

Mechanical properties of cellulose acetate/hydroxyapatite nanoparticle composite fiber by electro-spinning process

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Synthetic biodegradable polymer matrix composites including bioactive ceramic phases are being increasingly considered for use as tissue engineering scaffolds due to their improved physical, biological and mechanical properties. Cellulose acetate composite fibers were prepared by electro-spinning of cellulose acetate doped with from 2.5 to 40 vol.% hydroxyapatite nano powder. The structure of the electro-spun web varied depending on the solvent types. The cross-linked morphology between fibers was obtained by the addition of benzyl alcohol. In this study, the effect of the spinning dope composition and the filler concentration on the morphology of electro spun cellulose acetate fibers was evaluated. The mechanical properties of the electro-spun single fiber were measured using a Thermo Mechanical Analyzer (TMA). The tensile strength of electro-spun fibers depended on the filler content.

Key words: Cellulose acetate, Hydroxyapatite, Electro-spinning, Tensile test, Hybrid composites.

Introduction

Ceramic biomaterials are often used to alleviate pain and restore function to diseased or damaged body parts. In particular, they are widely used as artificial supports for bone regeneration [1]. The required characteristics of an artificial bone material are as follows. First, it needs to contain an appropriate extracellular matrix structure made from biocompatible or biodegradable material. Second, and most importantly, artificial bone must have a high mechanical strength. To achieve this, biomaterials for bone substitution must be made from materials with appropriate mechanical properties such as an elastic modulus and deformability. While all ceramics are more brittle than bone, ideal bone substitute materials can be derived from organic-inorganic hybrid composites through the combination of bioactive ceramics and polymers with appropriate mechanical properties. Therefore, the addition of bioactive ceramic particles to polymeric materials can improve the mechanical and biological properties of cellulose-ceramic composites for a broad range of applications [2, 3]. Various techniques can be used to fabricate organic-inorganic hybrid composites [4, 5, 6]. For example, electrospinning is a very simple process that can be used to fabricate composites with fiber morphologies with comparative ease. As mentioned above, the mechanical properties of the composite are very important for bone substitute materials, but so far,

the mechanical properties of electrospun fiber composite materials have mostly been evaluated only for films or mats. In mats, many factors such as the fiber orientation and porosity affect the mat elongation during tensile tests and thus the subsequently calculated Young's modulus. Furthermore, direct measurement of the mechanical properties of single electrospun fibers is very difficult because the electrospun fabric has random fiber orientations. In particular, tensile testing is considerably more difficult than performing bending tests because of the difficulty in gripping and holding single cellulose fibers that have micro- or nanoscale diameters. Nevertheless, an understanding of the mechanical properties of single fibers is very important for quality control, because it is essential to obtain the mechanical properties of the individual fibers that make up the scaffold in order to predict the mechanical behaviour of scaffolds under various loading conditions. However, the mechanical properties of single composite fibers have not been widely characterized because of the aforementioned difficulty in handling micro- and nanoscale fibers and the small load required for mechanical strength measurements. In this study, we measured the mechanical properties of electrospun single fibers using a thermomechanical analyzer (TMA) and found that the tensile strength of the electrospun fibers depended on the filler content.

Materials and Methods

As the starting material, we used cellulose acetate powder (Aldrich, USA). Solvents used included benzyl alcohol, methyl ethyl ketone (MEK), and acetone (Samchun chemicals, South Korea). The hydroxyapatite

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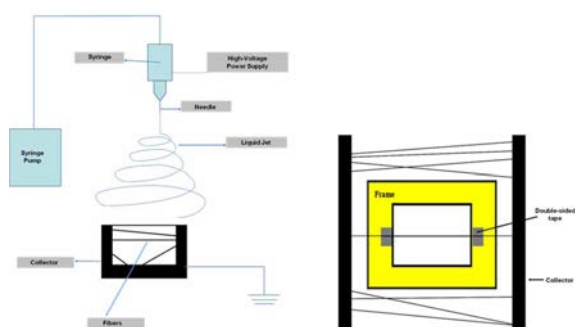


Fig. 1. Schematic of the sample preparation used for the mechanical properties of the fiber.

