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Interrupted Wet-Spinning Process for Chitosan Hollow Fiber Elaboration

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Summmary: Chitosan hollow fiber formation with a variable internal diameter was performed from a new wet-spinning method in interrupted coagulation conditions by means of water washings. The main objective of the present study is to provide a better understanding of the physicochemical events involved during the chitosan fiber formation by this new wet-spinning method.

Keywords: chain reorganization; chitosan; diffusion; hollow fiber; interrupted wet-spinning

Introduction

Chitosan is a linear co-polysaccharide consisting in β-(1 $\rightarrow$ 4) linked D-glucosamine and N-acetyl-glycosamine residues randomly distributed. The degree of acetylation (DA) represents the molar fraction of N-acetyl-glucosamine residues with respect to the total number of units. The DA is an important structural parameter which influences the physicochemical, physical and biological properties of chitosan. Among natural polymers, glycosaminoglycans, especially chitosan, constitute a very interesting family having a remarkable bioactivity.

Chitosan hydrogels are biomaterials with high potential for application in skin regeneration[1] and cartilage repair.[2] Additionally, tubular chitosan hydrogels are interesting systems for the regeneration of tissue with a complex architecture, like blood vessels and nerve tissue.

There exists numerous equipments/ for chitosan fibers and hollow fibers formation that are based on the wet-spinning technique. The wet-spinning is the most appropriate method for the chitosan hollow fiber formation because of the chitosan ability to form a continuous and stable macrofilament owing to its high viscosity in aqueous acetic acid solution. Nevertheless, the methods proposed are not really versatile since the equipments are complex [3–5] and because the internal diameter of hollow fibers is pre-determined by the annular spinneret fixed geometry.

In order to attempt the regeneration of tissues of tubular architecture, we propose a simple method based on the interrupted coagulation for the elaboration of hollow tubular chitosan fibers with variable internal diameter. The interrupted wet-spinning method implies to stop the coagulation step by means of successive water washings. Therefore, the main objective of the present work is to elucidate the physicochemical events involved during the chitosan fiber formation.

Materials and Methods

Chitosan Characterization

The chitosan sample was from Mahtani Chitosan Pvt. Ltd (batch No. 113). The degree of acetylation of this sample (DA = 1.5%) was deduced from the method developed by Hirai et al.[6] based on ^{1}H nuclear magnetic resonance (NMR) spectroscopy measurements. The chitosan weight-average molecular weight ($\overline{M}_w = 516\,800$ g/mol) was

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determined by size exclusion chromatography (SEC) coupled on line with a Waters 410 differential refractometer and a multi-angle laser light scattering (632.8 nm; Wyatt Dawn DSP) detector.

Preparation of Chitosan Dope and Coagulation Bath

The dope was an aqueous chitosan solution of 5% (w/w). For the dope preparation, chitosan was dissolved in a solution with a stoichiometric amount of acetic acid necessary to achieve the exact protonation of amine residues. On the other hand, the coagulation bath was an aqueous solution of sodium hydroxide at different concentrations (0.10, 0.50, 1.0 and 4.0 mol/L).

Membrane Thickness

Fibers were cross-sectioned with a razor blade to measure the thickness of the outer membrane gel formed at the periphery of the fibers. The membrane thickness was measured at different periods of coagulation by optical microscopy (Olympus BX41, 20X) (Figure 1)

Nanostructural Analysis Across the Fiber Section

The nanostructure of the fibers was determined by small-angle X-ray scattering (SAXS) performed on the BM2-D2AM beamline at ESRF (Grenoble, France). A synchrotron source (16 keV, 200 mA) was used in our study in order to determine the intensity scattered across the fiber section. The analysis was realized across the cross section of the fiber at different points separated by 200 μm.

