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Coaxial poly(lactic acid) electrospun composite membranes incorporating cellulose and chitin nanocrystals

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In this study, we used electrospinning to produce core-shell nanofibers of poly(lactic acid) as core and poly-acrylonitrile/cellulose nanocrystals (CNC) or polyacrylonitrile/chitin nanocrystals (ChNC) as shell. Electrospun materials prepared at different nanocrystal concentrations were tested and assayed as microfiltration membranes. The coaxial membranes presented a maximum pore size in the 1.2–2.6 μm range and rejections > 85% for bacterial cells (0.5 × 2.0 μm) and > 99% for fungal spores (> 2 μm). The morphological and mechanical properties and the water permeability of the nanocomposite membranes were studied. The morphological characterization showed random fibers of beadless and well-defined core/shell structured fibers with diameter generally below the micron size with presence of secondary ultrafine nanofibers. Tensile strength and Young's modulus of elasticity improved with respect to coaxial membranes without nanocrystals with best mechanical properties achieved at 5 wt% CNC and 15 wt% ChNC loadings. The enhancement was attributed to the reinforcing effect of the percolating network of cellulose nanocrystals. Water permeability increased for all membranes loaded with nanocrystals with respect to the coaxial fibers without nanocrystals, the highest corresponding to ChNC composites with up to a 240% increase over non-loaded membranes. Composite membranes prepared with CNC in their shell were hydrophilic, in contrast with the hydrophobic PLA core, while coaxial fibers with ChNC were superhydrophilic. CNC membranes were negatively charged but ChNC originated neutral or positively charged membranes due to the contribution of deacetylated chitin structural units. Upon exposure to *E. coli* cultures, composite membranes containing ChNC showed a high antimicrobial action and were essentially free of bacterial colonization under strong biofilm formation conditions.

1. Introduction

Electrospinning is a versatile procedure for producing polymeric fibers below the micron scale [1]. The technique has been recently investigated in view of its potential to generate high surface-to-volume ratio materials functionalized in the nanoscale [2,3]. By controlling operating conditions and solution parameters, electrospinning can be used to produce a variety of non-woven porous or smooth nanofibrous structures suitable for their use as filtration media [4]. Opposite to conventional membrane preparation technologies, such as phase inversion, the high pore interconnectivity and porosity of electrospun membranes make them promising materials for filtration processes [5]. However, filtration using electrospun fibrous membranes must overcome the hurdle of their lower mechanical strength compared to polymeric films, which is particularly critical in pressure-driven filtration for water treatment applications [6]. The reason is the low degree

of molecular orientation in electrospun polymers, which is a consequence of the competition between flow-induced chain orientation and chain relaxation before fiber solidification [7]. The mechanical properties of electrospun fibers can be improved using post-treatments, such as stretching and annealing, that increase molecular orientation and crystallinity [8]. Alternatively, the co-electrospinning of polymers and fillers can produce composite fibers with enhanced mechanical properties [9,10].

Biofouling, is one of the main factors determining membrane performance in many practical applications [11]. It refers to the growth of microorganisms on membrane surface, and results in loss of permeability, increased transmembrane pressure, reduced membrane life and risk of pathogen dissemination [12]. Two approaches can be followed to minimize biofouling: Proper surface design to prevent primary adhesion, or the use of cleaning strategies including the use of biocides [13]. The manipulation of the physicochemical properties of

membranes allow creating surfaces hostile for microbial attachment targeting the initial stage of microbial colonization, before biofilm formation [14]. Biofilms are complex communities of cells embedded in an extracellular polymeric matrix formed by polysaccharides, proteins, and nucleic acids, which protect cells from adverse conditions [15]. Once formed, biofilms are very difficult to remove. In fact, biofilm formation constitutes an advantageous strategy for survival and growth in hostile environments and represents a degree of complexity in structure and metabolism similar to the tissues of higher organisms [16]. The high tunability of electrospun membranes offers new ways of creating antimicrobial environments. The incorporation of functional agents with antibiotic properties [17], the use of polymers with intrinsic antibacterial properties such as chitosan [18] and different treatments for surface modification [19] have been explored to create biofouling resistant electrospun fibers.

Poly(lactic acid), PLA, is a biodegradable thermoplastic aliphatic polyester derived from renewable resources, which, despite being hydrophobic, displays higher natural hydrophilicity than conventional hydrophobic thermoplastic polymers due to the better access of water molecules to the polar oxygen linkages of its backbone. Higher water fluxes and reduced biofouling tendency of PLA-based membranes offer a good option to replace conventional membranes made of petrochemical polymers [20]. However, electrospun PLA in membrane applications presents some limitations due to the poor mechanical properties of pure PLA fibers [5].

Cellulose and chitin fibrils in the nanometer range are biobased nanoparticles that expanded the possibilities of natural polymers in the field of engineered sustainable nanocomposites [21]. The dimensions of cellulose and chitin nanocrystals and nanofibers offer a high surface area filler and the possibility of creating functional materials with exceptional physical, chemical and mechanical properties [22]. Cellulose nanocrystals from microcrystalline cellulose were previously reported to substantially improve the mechanical properties of electrospun nanocomposites prepared from PLA [23], polyethylene oxide [24], and polyacrylamide [25].

