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Short communication

An in situ hydrothermal fabrication process of poly (vinyl alcohol)/apatite-like nanocomposites with improved thermal and mechanical properties

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Abstract

In this communication, a novel poly(vinyl alcohol) (PVA)/apatite-like nanocomposite films were successfully synthesized using an in situ hydrothermal process at low temperatures and a solution casting method for a facile and effective fabrication process. One step in situ process, comprising nucleation and precipitation of apatite-like nanoparticles in the presence of PVA molecules of obtained PVA/apatite-like nanocomposites. The morphological, structural, thermal, and mechanical properties of the nanocomposites were studied. The morphological analysis confirmed that this process produced amorphous apatite-like nanoparticles in the PVA solution that were homogenously distributed with controlled particle sizes of less than 20 nm in diameter. The incorporation of low quantities of apatite-like nanoparticles into the PVA matrix could significantly improve the mechanical strength of the resultant biocomposite film, which suggests an excellent load transfer between the apatite and the PVA matrix. This improvement in mechanical strength is due to the effective bonding of the filler nanoparticles in the PVA matrix during the hydrothermal reaction, which is supported by the FTIR and TGA/DSC data. This proposed process offers the possibility of using these synthesized nanocomposite materials in biomedical applications.

Keywords: Bionanocomposite; Bioceramic; Poly(vinyl alcohol)

1. Introduction

Poly(vinyl alcohol) (PVA) has gained popularity as a scaffold supporting material for tissue engineering and in the treatment of defects in load-bearing joint applications [1,2]. PVA has also been employed for several biomedical purposes including tendon repair and drug delivery [3]. This utility is because of their inherent non-toxicity, non-carcinogenicity, good biocompatibility, and desirable physical properties [4]. More recently, organic/inorganic nanocomposites have attracted significant attention from both academia and industry applications, especially for their uses in tissue regeneration [5,6]. Such nanocomposites have the potential for greater function and performance than pure organic or inorganic materials. Many researchers have been trying to incorporate inorganic components into PVA polymer matrices at the nanoscopic level in order to enhance the matrix properties, as the physical properties of nano-sized scales are considerably different from those in their bulk form [7,8]. For example, when ceramic filler, which is a stiff material, is added into the PVA matrix, the swelling ratio of the PVA/ceramic composite polymer is effectively reduced [9].

Calcium phosphates (CaP) families such as hydroxyapatite (HA) have long been used as an implant material owing to their good biocompatibility, bioactivity, and chemical stability. A similar type of bioactive ceramics can be obtained in a simulated body fluid (SBF). The SBF is an aqueous solution that has almost the same constituents as human extracellular fluid. The bioactive ceramic formed in SBF has been called bone-like apatite because its composition and structure are similar to those of bone mineral rather than of sintered stoichiometric HA, and have important characteristics such

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as low crystallinity and nanoscale sizes that are important for the reabsorption and remodeling found in bone [10,11]. However, the concentrations of the constituents of standard SBF are slightly different from those of human blood plasma. The apatite formed in this SBF is believed to exhibit even higher bioactivity and biocompatibility than sintered HA [11,12].

Several techniques to introduce CaP phase nanoparticles (NPs) into PVA matrices have been developed. It is now well established that the properties of the composites depend on the dimensions of the supporting material, the shape and size of the fillers clusters, and in particular, the distribution and preparation method [13]. In fact, it is extremely difficult to homogenously disperse nanomaterials into the polymer matrix by conventional preparation methods because of the easy agglomeration of NPs and the high viscosity of the polymer solution [1,4]. The conventional preparation method of PVA/bioceramic composites lacks many desired biological functions such as, bioactivity and biocompatibility, mechanical and physical properties [1] due to the weak interaction bonding between the polymer molecules and the bioceramic groups. Hence, the synthesis of PVA/apatite nanocomposites via a novel fabrication method may establish and add new physical and mechanical properties to the PVA matrix.

