Preparation of Hydroxyapatite/Poly(vinyl alcohol) Composite Fibers by Wet Spinning and Their Characterization

Yong Sik Chung,[1] Sung Il Kang,[1] Oh Wook Kwon,[2] Dong Soo Shin,[2] Se Geun Lee,[3] Eun Joo Shin,[3] Byung Gil Min,[4] Han Jo Bae,[2] Sung Soo Han,[2] Han Yong Jeon,[5] Seok Kyun Noh,[6] Won Seok Lyoo[2]

[1]Department of Textile Engineering, Chunbuk National University, Jeonju 561-756, Korea
[2]Division of Advanced Organic Materials, School of Textiles, Yeungnam University, Gyeongsan 712-749, Korea
[3]Polymer Gel Research Cluster Center, Yeungnam University, Gyeongsan 712-749, Korea
[4]Department of Textile and Fashion Engineering, School of Advanced Materials and System Engineering, Kumoh National Institute of Technology, Kumi 730-701, Korea
[5]Division of Nano-Systems Engineering, Inha University, Incheon 402-751, Korea
[6]School of Chemical Engineering and Technology, Yeungnam University, Gyeongsan 712-749, Korea

ABSTRACT: To prepare hydroxyapatite (HA)/poly(vinyl alcohol) (PVA) composite fibers with high processibility applicable to various biomedical fields, HA/PVA composite powders were synthesized through a coprecipitation method and then mixed with pure PVA in dimethyl sulfoxide at 90°C for 2 h to prepare wet-spinning dopes. HA/PVA solutions with HA contents of 0, 1, 3, 5, 10, and 15 wt % were analyzed with a rheometer to elucidate the effect of HA particles on the shear viscosities of the spinning dopes. The spinning dopes with pure PVA and an HA/PVA concentration of 12 wt % showed non-Newtonian flow behaviors, and as the HA content increased from 1 to 15 wt %, the shear viscosities increased simultaneously because of the complex formation between PVA chains, citric acid, and HA particles acting as crosslinkers. The increased viscosities of the spinning dopes diminished the breakage of PVA fibers and enhanced the spinnability. Through the addition of citric acid interacting with both PVA and HA particles, the aggregation of HA particles was suppressed, and it was possible to prepare HA/PVA composite fibers with smooth surfaces. An adequate amount of HA in the PVA fibers improved the thermal and mechanical properties of the fibers because uniformly dispersed HA particles interacting with PVA chains through hydrogen bonding in the PVA matrix complemented the structural defects. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3423–3429, 2007

Key words: HA/PVA; composites; fibers

INTRODUCTION

Poly(vinyl alcohol) (PVA) fibers are employed profitably as high-performance substances and are the best replacement materials for natural, carcinogenic asbestos fibers and iron rods in ferroconcrete because they have high tensile and impact strengths, high tensile moduli, high abrasion resistance, excellent alkali resistance, oxygen barrier properties, and good binding properties.[1–3] Recently, PVA gels and films have attracted great attention for various applications because of their easy preparation, excellent chemical resistance and physical properties, biocompatibility, and low price. Furthermore, the high water content and elastic properties make PVA gels advantageous for many biological applications, including wound dressings, bioreactors, controlled release matrices, and bioadhesives.[4–7]

Hydroxyapatite [HA; $Ca_{10}(PO_4)_6(OH)_2$], partially ionically substituted HA, and their composites have attracted much attention as materials suitable for repairing and substituting for hard tissues, and their clinical applications are gradually expanding because of their excellent biocompatibility and overall safety and the fact that they have a chemical structure similar to that of the mineral found in hard tissues of the body.[8–11] An ideal prosthetic material must fulfill such basic requirements as biocompatibility with bone tissue, sufficient initial strength, strength retention over an adequate period of time, and nontoxicity of degradation byproducts.

PVA has been used extensively in the treatment of defects in load-bearing joints such as cartilage because of the similarity of its tensile strength to that of human articular cartilage and its good lubrication.[12–15]

There have been several studies on the preparation of polymer/HA composite films using a soaking pro-

cess[16–18] and a casting process with polymeric solutions containing HA.[19] However, HA particles are readily aggregated and have poor dispersibility in polymeric matrices. Moreover, most inorganic materials are available as powders and granules; macroscopic morphology control is desirable and allows for easier processing and handling of the materials.

There have been some reports on the formation of inorganic–organic hybrid fibers with HA. Granqvist et al.[20] prepared biodegradable and bioactive hybrid organic–inorganic poly(ethylene oxide)/siloxane fibers using a sol–gel transition method. Ito et al.[21] immersed electrospun biodegradable nanofibers in an inorganic suspension to prepare mats with enhanced cell adhesion. However, there have been few results reported on the spinning of polymeric solutions mixed with HA nanoparticles.

