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Fabrication and Characterization of PCL/Chitosan and PCL/AgNPs Electrospun Nanofibers for Surface Modification of Cotton Textile

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In the textile industry, particularly for hospital applications, ensuring optimal mechanical properties, balanced hydrophilicity/hydrophobicity, and infection resistance is essential to prevent cross-contamination. Nanofibers offer a promising solution due to their biocompatibility, high surface-to-volume ratio, porosity, tensile strength, and functionalization potential for added properties like antimicrobial. This study electrospinning was used in the fabrication of polycaprolactone/chitosan (PCL/CHT) and polycaprolactone/silver nanoparticles (PCL/AgNPs) nano/microfibers, applied to commercial cotton fabric. Characterization via scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR), confirming the presence of nano/microfibers in cotton, while tensile tests showed improved fabric strength with binder pre-treatment, maintained after coating. The finished textiles exhibited hydrophobic properties, as evidenced by contact angle measurements. Microbiological tests with both gram-negative (*Escherichia coli*) and gram-positive (*Staphylococcus aureus*) bacteria, demonstrated that AgNPs effectively inhibited bacterial growth. The antibacterial properties of PCL/CHT were lower than those of PCL/AgNPs but like those reported in the literature. These findings highlight the potential of nano/microfibers in advanced healthcare textiles.

1. Introduction

Antibacterial textiles have been significant throughout human history. Since ancient times, the Egyptians functionalized textiles with spices and herbs to wrap mummies, preventing bacteria and fungi from decomposing the body. The availability of such textiles allows for a more strategic response to epidemics and pandemics (Schneider et al., 2021). The demand for manufacturing antibacterial textiles is on the rise, with various polymeric and hybrid nanomaterials emerging as promising candidates for surface functionalization, thus aiding in the prevention and control of healthcare-associated infections. This growing market presents an attractive opportunity for several developing countries, prompting them to focus on policy development and incentives for their textile industries, especially in the realm of technical textiles, to compete with highly industrialized nations in textile production. To impart desired properties to these textiles, inorganic or organic antimicrobial agents are employed. Among the most extensively researched agents for conferring antimicrobial properties to textiles are AgNPs . Alternatively, the manufacturing of natural polymer nanofibers presents itself as a viable option, capable of conferring antibacterial activity, typically in fiber diameters smaller than 800 nm (Herrero-Herrero et al., 2021), much smaller than those of common textiles, natural and/or synthetic, which generally have fibers with diameters ranging from 7 to 20μm or fibers produced by melt-blowing and flash spinning with diameters around 1μm (Pohl, 2010). The antibacterial properties of nanofibers are important not only for this sector but also for tissue engineering, as they enable the manufacturing of dressings or wound healing devices (Li et al., 2021). Various techniques have been used for nanofiber manufacturing; however, due to its low cost and reproducibility, electrospinning is one of the most widely used today. In this technique, a polymer solution is subjected to high voltage. By adjusting variables inherent to the solution used (surface tension, viscosity, solute and solvent

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characteristics, among others), process variables (voltage, solution flow rate, collector distance), and environmental variables (relative humidity and temperature), it is possible to obtain fibers with desired characteristics (Clavijo-Grimaldo D. et al., 2022). Leveraging metallic NPs and polymeric nanofibers has been of interest to researchers in recent years, as it facilitates the controlled release of the antimicrobial effect of the nanofibers, ensuring durability (Avci et al., 2022). Challenges arise when AgNPs are dissolved in polymer solutions, such as precipitation or solvent incompatibility with the electrospinning polymer (Villarreal-Gómez et al., 2021). One solution is the one-step synthesis of AgNPs, synthesizing the NPs in the polymer solution to promote solution homogenization and the electrospinning process (Shi et al., 2011). A more environmentally friendly approach includes natural antimicrobial agents such as CHT (Antaby et al., 2021). However, due to the low conductivity and high viscosity of CHT solutions, mixing with other polymers more conducive to electrospinning, such as PCL, is common practice—a polymer widely used in the biomedical industry due to its degradability and biocompatibility. This study conducts a comparative analysis of cotton coatings with PCL/Ag and PCL/CHT nanofibers. The objective is to evaluate their impact on mechanical and wettability properties, as well as antibacterial effectiveness and to demonstrate the potential of each application to enhance the characteristics of textiles used in healthcare.

