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Electrospinning and Electrospraying Techniques for Designing Antimicrobial Polymeric Biocomposite Mats

Heriberto Rodríguez-Tobías, Graciela Morales and Daniel Grande

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Abstract

Tissue engineering is an interdisciplinary area in which polymeric nanofibers have been exploited either as scaffolds or wound dressings. This chapter overviews the use of versatile electro-hydrodynamic processing techniques for developing antimicrobial nanofibrous mats derived from polymeric biocomposites. The influence of well-known antimicrobial nanoparticles on the physical properties of precursory polymeric solution is discussed, and the consequences of their variations on several important morphological parameters, namely average fiber diameter and orientation, porosity, pore size, among others, are considered. Moreover, other specific properties of composite fibers conferred by the nanoparticles are reviewed as well as their use toward the design of multifunctional polymeric mats.

Keywords: antimicrobial nanoparticles, biocomposites, electrospinning, electrospraying, polymeric nanofibers

1. Introduction

Electro-hydrodynamic techniques, i.e., electrospinning and electrospraying, have been extensively explored in the biomedical area for the last 15 years, probably due to the submicrometric diameter exhibited by the obtained fibers; and consequently, to the large surface area to volume ratio and high porosity with interconnected voids formed between the fiber structures. These morphological features and size scale are suitable to mimic the natural extracellular matrix (ECM), thus promoting cell attachment and proliferation. Therefore, fibrous materials have been catalogued as excellent materials for tissue engineering, and a vast

number of publications related to their applications as wound dressings and/or cell-based scaffolds have been recorded [1, 2].

Electrospinning and electrospraying techniques are based on identical principles and the equipment typically consists of a syringe containing the solution that passes through a capillary (needle) and the flow rate is controlled by a pump. In turn, a power source applies several tens of kV on the needle, and therefore on the polymer solution. The applied high voltage causes a significant density of charges on the droplet which protrudes into the tip of the needle up to a point where the repulsive forces of the charges exceed the surface tension and polymer jet or drop is eventually produced and then captured in the grounded collector, and the solvent being evaporated during the passage from the tip of the needle to the collector. The final morphology of the obtained polymeric material depends on the physical properties of the polymer solution as well as the electro-hydrodynamic device parameters [3, 4]. The effects of these parameters on the fiber diameters and morphologies are gathered in **Table 1**. When the polymer solution concentration is enough to promote chain entanglements, a polymer jet is formed. On the contrary, if the polymer solution concentration is too low, chain entanglements will not occur and droplets will be sprayed from the needle, and the electro-spraying process takes place [5–7].

Parameter	Effect on fiber morphology
Increase in applied voltage	Fiber diameter initially decreases, then increases (not monotonic)
Increase in flow rate	Fiber diameter increases (beaded morphologies occur if the flow rate is too high)
Increase in needle-to-collector distance	Fiber diameter decreases (beaded morphologies occur if the needle-to-collector distance is too short)
Increase in polymer concentration (viscosity)	Fiber diameter increases (within optimal range)
Increase in solution conductivity	Fiber diameter decreases (broad diameter distribution)
Increase in solvent volatility	Fibers exhibit surface microtexture (pores on their surfaces, which may increase surface area)

Source: Ref. [3].

Table 1. Effect of different parameters on the morphology of polymeric fibers derived from electrospinning process.

Currently, there is a trend to develop nanocomposite fibers by means of the incorporation of nanoparticles in a polymer solution; the resulting materials consist of nanoparticles-embedded polymeric fibers with enhanced or new properties. On the other hand, an innovative approach has been recently employed in order to obtain nanoparticles-coated polymeric fibers that involve a tandem process, i.e., simultaneous electrospinning of a polymer solution and the electrospraying of a nanoparticles dispersion, whose configuration is illustrated in **Figure 1**. This combination of electro-hydrodynamic techniques gives rise to a higher extent

of exposed nanoparticles, thus increasing the surface-dependent properties of nanocomposite fibers, such as antimicrobial, optical, and catalytic properties, among others [5–10].

