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Spinning of hydroalcoholic chitosan solutions

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ABSTRACT

We investigated the spinning of hydroalcoholic chitosan solutions. The dope composition was optimized in order to obtain a continuous alcogel fiber by water evaporation on heating the extruded hydroalcoholic solution. This alcogel fiber was then neutralized in aqueous alkali baths and washed in water to eliminate the residual alcohol and salts before final drying. Depending on the alcohol content in the filament at the neutralization step, on specific alcohol–chitosan interactions and on the nature and concentration of the coagulation base, the process yielded semicrystalline chitosan fibers with different proportions of anhydrous and hydrated allomorphs. Contrarily to the classical annealing method, the formation of mainly anhydrous crystals was obtained without significant molecular weight decrease by neutralizing the polymer in hydrophobic conditions. The control of allomorph content was shown to be related to the hydrophobicity of the solvent (alcohol fraction) at the neutralization step.

1. Introduction

In recent years, "new generation" medical textiles based on biomaterials with bioactive properties have received growing interest in biomedical research (Boateng, Matthews, Stevens, & Eccleston, 2008). These technologies usually involve either the incorporation of pharmaceutical or biological molecules (*e.g.* antiseptics (Meaume, Vallet, Morere, & Teot, 2005), growth factors (Puolakkainen et al., 1995)) or the use of natural polymers such as proteins (*e.g.* collagen (Parenteau-Bareil, Gauvin, & Berthod, 2010), silk fibroin (Min et al., 2004)) or polysaccharides, especially those that can express the rare property of bioactivity (*e.g.* hyaluronic acid (Chen, & Abatangelo, 1999), chitosan (Muzzarelli, 2009)). Hence, the main strategies to produce such "bioactive" fiber-based devices are: (i) the coating of conventional fibers or textiles with these biopolymers (*e.g.* Parietex®composite, Promogran®) or pharmaceutical agent (Blanchemain et al., 2008; Ravindra, Mohan, Reddy, & Raju, 2010), (ii) the incorporation of bioactive molecules into the dope to be spun (Schneider, Wang, Kaplan, Garlick, & Egles, 2009), or (iii) the direct spinning of natural bioactive polymer solutions into fibers (Agboh & Qin, 1997; Meyer, Baltzer, & Schwikal, 2010; Wang et al., 2005).

Among spinnable polysaccharides, chitosan is well-known for its biocompatibility, haemostatic, bacteriostatic and fungistatic properties, bioresorbability as well as its healing bioactivity (Domard & Domard, 2002, chap. 9), and thus constitutes an excellent candidate for smart biomedical textile applications. Indeed, chitosan fibers could be used into many product forms such as woven/non-woven dressings to limit fungal and bacterial proliferation and promote tissue regeneration (Agboh & Qin, 1997; Jayakumar, Prabaharan, Kumar, Nair, & Tamura, 2011; Muzzarelli, 2009) (*e.g.* in the case of chronic wounds); as knitted textiles to be incorporated in synthetic fiber-based textile implants to improve their biocompatibility and stimulate healing mechanisms (Burger, Halm, Wijsmuller, ten Raa, Jeekel, 2006; Earle & Romanelli, 2007); as yarns for bioresorbable surgical sutures (Ravikumar, 1999). This polysaccharide is produced from the N-deacetylation of chitin which is the most abundant polymer in biomass with cellulose (Roberts, 1992). Chitin and chitosan are linear copolymers of 2-amino-2-deoxy-β-D-glucan (GlcN) and 2-acetamido-2-deoxy-β-D-glucan (GlcNAc) residues. A key structural parameter is defined by the degree of acetylation (*DA*) corresponding to the molar fraction of GlcNAc residues. Chitosan refers to polymers soluble in dilute acid aqueous solutions at pH < 6 and thus to *DA*s below 60% for statistical copolysaccharides (Domard & Domard, 2002). The presence of only β(1→4) type glycosidic linkages along the polymer backbone (as found in the cellulose structure) yields filmogenic and fiber-forming ability useful for fiber spinning applications (Hudson,