2. Materials and Methods

2.1 Materials

Polycaprolactone (PCL) (CAS # 134490-19-0 and average Mn = 80.000 g/mol), 100 % acetic acid (AA) (CAS # 64-19-7), formic acid (FA) (CAS #64-18-6), chitosan 85 % deacetylated (CHT) (CAS # 9012-76-4) and silver nitrate (CAS # 7761-88-8) were used. All these chemical agents used were supplied by Sigma-Aldrich. The substrates used were commercial 100 % cotton fabric (F) treated with the binder Aprettan NTR ® (B) (N92201) supplied by Archroma.

2.2 Textile pretreatment and solutions preparations

The F samples were cut into 1 cm diameter circles and immersed in a 50:50 v/v solution of Aprettan NTR® and deionized water. They were then dried at 70°C for 8 minutes. To manufacture the nanofibers, a base solution of PCL at 8% w/v in a 50:50 v/v mixture of FA and AA was prepared and stored at room temperature for 48 hours. CHT was dissolved in the PCL solution at concentrations of 5, 10, and 20% w/v (labelled as PCL/5%CHT, PCL/10%CHT, and PCL/20%CHT, respectively). PCL/Ag solutions were prepared by adding AgNO3 to the solution at concentrations of 0.25, 0.5, and 1% w/v (labelled as PCL/0.25%Ag, PCL/0.5%Ag, and PCL/1%Ag, respectively). The resulting solutions were homogenized using ultrasound at a frequency of 50 Hz for 180 minutes at 21°C.

2.3 Nanofiber fabrication and cotton fabric functionalization

The fibers were developed in a vertical electrospinning equipment composed of a high voltage source (CZE1000R, Spellman), a dosing pump (NE-300, Micrux), a syringe and a needle (21 gauge). The deposition time of the fibers on the F substrates was 60 min over the rotary collector. Applied voltage, needle-collector distance and solution flow were the parameters of the electrospinning process that were adjusted until obtaining uniform fibers without defects. The parameters of the electrospinning process are found Table 1.

Table 1: PCL/Chitosan and PCL/Ag electrospinning parameters.

Sample	Flow (ml/h)	Collector Distance (cm)	Voltage (kV)
PCL	0.2	18	10
PCL/5%CHT	0.2	18	10
PCL/10%CHT	0.2	15	10
PCL/20%CHT	0.1	12	12
PCL/0.25%Ag	0.2	18	10
PCL/0.5%Ag	0.2	18	10
PCL/1%Ag	0.2	18	10

2.4 Physicochemical characterization

The fiber morphology was studied using Jeol JSM-6010LA (Mitaka, Tokyo). The fiber diameter was analyzed using the public domain image analysis software ImageJ software. Mechanical properties were analyzed through tensile testing (ASTM D5034:2009). Chemical properties were determined using FTIR (Nicolet iS5) in

attenuated total reflectance mode (ATR). Contact angle tests (ASTM D5725-99/2008) were conducted on all samples and were calculated using Image J software.

2.5 Antibacterial Test

Reference strains of *S. Aureus* (ATCC 29213) and *E. Coli* (ATCC 25922) were used, supplied by the Microbiology Laboratory of Keralty. Textile were sterilized using ultraviolet radiation. To assess antimicrobial activity, the qualitative method JIS L 1902:2008-Halo was performed. Bacterial strains were placed in contact with the textile on nutrient an agar Mueller Hinton (Ad-bio AD-MP16-3) and incubated for 24 h at 37 °C. Bacterial viability was evaluated at 48 h of incubation using the LIVE/DEAD™ BacLight™ Bacterial Viability Kit for Microscopy (Molecular Probes™). The biofilm formation capacity was determined by detecting exopolysaccharides using a 0.02% calcofluor stain.

3. Results and Discussion

3.1 Morphological characterization

Figures 1a and 1b depict that F exhibits a typical woven structure with a flattened morphology and twisted ribbon-like fibers, showing a wide diameter distribution with micrometer-sized fibers, consistent with literature reports. The manufactured PCL fibers (Figure 1c) have uniform diameter distribution (592.44 ± 138 nm). Figure 1d illustrates the PCL fibers deposited onto F.