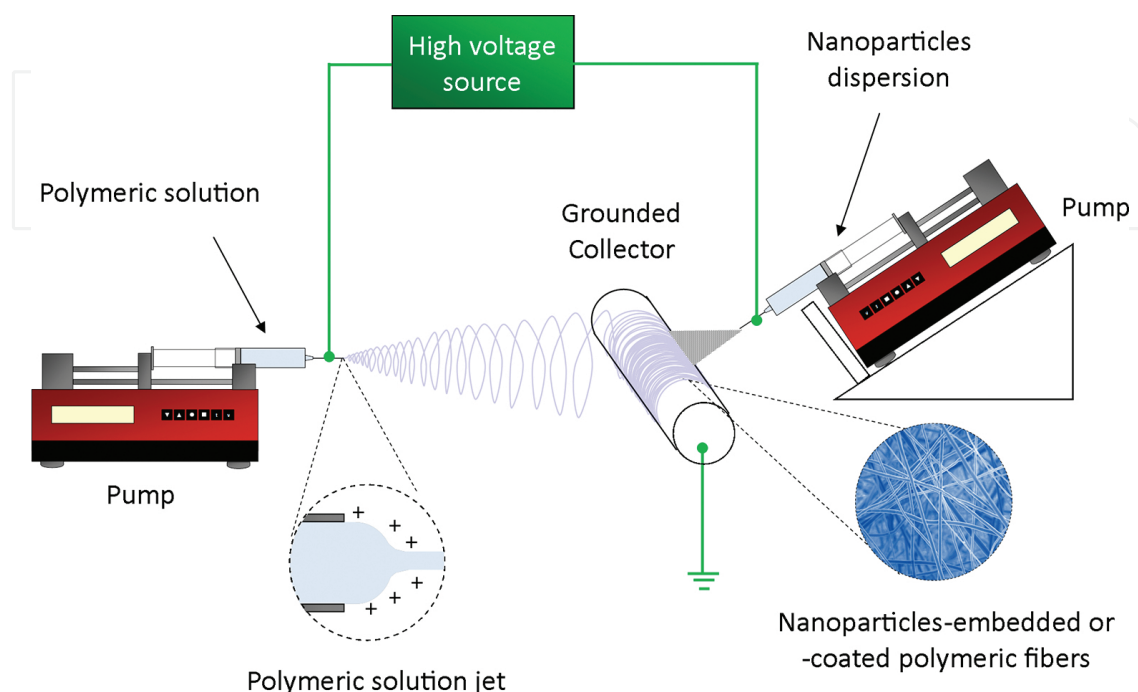


Figure 1. Typical configuration of an electrospinning/electrospaying tandem equipment.

2. Antimicrobial biopolymeric nanofibers by electrospinning and electrospaying

Materials designed by electrospinning and electrospaying techniques are predominantly used as mats in tissue engineering. The mats derived from electro-hydrodynamic techniques indeed possess morphology similar to the natural ECM that is composed of a submicron fiber network of proteins and glycosaminoglycans. Electrospun nanofibrous scaffolds may act as a support for cell adhesion and subsequent proliferation, thus providing cells with the appropriate microenvironment of chemical and physical cues, including cell-matrix and cell-cell interactions, and eventually forming tissues with suitable mechanical and biological properties [3, 4].

Regarding the polymeric matrix, biocompatible, biodegradable, and/or bioabsorbable polymers are desirable, since the mats gradually degrade leaving only the new tissue and also avoid a subsequent surgery [2–4]. Several aliphatic polyesters possess the aforementioned features, among which poly(ϵ -caprolactone), poly(3-hydroxybutyrate), poly(4-hydroxybutyrate), the corresponding copolymers with 3- and 4-hydroxyvalerate, poly(lactic acid), and the

respective copolymer with glycolic acid could be cited. Some polysaccharides have also been used, chitosan being the most noticeable.

However, polymeric mats derived from electro-hydrodynamic techniques entail a huge inconvenience, their fibrous/porous morphology is also prone to the adhesion of pathogenic microorganisms, thus facilitating the occurrence of serious infections [11–13]. Several strategies have been considered in order to overcome one such drawback, the incorporation of organic compounds being the most prominent, and more recently, nanoparticles with well-recognized antimicrobial properties. Polymeric nanofibers containing antimicrobial nanoparticles can exhibit several advantages compared to typical organic compound-loaded polymeric analogues, such as higher thermal stability, enhanced mechanical performance, or biocompatibility, depending on the chemical nature of nanoparticles [14–17]. In this context, the design of antimicrobial polymeric fibers containing different nanoparticles will be addressed in the next subsections.

