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Communications

Native Chitosan/Cellulose Composite Fibers from an Ionic Liquid via Electrospinning

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Introduction

The demand for novel polysaccharide-based hybrid biomaterials has recently gained worldwide attention in the field of tissue engineering and medical applications owing to their inherent biocompatibility and biodegradability.[1-8] Polysaccharide-based biomaterials can be designed into various forms and shapes, including membranes,[9] tubes,[10] fibers,[11,12] and beads,[13] for use in medical devices or implants. In particular, nanofibers prepared by electrospinning various synthetic or natural biocompatible polymers are useful as tissue engineering scaffolds, wound healing materials, and as a drug delivery carriers in medical science.[14] Electrospinning, considered as a derivative of the electrospray process, is a fascinating and simple technique capable of producing nanometer- to micrometer-sized fibers of various polymers. In particular, rapid progress of cellulose fiber-based hybrids prepared by electrospinning, any combination of polysaccharides, such as starch, chitin, chitosan, pectin, heparin, fucan, or carageenan, has been achieved in a range of applications, including drug delivery systems, vascular grafts, scaffolds, and wound-healing for tissue engineering.[15,16] The usefulness of cellulose-based hybrid fibers is obvious because the intra- and intermolecular hydrogen bonds in cellulose offer an excellent mechanical strength that stabilizes the entire fiber-structured matrix into the form of gauze during the healing process.[17]

Undoubtedly, blending chitosan and cellulose through an electrospinning process represents a viable opportunity to invent novel antibacterial three-dimensional fibrilar-structured wound-healing gauzes. Although Du *et al*. reported that ester derivatives of cellulose and chitosan, which are the two most abundant natural polysaccharides, could be electrospun together,[11,12] non-derivatized polysaccharide hybrids via electrospinning, including chitin, chitosan, cellulose, and heparin are highly challenging due to both the limited availability of volatile solvents and their poor ability to dissolve biopolymers in most common organic and aqueous solvents.[18-22]

Hence, in this report, we demonstrate for the first time that it is possible to electrospin non-derivatized chitosan-cellulose composite fibers from an ionic liquid (IL), 1-ethyl-3-methylimidazolium acetate ([EmIm][Ac]). Ionic liquids, organic liquid salts capable of dissolving both polar and nonpolar compounds, are useful in overcoming the poor solubility of polysaccharides in conventional organic solvents, resulting in potential applications in the chemical and biotechnology industries.[17] Given that ILs are low-melting salts with very low vapor pressure, the IL was removed from chitosan and cellulose by dissolution in an ethanol cosolvent. The chitosan-cellulose composite fibers fabricated were directly electrospun in the ethanol cosolvent, where IL, [EmIm][Ac] used in dissolving both non-derivatized cellulose and chitosan, can completely be dissolved where neither chitosan nor cellulose is soluble (Figure 1). Therefore, IL is capable of affording pure chitosan-cellulose composite fibers after the cosolvent ethanol removes the IL. These chitosan-cellulose composite fibers from IL were manufactured into a three-dimensional form possessing antimicrobial activity to treat burns, bedsores and skin ulcers. They can also be used with frequent dressing-changes on wounds in biomedical and pharmaceutical areas and have the potential for application as antimicrobial materials for food coatings.[23,24]

Results and Discussion

Electrospinning of chitosan-cellulose solution in ILs is hard to control for continuous jets and fiber production because of the high viscosity, high ionic strength and non-volatility of ILs.[18] Moreover, it was not possible to prepare pure chitosan fibers from [EmIm][Ac]. Electrospinning of chitosan using [EmIm][Ac] is very difficult because of its limited solubility (about 1% w/w chitosan in [EmIm][Ac]) and its polycationic nature in solution, resulting in excessively enhancing the surface tension of the resultant solution.[25] Hence we optimized a final concentration of 0.5%

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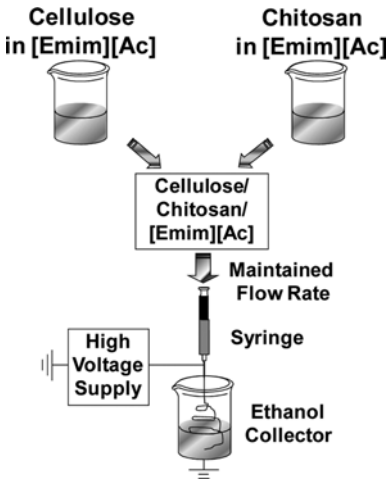

Figure 1. Schematic representation of the electrospinning process from a cellulose-chitosan-ionic liquid solution.

