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Whisker Nanohydroxyapatite Synsthesis in Casein Medium and the Effect of Protein Solution Concentration on the Morphology and Structure of Nanohydroxyapatite

A. V. Severin[a], V. E. Bozhevolnov[a], and I. T. Smykov[b]

[a] *Department of Chemistry, Moscow State University, Moscow, Russia*

[b] *Department of Physical Chemistry, All-Russia Research Institute for Butter- and Cheesemaking of the Russian Academy of Agricultural Sciences, Uglich, Russia*

e-mail: severin@radio.chem.msu.ru

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Abstract—The means of hydroxyapatite nanoparticles (n-HAP) preparation in biopolymer modifiers solutions under ultrasonic activation have been investigated. The use of casein as a modificator was suggested. It was shown that a protein solution with a concentration of 0.2% provides whisker n-HAP with a diameter of 2 nm and a length of 10 nm. This size of n-HAP is correlated to colloidal calcium phosphate in milk casein micelles. Synthesized nanoparticles can be used for the intensification of technologies processes in the dairy industry and for the fortification of food with calcium in the natural form.

Keywords: synthesis, milk, casein micelles, colloidal calcium phosphate, hydroxyapatite

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Calcium compounds are the main component for the formation of bone tissue of animals and humans. They are present in milk, eggs, caviar and other food products, from which they are received by the human body. However, a large number of patients with bone injuries and osteoporosis, as well as dental patients, need special biooptimized calcium-containing drugs and biologically active agents.

Synthetic nanohydroxyapatite (n-HAP) is one of the most suitable materials to solve the above problems, because it is a natural component of the human body [1]. Depending on the application, it is possible to create composite materials based on n-HAP with an inorganic and organic biologically active substance [2]. To solve specific practical problems, it is required to synthesize n-HAP with a defined size closest to its natural functional size. It is known that the stability of milk (a primary natural source of calcium for the human body) as a dispersion system is provided by colloidal calcium phosphate (n-HAP nanoparticles with a size of 2–5 nm), which binds the individual protein molecules in the globules with size of 100–150 nm [3,4]. This fact led many researchers around the world to use synthetic n-HAP for improving the quality of dairy products. The size of these hydroxyapatite particles is generally about 60–100 nm, which is considerably greater than the size of the particles in milk. Synthesis of smaller n-HAP nanoparticles is associated with technical difficulties because of its extremely high aggregative activity. Reducing the size of nanoparticles can be obtained by ultrasonic treatment of the system during synthesis [5] or by the synthesis in a medium with modifiers, the role of which is filled by biopolymers [6, 7]. In this paper, the main milk protein, casein, in the form of sodium caseinate at different concentration, was used for the synthesis of n-HAP with a particle size less than 10 nm.

PROCEDURE OF THE EXPERIMENT

The synthesis of n-HAP was performed as described [8], in a special reactor allowing the use of sonication in the synthesis (Fig. 1). The reactor consists of a cylindrical Teflon vessel, with a mounted high-frequency transducer on the side wall. A supply of phosphoric acid was carried out continuously by means of a special node in a ceramic tube (diameter 1 mm) passing through the wall of the reactor opposite the high-frequency transducer and perpendicular thereto. The pH and temperature sensors are mounted in the reactor cover. The cover has a central hole, through which additional stirring was performed with a paddle stirrer or an additional low frequency transducer.

In this work, pure β-sodium caseinate was used. The water solutions of the modifier were prepared at a concentration of 0.05, 0.2, 1.0 and 3 %. Before synthesis they were stirred vigorously for 1 hour. Then n-HAP synthesis was performed with the pH control metric. After synthesis (pH 6.5–7.0), the samples were