

BIOMATERIALS CENTER

Laboratories:

- Biomaterials Synthesis Laboratory
- Thermal and Structural Characterisation Laboratory
- Biomaterials – Biofluids Interfaces Laboratory (Bio-interfaces Laboratory)
- Morfological and Surface Area Analysis Laboratory

Research topics:

The Biomaterials Center is mainly devoted to the enhancement of post graduate education in the field of biomaterials. Research programs are strongly focused on synthesis and characterization of systems which are of interest as potential biomaterials. The preponderantly investigated systems are vitreous and vitroc ceramic materials obtained by melting method, sol-gel route, or by spray drying; composite systems consisting of polymers and inorganic phases; hybrid systems obtained by enclosure of pharmaceuticals in microspheres or surface functionalisation with biomolecules; systems for drugs encapsulation and release. The most provocative application of the investigated systems are related to their integration in scaffolds for tissue regeneration.

Research team:

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Main equipments / Facilities:

- ***DTA&DSC Thermal analyzers, Shimadzu***

The DTA analyzer delivers differential thermal (DT) and thermogravimetric (TG) data from ambient temperature up to 1600°C. Differential Scanning Calorimeter DSC-60 provides high sensitivity with excellent resolution and signal-to-noise ratios. The temperature range is -150 to 600°C. A built-in liquid nitrogen bath enables low temperature measurements without any accessories. Detector cleaning is fast, easy, and accomplished automatically by using a built-in cleaning program. Windows-based operating software enables customized operation and applications.

- ***X-ray Diffractometer, Shimadzu XRD – 6000***

The Bragg/Bretano type system is working in $\Theta/2\Theta$ operation mode; the measurements are in transmission or reflection, the maximal power of the X-ray generator is 3 kW, the anodes are of Cu and Cr, the data base is JCPDS. The systems allows identification and quantitative estimation of the crystalline phases included in the JCPDS data base.

This equipment is used for the structural characterisation of the layers on biomaterials surface before and after immersion in simulated body fluids.

- ***BET Surface Area Analyser, QSURF M3***

The equipment is designed for specific surface areas ranging from 0,10 to 2000 m²/g, cu with an accuracy of 0,01 m²/g; automatic calibration, maximum degassing temperature 300 °C.

- ***Particle Size Analyser, Shimadzu SALD-7001***

The equipment allows the size determination of particles from 15nm to 500 µm by laser diffraction method. A single light source of violet semiconductor laser (405nm wave length) is combined with a single optical system for wide angle scattered light signals. The sampler unit is provided with a ultrasound (42 kHz) sonicator of 40 W output power. The inner volume of the dispersing bath is about 280 cm³.

- ***Mini Spray Dryer, Buchi B – 290***

The spray dryer is a top system for quick and easy drying of aqueous and organic solutions and suspensions. The equipment is very useful to produce small samples of dried product. An easy operation enables to obtain optimized processes within a short time. The spray dryer can be used in fields like glass, ceramics and pharmaceutical products. In standard setup, the spray dryer allows to obtain particles and microcapsules of diameters ranging between 1 and 25 µm. The evaporative capacity is 1.0/hr for H₂O and higher

for organic solvents, the maximal temperature input is 220° C, heating capacity - 2300 W, heating control accuracy +/- 3° C, nozzle diameter - 0.7 mm. The spray drying can be achieved by means of a rotary system and the particles diameter can be controlled by rotation speed or nozzle pressure.

- ***FP-6300 Fluorescence Spectrometer***

FP-6300 is a middle-range spectrofluorometer with a minimum 2.5 nm resolution. The signal to noise ratio for Raman band of water at 350 nm is greater than 550:1. The optical system utilizes a DC-powered 150W Xenon lamp (in a sealed housing), holographic concave grating monochromators, variable slits and horizontal sample illumination. Minimum spectral bandwidth on monochromators is of 2.5 nm.

