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Influence of the value of the pH on the preparation of nano hydroxyapatite – poly vinyl alcohol composites

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Many investigators have reported the incorporation of PVA with HA via in situ formation of HA crystals in a PVA solution which leads to the formation of a biodegradable and biocompatible nanocomposite. However a detailed study of the effect of the value of the pH of the reactive solution on the synthesis of HA/PVA composites had not yet been made. Using extensive FTIR and XRD analyses, the aim of the present study is to investigate the affection of the value of the pH on the formation and interaction of organic and inorganic compartments of the composite.

Key word: Poly vinyl alcohol, Hydroxyapatite, Nanocomposite, pH.

Introduction

Hydroxyapatite (HA), as a main constituent of human body hard tissue, has been subjected to numerous investigations. As a biocompatible, bioactive and osteoconductive material, HA has been the first choice for bone tissue engineering scaffold compartments. Unfortunately, fabricated materials based solely on HA cannot be used in load-bearing applications due to the low mechanical properties of HA. Introducing a polymeric component into HA in order to form an organic - inorganic composite is the method most commonly used to overcome the mechanical weakness of HA-based scaffolds.

Poly vinyl alcohol (PVA) is one of the most commonly used polymers in the case of biomedical applications [1]. PVA has a hydroxyl pendant group on every second carbon atom on its backbone. Such a high concentration of hydroxyl pendant groups makes PVA uniquely capable of being crosslinked physically and without the incorporation of any chemical additives [1]. The physical crosslinking process of PVA (known as the freeze thaw process) may be applied by freezing the samples at a temperature around -30 °C and subsequently thawing the samples at ambient temperature. The more freeze thaw cycles applied to the sample, the more hydrogen bonds will be established among hydrogen and oxygen atoms in two parallel PVA polymeric chains. The formation of such bonding among polymer chains initiates crystal clusters known as "crystallites" which are randomly dispersed among an amorphous background. Such crystallite clusters have a crystallographic nature and can be characterized using X-ray diffraction patterns [2].

Featuring such a relative simple crosslinking mechanism which avoids the necessity to use chemical crosslinkers, PVA is an attractive candidate for biomedical applications. Incorporation of PVA with HA via the in situ formation of HA crystals in a PVA solution has been reported to form a biodegradable and biocompatible nanocomposite [3-6]. However, a detailed study of the effect of the value of the pH of a reactive solution on the synthesis of HA/PVA composites has not yet been made. Using the in situ synthesis of nano hydroxyapatite particles inside a poly vinyl alcohol solution, value of the pH would affect both the formation of HA and the incorporation of PVA by affecting the hydroxyl pendant groups of PVA. The aim of the present study was to investigate the effect of the variation value of the pH in the synthesized HA structure, Organic-inorganic phase interactions and poly vinyl alcohol crystallites introduced by freeze thaw crosslinking.

Materials and Methods

Poly vinyl alcohol (Merck, $M_w = 72000$) was dissolved in distilled water to obtain a 10 wt.% PVA solution. Hydroxyapatite synthesis was implemented using the in situ precipitation of HA nanoparticles in the prepared solution. To do so calcium nitrate tetra hydrate (Biolab) was added to the PVA solution to make a 0.29 M solution then an as-prepared diammonium hydrogen phosphate (Merck) 0.24 M solution was added to the calcium and PVA mixed solution drop wise. By introduction of the phosphate solution, HA synthesis commenced automatically making the solution pH value descend. To control the pH value around a desired value 1M NaOH (Merck)

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was added to the solution as needed. To compare the affect of the value of the pH, 3 different pH values of 7, 9 and 11 were chosen. These samples were designated PHV7, PHV9 and PHV11. By the end of the synthesis nanocomposites with a composition of 50 Wt.% PVA-50 Wt.% HA were attained. The nanocomposites prepared underwent a single freeze-thaw cycle, including 15 hours at -30 °C and a 9 hours thaw at ambient temperature. Physically cross-linked samples were examined using Fourier-Transform infrared spectroscopy (FTIR; Beckam, USA) and X-Ray diffractometry (XRD; Siemens; Germany).