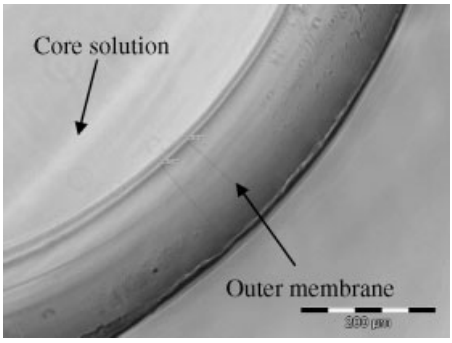

Figure 1.
Chitosan fibers with two distinguishable parts: a chitosan outer membrane and a core chitosan solution.

Results and Discussion

Depending on the initial dope concentration, two different strategies based on the wet-spinning process are possible for the elaboration of hollow chitosan fibers: the interrupted wet-spinning process [7] and the precipitated chitosan core.

Interrupted Wet-Spinning Methodology

In the interrupted wet-spinning process, a concentrated chitosan dope (from 2.5 to 5% w/w) is required. Chitosan dope was first degassed and placed into a polypropylene syringe with an inside spout diameter of 1.90 mm.

The dope was then extruded through a spinneret by means of a metering pump. In turn, the extruded solution was poured into a sodium hydroxide coagulation bath where the chitosan coagulation occured. In the coagulation bath, chitosan neutralization was not fully achieved because the reaction was interrupted by water washing baths in order to obtain a fiber with two distinguishable parts: a chitosan outer membrane gel and a core chitosan solution (Figure 1).

Finally, hollow fibers were obtained after the elimination of the core chitosan solution. There are two possiblilities for this purpose. The first one, consists in removing the core chitosan solution from the outer membrane gel by water washing baths and the second implies the neutralization of the core solution by means of a second coagulation bath and then removing it from the outer membrane. Hollow chitosan fibers of small-external diameter (2.0 mm) with an internal diameter which lower limit close to 200 μm were obtained by the interrupted wet-spinning process. The internal diameter size of the hollow chitosan fiber was determined by controlling the thickness of the outer membrane gel. In turn, the outer membrane thickness

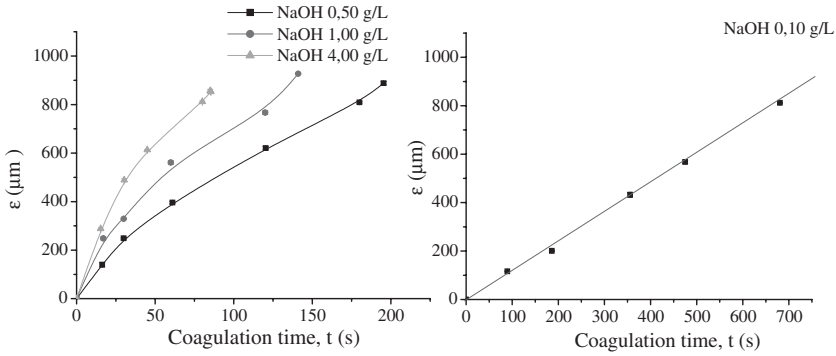

Figure 2.
Membrane thickness as a function of the time of coagulation (s).

depends on the time passed in the coagulation bath. The evolution of the membrane thickness was then determined by optical microscopy.

In Figure 2 is presented the evolution of the outer membrane formation with time for the different concentrations of the coagulation bath. The formation of the membrane results from the diffusion of the coagulant into the chitosan macrofilament.

According to the Fickian diffusion theory,[8] the thickness of the outer membrane gel should be initially proportional to the root square of the coagulation time. In our study, a linear behaviour was observed in the concentrated coagulation baths (above 0.5 g/mol NaOH) at all the investigated coagulation times (Figure 3a).