2.1. Polymeric mats containing silver nanoparticles as antimicrobial additives

Silver nanoparticles (nano-Ag) have extensively been investigated as antimicrobial agents against a broad variety of microorganisms, from bacteria to viruses [18]. Silver in its metallic state is inert but it reacts with the moisture in the skin and the fluid of the wound and gets ionized. The ionized silver is highly reactive, as it binds to tissue proteins and brings structural changes in the bacterial cell wall and nuclear membrane leading to cell distortion and death. Silver also binds to bacterial DNA and RNA by denaturing and inhibits bacterial replication. The antimicrobial performance of silver is related to the amount of silver and the rate of silver ions released [19]. Although silver nanoparticles have been used as cream or gel, there is a trend to incorporate them into polymeric wound dressings in order to prevent infections, and in turn, promote wound healing [20–22].

Poly(vinyl alcohol) (PVA) is a biocompatible and nontoxic polymer suitable for the design of antibacterial wound dressings derived from electro-hydrodynamic techniques. Additionally, PVA is a water soluble polymer, thus making its fibers elaboration an ecofriendly and innocuous process. Hong [23] engineered PVA-based mats containing nano-Ag by means of precursory solution of the corresponding polymer and AgNO_3 with a subsequent thermal or ultraviolet (UV) posttreatment. The obtained PVA-based mats exhibited excellent antibacterial activity against *Staphylococcus aureus* and *Klebsiella pneumoniae*. Although the water solubility of PVA might be a drawback when using it as wound dressing, this can be overcome by simple thermal treatment without negative effect on final properties.

Likewise, PVA solutions have also been mixed with nano-Ag and montmorillonite (MMT) in order to obtain the corresponding fibers with antibacterial properties and enhanced thermal stability (conferred by MMT). At a fixed MMT concentration, an increase in nano-Ag from 1 to 5 wt% led to higher average fiber diameters, which was attributed to an increase in solution viscosity, thus illustrating that nanoparticles seriously affected the final morphology of mats. Nano-Ag triggered the inhibition growth of both *Staphylococcus S. aureus* and *Escherichia coli* [24].

In other studies, nano-Ag was embedded into electrospun nanofibers based on chitosan. This polysaccharide has attracted the industrial and academic attention, as it is a bio-sourced material and possesses inherent antimicrobial activity. Nonetheless, electrospinning of neat chitosan is complicated due to its limited solubility; therefore, it has typically been mixed with other biocompatible polymers such as poly(ethylene oxide) (PEO) and PVA. An et al. [25] designed antibacterial chitosan/PEO nanofiber by means of incorporation of nano-Ag. The results led to the conclusion that viscosity and surface tension of the precursory solution were not affected by the nano-Ag concentration, but the electrical conductivity was proportionally increased by the augmentation of the metallic nanoparticles. The authors argued that residual Ag^+ ions were responsible for this behavior. Another important fact was that the presence of nano-Ag promoted the formation of fibers with smooth surface and the average fiber diameter was decreased, as expected by the increase in electrical conductivity. Furthermore, the obtained polymeric mats with embedded nano-Ag (2.2 wt%) exhibited higher tensile strength than that for neat mats, while the corresponding elongation was reduced. Regarding the antibacterial activity against *E. coli*, the chitosan/PEO-based mats significantly decreased the proliferation of this bacterium in a short period of time (6–8 h). Penchev et al. [26] have developed a one step-procedure for the preparation of cross-linked chitosan/PEO/Ag mats whose stability in aqueous environment render these new materials promising candidates for applications, such as wound-healing dressings or antibacterial filters.

Other biodegradable polyesters, such as poly(lactic acid) and poly(ϵ -caprolactone) have been used as matrices for the elaboration of nanofibers with Ag nanoparticles. Kim et al. [21] investigated the influence of AgNO_3 concentration on the viscosity, electrical conductivity, and surface tension of precursory polymeric solution, and a relationship with the final morphology was proposed. It is important to mention that after electrospinning process, AgNO_3 was reduced to Ag. The incorporation up to 9 wt% of AgNO_3 did not alter the viscosity or surface tension, but the electrical conductivity was considerably increased, as observed in other polymeric systems. Regarding the morphology, the increase in AgNO_3 concentration (i.e., electrical conductivity) from 3 to 6 wt% led to thinner PLA fibers, interestingly, an optimal AgNO_3 concentration was perceived since thicker fibers were formed at 9 wt% AgNO_3 . The mats containing nano-Ag showed growth inhibition values higher than 99%, regardless of the type of bacterium and nanoparticles concentration. Xu et al. [27] conducted a similar investigation but with higher content of nano-Ag from 9 to 32 wt%. The author demonstrated that at high nano-Ag concentration, average fiber diameter increased probably due to interactions with PLA, and consequently increased the solution viscosity. The antibacterial activity against *E. coli* and *S. aureus* was practically identical to that for PLA mats with lower nano-Ag concentration as that reported by Kim.