In this communication, the complete mineralization of apatite was achieved in a very short time (1 h) with a reaction temperature of 150 °C in a simple and effective in-situ hydrothermal process, incorporating apatite-like materials in the surrounding PVA solution. This process produced a biomineralization–biopolymer nanocomposite film with adequate electrostatic attractive force effective for apatite nucleation and strong hydrogen bonding between the polymer molecules and nucleation compounds. Accordingly, it is clear that we are mixing SBF with PVA solution in order to enable simultaneous scaffold formation and mineralization, which is the novel aspect of the work, the PVA maintains the native structure and the in situ synthesis of apatite NPs allows the synthesis of PVA/apatite nanocomposites materials with special morphology. The special morphology can be explained due to the presence of strong interactions between apatite NPs and polyvinyl alcohol. Consequently, this approach may not only be useful in fashioning promising bioactive scaffolds (bone substitute) and bone grafts materials with good biological properties (biocompatibility), but also provide a novel and smart way for preparing PVA/inorganic and/or PVA/metallic (such as Ag, Pt, and so on) nanocomposites in a good-uniform distribution. The findings suggest that the introduction of apatite-like NPs into PVA alter its mechanical properties.

2. Experimental methods

A systematic increase in the concentration of the ions constituting apatite results in the increased in situ synthesis of apatite in PVA/apatite composite films. To carry out a comparative study, three samples of PVA/apatite composite films comprising 15, 25, and 50 wt% simulation body fluid solution (SBF), Hank's balance salt solution, (wt% based on PVA solution; pH = 7.54) were synthesized in 8 wt% PVA solution. The SBF was carried out in the presence of PVA (Mw, 146,000–186,000, Sigma Aldrich) for the *in situ* synthesis of apatite NPs. For each experiment, PVA was dissolved in distilled water. The chemical composition of SBF solution to nucleated biological compounds (apatite-like) is given in the literature [14]. 50 ml of PVA/apatite solution was transferred to a Teflon-lined autoclave container and heat-treated at 150 °C for 1 h. After the reaction process, the composite solution was cast into a 3-D mold. The three composite and plain PVA films obtained were designated as F_1, F_2, F_3, and F_0, respectively. The resultant films were left to dry at room temperature for four days and then introduced into a vacuum oven (10 mbar) at 45 °C for 72 h. Dry samples were later morphologically-characterized by FESEM (Hitachi S-7400) associated with energy dispersive spectroscopy (EDS), X-ray diffraction (GA-XRD, Philips X'Pert, Holland), and Fourier transform infrared spectroscopy (FT-IR, Jasco FT-IR-300 E). The thermal behavior of the films was investigated using Simultaneous Thermogravimetry-Differential Scanning Calorimetry TGA/DSC (SDT Q600 V20.9 Build 20), which measured both heat flow and weight changes in the samples as a function of temperature. Using an Instron mechanical tester (LLOYD instruments, LR5K plus, UK) in tensile mode, the mechanical properties of the cast films were measured according to ASTM D-638. The thickness of the specimens was around of 300 ± 22 μm which was measured using a digital micrometer with a precision of 1 μm. The extension rate was 10 mm/min and the five specimens were tested with their average values for each film.

3. Results and discussion

In this study an attempt has been made in the application of this so-called biomimetic method in the processing of synthetic apatite particles. Specifically the biocompatible PVA polymer has been chosen as templating agent for the in situ precipitation of apatite-like crystals. Fig. 1 shows FESEM cross section images of fabricated PVA/apatite samples under different concentrations from biological SBF solution. The prominent microstructural features demonstrate the effect of apatite concentration on particle size and its nucleation and distribution. It was observed that apatite NPs were well uniformly dispersed in the PVA matrix and the apatite NPs distribution in each part of the PVA matrix was well controlled by the hydrothermal process. It was found that the mineral phase uniformly grew with well-uniform distributions in PVA/apatite matrices, as shown in Fig. 1A–D. In Fig. 1A and B, very fine NPs, in tens nanometers, were observed to be nucleated within the PVA matrix with 15 wt% SBF solution. As the apatite concentration increased, the effects of the hydrothermal reaction on apatite NPs growth became more obvious due to the further nucleation and assembling of apatite NPs. An increase of apatite concentration to 50% resulted in increases in the particle diameter of the mineralized compounds ranging from 150–300 nm (Fig. 1C and D), with the samples of PVA/apatite nanocomposites providing free voids and pores inside the matrix. To further support the well distribution of

