키토산/피브로인 나노섬유웹 제조와 그 특성화

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Production of Electrospun Chitosan/Fibroin Nano-sized Fiberwebs and Their Characterization

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1. Introduction

Chitin is the most abundant natural amino polysaccharide and is estimated to be produced annually almost as much as cellulose. It has become of great interest not only as an under utilized resource, but also as a new functional material of high potential in various fields. In addition, chitin and chitosan are recommended as suitable functional materials, because these natural polymers have excellent properties such as biocompatibility, biodegradability, non-toxicity and adsorption properties, etc. And silk fibroin is one of the typical natural protein polymers. It has been investigated as a potential biomaterials such as a matrix for the enzyme immobilization and mammalian fibroblast cell culture. Recently, there has been increased interest in another method of fiber production, electrospinning, which can consistently produce fibers that are sub-micron and nano-size in diameter. Electrospun fibers have small pore size and high surface area. So, it can usefully used in biomedical applications such as wound dressing in medical industry. At first, electrospinning method was studied by Zeleny and patented by Formhals. Taylor found the critical voltage and semi-vertical angle. Great efforts have been made to study the effects of processing parameters on the structure and morphology of electrospun fibers. The electrospinning technology is well suitable to process natural biomaterials and synthetic biocompatible or bioabsorbable polymers for biomedical applications. Thus, the aim of this study is to establish the manufacturing technique of chitosan, silk fibroin and chitosan/silk fibroin nanofiberweb and to investigate of the spinning behavior and processing condition as well as to characterize the microstructure and physical properties of electrospun nanowebs.

2. Experimental

2.1 Sample preparation

The used chitosan(Chitolife Co.) contained a weight average molecular weight(Mw) of 2.5×10^4g/mol. The chitosan solution(50wt.%) and silk fibroin solution(20wt.%) were prepared. Both solutions, formic acid was used as the solvent. Also, the chitosan/silk fibroin solution(10:3) was prepared using the formic acid. The applied electrical potential was in a range of 0~40kV. And, the spinning distance was 6~8cm.

2.2 Electrospinning behavior

To observe the electrospinning behaviors of chitosan, silk fibroin and chitosan/silk fibroin fibers, we used the digital video camera(VL-NZ100U, Sharp Co.). When we used the chitosan solution for

electrospinning, the feeding rate was 10㎕/h and the applied electrical potential was 15㎸. In the case of silk fibroin solution, the feeding rate was 0.4㎕/h and the electrical potential was 13㎸. And in the case of chitosan/silk fibroin solution, the feeding rate was 15㎕/h and the electrical potential was 15㎸.

2.3 Morphological structure

Morphological structures and diameters of electrospun fibers were observed by SEM (JSM-5410, JEOL Co.) and the Image Analyzer(BMI plus Co.).

2.4 Thermal property

To measure the weight reduction with changing temperature of chitosan, silk fibroin and chitosan/silk fibroin fiberweb, it used the Thermogravimetric Analysis(TGA-7, Perkin-Elmer Co.).

2.5 X-ray diffraction

For observation of crystallization difference of chitosan, silk fibroin and chitosan/silk fibroin fiberwebs, we used the X-ray diffraction(XDS 2000, Sintag Co.). The used wavelength was 1.544㎝$^{-1}$.

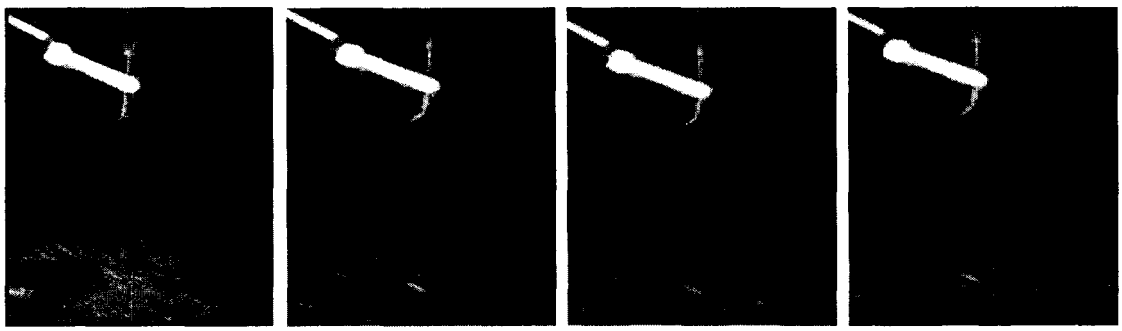
2.6 IR spectroscopy

IR spectra were obtained using a MAGNA 560 spectrometer(Nicolet instrum Co.) in the spectral region of 400~4000㎝$^{-1}$.