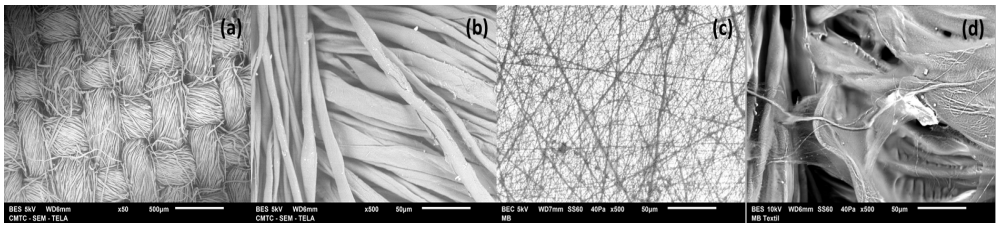

Figure 1: Morphology of F, nanofiber and F with nanofibers observed by SEM of (a) initial F 50X, (b) initial F 500X (c) PCL nanofibers 500X, (d) PCL nanofibers on the F 500X.

Figures 2 and 3 show independent PCL/CHT and PCL/Ag nanofibers and those deposited on F. In general, nanofibers exhibit a smooth, bead-free surface, distributed uniformly. The electrospinning process with the incorporation of fabric with a binder in the rotary collector reduced electrostatic charge, resulting in some beads appearing on F. When 5 % CHT is added to the PCL, Figures 2a and 2b show smooth nanofibers, but with a 10 % CHT addition in Figure 2c, beads are observed distributed along the fibers. Regarding the fiber diameter distribution, the addition of 5 % CHT results in a diameter of 2300 ± 794 nm. With a 10 % CHT addition, there is a substantial decrease in the mean diameter (349 ± 87 nm).

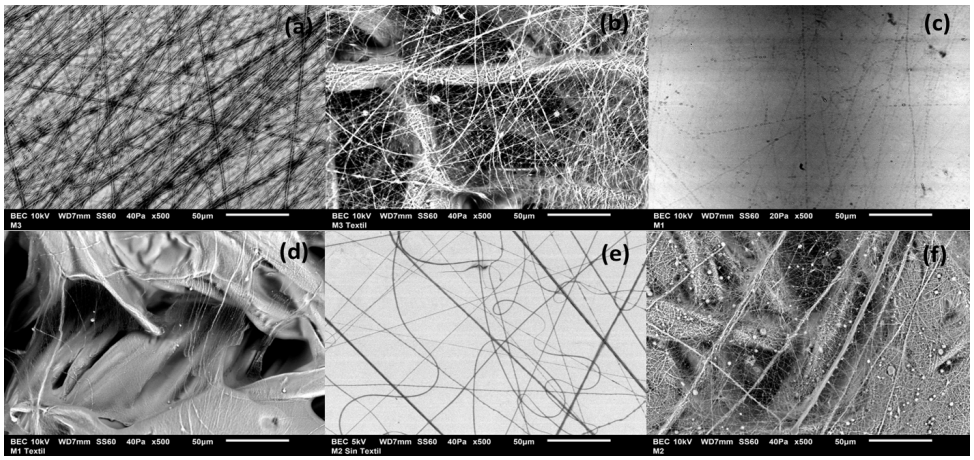

Figure 2: Morphology of PCL/CHT nanofibers and PCL/CHT nanofibers on F observed by SEM: (a)PCL/ 5,0% CHT (b) PCL/5,0% CHT on F (c)PCL/ 10% CHT (d) PCL/10% CHT on F, (e) PCL/20% CHT, (f) PCL/20% CHT on F.