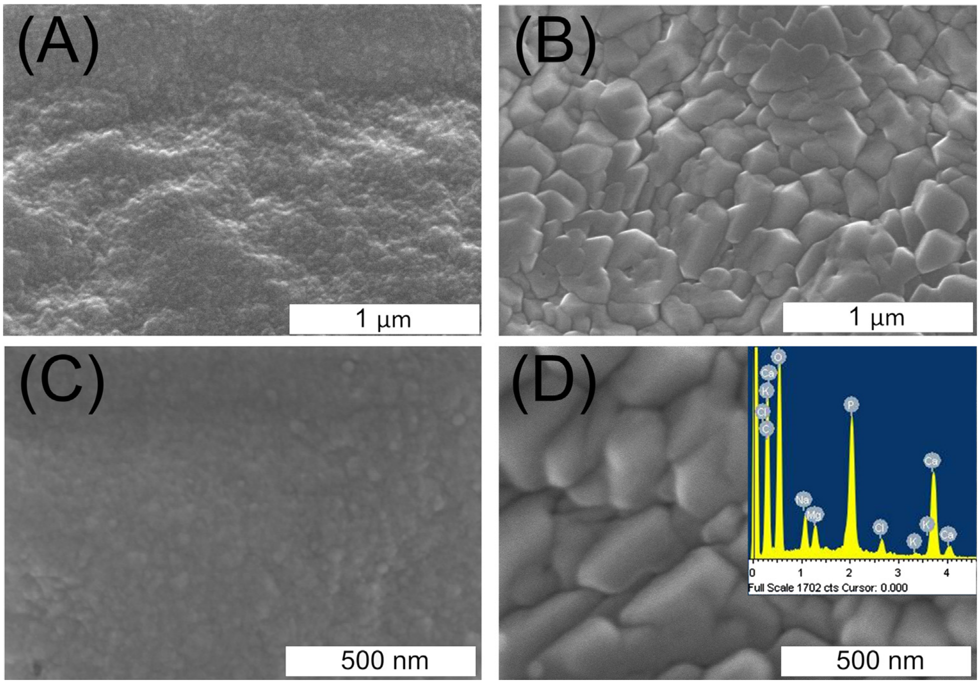

Fig. 1. FESEM morphologies of the PVA/apatite nanocomposite films with different apatite contents (A, C) 15 and (B, D) 50 wt%. The inset of panel D shows its EDS spectra.

nucleated apatite NPs within PVA matrix, the composite films were transparent and slightly yellow (see supporting information, Fig. S1). whereas pure PVA films appeared only transparent (data not shown). From this figure, with further SBF concentration the yellow of the as obtained composite samples gradually transferred to slightly brown, Fig. S1, F_3. The transparent appearance of apatite/PVA composite by in situ biomineralization indicates the uniformity of apatite dispersal in the PVA matrix, and that the size of apatite particles synthesized and nucleated simultaneously in the presence of PVA were smaller than that of wavelength of visible light [15]. These results indicate that the NPs grow uniformly in the PVA solution with this fabrication method. Free porosity in the PVA matrix may help inhibit the diffusion of the water molecules into the matrix, thereby reducing the swelling and the degradation rate of the PVA nanocomposite [9,16]. The biodegradability of the popular bioactive inorganic CaP material, is strongly correlated with the crystallinity of the CaP, lower crystalline CaP shows faster biodegradability and higher crystalline CaP shows slower or no biodegradability as was documented by Tadic.et.al [17]. It seems that the biodegradability of the apatite in the PVA/apatite nanocomposites can be controlled by the using of the present nanocomposite materials. The biodegradability of the as-obtained samples will be deeply studied as a future work.

The precipitation of the nanosized apatite particles could be explained based on surface-induced high nucleation rate of the polymer followed by sluggish growth [18]. These results suggested that the apatite NPs could be introduced into the PVA/apatite composites using the simple method of SBF solution and the morphology properties could be controlled by the concentration of SBF.

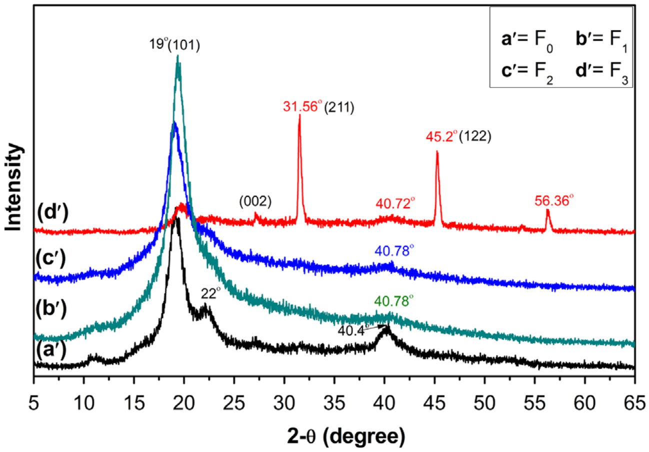

Fig. 2. XRD patterns of plain PVA and PVA nanocomposite films.