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1998; Rathke & Hudson, 1994). Thus, chitosan yarns have been mainly produced by wet-spinning (like regenerated cellulose or viscose). Other methods have been developed such as dry-jet-wet spinning (Agboh & Qin, 1997), pseudo-dry-spinning (Notin, Viton, Lucas, & Domard, 2006), later referred to as gel-spinning (Notin, Viton, David, et al., 2006), and electrospinning (Lee, Jeong, Kang, Lee, & Park, 2009; Pillai & Sharma, 2009). Except from electrospinning that is limited to the production of nanofiber mats such as non-wovens and not easily to the production of yarns, all the above techniques are based on the coagulation of aqueous chitosan solutions in alkali media. Chitosan must be dissolved in a dilute aqueous acid solution inducing the protonation of the free amino groups of glucosamine (GlcN) residues. The resulting polyelectrolyte solution is used as a spinning dope and is converted to chitosan fibers by coagulation of the polymer solution induced at pH > 6.5 (*i.e.* above the pK_0 value for chitosan with $DA < 25\%$ (Domard & Domard, 2002)) due to the regeneration of the free amino form. The alkali media is either an alkali bath (NaOH (East & Qin, 1993; Knaul & Creber, 1997) or NaOH/alcohol mixture (Molloy, 2002), KOH (El-Tahlaway & Hudson, 2006; Knaul & Creber, 1997), ammonia (Knaul & Creber, 1997)...) for wet-spinning and dry-jet-wet spinning or ammonia vapors for gel-spinning (Notin, Viton, David, et al., 2006). After washing and drying, typical tenacity can be closed to 2 g/denier in the dry state (the denier represents the mass in grams per 9000 meters of fiber). Besides their remarkable biological features, the well-known drawback of chitosan fibers is the lower mechanical properties compared with synthetic fibers. This makes difficult to perform post-operations such as weaving or knitting. Moreover, an important loss of mechanical properties is observed in wet environment (East & Qin, 1993). Improving mechanical properties both in the dry state and in contact with physiological fluids is a real challenge and brings to develop new chitosan spinning processes. Current approaches are based on chemical crosslinking (*e.g.* epichlorohydrin (Lee, Kim, & Kim, 2007; Wei, Hudson, Mayer, & Kaplan, 1992), phthalate or phosphate ions (Knaul, Hudson, & Creber, 1999a), dialdehydes such as glutaraldehyde or glyoxal (Knaul, Hudson, & Creber, 1999b; Yang, Dou, Liang, & Shen, 2005) or physical post-treatments (East & Qin, 1993; Knaul et al., 1999a; Notin, Viton, David, et al., 2006)) (*e.g.* drawing at coagulation or drying step). But the increase of mechanical properties obtained by these methods remains low (maximum tenacity of 2.4 g/denier) and other spinning routes still need to be developed to improve and control physical and biological properties of chitosan fibers.

Most of natural polymer fibers are formed from coagulated hydrogel materials (*i.e.* alginates (Qin, 2008), cellulose (Woodings & The Textile Institute, 2001), chitosan (Agboh & Qin, 1997)). The solid fibers obtained from drying a coagulated filament should inherit part of the morphology of the hydrogel (Robitzer, David, Rochas, Di Renzo, & Quignard, 2008). More precisely, the physical properties of the fibers in the dry state should depend on the polymer chain ordering resulting from intra- and intermolecular interactions in the hydrogel fiber (entanglements, hydrogen bonding, hydrophobic interactions, and electrostatic interactions if ionic complexes with the polyelectrolytes are present). Thus, the mechanical properties of final fibers should be improved by generating and preserving the maximum of polymer intra- and interchain interactions all through the fiber spinning process, from the initial solution, to the gel fiber, and in the dry fiber (Popa-Nita, Alcouffe, Rochas, David, & Domard, 2010).

