

Electrospinning chitosan blends for nonwovens with morphologies between nanofiber mat and membrane

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Abstract. Chitosan belongs to the biopolymers possessing a broad spectrum of intrinsic physical and chemical properties which make it useful for diverse applications, such as filters or tissue engineering. For both areas it is necessary to control not only the chemical composition of the polymer, but also the shape of the surface which is in contact with the filtered medium or the growing cells, respectively. Depending on the desired form, chitosan and other biopolymers can be sprayed, coated, or spun, with few possibilities to vary their morphology between droplets, thin layers, and fibres. One possibility to mix thin films and fibres consists in using an electrospinning process which normally produces fine fibres, but depending on spinning solution and process, also membranes can be created. The article gives a short overview of the possibilities to vary a chitosan nonwoven between nanofiber mat and membrane, resulting in significantly different surface shapes.

1. Introduction

Chitosan is used in a broad field of different applications. Due to its antifouling properties under visible light, chitosan was used for the production of filters which showed high methylene blue degradation efficiency. To optimize mechanical properties and the porous structure, the chitosan was mixed with Cr-doped TiO₂ [1].

In air filtration, chitosan nanofibers blended with TiO₂ or Ag nanoparticles showed a significant increase in filtration of nanoparticle aerosols, compared with commercially available filters, combined with antibacterial activity [2]. For water filtration, composites of a PHBV (poly (hydroxybutyrate-cohydroxyvalerate)) nanospun mat and a chitosan casted barrier layer were found to reach up to 99 % filter efficiency for different disperse dyes [3]. As a coating on a cotton fabric, chitosan was used as a biological water filter for Gram-positive and Gram-negative bacteria [4-5]. Blended with PCL (polycaprolactone), chitosan nanofiber membranes were used for antibacterial water filtration [6].

More special filter demands can be found, e.g., in filtering silver from the waste of X-ray film processing. Here, chitosan membranes were found to have filtration coefficients of up to 99.9 % [7]. In solid phase extraction cartridges, chitosan can be used for perchlorate removal [8]. Dissolved pharmaceuticals could be removed from water by chitosan better than by cellulose or sodium alginate [9].

On the other hand, chitosan belongs to the biopolymers which are typically used for production of scaffolds in biotechnological or medical applications. Human mesenchymal stem cells, e.g., were grown on chitosan thin films after enzymatic modification [10]. Genipin-crosslinked chitosan is used



as a hydrogel due to its antibacterial activity for different medical purposes, such as scaffolds for human mesenchymal stem cell growth, but also for cartilage engineering and similar applications [11].

In several investigations, chitosan was used for electrospinning nanofiber mats. For chitosan/ poly (ethylene oxide) (PEO) blends, some research groups found nanofiber membranes with varying morphologies, depending on the chitosan:PEO ratio [12]. Another group, working with needle-electrospinning, produced fibres and/or beads, depending on the chitosan:PEO ratio [13].

Most of the aforementioned investigations, however, were performed for special morphologies of the chitosan, such as nanofibers, membranes, or hydrogels, without the possibility to examine the influence of the surface structure in detail. In an earlier investigation, however, we found a first indication that nanofibers as well as thin film membranes could be produced by needleless electrospinning, depending on the chitosan:PEO ratio [14].

This is why in the recent project, we studied the influence of different spinning solution and process parameters on the created chitosan nonwovens, resulting in structures between nanofiber mats and thin film membranes.

2. Experimental

The needleless nanospinning machine “Nanospider Lab” (Elmarco, Czech Republic) was used to produce electrospun nanofiber mats. The spinning parameters were as follows: voltage 80 kV, carriage speed 250 mm/s, nozzle diameter 0.9 mm, electrode-substrate distance 160 mm, relative humidity in the chamber 38 %, temperature 22.5 °C. The substrate speed was varied between 0 and 30 mm/min to create mats of different densities.

For the spinning solutions, a chitosan solution of 2 wt% medium molecular weight chitosan (190-310 kDa; 200-800 mPa·s; Sigma Aldrich) with 1 % acetic acid was prepared. The chitosan was solved in aqueous solution with sodium bicarbonate (NaHCO_3), using a concentration of 20.16 g/l. PEO (poly (ethylene glycol)) with a molecular weight of 600,000 daltons (concentration 8 %) purchased from S3 Chemicals was added as a spinning agent. Water was added to modify the viscosity of the polymer solution; the respective amounts of H_2O are given in the descriptions of the results. Viscosities were not measured but varied in a range which was suitable for electrospinning with the chosen nozzle.

