Preparation of Hydroxyapatite/Poly(vinyl alcohol) Composite Film with Uniformly Dispersed Hydroxyapatite Particles Using Citric Acid

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ABSTRACT: Biocompatible hydroxyapatite (HA)/poly-(vinyl alcohol) (PVA) composites and their transparent films were prepared by the coprecipitation and solvent casting method. The formation of HA in PVA composite powder was confirmed by the characteristic phosphate bands at 1100–1032 and 565 cm^{-1} at FT-IR spectra, and the weight ratio of HA to PVA was 50/50 examined by TGA. The crystal melting temperature of HA/PVA decreased compared with that of pure PVA. HA/PVA (50/50) composite powder and pure PVA were dissolved in dimethyl sulfoxide to obtain a film with HA/PVA weight ratio of 10/90. To improve HA particles' dispersity, which is one of the major factors affecting the mechanical properties of composite materials, various contents of citric acid were used for the preparation of HA/PVA films. At a citric acid concentration of 5 wt %, HA/PVA film with good dispersity of HA particles was obtained. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3240–3244, 2007

Key words: hydroxyapatite/poly(vinyl alcohol); composite films; citric acid; dispersity

INTRODUCTION

Because of its excellent biocompatibility and overall safety, and chemical structure similarity with the mineral found in hard tissues of the body, hydroxyapatite (HA; $Ca_{10}(PO_4)_6(OH)_2$), partially ionic 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.[1–4] 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 by-products.

Rigid glass and ceramic materials, however, cannot be utilized for the replacement of ligament, tendon, intercerebral disc, and periodontium even if bioactive, because they basically have should a flexibility and elasticity that rigid glass and ceramic cannot provide. Therefore, attempts have been made to render the bone-bonding ability to flexible, tough polymeric substrates, in which various polymers such as copoly(ether-imide),[5] polyethylene,[6] gelatin,[7] poly(α-hydroxyl acid),[8,9] poly (vinyl phosphonate),[10] poly(vinyl acetate),[11] and poly (vinyl alcohol) (PVA)[12–14] have been used.

PVA is obtained by the saponification of a poly(vinyl ester), such as poly(vinyl acetate) or poly(vinyl pivalate). PVA fibers and films have high tensile and compressive strengths, a high tensile modulus, and good abrasion resistance owing to the large crystalline lattice modulus.[15–21] PVA has been used extensively in the treatment of defects in load-bearing joints such as cartilages because of its relatively similar tensile strength to human articular cartilage and its good lubrication.[22–24] In addition, the ability of PVA to form complexes having suitable adhesion makes it one of the ideal materials to treat complex craniofacial defects.[25]

There have been several studies on the preparation of polymer/HA composite films using a soaking process[11,26–28] and a casting process of polymeric solution containing HA.[29] However, HA particle is readily aggregated and has a poor dispersibility in polymeric matrix.

In this study, to improve the dispersibility of HA particle, HA was synthesized in PVA solution and the resulting HA/PVA composite powder was blended with homo-PVA in water and then casted to prepare film. The phases in the composite matrix, thermal degradation, and crystal melting temperature of HA/PVA powder were characterized. Finally, the effect of the concentration of citric acid interacting with the surface of HA particles on the dispersity of HA particle in PVA matrix was investigated.

EXPERIMENTAL

Materials

Calcium hydroxide ($Ca(OH)_2$, Showa Chemical Co. Ltd., Japan) and phosphoric acid (H_3PO_4, Samchun Pure Chemical Co. Ltd., Korea) were used as-received. PVA with degree of polymerization of 1700 and degree of saponification of 99.3% was purchased from Unitika Co. Ltd. (Japan). Citric acid (Showa) was used as an aggregation-preventing agent for HA particles. Other extrapure-grade reagents were used without further purification and distilled water used.

