New Bioactive Ceramics Obtained by Heat Treatment of Modified Polymeric Precursors

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Summary: The aim of this work was to obtain pseudowollastonite-based ceramics and to determine its bioactive features. The materials were obtained by new method, namely thermal treatment of ceramic active fillers-containing polysiloxane polymeric precursor. As active fillers, commercially available $Ca(OH)_2$ and silica nanopowders (SiO_2) were used. The phase composition of ceramic products were analysed by the means of Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction analysis (XRD). The microstructure of ceramic products were studied by scanning electron microscopy (SEM) with EDS point analysis. The bioactivity was determined in ''in vitro'' conditions, by immersing of ceramic samples in simulated body fluid (SBF). The results presented in this work indicate that heat treatment of active fillers-containing polysiloxane precursor is an alternative method for receiving of pseudowollastonite-containing materials. Such obtained samples demonstrate bioactivity in ''in vitro'' conditions.

Keywords: active fillers; bioactive ceramic; polymeric precursors; polysiloxanes; pseudowollastonite

Introduction

The approaches to bone reconstructive surgery include utilization of autografts or allografts, as well as synthetic materials. The main drawbacks of autografts are limited donor bone supply, anatomical and structural problems and also donor site damage. In using allografts, the disadvantage are the risk of inducing transmissible diseases eliciting and immunological response due to genetic differences. Therefore, a number of synthetic materials have been investigated as substitute parts of hard tissues.[1–6] Among those materials, so-called surface reactive or bioactive ceramics, such as dense synthetic hydroxyapatite, bioglasses, glass-ceramics and composites basing on those materials, have drown attention, because of their unique capability to forming biological interface with surrounding tissue.[1–6]

Pseudowollastonite-based ceramics ($Ca_3[(Si_3O_9)]$) is also found to be bioactive and therefore could be also considered as hard tissue replacement material.[4,6] What is more, in comparison with the other types of bioactive ceramics, pseudowollastonite-based ceramics represent improved load-bearing features, especially fracture toughness, that is explained by the presence of precipitation of the pseudowollastonite phase.

Bioactive pseudowollastonite-containing ceramics is made by traditional high temperature melting of oxide components (CaO, SiO_2, P_2O_5, MgO) followed by controlled crystallization of the glass. In this method, melting temperature is usually about 1450 °C.[7,8] The next step of sample preparation is grinding and sintering of as-received powder at about 1500 °C. The main drawbacks of melting method are multistep

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preparation procedure (melting, grinding, forming and sintering), relatively high processing temperatures and the presence of impurities in the final product. Bioactive pseudowollastonite-containing glass-ceramics can be made also by chemical method called sol-gel. In this method glass components are introduced as organic compounds of suitable elements.[9,10] In comparison with the traditional melting method, sol-gel method offer possibility for obtaining of homogenous product in the temperatures not exceeding 1200 °C. However, the sol-gel method has low efficiency and do not allow to obtain complex shapes.

The new and very promising way that could be applied for obtaining bioactive pseudowollastonite containing ceramics is controlled heat treatment of silicon-containing polymer precursor with suitable ceramic active fillers.[11,12] Heat treatment of such mixtures, depending on the type of polymer precursor, type of active fillers and final heat treatment temperature, may lead to formation of pseudowollastonite-containing ceramic material already at about 1000 °C. This is a relatively inexpensive and efficient method and makes complex shaping possible. Preliminary results on heat treatment of polysiloxane polymer precursor with active fillers was described an analysed in.[11,12] It was shown that different combination of $CaCO_3$, $Ca(OH)_2$, $NaHPO_4$ and SiO_2 active fillers led to formation of ceramic materials – e.g. bioactive pseudowollastonite or mixture of pseudowollastonite with other silicates. The addition of SiO_2 filler promoted pseudowollastonite formation.

Therefore, the aim of this work was to study and to set up preparation method of pure pseudowollastonite ceramics materials by the new method - heat treatment of active fillers-containing polysiloxane polymer. In this work, the studies was focused on using of different weight ratios of two types of active fillers, namely $Ca(OH)_2$ and SiO_2. The effect of weight ratio of polymer/$Ca(OH)_2$/SiO_2 on the quantity of pseudowollastonite formed in the process was studied. The phase composition of obtained ceramic products as well as bioactivity in ''in vitro'' conditions were determined.

