Nanofibers and thin films as a selective membrane for sensors and microTAS

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Abstract. A composite material of PAN (polyacrylonitrile), starch granules and dimethylformamide as solvent was used as a selective membrane for volatile organic compounds (VOCs) in gaseous phase. This composite was produced as a thin film obtained by spin-casting and as a fiber mat produced by electrospinning. The fiber mat was tested for adsorption of VOCs and water. Characterization used microscopy (electron scanning and optical) in order to evaluate the fiber morphology and the starch incorporation in the PAN matrix. Infrared spectroscopy was intended to determine the starch presence. Relative viscosity of the starch/PAN suspensions was measured in order to provide a model of composite fiber formation. Quartz crystal microbalance experiments determined VOCs and water adsorption. Fibers incorporated the starch granules, making the composite sensible to water; but VOCs were not detected. Therefore, the composite was found to be a good choice as selective barrier on sensors or microTAS protection purposes.

1. Introduction
Electronic devices use membranes in several applications, such as protective layers [1] to electronic tongue or nose developments [2,3,4]. Composite membranes can merge different functions in one material, which is useful for micro-unit operations, such as microreactors, mixers, micro and nanofiltration, or as active parts on a microTAS (micro total analysis system)[5]. As an example, nanoparticles can be distributed in a porous polymeric matrix; in this case the disturbance in the flow through the porous improves mixing in microreactors. Another possibility is an online control of VOCs contamination in air or water flow using starch granules protected by a fluorinated film [6,7].

Due to the small dimension of electronic devices, the polymeric membranes must be thin (sub micrometer range) and able to cover a rough topography. On such approach, nanofibers are good candidates for protection/modification of such sensors and devices. The disturbance in flow caused by the nanofiber membrane will provide mixing and, eventually, removal of some contaminants. Additional advantages are low diffusion effects, which will not occur in conventional or in tunneling systems such as the one proposed by Macagnano [8].

Nano and microfibers can be produced by several different methods, with electrospinning being an

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ease and cost-effective process [9,10]. Several research and technological applications use polymer fibers varying the compound and geometry of the fiber. The inherent large fiber surface is explored in sensors. The fibers can be modified in different ways, e.g. metals can be electroless-deposited or active particles can be incorporated into electrospun fibers. The incorporation of particles is a promising field of research in microreactor and pre-concentrators.

As far as we know, this work proposes for the first time the production of PAN/starch electrospun fibers. They were deposited on miniaturized structures for water detection.

2. Experimental

Fibers were produced by electrospinning using dispersion of starch granules from Cassava (*Manihot esculenta* Crantz, 5μm diameter, homemade produced) [6] and polyacrylonitrile (PAN, Sigma Aldrich) in N,N-dimethylformamide (DMF, Sigma Aldrich). PAN/starch mass ratio was: 1:0.1; 1:1; 1:3; 1:5 and 1:7. The electrospinning setup was described elsewhere [11]. To establish a model for starch incorporation, D-glucose (Casa Americana Ltda)/PAN in DMF was also electrospun. Films were obtained by spin-casting the same suspensions on silicon substrates at 1000 rpm, 6 minutes.

Fibers were characterized by optical (Leica Mycrosystem GMB) and scanning electron microscopy (SEM, Jeol JSM-6360); infrared spectroscopy (Thermo Nicolet Nexus 870) helped to determine the starch presence.

Adsorption of volatile organic compounds (VOCs) and water was verified using Quartz Crystal measurements (QCM) [6]. The relative viscosity of starch/PAN dispersions was measured, using an adapted Ford cup rheometer.

3. Results and Discussion

This narrative describes the experimental results in the following sequence:
- The film production and preliminary characterization;
- The establishment of a model for starch/fiber composite formation;
- The use in miniaturized structures.

![Figure 1](image)

**Figure 1.** Optical image of films of a) starch; b) PAN; c) PAN:starch granules (1:1 w/w)

Figure 1 shows optical images of films produced by spinning process. The films appear homogeneous and similar. The PAN/starch sample presents more granules because starch is insoluble in DMF. Samples stocked for six months did not peel or change optical appearance, which pointed out the stability and low stress state of the PAN/starch composite.

Figure 2 shows optical microscopy for PAN/starch composite fibers in several mass ratios; it is noticeable that starch is incorporated into the fibers. Nonetheless, for mass ratio higher than 1:4, the starch granule coalescence is significant and, as can be seen in figure 2 (e), big clusters are detected. However, these clusters showed a surface quite different from the starch film of Figure 1 (a), suggesting strong interaction among nitrile groups from PAN and OH radicals from starch. Probably the PAN chains involve starch granules in the liquid dispersion, remaining attached even if precipitation of starch occurs.
Figure 2. Optical microscopy for PAN/starch composite fibers with different mass proportions (w/w).

SEM images reinforce the assumption of strong interaction, probably hydrogen bond formation, between starch granules and PAN chains. As can be seen in Figure 3, the starch incorporation promotes the formation of nodules along the fiber. If low PAN/starch w/w ratios are employed, some starch grains could not be covered by the polymer chains, as the arrow in figure 3 (b) indicates. In figure 3 (b) the biggest granule shows a crack possibly due to charged particles desorption, suggesting the using of starch as an absorber inside the fiber [6].

Figure 3. (a) The starch granules incorporated to the polymeric fibers. (b) The agglomerated granules covered by the polymer and an individual uncovered starch granule (dashed arrow). PAN/starch ratio (1:7)

The fiber morphology and diameter were strongly dependent of the amount of starch in the liquid dispersion as can be seen in Figure 4.