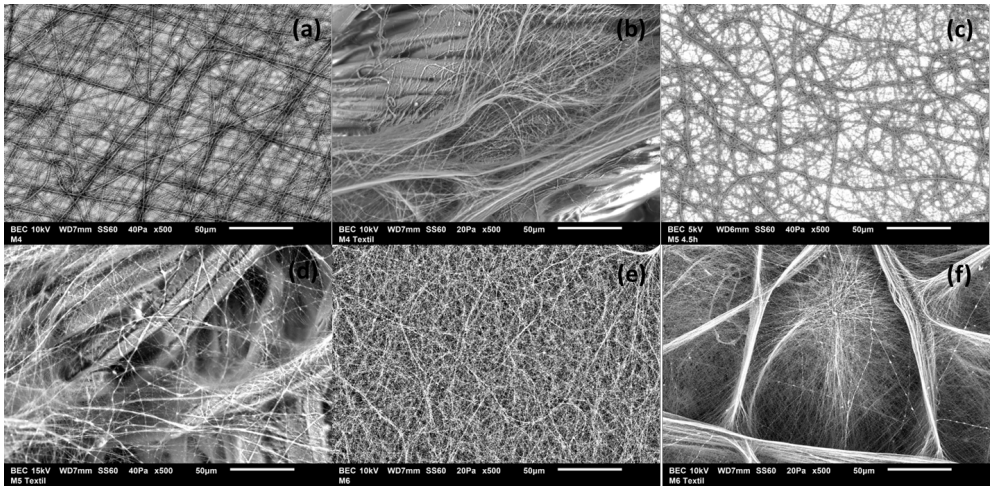

Figure 3: Morphology of PCL/Ag nanofibers and PCL/AG nanofibers on the F observed by SEM of (a) PCL/0,25% Ag, (b) PCL/0,25% Ag on F, (c) PCL/0,5% Ag, (d) PCL/0,5% Ag on F (e) PCL/1,0 % Ag, (f) PCL/1,0% Ag on F.

The addition of 20 % CHT shows a slight increase in the diameter (532 ± 256 nm), change in trend may be due to the change in the electrospinning parameters to achieve smooth fibers. PCL/Ag nanofibers reveal a uniform and better-distributed diameter than PCL/CHT fibers, as shown in Figure 3a–f. The obtained diameters decrease with the addition of Ag to the fibers, reaching 611 ± 112 nm for 0.25 % Ag, 532 ± 256 nm for 0.5 % Ag, and 453 ± 84 nm for 1.0 % Ag. This behaviour is attributed to the increased electrical conductivity of the polymeric solution, resulting in a smaller diameter due to the enhanced charge transport (Avci et al., 2022). The reduction in diameter size is a desirable effect as it increases the surface area-to-volume ratio.

3.2 Mechanical testing evaluation

The textile without any treatment (F) shows more stiffness and less deformation than textile with binder (F+B) and textile with binder and PCL (F+B+PCL). Finding that the addition of the binder does generate significant changes in the properties of the textile. On the other hand, when adding the nanofiber coating to the (F+B), there no significant change ($p<0.05$). Additionally, the tensile properties of the textile samples with nano/microfibers of PCL/chitosan and PCL/Ag were not significantly different ($p<0.05$); differing in some tests in the breaking point, showing that the coating of nano/microfibers does not generate significant changes in the mechanical behavior of the textile with binder. In comparison, the tensile properties of nanofibers with F are higher, because of the summation of the mechanical properties of the fabric and the aligned nanofiber of PCL, which contributes to enhancing the tensile stretch because of the anisotropy. Finally, there is no difference between PCL/CHT and PCL/Ag nanofibers with F, due to the fabric strength, which is so much higher than the PCL nanofibers by themselves (Table 2).

Table 2: Strength, strain and Young's Modulus of F, F with blinder, and F with blinder and coaching of PCL nano/microfibers.

Sample	Tensile Strength (MPa)	Strain (%)	Young's Modulus (MPa)
F	103.5 ±3.4	11.1 ±0.3	9.2 ±0.2
F+B	101.9 ±1.8	13.3 ±0.2	8.4 ±0.2
F+B+PCL	104.3 ±3.4	13.8 ±1.1	8.4 ±0.4

3.3 FTIR spectroscopy

In the spectrum corresponding to initial F (Figure 4a), a peak at 3250 cm^{-1} (O-H bonds of cellulose) and a peak at 1045 cm^{-1} (O-C bonds) were recognized. On the other hand, upon adding the nano/microfiber coating with PCL (spectra b-g), the characteristic peaks of PCL at 2954 and 2870 cm^{-1} (asymmetric and symmetric CH2 stretching) and a peak at 1732 cm^{-1} (C=O bond) are observed. In the case of spectra (b-d), the presence of CHT is recognized by the appearance of the band centered around 3441 cm^{-1} and 3435 cm^{-1} (O-H and N-H bonds). Regarding the spectra (e-f) corresponding to the samples with silver nanoparticles (AgNPs), only the base PCL polymer can be identified since it is not possible to recognize the presence of Ag using this technique.