- ***Consort C833 multimeter***

The Consort C833 functions as electrochemical multimeter and can read up to seven different parameters regarding pH, mV, ion, conductivity, resistivity, salinity; temperature.

- ***Digital microscope - Motic***

The Motic Digital/Analog Research Microscope is equipped with a 1.3 megapixel resolution digital camera that transmits microscopic images at ultra high speed through the included IEEE 1394 firewire cable system to a PC.

- ***Ball mixer mill - Retsch MM300***

Used for size reduction (dry and wet grinding), mixing, homogenizing, emulsify samples construction materials, soil, chemical products, glasses, minerals, pharmaceuticals. The feed materials can be sized up to 10 mm (soft, medium hard, hard, brittle).

- ***Thermostat, RAYPA***

For adjustable temperatures from ambient to 99.9°C. Stability of temperature ±0.05°C, resolution 0.1°C.

- ***Incubation Oven, RAYPA Incuterm***

For adjustable temperatures from ambient to 80°C, with natural air convection, temperature homogeneity ±2%, temperature stability ±0,5°C.



DTA&DSC Thermal analyzers



X-ray Shimadzu XRD 6000 Diffractometer



Mini Spray Dryer



BET Surface Area Analyser,
QSURF M3

Current research projects:

- “Composite biomaterials for simultaneous radiotherapy and hyperthermia”, BIORADHIP, CEEEX grant 100/2006, MATNANTECH programme (coordinator);
- “New ionomere biocomposite based on polyalchenoic acids modified with resins and glasses with multiple applications in medicine”, IONPOL, CEEEX grant 132/2006, RELANSIN programme (partner);
- “Osteoinductive potential of fallen deer antler usable in bone regeneration”, CERBO-REGEN-OS, CEEEX grant 73/2006, VIASAN programme (partner);
- “Reconstruction of the intestine using tissue engineering and biotechnologies - a multidisciplinary approach”, BIOINTTECH, CP 42-118 /2008, partner.

Partners and collaborators:

- Research Centre in Biomedical Materials, Queen Mary, University of London, UK
- Faculty of Physics, University of Osnabrueck, Germany.
- Iuliu Hatieganu University of Medicine and Pharmacy Cluj-Napoca,
- Technical University, Cluj-Napoca,
- Ion Chiricuta Oncological Institute, Cluj-Napoca,
- University of Agricultural Sciences and Veterinary Medicine, Faculty of Veterinary Medicine, Cluj-Napoca,
- Victor Babes University of Medicine Timisoara,
- University of Oradea, Romania

Publications:

1. V. Simon, R.V.F. Turcu, D. Eniu, S. Simon
Short range order changes induced by heat treatment in yttrium aluminosilicate glasses
Physica B, 403, 139-144 (2008)
2. V. Simon, C. Albon, S. Simon
Silver release from hydroxyapatite self-assembling calcium-phosphate glasses
J. Non-Cryst. Solids, 354, 1751–1755 (2008)
3. M. Tamasan, T. Radu, S. Simon, I. Barbur, H. Mocuta, V. Simon
Thermal analysis of sol-gel aluminosilicate systems
J. Optoelectr. Adv. Mat., 10, 4, 948-950 (2008)
4. T. Radu, S. Simon, C. Prejmerean, V. Simon, A. Colceriu, C. Tamas, L. Silaghi-Dumitrescu
Thermoanalytical characterisation of new dental ionomer biocomposites
J. Optoelectr. Adv. Mat., 10, 4, 958-960 (2008)
5. K. Magyari, C. Tănăselia, V. Simon
Dynamics of calcium, phosphorus and sodium ions at the interface of sol-gel hydroxyapatite with simulated body fluid
J. Optoelectr. Adv. Mat., 10, 4, 951-953 (2008)
6. V Simon, S Cavalu, M Prinz, E Vanea, M Neumann, S Simon
Albumin adsorption on the surface of iron containing aluminosilicates