Thus, in this study, to prepare HA/PVA composite powders, HA was synthesized in PVA solutions and coprecipitated with PVA. Then, HA/PVA spinning dopes with various HA contents were prepared and analyzed with a rheometer to elucidate the effects of HA/PVA complexes on the shear viscosities. The HA/PVA composite fibers prepared by wet spinning were characterized with various instrumental techniques.

EXPERIMENTAL

Materials

Calcium hydroxide [$Ca(OH)_2$; Showa Chemical Co., Ltd., Tokyo, Japan] and phosphoric acid (H_3PO_4; Samchun Pure Chemical Co., Ltd., Seoul, Korea) were used as received. PVA with a number-average degree of polymerization of 1700 and a degree of saponification of 99.3% was purchased from Unitika Co., Ltd.
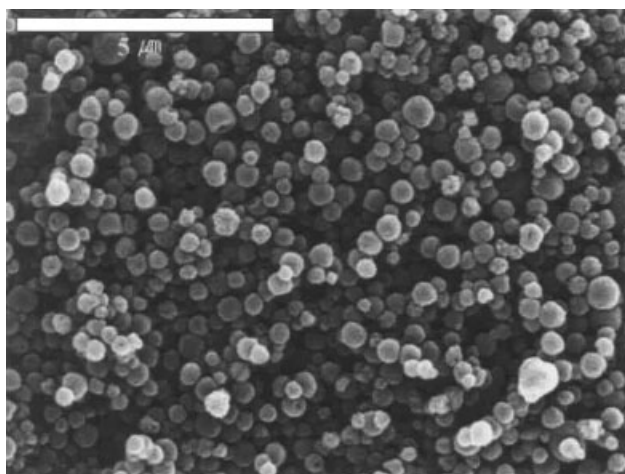

Figure 1 SEM image of pure HA particles prepared through the dissolution of HA/PVA with a weight ratio of 50 : 50 in hot water at 100°C, washing, and freeze drying.
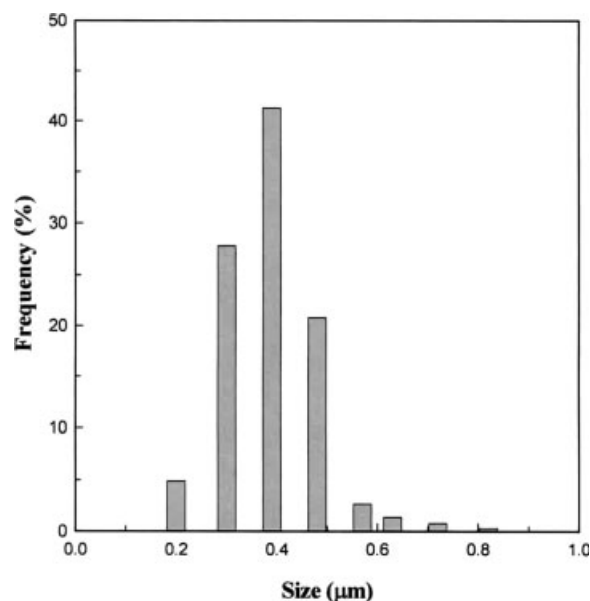

Figure 2 Particle size distributions of pure HA particles prepared through the dissolution of HA/PVA with a weight ratio of 50 : 50 in hot water at 100°C, washing, and freeze drying.

(Osaka, Japan). Citric acid (Showa Chemical) was used as an aggregation-preventing agent for HA particles. Other extrapure-grade reagents were used without further purification, and distilled water was used.

Preparation of the HA/PVA powder and HA powder

$Ca(OH)_2$ (8.2 g) was completely dissolved in 1 L of a 10 wt % PVA aqueous solution at 60°C with a mechanical stirrer to yield a concentration of 0.5M. A solution of H_3PO_4 with a concentration of 0.3M was added to the $Ca(OH)_2$/PVA solution dropwise at a speed of 3.2 mL/min at 60°C, and the pH of the system was maintained at 9.1 ± 0.5 with an ammonium solution. To prepare HA/PVA with a weight ratio of 50:50, the overall weight of $Ca(OH)_2$ and H_3PO_4 was fixed to that of PVA. After the reaction mixture was aged for 24 h at 30°C under stirring, it was poured into methanol. The obtained HA/PVA composite was washed with methanol several times and then freeze-dried. To obtain the homo-HA powder, the prepared HA/PVA with a weight ratio of 50 : 50 was dissolved in hot water at 100°C, washed with hot water several times, and then freeze-dried. Figures 1 and 2 present scanning electron microscopy (SEM; JSM-6300, JEOL, Tokyo, Japan) images and particle size distributions of pure HA prepared by the method described previously, respectively.