The compositions of the films were analyzed by means of EDS (Fig. 1D inset). EDS spectrum detected same peaks for all composite samples in a different intensity. It is obvious from the EDS spectrum that calcium and phosphorus are the dominant inorganic constituents of F_3 composite sample, which contains small peaks of Mg, Cl, and Na similar to bone mineral. This result supports the proposition that the nucleation NPs are apatite-like. XRD diffractograms of the resulting nanocomposite materials (Fig. 2) are useful for the identification of the deposited mineral phase, the as obtained samples consist of pure PVA (F_o) and PVA/apatite nanocomposites at different SBF concentrations and for the study of the material crystallinity. It was found that the exact crystalline structure of the samples revealed the formation of a calcium-hydroxyapatite phase in composite film F_3, Fig. 2(d') and yielded main reflection forms (002) and (211) planes. The relative intensity of these diffraction patterns correlate with the relative presence of the apatite phase in the composite. In this regard, the more growth and nucleation achieved by the apatite NPs synthesized in the reaction vessel, the stronger the incident peaks became. Fig. 2(b') shows that the strong and sharp crystalline peak at 19° are attributed to the (101) crystallographic plane of PVA. However, at low SBF concentration (15%), in the F$_1$ film, the intensity of this diffraction peak was significantly increased compared to that of the plain F$_0$ film (pure PVA) peak. This increased crystallinity of the composite film synthesized by the hydrothermal reaction can significantly enhance the properties of PVA film. It should be emphasized that the strong effects of such low concentration of apatite on the matrix chains are unusual. Our results are in opposition to the previous literature, which reported that the incorporation of bioceramic materials into a PVA matrix decreased its crystallinity [9]. This difference results from the hydrothermal reaction used in this study. With apatite concentrations, the intensity of this diffraction peak slightly decreased due to the high nucleation rate of amorphous apatite. In general, amorphous materials typical showed hollow patterns in their XRD peaks. The apatite-like material formed in this study has poor crystallinity, which is similar to the apatite found in natural bone as shown in Fig. 2. The biodegradability of the popular bioactive inorganic CaP materials, is strongly correlated with the crystallinity of the CaP, lower crystalline CaP shows faster biodegradability and higher crystalline CaP shows slower or no biodegradability as was documented by Tadic.et.al [17]. It seems that the biodegradability of the apatite in the PVA/apatite nanocomposites can be controlled by using the present nanocomposite materials. The biodegradability of the as-obtained samples will be deeply studied as a future work.