Recently, Augustine et al. [28] prepared PCL fibers containing embedded silver nanoparticles. Regarding the morphological features, the fiber diameter was decreased by the presence of nanoparticles. The authors claimed that nanoparticles increased the electrical conductivity; however, no evidence was given. EDX analysis showed that the higher the silver content, the more significant the formation of aggregates, and the latter were exposed on the surface of the PCL fibers. The aggregation of silver nanoparticles had an impact on the

mechanical properties of the fibrous materials, since at relatively low concentrations (0.05 and 0.5 wt%) both; elongation and fracture resistance were enhanced, while incorporating 1 wt%, the mechanical properties had no changes compared with blank PCL fibers. Concerning the performance of the fibers as antibacterial materials, disk diffusion tests proved that the growth inhibition area of *S. aureus* is doubled at a nanoparticles concentration as low as 0.5 wt%, while the bacterium *E. coli* showed greater resistance.

Actually, there is a limited investigation related to the use of mere electrospraying or its combination with electrospinning for obtaining antimicrobial nanocomposites mats with Ag nanoparticles. Park et al. [29] successfully obtained PVA/montmorillonite/silver hybrid particles by means of an aqueous solution of the corresponding polymer and inorganic nanoparticles subjected to electrospraying. The composite polymeric particles were formed only at low PVA molar mass and concentration, and the transmission electron microscopy (TEM) images evidenced the exfoliated montmorillonite and well-dispersed Ag nanoparticles, regardless of their concentration in the precursory solution. The hybrid polymeric particles containing the combination of nanostructures possess a higher thermal stability attributed to montmorillonite, and no interference of Ag was perceived. Electrosprayed materials having Ag nanoparticles inhibited the proliferation of the *S. aureus* strain, while those without the mentioned metallic nanoparticles failed, thus showing the potential of electrospraying technique for obtaining polymeric nanoparticles with antibacterial activity.

2.2. Antimicrobial polymeric mats containing metal oxides nanoparticles

Metal oxides nanoparticles are another type of particles not only used as antimicrobial agents but also they can also impart other interesting optical and electrical properties, which can potentiate their use as semiconductors, electroluminescent devices, thermoelectric materials, and for environmental decontamination applications [30–32]. Among the main metal oxide nanoparticles used as antimicrobial agents, zinc oxide (ZnO) and titanium dioxide (TiO₂) can be mentioned. They are addressed in the following subsections.

In this context, TiO₂ has also been embedded in biopolymer fibers to confer antimicrobial properties and its potential use in tissue regeneration. Lee et al. [33] developed multifunctional PVA fibers with excellent growth inhibition against *S. aureus* and *K. pneumoniae*. Furthermore, the obtained fibrous materials functioned as UV filter membranes and degrading agents of ammonia and formaldehyde. These features were accomplished with relatively low nanoparticles content (2–3 wt% respect to the polymer). It is noteworthy that the effect of the presence and/or concentration of the nanoparticles on the precursory solution properties was not studied.

Son et al. [34] have also exploited the antibacterial activity of TiO₂ to prepare polymeric fibers based on chitosan/PVA blends. The experimental results demonstrated a direct relationship between the content of chitosan and the viscosity of the precursory solution. The authors also found that at chitosan concentration greater than 7 wt% (relative to volume of solution), it was not possible to obtain uniform morphology, i.e., fibers with numerous ovoid defects were obtained. Interestingly, the presence of TiO₂ nanoparticles did not change the morphological features, namely average fiber diameter. Authors also established that the diameter of the

fibers (270–360 nm) had no significant effect on the antibacterial activity against *E. coli* and *S. aureus*. Furthermore, good growth inhibition (approximately 83–85%) was obtained with TiO_2 concentrations as low as 0.04 wt% into the polymeric blend. When comparing these results with those for fibers containing silver nitrate, it was evidenced that the presence of the latter was more effective for growth inhibition of both bacteria.

