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THE EFFECT OF BINDER ON CHEMICALLY PRECIPITATED HYDROXYAPATITE DURING SPRAY DRYING

VPLIV VEZIVA NA KEMIJSKO IZLOČENI HIDROKSIAPATIT MED ATOMIZACIJO

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The synthesis of appropriate calcium phosphate powders for thermal-spraying applications is a fundamental, crucial stage in the production of bioceramical coatings coupled with the desired characteristics. The performance, lifespan and quality of the resulting biological coating in-vivo is largely dependent on the coating morphology, phase composition, particle size and the crystallites of the spray powders. In order to achieve very reliable coatings from thermal-spray processes, spherical powders of a specified size distribution are recommended. The aim of this work was to produce hydroxyapatite powder with a chemical precipitation method and to reshape it in a spray dryer and investigate the effect of binder on the powder structure to provide an insight into the preparation and characterization aspect of HA powders using the spray-drying process. Ethanol, pure water and polyvinilalcohol (PVA) + ethanol were used as the binder. Different temperatures were applied in the spray dryer. Then, the precipitated, spray-dried powders were examined for morphology. Scanning electron microscopy (SEM), X-ray diffraction (XRD), (EDX) and ICP were used to characterize the specimen powders.

Keywords: hydroxyapatite, chemical precipitation, spray dryer, ICP (Inductively Coupled Plasma)

Sinteza primernega prahu kalcijevega sulfata za termično naprševanje, povezana z želenimi lastnostmi, je osnovna in ključna faza pri izdelavi biokeramičnih prevlek. Uspešnost, zdržljivost in kvaliteta biološke prevleke v živo je močno odvisna od morfologije prevleke, fazne sestave, velikosti delcev in kristalnih zrn napršenega prahu. Za zagotovitev zelo zanesljivega premaza se priporoča uporaba prahu z okroglimi delci določene porazdelitve velikosti zrn. Cilj tega dela je izdelati prah hidroksiapatita (HA) z metodo kemijskega izločanja, s preoblikovanjem z atomizacijo in preiskati učinek veziva na strukturo prahu, da bi dobili vpogled v načine priprave in karakterizacijo HA-prahov z atomizacijo. Kot veziva so bili uporabljeni etanol, čista voda in polivinil alkohol, (PVA) + etanol. Pri atomizaciji so bile uporabljene različne temperature. Nato je bila pregledana morfologija atomiziranega prahu. Karakterizacija vzorcev prahov je bila izvršena z vrstično elektronsko mikroskopijo (SEM), rentgensko difrakcijo (XRD), energijsko disperzijsko rentgensko spektroskopijo (EDX) in induktivno sklopljeno plazmo (ICP).

Ključne besede: hidroksiapatit, kemijsko izločanje, atomizacija, induktivno sklopljena plazma ICP

1 INTRODUCTION

Bone is formed by collagen fibres and hydroxyapatite natural bone tissue can be considered as a composite consisting of a mineralized collagen matrix.[1] Hydroxyapatite (HAp) $Ca_{10}(PO_4)6(OH)_2$ and other related calcium phosphate minerals have been evaluated as implant materials for many years due to their good biocompatibility and bioactivity as well as their similarity with the inorganic components of the hard tissues in natural bones. Their Ca/P ratio of 1.5–2.0 makes them an excellent choice for most dental and orthopedic applications in the form of bioceramic coatings. Moreover, HA has been used as a biological chromatography support in protein purification and DNA isolation. Also, HA is currently used for the fraction and purification of a wide variety of biological molecules, such as subclasses of enzymes, antibodies fragments and nucleic acids.[2–6]

Several methods, such as precipitation, solid-state synthesis, hydrolysis, wet chemical, hydrothermal and sol-gel methods have been used to prepare synthetic HAp. The synthetic HAp is used for coating in medical applications.

The HAp coating produced by plasma-spraying technology combines the mechanical advantages of a metal substrate with the excellent biological properties of HAp. Some important factors are the particle size, particle size distribution and particle morphology, which affect the lifetime and quality of the resulting biological coating.[7,8]

These important factors determine the flow characteristics in the powder-feeding systems and the melting behavior in the plasma jet.[2,3]

The hydroxyapatite powder size is very important for a thermal-spray coating system. Therefore, we have to increase the size of the powder for a good flow rate. The spray-dryer system was used to adjust the particle size. The spray-drying method is a kind of granule production technique. The advantages of this method are very simple and the particle size can be controlled quite easily. The process parameters are the slurry concentration, the compressed-air flow rate and the liquid flow rate, which are affected by the specific surface area and size distribution of the final products.[4] The morphology of the powders is generally spherical, the other morphologies are, for example, mushroom-like,[9] doughnut-like,[9] hollow structures[10] etc.

