A study of expanded perlite for biomedical composites

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Natural volcanic perlite was investigated with respect to its properties as component of composite systems considered for biomedical applications. Beside the overwhelming vitreous phase, $(Na,K)AlSi_3O_8$ anorthoclase crystallites were also identified in the structure of the investigated perlite. The electron paramagnetic resonance and energy dispersive X-ray spectroscopy highlighted the presence of iron impurities. The specific surface area and high magnification micrographs point out the porosity of the grains. The results obtained both by differential scanning calorimetry and infrared spectroscopy indicated that perlite is highly inert in simulated body fluid containing serum albumin.

(Received April, 30, 2013; accepted July 11, 2013)

Keywords: Perlite, Aluminosilicate glasses, Simulated body fluid

1. Introduction

Perlite is a natural compound with vitreous structure, formed in the wake of the volcanic activity, and its main components are SiO_2, Al_2O_3, Na_2O, K_2O and CaO. Perlite is free of organic substances, grainy, has a porous structure and is non-toxic. When heated to a suitable point in its softening range, it expands up to twenty times its original volume and can be transformed in fine hollow microspheres [1]. Rapidly heating perlite to temperatures of about 900°C softens the volcanic glass causing entrapped water molecules in the rock to turn to steam and expand the particles like popcorn [2].

In the last years perlite composites were considered for biomedical applications [3] and the results obtained in an in vitro model with human primary osteoblasts cultured directly on the perlite composites indicated they could be usable in the field of bone substitution. In fact, the interest for medical applications of composite materials containing natural porous inorganic components like clays, for exemple, opened new research topics intensly explored in the last time [4-7].

Our present study is focussed on the investigation of physical properties of perlite and on perlite bioactivity tested in simulated body fluid.

2. Experimental

The material taken into consideration in this study is an expanded perlite commercially available. The content of the main oxides in the investigated perlite granules is indicated in Table 1, according analysis data delivered by the supplier.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were used to explore the morphology and to determine the elemental composition of the investigated perlite. SEM images were obtained with a FEI QUANTA 3D FEG dual beam microscope; the elemental analysis was carried out with an EDX system attached to the microscope.

Table 1. The composition of the perlite grains.

Components	% mol
SiO_2	74,0-77,0
Al_2O_3	12,0-15,0
Fe_2O_3	1,1-1,6
Na_2O+K_2O	5,0-8,0
CaO	1,3-1,7
MgO	0,1-0,7

The textural characterization was made on the basis of the Brunauer, Emmet and Teller (BET) theory for multilayer adsorption of nitrogen [8] by means of a QSurf S1 Thermo Fischer Scientific Surface Area Analyzer instrument.

X-ray diffraction analysis was carried out on a Shimadzu XRD-6000 diffractometer in theta-2theta geometry using Ni-filtered CuKα radiation (wavelength λ = 1.5418 Å) at a scanning speed of 2º/min, a step of 0.02, in a 2θ scan range from 3 to 80°, using a X-rays generator voltage of 40 kV and a current of 30 mA. FTIR spectra in the middle IR region (4000–400 cm^{-1}) were recorded in a reflection configuration on a Jasco IRT-5000 FT-IR spectrometer with a resolution of 4 cm^{-1} and 256 scans, from pellet samples pressed with KBr (2 mg of sample and 200 mg KBr).

Differential scanning calorimetry analyses DSC were performed with Shimadzu DSC - 60 equipment with 10 ºC/min heating rate, from room temperature up to 560ºC, in nitrogen and air dynamic atmosphere at 70 ml/min flow. The reference material was α-alumina (Al_2O_3) and as

samples and reference support aluminum open crucibles were used.

Electron paramagnetic resonance (EPR) measurements were performed at room temperature on an ADANI spectrometer operating at 9.4 GHz (X-band). The magnetic field was modulated at 100 KHz, and the spectra were displayed as the first derivative of the absorption curve. The EPR signal of diphenylpicrylhydrazyl (DPPH) at g=2.0036 was used as g-value standard.

The bioactivity was tested in simulated body fluid (SBF) prepared according to Kokubo protocol [9], enriched with 20 mg/ml bovine serum albumin (BSA). 100 mg perlite grains were immersed in 15 ml SBF enriched with BSA, for 2 days, at 37 ^{o}C, under static conditions. Part of the grains were immersed for 7 days obly in SBF under similar conditions.

3. Results and discussion

The specific surface area of the expanded perlite measured by both 1 point and 3 points methods is 1.075 m^2/g. This value is in agreement with the data reported for perlite samples [10]. SEM images (Fig. 1) evidence the perlite porosity. The elemental composition of the perlite determined by SEM/EDX spectroscopy is presented in Table 2. Iron impurities were detected in a content of 0.47 at%. Otherwise, the presence of ferric ions was clearly evidenced by electron paramagnetic resonance.