The base parameters were chosen as follows: 1 ml chitosan solution (2 wt%), 1 ml NaHCO_3 , 3 ml H_2O ; 0.5 mL PEO solution (8 wt%). The amounts of water and of PEO solution were varied in the experiments.

The resulting samples had dimensions of approx. 30 cm x 50 cm of which the middle area was chosen for further investigation. Images were taken using a confocal laser scanning microscope VK-9000 (Keyence), using a nominal magnification of 2000 x.

3. Results and discussion

In a first test series, chitosan/PEO nonwovens were produced using different amounts of H_2O with 1 ml chitosan solution, 1 ml NaHCO_3 solution, and 0.5 ml PEO solution. In Figure 1, the results are depicted. For the smallest amount of water (1 ml H_2O), a relatively closed mat with some pores is produced, partly showing the rainbow colours typical for diffraction in thin films, while other parts seem to be more solid.

A middle quantity of water (3 ml H_2O) results in evenly thin films, showing rainbow diffraction colours in several areas, with apparently more holes in which only very fine fibres are formed. The highest amount of water (5 ml H_2O) leads to an open-pore structure with several thicker and thinner fibres and a few membrane areas. Apparently, the middle amount of water results in creation of thin membranes, while less water produces more fibrous structures.

As visible by the scales in the images, the pores in the membranes are of the order of magnitude of 10-50 μm , while the fibre diameters vary between approx. 100 nm and 1 μm .

In the next test series, the quantity of PEO solution was modified, while the other parameters (1 ml chitosan solution, 1 ml NaHCO_3 solution, 3 ml H_2O) were kept constant. The results are presented in Figure 2. For the lowest amount of PEO solution (0.2 ml), only a web of fine fibres is shown, covered

with small droplets. In some parts of the web, however, thin films are visible. By increasing the fraction of PEO solution to 0.5 ml, the already known membrane structure with some holes is achieved. By increasing the quantity of PEO solution further (0.8 ml), more areas are covered with fibre structures and fewer thin film areas. Finally, adding 1.1 ml PEO solution, most areas are covered with fine fibres, while the areas covered with thin films are again reduced. Apparently it is possible to tailor the ratio of nanofiber and membrane areas by modifying the amount of PEO in the spinning solution.

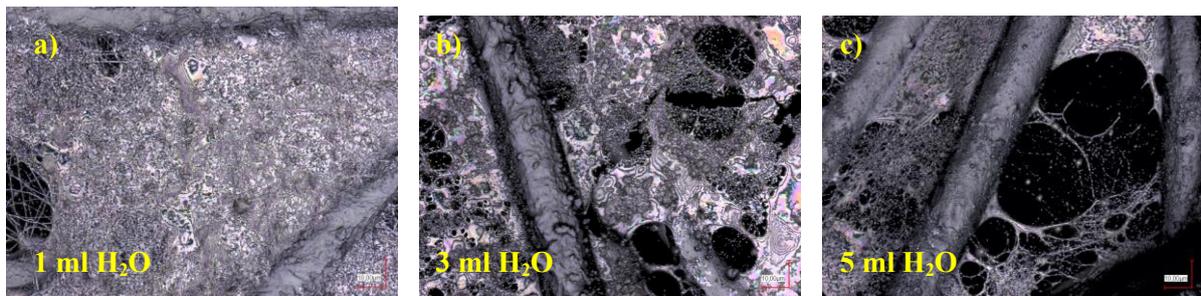


Figure 1. Chitosan nanofiber mats, produced from 1 ml chitosan solution, 1 ml NaHCO_3 solution, 0.5 ml PEO solution, and different amounts of H_2O .