European Cells & Materials, 16, S1, 55 (2008)

7. S. Simon, H. Mocuța, D. Lazăr
Structure and thermal behaviour of apatitic calcium phosphates: glass melting versus sol-gel synthesis
Studia – Physica, LIII, 1, 17-24 (2008)
8. V. Simon, S. Simon, M. Prinz, M. Neumann, H. Mocuta, E. Vanea
Synthesis and surface characterisation of biomaterials functionalised in protein enriched simulated body fluids
Studia – Physica, LIII, 1, 25-32 (2008)
9. E.S. Vanea, V. Simon
EPR Study of Radiation Induced Paramagnetic Species in Aluminosilicate Compounds
Studia – Physica, LIII, 2, 389 (2008)
10. M.Tamasan, S. Simon, M. Baciut, G. Baciut, V. Coman, V. Simon
Thermal investigation of nanocrystalline bone phases
Studia – Physica, LIII, 2, 9-16 (2008)

Abstracts:

V. Simon, R. V. F. Turcu, D. Eniu, S. Simon
Short-range order changes induced by heat treatment in yttrium-aluminosilicate glasses
Physica B, 403, 139-144, 2008

Short-range order and local atomic configuration in yttrium–aluminosilicate glasses doped with gadolinium were studied by infrared (IR) spectroscopy, ^{27}Al magic-angle-spinning nuclear magnetic resonance (MAS-NMR) and Gd^{3+} electron spin resonance (EPR) on as-prepared and heat-treated samples. A small amount of yttrium was replaced by gadolinium in the host glass because Y^{3+} and Gd^{3+} cations are quite similar and gadolinium ions can be used as structural sensor in electron paramagnetic resonance measurements. The results evidence weak changes in the structure of as-prepared glasses with respect to the coordination of aluminium atoms produced by gadolinium doping (0.2 and 0.5 mol%). New IR bands recorded from heat-treated samples are associated with stretching modes of hexacoordinated aluminium in AlO_6 octahedra. The effect of the heat treatment on aluminium environment is estimated by analyzing the relative intensity of the component lines of simulated ^{27}Al MAS-NMR spectra. High-coordinated AlO_n species were identified in all samples. EPR results evidence the increase of the number of gadolinium sites with weak crystal field as effect of the structural relaxation.

Keywords: Glasses; Short-range order; IR; EPR; NMR

V. Simon, C. Albon, S. Simon

Silver release from hydroxyapatite self-assembling calcium–phosphate glasses

Journal of Non-Crystalline Solids 354, 1751–1755, 2008

The in vitro behavior of $x\text{Ag}_2\text{O}(100 - x)[50\text{P}_2\text{O}_5 \cdot 30\text{CaO} \cdot 20\text{Na}_2\text{O}]$ glasses ($0.14 \leq x \leq 20$ mol%) is investigated in simulated body fluid (SBF) mainly with respect to bioactivity and silver ions release. In order to estimate the biodegradability and bioactivity, the samples were soaked in SBF, which has almost equal ions concentration to those of human blood plasma, and kept at 37°C for fixed periods of time up to 18 days. After the fixed periods of time analyses were performed on the SBF solutions. Calcium and silver ions concentration of SBF after different soaking times of the glass samples were primarily examined. Conductivity data support the assumption that the released silver ions are reduced in SBF and their release is obstructed by growth of the bioactive layer on the glass surface. X-ray diffraction and infrared analysis attest the development on glass surface of a hydroxyapatite type layer.

