UDC 541.64

[1] G.E.Temyrkhanova*, [2] M.A. Trubitsin, [1] G.A. Mun, [1]P. YUrkymbaeva

[1] Faculty of Chemistry and Chemical Technology, al-Farabi Kazakh National University, Almaty, Kazakhstan
[2]National Research Institute, Belgorod State University, Belgorod, Russia

Synthesis of composite based on vinyl ether of ethylene glycol structured by hydroxyapatite nanoparticles

Abstract

Millions of people are suffering from bone defect arising from trauma, tumor or bone diseases. Therefore, there is a growing need for the development of biocomposites with excellent bioactivity and compatibility. In this study hydroxyapatite (HAp) nanorod embedded composite was prepared using vinyl ether of ethylene glycol (VEEG) as a matrix. The role of VEEG composition on the crystallite size, degree of crystallinity, functional groups and morphology of nanocomposites were characterised by TEM analysis. The results indicated that the size and crystallinity of Hapnano particles decreases with increase in VEEG concentration in the composite. This shows the size control effect of VEEG concentration on HApnanorods. Due to the chemical bond interactions between HAp and VEEG. TEM micrograph confirms the presence of Hapnano rod crystals in VEEG matrix.

Introduction

The calcium phosphate based bioceramics particularly hydroxyapatite (HAp) play an excellent role in biomedical applications owing to their excellent biocompatible, osteoconductive and bioactive properties, and its close chemical and physical resemblance to mineral component of bone tissue, enamel and dentin. The major mineral phase of bone is hydroxyapatite (HAp) with a ratio of calcium-to-phosphate is 1.67 which is embedded as nanocrystalline form in collagen triple helix structure. Currently, researchers are trying to mimic this natural nano composite system for tissue engineering applications. Since, the nanoHAp with high surface area to volume ratio is more desirable to increase their contribution in bone/tooth implants, adsorbents, gene delivery and immune sensor. However, the brittleness and poor performance of mechanical stability of pure HAp limit its use for the regeneration of non-load-bearing bone defects and tissue engineering applications.Composite biomaterials like metal and polymer matrix are used to improve the mechanical compatibility of nanoHAp (n-HAp). Generally, the composite biomaterials are prepared by using biocompatible/biodegradable synthetic/ natural polymers [1].

The inorganic minerals such as hydroxyapatite, bioactive glasses, metal oxides, and carbon nanotube are incorporated into polymer matrixes to impart bioactivity. This enables us to developed the composite with desired properties. The addition of nanosized particles is desirable to develop the composite with a good mechanical strength since the natural bone contains mineral crystals which are at the nanometer scale and embedded in the collagen matrix. The polymer composites are designed to meet the specific requirement of biomedical applications like tissue engineering and drug delivery system. The right choice of the composition of both filler and polymer matrix are essential in addition to the process method to obtain suitable biopolymer composites. Recently, attempts have been made to develop nanocomposites, wherein n-Happarticles are embedded in VEEG polymeric matrices [2].

An extensive study have been made on both natural (collagen, gelatin, silk fibroin) and synthetic (polyethylene, polyamide, chitosan, polystyrene, poly (vinyl alcohol) and polyetherethilenglicole)

*E-mail: guldenka_t@mail.ru

 Printed in Kazakhstan

polymers to overcome the mechanical problems associated with bioceramics in bone tissueengineering applications [3-5].Among the above polymers, VEEG remain one of the widely used polymer group of biomaterials applied for medical implants. This usage is due to its segmented block co-polymer character. This wide range of versatilityin terms of tailoring their applications such as tissue scaffolding, artificial cartilage and biodegradable scaffolds.

With the superior combination of the synergic effect and biocompatible HAp and the adjustable biodegradability of polymer matrix, Hap nanorod embedded VEEG composites were prepared under controlled environment. The obtained nanoHAp/ VEEG composites were characterised in light of crystallite size, degree of crystallinity, morphology, biological and mechanical properties [6].

Materials and methods

Materials

The work was refined feedstock purification technique: monomer – vinyl ether glycol and a cross-linking agent – diethylene glycol divinyl ether in the laboratory.

Original monomer monovinyl ether glycol containing 99.5% of the main product was purified by distillation in the vacuum distillation unit «Distillation unit for normal laboratory quantities», (Normschliff, Germany) equipped with a distillation column. As a result of the distillation were two factions, the first of which is an azeotropic mixture containing monomer and water. The main product contained in the second fraction. Boiling point fractions were determined by the NG to determine the boiling point of the liquid at any given pressure. The first fraction was selected below 49.80 C at atmospheric pressure of 100 mbar. The second fraction was selected below 600C at 25 mbar, with the main product to stand at 540S and a given pressure of 25 mbar. For purified monomer was defined refractive index (nD20 = 1.4360) on the instrument IRF-22 (№ 710 408), which coincided with the reference data (nD20 = 1.4360, bp = 139.9-1400S/720mm. rt.st or 960 mbar). The chemicals used in the present investigation were of AR grade calcium hydroxide ($Ca(OH)_2$, Merck GR, 96%), ortho-phosphoric acid (H_3PO_4, Merck GR, min. 88%) and vinyl ether of ethylene glycol are was synthesized. All the high purity chemicals were used without any further purification.