In this study we fabricated HAp powders with the chemical precipitation method and the produced powders were granulated as spherical powders using the spray-drying method by controlling the process parameters. Different binders (pure water, PVA (polyvinyl alcohol) and ethanol) were used for the slurry. The resultant spherical powders were investigated to see the effect of binders on the powder properties (morphology and particle size distribution). The final spherical powders were prepared as bulk materials and sintered. Scanning electron microscopy (SEM), X-ray diffraction (XRD) and inductively coupled plasma (ICP) were used to characterize the powders and the bulk materials.

2 MATERIALS AND METHOD

HAp particles were synthesized by a chemical precipitation method, with calcium nitrate tetrahydrate ($Ca(NO_3)2{\cdot}4H_2O$) as the calcium source, phosphoric acid (H_3PO_4) as the phosphorous source, and ammonium hydroxide(NH_4OH) as the pH regulator. ($Ca(NO_3)_2 \cdot 4H_2O$) and (H_3PO_4) were separately dissolved in distilled water continuously for 30 min. The dissolved solutions were mixed together and added (NH_4OH) to obtain the initial pH values of the reaction solutions as 11.00. The mixture was stirred at a speed of 250 r/min. The resulting suspension was aged for 24 h at room temperature and then filtered. The product was washed with water to remove the residual impurities. The precipitated powders were dried at 105 °C to remove the undesired impurities. The dried powders were mixed with pure water, and PVA and ethanol were used as a binder to obtain a slurry for the spray dryer. Inlet temperatures of 175 °C, 190 °C and 200 °C and a 1.5 bar pressure were chosen for the spray drying. The final product was shaped as a bulk material and sintered at 1050 °C for 1 h.

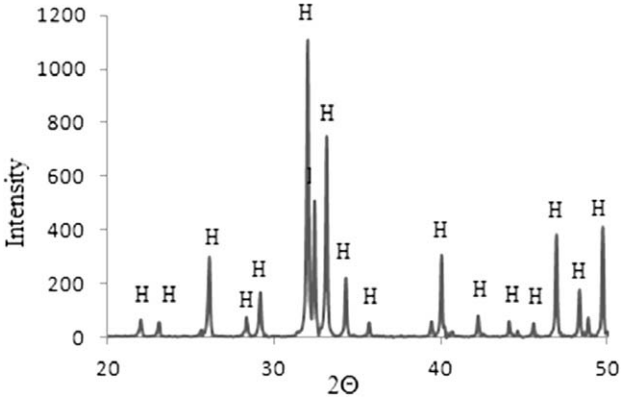

Figure 1: XRD peaks after sintering
Slika 1: XRD-spekter po sintranju

Table 1: ICP analysis result
Tabela 1: Rezultati ICP-analize

Composition	Amount in mass fractions, *w*/%
PO_4	61.05
Ca	38.50
Fe	0.0030
Mg	0.12
Zn	0.0068

3 RESULTS AND DISCUSSION

The XRD result of the hydroxyapatite after the sintering process is shown in **Figure 1**. The peaks are sharp and match with the reference hydroxyapatite peaks. The powder has a crystalline structure. These results revealed that hydroxyapatite with a chemical precipitation method could be produced. Also, the composition of the powder was given in **Table 1** (i.e., the results of the ICP). It was shown that the powder not only has Ca and P elements, but also has Fe, Mg and Zn.

Figue 2a shows that the powders had an irregular, and an angular shape distribution, and also range widely.

The SEM micrographs of the powder in **Figures 2b** and **2c** revealed that the powders produced by spray drying had a less spherical and porous microstructure. The high degree of porosity could be due to the elimination of the binder that was used in the binding and agglomeration of the spray-dried powder. Moisture and gases were also released and eliminated as a result of spray drying at an elevated temperature of 200 °C.[11]

Also, these porosities appear as a small surface depression (**Figures 2c** and **2d**), which may be minimized and the material restored to a denser structure through calcination or sintering. Visible colour changes were seen in powder. The colour changes were due to the presence of manganese ions or other transition-metal elements located in the crystal lattice structure. Although they may not have any significant effect on the biocom-

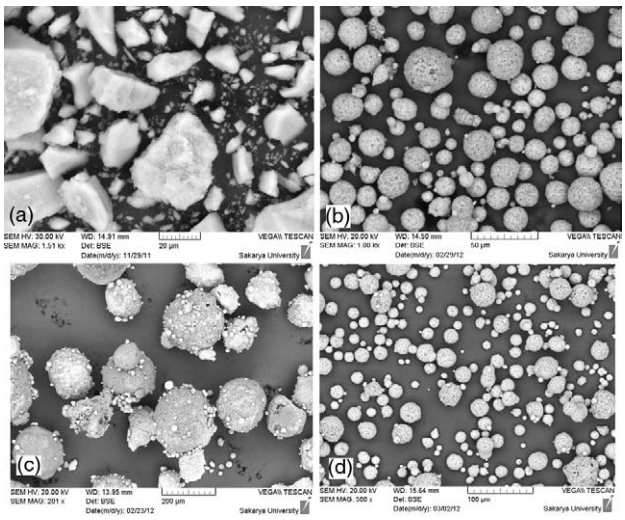

Figure 2: a) Hydroxyapatite microstructure before spray drying, b) after spray drying (175 °C, 1.5 bar, ethanol), c) (200 °C, 1.5 bar, ethanol), d) (175 °C, 1.5 bar, ethanol + PVA)
Slika 2: a) Mikrostruktura hidroksiapatita pred atomizacijo, b) po atomizaciji (175 °C, 1,5 bar, etanol), c) (200 °C, 1,5 bar, etanol), d) 175 °C, 1,5 bar, etanol + PVA)

