

Thermal stability of brushite with chitosan samples

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Abstract. In this paper, the powders of brushite from an aqueous solution of $\text{Ca}(\text{NO}_3)_2 \cdot (\text{NH}_4)_2\text{HPO}_4$ with different content of chitosan were synthesized. XRD data revealed that all samples are single-phase and are brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$). By FT-IR spectroscopy and BET methods, it was found that chitosan adsorbs onto the surface of powders. With increase of the content of the additive, the average size of crystallites increases 4.0 – 4.8 – 11.8 μm , respectively, and the dissolution rate in isotonic solution also decreases. The thermal stability of the composite powders was studied. It was established that the highest destruction of samples occurs in the range 473-673 K by removing of adsorption and crystallization water and partial change of the structure of the mineral and chitosan. At a temperature of 873 K, carbonization of the organic additive occurs.

1. Introduction

In the world of modern osteoplastic materials, much attention focuses on the creation of composite aggregates [1-3]. For this purposes, pure or mixed variants of calcium phosphates with various organic polymers are often used. For example, calcium phosphate cements with polyamides are used in tissue engineering to restore bone defects [4]. Phosphate based composite with polymethyl methacrylate is used to affix an antibiotic to reduce the risk of bacterial infection development during transplantation [5].

Chitosan, the deacetylated chitin derivative, is of particular interest as a biopolymer thanks to its multifunctionality, molecular structure (figure 1), presence of free amino groups, antibacterial properties and biocompatibility [6]. Chitosan is also a suitable object for immobilization of various compounds, particularly medical agents [7]. In this regard, it is important to synthesize and study the composite connections on the basis of chitosan and calcium phosphate of different nature. Therefore, the aim of this work is to obtain brushite samples with chitosan and study their properties and thermal stability.

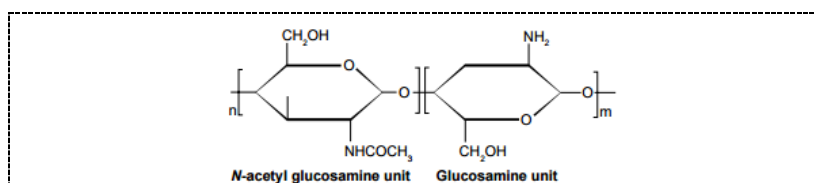
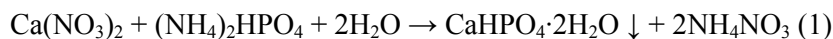


Figure 1. Chemical structure of chitosan [6].

2. Material and methods

2.1. Synthesis of powders

Brushite crystals in a chitosan matrix were synthesized by precipitation from aqueous solution at pH = 5.50±0.05, t = 25 °C by spontaneous crystallization. The powders were prepared by mixing of dilute solutions of calcium nitrate and ammonium hydrophosphate with equimolar concentrations (50 mmol/l) in accordance with equation (1).



The synthesis was carried out on three samples. The mass of chitosan varied in each sample by 0.01g, 0.04g and 0.08g. After each solution was left standing for 72 hours, the precipitate was filtered off and dried in the drying chamber at T = 80 °C until the complete removal of water.

2.2. XRD-analysis

The study by X-ray diffraction (XRD) method was performed on the powder X-ray diffractometer D8 Advance, Bruker in Cu- α radiation (wavelength 0.15406 nm) using a position-sensitive linear detector LynxEye. The following measurement modes were used: scanning step – 0.05°, integration time – 5 seconds/point, the voltage and heater current are 40 kV and 40 mA, respectively. Scanning area 2 θ : 4 – 90°. Interpretation of the obtained diffractograms was conducted using the database of powder diffraction ICDD PDF-2, 2006.

2.3. FT-IR spectroscopy

The study of powders by FT-IR spectroscopy method was carried out on the device FSM-2202. The scanning range was 400-5000 cm⁻¹, resolution was 8 cm⁻¹. Tablets of the sampling material with potassium bromide were made to conduct the study.

2.4. Specific surface area

The determination of the specific surface area of the samples was performed by the classical adsorption method. The specific surface area of the samples was measured by the method of one-point nitrogen adsorption at 77.4 K on the adsorption apparatus “Sorbometer”, production by Katakon LLC, Russia. Calculation of the obtained values of S_{BET} (m²/g) was made by the BET method.

2.5. Optical microscopy

The synthesized powders were analyzed on the optical binocular microscope XSP-104, magnification 100. The images with the resolution of 2048*1536 were taken on the video ocular ToupCam UCMOS03100KPA.