Preparation of the HA/PVA composite fibers

The PVA/HA/dimethyl sulfoxide (DMSO) spinning dopes were prepared at 90°C for 2 h through the mix-
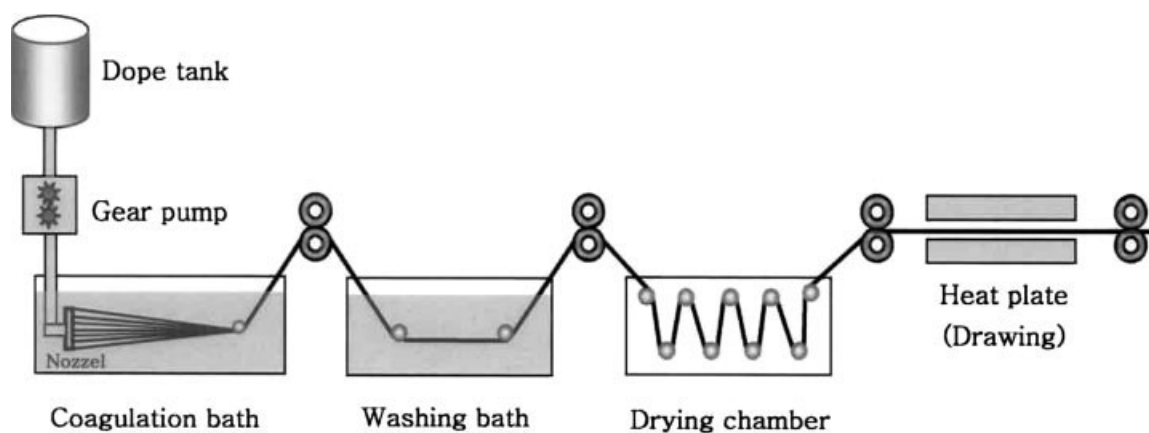
Figure 3 Schematic diagram of the wet-spinning procedure.

ing of PVA and HA/PVA composite powders. The total concentration of PVA and HA was 12 wt %, and the weight ratios of HA to PVA were 0/100, 1/99, 3/97, 5/95, 10/90, and 15/85. To suppress the aggregation of HA particles, 5 wt % citric acid with respect to the weight of HA was added to the spinning dopes and then filtered, and the bubbles were removed. Wet spinning was performed by the extrusion of the dopes from a nozzle with 200 holes, of which the diameter was 0.1 mm and the length/diameter ratio was 2. The dopes were extruded in methanol and then washed, dried, and drawn, and their draw ratios were 2, 4, and 6, respectively. The obtained fibers were immersed in methanol for 1 day to remove DMSO thoroughly and dried. The overall procedure for the spinning of the HA/PVA composite fibers is shown in Figure 3.

Characterizations of the HA/PVA fibers

To evaluate HA/PVA composite formation in the fibers, they were analyzed with Fourier transform infrared (FTIR) spectroscopy (FTS, Bio-Rad Co., Ltd., Cambridge, MA). The thermal characteristics of the HA/PVA composite fibers were analyzed with a TA Instruments (New Castle, DE) model 2050 and differential scanning calorimetry (DSC) under an atmosphere of flowing nitrogen gas at a heating rate of 20°C/min from 30 to 800°C for thermogravimetric analysis and at a heating rate of 10°C/min from 20 to 250°C for DSC, respectively. HA/PVA fibers with different amounts of HA were observed with SEM (JSM-6300, JEOL) to investigate the surface morphology of the HA/PVA composite fibers. Load–elongation curves were recorded on a tensile strength meter (TSM-02, Search Co., Ltd., Tokyo, Japan) with a sample length of 25 mm and a crosshead speed of 20 mm/min to determine the tenacities and elongations at break of the wet-spun HA/PVA composite fibers.