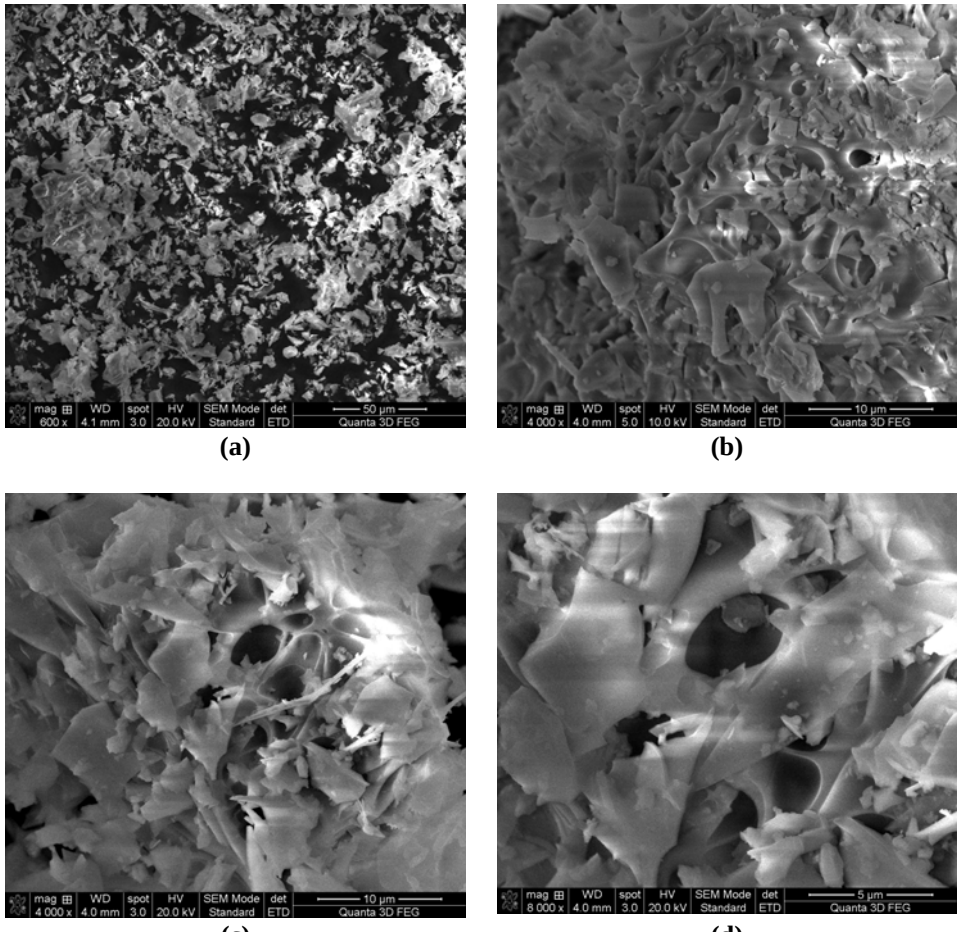

Fig. 1 SEM of perlite at different magnifications; scale bars: 50 µm (a), 10 µm (b) and (c), 5 µm (d).

Table 2. Elemental composition of the perlite grains.

Element	wt %	at %
O	36.98	51.24
Si	46.01	36.32
Al	8.28	6.80
Na	2.26	2.18
K	5.29	3.00
Fe	1.18	0.47

XRD analysis revealed the prevalent amorphous structure, but few weak diffraction peaks (Fig. 2) that could arise from crystals of $Na(AlSi_3)O_8$ (albite)–$Ca(Al_2Si_2)O_8$ (anorthite) plagioclase [11, 12] or from $(Na,K)AlSi_3O_8$ anorthoclase [13] were also recorded. Based on the elemental composition determined by EDX analysis (Table 2), the lack of calcium exclude the presence of plagioclase and support that of anorthoclase (ICDD 9-478).

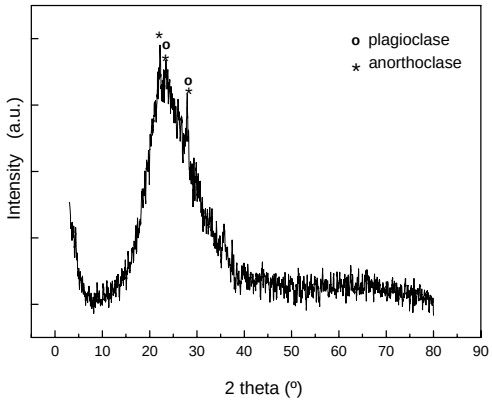

Fig. 2. XRD pattern of the expanded perlite.

The DSG curve of expanded perlite (Fig. 3) indicate a good thermal stability with no relevant deviations from the baseline except a slight decrease of the signal in the range 300-600 °C which could correspond to a weak structural rearrangement of the anorthoclase crystalline phase.