2.6. Dissolution

To study the kinetic parameters of dissolution, 0.2 g of powder was poured with 100 ml of 0.9% NaCl at T=298 K and a constant stirring speed. After that, the pCa values (unit I-160-MI, LLC “Measuring equipment”, Russia) and pH (pH unit 150 MI, LLC “Measuring equipment”, Russia) were fixed at regular intervals before output of the value on the plateau.

2.7. TG analysis

Powders of m=0.2000±0.0005 were selected into dry ceramic crucibles. Then these samples were placed in a muffle furnace for 2 hours. The calcination temperature was 473-873 K. After a prespecified heat time, the crucibles were cooled to room temperature then weighed on the analytical balance. The samples were transferred to a specially marked container and dispatched for physical analysis.

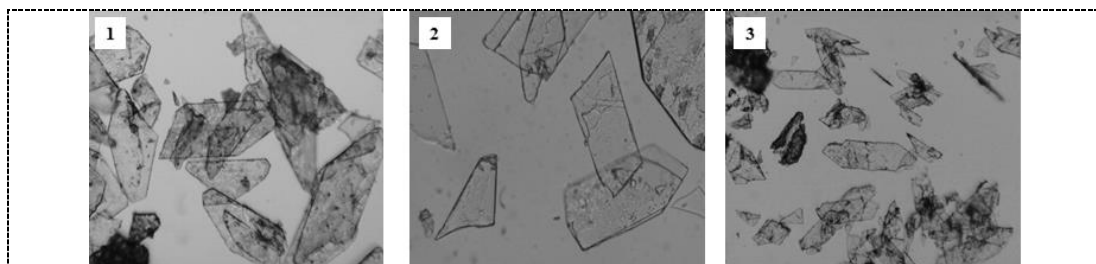


Figure 4. Optical microscopy of precipitation: weight of chitosan 1 – 0.01 g, 2 – 0.04 g, 3 – 0.08 g.

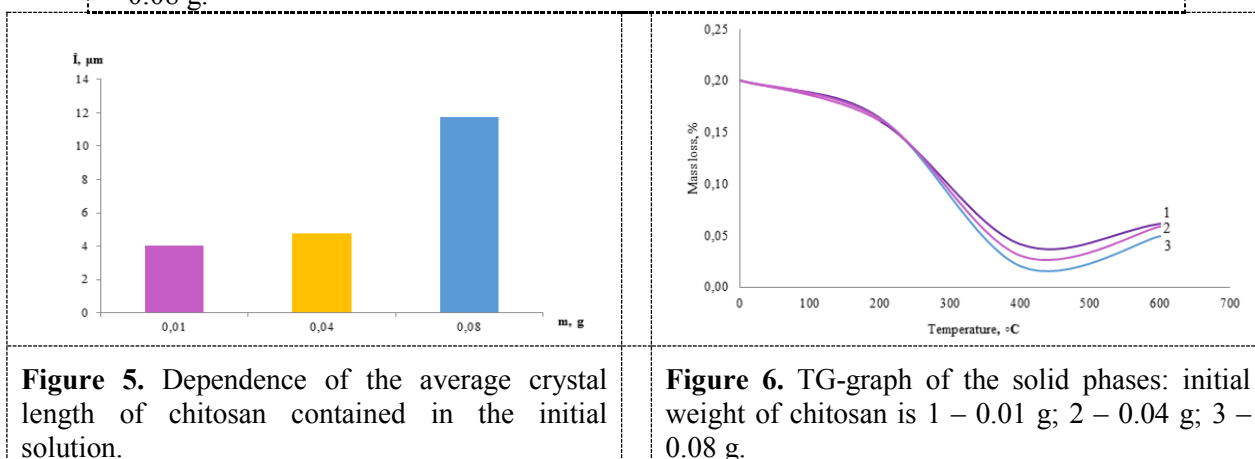


Figure 5. Dependence of the average crystal length of chitosan contained in the initial solution.

Figure 6. TG-graph of the solid phases: initial weight of chitosan is 1 – 0.01 g; 2 – 0.04 g; 3 – 0.08 g.