Results

FTIR analysis

Fig. 1 shows FTIR spectra of PVA-HA nanocomposites prepared at different pH values. As can be seen, the spectrum from PHV9 has a relatively stronger absorption around 2900 cm⁻¹, which originates from the C-H interaction in the alkyl groups on the PVA backbone [7]. Also, compared with the two other samples, in spectrum from PHV9 a red shift in the absorption around 1400 cm⁻¹ is detectable, which corresponds with the bending vibration of methyl groups on PVA backbone [7]; such a shift may be because of the interaction between the absorption due to the HA phosphate group around 1100 $\text{cm}^{-1}[8]$ and the original PVA methyl group bending vibration around 1400 cm^{-1} . The inset section of Fig. 1 shows an enlarged portion of the main spectra between 2800-2100 cm⁻¹; which is of great concern since it covers the absorption peak around 2430 cm^{-1} , which corresponds with P-H interactions [9, 10].



Fig. 1. Influence of pH value on FTIR spectra of PVA-Hydroxyapatite composite. Inset section shows variation around 2430 cm⁻¹.



Fig. 2. Variation of relative absorption intensities at 2430 cm^{-1} as a function of the value of the pH.

Here the interaction between phosphorous atoms in the HA structure and hydrogen atoms in the PVA macromolecules correlates with the interaction between the organic and inorganic phases of the composite. Thus, the stronger the absorption is around 2430 cm⁻¹, the stronger is the interaction between two comportment of the composite. Using FTIR spectral raw data, Fig. 2 shows the relative absorption intensity variation occurring around 2430 cm⁻¹. To record the peak intensities, the intensity at 2430 cm⁻¹ was normalized with respect to the intensity of the spectrum baseline and reported as the relative intensity at each pH value. Compared with PHV7, the relative intensity experiences a sharp decline for the PHV9 sample.



Fig. 3. Influence of pH value on XRD patterns of PVA and hydroxyapatite composites.

Sample	PVA crystallite main peak angle (001)	Peak width at half height	PVA crystallite size (nanometre)	Interplaner distance (Å)	31.7 angle intensity
PHV7	12.6	4.375	1.574	6.798	31.21
PHV9	13.01	5.76	1.3879	6.716	31.69
PHV11	13.17	5.08	1.82	7.018	31.82

 Table 1. influence of pH value on XRD diffraction patterns of PVA – HA composites

XRD analysis

Fig. 3 shows X-Ray diffraction patterns of the nanocomposites prepared at different pH values. Table 1 includes diffractometry data of each sample. By applying Bragg's law (Equation 1) interplanar distances between poly vinyl alcohol crystallites were calculated (Table 1).

$$n\lambda = 2d\sin\,\theta\tag{1}$$

where λ , d and θ are the diffraction wavelength (1.5404 Å), interplanar distance (Å) and diffraction angle (degree), respectively. Also using the diffraction patterns, *Debye-Scherrer law* (Equation 2) was applied to estimate the PVA crystallites size:

$$d = \frac{0.9\lambda}{B\cos\theta} \tag{2}$$

where d, λ , B and \dot{e} are crystallite size (nanometre), diffraction wavelength (0.15404 nanometre), the peak width at its half height (degree) and diffraction angle (degree), respectively. Table 1 summarizes results of the calculations. Increasing the crystallinity of the PVA samples by either implementing mechanical stretching or freezethaw crosslinking, changes the X-ray diffraction patterns from the halo characteristics of an amorphous material into defined crystalline peaks which imply increasing periodicity [11]. Accordingly, diffraction at a 2θ angle of 13° corresponds with the (100) plain [2]. Fig. 4 shows the trend in variation of interplanar distance of poly vinyl alcohol crystallites. Fig. 5 shows the variation of PVA crystallite size with the variation of pH. As can be seen the crystallite sizes experience a minima at pH value of 9.

