Hydroxyapatite/키토산 복합재료 및 그 응용

정용식
전북대학교 섬유공학과

Hydroxyapatite/Chitosan Composites and its Application

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1. Introduction

Hydroxyapatite(HAp, $Ca_{10}(PO_4)_6(OH)_2$, is a compound with structural and chemical resemblance bone mineral and of particular importance in the field of biomaterials. In addition to the non-toxicity and high compatibility with hard and soft tissue, HAp exhibits strong affinity to host hard tissues and protein molecules. However, HAp is difficult to shape in the specific forms due to its hardness and brittleness. Therefore, novel composites of HAp and polymers that can compensate for the weak mechanical properties of HAp have become of great interest. In recent years, biodegradable HA/polymer composites can be made by using a biodegradable polymer matrix. Such biodegradable composites have the ability to induce new bone growth and gradually to degrade, thus enabling the load gradually to transfer from the material to the newly grown bone.

Chitosan consists of glucosamine and *N*-acetylglucosamine units linked through 1-4 glycosidic bonds. In commercial chitosan products, the acetyl group content varies from 5 to 30 % due to imperfect *N*-deacetylation of chitin. The most important feature of chitosan is its biodegradability, but it also has good solubility in various organic acid solutions and sufficient resistance in alkali environments. In addition, chitosan is flexible and has a high resistance upon heating due to the intramolecular hydrogen bonds formed between hydroxyl and amino groups.

Therefore, the composites of HAp and chitosan is expected to show increased mechanical properties and biodegradation. The incorporation chitosan with HAp can transform the physical shape of HAp into the different forms such ac liquids, membranes, and fibers etc., and thus expand the application area of both HAp and chitosan.

The object of this study is firstly to prepare homogeneous HAp/chitosan composites using a co-precipitation method, secondly to transform HAp/chitosan composites into liquids, films, and fibers, finally to utilize the advantages of HAp and chitosan as a biomaterial.

2. Experimental

2.1. Materials

Chitosan powder was from TaeHoonBio Co. The degree of deacetylation is 92 % and the viscosity is 600 cps in 0.5 % chitosan solution. Citric acid, $Ca(OH)_2$ and H_3PO_4 are of analytic grade and used without further purification.

2.2. Preparation of HAp/chitosan composite

A chitosan aqueous solution of 2 wt % was prepared by dissolving the chitosan powder into 1 mM aqueous acetic acid solution. The chitosan solution was added into 60 mM H_3PO_4 solution. The ratio of chitosan to H_3PO_4 was adjusted for the final HAp/chitosan composition; 80/20. Then the chitosan/H_3PO_4 solution gradually was added drop-wise to a $Ca(OH)_2$ suspension of 100 mM with stirring until pH 9±0.2 was achieved. The reaction temperature was kept at 30 ℃. The resulting slurry was aged with stirring for 24 hours. The precipitate was filtered, washed , and dried.

$$10Ca(OH)_2 + 6H_3PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2$$

$$Chitosan\text{-}NH_3^+ + CH3COO^- + Ca(OH)_2 \rightarrow Chitosan\text{-}NH_2 + (CH_3COO)_2Ca$$

Fig. 1. Co-precipitation synthesis of HAp/Chitosan composite.

2.3. Preparation of HAp/chitosan composite film

The HAp/chitosan composite was dissolved in acetic acid solution with additional chitosan. The chitosan content was adjusted final HAp/chitosan composition ranging from 10/90 to 50/50. I added citric acid to the solution to inhibit nucleation of HAp. The final solutions were poured into petri dish which was covered with Teflon sheet to peel off easily and dried for 24 hours at room temperature. The obtained films were rehydrated in 5 % NaOH solution, washed, and dried.

2.4. Preparation of HAp/chitosan hybrid fiber

The HAp/chitosan composite was diluted with the procedure above mentioned. The final content of HAp/chitosan in spinning dope was adjused to 5 %. The

obtained dopes were extruded through a spinneret into 10 % NaOH solution. The coagulated fibers were washed and dried.