The results of the thermogravimetric analysis of the powders obtained at different weight of chitosan in the initial solution are shown in figure 6. As can be seen, the dependent variables are similar, but there are some differences. For example, a slight increase in the loss of mass at 473 K and a reduction in the range of 673–873 K with the increase of the initial mass of chitosan in the initial solution, the greatest mass loss is observed in the range of 473–673 K. The degradation of chitosan, forming part of the powders, starts from a temperature of 473 K. At that temperature, the color of the samples changes (figure 7.): beige (0.01g), pink (0.04g) and dirty pink (0.08g). At a temperature of 673 K, the discoloration is more intense. At a temperature of 873 K, chitosan burns out and carbonates.

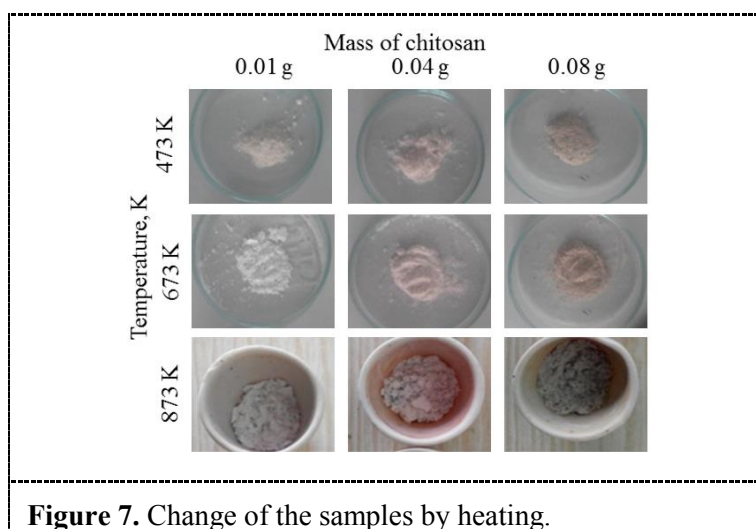


Figure 7. Change of the samples by heating.

The main processes that occur during the calcination of composites are presented in table 1 and are confirmed by IR spectroscopy (figure 8). Thus, for the further use of the composites as an additive to

biomaterials or creation of ceramics based on them, the processing temperature must not exceed more than 673 K.

Table 1. Change of powders at calcination.

T, K	DCPD [8]	T, K	Chitosan [9]
298 – 373	Removal of free water $[\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}]\text{H}_2\text{O}_{(\text{TB})} \rightarrow \text{CaHPO}_4 \cdot 2\text{H}_2\text{O}_{(\text{TB})} + \text{H}_2\text{O}_{(\text{u})} + \text{Q}$	298 – 373	Removal of free water
353 – 503	Removal of adsorption and crystallization water $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}_{(\text{TB})} \rightarrow \text{CaHPO}_4 + 2\text{H}_2\text{O}_{(\text{r})} + \text{Q}$	373 – 473	Removal of adsorption and chemically bounded water
473 – 633	Disintegration of ammonium nitrate $\text{NH}_4\text{NO}_3_{(\text{TB})} \rightarrow \text{N}_2\text{O}_{(\text{r})} + 2\text{H}_2\text{O}_{(\text{r})} - \text{Q}$ $\text{NH}_4\text{NO}_3_{(\text{TB})} \rightarrow \text{N}_{2(\text{r})} + 1/2\text{O}_{2(\text{r})} + 2\text{H}_2\text{O}_{(\text{r})} - \text{Q}$	473 – 673	Thermal decomposition with the weight loss up to 40%
633 – 733	Melting of monetite and formation of calcium pyrophosphate $2\text{CaHPO}_4_{(\text{TB})} \rightarrow \text{Ca}_2\text{P}_2\text{O}_7_{(\text{TB})} + \text{H}_2\text{O}_{(\text{r})} - \text{Q}$	> 673	Partial carbonization and burnout