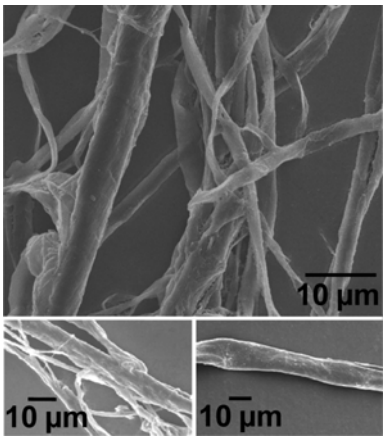

Figure 2. SEM images of chitosan-cellulose composite fibers (0.5% (w/w) cellulose + 0.25% (w/w) chitosan in [EmIm][Ac]).

(w/w) cellulose and 0.25% (w/w) chitosan in [EmIm][Ac]. After the electrospinning process, the dried chitosan-cellulose composite fibers were structurally characterized using scanning electron microscopy (SEM), as shown in Figure 2. Homogeneous distributions of chitosan on the surface were observed by EDS nitrogen mapping. The three-dimensional chitosan/cellulose fiber film was comprised of randomly arranged micron-sized fibers because the newly fabricated fibers were sinking much slower than they were piling up on the surface of the cosolvent.[18] Although the morphology and diameter distribution of fibers created through an electrospinning process can be varied by controlling process parameters such as the pump feed rate, voltage, solution concentration, various collection and solidification processes, and the surface tension of the solvents, highly viscose and non-volatile ILs allow the fibers to have mostly micron-sized diameters. These electrospun fibers have potential applications as an antibacterial textile on wounds. Essentially, microfibrils of chitosan-cellulose composites create an extensive surface area, allowing it to hold a large amount of water as a high-quality wound dressing during the healing process while maintaining a high degree of conformability.

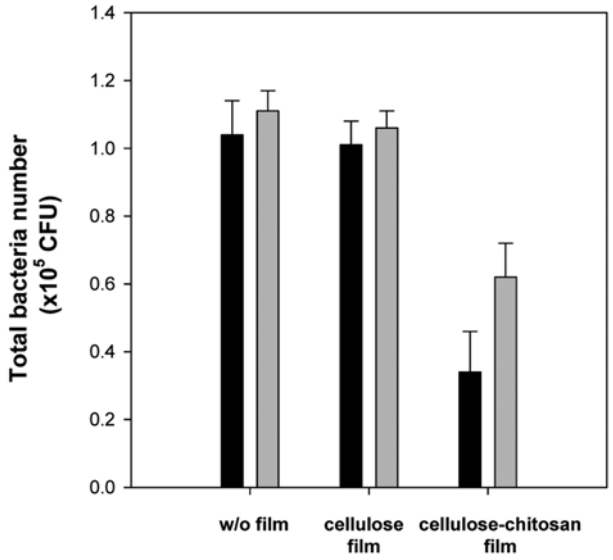

Figure 3. Effect of cellulose/chitosan film, cellulose film, and incubation without film on *E. coli* in 24 h incubation at different pH levels. The black and gray bars indicate incubation at pH 6 and 7, respectively.

Figure 3 shows the total number of viable cells after incubation with the cellulose and cellulose/chitosan electrospun fiber film. The percentage of viable cells was over 95% for incubation with cellulose film compared to a control group incubated without film. This indicates that cellulose film did not demonstrate an antibacterial effect and that the adsorbed cells into the cellulose film comprised less than 5% of the total. On the other hand, the cellulose/chitosan film showed an antibacterial effect when challenged with *E. coli*, affording 65% and 36% bacterial resistance at pH 6 and 7, respectively, compared to a cellulose film. The higher antibacterial effect at a lower pH may be caused by the increased solubility of the chitosan. Chitosan is a well-known antibacterial compound, as positive charges of the chitosan interface with the negatively charged residues of the macromolecules at the bacterial cell surface lead to bacterial cell death.[26]

In conclusion, a novel non-derivatized electrospun chitosan-cellulose composite film was created from an ionic liquid [EmIm][Ac]. This chitosan-cellulose hybrid film could be useful as an antibacterial reagent for wounds where antimicrobial activity is required to treat skin ulcers. This textured fabric material, which is unlike conventional dressings, can be placed on the wound site as a bandage or can be incorporated into other absorbents or gauzes that are meant for immediate use as a frequently changed wound dressing. Further studies are necessary to produce well-separated smooth chitosan/cellulose fibers using a rotating wire drum that can quickly remove ILs[18] and determine the efficacy of

this material with regard to wound healing applications.

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Supporting Information: Information is available regarding the experimental procedure for the preparation of chitosan/cellulose in [EmIm][Ac], the electrospinning of the chitosan/cellulose/[EmIm][Ac], and the antibacterial activity tests. The materials are available via the Internet at http://www.polymer.or.kr.

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