RESULTS AND DISCUSSION

Rheological characteristics of the HA/PVA spinning dopes

Polymeric solutions are inevitably deformed because of viscoelastic properties originating from their huge molecular size, which makes it difficult to analyze the spinning process. Furthermore, the final properties of a product are affected not only by the inherent chemical structure but also by physical properties such as the crystallinity and degree of orientation determined during the spinning process. Thus, before spinning, it is very important to understand the rheological properties of polymeric materials for the improvement of the final products through the optimization of the spinning process. Figure 4 shows the shear viscosities
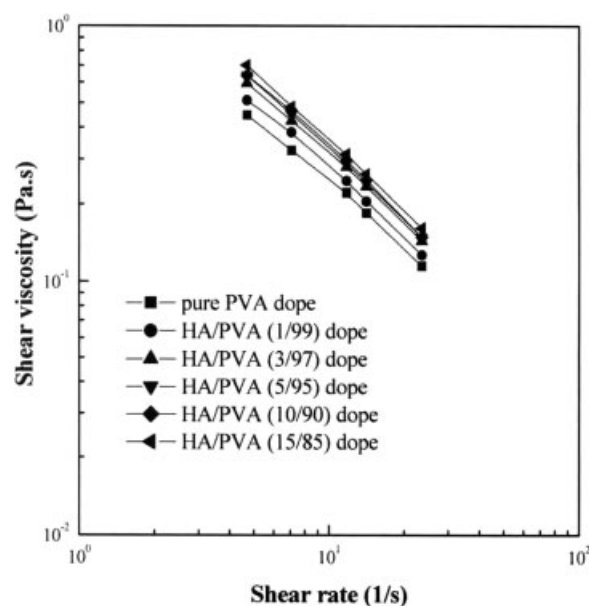

Figure 4 Shear viscosities of pure PVA and HA/PVA (10/90) spinning dopes as a function of the shear rate.

of HA/PVA spinning dopes with different HA contents according to the shear rates. Pure PVA and HA/PVA composite solutions showed typical non-Newtonian flow behavior, and at the same shear rate, the shear viscosities increased with increasing HA contents.

In this study, citric acid was added to PVA/HA suspensions after the formation of the composites. Citric acid has the highest salting-out effect of the so-called Hofmeister series. The multivalent ion may absorb by physicochemical interactions and change the surface potential of the particles. Additionally, the ion competes with the colloid for the hydration water, dehydrating the lyophilic particles.[22–24] Therefore, citric acid is able to lower surface-charged layers or shorten the distance between charged particles by adsorbing oppositely charged ions and/or eliminating surface hydration water. Thus, a small amount of citric acid was added to the PVA/HA suspensions after the formation of the composites. PVA has good linearity because most branches are cut during saponification. The number of complexes of PVA chains, citric acid, and HA particles, however, increased with increasing HA contents, and these acted as branches and crosslinkers. Thus, the viscosities of the HA/PVA spinning dopes increased with increasing HA contents. HA/PVA complexes in spinning dopes with citric acid formed a similar structure with a branched polymer, which increased the resistance against the drawing tension when PVA chains were oriented by the tension loaded during the spinning process. This tension-stiffening phenomenon had the advantage of diminishing a local stress concentration effect arising from an unstable drawing flow. Thus, it is possible to prepare uniform fibers without breakage of the fibers during the spinning process. In this study, HA/PVA fibers with higher HA concentrations were less bro-
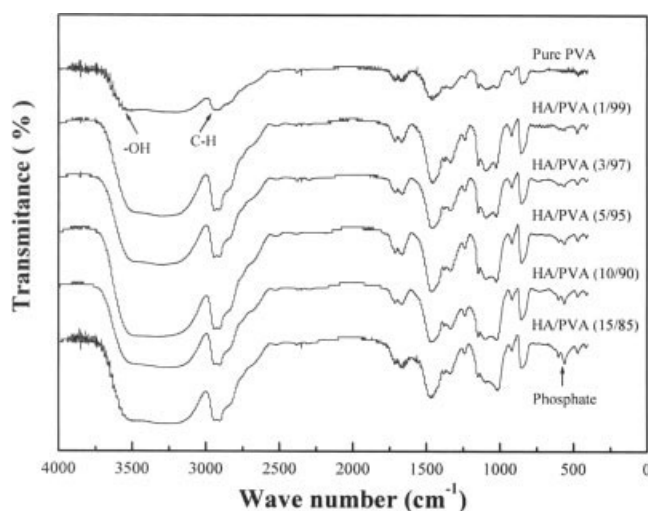