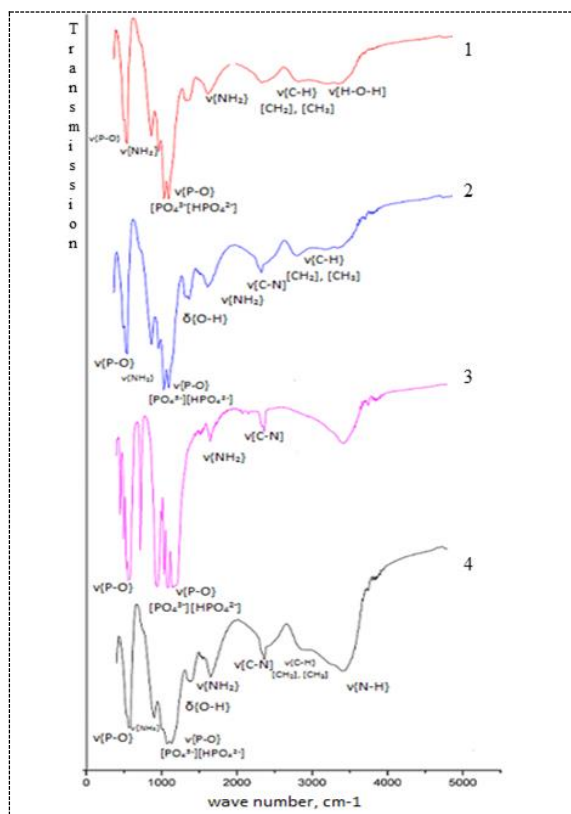


Figure 8. IR-spectra of the samples after heating: 1 – initial weight of chitosan is 0.04 g, T=473 K; 2 – initial weight of chitosan is 0.04g T=673 K; 3 – initial weight of chitosan is 0.04g, T=873 K; 4 – initial weight of chitosan is 0.08g, T=473 K.

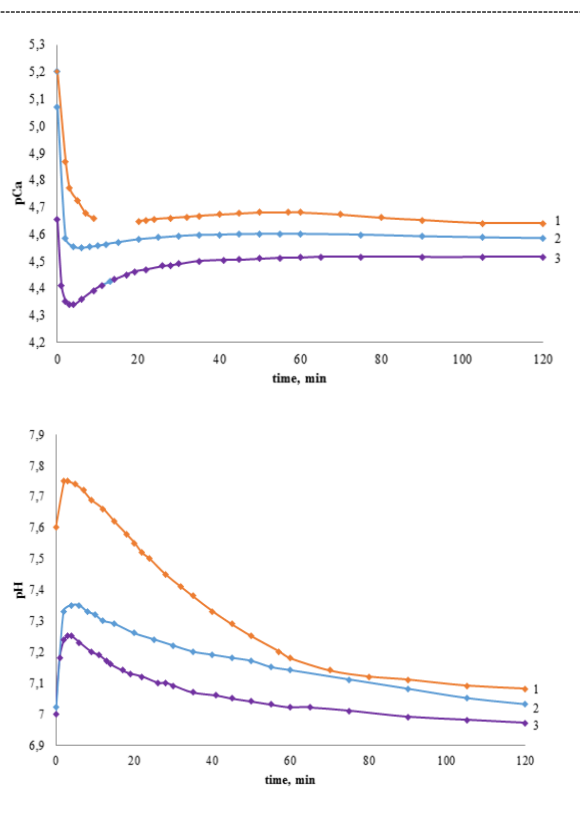


Figure 9. Kinetic dissolution curves. Initial weight of chitosan is 1 – 0.01 g; 2 – 0.04 g; 3 – 0.08 g.

In the study of the dissolution of powders in an isotonic solution (figure 9), it was revealed that the kinetic curves have the same dependences; the functions $pCa = f(t)$ and $pH = f(t)$ can be used to describe the process. As seen in Fig. 9, the maximum dissolution rate is observed in the first phase (up to 10 min.) Therefore, this curved segment is of interest. The equations calculated by the graphical method and the rate are presented in table 2. The values indicate that with the increase of the mass of chitosan in the initial solution, the dissolution rate decreases. The additive with a long acting (but not too slow) 0.01g and 0.04g is desirable for the use.

Table 2. Kinetic parameters of dissolution of powders in 0.9% NaCl.

Mass of chitosan, g	Kinetic equation	Rate
0.01	$pCa = -0.0524t + 5.043$	0.0524
0.04	$pCa = -0.0382t + 4.834$	0.0382
0.08	$pCa = -0.009t + 4.447$	0.009

4. Conclusion

Thus, the micro-sized composites of chitosan-brushite from the system $Ca(NO_3)_2-(NH_4)_2HPO_4-H_2O$ were obtained in the work. Their morphology and composition were established. It was found that with the increase of the weight of chitosan in the initial solution, the size of crystallites increases, but the values are smaller compared to pure dicalcium phosphate dihydrate. The thermal stability of the powders was studied. The highest mass loss occurs in the range of 473–673 K. This is due to the removal of adsorption and crystallization water from the structure of samples and also due to the thermal decomposition of chitosan. The dissolution rate of the samples in an isotonic solution was determined. It is found that it decreases with the increasing mass of the organic additive.

Acknowledgments

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