A change of slope with two regimes was observed in the dilute coagulation bath of 0.10 g/mol, NaOH, where the kinetics of coagulation is slower (Figure 3b). The change of slope reveals that the coagulation is a complex mechanism, involving the osmosis and Donnan effects, and is preceded by the neutralization of the chitosan chains. Indeed, the chitosan chains reorganisation occurs as the coagulant agent diffuses into the chitosan solution. The protonated amine residues are neutralized and as a result a decrease of charge density of chitosan. Then, the solvophobic interactions and hydrogen bonding are favored, inducing the formation of physical junctions of the gel.[9]

A relevant parameter that could be obtained from the previous plot is the apparent coagulation rate $(\varepsilon/\sqrt{t})$ which is the slope of the $\varepsilon(t)$ vs $\sqrt{t}$ curves. In fact, the apparent coagulation rate is the most direct

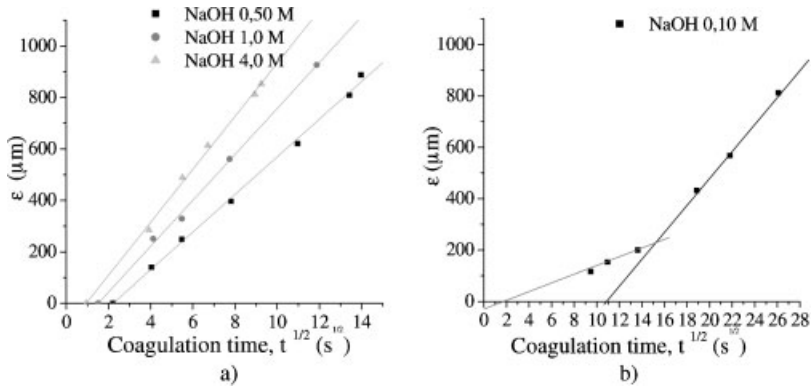

Figure 3.
Membrane thickness as a function of $\sqrt{t}$ for different concentrations of the coagulation bath.

measure of the external membrane rate formation.

Modeling

A phase separation occurs from the periphery to the membrane limit (ε) of the fiber up to the coagulant reaches a critical concentration, C_ε, causing the chitosan coagulation from the solution. Then, from Equation 1 which is the solution of the Fick's second law in a semi-infinite medium at the position of the membrane limit (ε),[10] the concentration C_ε at the membrane limit-solution interface was modeled by means of the Equation 2.

$$\frac{C_{NaOH,0} - C_\varepsilon}{C_{NaOH,0}} = \mathrm{erf}\left(\frac{\varepsilon}{2\sqrt{Dt}}\right) \quad (1)$$

$$erf\left(\frac{\varepsilon}{2\sqrt{D(t-t_i)}}\right) = 1 - \frac{C_\varepsilon}{C_{NaOH,0}} \quad (2)$$

Where erf () is the error function, /D/ the coefficient of diffusion of sodium hydroxide into the chitosan dope, /ε/ the thickness of the outer membrane, /$C_{NaOH,0}$/ the initial concentration of coagulation bath, /C_ε/ the concentration of coagulant at the membrane limit and /t_i/ the time of induction for chitosan neutralization.

The determination of the parameters C_ε and D was performed by a fitting of the data presented in Figure 4 and 5. After a first estimation of the value of coefficient of diffusion ($D = 4 \times 10^{-10}$ m^2/s), equation 2 could be graphically represented in Figure 4. C_ε corresponds to the slope of the plot. In the present conditions of elaboration, it was found close to 8.9×10^{-3} g/L.

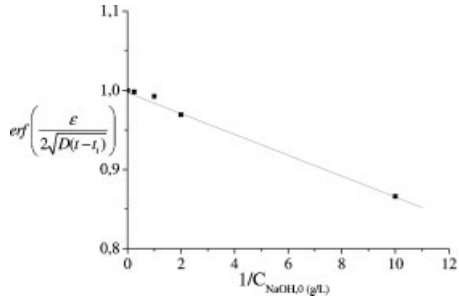

Figure 4.
Regression plot for predicting C_ε by estimating the coefficient of diffusion ($D = 4 \times 10^{-10}$ m^2/s).