Since diffraction at 31.7° is the most intense diffraction peak in the HA diffraction pattern, the relative intensity of the diffraction pattern at 31.7° correlates with the relative presence of the HA phase in the composite [10]. In this regard, the more HA crystals synthesized in the reaction vessel, the stronger the incident peak at 31.7° becomes. Fig. 6 shows the variation in relative intensities of incident peak at 31.7 degree for different samples.

Discussion

Based on FTIR results and the intensity of the absorption peak around 2430 cm⁻¹; it is ratified that the organicinorganic interaction between compartments of the composite varies with a change in the value of the pH. In this regard, the two components of the composite experience an optimum interaction in the PHV9 sample.



Fig. 4. Variation of interplaner distance (nm) of PVA crystallites as a function of the value of the pH.



Fig. 5. variation of crystallite size with changes in the pH.



Fig. 6. Variation of the relative intensity of diffraction at 31.7° corresponding with the synthesis of HA as a function of the value of the pH.

Accordingly, the interaction between PVA and HA remains at similar intensities in the PHV7 but decreases sharply in PHV11 sample. Also, in the PHV9 sample a larger amount of PVA contributes to the FTIR spectrum, as there is an evident absorption around 2900 cm⁻¹ to the PHV9 sample. To explain this, it can be concluded that hydroxyl pendant groups on the PVA backbone can operate as nucleation sites for HA crystals. Since hydroxyl pendant groups are negatively charged they can attract Ca²⁺ ions and by introduction of phosphate ions to the reaction vessel, hydroxyapatite crystals start growing by interaction with the PVA polymeric chains. Increasing the value of the pH by introduction of more NaOH to the solution will increase the overall hydroxyl concentration in the reaction vessel which reduces the effectiveness of PVA hydroxyl groups as nucleation sites for HA crystals. This reduces the interaction between the organic and inorganic portions of the composite abruptly, which is reflected in a sharp decline in the 2430 cm⁻¹ absorption (Fig. 2).

As can be seen in Table 1, by increasing the value of the pH, the diffraction peak (100) from the crystal plane in the PVA crystallite structures gradually shifts to larger diffraction angles, which can suggest more closely packed crystallites with less imperfections in more acidic environments. This finding is in agreement with the FTIR data, since by increasing the value of the pH the interactions between the two portions of the composite are reduced, which means less interference by HA crystals in the PVA crystallite structures. This phenomenon leads to denser structures being formed by PVA crystallites in the PHV11 sample. A denser structure leads to smaller interplanar spacings in the PHV11 sample (Fig. 4). Accordingly the crystallite size is reduced to its lowest value for the PHV9 sample (Fig. 5). This also ratifies the increased interaction of HA-PVA at this pH, since more interference from the HA structure prevents PVA crystallites from growing and joining each other to reach a more thermodynamicallystable structure and because of this the crystallite size remains the smallest compared with the PHV11 sample where the crystallites have been let grow and joined with each other to form the biggest crystallites in the series. According to Fig. 6, there is an increase in the amount of HA incorporated in the composite structure with an increase of the value of the pH in the reaction vessel. It is well known that synthesis of HA at a more basic pH value is enhanced [10]. This is in good agreement with the Fig. 6.

Conclusions

As anticipated, changes of the value of the pH can manipulate the role of hydroxyl pendant groups on the PVA backbone as a nucleation site for HA crystals. While a more basic pH enhances the formation of HA in the reaction vessel, it will hinder absorption of Ca^{+2} on hydroxyl pendant groups located on the PVA backbone. By contrast with a more acidic pH value, the formation of HA crystals would be more sluggish while there would be more intimate interaction between the organic and inorganic phases in the composite. In this regard a pH value of 9 can be an optimum value for the best interaction between both compartments while at the same time allowing acceptable formation of HA nano crystals within the structure.

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