3. Results and Discussion

3.1 Spinning behavior

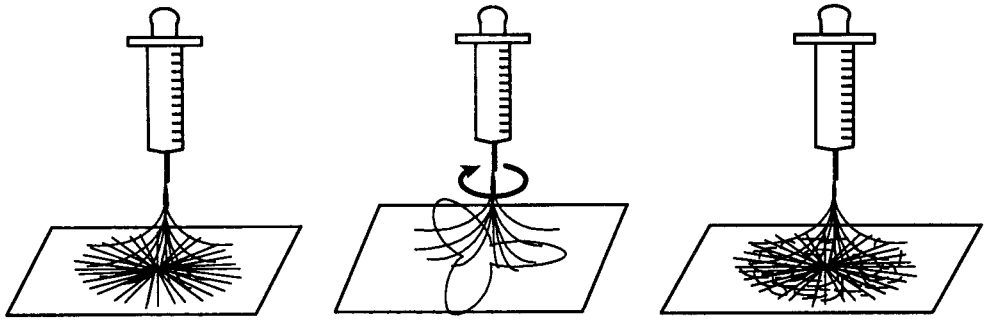
According to the TGA curve, it observed about 10% weight loss around 160℃ and about 50% weight loss around 250℃ by thermal decomposition. To use chitosan, silk fibroin and chitosan/silk fibroin solution, electrospinning was performed at spinning distance of 6~8cm. When we used the chitosan solution for electrospinning, the spinning behaviors were showed in Fig.1. Fig.1(a) shows the formation of chitosan solution jet. And, Fig.1(b) and (c) appears two and three branches of the jet each other. The Fig.1(d) shows the multiple jet. Fig.1 appears a cycle of formation of chitosan fiberweb.



(a) (b) (c) (d)

Figure 1. Photographs of formation cycle of chitosan fiberwebs.

Fig.2 shows the difference of collected forms among the chitosan, silk fibroin and chitosan/silk fibroin fiberwebs. (a) shows the collected chitosan fiberweb. According to the (a), chitosan fiberweb was collected with radial form. (b) is the silk fibroin fiberweb and it has the circle form. And (c) shows the collected chitosan/silk fibroin fiberweb having net shape.

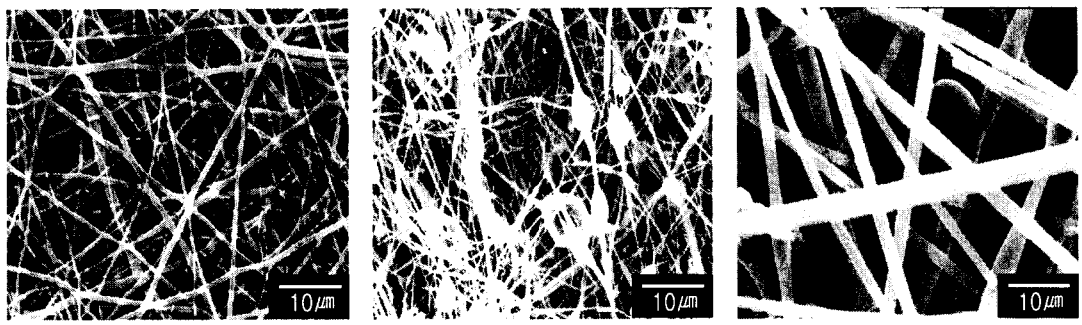


(a) (b) (c)

Figure 2. Spinning behaviors of electrospun fiberwebs.
(a : chitosan , b : silk fibroin, c : chitosan/silk fibroin)

3.3 Morphological structure

Fig.3 shows the morphological structures of chitosan, silk fibroin and chitosan/silk fibroin fiberwebs. According to Fig.3, chitosan fibers were produced without beads. But, silk fibroin fibers were produced with beads and fiber diameters were very small. The chitosan/silk fibroin fibers were produced with some beads and fiber diameters were the largest of the three cases. The diameters of chitosan, silk fiborin and chitosan silk fibroin fibers were 700, 300 and 2000㎚, respectively.