Preparation of HA/PVA powder

In 1 L of 10 wt % PVA aqueous solution 8.2 g of $Ca(OH)_2$ was completely dissolved at 60°C using a mechanical stirrer to yield a concentration of 0.5M. H_3PO_4 solution with concentration of 0.3M was added into the $Ca(OH)_2$/PVA solution dropwise at the speed of 3.2 mL/min at 60°C and the pH of the system was maintained at 9.1 ± 0.5 by using ammonium solution. To prepare HA/PVA with same weight of 50:50, 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. Obtained HA/PVA composite was washed with methanol several times and then freeze-dried.

Preparation of HA/PVA composite film

HA/PVA powder and pure PVA was dissolved in dimethyl sulfoxide at 90°C for 2 h. The concentration of PVA was 10 wt % and the weight ratio of HA to PVA was 0.1. To suppress the aggregation of HA particle, citric acid with various weight ratios to HA as 0.05, 0.1, 0.15, 0.3, 0.5, and 1 was added to the blend solution. Same amount of HA/PVA solutions with different citric acid concentrations were spread in a Petri dish and then immersed in methanol sufficiently to extract remaining water and solidified. HA/PVA (10/90) films with different amounts of citric acid were obtained.

### Characterizations of HA/PVA composite powder and films

To evaluate HA/PVA composite formation, we used Fourier transform infrared spectroscope (FT-IR, FTS, Bio-rad Co. Ltd). Thermal degradation behavior of HA/PVA composite powder compared with pure PVA powder, the content of HA, and crystal melting temperature (T_m), and heat fusion were determined using a differential scanning calorimeter (DSC, TA Instrument 2050, Dupont, USA). HA/PVA films with different amounts of citric acid were observed by optical microscope (icamscope, Sometech Vision Co. Ltd., Korea) and by scanning electron microscope (SEM, JSM-6300, JEOL) to check the dispersity of HA particle and to observe the surface morphology of HA/PVA composite films.

RESULTS AND DISCUSSION

Properties of HA/PVA composite powder

The HA/PVA (50/50) composite powder was prepared in aqueous PVA solution. The FT-IR spectra of pure PVA and HA/PVA composite powder are shown in Figure 1. HA/PVA powder exhibits typical peaks of the phosphate bands in the HA (1100–1032 and 565 cm^{-1})[30] and —OH bands at 3571 and 632 cm^{-1}. It was confirmed that owing to the —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.