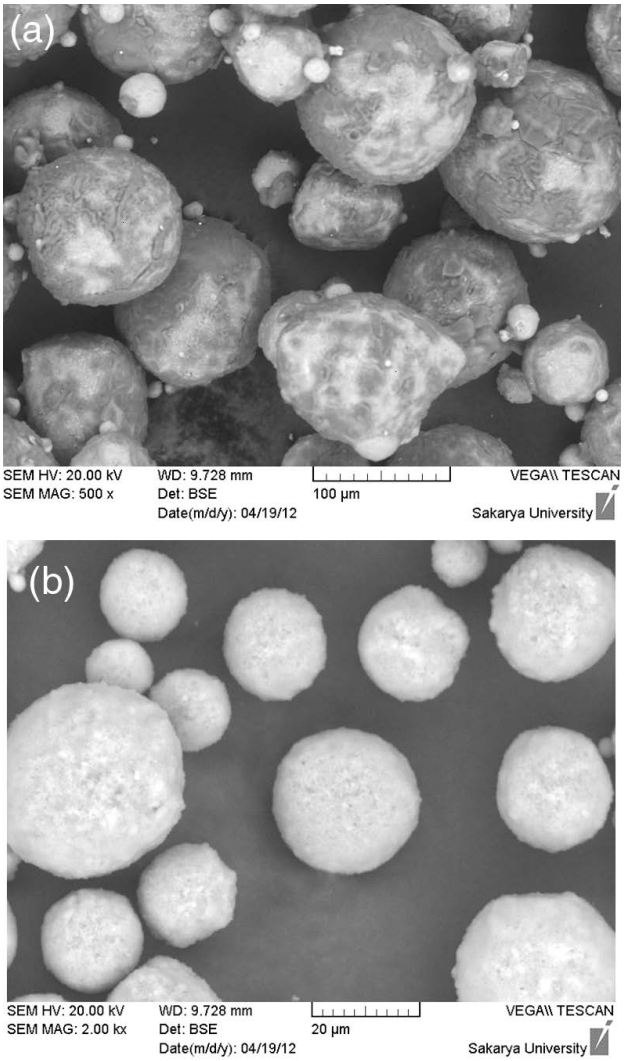

Figure 3: a) After spray drying (175 °C, 1.5 bar, pure water), b) (190 °C, 1.5 bar, pure water)
Slika 3: a) Po atomizaciji (175 °C, 1,5 bar, čista voda), b) (190 °C, 1,5 bar, čista voda)

patibility of HA, the consumer acceptance should be duly considered.[12]

When the binder is ethanol for drying, the optimal parameters are 175 °C inlet temperature and 1.5 bar pressure, for pure water the optimal parameters are 175 °C inlet temperature and 1.5 bar pressure.[13] Spherical particles are seen in **Figure 2b**. The powders have a porous structure because of the early evaporation of the ethanol. A porous and hollow structure with the slow diffusion of solute and a quick solvent evaporation were obtained.[14] Irregular particles are seen in **Figure 2c**. Increasing the inlet temperature results in quick evaporation of the moisture, but a high temperature may cause chemical/physical distortion.[15] The spherical and porous particles are seen in **Figure 3**. Ethanol + PVA were chosen as binders. The results are same as those obtained from the ethanol-added samples. The PVA affected only the particle size. After the particle size analysis, it was seen that the particle size increases with increasing PVA addition for a good binding. The average particle sizes were 27 µm and 41 µm for the ethanol and ethanol + PVA, respectively.

It was shown in **Figures 3a** and **3b** that spherical particles were obtained at both 175 °C and 190 °C, but it seems that particles have moisture because of the insufficient inlet temperature for drying in **Figure 3a**. Increasing the temperature made the particles dry. Particles have less porosity when using pure water for the binding. Because the pure water's evaporation temperature is higher than the ethanol's, the binder holds together all particles during the process.[15]

4 CONCLUSIONS

Hydroxyapatite powders could be produced by a chemical precipitation method and reshaped with a spray dryer. The change in the binder impacted on the spray-drying parameters. The optimal inlet temperatures are 175 °C for ethanol and 190 °C for pure water. The type of binder was affected by the particle structure. A volatile binder resulted in a lower particle density and the particles had more porosity. The binder holds together all the particles, and increasing the amount of the binder (like PVA) increases the particle size.

Spray-dried powder with the correct particle size is converted to flame spheroidized powder so as to improve the microstructural characteristics and the stability of the powder. A spherical geometry is very desirable for enhanced flowability and deposition consistency, which would eventually give rise to high-quality bioceramic coatings.

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