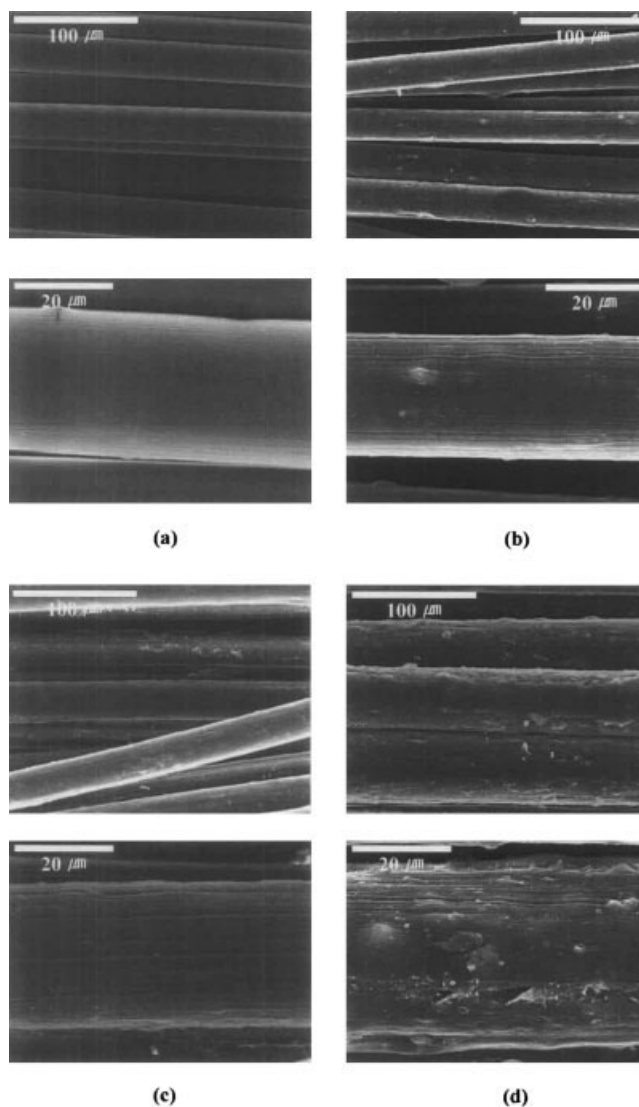**Figure 5** FTIR spectra of pure PVA and HA/PVA composite fibers with various HA contents.

Figure 6 SEM images of pure PVA and HA/PVA composite fibers with various HA contents in the absence of citric acid. The HA concentrations were (a) 0, (b) 5, (c) 10, and (d) 15 wt %.

ken by drawing tension in the coagulation bath than those with lower HA concentrations and pure PVA.

Characteristics of the HA/PVA composite fibers

The FTIR spectra of pure PVA and HA/PVA composite fibers prepared by wet spinning are shown in Figure 5. The HA/PVA fibers exhibited typical peaks of the phosphate bands in HA (1100–1032, 565, and 632 cm^{-1})[25] and —OH bands at 3571 cm^{-1}. It was confirmed that because of —OH groups both in PVA and in HA, the intensity of the band at 3200–3500 cm^{-1} corresponding to the hydrogen bond was significantly increased.

The surface morphologies of composite fibers with various HA contents are shown in Figure 6. The
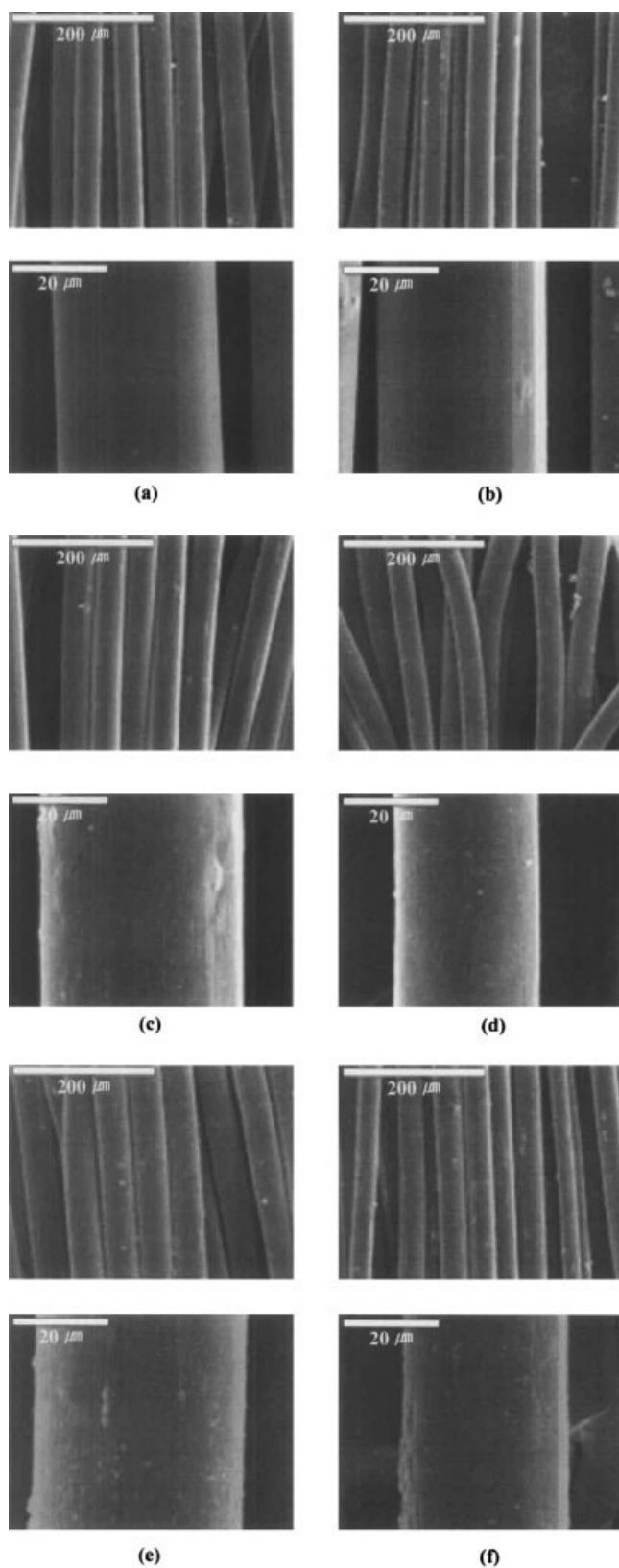
Figure 7 SEM images of pure PVA and HA/PVA composite fibers with various HA contents in the presence of citric acid. The HA concentrations were (a) 0, (b) 1, (c) 3, (d) 5, (e) 10, and (f) 15 wt %.