(HAp) nanoparticles were synthesized using the hydrothermal method (Seoul National University, Korea). The HAp powder was mixed with a solvent in a SPEX mill for 1 h, and the solvent was then separated from the HAp powder suspension using a centrifugal separator. Next, solutions of 14 wt.% cellulose acetate in acetone, 6 wt.% MEK in acetone, and 6 wt.% benzyl alcohol in acetone were prepared. The spinning dopes were prepared by mixing the 14 wt.% cellulose acetate with various amounts of HAp (up to 40 vol.%). Fig. 1 shows a schematic illustration of the basic setup for electrospinning. It consists of three major components: a high-voltage power supply, a spinneret (needle), and a collector. Direct current power supplies were usually used for electrospinning, although the use of alternating current is also feasible [7]. The spinneret was connected to a syringe containing the spinning dope. With a syringe pump, the solution could be fed through the spinneret at a constant and controllable rate. The spinning dope was injected onto a collector at an injection rate of 2 ml/h. When a high voltage (usually in the range of 10 and 15 kV) was applied, the pendent drop of the spinning dope at the nozzle of the spinneret became highly electrified, and the induced charges were evenly distributed over its surface. Single electrospun fibers were detached carefully from the collector and subsequently dried for 24 h at room temperature to remove the solvent completely. Finally, the mechanical properties of a single electrospun fiber were measured using the Thermo Mechanical Analyzer (TMA, Seiko Exstar 6000, Seiko Inst., Japan) with a loading rate of 10 mN/min. A collector consisting of two parallel conductors and a rubber body was used to collect the aligned fibers. For testing, the fibers were affixed to a paper frame with a rectangle cut-out using double-sided tape.

Results and Discussion

During electrospinning, the pendant drop of the spinning dope undergoes two major electrostatic forces: electrostatic repulsion between the surface charges and the Coulombic force exerted by the external electric

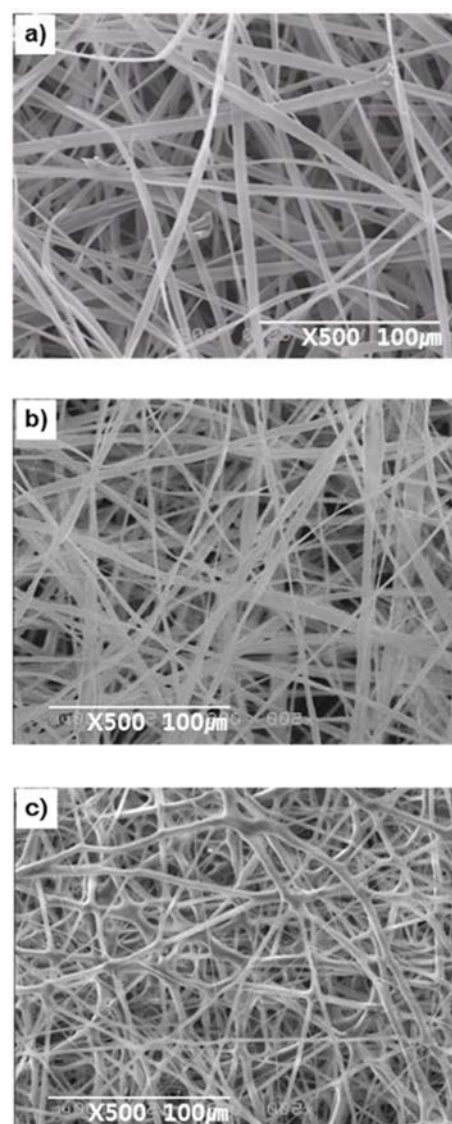


Fig. 2. Influence of solvent type on electro-spun cellulose fibers structure: a) acetone, b) acetone and MEK and c) acetone and benzyl alcohol (electro-spun at 10 kV).

field. Under the action of these electrostatic forces, the polymer dope is ejected from the tip in the shape of a Taylor cone [8, 9, 10]. Fig. 2 shows the morphologies of fibers prepared with different cosolvents. As can be seen, randomly oriented fibrous matrices were formed in all cases. Furthermore, all electrospun fibers had homogeneous, continuous fiber morphology, and no beads were formed. However, the properties of the cosolvent had a remarkable effect on the obtained electrospun fibers. For example, figs. 2a and 2b do not show cross-link fibers because acetone and methyl ethyl ketone have a low vapour pressure and boiling point. However, acetone, which has a relatively low vapour pressure, led to a smaller fiber diameter. Cross-linked fibers were obtained when both acetone and benzyl alcohol were used (fig. 2c). This is because mixing benzyl alcohol with acetone can retard acetone