Figure 5 shows the fiber diameter as a function of the PAN/starch w/w ratio. The non linearity shown in the graph is consistent with two different regimes of starch incorporation, as pointed out by microscopy, and presents good agreement with a slope change at PAN/starch 1:3 mass ratio.
In order to get insight on starch/PAN chemical interaction, FTIR analysis was carried out; the FTIR results are shown in Figure 6. In this figure, bands for PAN fiber spectrum (continuous line) are consistent with the assignment made by Serkov [12]; bands are well defined, indicating a high ordered polymer structure. However, even for mass ratio of 1:0.1, the inclusion of starch granules broads the bands showing the interaction among fiber components. Bands assigned to CO (1190-950 cm\(^{-1}\)) and OH (3600-3000 cm\(^{-1}\)) species are characteristic of cassava starch [13]. The CH\(_n\) bands (2933 and 2881 cm\(^{-1}\)) are merged due to strong interaction of starch and PAN chains. The nitrile radicals’ interaction no longer plays an important role since the band at 2245 cm\(^{-1}\) almost disappears and the band at 1590 cm\(^{-1}\) shifts to lower wavenumbers. In other words, hydrogen bonds with starch radicals predominate. These results agree with the SEM analysis. The increase in diameter is owing to particle insertion on the fiber and correlated with bead formation due to the strong interaction among PAN chains and starch.

The two different regimes showed in figure 5 correlated with viscosity data. As can be seen in the figure 7, whereas the relative viscosity is almost constant in the range of 1:0 to 1:3 of PAN/starch w/w ratio, additional starch suddenly increases the viscosity. The detail on the graph shows a minimum on the relative viscosity at a ratio of 1:0.3. Therefore, up to a 1:0.3 ratio, the inclusion of starch granule in the dispersion decreases the relative viscosity probably due to the adsorption of the polymer molecules on the surface of the granule that might even precipitate. Thus, the system acts as if lower amounts of polymer were present in the liquid dispersion.
After the 1:0.3 ratio, additional starch enhances the interaction among granules and viscosity strengthens. When PAN/starch ratio overpasses 1:5, the starch and PAN in the dispersion act as a network; as a consequence, the viscosity increases suddenly. When that occurs, the fiber formation is difficult and higher fiber diameters will be achieved.

![Figure 7](image.png)

**Figure 7.** Relative viscosity in function of starch concentration.

This model for the PAN/OH-radical interaction was evaluated using D-glucose as a substitute for starch granules. D-glucose was selected because it is the monomer responsible for starch production and it also dissolves in DMF up to 0.7% w/w (determined experimentally), which will favour hydrogen bond formation on PAN dispersion.

![Figure 8](image.png)

**Figure 8.** Relative viscosity as function of D-glucose concentration a) up to 1:1.0 (w/w), b) up to 1:5 (w/w). c) PAN/D-glucose dispersions. The solid phase is apparent on the right bottle.

Figure 8 shows typical results for relative viscosity as a function of D-glucose concentration. Up to 1:0.7 the 5% increase on viscosity is consistent with the existence of soluble D-glucose molecules. Additional D-glucose will not be solubilized, but the increase on relative viscosity will remain, i.e., up to the 1:2.5 range, addition of D-glucose promotes the formation of solid precipitates in a highly viscous medium. Furthermore, on the 1:3 region the strong interactions among these precipitates create a net, i.e., an almost solid material (Figure 8c), which hinders viscosity measurements.

SEM analysis (Figure 9) of PAN:D-glucose fibers shows rough surfaces and D-glucose crystal completely covered by the polymer, which points out strong interactions between PAN and D-glucose molecules in the whole material.
Figure 9. Fibers electrospun from dispersion of PAN and D-glucose. a) the D-glucose granules on the fibers surface at 2500 X and. b) at 30000 X, in this case it is possible to see the rough surface of the fiber due to the incorporation of the D-glucose.

In order to validate the use of PAN/starch fiber as an active material for detection, few fibers were electrospun directly on a) quartz crystals for QCM and b) in 3D-microchannels [6]. The fiber exposure to n-hexane or 2-propanol did not change the QCM signal; however, 10% of relative humidity caused a reversible change of the signal by 10 Hz. This means that water molecules could permeate the PAN chains (probably due to hydrogen bonds formation), while 2-propanol molecules could not, probably owing to the molecule size. Figure 10 shows typical results for QCM experiments.

Figure 10. QCM measurements

A strong hydrogen bond linking nylon-6 nanofibers was already proposed [14], which reinforces the idea of water selective permeation from PAN fibers. Inside the fibers, starch will act as a scaffold and will retain a number of water molecules, which explains the 10Hz variation in the quartz oscillating frequency that means approximately 10% variation on the fiber weight. This phenomenon could be used in several ways, such as promoting preconcentration on microTAS or in a sensible layer for sensor applications.

The behavior of cassava starch granules was different on PAN/starch electrospun fibers than in a plasma polymeric thin composite film with fluor radicals obtained by Lima [6]. In fluorinated/starch composites, the permeable thin film allows the adsorption of 2-propanol. The use of fibers is more advantageous since it avoids diffusion effects that delay QCM measurements, such as the results found out using Zn-porphyrin film in similar devices [7].
The ability of the PAN/starch fibers to deposit on 3D-microchannels is shown in the figure 11. Most of the fibers link the edges of each thread, forming a mat around the screw; however, some of these fibers were deposited in the channel, which is also interesting since it provides an easy way to insert adsorptive material in small spaces.

4. Conclusions
This work showed an easy way to produce PAN fibers modified with starch. Tests revealed that fibers completely cover the starch grains and a model was proposed to explain the experimental results. The produced composite fibers are sensible for water but not to VOCs, which means that these fibers can be a useful material for production of selective membranes. Electrospun fiber over the miniaturized structures showed a good coverage over the topography, which means that the fibers mat is a good choice as selective membrane for sensors or to protect microTAS surfaces.

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5. References
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