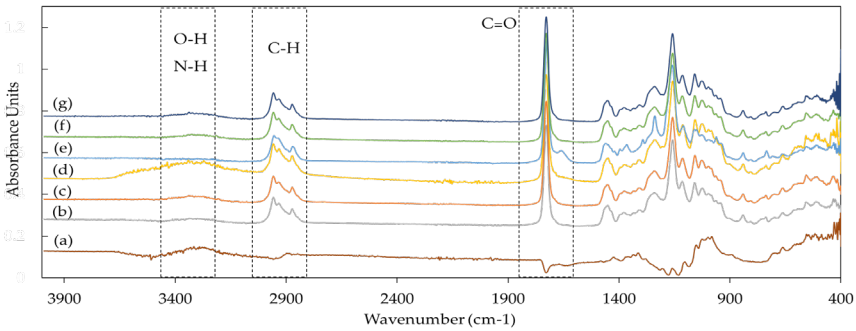

Figure 4: FTIR Spectra (a) initial F, (b) PCL/5% CHT, (c) PCL/10%CHT, (d) PCL/20%CHT, (e) PCL/0,25% Ag, (f) PCL/0,5% Ag, (g)PCL/1% Ag.

3.4 Wettability of fibers

The sample of F is completely hydrophilic, since, by adding the drop of water, it is immediately impregnated in the fabric. On the other hand, when adding the surface modifier with PCL nano/microfibers, is observed a contact angle of 112 ±2° , indicating that the textile now has hydrophobic properties. This result is due to the hydrophobic character of the base polymer of the PCL nanofibers, as it is known in the literature for the molecular composition of PCL nanofibers (Tiyek et al., 2019). The contact angles were PCL/5%CHT (115 ±2°), PCL/10%CHT (111 ±2°), PCL/20%CHT (114 ±2°), PCL/0.25%Ag (111 ±3°), PCL/0.5%Ag (115 ±0.4°) and, PCL/1%Ag (74 ±12°). Except for the last-mentioned sample, functionalization with PCL/CHT and PCL/Ag shows a significant increase in the hydrophobicity of the textile.

3.5 Antibacterial Test

In the PCL/CHT samples, bacterial growth was observed before washing. The antibacterial mechanism of CHT is based on the interaction between positively charged chitosan molecules and negatively charged entities on the bacterial surface. Since this polymer is insoluble in the culture medium, CHT can only act against bacteria in the tissue and not those in the medium. After washing, bacterial growth was not observed (Sathiyaseelan et al., 2022). In the PCL/Ag samples, there was no evidence of microbial growth on the textile before or after washing, showing a better effect (Table 3). Previous studies have shown that PCL fibers possess intrinsic antibacterial activity (Clavijo-Grimaldo et al., 2019). Functionalization was not effective in preventing biofilm formation, even at higher concentrations (PCL/20%CHT and PCL/1%Ag), as reported in other studies (Vukoje et al., 2014). The strains used were highly resistant bacteria, as they were obtained from a reference microbiology laboratory at a hospital institution. Therefore, the qualitative observation of the antibacterial properties is valid, as it allows for macroscopic identification of population changes due to the effect of the material used (Alven et al.,2021). In this study, no quantitative analysis of Ag retention after washing was performed, as previous research has shown that PCL nanofibers with AgNPs, fabricated via electrospinning, retain a significant number of nanoparticles both within the nanofiber structure and after washing (Korniienko V, et al., 2024). This supports the interpretation that the results observed in this study indicate sufficient nanoparticle retention to achieve effective antibacterial performance (Permyakova et al., 2023).

Table 3: Results of proliferation of Staphylococcus aureus or Escherichia coli bacteria on the textile samples. (+/-) corresponds to samples where microbial growth/absence of bacterial growth.

Sample	*S. aureus*		*E. coli*	
	Pre-washing	Post-washing	Pre-washing	Post-washing
F	+	-	-	+
PCL	-	-	+	-
PCL/5%CHT	+	-	+	-
PCL/10%CHT	+	-	+	-
PCL/20%CHT	+	-	+	+
PCL/0.25%Ag	-	-	-	-
PCL/0.5%Ag	-	-	-	-

4. Conclusions

Nano-microfibers PCL/chitosan and PCL/AgNPs were successfully deposited and adhered to a cotton textile. The functionalization increased hydrophobicity, thus providing greater protection against potential contamination

with fluids from patients. This change is important to enhance user biosecurity. The addition of the binder in the fabric pre-treatment resulted in increased load resistance in the tensile mechanical test and enhanced deformation and resilience of the textile, essential characteristics for specific applications (e.g., hospital bedding). As reported in the literature, the antibacterial properties of silver nanoparticles were superior to those of chitosan, both before and after washing the textile. Future studies combining both agents are needed, expecting a greater antimicrobial effect.

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