Rashkov's group has thoroughly studied the combination of electro-hydrodynamic techniques. In 2013, this group prepared submicrometric fibers based on PHB and TiO_2 nanoparticles by mere electrospinning and electrospinning/electro spraying tandem technique [35]. The fibers obtained by mere electrospinning of PHB/ TiO_2 presented defects along them, which were attributed to the formation of agglomerates, and consequently, disturbance of the solution flow. Furthermore, the nanoparticles were successfully deposited on PHB fibers by the tandem process, although some aggregates were perceived with up to 1 μm in size. In order to overcome the aggregation of nanoparticles, the authors added chitosan oligomers to the precursory solution, keeping in mind that it might act as a dispersant. However, the selected approach was not favorable, since aggregates as big as 10 μm were detected, which was attributed to the increase in the dispersion viscosity, thus forming large droplets during the electro spraying process. The authors also implemented an impregnation process in order to obtain the TiO_2 -covered PHB fibers, whose morphological results were not encouraging due to the formation of large aggregates. The materials obtained showed excellent pigment degradation of pollutants; methylene blue (used as pigment model) was entirely degraded after only 3 h in the presence of the electro spun materials. The composite fibers obtained by the different strategies showed significant antibacterial activity against *E. coli*, with the advantage of allowing for the adhesion and development of human mesenchymal stem cells, which was attributed to the morphological characteristics suitable for applications in the field of tissue engineering.

Another contribution from Rashkov's group was also related to the combination of electro-hydrodynamic techniques, by which a series of PHB-based fibers with TiO_2 and iron oxide (Fe_3O_4) nanoparticles were designed in order to obtain multifunctional mats [36]. The authors carried out the electrospinning of PHB containing TiO_2 and Fe_3O_4 , the combination of electrospinning of PHB and electro spraying of Fe_3O_4 or $\text{Fe}_3\text{O}_4/\text{TiO}_2$ dispersion, and electrospinning of PHB/ Fe_3O_4 combined with electro spraying of TiO_2 . In order to stabilize the nanoparticles dispersions, low amounts of chitosan or its oligomers in acetic acid were used (0.5–2%, w/v). Regarding the morphology, the composite PHB fibers derived from electrospinning exhibited a significant number of beads, while the materials produced by the combined techniques of electrospinning/electro spraying showed aggregates on the surface. Furthermore, a smaller amount of nanoparticles than initial feed was determined by X-ray photoelectron spectroscopy (XPS), which was ascribed to the formation of a dense layer of the stabilizing agent used (chitosan or oligomers). Since the antibacterial activity of identical materials had already explored, the new series of electro spun PHB fibrous mats were used as membranes for the degradation of pollutants pigments. The degradation activity was higher for the fibrous materials obtained by the conjunction of electro-hydrodynamic techniques, due to higher surface area exposed to the solution containing the pigment. It is noteworthy that no

information of the effect of metal oxide nanoparticles on viscosity or electrical conductivity was reported in this work.

Zinc oxide (ZnO) nanoparticles are considered as antimicrobial agents that can strongly compete with silver nanoparticles, especially for their simple and inexpensive synthesis as well as its effectiveness in eliminating several pathogen microorganisms [37–40]. ZnO nanoparticles have been exploited for the development of fibrous materials based on biodegradable polymers, and some of these reports shall be addressed next.

Sodium alginate is a polyelectrolyte that has excellent biocompatibility, biodegradability, and ease of dissolution in water; however, it is not suitable for the preparation of fibers by electrospinning. In order to facilitate the fiber formation, Shalumon et al. [41] mixed sodium alginate with different proportions of PVA, which lowers the inherent brittleness of the sodium alginate, and the authors used ZnO nanoparticles (diameter = 100 nm) as an antibacterial agent. The resulting fibers were crosslinked using glutaraldehyde to increase their dimensional stability. Since sodium alginate is a polyelectrolyte, this increased electrical conductivity of the solution. This behavior was also observed when the nanoparticles were incorporated; however, the effect was not so marked but until a nanoparticles concentration higher than 5 wt%. Similarly, the viscosity of the solution was increased, due to the presence of alginate or nanoparticles, and this parameter had the most important effect on fiber morphology, specifically, the fiber diameter which slightly increased. The authors also demonstrated that the presence of the alginate promoted higher thermal stability of the fibers, while the nano-metal oxide did not contribute significantly to the retard in thermal degradation. Concerning the antibacterial properties, the fiber materials showed excellent antibacterial activity against *E. coli* and *S. aureus*, which was proportional to the content of nanoparticles. Conversely, the adhesion of mice fibroblasts was diminished as the concentration of ZnO was increased.