higher the contents were of HA, the rougher the surfaces were of the fibers and the more severe the aggregation was of the HA particles. However, composite fibers that were wet-spun with dopes with citric acid had few HA particle aggregates and rather smooth surfaces in comparison with fibers with no citric acid addition, as shown in Figure 7. There was such a strong coagulation tendency of HA particles by hydrogen bonds that it was difficult to separate the HA particles once they aggregated. In this study, HA was synthesized in a 10 wt % PVA solution, in which the growth of the HA particles could proceed more slowly because of the decreased mobility of the reactants and the aggregation was suppressed by PVA. Chung et al.[26] reported that the role of citric acid in an HA/chitosan solution was to prevent the aggregation of HA particles, and transparent HA/chitosan films were obtained at a citric acid concentration over 50% with respect to HA. Citric acid, having one hydroxyl group and three carboxylic groups, is ionized in HA/PVA composite aqueous solutions. Hydroxyl groups of citrate ions can interact with those of PVA through a hydrogen bond, and carboxyl groups can interact with Ca^{2+} on the surface of HA particles through an ionic bond. Thus, PVA chains, bridged through citrates to the surface of HA particles, are capable of preventing the aggregation of HA particles.[27–29]

There were no aggregates of HA particles in the cross sections of composite fibers with HA contents of 1–5 wt %, as shown in Figure 7. However, some aggregated HA particles were observed at 10 and 15 wt %. The cross sections of most fibers had a circular contour, but the fiber with 15 wt % HA had voids and a somewhat loose structure because of the hindered orientation of PVA chains and crystallization due to the complex formation.
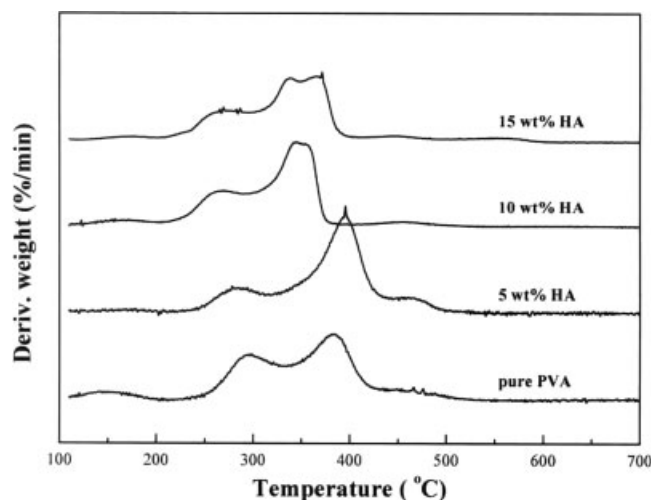

Figure 8 DTG thermograms of HA/PVA composite fibers.

