**EULA-NETCERMAT**
**SEVENTH FRAMWORK PROGRAMME**

# FIRST YEAR REPORT AND WORKING PLAN OF INTEMA

**OCTOBER 2012 – NOVEMBER 2013**

**Full Title:** EULANETWORK IN CERAMIC MATERIALS WITH ENVIRONMENTAL AND INDUSTRIAL APPLICATIONS
**Acronym:** EULA-NETCERMAT
**Proposal Number:** 295197
**Grant Agreement Number:** PIRSES-GA-2011-295197
**Duration of the project:** 48 months
**Starting date:** 1-10-2012
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## I. Secondments until September 2014

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| **Pablo Botta**: | October - December 2013 (ICMAB/UAB) |
| Miriam Castro: | 2015 |
| **Alejandra Fanovich**: | September - November 2013 (ICMAB) (two months) |
| Rodrigo Parra: | July - September 2014 (KTH) (two months) |
| Sergio Pellice: | July - September 2014 (KTH) (two months) |
| **Raúl Procaccini**: | September - December 2013 (KTH) (four months) |

## II. Activities developed to date

### II.1. Biocide sol-gel coatings

In recent works, held at INTEMA, we had investigated silver doped sol-gel coatings obtained from tetraethoxysilane (TEOS), methyl-trimethoxysilane (MTES) and 3-glycidoxypropiltrimethoxysilanes (GPTMS). Silver was added to the sol by mean of an alcoholic solution of silver nitrate stabilized to obtain biocide activity. The main obtained results are:

Colorless and highly stable sols, without gelling, neither precipitations nor loosing of transparency for more than two weeks of cold storage were observed.

UV-visible spectroscopy tests showed the presence of intense bands at 275 and 310 nm attributed respectively to $(Ag_4)^{2+}$ and $(Ag_2)^{+}$ clusters in the sols. Also, the UV-visible technique revealed the presence of an extremely weak plasmonic band at 420 nm indicating the development of silver nanoparticles.

X-ray fluorescence tests (XRF) showed that silver remains into the coatings after the deposition process and the thermal treatment of samples and that silver ions were steadily released from the hybrid coatings during the firsts two months of immersion in water at 30°C. $Ag^{+}$ ions present in coatings are able to migrate through diffusion processes.

Small Angle X-ray Scattering (SAXS experiments performed in the National Laboratory of Synchrotron Light, LNLS-Campinas, Brazil), revealed the presence of silver sub-nanometric clusters and higher nanoparticles.

Transmission electron microscopy verified the presence of spherical silver nanoparticles whose size distribution is highly dependent of the thermal treatment. Images were analyzed extracting the size distribution of particles using techniques of digital image processing. An algorithm for detection and measurement of the diameter of these particles was developed.

Biocide tests by mean of inhibition halos on *Escherichia coli* cultures on agar and of silver release in water indicated the tight relationship existing between the size of silver particles, the chemistry of the matrix and the biocide activity of the synthesized coatings at medium and long-term.

All the obtained results in this research line led to the following works:

- R.A. Procaccini, C.A. Studdert, S.A. Pellice. *Silver doped silica-methyl hybrid coatings. Structural evolution and antibacterial properties*. *Surface and Coatings Technology* [*Sent 02/2013*]
- Procaccini R.A., Pellice S.A. *Silver doped silica-methyl hybrid coatings. Structural evolution and antibacterial properties*. LNLS 2011 Activity Report. ABTLuS / Brazilian Synchrotron Light Laboratory, Editora Cubo. ISSN: 1518-0204.
- R. Procaccini, S. Pellice. *Evolución térmica de recubrimientos híbridos sílice-epoxi dopados con plata*. XVIII Congreso Argentino de Fisicoquímica y Química Inorgánica. 9-12 de Abril de 2013, Rosario, Argentina.
- Raul A. Procaccini, Sergio A. Pellice. *Thermal evolution of silver doped silica-epoxy hybrid coatings*. XVII International Sol-Gel Conference. 25-30 de Agosto de 2013, Madrid, España.

II.2. *Preparation and characterization of hydroxyapatite and polycaprolactone nano and micro composites for tissue engineering*.

