



Synthesis and characterization of nanocomposite based on hydroxyapatite and monetite



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ABSTRACT

A mixture of hydroxyapatite (HAp) and monetite (DCPA) was synthesized under conditions of precipitation without pH adjustment by varying the ripening time of 0, 32, 76 and 144 h, followed by a hydrothermal process. The prepared samples were characterized by different techniques. It was concluded that the crystallinity and the morphology of the nanoparticles was dependent on the ripening time, hydroxyapatite crystalline phase and needle-like morphology was favored by higher ripening times. Subsequently the sample with a maturation period of 144 hours was incorporated in a polyurethane matrix, and it was observed that nanoparticles increased the dispersive component of the surface free energy of the composite.

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1. Introduction

Polyurethanes (PU) are polymers that have rigid and soft segments. The microphase separation that occur among them allows PU to withstand mechanical stress, making them suitable in different applications where dynamic loads are present, for example bone tissues. PU have been broadly used in biomedical applications such as wound dressings, artificial organs, and vascular stents, among others. The main advantages of PU are the widely variable mechanical properties and the excellent biocompatibility [1]. On the other hand calcium phosphates (CaP) are the principal component of bone and teeth, where the most representative salts are octacalcium phosphate, dicalcium phosphate anhydrous (monetite), dicalcium phosphate dehydrate (Brushite), α and β tricalcium phosphate and hydroxyapatite (HAp) [2]. Naturally occurring CaP are carbonated and calcium-deficient HAp with a Ca/P ratio less than 1.67. Therefore, synthetic CaP is of high interest in research related to bone tissue and biomedical applications [2–5].

Due to the characteristics of the polymers and the hydroxyapatite, the creation of composite materials that can be used for biomedical applications have increased. In a previous work, other authors [6] have synthesized materials based on polyurethane with a variety of inorganic fillers, including hydroxyapatite, trying to improve the abrasive properties of obturation materials. Some other examples of the applications are: non-toxic and degradable porous scaffold were made from nanohydroxyapatite and

polyurethane [7], a composite scaffold from nanosize hydroxyapatite/poly(ester-urethane) was biocompatible due to the presence of HAp [8], a porous scaffold were prepared with nanohydroxyapatite and showed cell affinity and cytocompatibility [9].

The aim of this paper is to study the influence of ripening time and hydrothermal treatment in the crystallinity and morphology of a mixture of hydroxyapatite and monetite and to use this mixture to prepare composites with polyurethane.

2. Material and methods

2.1. Materials

For the synthesis of polyurethane methylene bis(p-phenyl isocyanate) (MDI) and 1,4-butanediol (BDO) were used as hard segments, and poly(tetramethyleneoxide) diol (PTMO) with molecular weight of 1000 g/mol for the soft segments. The materials used in the synthesis of hydroxyapatite were calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and monohydrogen ammonium phosphate ($(\text{NH}_4)_2\text{HPO}_4$). All reagents were purchased from Sigma Aldrich (98% purity).

2.2. Synthesis of HA and DCPA

Solutions of Ca^{2+} and HPO_4^{2-} with a concentration of 0.1 M were prepared by dissolving appropriate amounts of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ in deionized water, respectively. The phosphate ion solution was then added into the calcium ion solution at a rate 0.1 mL/min under continuous stirring, the Ca/P molar ratio was

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kept constant at 1,67. After completing the addition of the phosphate solution, the samples were ripened under stirring at times for 0, 32, 72 or 144 h, at the end of the ripening time the samples were transferred to a 500 mL autoclave and hydrothermally treated at 110 °C for 72 h. Finally all samples were washed four times with distilled water and separated by filtering, then they were dried at 60 °C.

2.3. Synthesis of polyurethane

The synthesis used was the prepolymer method. For the first step, the molten MDI was placed in a reactor and heated to 70 °C under continuous stirring and a nitrogen atmosphere to avoid oxidative reactions. Afterwards, the macrodiol was added to the reactor over a period of 30 min. Upon completion of the macrodiol addition, the temperature of the mixture was increased to 85 °C and held during 90 min. Then, polymer extension was carried out by quickly adding BDO to the prepolymer and stirring for 5 min. The polymer was then poured onto a Teflon plate and cured at 110 °C for 4 h in a nitrogen-circulating oven. A constant weight fraction of 60% soft segment was used for all synthesis and a molar ratio of isocyanate/hydroxyl groups of 1.03 was employed.

2.4. Synthesis of composite

The addition of nanoparticles was carried during the polymerization. The procedure was the same that the one described for the polymer, with the exception that in the last step, a dispersion of 2%wt nanoparticles in BDO was used.

2.5. Characterization

FTIR spectroscopy Attenuated Total Reflectance (ATR) was performed on a Shimadzu Affinity spectrometer with an angle of incidence of the IR radiation of 45° in a ZnSe crystal in the wavenumber range 4000–650 cm^{-1} , 200 scans were obtained and averaged with a resolution of 4 cm^{-1} .

