Ultrasound Synthesis of Poly-DL-lactide-co-glycolide/Hydroxyapatite Core-shell Nano-spheres

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INTRODUCTION

Poly-DL-lactide-co-glycolide/hydroxyapatite (PLGA/HAp) is a very perspective polymeric/ceramic composite biomaterial. Micro- and nano-particles of PLGA/HAp composite showed excellent behavior during its application in reparation and reconstruction of human bone tissue [1,2]. Application of new technologies during the process of formation of this material can influence its morphology [3]. Special design of PLGA/HAp composite with large polymeric part, highly regular structure and increased particle size can improve its application as a carrier system for local drug delivery.

This paper investigates possibilities for new methods of synthesis of PLGA/HAp composite biomaterial in the form of spherical nanoparticles using ultrasound field.

MATERIALS AND METHODS

In this work, the ultrasonic processing method was applied for the preparation of PLGA/HAp nano-spheres. This method consists of three steps [3]. In the first step, homogeneous precipitation method in the field of ultrasound was applied with urea as homogeneous precipitation agent (more details in [4]). The obtained powder was dispersed in 15 ml of ethanol by high-intensity ultrasonic field in order to obtain grained superstructures in the second step and coat them with poly-DL-lactide-co-glycolide in the final, third step. The synthesis process was carried out in an ultrasonic processor for high volume applications (VCX 750, Newtown, Connecticut, USA). Shematic illustration of the apparatus applied for ultrasonic processing is represented in Figure 1. Samples were characterized by infrared spectroscopy, X-ray diffraction and scanning electron microscopy.

Figure 1. Schematic illustration of the apparatus used for ultrasonic processing

RESULTS

Figure 2 represents infrared spectra of (a) pure hydroxyapatite, obtained in the first step of the synthesis process and (b) poly-DL-lactide-co-glycolide/hydroxyapatite composite material as the final product. Phase composition of powders obtained during ultrasonic processing was determined using diffractogram analysis of pure hydroxyapatite and poly-DL-lactide-co-glycolide/hydroxyapatite composite material, represented in Figures 3a and 3b, respectively. The morphology of hydroxyapatite particles obtained during sonochemical synthesis and during treatment in the field of ultrasound are represented in Figures 4a and 4b, while the morphology of grained ceramic particles coated with polymer in PLGA/HAp biocomposite are presented in Figures 4c and 4d.

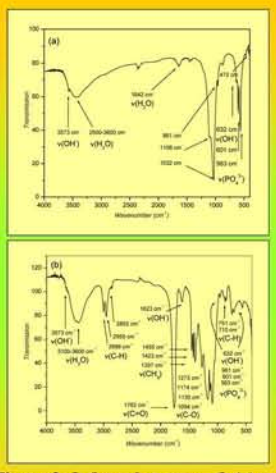

Figure 2: Infrared spectra of: (a) pure hydroxyapatite and (b) poly-DL-lactide-co-glycolide/hydroxyapatite composite processed in the field of ultrasound.

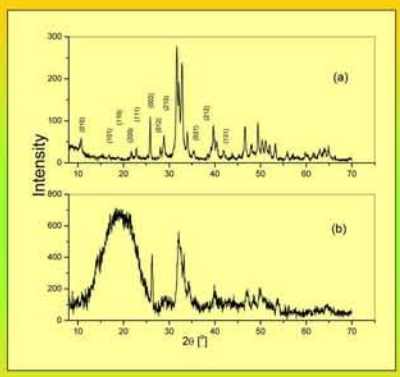

Figure 3: Diffractograms of: (a) pure hydroxyapatite and (b) poly-DL-lactide-co-glycolide/hydroxyapatite composite processed in the field of ultrasound

DISCUSSION

Identification of materials confirmed the presence of hydroxyapatite and poly-DL-lactide-co-glycolide in the composite material (Figure 2). The broadening of the peak at 2θ=26° in PLGA/HAp, in contrast to pure hydroxyapatite, indicates smaller crystallite size in the growth direction of these nano-rods (Figure 3). These data were confirmed by SEM micrographs of the as-obtained and ultrasonically treated HAp (Figs 4a and 4b).

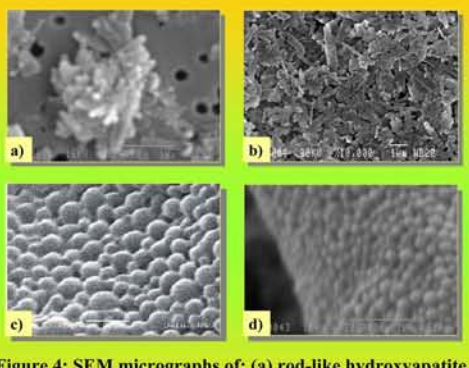

Figure 4: SEM micrographs of: (a) rod-like hydroxyapatite after ultrasonic treatment, (b) plate-like as-obtained hydroxyapatite, (c), narrow size distribution of spherical particles of PLGA/HAp and (d) planar spatial organization of spheres of PLGA/HAp

Plate-like particles formulated from parallelly oriented nano-rods, obtained during sonochemical synthesis [5] were converted into rod-like products with reduced sizes. In contrast to the rod-like morphology of pure hydroxyapatite, PLGA/HAp particles were highly regular spheres with smooth surfaces, very narrow size distribution and characteristic planar spatial organization.

CONCLUSION

In this work, we focus on the comparison between the structure of poly-DL-lactide-co-glycolide/hydroxyapatite composite material and that of pure hydroxyapatite processed in the field of ultrasound. Plate-like particles of hydroxyapatite were significantly changed in size and shape after ultrasonic deaglomeration. The small size of hydroxyapatite nano-rods was maintained after they were coated with polymer. Due to thermal instability and degradation of the polymeric part of the composite, it was very difficult to determine the structure and internal organization of the component parts within the composite through the direct method. However, the fact that only sphere-like morphology of the composite material, as opposed to rod-like apatite crystals, was detected, we may presume that the application of ultrasonic processing resulted in core-shells of PLGA with hydroxyapatite distributed inside them.

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