Thermal degradation behaviors of HA/PVA and pure PVA are shown in Figure 2. Initial degradation temperatures of PVA and HA/PVA were identical to 250°C. However, PVAs in both pure and composite form were completely decomposed over 600°C and the amount of the relict for HA/PVA composite powder,
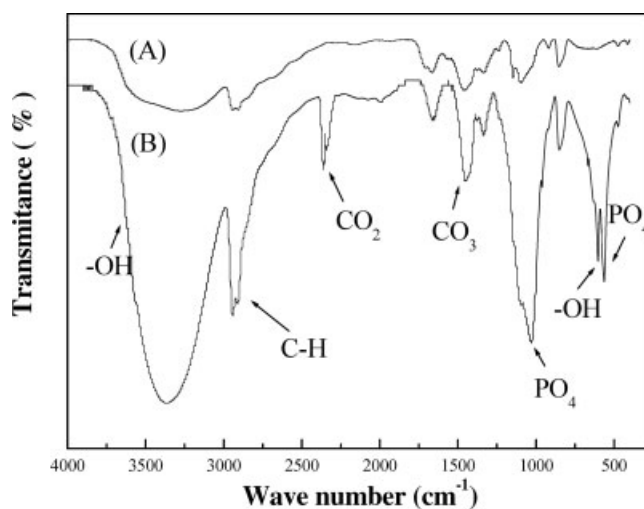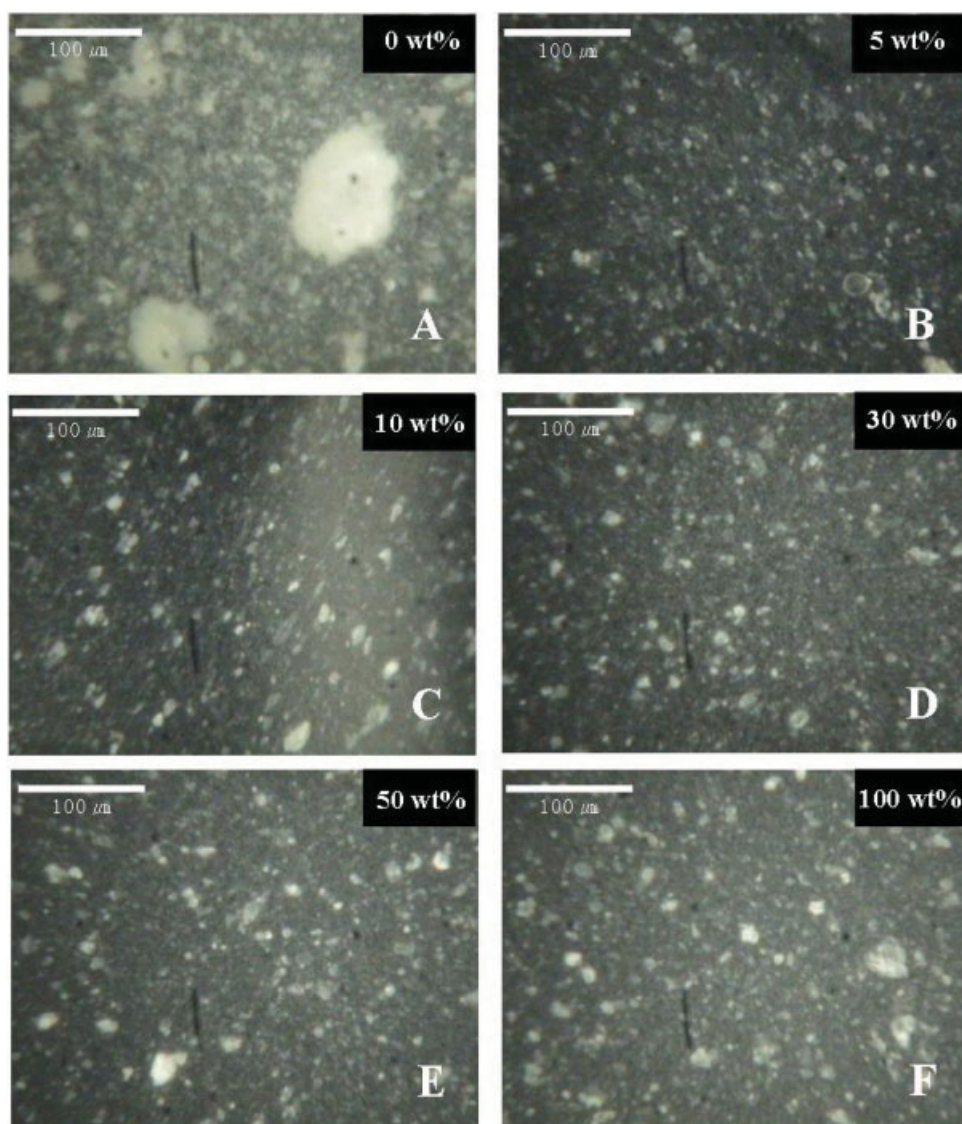