Augustine et al. [42–44] have intensively investigated the influence of ZnO nanoparticles on the morphology, bactericidal performance, and cell proliferation on mats based on PCL fibers. In 2014, these authors reported that the incorporation of a relatively low amount of nano-ZnO (0.1–0.9 wt%) did not significantly affect the morphology of PCL fibers. Conversely, when a concentration of 1 wt% is exceeded, the morphology undergoes significant changes mainly in the appearance of pores and the fiber diameters, which they attributed to the increased viscosity of the precursor solution and the charge density; however, electrical conductivity or rheological analyses were not presented. EDX spectroscopic studies showed that by increasing the concentration of ZnO nanoparticles, they can be exposed on the surface of the PCL fibers, while the existence of hydrogen bond interactions between hydroxyl groups on nanoparticles surface and the carbonyl groups of the PCL was established by Fourier transform infrared (FTIR). Regarding antibacterial activity, it was determined that a lower concentration of 5 wt% was not enough to inhibit the proliferation of *E. coli* and *S. aureus*. Interestingly, PCL/ZnO fibrous mats did not show cytotoxicity against adult goat fibroblasts (*in vitro* study), which makes them promising as antibacterial biodegradable scaffolds [43]. Concurrently, Augustine et al. showed that the PCL/ZnO composite fibers had the ability to heal wounds on the skin of animals without showing inflammation of tissues when ZnO nanoparticles was

below 4 wt%, which allows for further use as wound dressings and/or scaffolds with bactericidal properties [44].

Poly(L-lactide) has also been subjected to both the electrospinning process and the electrospinning/electro spraying tandem technique. Rashkov's group [45] designed fibrous mats whose inorganic phase consisted of ZnO nanoparticles. The authors took advantage of the photocatalytic and antibacterial properties of ZnO to generate purifying membranes. The fibers obtained by mere electrospinning showed high efficiency to degrade methylene blue and an azo pigment (95% and 65% degradation, respectively) in only 300 min. Meanwhile, the fibers resulting from electrospinning/electro spraying degraded both pigments in a shorter time (approximately 180 min). This behavior was explained in terms of a larger nanoparticles surface area prone to degrade the pigments. Furthermore, the materials had a considerable efficiency for killing *S. aureus*, in a greater extent for the PLA/ZnO fibers derived from the combined technique. Considering the biocompatibility, the content of nanoparticles was significantly high (greater than 45 wt%), which is not beneficial when trying to use such materials as surgical implants, since it has been shown that ZnO nanoparticles contents higher than 5 wt% is not suitable for adhesion and proliferation of tissue cells.

In order to get further insight into the antibacterial activity of PLA-based fibers containing ZnO nanoparticles, our research groups in Mexico and France have developed electrospun and electrospun/electro sprayed mats derived from poly(D,L-lactide) and low amounts of ZnO nanoparticles [10]. Scanning electron microscopy (SEM) images of the obtained mats are disclosed in **Figure 2**. It was noted that the incorporation of nanoparticles provoked slight variations in viscosity and conductivity of precursory solutions, and no significant effect on the morphological parameters (namely, average fiber diameter, pore size, and porosity) of electrospun PLA-based mats was observed. Furthermore, the presence of nano-ZnO enhanced the mechanical performance of these materials, exhibiting an optimal concentration of nanoparticles for 3 wt%, probably due to hydrogen bonds between hydroxyl groups on ZnO nanoparticles and carbonyl groups of PLA. Regarding the antibacterial properties of mats, they were shown to be dependent on the type of bacteria, being *E. coli* less sensitive to the presence of nanoparticles. On the other hand, when electrospinning/electro spraying was used with at least 1 wt% of ZnO nanoparticles, values higher than 94% of growth inhibition of *S. aureus* were achieved, while simple electrospun mats did not inhibit the bacterium growth for the same ZnO concentration. The results obtained make ZnO-coated fibrous PLA mats potential candidates for applications related to wound dressing materials.