Materials and Methods

Lukosil 901 polymethylphenylsiloxane resin characterized with 3.14 C/Si molar ratio (Lucebni Zavody, Kolin, Czech Republic) and active fillers (amorphous silica - SiO_2 - of ca. 100 nm in grain size and calcium hydroxide - $Ca(OH)_2$ - 0.5–2 μm in grain size) were used. The resin and active fillers were mixed and cured during the time of 7 days up to 150 °C. The cured samples were ground. Then, from as received powders pellets were formed and heat treated at 1000 °C in an inert atmosphere at the mean heating rate of 0.7 °C/min (total time of heating - 24 hours). By this method three types of ceramic samples containing various weight ratio of fillers were prepared (Table 1).

The study on heat treatment product was led by means of Fourier transform infrared absorption spectroscopy (FTIR) in the range from 4000 to 400 cm^{-1} with 4 cm^{-1} resolution on FTS-60 V Bio-Rad spectrometer. A standard KBr pellet technique was used. The structure of ceramic samples was carried out on XRD diffractometer (Cu K_α radiation, Ni-filtered). The average grain size of ceramic products were calculated by using of Scherrer equation:

$$L_c = k\lambda/(B\cos\theta) \quad (1)$$

Table 1.
Weight ratio of active fillers used for the preparation of ceramic samples.

Ceramic sample	Resin/fillers ratio [wt%]	Resin/$Ca(OH)_2$/SiO_2 ratio [wt%]
S1	84.5/15.5	84.5/2.7/12.8
S2	73.9/26.1	73.9/13.6/12.5
S3	56.5/43.5	56.5/31.1/12.4

where: L_c – average crystal size; k - the Scherrer constant; λ - wavelength of the CuK_α radiation; B - peak width at half maximum; θ - Bragg diffraction angle.

Microstructure of the materials was examined by scanning electron microscopy JEOL 5400 with LINK AN 10000 point microanalyzer of X-ray radiation (EDS).

Study on in vitro bioactivity of the ceramic sample were carried out by their soaking in simulated body fluid (SBF), that ion concentration was nearly equal to that of human blood plasma, at the temperature of 37 °C during the time of 4 weeks under static conditions. SBF was exchanged every 3–4 days. After this period of time the surface of the ceramic samples was studied by SEM and EDS analysis.

Results

Figure 1 shows FTIR spectra of ceramic samples obtained by heat treatment of pure polysiloxane resin with different ratios of active fillers - the concentration of $Ca(OH)_2$ filler in the polymer/fillers mixture was the highest in the sample S3 and the lowest in the sample S1 (see Table 1). The spectra indicate that after heating process, in all the systems studied pseudowollastonite, i.e. ring silicate of the formula $Ca_3[(Si_3O_9)]$, is formed. This is confirmed by the appearance of the analytical band for the three-membered ring at 719 cm^{-1} as well as the bands at 1090 cm^{-1} (Si–O(Si) stretching bridging) 1069 cm^{-1} ($Si–O^-$ stretching non-bridging), 992, 940, 923cm^{-1} (Si–O(Si) stretching), 564cm^{-1} ($^-O–Si–O^-$ bending) and 471 and 433cm^{-1} ((Si)O–Si–O(Si) bending).[13]

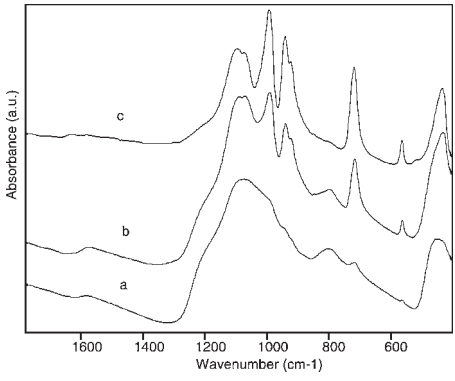

Figure 1.
FTIR spectra of: a) sample S1, b) sample S2, c) sample S3.

It should be noted that the analytical band 719 cm^{-1} corresponding to pseudowollastonite shows the highest intensity in the spectra of sample S3 presented in Figure 1c. This suggest that the sample contains high amount of $Ca(OH)_2$ compound and is the most interesting from the point of view of pseudowollastonite concentration. It is worth to note that the highest quantity of $Ca(OH)_2$ filler in polymer/fillers system is, the highest concentration of pseudowollastonite in its ceramic product can be observed (sample S3—see Table 1 and spectra in the Figure 1).