Finally, by considering the calculated values of C_ε and D, the chitosan membrane formation could be modeled from Equation 3. The modeled curves are presented in Figure 5.

$$\varepsilon = \mathrm{erf}^{-1}\left[\frac{C_{NaOH} - C_\varepsilon}{C_{NaOH}}\right] 2\sqrt{D}\sqrt{t - t_i} \quad (3)$$

Gel Nanostructure Across the Fiber Section and Precipitated Chitosan Core Strategy

The chitosan nanostructure across the fiber was estimated by small-angle X-ray scattering. The scattered intensity (I_o) was studied across the fiber section at different distances from the center of the fiber. From

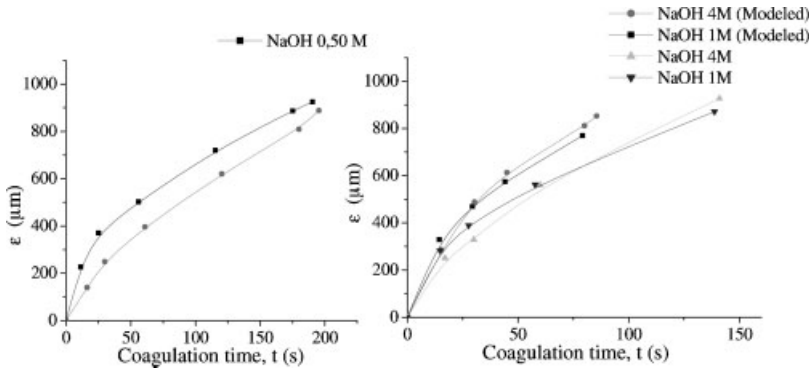

Figure 5.
Modeled external membrane with approximative values of $D = 4 \times 10^{-10}$ m^2/s and $C_\varepsilon = 8.9 \times 10^{-3}$ g/L.

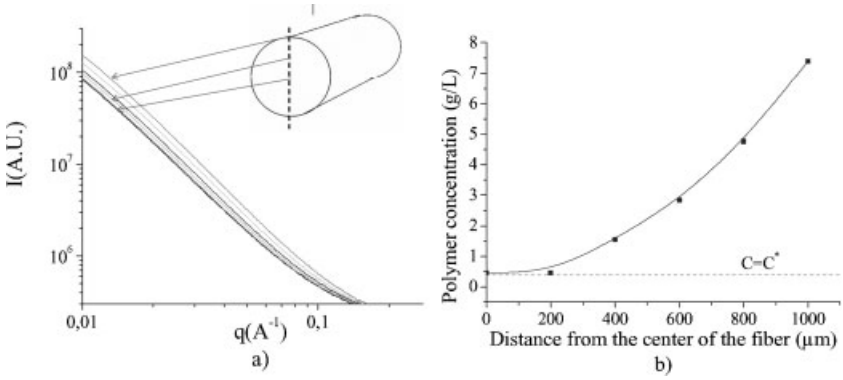

Figure 6.
a) SAXS intensity curves and b) polymer concentration across a coagulated chitosan fiber.

the measured I_o values, the chitosan concentration across the fiber was deduced. A typical small angle scattering intensity profile is shown in Figure 6a. All the investigated points across the fiber section presented a similar scattering pattern with a $I = I_o q^{-\alpha}$ law. The scattered intensity was found more intense at the periphery, as a result of a decrease of chitosan concentration from the periphery to center of the fiber (Figure 6b). In fact, the final chitosan concentration at the center (0.4 g/L) was found close to the critical concentration for chains entanglement ($C^* \cong 0.1$–0.4 g/L)[1]. It means that a precipitate was formed at the core of the fiber. In a dilute chitosan dope under 2.5% (w/w), hollow chitosan fibers with a small internal diameter (<200 μm) could be yield by the removal of the precipitated chitosan core.

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