(a) (b) (c)

Figure 3. SEM microphotographs of electrospun fibers.
((a) chitosan, (b) silk fibroin, (c) chitosan/silk fibroin))

3.4 X-ray diffraction

Fig.4 shows x-ray diffraction curves of chitosan, silk fibroin and chitosan/silk fibroin. The chitosan fiberwebs from chitosan solution showed a major diffraction peak at about 22.5° and two minor peaks at about 14.5° and 29.5°. On the other hand, silk fibroin fiberwebs exhibited diffraction peak at 16.2°. Diffraction peaks of Chitosan/silk fibroin fiberwebs similar to peaks of chitosan fiberwebs. Because concentration of chitosan is higher than that of silk fibroin, these diffraction peaks were investigated. The degrees of crystallization of chitosan and chitosan/silk fibroin fiberwebs were higher than silk fibroin fiberwebs. The beads of silk fibroin fiberwebs were the reason of low degrees of crystallization.

3.5 IR spectroscopy

The IR spectra of chitosan, silk fibroin and chitosan/silk fibroin fiberwebs are shown in Fig.5.

Chitosan fiberweb was showed strong absorption bands at 1032cm^{-1}. It assigned to the skeletal vibrations involving the C-O stretching. The absorption band at 1151cm^{-1} was assigned to the anti-symmetric stretching of C-O-C bridge, and 1589 and 1647cm^{-1} absorption bands attributed to the C=O and -NH_2 stretching. Silk fiberweb showed strong absorption band at 2700 and 3000cm^{-1} (amides).

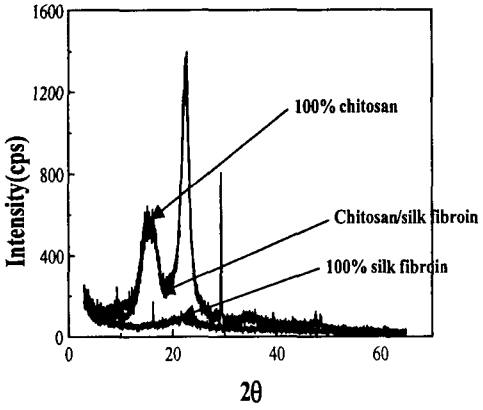


Figure 4. X-ray diffraction curves of fiberwebs

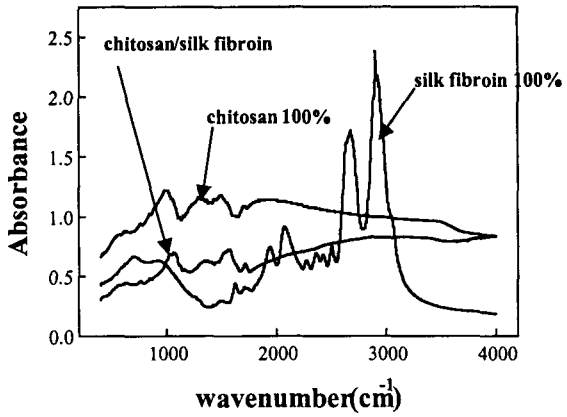


Figure 5. IR spectra of fiberwebs.

4. Conclusions

To use chitosan, silk fibroin and chitosan/silk fibroin solution, electrospinning was performed. The effects of solution properties and processing parameters on the structure and morphology of electrospun fibers were investigated. It showed the difference of collected forms among these fiberwebs. Collected chitosan fiberweb appeared radial form, silk fibroin fiberweb showed circle form and chitosan/silk fibroin fiberweb appeared net shape. Because chitosan concentration is higher than that of silk fibroin, diffraction peaks of chitosan were similar to chitosan/silk fibroin. Chitosan/silk fibroin peaks included chitosan and silk fibroin peaks. According to Fig.3, chitosan fibers were produced without beads. But silk fibroin fibers were produced with beads and fiber diameters were very small. The chitosan/silk fibroin fibers were produced with some beads and fiber diameters were the largest of the three cases. The X-ray results appeared the fiberwebs included chitosan has high degrees of crystallization. And according to the IR spectra, absorption band of chitosan/silk fibroin was included to the chitosan and silk fibroin absorption bands.

5. References

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