Keywords: Bioglass; Biomaterials; Corrosion; Electrochemical properties; Ion exchange; Crystal growth; Nucleation; X-ray diffraction; Conductivity; Optical spectroscopy; Optical microscopy; FTIR measurements; Phosphates

M. Tamasan, T. Radu, S. Simon, I. Barbur, H. Mocuta, V. Simon

Thermal analysis of sol-gel aluminosilicate systems

Journal of Optoelectronics and Advanced Materials, Vol.10, No.4, p.948–950, 2008,

Aluminosilicate systems containing radioactivable elements (Y or Dy) and/or Fe are investigated for possible applications in internal radiotherapy and hyperthermia, or in combined therapies. The samples were prepared by sol-gel method, using two SiO_2 , Dy_3O_2 , $\text{Y}_3\text{O}_2\text{O}$ (silicic acid), and nitrates sources of $\text{Al}_2\text{xH}_2\text{Si}$ (TEOS) and $\text{SiO}_4\text{O}_2\text{H}_8$: C2 different sources for SiO

and Fe_2O_3 , added in different ratios. The dried gels were heat treated at 500°C for 1 hour and at 1200°C for 24 hours, in order to engineer their structure. The samples were studied by differential thermal analysis/thermogravimetry and differential scanning calorimetry and the results were correlated with the data obtained by X-ray diffraction analysis.

T. Radu, S. Simon, C. Prejmorean, V. Simon, A. Colceriu, C. Tamas, L. Silaghi-Dumitrescu,

Thermoanalytical characterisation of new dental ionomer biocomposites

Journal of Optoelectronics and Advanced Materials Vol.10, No.4, p. 958–960, 2008

Thermoanalytical properties of four new glass ionomer cements were investigated using thermal techniques such as thermogravimetry (TG) and differential thermal analysis (DTA). The materials contain in the same ratio different copolymers and a mixture of two glass powders with preponderance of a fluoroaluminosilicate type glass. The X-ray diffraction analysis shows that these materials are all in the vitreous state. The thermal analysis traces have similar characteristics and indicate water removal, decomposition of hydroxyl groups, thermal decomposition process of the polymeric network and a dissociation process without mass loss. The last process is more likely to point out the glass transition taking place in the

inorganic glass phase.

Keywords: Thermal analysis, Biocomposites, Glass ionomer cements

Klára Magyari, C. Tănăselia, V. Simon,

Dynamics of calcium and phosphorus ions at the interface of sol-gel hydroxyapatite with simulated body fluid

Journal of Optoelectronics and Advanced Materials Vol.10, No.4,p.951-953, 2008

Hydroxyapatite [Ca₁₀(PO)₄(OH)₂] type calcium phosphate powders were prepared by sol-gel method. By filtering and washing several times with deionized water samples with pH 6.5, 8 and 11 were obtained. In order to prove their bioactivity, the samples were soaked at 37 °C for several periods in simulated body fluid with almost equal ion concentrations to those of human blood plasma. Data on conductivity, calcium and phosphorus concentrations in SBF were used to estimate the dynamics of these cations on the hydroxyapatite interface with the simulated body fluid. The scanning electron microscopy evidences morphological changes on the sample surfaces after immersion in SBF.

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Keywords: Hydroxyapatite (HA), Simulated body fluid, Biomaterials

V Simon, S Cavalu, M Prinz, E Vanea, M Neumann, S Simon

Albumin adsorption on the surface of iron containing aluminosilicates

European Cells & Materials, 16, S1, 55 (2008)

The paper reports on proteins uptake on the surface of iron containing aluminosilicate samples tested in simulated body fluids enriched with bovine serum albumin. Non-crystalline samples with 60SiO₂·20Al₂O₃·20Fe₂O₃ composition obtained by sol-gel method were subjected to partial crystallisation by heat treatment in order to developed proper magnetic crystalline phases. After fine grinding the powder samples were immersed in simulated body fluid (SBF) enriched with bovine serum albumin (BSA) in two concentrations. Fourier transform infrared (FTIR) attenuated total reflectance (ATR) and Xray photoemission spectroscopy (XPS) were used to inspect the albumin adsorption on the sample surface. X-ray photoelectron spectroscopy appears more sensitive than IR ATR spectroscopy to the changes occurred on the sample surface after immersion in simulated body fluids. The C 1s and N 1s core level XPS spectra show the BSA attachment to the surface of aluminosilicate samples already after one day immersion even in the low BSA enriched SBF.