Synthesis of VEEG

The preparation of the reaction mixture was as follows: the estimated number of monomer and crosslinking agent is poured into the container of 500 ml. To remove the oxygen reaction mixture in the vessel was purged with an inert gas (argon) for 0.5 hours, after which the container is sealed and transported to the site of radiation treatment. For radiochemical synthesis module irradiation container with the reaction mixture plunged irradiation by fast electrons on the electron accelerator ELV-4. 60-80 KHz radiation dose.

Synthesis of HAp/VEEG nanostructured composites

The HAp with rod like morphology embedded composite was prepared using different weight percentages of VEEG. The VEEG was dissolved in 100 ml ultrapure water with continuous stirring for 1 h to obtain a homogeneous solution. Similarly, 0.5 g of calcium hydroxide was dissolved in 150 ml ultrapure water with continuous stirring for 1,5 h. After obtaining the homogeneous solution, the calcium solution was added into the VEEG solution drop-by- drop under constant stirring for 2 h and kept it for 12 h in constant room temperature. During the stirring process, the prepared phosphate solution (10% of H_3PO_4) was added drop wise for a period of 40 minutes to the above polymer mixed solution. After adding the phosphate solution, the pH value is measured for all VEEG concentrations. The final solution was stirred continuously for 5 h and then it was kept for 24 h for sedimentation. Then filtered through filter paper.

Results and Discussion

A draft of production schedules for the production of polymeric implant material IPIM (Appendix C – Draft Technical specifications for the production IPIM). Injectable polymeric implant material IPIM intended for use in endoscopic correction of vesicoureteral reflux in pediatric urology, prosthetics soft tissue in plastic and reconstructive surgery. IPIM prepared by the following chemical scheme:

Injectable polymeric implant material, which is a colorless, greasy composition based on a three-dimensionally cross-linked non-toxic, biocompatible hydrophilic copolymer of vinyl ether ethylene glycol (VEEG) with diethylene glycol divinyl ether (DEGDE) and water. No irritating, allergenic, general toxic, carcinogenic, mutagenic and embryotoxic action is fully consistent with medical-technical and sanitary requirements for materials, long-term contact with the tissues of the human body.