A similar protocol used for PLA/ZnO mats was adapted for developing PHB-based antibacterial fibers [46]. The analysis of the physical properties (viscosity and electrical conductivity) showed that the presence of ZnO nanoparticles had an insignificant effect at low concentration (1 and 3 wt%) and a slight effect at ZnO content of 5 wt%. Consequently, the final morphology of corresponding nanofibers was not altered. The obtained PHB/nano-ZnO mats showed uniform fiber morphology with an average porosity *ca.* 85% with enhanced thermal stability compared to that of pristine PHB. Differential scanning calorimetry was also used to determine the influence of ZnO nanoparticles on the phase transitions of as-spun PHB nanofibers; it was thus shown that the nanoparticles promoted the formation of different

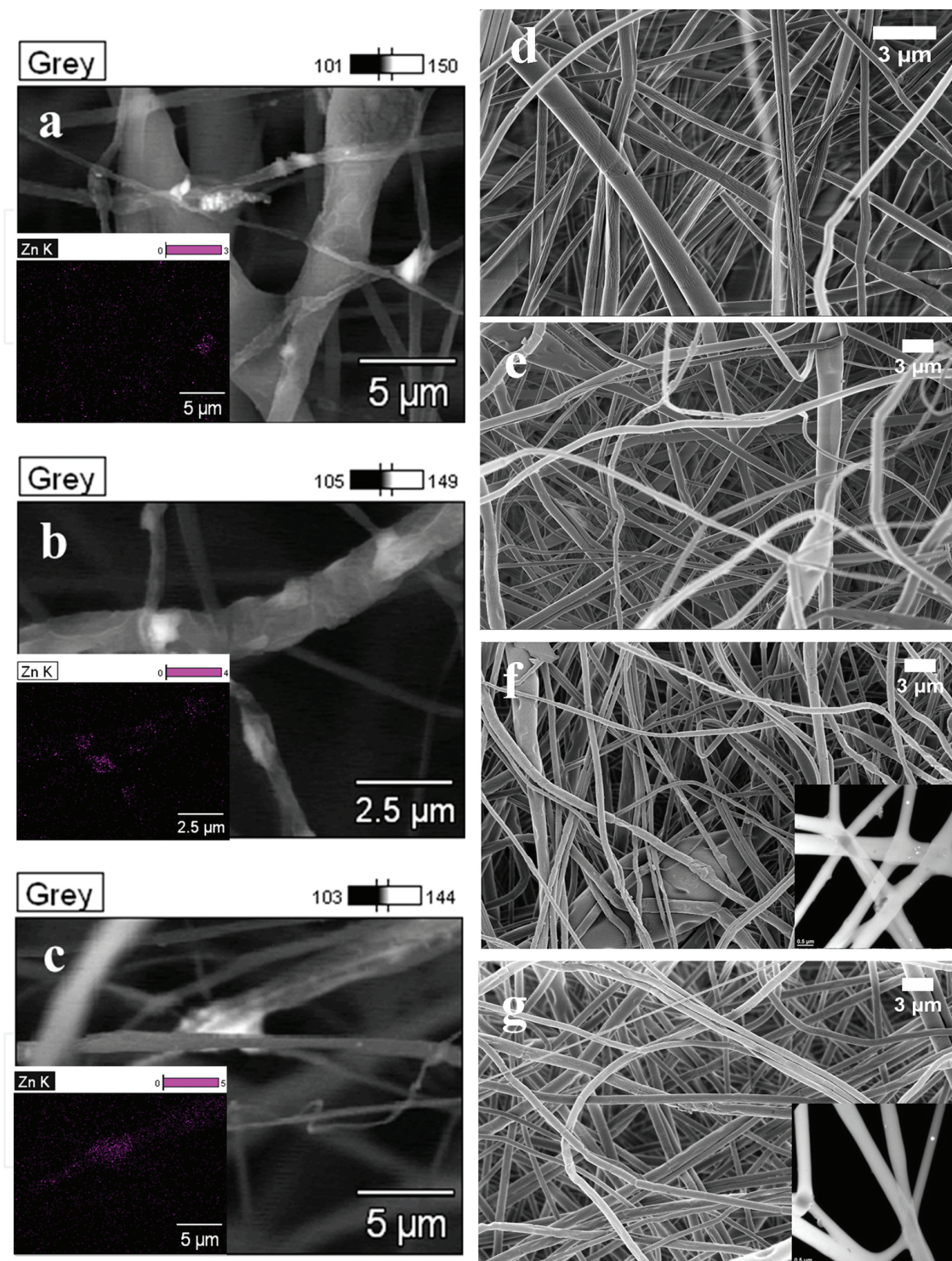


Figure 2. SEM images of PLA/ZnO mats obtained by means of electrospinning/electrospraying with (a) 1, (b) 3, and (c) 5 wt% ZnO, respectively, and simple electrospinning with (d) 0, (e) 1, (f) 3, and (g) 5 wt% ZnO, respectively. Insets: (a)-(c) EDX maps; (f), (g) TEM images.

crystalline entities. Furthermore, the antibacterial performance against *E. coli* and *S. aureus* was proved to be dependent on the elaboration technique, being higher for electrospinning/

electro spraying tandem technique, thus permitting the design of novel bacteriostatic or bactericidal PHB/nano-ZnO nanofibrous composites.