Name: *María Alejandra Fanovich*

Institution of Origin: *Instituto de Investigaciones en Ciencia y Tecnología de Materiales (INTEMA)*

Institution of Destination: *Institut de Ciència de Materials de Barcelona (ICMAB)*

Starting date and duration of the secondment: 2/9/2013, two months.

Main research issue covered by the Exchange:

- Objectives: (initial specific objectives).

1) To cooperate in the methodology of synthesis and processing of ceramic-polymer composite materials for tissue engineering applications.

2) To develop a procedure for increase the ceramic load into the porous devices.

3) To study the effect of cosolvents in the foaming of nano and micro composites of HA and PCL for scaffolds production by using supercritical fluids technology.

- Activities: (report of the activities developed during your stay). **Please, specify training and R&D knowledge transfer activities performed concerning advanced ceramics synthesis, characterization and application**

The tasks performed in these two months were focused on the preparation and characterization of composite materials from synthesized materials in INTEMA and those provided by ICMAB:

- Preparation of suspensions of hydroxyapatite in polycaprolactone solution with diferent %wt/wt of nano and micro powders.
- Processing of composites by supercritical carbon dioxide. Effect of temperature, time, cosolvent (ethyl lactate and ethyl acetate) and procedure for adding the cosolvent (in the reactor and in the material like dough) according to the following scheme:

| Test | Sample composition | Blowing agent | Sample preparation | Saturation time [h] | Temperature [°C] | Pressure [MPa] |
|---|---|---|---|---|---|---|
| 1 | PCL<br>PCL-HA-M (5,10%)<br>PCL-HA-N (5,10%) | $CO_2$ | Disc | 1 | 40 | 20 |
| 2 | PCL<br>PCL-HA-M (5,10%)<br>PCL-HA-N (5,10%) | $CO_2$ | Disc | 1 | 45 | 20 |
| 3 | PCL<br>PCL-HA-M (5,10%)<br>PCL-HA-N (5,10%) | $CO_2$+EL | Disc | 1 | 40 | 20 |
| 4 | PCL<br>PCL-HA-M (5,10%)<br>PCL-HA-N (5,10%) | $CO_2$+EL | Disc | 1 | 45 | 20 |
| 5 | PCL<br>PCL-HA-M (5,10%)<br>PCL-HA-N (5,10%) | $CO_2$+EA | Disc | 1 | 40 | 20 |
| 6 | PCL<br>PCL-HA-M (5,10%)<br>PCL-HA-N (5,10%) | $CO_2$+EA | Disc | 1 | 45 | 20 |
| 7 | PCL<br>PCL-HA-M (5,10%)<br>PCL-HA-N (5,10%) | $CO_2$+EL | Mix + Disc | 1 | 40 | 20 |
| 8 | PCL<br>PCL-HA-M (5,10%)<br>PCL-HA-N (5,10%) | $CO_2$+EL | Mix + Disc | 1 | 45 | 20 |
| 9 | PCL<br>PCL-HA-M (5,10%)<br>PCL-HA-N (5,10%) | $CO_2$+EA | Mix + Disc | 1 | 40 | 20 |
| 10 | PCL<br>PCL-HA-M (5,10%)<br>PCL-HA-N (5,10%) | $CO_2$ | Disc | 17 | 45 | 20 |
| 11 | PCL<br>PCL-HA-M (5,10%)<br>PCL-HA-N (5,10%) | $CO_2$+EL | Disc | 17 | 45 | 20 |
| 12 | PCL<br>PCL-HA-M (5,10%)<br>PCL-HA-N (5,10%) | $CO_2$+EA | Disc | 17 | 45 | 20 |
| 13 | PCL<br>PCL-HA-M (5,10%)<br>PCL-HA-N (5,10%) | $CO_2$+EL | Mix + Disc | 17 | 45 | 20 |
| 14 | PCL<br>PCL-HA-M (5,10%)<br>PCL-HA-N (5,10%) | $CO_2$+EA | Mix + Disc | 17 | 45 | 20 |

The discussion of the obtained results of this work is underway. The first results will be presented in the *III Reunión Interdisciplinaria de Tecnología y Procesos Químicos* – RITeQ 2014, Los Cocos, Córdoba, Argentina.

