V Iberoamerican Chitin Symposium
Iberoamerican Chitin Society
March, 2010, Santiago, Chile

NEW CHITOSAN FIBER SPINNING PROCESS WITH SEMICRISTALLINE MICROSTRUCTURE CONTROL

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In recent years, "new generation" medical textiles for wound dressings have received growing interest in biomedical research. In addition to their fundamental functions such as protective barrier, high surface area associated with trombogenic properties, softness and absorbency, the "ideal" wound dressing should help shorten wound healing process, reduce scars and should require easy and less frequent changes. In this context has emerged the use of new fibers with bioactive properties.

Among spinnable polysaccharides, chitosan is well-known for its biocompatibility, haemostatic, bacteriostatic and fungistatic properties, bioresorbability, bioactivity, and thus constitutes an excellent candidate for wound dressing applications. Chitosan fibers could be used into many fabrics such as yarns for bioresorbable suture or as woven/non-woven dressings for example to promote cell proliferation and tissue regeneration in chronic wounds. Different spinning routes based on the coagulation of aqueous chitosan solutions in alkali media are reported in literature[1]. The most commonly used process to produce chitosan yarns is wet-spinning using alkali baths. Besides their remarkable biological features, the main drawback of chitosan fibers is their lower mechanical properties compared to synthetic fibers especially in wet environment. Current approaches to improve chitosan fiber mechanical properties are based on chemical cross-linking (*e.g*. epichlorohydrin) or physical post-treatments (e.g. drawing during coagulation or during the drying step) which are more relevant for biomedical applications as they lead to pure chitosan fibers. Nevertheless, other processing routes still need to be developed to improve or control the physical and biological properties of chitosan fiber.

In the frame of material development, microstructural parameters such as molecular orientation, intra- and intermolecular interactions (hydrogen bonding, hydrophilic/hydrophobic interactions), micro/nano fibrillar and semi crystalline morphology (cristallinity index, allomorph type) are the key for final fiber properties. Crystallites act as a physical fillers and crosslinks of high functionality that are known to contribute to the reinforcement of the material. Chitosan can crystallize in two forms: the hydrated form (tendon structure) and the anhydrous form ("annealed" structure) which is harder to obtain without chain degradation. To our knowledge, the influence of allomorph content in chitosan fibers on mechanical properties has never been reported. In our approach, we investigated the spinning of hydroalcoholic chitosan solutions in order to control the anhydrous/hydrated allomorph balance. Two coagulation methods were explored. In a first set of experiments, gelation was induced by water/alcohol solvent exchange followed by neutralization of the alcoholic gel fiber in alkali bath. A similar process was used for chitosan gel formation and led to improved mechanical properties compared to aqueous process[2]. In a second step of the study, direct neutralization of hydroalcoholic chitosan dope was considered. In both cases, after washing in water and air-blow drying, final fibers contained only chitosan and water. Chitosan dope composition (polymer concentration, water/alcohol ratio, alcohol structure and chitosan salt form) as well as neutralization conditions (base nature and concentrations) were optimized for spinning. We focused on the influence of all these physico-chemical parameters on the final semi crystalline microstructure of chitosan fibers using synchrotron WAXS technique. Chitosan allomorph type was evidenced to be controlled by both alcohol proportion in dope at neutralization step and neutralization conditions. Thus, using such processes, chitosan fibers containing from mainly hydrated crystals to mainly anhydrous crystals can be obtained without any significant decrease in molecular weight compared to classical annealing method[3] *i.e.* heating at 240°C in water. In particular, annealed allomorph chitosan fibers could be attractive to play both on bioresorption and mechanical properties when fibers are in contact with physiological fluids.

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