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Pseudo-dry-spinning of chitosan

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Abstract

A pseudo-dry-spinning process of chitosan without any use of organic solvent or cross-linking agent was studied. A highly deacetylated chitosan (degree of acetylation = 2.7%) from squid-pens, with a high weight-average molecular weight (M_W = 540 000 g/mol) was used. The polymer was dissolved in an acetic acid aqueous solution in order to obtain a polymer concentration of 2.4% w/w with a stoichiometric protonation of the $-NH_2$ sites. The coagulation method consisted of subjecting the extruded monofilament to gaseous ammonia. The alkaline coagulation bath classically used in a wet-spinning process was therefore not useful. A second innovation dealt with the absence of any aqueous washing bath after coagulation. The gaseous coagulation was then directly followed by a drying step under hot air. When the chitosan monofilament coagulated in the presence of ammonia gas, ammonium acetate produced with the fiber could be hydrolyzed into acetic acid and ammonia, easily eliminated in their gaseous form during drying. The pseudo-dry-spinning process did not give rise to any strong degradation of polymer chains. After 2 months at ambient atmosphere, chitosan fibers could then be stored without any significant decrease in the M_W, which remained at a rather high value of 350 000 g/mol. The obtained chitosan fibers showed a smooth, regular and uniformly striated surface.

Keywords: Chitosan fibers; Pseudo-dry-spinning; Ammonium acetate hydrolysis

1. Introduction

Among polysaccharides, only glycosaminoglycans, including chitosan, show the rare property of bioactivity [1]. The latter is produced from the *N*-deacetylation of chitin, the most abundant naturally occurring polysaccharide along with cellulose [2]. Chitin occurs mainly in the cuticles of arthropods, endoskeletons of cephalopods and fungi. Chitosan, as chitin, belongs to the family of the linear copolymers of (1 → 4)-2-amino-2-deoxy-β-D-glucan (GlcN) and (1 → 4)-2-acetamido-2-deoxy-β-D-glucan (GlcNAc). Due to the β, (1 → 4) linkages distributed all along its chain, chitosan gives rise to: very good mechanical properties; a high chain stiffness; filmogenic, gelation and fiber-forming properties responsible for an important part of its applications [3]. Chitosan is widely used in pharmaceutical and biomedical fields for its bioresorbability [4], biocompatibility [5] and non-toxicity [6]. Moreover, it plays an important role in cell regulation and tissue regeneration [7,8].

The textile industry has developed processes avoiding the use of toxic chemicals. From this point of view, the chitosan fiber seems to be an excellent candidate for biomedical applications [9]. Our work deals with developing a new concept of reinforcing plates principally made from chitosan fibers which will prevent post-operative adhesion and promote tissue regeneration, in addition to their stiffening function [10]. Additionally, these fibers should also find applications in suturation and wrinkle filling.

Contrary to synthetic fibers, which can be produced by melt-, dry- or wet-spinning, the most commonly used process for natural polymers, is wet-spinning. Thus, chitosan cannot be melt-spun, due to extensive hydrogen bonding,

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which is responsible for glass transition and melting temperatures well over its temperature of thermal decomposition [11]. In a wet-spinning process, the polysaccharide is dissolved in a solvent, then extruded through a spinneret immersed in a coagulation bath, where the polymer precipitates [12]. In dilute acids, the free amino groups of the glucosamine residues are protonated and the molecule becomes fully soluble below pH 6. Chitosan is thus dissolved in an acidic solution to form the spinning dope. Viscous solutions can be transformed into fibers in different coagulation solutions such as aqueous solutions of: NaOH [12–15], KOH [16,17], cupric ammonia [18], alcohol, calcium chloride or acetate [19], NaOH–Na_2SO_4, NaOH–AcONa [20], NaOH–40% methanol [21], $CuSO_4$–concentrated ammonia [22], etc. The coagulated fiber can be subsequently washed in water to remove the excess of coagulant, dried and collected on a winder. The washing bath is constituted of distilled water [17], aqueous methanol or ethanol [18,19]. The last mixtures often play the role of a pre-drying bath. A pure chitosan fiber processing has rarely been reported in the literature. The formation of chitosan fibers cross-linked by epichlorihydrin [15] has been described and numerous papers detailed the preparation of composite chitosan fibers like *N*-acylchitosan-cellulose fibers [23,24], fragrant chitosan derivatives [25], chitosan–collagen fibers [26], or chitosan/poly(vinylalcohol) blend fibers [27]. Moreover, post-treatments were performed on chitosan fibers with solutions containing phthalate or phosphate ions [17], EDTA-4Na or Na_2HPO_4 [19], and even aldehydes including vanillin [20].