Copper oxide nanoparticles are other well-recognized antibacterial agents that have been incorporated into polymeric matrices, but not specifically biodegradable. The studies related to copper nanoparticles used as antimicrobial agent in electrospun polymers are limited, probably due to the instability of this metal oxide to environmental conditions, which can change the oxidation state of copper, thus changing its final properties.

However, Ungur and Hruza [47] used a semi-industrial scale electrospinning (roller spinning method) for developing poly(urethane) (PU) nanofibers modified with copper oxide (II) (CuO). The roller spinning method consists of an aluminum rotating cylinder body with spikes which was partially immersed into the polymer solution. High voltage is connected to the rotating roller. As the solvent evaporates, the jets of polymer solution are transformed and the solid nanofibers are obtained before reaching the collector electrode. The nanofibers were collected on polypropylene (PP) spun bond nonwoven antistatic material. Regarding the physical properties of PU solutions, the authors demonstrated that low CuO content (2.5 and 5 wt%) have no noticeable influence on the rheological behavior of solutions within time at low shear rate. However, the viscosity of PU solutions was increased in the presence of higher concentrations of antimicrobial agent (7, 9.5, 12, and 15 wt%). On the other hand, electrical conductivity was identical for all solutions, i.e., the presence of CuO did not affect this physical property. Interestingly, despite the increase in solution viscosity by the incorporation of CuO, average fiber diameter of pristine PU and PU/CuO mats exhibited a slight variation ranging from 250 to 300 nm. The result of EDX analysis demonstrated the significant decrease in the amount of Cu on the nanofiber surface for the fibers with 15% CuO, probably due to their aggregation within the fiber structure. The obtained materials demonstrated high antibacterial activity against Gram-negative bacterial strain *E. coli* and Gram-positive strain *S. aureus* at relatively low CuO contents (2.5 wt%) and it was also demonstrated that the incorporation of higher amount of nanoparticles did not improve the antibacterial properties.

Poly(acrylonitrile) (PAN) possesses good mechanical and thermal properties; therefore, it is a suitable polymer for designing purifying filters and (no biodegradable) wound dressings by electro-hydrodynamic techniques. For instance, Zhang et al. [48] employed a method that allowed for the synthesis of zero-valent copper (Cu⁰) nanoparticles in/on PAN nanofibers by two steps, including the preparation of polyacrylonitrile/copper(II) (PAN/Cu²⁺) nanofibers by electrospinning, and the preparation of PAN/Cu⁰ nanofibers by high-pressure hydrogenation reduction. Regarding the morphology of PAN/Cu²⁺ nanofibers, the average diameter ranged from 200 to 600 nm, and the nanofibers were becoming more and thicker with the increase in copper nitrate. The authors also demonstrated that the use of high-pressure hydrogenation reduction chamber did not change the fiber morphology, and a good dispersion of nanoparticles was preserved, showing Cu⁰ aggregates lower than 20 nm. The PAN/Cu⁰ showed bacteriostatic effect against *S. aureus* (i.e., the survival bacteria population was lower than those counted in pristine polymer, but higher than the bacteria population inoculated), thus showing the potential use of these fibers as antifouling materials.

3. Conclusions and perspectives

Electro-hydrodynamic techniques, namely electrospraying and electrospinning, are powerful approaches for developing material with morphological features suitable for tissue engineering applications. The incorporation of nanoparticles allows for the generation of multifunctional mats that can be used in different applications ranging from filters for pollutant removal to wound dressings. Regarding the pollutant removal, metal oxides (mainly ZnO and TiO₂) are the more promising nanoparticles, while for tissue engineering a further insight into the biocompatibility should be obtained. Comparing the electro-hydrodynamic techniques, the electrospraying process enables higher nanoparticles surface area prone to act as antibacterial agents or degrading materials, regardless of the presence of aggregates obtained in most of the cases. Finally, certain nanoparticles promote other specific properties, such as thermal stability, original crystallization behavior, enhanced mechanical properties, etc. which can lead to the diversification of polymeric/nanoparticles-based mats.

Electro-hydrodynamic techniques have a great potential in many applications; however, there is a need for developing novel or adapted equipment that enables the fabrication of polymeric mats in a higher scale.

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