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SYNTHESIS OF BIOMIMETIC HAp-PAA/PEG HYDROGEL COMPOSITES

SYNTEZA BIOMIMETYCZNYCH KOMPOZYTÓW HYDROŻELOWYCH HAp-PAA/PEG

Abstract

In the present study we synthesized a series of HAp-PAA/PEG hydrogel composites with various HAp contents under microwave irradiation. Novel composites were characterized using Fourier transform infrared spectroscopy (FT IR) and in vitro investigations (Ringer's solution).

Keywords: hydroxyapatite, hydrogels, poly(acrylate acid), poly(ethylene glycol)

Streszczenie

W artykule przedstawiono syntezę w polu promieniowania mikrofalowego serii kompozytów hydrożelowych z różną zawartością HAp. Nowoczesne kompozyty scharakteryzowano z zastosowaniem spektroskopii w podczerwieni z transformacją Fouriera (FT-IR) oraz badaniami in vitro (roztwór Ringera).

Słowa kluczowe: hydroksyapatyt, hydrożele, polikwas akrylowy, poliglikol etylenowy

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1. Introduction

Biomaterials can be divided into four major classes of materials: polymers, metals, ceramics (including carbons, glass-ceramics, and glasses) and natural materials (including those from both plants and animals). Sometimes two different classes of materials are combined together into a composite material, such as silica-reinforced silicone rubber or carbon fibre- or hydroxyapatite particle-reinforced poly(lactic acid). Such composites are the fifth class of biomaterials [1].

Many types of polymers are widely used in biomedical devices that include orthopedic, dental, soft tissue, and cardiovascular implants. Polymers represent the largest class of biomaterials. In this section we will consider the main types of polymers, their characterization, and common medical applications. Polymers may be derived from natural sources, or from synthetic organic processes. Hydrogels are water-swollen, cross-linked polymeric structures containing either covalent bonds produced by the simple reaction of one or more co-monomers, physical cross-links from entanglements, association bonds such as hydrogen bonds or strong van der Waals interactions between chains, or crystallites bringing together two or more macromolecular chains. Hydrogels have received significant attention because of their exceptional promise for biomedical applications. The physical properties of hydrogels make them attractive for a variety of biomedical and pharmaceutical applications. Their biocompatibility allows them to be considered for medical applications [1–5].

Within the past 20–30 years interest increased in the use of calcium phosphates as biomaterials, but only certain compounds are useful for implantation in the body since both their solubility and speed of hydrolysis increase with a decreasing calcium-to-phosphorus ratio.

The main crystalline component of the mineral phase of bone is a calcium-deficient carbonate hydroxyapatite. Hydroxyapatite may be processed as a ceramic using compaction (die pressing, isostatic pressing, slip casting, etc.) followed by solid-state sintering. When reporting methods for the production and sintering of hydroxyapatite powders, it is very important to adequately characterize the morphology of the product including the surface area, particle size distribution, mean particle size and physical appearance of the powders, since this will greatly influence the handling and processing characteristics of the material. There is a great deal of variation in the reported mechanical performance of dense hydroxyapatite ceramics, dependent on phase purity, density and grain size [1].

2. Experimental

2.1. Preparations of composites

Acrylic acid, ammonium persulphate (APS), potassium hydroxide (KOH) and poly(ethylene glycol) (PEG) M_w = 6000 were purchased from POCh. Polyethylene glycol diacrylate (PEGDA) M_w = 256 was purchased from Sigma Aldrich. All the chemicals were of analytical grade and were used without further purification.

HAp was of natural origin, obtained from bone sludge via a two-step calcination method at 650 and 850°C, with calcination time reaching 3 hours [6]. For preparation of biomimetic hydrogel composites a sieve fraction below 150 μm was applied.

SAP/HAp composites were synthesized under microwave irradiation in aqueous solutions. An appropriate amount of acrylic acid monomer was added to the solution containing KOH. Then the mixture was cooled slowly until the temperature dropped to 30 °C and next PEG and HAp were added. Then an initiator APS and a crosslinker PEGDA were added.