In our previous paper[11] products of heat treatment of Lukosil 901 polymethylphenylsiloxane resin and commercially available active fillers, namely powders of $Ca(OH)_2$, $CaCO_3$, Na_2HPO_4 and SiO_2, were investigated. The results of those studies showed that in all investigated heat-treated resin/filler systems, such as resin/$Ca(OH)_2$, resin/$CaCO_3$, resin/SiO_2+$Ca(OH)_2$ and resin/SiO_2+$Ca(OH)_2$+Na_2HPO_4, pseudowollastonite appeared. However, ceramic samples originated from resin/SiO_2+$Ca(OH)_2$ and resin/SiO_2+$Ca(OH)_2$+Na_2HPO_4 systems contained large amounts of pseudowollastonite compound and were the most interesting from the point of view of its concentration. It was proved that the addition of SiO_2 filler promoted pseudowollastonite formation.[11]

In the presented studies, the influence of $Ca(OH)_2$ filler on the formation of pseudowollastonite was investigated. Therefore, it can be concluded that high concentration of $Ca(OH)_2$ filler also promotes pseudowollastonite formation.

Figure 2 show diffraction pattern of the sample S3 heat treated at 1000 °C. XRD analysis reveals that heat treatment product of the active fillers-containing polysiloxane

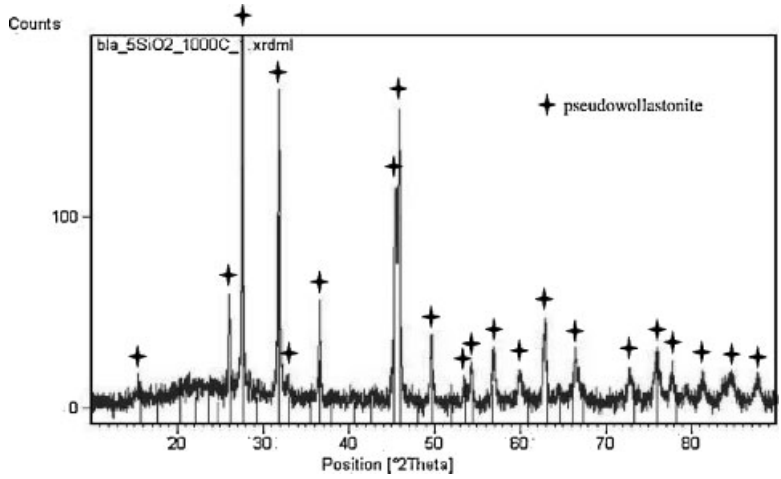

Figure 2.
XRD pattern of the sample S3.

precursor contains pure pseudowollastonite $Ca_3[(Si_3O_9)]$. The crystallite size of pseudowollastonite, calculated from diffraction peak using the Scherrer Equation (1), is about 52 nm. Due to the presence of the highest concentration of pseudowollastonite, sample S3 was chosen for bioactivity test.