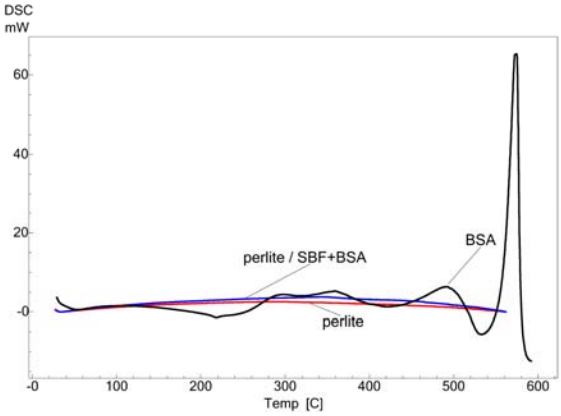

Fig. 3 DSC runs of perlite before and after 2 days of immersion in SBF with BSA compared to that of the BSA.

The EPR spectrum recorded at room temperature (Fig. 4) is delivered by Fe^{3+} ions occurring in perlite as iron impurities. The spectrum is dominated by a large, relatively symmetric resonance line with $g_{ef} = 2.1$. A weak resonance signal is recorded at $g_{ef} = 4.3$ and is assigned to Fe^{3+} ions in sites of thetrahedral or rombohedral symmetry characterized by high crystal fields. Both resonance lines are typical for Fe^{3+} ions in glasses [14, 15].

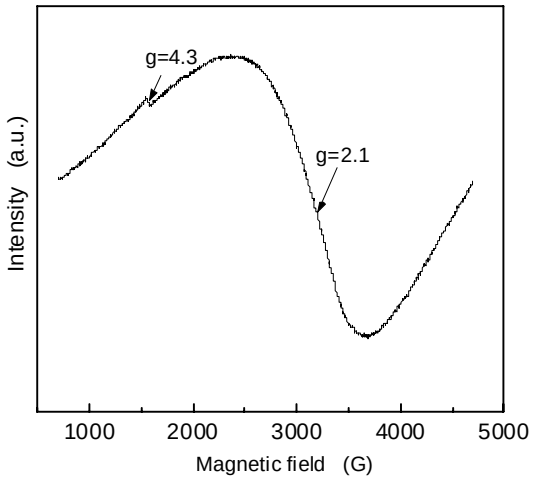

Fig. 4 EPR spectrum of expanded perlite

The FTIR spectra of perlite prior to immersion and after immersion in simulated body fluid enriched with protein (Fig. 5) show no difference between the samples, indicating that the protein was not attached on the surface of the perlite. This conclusion is also sustained by the results obtained from the analysis of DSC runs (Fig. 3), where no events related to BSA decomposition peaks are spotted in the curve recorded after perlite immersion in simulated body fluid enriched with bovine serum albumin. On the other hand, nearly no changes were observed even after 7 days of immersion in SBF (Fig. 5). The only difference is related to a weak decrease of the shoulder recorded at 1186 cm^{-1}.

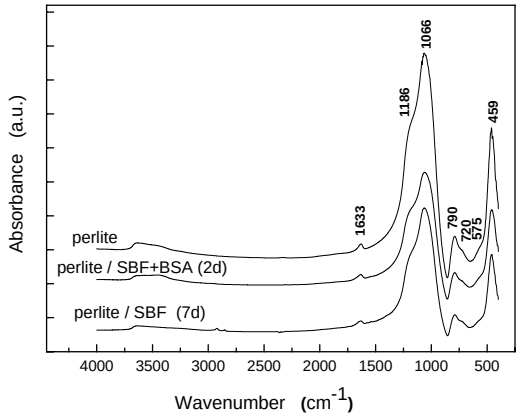

Fig. 5 FTIR spectra of perlite before and after 2 days of immersion in SFB enriched with BSA, and after 7 days of immersion only in SFB.

The absorption band close to 460 cm^{-1} is assigned to Si–O-Si bending vibrations, the sholder at 575 cm^{-1} to symmetric stretching of Si-O-Si or Si-O-Al bonds, the at 720 cm^{-1} to bending of Si-O-Al, the absorption at 790 cm^{-1} to symmetric stretching of Si-O-Si, while the intense band and shoulder at 1066 and 1186 cm^{-1} are attributed to asymmetric stretching of Si-O-Si and Si-O-Al bonds [10, 16, 17]. The weak infrared absorption band recorded at 1633 cm^{-1} and the large one recorded between 3400 and 3600 cm^{-1} are due to water molecules.

4. Conclusions

The investigated perlite contains beside the overwhelming vitreous phase also (Na,K)AlSi3O8 anorthoclase crystallites. The value of specific surface area and SEM images point out the porosity of the grains. Electron paramagnetic resonance and energy dispersive X-ray spectroscopy highlighted the presence of iron impurities. Both differential scanning calorimetry and infrared spectroscopy indicated that perlite is highly inert in simulated body fluid containing serum albumin. These properties recommend the investigated perlite as a stable component for biomedical composites.

Acknowledgements

This research was accomplished in framework of PNII PCCE-248/2008 project granted by Romanian National University Research Council.

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