2.2. Immersion in Ringer's solution

The in vitro research was conducted for 10 days in Ringer's solution (the solution of calcium, potassium and sodium chlorides in proper ratio) at the temperature of 37 °C using the multifunction device CX-742 produced by the Elmetron company for pH control and analyses. The chemical stability and biological activity of the samples were evaluated on the basis of changes in the pH; Fig. 1 shows the pH value in dependence on the immersion time.

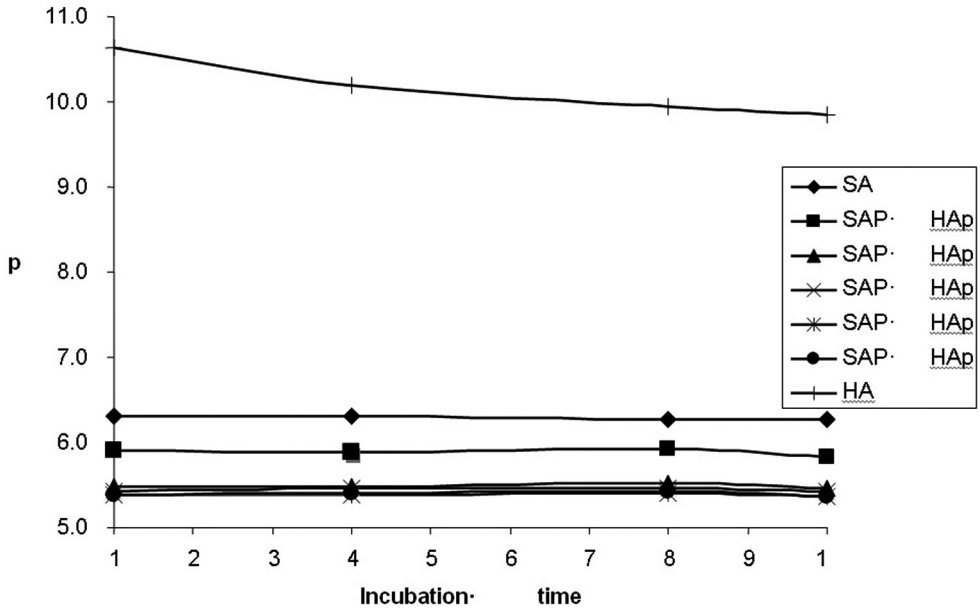

Fig. 1. Changes in pH value of Ringer's solution

Rys. 1. Zmiany pH w roztworze Ringera

Pure hydroxyapatite is characterized with a pH value at a level of 8–9. The pH value for the HAp sample was the highest since the CaO content in hydroxyapatite powder amounted to 0.025%. A low content of CaO allows to use this material as biomaterial according to standard ISO 13779 (2008).

For all the SAP/HAp samples a constant pH value in the period of incubation in Ringer's solution was observed. The pH value of pure Ringer's solution was 7.185. The samples containing SAP immersed in Ringer's solution had lower pH values because the polymer matrix was used which was anionic hydrogel.

2.3. Fourier transform infrared spectroscopy (FT-IR)

FT-IR infrared analyses were conducted with the use of Scimitar Series FTS 2000 spectrophotometer produced by the Digilab company within the basic infrared range of 400–4000 cm^{-1}. The samples were investigated before and after immersion in Ringer's solution.

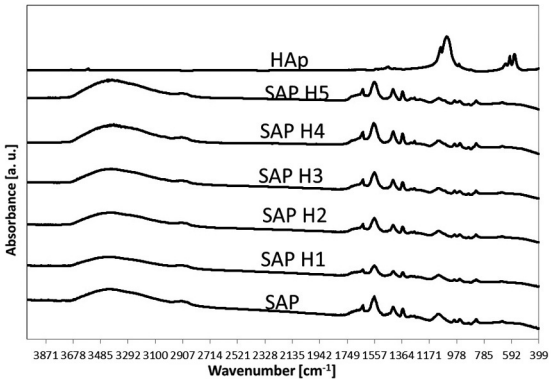

Fig. 2. FTIR spectra of HAp/PVA-H composite before immersion in Ringer's solution