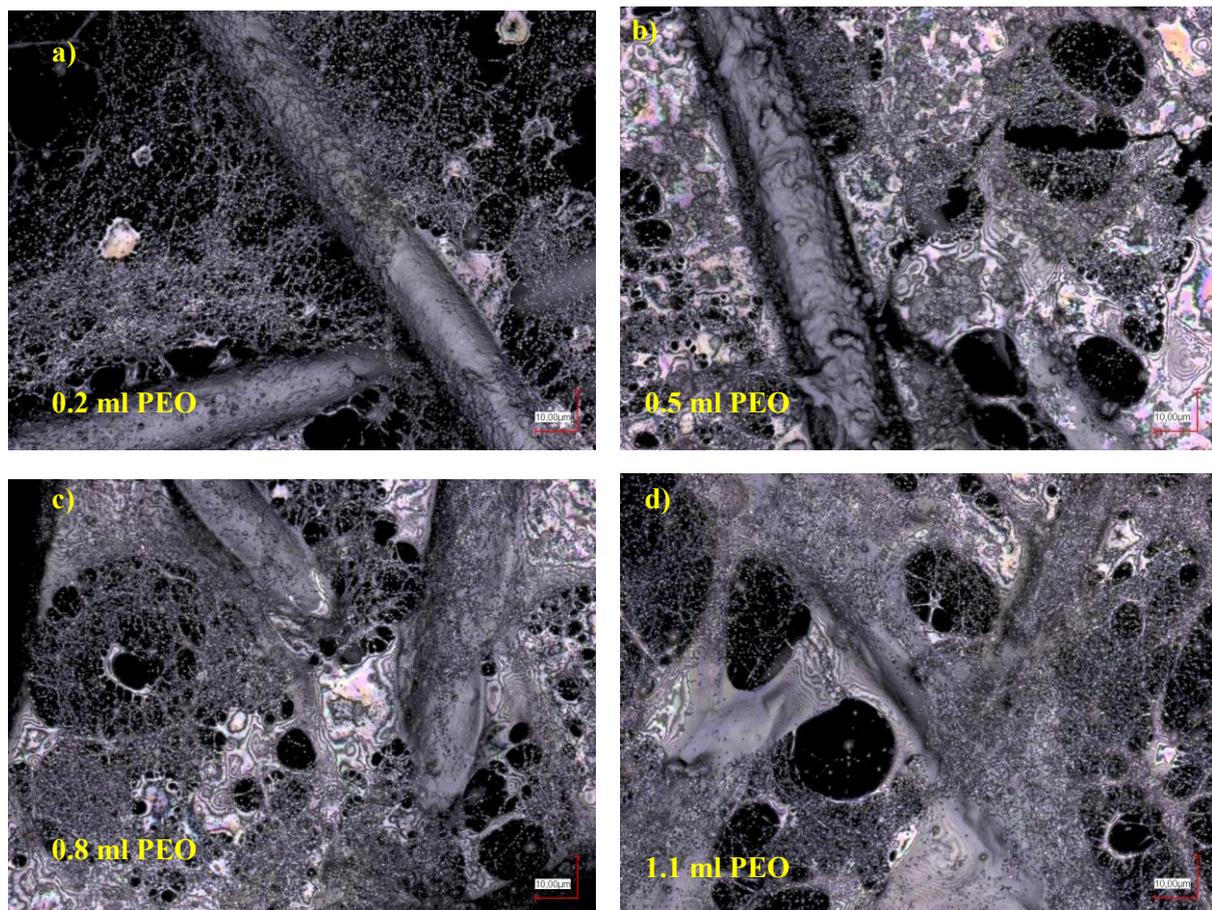


Figure 2. Chitosan nanofiber mats, produced from 1 ml chitosan solution, 1 ml NaHCO_3 solution, 3 ml H_2O , and different amounts of PEO solution.

Interestingly, the formation of droplets seems to be independent from the amount of PEO in the polymer solution. This is correlated with the observation found in literature that chitosan tends to forming droplets or beads along the nanospun fibres [13]. Apparently this behaviour cannot be changed by adding more PEO as a spinning agent. Future tests will show whether modifications in the preparation of the spinning solution may reduce the number of these droplets.

Another interesting effect, influencing the ratio between thin film and nanofiber parts in the produced nonwoven, is depicted in Figure 3. Nonwovens of different density were produced from 1 ml chitosan solution, 1 ml NaHCO_3 solution, 3 ml H_2O , and 0.5 ml PEO solution, by varying the substrate speed between 0 and 30 mm/min. In this way, very fine as well as very dense chitosan mats were created.

For the finest mat shown in Figure 3a, only fibres are visible with droplets adhered on them, as recognized before. By increasing the density slightly by enhancing the spinning time, first membrane areas become visible (Figure 3b). Further increase of the density leads to larger areas with membranes, still showing several completely open parts (Figure 3c). Finally, for the densest mat, the nonwoven does not show open areas anymore, but completely consists of a mixture of fibres and thin films (Figure 3d).