Figure 1 FT-IR spectrum of pure PVA powder (A) and HA/PVA (50/50) composite powder (B).
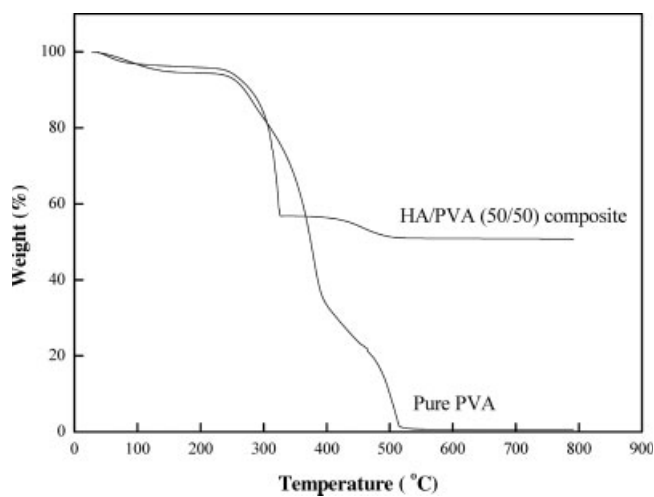
Figure 2 TGA curves of pure PVA powder and HA/PVA (50/50) hybrid composites.
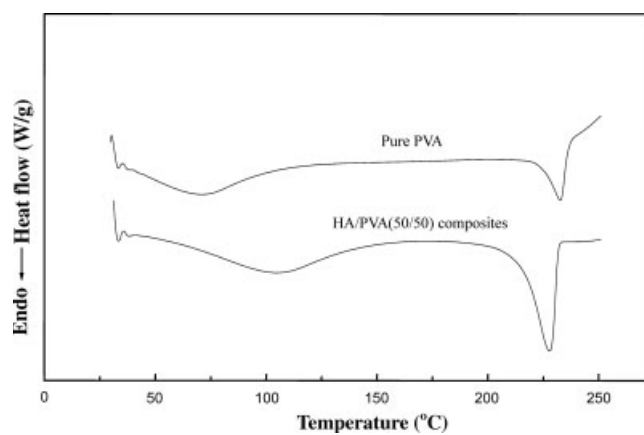
Figure 3 DSC curves of pure PVA powder and HA/PVA (50/50) hybrid composites.

Figure 4 Optical microscopic images of HA/PVA (10/90) film with citric acid contents.

which should be HA, was about 50% identical to the weight ratio in the composite. Figure 3 shows DSC thermogram of pure PVA and HA/PVA composite powder. The crystal melting temperature of HA/PVA decreased when compared with that of pure PVA.

### Effects of citric acid concentration on the dispersity of HA particles

One of the main factors in the preparation of inorganic/organic composite is to suppress aggregation between inorganic particles and to disperse them uniformly in the organic matrix because the amount of inorganic particles and the dispersity deeply affect the mechanical properties of the composite.

There is a so strong coagulation tendency of HA particles due to hydrogen bond and so it is difficult to separate HA particles once aggregated. In this study, HA was synthesized in 10 wt % PVA solution in which the growth of HA particles might proceed more slowly due to decreased mobility of reactants and the aggregation would be suppressed by PVA.

Chung et al. reported that the role of citric acid in HA/chitosan solution was to prevent the aggregation of HA particles and transparent HA/chitosan films were obtained at the citric acid content to HA over 50%.[31] Citric acid having one hydroxyl group and three carboxylic groups is ionized in HA/PVA composite aqueous solution. Hydroxyl group of citrate ion can interact with that of PVA through a hydrogen bond and carboxyl groups with Ca^{2+} on the surface of HA particles through a ionic bond. Thus, PVA chains bridged through citrates to the surface of HA particles are capable of preventing the aggregations of HA particles.[32–34]

