum (Figure 7b) shows a well-defined doublet (3d5/2 at 368.06 eV and 3d3/2 at 374.07 eV) with a spin–orbit separation of 6.0 eV, indicating the presence of metallic silver (Ag⁰). Notable in this sample is the simplification of the Cu2p spectrum towards a predominantly reduced state (Cu^0/Cu^+), accompanied by the practical disappearance of the “shake-up” satellites of Cu^{2+} , which suggests an electronic interaction or a process of silver deposition in a bimetallic form, leaving mainly Cu^0/Cu^+ species exposed during the formation of the bimetallic structure.

3.7. Microbiological Tests

The antibacterial capacity of films loaded with PETNH–Cu@Ag nanoparticles was evaluated against Gram-positive *Staphylococcus aureus* and Gram-negative *Escherichia coli* at 37 °C and pH 7 (Figure 8). The study included PET, PETNH, PETNH–Cu, and PETNH–Cu@Ag films. Cu@Ag nanoparticles loaded on PETNH exhibited significantly enhanced antimicrobial activity against *S. aureus* compared to *E. coli*, with inhibition zones

reaching maximum areas of 1.14 cm² and 0.35 cm², respectively. In contrast, PETNH-Cu films showed substantially smaller inhibition zones, 0.33 cm² (*S. aureus*) and 0.21 cm² (*E. coli*). These findings emphasize the critical role of silver nanoparticle coating in significantly enhancing the antimicrobial properties of PET films, highlighting their potential for applications requiring effective microbial inhibition.

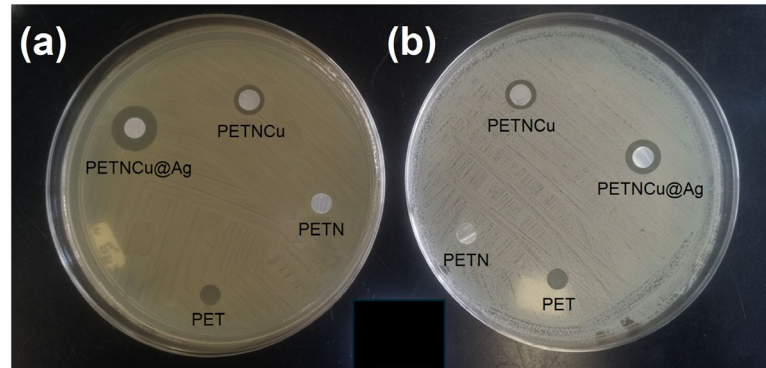


Figure 8. Photograph of the evaluation of the antimicrobial activity (37 °C, pH = 7) of PETNH-Cu and PETNH-Cu@Ag films against *S. aureus* (a) and *E. coli* (b) as models of Gram-positive and Gram-negative bacteria. PET and PETNH films were used as controls that did not exhibit antimicrobial activity.

4. Conclusions

The functionalization of PET with amino groups was successfully achieved via aminolysis with an optimized degradation matrix, yielding a maximum density of 276.13 pmol/mm². This modification allowed for the formation, loading, and stabilization of Cu@Ag nanoparticles on the surface of the PETNH films. SEM micrographs revealed the appearance of surface cracks in the PETNH films, attributable to the partial degradation of the PET, and confirmed the presence of the Cu@Ag nanoparticles. EDS studies showed homogeneous functionalization of the PET surface with amino groups, as well as a uniform distribution of the Cu@Ag nanoparticles. The mechanical and thermal properties of the PETNH-Cu@Ag films showed minimal changes compared to unmodified PET, suggesting that the functionalization was limited to the surface of the material. In conclusion, the aminolysis process and the incorporation of nanoparticles did not significantly affect the intrinsic properties of PET and provided effective antimicrobial activity against Gram-positive and Gram-negative bacteria, expanding its potential applications where bacterial inhibition is needed.

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