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Morphology and mechanical properties of chitosan fibers obtained by gel-spinning: Influence of the dry-jet-stretching step and ageing

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Abstract

The morphology and mechanical properties of chitosan fibers obtained by gel-spinning are reported. The objectives were both to understand how the microstructure of the fibers could be modified and how the mechanical properties were improved by means of a dry-jet-stretching step. 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 dissolved in an aqueous acetic acid solution, spun using gaseous ammonia as the coagulant, and then directly dried under hot air. A "post-drying" of 1 week was necessary to stabilize the fibers in ambient atmosphere. A dry-jet-stretching ratio applied during the monofilament coagulation (maximal value of 4.3) allowed us to increase the density and favor the orientation of chains along the fiber axis. This allowed us to improve the mechanical properties of the fibers (Young's modulus of 82 g/denier and tenacity of 2 g/denier). The ageing in ambient atmosphere played an important role in the crystalline microstructure in relation to: the kinetics of ammonium acetate hydrolysis, the formation of a weak fraction of the anhydrous allomorph of chitosan, and an increase of the crystallinity index, whereas the Young's modulus was increased and the tenacity was slightly lowered. In addition, gel-jet-stretched or dry-jet-stretched fibers could be stored at least 3 months in ambient atmosphere without any significant degradation.
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Keywords: Chitosan fibers; Mechanical properties; Dry-jet-stretching ratio; Ageing

1. Introduction

Among polysaccharides, only glycosaminoglycans, including chitosan, show the rare property of bioactivity [2]. By bioactivity we mean that these structures activate biological media in such a way that tissue is regenerated [3,4]. Chitosan is produced from the *N*-deacetylation of chitin, the most abundant natural polysaccharide along with cellulose [5]. 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 along its chain, chitosan gives rise to very good mechanical properties, together with the filmogenic, fiber-forming and gelling ability that are responsible for an important part of its

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applications [6]. Chitosan is widely used in pharmaceutical and biomedical fields for its bioresorbability [7], biocompatibility [8] and non-toxicity [9]. Moreover, it plays an important role in cell regulation and tissue regeneration [10,11].

The textile industry needs to develop materials and industrial processes that respect the environment, i.e. by avoiding the use of toxic substances. In this context, chitosan fibers seem to be excellent candidates, especially for biomedical applications [12]. Our work deals with developing a new concept of reinforcing plates principally made from chitosan fibers, which prevent post-operative adhesion and promote tissue regeneration, in addition to their mechanical functions [13]. Additionally, these fibers should also find applications in suturation and wrinkle filling [14].

In previous work [1], we aimed to develop a new method of chitosan spinning corresponding to gel-spinning. This method [15] consisted of using a chitosan acetate solution as dope, then, by operating a coagulation thanks to ammonia gas and a direct drying, allowing a simultaneous elimination of a part of the water and ammonium acetate generated during coagulation.

The poor tensile strength of chitosan fibers, especially in the wet state, is a key deficiency. Numerous methods are available for improving the mechanical properties of chitosan fibers. Chemical modifications of wet-spun chitosan fibers, widely studied, involve the use of cross-linking agents such as epichlorohydrin [16,17] during the coagulation step, post-treatments with glyoxal [18–20] or glutaraldehyde [19], or the immersion of fibers in solutions containing phosphate and phthalate ions [21].

Even though fiber stretching has been common in fiber technology for a long time, the literature provides no significant information regarding physical treatments to improve the mechanical properties of wet-spun chitosan fibers. The studies of Qin [22] and Knaul [23] demonstrated that the Young's modulus and tenacity could be improved by increasing the draw ratio in the washing and drawing baths, and possibly via the drying step, whereas the influence of the jet-stretching ratio was not really discussed. The objectives of the present work were numerous. We particularly wanted to study the microstructure in terms of the characteristic dimensions of the morphologies and the crystallographic organization of the nano-fibrillar structures of the gel-spun fibers. These investigations were performed as a function of ageing in ambient atmosphere, including the preliminary "post-drying" and gel-jet-stretching or dry-jet-stretching ratio. The latter was applied during the coagulation step of the monofilament with ammonia gas. The microstructural characterization of the morphology allowed us to explain and understand the evolution and the improvement of the mechanical properties of our fibers using only a spinning physical parameter, namely the stretching ratio of the fibers, as a function of ageing. Although it has never been really studied, the influence of ageing seemed to be a key factor in considering the fibers for applications in the biomedical area.

2. Materials and methods

2.1. Materials

2.1.1. Purification

The sample of chitosan, produced from squid pens, was purchased by Mahtani Chitosan (batch No. 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 from Millipore. Then, dilute ammonia was added to fully precipitate the polymer. The latter was repeatedly rinsed with distilled de-ionized water and centrifuged until a neutral pH was achieved, then lyophilized.

2.1.2. Chitosan characterization

2.1.2.1. ^1H NMR spectroscopy. The degree of acetylation (DA) of the sample, calculated by ^1H nuclear magnetic resonance (NMR), 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. [24], the DA was deduced from the ratio of the area of the methyl protons of the *N*-acetylglucosamine residues to that of all the H_2 to H_6 protons of both glucosamine and *N*-acetylglucosamine.

2.1.2.2. SEC-MALLS. The weight-average molecular weight M_w was determined by size exclusion chromatography (SEC) [25]. 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 MALLS detector operating at 632.8 nm (Wyatt Dawn DSP) were connected on line. Depending on the DA, the refractive index increment d*n*/d*c* ranged from 0.183 to 0.190 $cm^3\ g^{-1}$ [26]. 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 with a DuPont Instrument 2950 thermogravimetric analyzer (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 Ubbelhode capillary viscometer (Viscologic TI.1, SEMATech) with an inner diameter of 0.53 mm. The intrinsic viscosity [η] was calculated on extrapolating to zero concentration the Huggins or Kraemer equation, then considering the average of the two results.

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