

Effect of Concentration of Sodium Acetate(SA) on Crosslinking of Chitosan Fiber by Epichlorohydrin(ECH) at a Wet Spinning System

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INTRODUCTION

Chitin, (1→4)-linked 2-acetamido-2-deoxy-β-D-glucan, is the second most abundant natural polymer. Chitosan is the deacetylated product of chitin. Both polymers have attracted much attention, due to their unique properties and renewed interest in natural polymers. Chitosan is an under-utilized polymer which possesses many of the desired characteristics for this application; i.e., it is readily mineralized in the environment through the actions of microbes and weathering. These biopolymers are biocompatible, biodegradable, and biofunctional and are therefore utilized to good effect as special products in the surgical treatment of the human body.

Chitosan fibers are typically spun from viscous, concentrated polymer solutions commonly referred to as spinning dopes. Melt spinning cannot be used because the chitosan polymers degrade upon heating. The spinning process most commonly used for chitosan fibers is wet-spinning. In wet-spinning, the spinning dope is extruded through a spinneret immersed in a coagulation bath containing a nonsolvent.

This article describes our work to crosslink chitosan fibers. It is our objective to improve the functional properties of this material. Chitosan is less easily defined as it is difficult to fully deacetylate chitin. Chitosan is the preferred form of the polymer, as it is more readily processed into fiber and film forms than is chitin. A drawback of chitosan is its enhanced hydrophilicity compared to chitin, which results in a considerable loss of tensile strength when wet.

ECH was selected as a convenient base-catalyzed crosslinking agent. An advantage of ECH is that it does not eliminate the cationic amine function of chitosan. The use of ECH to crosslink amylose was reported by Luby. This methodology was adapted to crosslink chitosan films and, in this work, fibers. Most notably, crosslinking by ECH considerably improves the strength of the chitosan films and fibers. In our previous work, crosslinked chitosan fiber in a wet spinning system were prepared by ECH in a wet spinning system. The wet tenacity at breaking point was increased with increasing

concentration of ECH for spinning dope. On the other hand, SA was selected as a coagulation retardant. An advantage of SA is that it is expected slow coagulation in fiber formation by neutralization reaction of acetic acid and sodium hydroxide. As a result, promotion of degree of crosslinking is expected by ECH. In this study, the fiber formation and the fiber characteristics crosslinked by ECH in a wet-spinning system(SA addition in coagulation bath), a one step system, have been investigated.

EXPERIMENTAL

Materials

Chitin from red crab of the east sea was acquired from the Dongbo Chemical Company of Korea. Acetic acid (Aldrich), sodium hydroxide (Fluka), ECH (Sigma), and urea (Sigma) were used as reagent grade.

Preparation of chitosan fiber by wet spinning

The fiber formation process will be described with emphasis on the development of the optimum fiber structure for commercial applications. By fiber formation, we mean the process by which the spinning dope is converted into fiber in the spin bath. Wet spinning is the most widely used spinning process in solution spinning.

Figure 1 depicts a schematic drawing of the wet spinning system used in this study. The solutions were mechanically stirred for 60sec. in order to be homogenized; then the dope solutions were degassed and filtered in a vacuum system and were left standing for 5 hours at 20°C.

The chitosan dope was extruded through a stainless steel 300-hole spinneret by means of a variable speed infusion metering pump. Spinneret dimensions were 0.1mm in diameter and a capillary length-to-diameter ratio of 2. A 400 mesh(pore size, 37µm) stainless steel filter was mounted behind the spinneret. The coagulation bath was a 10% w/w NaOH aqueous solution. The coagulation and the crosslinking of chitosan fiber occurred in this coagulation bath at the same time. As a result, the crosslinking reaction started at the surface and worked its way to the core of the fiber(polymer jet). As such, depending on the residence time in the coagulation bath, the fiber may not have been crosslinked through out its entire cross-section. The fibers emerging from the wet-spinning coagulation bath were unoriented and had little strength. Development of the anisotropic mechanical properties required of textile fibers is accomplished largely in the orientational drawing operation. Therefore, the fibers obtained by the coagulation bath were washed in water and drawn or stretched in a suitable stretching ratio at

99±1°C in a water bath. The take-up velocity at the end of the coagulation bath was maintained at 3.0 m/min for all experiments.

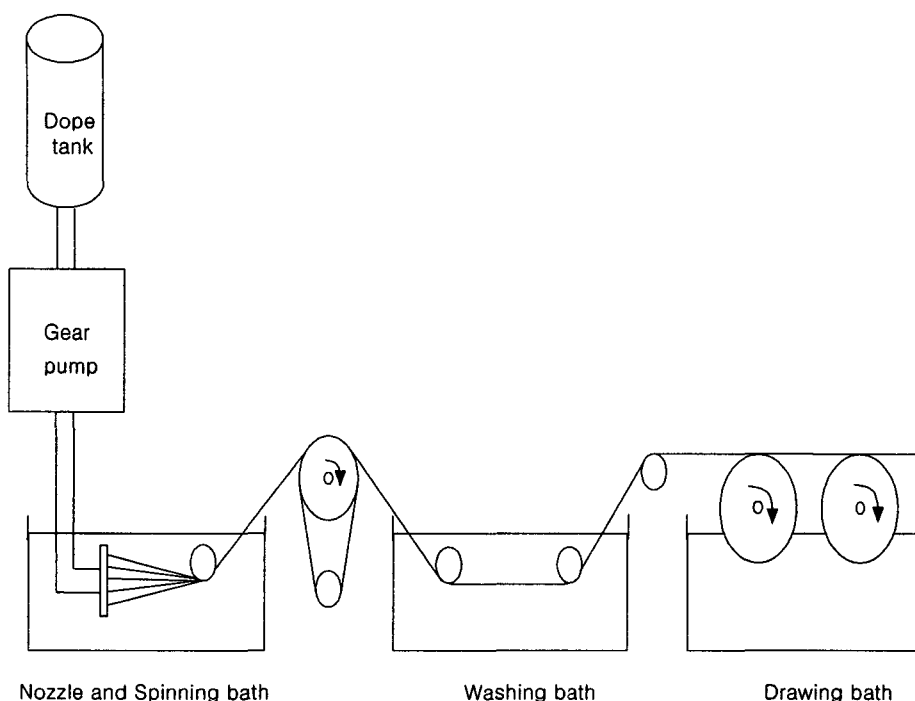


Figure 1. Schematic diagram of wet-spinning apparatus.

MEASUREMENTS

Tensile properties of monofibers were measured using a tensilon (Fafegraph, M) with a crosshead speed of 20 mm/min at room temperature. The degree of swelling of fiber was measured by a moisture percentage measuring instrument (HR73 Moisture Analyzer, Mettler Toledo) at standard condition. The thermal behavior of the chitosan fibers was investigated using a differential scanning calorimeter, model TA Dupont 9900. The measurements for the chitosan fiber were performed at a scanning rate of 20°C/min at a temperature range of 35 to 450°C in a nitrogen atmosphere. X-ray diffractograms of the chitosan fiber samples were obtained using a Rigaku XG X-ray generator working at 35 KV, 20 mA. The scattered X-ray in WAXD mode was monochromatized to a Cu-K_α ray with a graphite monochromator, and counted with a Rigaku Denki scintillation counter at intervals of 2° of scattering angle using a Rigaku Rint 2000 goniometer. The fractured samples were prepared by stretching the fibers to breaking on a Tensilon at standard condition. Morphologies of the fractured fibers were studied by

scanning electron microscopy(SEM, JSM 6400).

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