Figures 4 and 5 are the optical and SEM images of HA/PVA (10/90) films with different citric acid weight percentages to the HA of 0, 5, 10, 30, 50, 100
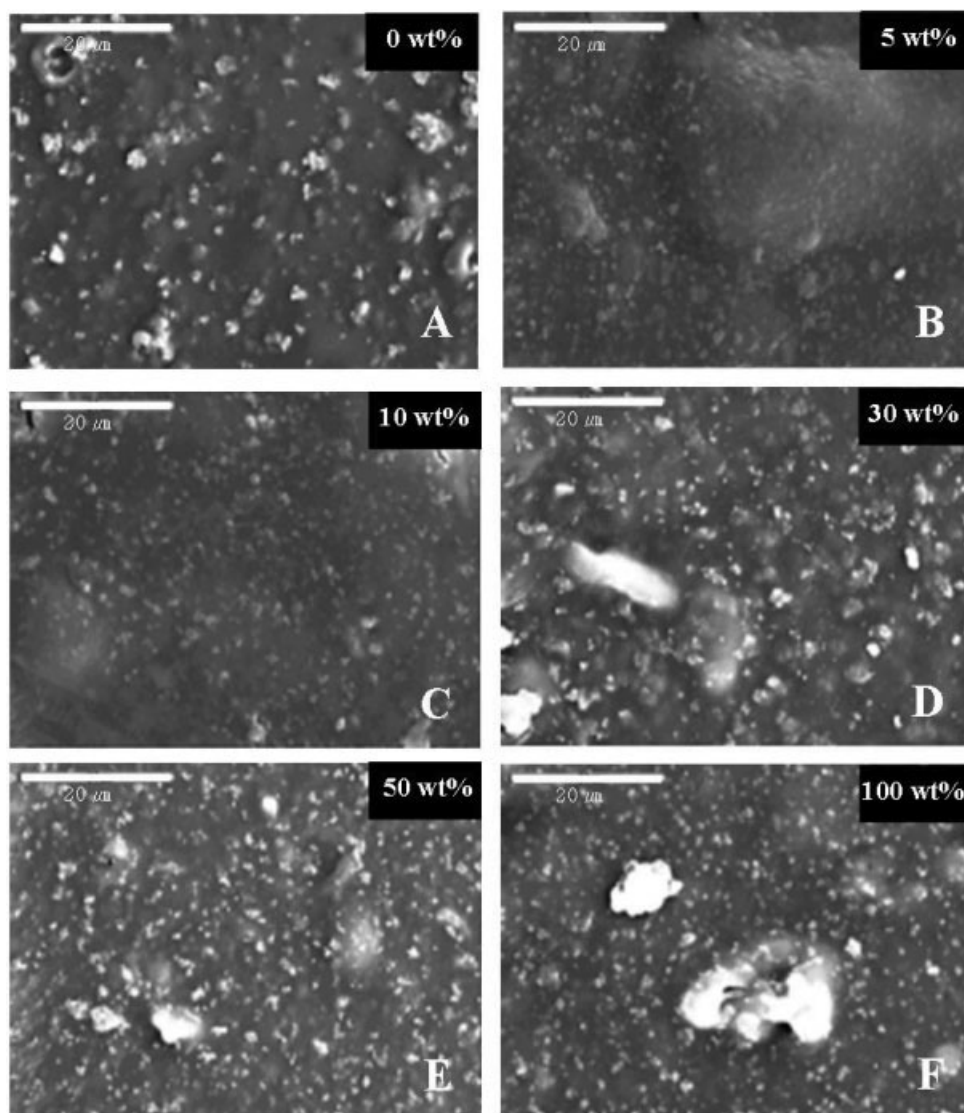
Figure 5 SEM images of HA/PVA (10/90) film with citric acid contents (×2000).

wt %. HA particles were significantly aggregated in film without citric acid. As shown in Figures 4(B) and 5(B), HA/PVA film with a uniform dispersity was obtained at 5 wt % citric acid content. With increasing content of citric acid, the aggregation became slightly frequent, because a large amount of citric acid might give more chances to HA particles to encounter each other. From these results, it was concluded that there was an optimum concentration of citric acid, and in this study, it is 5 wt % for the effective preparation of HA/PVA film with uniformly dispersed HA particles.

CONCLUSIONS

HA/PVA composite powder with weight ratio of 50/50 was successfully prepared through the coprecipitation method and an interaction between PVA and the surface of HA particles was examined by FT-IR. Thermal analysis reflected that the composite had weight ratio of HA/PVA of 50/50 and lower T_m than pure PVA. HA/PVA (50/50) composite powder and pure PVA were dissolved in dimethyl sulfoxide for a film with HA/PVA weight ratio of 10/90. To improve HA particles' dispersity which is one of the major factors affecting the mechanical properties of composite materials, various contents of citric acid were used for the preparation of HA/PVA films. At citric acid concentration of 5 wt %, HA/PVA film with good dispersity of HA particles was obtained. This HA/PVA (50/50) composite powder would be expected to be useful for the improvement of processibility of hybrid composite system. In the near future, we will report on the preparation of HA/ high molecular weight and high stereoregular PVA composite film.

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