Thus, physical chitosan hydrogels with a relatively high mechanical strength can be obtained by neutralizing concentrated aqueous chitosan solutions of high molecular mass in alkali baths (Araiza, Rochas, David, & Domard, 2008) or in ammonia vapors (Montembault, Viton, & Domard, 2005a). Indeed, most chitosan spinning techniques are based on these gelation methods (Agboh & Qin, 1997; Notin, Viton, David, et al., 2006; Rathke & Hudson, 1994; Ravikumar, 1999). A second route to obtained physical chitosan hydrogels is the neutralization in alkali baths of alcoholic chitosan gels (that will hereafter be referred to as alcogels) produced hydroalcoholic chitosan solutions by water evaporation (Montembault, Viton, & Domard, 2005b). In that case, the mechanical properties of chitosan hydrogels are significantly improved compared with the aqueous process, suggesting a higher density of chain entanglements and junctions inherited from the alcogel (Montembault et al., 2005b; Montembault, Viton, & Domard, 2005c). Therefore, in the present work, we investigated the spinning of hydroalcoholic chitosan solutions. The gelation of the extruded solution was induced by selective solvent evaporation (water evaporation) at moderate temperature ($T \sim 130\,^{\circ}C$) to form an alcoholic chitosan gel fiber. This alcogel fiber was then neutralized in an alkali bath to obtain a stable physical hydrogel. After washings in water and drying, the process led to a pure chitosan fiber. In this work, the chitosan dope composition (*i.e.* polymer concentration, water/alcohol ratio in the initial solvent, alcohol nature and chitosan salt form), the post-extrusion thermal treatment, as well as the neutralization conditions (*i.e.* base nature and concentration) were studied and optimized for spinning. In addition, thanks to X-ray diffraction techniques, we studied the influence of all these physico-chemical parameters on the final semi-crystalline microstructure of chitosan fibers. We evidenced different semi-crystalline morphologies that provide new perspectives in controlling the morphology, and thus the physical and biological properties of chitosan fibers.

2. Materials and methods

2.1. Materials

A weakly acetylated chitosan with a high molecular weight produced from squid pens was supplied by Mahtani Chitosan Pvt. Ltd. (batch type 113, dated 17/12/2004) and characterized as previously described (Boucard, Viton, & Domard, 2005; Montembault et al., 2005b) (Table 1). All the polyols (purity of 99%) used to prepare hydroalcoholic chitosan solutions as well as concentrated ammonium hydroxide solution and sodium hydroxide pellets were purchased from Acros organics or Sigma Aldrich.

2.2. Preparation of hydroalcoholic chitosan dopes and rheological measurements

2.2.1. Preparation

Chitosan was dispersed in deionized water. Acetic acid (or hydrochloric acid in some experiments) was added to achieve the stoichiometric protonation of free amine sites of D-glucosamine residues. Stoichiometric protonation conditions (*i.e.* no acid excess) were chosen in order to avoid the polymer degradation and the neutralization kinetics decrease (El-Tahlaway & Hudson, 2006). Alcohol (*e.g.* 1,2-propanediol) was added slowly (3 additions over 2 h) only after complete dissolution of chitosan in aqueous media and the blend was stirred for 5 h to complete homogenization. In all hydroalcoholic chitosan solutions, the polymer concentration is largely over the critical chain entanglement concentration ($C^* = 1/[\eta]$) = 0.06–0.1% (w/w) (Boucard et al., 2005; Montembault et al., 2005b). Different water/alcohol (w/w) ratios were tested. Thus, in the initial aqueous solution, the chitosan concentration was adjusted depending on the targeted water/alcohol ratio and the polymer concentration required in the final solution.

2.2.2. Rheological measurements

Rheological measurements were conducted on a stress-controlled rheometer (AR 2000, TA Instruments) at $22 \pm 2\,^{\circ}C$. The steady viscosity of chitosan solutions was assessed in static mode