S. Simon, H. Mocuța, D. Lazăr,

Structure and thermal behaviour of apatitic calcium phosphates: glass melting versus sol-gel synthesis.

Studia – Physica, LIII, 1, 17-24 (2008)

Apatitic calcium phosphate samples were synthesised by glass melting and sol-gel methods. Hydroxyapatite crystalline phase was developed in the heat treated glass sample. A nanostructured hydroxyapatite was obtained following the sol-gel synthesis route after

drying at 110°C. The structure and thermal behaviour were investigated by X-ray diffraction, thermogravimetric and differential thermal analyses.

V. Simon, S. Simon, M. Prinz, M. Neumann, H. Mocuta, E. Vanea

Synthesis and surface characterisation of biomaterials functionalised in protein enriched simulated body fluids.

Studia – Physica, LIII, 1, 25-32 (2008)

Iron containing aluminosilicate systems are investigated as potential biomaterials for hyperthermia. The samples were obtained following a sol-gel route. The X-ray diffraction data show for the heat treated samples the crystallisation of both hematite and magnetite crystals. The Fe 2p core level photoelectron spectrum confirmed the occurrence of iron ions both in Fe² and Fe³ valence states. The sample surface was functionalised in Kokubo simulated body fluid enriched with bovine serum albumin. The attachment of the protein was proved by X-ray photoelectron spectroscopy.

E.S. Vanea, V. Simon

EPR Study of Radiation Induced Paramagnetic Species in Aluminosilicate Compounds

Studia – Physica, LIII, 2, 389 (2008)

Electron paramagnetic resonance (EPR) spectroscopy was used to characterize paramagnetic centres occurring in gamma ray irradiated aluminosilicate systems containing rare earth and/or iron that may be used for biomedical applications. The investigated samples were obtained following the sol-gel route. After drying at 110°C the samples were heat-treated at 500°C or 1200°C. Usually the sterilisation of such biomedical compounds is realized with gamma rays. For this reason the samples were gamma irradiated and investigated with respect to possible occurrence of nocuous irradiation effects. The EPR studies demonstrate that various radiation-induced defects, like surface defects and peroxy-centres, are present in the analysed systems. A higher concentration of defects was detected for samples treated at 500°C, as compared to samples treated at 1200°C.

M.Tamasan, S. Simon, M. Baciut, G. Baciut, V. Coman, V. Simon

Thermal investigation of nanocrystalline bone phases

Studia – Physica, LIII, 2, 9-16 (2008)

The present study was carried out with the intention of thermally analyse bone samples of different origins and of determining heat treatment temperatures proper for developing a method to obtain hydroxyapatite (HAP) powder usable for biomedical applications. Bones studied here were deer antler, human skull, cattle, pig, fish, hen and turkey. The results show that the removal of the organic matrix can be achieved by heat treatments applied above 500°C. At the same time it was evidenced that the organic matrix has sensibly different content in the investigated samples, depending on the bone nature.

Conference communications:

1. V. Simon, S. Cavalu, M. Prinz, E. Vanea, M. Neumann, S. Simon
Albumin adsorption on the surface of iron containing aluminosilicates
14-th Swiss Conference on Biomaterials, May 8, 2008, Basel, Elveția
2. S. Cavalu, V. Simon, F. Banica
Structural investigation and biocompatibility evaluation on dysprosium-iron-aluminosilicate sol-gel derived systems
1st Portuguese-Spanish-British Joint Biophysics Congress, 10-13th July 2008, Lisbon, Portugal
3. V. Simon, D. Lazăr, H. Mocuta, K. Magyari, M. Prinz, M. Neumann, S. Simon
Atomic environment in sol-gel derived nanocrystalline biomaterials
5th International Conference on Nanosciences & Nanotechnologies - NN08, 14-16 July 2008, Thessaloniki, Greece
4. D. Lazăr, S. Simon, K. Magyari, V. Simon
Effects of synthesis conditions on bioactivity of implant nanostructured materials
5th International Conference on Nanosciences & Nanotechnologies - NN08, 14-16 July 2008, Thessaloniki, Greece
5. S. Cavalu, V. Simon, F. Banica
Dysprosium/iron aluminosilicate for simultaneous radiotherapy and hyperthermia: structural investigation and biocompatibility evaluation
XXIX European Congress on Molecular Spectroscopy, EUCMOS, August 31-September 5, 2008, Opatija, Croatia
6. E. S. Vanea, V. Simon
EPR Study on Paramagnetic Species Induced in Aluminosilicate Compounds by Gamma Ray Irradiation
22nd General Conference of the Condensed Matter Division of the European Physical Society, 25-29 August 2008, Roma, Italia
7. S. Cavalu, F. Banica, V. Simon
Comparison between nanostructured aluminosilicate systems with yttrium/dysprosium and iron: structural investigation and biocompatibility evaluation
3-rd Conference on Advanced Spectroscopies on Biomedical and Nanostructured Systems, 7-10 September 2008, Cluj-Napoca, Romania
8. K. Magyari, M. Prinz, M. Neumann, V. Simon
Spectroscopic studies on osteoconductive biomaterials
3-rd Conference on Advanced Spectroscopies on Biomedical and Nanostructured Systems, 7-10 September 2008, Cluj-Napoca, Romania

9. V. Simon, D. Lazar, R.V.F. Turcu, H. Mocuta, S. Simon, M. Prinz, M. Neumann
Spectroscopic evidence of atomic environment changes in nanocrystalline biomaterials
3-rd Conference on Advanced Spectroscopies on Biomedical and Nanostructured Systems, 7-10 September 2008, Cluj-Napoca, Romania

10. E. Vanea, V. Simon
EPR evidence of paramagnetic defects in nanostructured sol-gel derived aluminosilicates compounds
3-rd Conference on Advanced Spectroscopies on Biomedical and Nanostructured Systems, 7-10 September 2008, Cluj-Napoca, Romania

11. V. Simon, C. Popa, D. Eniu, S. Cavalu, R. Stefan, D.T. Eniu
Nanostructured composites designed for simultaneous radiotherapy and hyperthermia
3-rd Conference on Advanced Spectroscopies on Biomedical and Nanostructured Systems, 7-10 September 2008, Cluj-Napoca, Romania

12. C. Mirestean, R.V.F. Turcu, H. Mocuta, S. Simon
Structural characterization of hydroxyapatites before and after simulated body fluid soaking
3-rd Conference on Advanced Spectroscopies on Biomedical and Nanostructured Systems, 7-10 September 2008, Cluj-Napoca, Romania

13. M. Todea, M. Tamasan, H. Mocuta, O. Ponta, F. Turcu, S. Simon
Structure of silica and silica-aluminium sol-gel microspheres
3-rd Conference on Advanced Spectroscopies on Biomedical and Nanostructured Systems, 7-10 September 2008, Cluj-Napoca, Romania

14. K. Magyari, L. Urcan, V. Simon
Behaviour of iron containing aluminosilicate systems in simulated body fluids
Fourth Balkan Conference on Glass Science and Technology, 27 Sept. – 1 Oct. 2008, Varna, Bulgaria

15. V. Simon, C. Popa, D. Eniu, S. Cavalu, R. Stefan, D.T. Eniu
In vitro and in vivo behaviour of composite biomaterials for simultaneous radiotherapy and hyperthermia
International Conference “Biomaterials & Medical Devices” BiomMedD’2008, 13-16 November 2008, Bucharest, Romania