Rys. 2. Spektrogram FTIR kompozytów HAp/PVA-H przed inkubacją w roztworze Ringera

Composites containing PEG, and HAp were investigated using infrared spectroscopy (Fig. 2). In composite samples only absoprtion bands corresponding to organic compounds were observed. The broad band at a high wavenumber corresponded to acrylic acid. The range of 800–1800 cm^{-1} came from organic compounds. The absence of absorpiton bands corresponding to inorganic phases could be caused by the low hydoxyapatite content in the compositions.

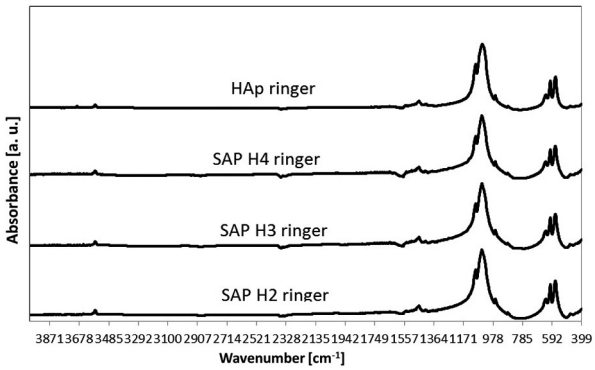

Fig. 3. FTIR spectra of HA/PVA-H composite after immersion in Ringer's solution

Rys. 3. Spektrogram FTIR kompozytów HA/PVA-H po inkubacji w płynie Ringera

The infrared investigations after 10 days of incubation in Ringer's solution confirmed that the degradation process of the polymeric matrix proceeded in the samples of composites (Fig. 3). These spectra were characterized by the absence of bands corresponding to the vibrations of C-H and C-C bonds present in organic compounds. Intensive bands corresponding to phosphate anions were present in these spectra. A low intensity band corresponding to carbonate groups could be observed, as well as a band in a high wave number range resulting from the vibration of O-H bonds. It was possible to notice an increase in the intensity of bands corresponding to a carbonate group that resulted from growing additional phases which came from Ringer's solution ions. The appetence of the new phases confirmed that hydroxyapatite exhibits bioactivity of biodegradable composite materials.

3. Conclusions

Hydroxyapatite biomaterials are characterized by the greatest biocompatibility and bioactivity of implantation materials. Solid HAp biomaterials have restricted applications, therefore the synthesis of HAp – matrix polymer composites is an innovative solution. A biologically active HAp, within short immersion in Ringer's solution, demonstrated high in vitro bioactivity of the new composites. The possibility of obtaining composites consist of HAp animal origin and the polymer matrix under microwave irradiation was confirmed. The SAP/HAp composites show the potential of a bioactive material for biomedical applications.

References

[1] Ratner B.D., Hoffman A.S., Schoen F.J., Lemons J.E., Biomaterials Science, Elsevier Academic Press, 2004.
[2] Kopecek J., *Hydrogel biomaterials: A smart future?*, Biomaterials 28, 2007, 5185-5192.
[3] Peppas N.A., Bures P., Leobandung W., Ichikawa H., *Hydrogels in pharmaceutical formulations*, Eur. J. Pharm. Biopharm. 50, 2000, 27-46.
[4] Hoffman A.S., *Hydrogels for biomedical applications*, Adv. Drug Deliv. Rev., 43, 2002, 3-12.
[5] Tyliszczak B., Lorenc I., Pielichowski K., *Microwave-assisted Synthesis and Characterization of Hydrogels Based on Acrylic Acid and PEG for Biomedical Applications*, Modern Polymeric Materials for Environmental Applications, 3, 2008, 243-246.
[6] Sobczak A., Błyszczek E., Kowalski Z., Wzorek Z., *Bone sludge as a raw material in the production of hydroxyapatite for biological applications*, Environmental Engineering III, CRC Press, Boca Raton, Taylor & Francis Group, New York 2010, 307-310.