Two thermal degradation peaks were observed, as shown in Figure 8. The former corresponded to that of soft segments like the chain ends of PVA or an amorphous region, and the latter corresponded to that of a dense crystalline region, respectively. The thermal degradation starting temperatures of the soft segments at 10 and 15 wt % were reduced in comparison with those of pure PVA. This was because an excess addition of HA caused the aggregation of HA particles and suppressed the crystallization. At lower HA contents, the thermal degradation starting temperature of the soft segments was almost the same, whereas that of the hard segments increased, and the peak became sharp, reflecting an increased degradation heat that might correspond to 1 and 5 wt % concentrations of HA. On the basis of these results, it was concluded that an adequate addition of HA particles to PVA filled the voids in the matrix and was helpful in making denser fibers because of increased intermolecular hydrogen bonding. DSC thermograms of pure PVA and HA/PVA composite fibers are shown in Figure 9. The crystal melting temperatures and heats of fusion were not significantly different. The glass-transition temperatures, however, largely increased at 5 wt % and then decreased at 15 wt %. These results corresponded to those of differential thermogravimetry (DTG).

The tenacities and elongations at break are presented in Figure 10. The tenacities of fibers increased with HA concentrations of 1–5 wt % and decreased with HA concentrations of 10 and 15 wt %. As for the elongations at break, they decreased significantly with HA concentrations greater than 3 wt %. As mentioned previously, these were affected by the balances between factors encouraging a denser structure of the composite and suppressing the crystallization of polymer chains by the addition of inorganic particles.
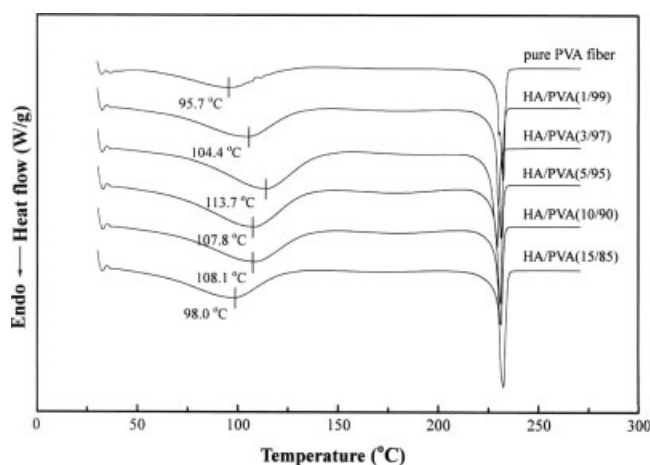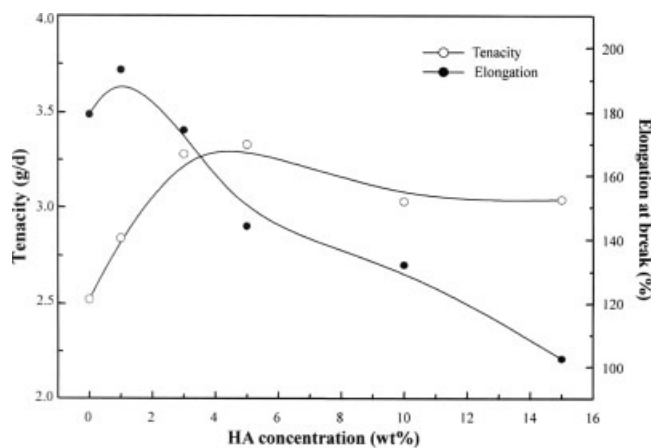

Figure 10 Effects of the HA contents on the tenacity and elongation at break of HA/PVA composite fibers.

When tension was loaded to a HA/PVA composite fiber, the PVA chains were under the tension, but the solid crystalline HA particles were not. The HA particles, acting as crosslinkers, depressed the elongations more significantly. For these reasons, the real elongation of some PVA chains became larger than the overall elongations of the composite fibers when tension was loaded; thus, it was concluded that the elongations at break decreased with increasing HA contents.

CONCLUSIONS

HA/PVA composite powders were synthesized through a coprecipitation method to prepare resins with finely dispersed HA particles. The HA/PVA composite powders were mixed with pure PVA in DMSO at 90°C for 2 h to prepare wet-spinning dopes. The spinning dopes with PVA and an HA/PVA concentration of 12 wt % showed non-Newtonian flow behaviors, and as the HA content increased from 1 to 15 wt %, the shear viscosities increased simultaneously because of the formation of complexes of PVA chains, citric acid, and HA particles acting as crosslinkers. The increased viscosities of the spinning dopes diminished the breakage of the PVA fibers and enhanced the spinnability. With the addition of citric acid, the aggregation of HA particles was suppressed, and it was possible to prepare HA/PVA composite fibers with smooth surfaces. An adequate amount of HA in the PVA fibers improved the thermal and mechanical properties of the fibers because uniformly dispersed HA particles interacting with PVA chains through hydrogen bonding in the PVA matrix complemented the structural defects. The HA/PVA composite fibers in this study are promising materials for various PVA applications. In the near future, we will report on the preparation of stereoregular PVA/HA composite fibers.