Thermal properties of the polyurethanes were measured by differential scanning calorimetry (DSC) in a TA Instruments Q100 device. To erase the thermal history of the samples, they were previously heated to 200 °C and then cooled at 10 °C/min up to –80 °C, after that they were heated to 230 °C with a heating rate of 10 °C/min and then cooled to 25 °C at 10 °C/min. The samples analyzed by DSC were polymers films obtained by compression molding at 200 °C.

2.6. The X-ray diffraction

Thin films of synthesized materials were analyzed by DRX using a transmission platform with a copper source ($K\alpha_1=1.540598$ and $K\alpha_2=1.544426$). Scanning was carried out from 10 to 50° (2 θ) with a step size 0.01° per step in a period 2 s. The analysis was carried out in an Empyrean (Panalytical, USA).

2.7. Scanning electron microscopy

All samples were analyzed by SEM using a JEOL FSEM 7100 or a JEOL JSM 6490LV microscope, powdered samples were loaded directly into the SEM holder using graphite tape and were covered with gold in a sputtering device.

2.8. Surface free energy (SFE)

All the samples were melted and compressed molded into thin films. These samples were analyzed by contact angle with two different liquids (water and diiodomethane). The contact angle

measurements were carried out using the Kruss K12 tensiometer by using Young equation [10]. The experimental temperature was hold at 25 °C.

3. Results and discussion

3.1. Synthesis of calcium phosphate

Fig. 1 shows the infrared spectra for the samples synthesized at different ripening times. All samples clearly exhibit several strong bands attributed to stretching vibrations of PO_4^{3-} groups (around 1090 and 1027 cm^{-1}). The samples with aging times of 0, 32 and 76 h show a band at 3400 cm^{-1} that is assigned to bending mode of OH^- vibration, at 1600 cm^{-1} appear the band assigned to bending and rotation of free water (H–O–H). The bands at 450 cm^{-1} , 800 cm^{-1} and 1100 cm^{-1} are ascribed to PO_4^{3-} . However, the sample with an aging time of 144 h shows different bands to the ones mentioned above, they appear at 550 cm^{-1} , 610 cm^{-1} and 900 cm^{-1} and can be attributed to PO_4^{3-} and –OH vibrations of the crystalline structure of HAp [5].

Fig. 2 shows the XRD patterns for the synthesis of calcium phosphate at different ripening times. The main phases present in the synthesized materials were monetite (CaHPO_4) and hydroxyapatite (HAp). It is observed that while the ripening time increases the diffraction peaks become sharper, therefore the crystallinity of the phases increases with the aging process, moreover the intensity of the peaks assigned to HAp rises with the ripening time, therefore ripening time favors the formation of HAp. The precipitation method depends on thermodynamic and kinetic factors which affect the presence of different phases or defects in the crystallinity of the synthesized materials.

Fig. 3 shows SEM photomicrographs for the sample synthesized at different ripening times. Different morphologies were observed in all samples; however, needle-like morphology was common to all samples. Fig. 3a shows that there are rod-like morphologies and sheets, with increasing aging time at 32 and 76 h (Fig. 3b and c) the quantity of sheets increases considerably. For ripening time of 144 hours, the population of needles increases and the population of sheet decreases. Besides the needles length is affected by the ripening time. It has been reported in the literature [5] that at pH 6 and low temperature for hydrothermal treatment the formation of sheets and needles is favored. The morphological changes occur due to the nucleation and growth processes, these could favor the production of hydroxyapatite. At pH 6 the monetite formation was observed in several samples. Nevertheless, at longer times the hydroxyapatite formation is observed, which leads to a

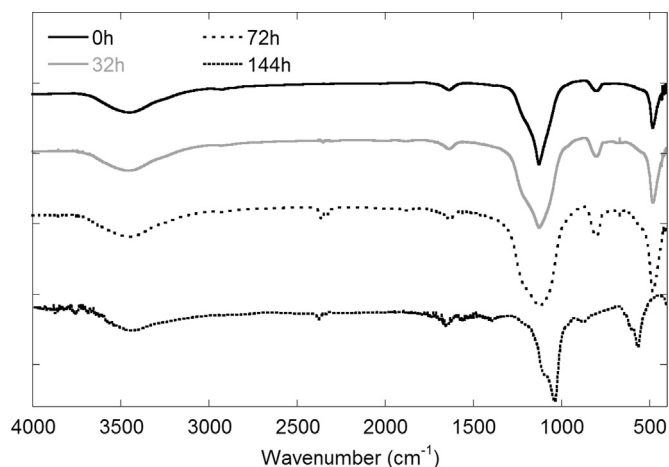


Fig. 1. FTIR of CaP powders of different phases.

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