Chitin, poly-β-(1-4)-N-acetyl-D-glucosamine, is a natural, renewable and biodegradable polymer, the second most abundant natural polymer after cellulose. Substantial amounts of this structural material can be found in animals, as part of exoskeletons, backbones and the cell walls of fungi and yeasts. Despite its easy accessibility, chitin is an underutilized resource because of its insolubility in water and common organic solvents [26]. However, in recent times the use of chitin has generated great interest due to its excellent mechanical and certain antibacterial properties. The incorporation of chitin derived nanocrystals to different polymeric membranes has been recently addressed with the purpose of enhancing their mechanical properties and antifouling performance [27,28].

In this work, structured electrospun PLA fibers reinforced with chitin and cellulose nanocrystals were prepared by means of coaxial electrospinning and used to prepare a microfiltration membrane with size exclusion in the low-micrometer range. Several works already reported the impact of nanocrystalline cellulose on the physical properties of PLA composites. It has been described that the resulting nanocomposites displayed a considerable improvement in mechanical properties, greater at temperatures below the glass transition temperature of PLA due to the enhancement of its crystallinity degree [29–32]. Our approach was to create core-shell fibers with nanocrystals on the fiber surface in order to deeply modify the physicochemical properties of membrane surface to enhance water permeability and resistance to microbial attachment. The described methodology aimed at combining the environmentally desirable properties of PLA with the unique characteristics of cellulose/chitin nanocrystals to create high flux and low biofouling membranes with enhanced mechanical resistance.

2. Materials and methods

2.1. Materials

Transparent PLA (marketed under trade name PLA Polymer 2002D) was acquired in pellets from NatureWorks LLC, UK, with melt index (MFR) of 5–7 g/10 min (at 210 °C/2.16 kg), molecular weight 121,400 g/mol, melting temperature 160 °C and 4% D-content (96% L-lactide). Polyacrylonitrile (PAN), molecular weight 150,000, melting temperature 317 °C, was obtained from Sigma-Aldrich. N, N-dimethylformamide (DMF, synthesis grade) and chloroform (synthesis grade) were purchased from Scharlab (Spain). Culture media components were biological grade reagents acquired from Conda-Pronadisa (Spain). Fluorescein diacetate (FDA), Live/Dead Bac-Light Bacterial Viability Kit and FilmTracer SYPRO Ruby were acquired from Invitrogen (Thermo Fisher, Waltham, USA).

The first type of cellulose nanocrystals, CNC_{H2SO4}, was prepared via sulfuric acid hydrolysis. Briefly, microcrystalline cellulose was mixed with sulfuric acid (63.5 wt%) under stirring in an ice bath. The suspension was heated up to 44 °C for 130 min under stirring. Then, the suspension was centrifuged for 10 min at 12,000 rpm until the supernatant became turbid. The nanocrystal suspension was neutralized against deionized water through dialysis. Thereafter, the suspension was sonicated in an ice bath to separate the nanocrystals [33].

The second kind of cellulose nanocrystals, CNC_{BE}, were obtained following the bioethanol processing route [34,35]. Unbarked wood was hydrolyzed using dilute acid in a bioethanol pilot plant at SP Processum, Örnsköldsvik, Sweden, and refined to obtain pure cellulose. The refining was done by Soxhlet extraction for 6 h at 150 °C using toluene/acetone mixture (2:1 ratio). This material was then bleached, washed with deionized water and concentrated by centrifugation to 17 wt%. The purified cellulose from bioethanol process was led to 2 wt% suspensions, mixed by shear mixture and passed through the homogenizer, 10 times to obtain a thick gel of cellulose nanocrystals (CNC_{BE}) as reported elsewhere [35].

Chitin nanocrystals (ChNC) were isolated from crab shells using hydrochloric acid hydrolysis. The raw material was boiled in 5 wt% KOH solution for 6 h under stirring to remove proteins. Afterwards, the suspension was washed with distilled water and then bleached with chlorite at 80 °C for 6 h. Thereafter, the bleached suspension was washed followed by bleaching during overnight treatment using 5 wt% KOH and then concentrated using centrifuge. After that, the purified chitin was hydrolyzed using HCl 3 N for 90 min at 80 °C under stirring. After hydrolysis, the excess acid was removed by centrifugation until the turbid supernatant was achieved. The isolation process was completed by neutralization against deionized water. Then, the suspension was sonicated to individualize the nanocrystals [36,37]. In what follows, CNC_{H2SO4} and CNC_{BE} will be jointly referred to as cellulose nanocrystals, CNC, while the term nanocrystals, NC, will include also chitin nanocrystals, ChNC. Water dispersed NC were solvent exchanged into DMF by distillation-assisted evaporation to facilitate the electrospinning process.

2.2. Coaxial electrospinning

Fig. 1 presents a schematic illustration of the experimental setup used for coaxial electrospinning. The spinneret consisted of a double capillary tube in which the smaller was concentrically inserted into the larger one. The inner fluid produced the core of the fiber, while the outer one formed the shell of core-shell or coaxial fibers. 7 wt% PLA in chloroform/DMF (3:2 v/v) was used for the core and 10 wt% of PAN in DMF with 5, 10, 15 or 20 wt% of NC (in solvent-free basis) was used to produce the PAN/NC fiber shell. The choice of PAN as shell-forming polymer was based on its compatibility with NC, that did not agglomerate during electrospinning. Besides, the shell solution must be spinnable by itself and viscous enough guide the core one to attain coaxial