Figure 9 DSC thermograms of HA/PVA composite fibers.

References

1. Lyoo, W. S.; Ha, W. S. Polymer 1996, 37, 3121.
2. Masuda, M. In Polyvinyl Alcohol—Developments; Finch, C. A., Ed.; Wiley: New York, 1991; p 403.
3. Lyoo, W. S.; Kim, B. C.; Ha, W. S. Polym Eng Sci 1997, 37, 1259.
4. Lyoo, W. S.; Ha, W. S. Polymer 1999, 40, 497.
5. Cho, J. D.; Lyoo, W. S.; Chvalun, S. N.; Blackwell, J. Macromolecules 1999, 32, 6236.
6. Lyoo, W. S.; Kim, B. C.; Ha, W. S. Polym J 1997, 30, 424.
7. Choi, J. D.; Lyoo, W. S.; Ko, S. W. Macromol Chem Phys 1999, 200, 1421.
8. Rehman, I.; Bonfield, W. J Mater Sci: Mater Med 1997, 8, 1.
9. Dalby, M. J.; Di Silvio, L.; Gurav, N.; Annaz, B.; Kayser, M. V.; Bonfield, W. Tissue Eng 2002, 8, 453.
10. Dalby, M. J.; Di Silvio, L.; Harper, E. J.; Bonfield, W. Biomaterials 2002, 23, 569.
11. Doi, Y.; Shibutani, T.; Moriwaki, T.; Kajimoto, T.; Iwayama, Y. J Biomed Mater Res 1998, 39, 603.
12. Chang, Y. S.; Gu, H. O.; Kobayashi, M.; Oka, M. Knee 1998, 5, 205.
13. Oka, M.; Ushio, K.; Kumar, P.; Ikeuchi, K.; Nakamura, T.; Fujita, H. J Eng Med 2000, 214, 59.
14. Bryant, S. J.; Nettelman, C. R.; Anseth, K. S. Biomed Sci Instrum 1999, 35, 309.
15. Chua, C. K.; Leong, K. F.; Tan, K. H.; Wiria, F. E.; Cheah, C. M. J Mater Sci: Mater Med 2004, 15, 1113.
16. Kato, K.; Eika, Y.; Ikada, Y. J Biomed Mater Res 1996, 32, 687.
17. Serizawa, T.; Kawanishi, N.; Akashi, M. J Biomater Sci Polym Ed 2001, 12, 1293.
18. Serizawa, T.; Tateishi, T.; Akashi, M. J Biomater Sci Polym Ed 2003, 14, 653.
19. Kobayashi, H.; Kato, M.; Taguchi, T.; Ikoma, T.; Miyashita, H.; Shimmura, S.; Tsubota, K.; Tanaka, J. Mater Sci Eng C 2004, 24, 729.
20. Granqvist, B.; Helmnen, A.; Vehvilainen, M.; Aaritalo, V.; Seppala, J.; Linden, M. Colloid Polym Sci 2004, 282, 495.
21. Ito, Y.; Hasuda, H.; Kamitakahara, M.; Ohtsuki, C.; Tanihara, M.; Kang, I. K.; Kwon, O. H. J Biosci Bioeng 2005, 100, 43.
22. Rosenholm, J. B.; Nylund, J.; Stenlund, B. Colloids Surf A 1999, 159, 209.
23. Cacace, M. G.; Landau, E. M.; Ramsden, J. J. Rev Biophys 1997, 30, 241.
24. Nakano, T.; Uasa, Y. H.; Kanaya, Y. Pharm Res 1999, 16, 1616.
25. Ogomi, D.; Serizawa, T.; Akashi, M. J Biomed Mater Res A 2003, 67, 1360.
26. Chung, Y. S.; Choi, C. Y.; Lee, K. W.; Choa, Y. H.; Pak, P. K. J Korean Fiber Soc 2002, 39, 383.
27. Rhee, S. H.; Tanaka, J. Biomaterials 1999, 20, 2155.
28. Brecevic, L.; Milhofer, H. F. Calcif Tissue Int 1979, 28, 131.
29. Anabel, L. M.; Jaime, G. M.; Rafael, R. C. J Colloid Interface Sci 1998, 200, 114.