As depicted here, modifications of the mat density significantly change the structure of the created nonwoven. Future experiments will reveal which of these structures are ideally suited for applications as filters or in tissue engineering.

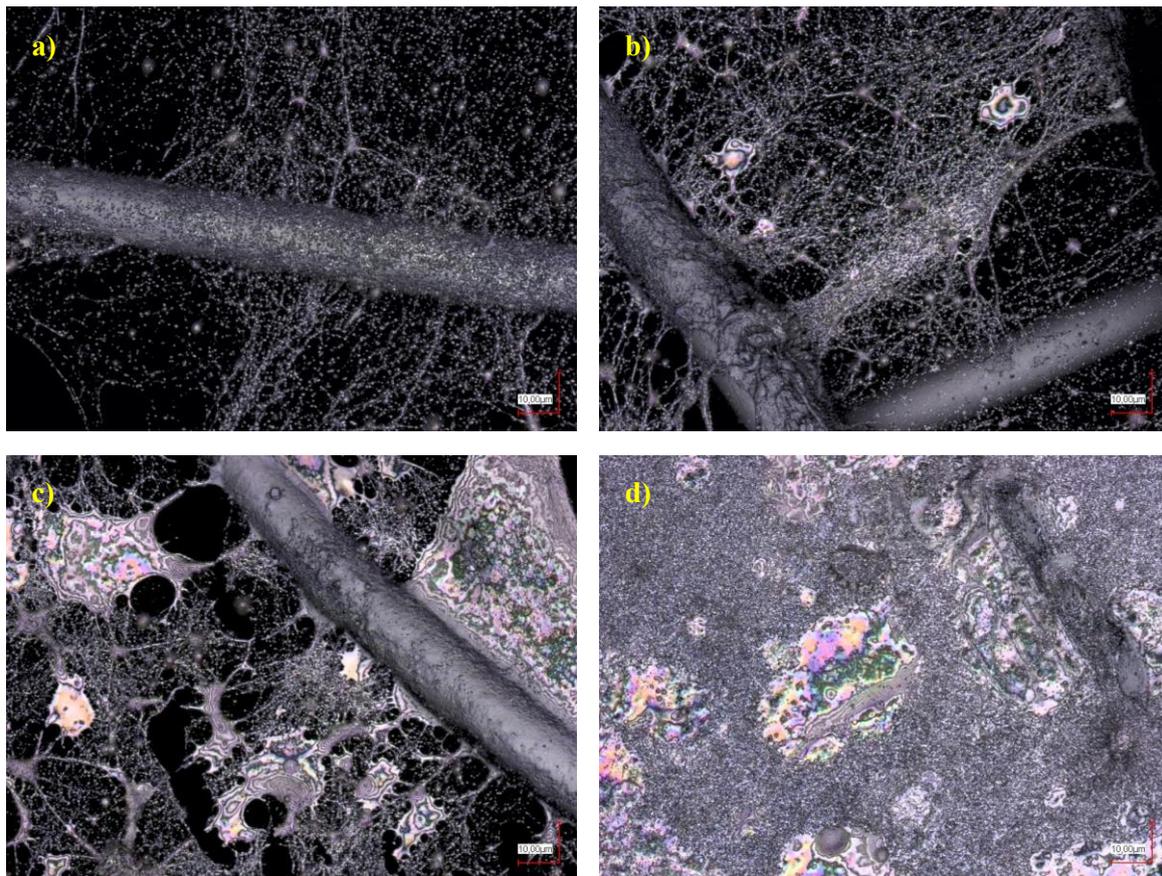


Figure 3. Correlation between mat density and membrane formation. Chitosan nanofiber mats of different densities, produced from 1 ml chitosan solution, 1 ml NaHCO_3 solution, 3 ml H_2O , and 0.5 ml PEO solution.

4. Conclusion

Needleless electrospinning was used to create chitosan/PEO blended nonwovens. Depending on the amount of water, the chitosan: PEO ratio and even the mat density, different surface morphologies between nanofiber mats and thin film membranes were created.

This possibility to tailor the structure of a nonwoven enables new applications in filter technology or for tissue engineering, allowing the creation of multi-layer filters with desired flow lines or choosing the ideal morphology for cells to grow. The “ideal” morphology thus depends on the desired application.

Future research will concentrate on measuring the mechanical and chemical properties of these chitosan/PEO nonwovens before and after stabilization of the chitosan for application in aqueous environments and testing the materials as filters and biotechnological scaffolds, depending on the created morphology.

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