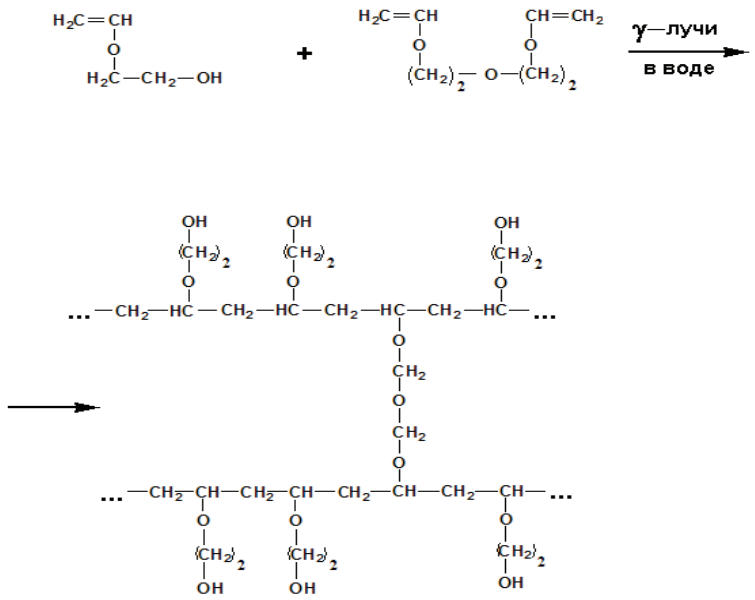


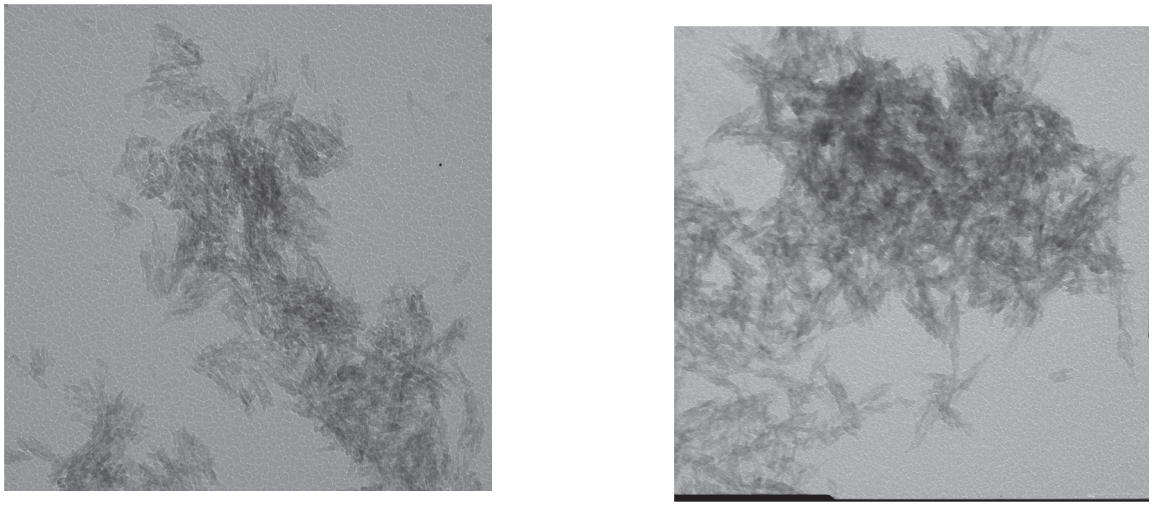
Figure 1 – Scheme of radiochemical obtain crosslinked copolymer VEEG-DVEDEG.

Formation mechanism of HAp/VEEG nanocomposite

Fig. 1 shows the schematic representation of the synthesis of HAp/VEEG nanocomposite. When the calcium hydroxide was added to the VEEG solution, the Ca^{2+} ions were attached with OH^-group in the VEEG matrix. Following the above step, orthophosphoric acid was added drop by drop into the above mixed solution. As a result, PO^{3-} ions bind to the $–OH^-$ and Ca^{2+} group to form hydroxyapatite particles and the VEEG matrix regulates the growth of c-axis of Hap nanorod.

Transmission electron microscopy analysis

TEM (Jeol JEM-2100) images of pure n-HAp and vinyl ether of ethylene glycol compositions are illustrated in Fig.2. The TEM picture shows that particles exhibit nanorod morphology. In case of composites, when the composition of VEEG is added to HAp, the rod-like morphology starts to disappear. According to TEM analysis, the particles are homogeneously dispersed in polymer matrix. Further, the micrograph does not show any notable indication for the existence of agglomeration.



а б

Figure 2 -TEM micrographs of the prepared nanohydroxyapatite samples: (a) without polymer, (b) with polymer.

Conclusion

In the present work, novel hydroxyapatite/vinyl ether of ethylene glycol nanocomposite is prepared by simple chemical route. It inferred that the composition of VEEG shows significant influence on particle size, degree of crystallinity and microhardness, which facilitate to optimize the composition of composite for particular applications. And we can safely say that our hypothesis was successful in practice. A polymer matrix we put calcium ions, which indicates the formation of nano HAP crystals.

Reference

1..Li M., Xiao X., Liu R., Chen C., Huang L. Structural characterization of zinc-substituted hydroxyapatite prepared by hydrothermal method // J. Mater.Sci: Mater. Med. – 2008. – 19. – P.797–103.

2. Bose S., Saha S.K. Synthesis and characterization of hydroxyapatite nanopowders by emulsion technique // Chem. Mater. – 2003. – 15. – P.4464-4469.

3. Ding Y., Liu J., Wang H., Shen G., Yu R. Apiezoelectricim munosensor for the detection of α-fetoprotein using an interface ofgold/hydroxyapatite hybrid nanomaterial // Biomaterials. – 2007. – 28. – P. 2147–2154.

4. Wang H., Li Y., Zuo Y., Li J., Ma S., Cheng L. Biocompatibility and osteogenesis of biomimetic nanohydroxyapatite/polyamide composite scaffolds for bone tissue engineering // Biomaterials. – 2007. – 28. – P.3338–3348.

5. Komlev V.S., Barinov S.M., Rustichelli F. Strength enhancement of porous hydroxyapatite ceramics by polymerimpregnation // J. Mater. Sci. Lett. – 2003. – 22. – P.1215–1217.

6. Meenakshi S.N., Girija E.K., Ashok M., Anee T.K., Vani R., Suganthi R. Crystallisation of hydroxyapatite nanocrystals under magnetic field // Mater. Lett. – 2006. – 60. – P.761-765.