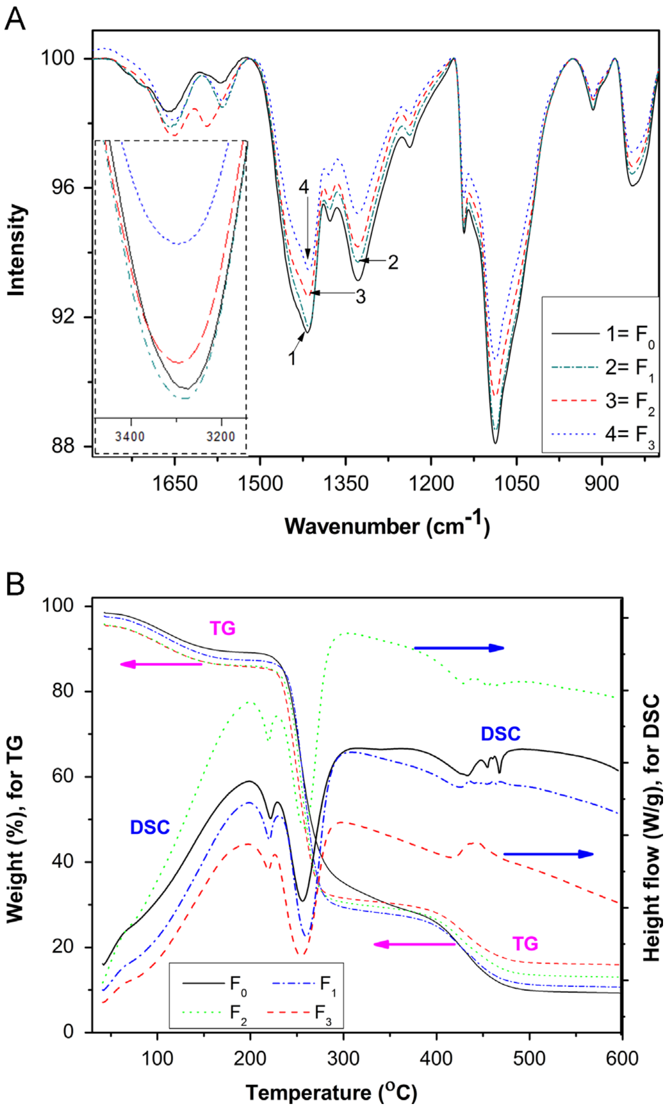

Fig. 3. (A) FTIR pattern and (B) TGA/DSC of plain PVA and PVA nanocomposite films. The inset section of A shows an enlarged portion of the spectra between 3278 and 3296 cm^{-1}.

To determine how the chemical bonding and crystalline changes between the PVA matrix and the apatite takes place, FTIR and TGA/DSC thermographs measurements of the pure PVA and the PVA/apatite nanocomposites with different contents of inorganic phase were performed (Fig. 3A and B). From IR spectra it was found that the characteristic PVA absorption bands have appeared at: 2940 cm^{-1} (CH$_2$ asymmetric stretching), 1408 cm^{-1} (CH$_2$ scissoring deformation); 1087 cm^{-1} (C–O stretching); 845 cm^{-1} (C–C stretching) and 1270 cm^{-1} (H–C–H bending in CH$_3$). The apatite characteristic absorption bands have to appear at 1010, 1041, 1087 cm^{-1} (ν3 antisymmetric P–O stretching, threefold degenerated); 962 cm^{-1} (ν1 symmetric P–O stretching, usually inactive in IR); 554, 570, 601 cm^{-1} (ν4 O–P–O bend, threefold degenerated), could not be detected on IR. Based on these bands, the deposited mineral phase can be concluded to be a non-stoichiometric hydroxyapatite. The most visible differences between the two types of materials that the incorporation of apatite into PVA films causes a shift of the predominant broad absorption band associated with the OH stretching of PVA from 3278–3296 cm^{-1} (Fig. 3A inset) [2]. Also, in comparison to plain PVA (F$_0$), many bands in the composite films significantly shifted towards the right side. For example, slight shifts in the spectrum of the composite films in the absorption around 1400 cm^{-1} is detectable, which corresponds with the bending vibration of the methyl groups in the PVA backbone [19]. PVA is a polar, water soluble polymer with CH, CH$_2$, and OH as side groups. Accordingly, it is worth to mention that the polar nature of PVA facilitates strong adhesion between the calcium phosphates and PVA. This result documents that the interaction bonding became stronger in PVA/apatite nanocomposites than pure PVA due to the increase in the number of OH groups by the addition of apatite. To explain this, the hydroxyl pendant groups on the PVA backbone can operate as nucleation sites for apatite compounds and initiating the crystallization process of apatite crystals. Since hydroxyl pendant groups are negatively charged, they can attract Ca^{2+} ions. A negatively charged surface promotes the heterogeneous nucleation of apatite, leading to a more uniform particles and dense film. The calcium ions can further attract negatively charged PO$_4^{3-}$ anions, and thereby formations of apatite like NPs within PVA matrix. This phenomenon is likely due to the specific interactions between the functional groups on the surface of a macromolecule and the ions on the surface of a crystal nucleus. By the combining of phosphate ions during the reaction vessel, apatite-like compounds (or hydroxyapatite crystals) start growing by interacting with the PVA polymeric chains. Overall, the exact role of PVA is supposed that it acts as a surface-regulating polymer to result in the NPs morphology of the apatite crystal. Specifically, the PVA molecules are believed to act as a site nucleation and growth of apatite crystal precipitated within a PVA matrix [2].