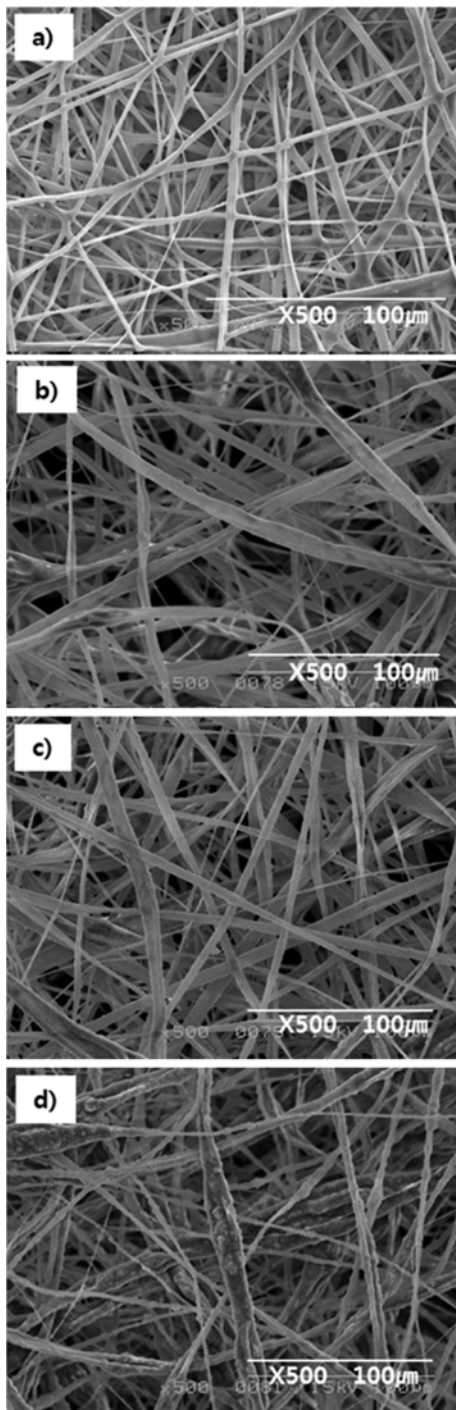


Fig. 3. SEM micrographs of electro-spun fiber with HAp filler: a) 5 vol% b) 10 vol% c) 20 vol% d) 40 vol% HAp filler.

evaporation, and thus the undried fiber struts were stacked on the surfaces of each other. The fibers were only dried after this cross-linking process. The three-dimensional pores formed between cross-linked fibers were distributed throughout the structure.

Fig. 3 shows the electrospun fibers with various amounts of HAp filler. All of the micrographs of the electrospun fibers with 5 to 20 vol.% HAp show cross-

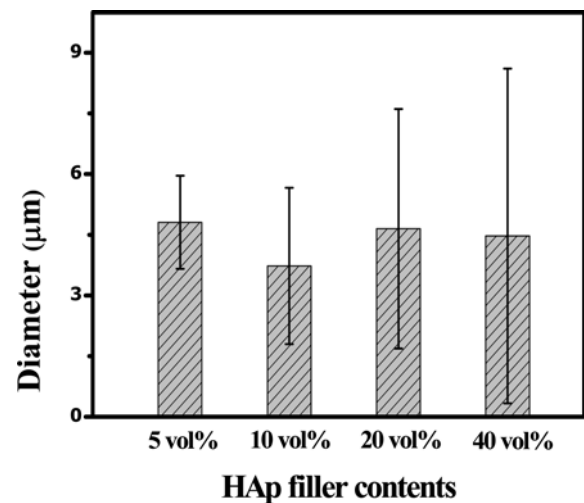


Fig. 4. Diameter graph of electro-spun fiber with HAp filler. a) 5 vol%, b) 10 vol%, c) 20 vol% and d) 40 vol% HAp filler.

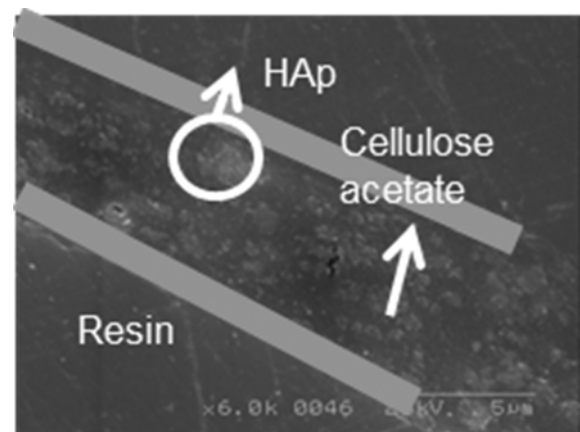
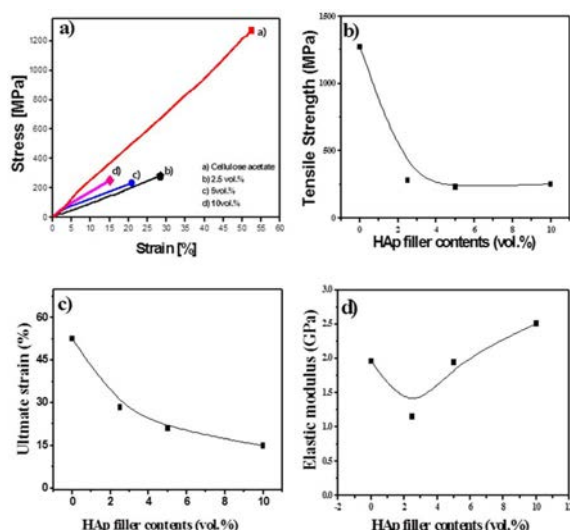