To our knowledge, a dry-spinning process of chitosan has never been reported in the literature, except, very partially, in one patent [28]. This dealt with preparing fibers by spinning a 20% chitosan aqueous solution into air at 15 kg/cm^2, then treating with gaseous NH_3 and washing before drying. The high dope concentration, impossible to achieve with a high molecular weight chitosan, makes the results impossible to repeat [29]. Additionally, this process, containing a washing step, cannot be considered as a true dry-spinning.

The aim of the work described in this paper was to describe for the first time a new method of spinning of polysaccharides in absence of any aqueous bath after the spinneret [30]. We applied this new process to chitosan and studied the role of several parameters to enable us to define the optimal spinning conditions.

2. Materials and methods

2.1. Materials

2.1.1. Purification

The initial chitosan produced from squid pens was purchased from Mahtani Chitosan (batch number 114). To obtain a high-purity material, chitosan was dissolved at 0.5% (w/v) in the presence of an amount of acetic acid necessary to achieve the stoichiometric protonation of the $-NH_2$ sites. After complete dissolution, it was filtered successively on 3, 1.2, 0.8 and 0.45 μm membranes (Millipore). Then, dilute ammonia was added in order to fully precipitate the polymer. The precipitate was repeatedly rinsed with distilled deionised water, centrifuged until a neutral pH was achieved, then lyophilized.

2.1.2. Chitosan characterization

2.1.2.1. ^1H nuclear magnetic resonance spectroscopy. The degree of acetylation (DA) of the sample, calculated from ^1H nuclear magnetic resonance (NMR) spectroscopy was found to be close to 2.7%. Spectra were recorded on a Bruker 250 spectrometer (250 MHz) at 25 °C. As proposed by Hirai et al. [31], the DA was deduced from the ratio of the area of the methyl protons of the *N*-acetylglucosamine residues to that of all of the H_2 to H_6 protons of both glucosamine and *N*-acetylglucosamine.

2.1.2.2. Size exclusion chromatography—multi-angle laser light scattering. The weight-average molecular weight M_W was determined by size exclusion chromatography (SEC) coupled online with a multi-angle laser light scattering (MALLS) detector [32]. SEC was performed by means of an IsoChrom LC pump (Spectra Physics) connected to Protein Pack glass 200 SW and TSK gel 6000 PW columns. A Waters R 410 differential refractometer and a multi-angle laser-light scattering detector, operating at 632.8 nm (Wyatt Dawn DSP) were connected online. Depending on the DA, the refractive index increment dn/dc ranged from 0.190 to 0.183 cm^3 g^{-1} [33]. A 0.15 M ammonium acetate/0.2 M acetic acid buffer (pH = 4.5) was used as the eluent. The flow rate was 0.5 mL/min. The polymer solutions were prepared by dissolving 1 mg of polymer in 1 mL of buffer, then filtered on a 0.45 μm pore size membrane (Millipore) before injection of 100 μL.

2.1.2.3. Thermogravimetric analysis. The water content of chitosan samples was evaluated on a DuPont Instrument 2950 thermogravimetric analyser (TGA), operating at a ramp of temperature of 2 °C/min under a flow of helium.

2.1.2.4. Viscometry. Viscometric measurements were performed at 22 °C by means of an automatic Ubbelohde capillary viscometer (Viscologic TI.1, SEMATech) with an inner diameter of 0.53 mm. The intrinsic viscosity [η] was calculated by extrapolating to zero concentration the Huggins or Kraemer equations. Since the differences between [η] values obtained from these equations were smaller than experimental errors, intrinsic viscosities were expressed as the average of the two methods.

All the characteristics of our studied chitosan are given in Table 1.

2.1.3. Preparation and rheology of chitosan solutions

The critical concentration of chain entanglement (C^*) for our samples was evaluated from the reverse of the intrinsic viscosity and found to be close to 0.06% (w/w).

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