The TGA curves of the PVA/apatite polymer films revealed that the incorporation of apatite does not significantly alter the thermal stability of the samples (Fig. 3B). The unimproved thermal stability can be explained through the increased mobility of the PVA chains in the nanocomposite. The composite samples remain much more stable at temperatures above 340 °C than pure PVA (F_0 film), so the residue left behind gives an indication of the apatite content. A close look at the DSC curves in the same figure reveals not only a shift of the slope in the heat capacity curve to higher temperatures with a decrease of the content of the inorganic phase, but also a broadening of its temperature range. These results indicate that the incorporation of apatite NPs using hydrothermal energy induces crystallinity and perfection of the crystal structure changes in the PVA polymer. It seems that the incorporation of uniformly distributed NPs into the polymer matrix affects the distribution of chain segments, most likely due to a change in chain packing density in the vicinity of the polymer solution. Collectively, these results suggest the presence of strong interactions between the polymer chains and the NPs which are induced by the well-uniform distribution, which results from the reaction temperature of the hydrothermal process. It is believed that this interaction can significantly affect the mechanical properties of the fabricated films. To verify this hypothesis we have investigated the mechanical properties of four fabricated films. Fig. 4 depicts typical stress–strain curves of pure PVA and nanocomposite films with different apatite contents. A change in the stress–strain behavior after the introduction of NPs in the matrix can be seen. Contrary to the pure matrix, where stress monotonically increases at lower apatite concentration in the initial elastic deformation of the matrix, the nanocomposite films exhibit higher Young's modules. Depending on the filler content, nanocomposite films show up to 1.5 times higher tensile strength than the plain matrix (Fig. 3b), explained by the high bulk-to-surface ratio of the uniform NPs (short interparticle distance) as well as the strong attachment of PVA chains to their surface. The stress–strain curves for the fabricated films also exhibit an increase in the Young's modulus by increasing the content of apatite in the composite. Because of the attachment of polymer segments, the transfer of mechanical energy from the matrix to the high-modulus filler will be significantly enhanced. This change is due to the effective size and distribution of the filler particles in the matrix, as well as due to the small distance between the NPs inside the matrix, which coalesce well (free voids and porosity). Finally, the strain at the breaking point gradually decreases with increasing apatite content (Fig. 4). Overall, it could be concluded that the binding between calcium ions and the charged groups in the polymer phase at this molecular level has been shown to have a positive effect on the mechanical behavior of the composite systems prepared in this manner.

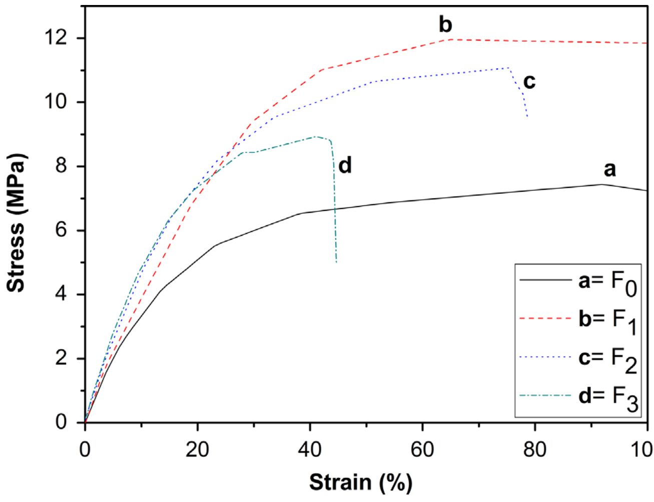

Fig. 4. Stress–strain behavior of the pure PVA and PVA/apatite nanocomposite films.

The way that this hydrothermal reaction nucleated, grew, and dispersed apatite NPs may give us some clues in the preparation of inorganic crystals with desired morphologies and/or sizes in water soluble polymer matrices. Therefore, this work provides another strategy for the preparation of apatite nanostructures with different sizes and morphologies [18].

4. Conclusion

Novel PVA/apatite nanocomposite films with well-uniform particle distributions with the chemical composition like of natural bone minerals were synthesized by a hydrothermal reaction with different apatite contents. The incorporation of synthesized apatite NPs into the PVA matrix induced significant changes in the physical and mechanical properties of the PVA. Our preliminary experimental results indicate that apatite content had a significant influence on both the size and the crystallinity of apatite NPs. PVA/apatite nanocomposite films of higher mechanical strength were achieved at lower apatite concentration in comparison with those found in pure PVA matrices. This higher tensile strength is mostly due to the effective distribution, free voids and pores, and strong bonding interactions of the NPs in the PVA matrix. These prepared nanocomposite materials may become potential candidates for different biomedical applications and its degradation rate and biological behavior in the context of tissue scaffold is the subject of a forthcoming publication.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://10.1016/j.ceramint.2013.08.057.

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