Figure 3 and 4 show microphotographs and EDS analysis of the samples before and

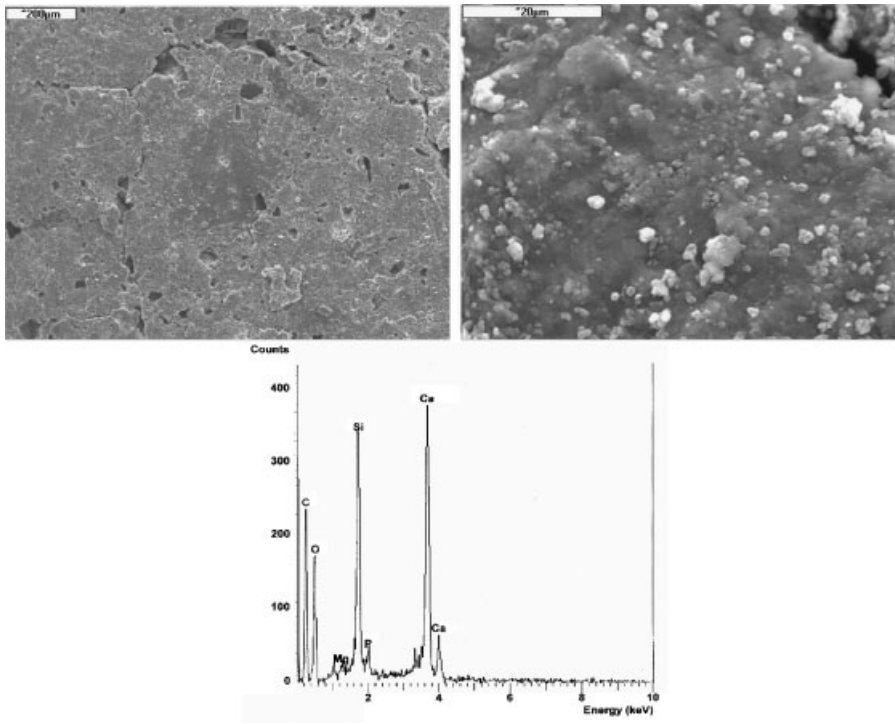

Figure 3.
SEM micrograph with EDS analysis of the pseudowollastonite-containing sample S3 before bioactivity test.

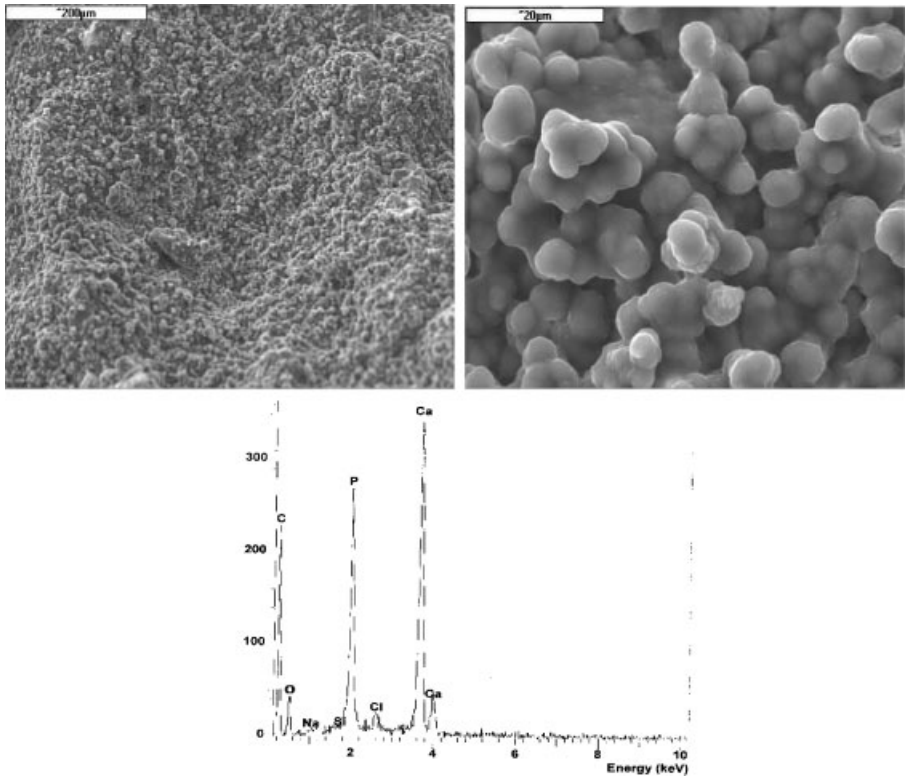

Figure 4.
SEM micrographs with EDS analysis of the pseudowollastonite sample S3 after bioactivity test.

after the bioactivity test. As it can be seen the samples before and after incubation in SBF show completely different surface morphology. The surface of the former one is smooth and dense (Figure 3.), whereas the latter is covered by so-called ''cauliflowers'' precipitations (Figure 4.). EDS analysis of the sample has revealed that onto the surface of ceramic sample calcium phosphate precipitates. It is evident that that the sample interact with SBF. Similar results, confirming formation of calcium phosphate after SBF test, have been presented by other authors for pseudowollastonite-containing ceramics obtained by melting or sol-gel methods.[7–10]

Conclusions

The results presented in this work indicate that heat treatment of $Ca(OH)_2$ and SiO_2 active fillers-containing polysiloxane precursor offers the alternative method for receiving of bioactive pseudowollastonite material, that can be useful in bone tissue regeneration. Moreover, high concentration of $Ca(OH)_2$ (over 13.6 wt%) in resin/active fillers system promotes pseudowollastonite formation.

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