Fig. 5. SEM micrographs of a) top (5 vol.% HAp) and b) cross-section (20 vol.%) view of electro-spun fiber. (white regions; hydroxyapatite, dark regions; Cellulose acetate).

linked structures. However, at a HAp content of 40 vol.%, the cross-linked structure could not be preserved. Instead, fine fibers forming electrospun mats were observed for higher filler contents. In addition, the diameter distribution of the electrospun fibers increased as the filler content increased (Fig. 4). In other words, the electrospun fibers were less uniform for higher filler contents. In particular, at higher filler contents, the fibers tended to form many beads, and the average fiber diameter was also larger. These phenomena occur because the filler cannot be mixed within the polymer matrix at very high filler contents and agglomerates. This agglomerated filler increases the flux density during the electro deposition and hinders the elongation of the polymer. We originally assumed that when a small amount of HAp filler was added to the dope, the increased charge carried by the dope solution would increase the stretching of the fiber. However, electrospun fibers with high concentrations of filler nanoparticles sometimes exhibit bulges due to nanoparticle agglomerates

Table 1. The mechanical properties of electro-spun cellulose acetate fiber with HAp filler contents.

Filler content	Tensile strength (σ , MPa)	Ultimate strain (ϵ , %)	Elastic modulus (E, GPa)
0 vol.%	1272	52.5	1.96
2.5 vol.%	280	28.4	1.15
5 vol.%	231	21.0	1.94
10 vol.%	253	15.0	2.51

**Fig. 6.** Mechanical properties of electro-spun fiber with filler contents: a) stress-strain curve b) Tensile strength, c) ultimate strain and d) elastic modulus.

that are easily formed as a result of the strong interfacial attraction between nanoparticles. This behaviour is consistent with the results previously reported in the literature [11, 12].

Fig. 5 shows the cross-section of an electrospun fiber, where the HAp filler is homogeneously distributed in the cellulose acetate matrix. However, in some regions, the HAp aggregates, and some voids can be observed.

Tensile tests on electrospun fibers with HAp filler were performed to study the effect of the filler content. To minimize the variation in the mechanical properties of the composites, single fibers with areas in the range of about 160–300 mm² were tested. The results of the single fiber tensile test are summarized in Table 1.

The tensile strength of the pure cellulose acetate fiber was 5 times higher than that of the composite fibers with 2.5, 5, and 10 vol.% HAp. Furthermore, the ultimate strains of the composite fibers were lower than that of the cellulose acetate fiber. The composite fiber with 2.5, 5, and 10 vol.% HAp have the ultimate strains of 28.4%, 21.0%, and 15.0%, respectively. The cellulose acetate fibers without filler have the ultimate strains of 52.5%. The elastic moduli of the composite fibers increased significantly with increasing filler content. The composite fiber with 2.5, 5, and 10 vol.% HAp have the elastic moduli of 1.15, 1.94, and

2.51 GPa, respectively.

This is consistent with the generally observed trend in which the elastic modulus increases with increasing filler content because of the restriction of the polymer molecule mobility by the HAp filler. However, as shown in Fig. 6, the elastic moduli of the composites with 2.5 and 5 vol.% HAp filler were lower than those of the pure cellulose acetate fiber, in spite of the filler addition. This decrease in the elastic moduli of fibers with filler can be explained by the presence of inner voids and the adhesion between the filler and matrix in the fiber [12, 13, 14, 15].

A number of experiments on cancellous bone and cortical bone have demonstrated that the elastic modulus of human bone ranges from 0.05 to 30 GPa [16, 17, 18, 19, 20, 21]. Thus, the electrospun cellulose acetate containing HAp filler prepared in this study has relatively appropriate mechanical properties for use as a bone substitute, and the mechanical properties can be controlled by changing the filler content.

Conclusions

In this study, cellulose acetate fibers with various HAp filler contents were prepared by electrospinning, and their mechanical properties were investigated. The diameters and structures of the fibers were controlled by the solvent composition, and cross-linked fibers could be obtained by using acetone and benzyl alcohol as the solvent. However, the cross-linked structure could not be preserved at a hydroxyapatite content above 40 vol.%. The tensile test showed that the tensile strength and ultimate strain decrease with increasing HAp filler content, while elastic modulus increases. In conclusion, the results suggest that electrospun cellulose acetate containing HAp filler has potential for use as a bone substitute, and its mechanical properties can be controlled by changing the filler content.

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