2.4. Application of HAp/chitosan composite to antimicrobial finish

The cotton fabrics were padded with the solutions of 1 % HAp/chitosan(50/50) and Ag^{+} doped HAp/chitosan composite at 80 % pick-up ratio, and cured at 170 ℃ for 2 min.

3. Results and Discussions

Fig. 2 and 3 show XRD diffraction patterns for HAp particle, HAp/chitosan composite(50/50), film(20/80), and fiber(30/70), respectively. All composites show the typical peaks of apatite crystal at 32° . The composites exhibit broadened X-ray diffraction trace due to the low degree of crystallinity.

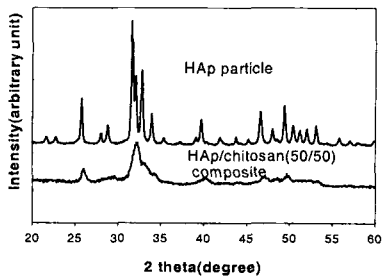


Fig. 2. XRD diffraction analysis of HAp particles and HAp/chitosan composite.

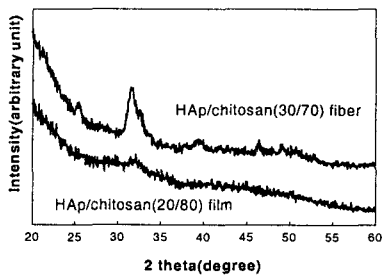
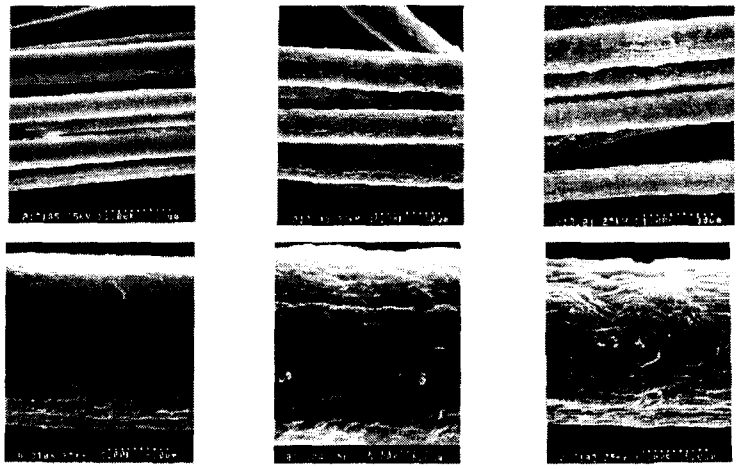


Fig. 3. XRD diffraction analysis of HAp/chitosan composite film and fiber.

Fig. 4 shows SEM observation of the surfaces of HAp/chitosan hybrid fiber with different HAp contents. 10/90 HAp/chitosan hybrid fiber shows that the particles of HAp anchored in the composite fiber and appears level and smooth surfaces, while with an increase in HAp content, it becomes rougher and rougher and uneven.

The Antimicrobial effects of the cotton fabrics treated with several composites containing HAp are indicated in Table 1. HAp has an affinity to proteins such as microbial or bacteria, and thus it hold and immobilize them. Therefore, the incorporation the substance having anitimicrobial activity into HAp can give anitimicrobial to textile fabrics.



(a) (b) (c)

Fig. 4. Scanning electron micrographs of HAp/chitosan hybrid fiber; (a) 10/90, (b) 20/80, and (c) 30/70 HAp/chitosan composites, respectively.

Table 1. Antimicrobial activity of cotton fabric treated with several composites containing HAp

Sample	Reduction of bacteria (%)	
Sample	*S. aureus*	*K. pneumoniae*
HAp	99.9	99.7
HAp/Ag^+	99.9	99.9
HAp/chitosan	99.8	99.8
HAp/chitosan/Ag^+	99.9	99.9

4. References

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