- **Have objectives been fulfilled?:** (difficulties and facilities to fulfill initial objectives. If any deviations occurred please, refer here).
  Yes.

- **State of the art and needs**, identifying the existing requirements and potentials in academia and industry at both EU and LA concerning MACs.
  A variety of polymer/ceramic composites have gained much recognition as scaffolds for bone tissue engineering not only due to their composition and structural similarity with natural bone, but also because of their functional unique properties. Ceramic phase increase the mechanical properties of the resulting composites, being suitable for orthopaedic applications. Moreover, the bonelike inorganic phase influences the general properties of many synthetic polymers.
  To study and improve the processing of foamed ceramic-polymer systems by supercritical fluids solvents is key to progress in the mass production of these materials, avoiding the use of organic solvents.

- **Methods for co-creating innovation on modern advanced ceramics (MACs)** applied to environment, health and aeronautics.

II.3. Nanostructured Electroceramics

- Epoxy/$BaTiO_3$-fibers composites

Composite materials made of epoxy resin and barium titanate ($BaTiO_3$, BT) electrospun nanostructured fibers were prepared. BT fibers were synthesized from a *sol* based on barium acetate, titanium isopropoxide, and poly(vinyl pyrrolidone). Mats of BT fibers heat-treated at 800° C (Fig. 1) were embedded in epoxy resin into suitable molds. The composites were characterized by SEM, and dielectric measurements were performed by means of dielectric spectroscopy. The dielectric permittivity and dielectric modulus of epoxy resin/BT-fiber composites were measured for two types of samples: with the electrodes parallel and perpendicular to the BT fiber layers. Interestingly, composite samples with electrodes perpendicular to the fiber layers and a BT content as low as 2 vol. % led to dielectric permittivities 3 times higher than that of pure epoxy resin.

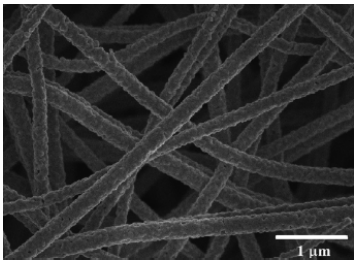


**Figure 1.** FE-SEM image of PVP/BT fibers heat-treated at 800° C.

- Transparent conducting oxide films

Transparent conducting $SnO_2$ films were deposited by spray-pyrolysis on glass slides. Films were calcined at 500° C and, afterwards, heat treated in a 5% $H_2$ atmosphere in order to decrease the electrical resistivity. Scanning electron microscopy showed 1μm, approximately (Fig. 2) thick films, whose sheet resistance was 600 Ω/sq. After a heat-treatment under reducing atmosphere a 2 Ω/sq sheet resistance was measured.

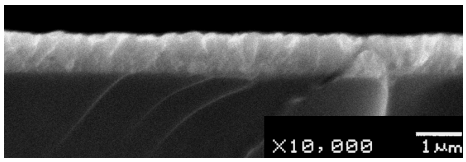


**Figure 2.** SEM image of a conducting $SnO_2$ film.

- Hierarchically structured porous films

On the other hand, low resistivity $TiO_2$-based films with oriented porosity were synthesized. Titanium dioxide (Degussa P25) aqueous dispersions were prepared with the addition of PVP. Films were deposited on alumina substrates by a dr. blade technique and were immediately dipped (vertically) into liquid $N_2$ at controlled rate for directional freezing. After lyophilisation, films were heat-treated at 1050° C in a 5% $H_2$ atmosphere in order to obtain electrically conducting titanium oxide Magnéli phases. X-Ray Diffraction analysis of the resulting blue/black films showed patterns associated with a mixture of Magnéli phases, mainly $Ti_9O_{17}$ (JCPDS 50-0791) among traces of $Ti_4O_7$, $Ti_5O_9$, $Ti_6O_{11}$ and $Ti_7O_{13}$. Resistance values of about 3 kΩ were measured within a distance of 1 cm, along the freezing direction, in ~2 μm-thick films. These films may find application in residual water purification.

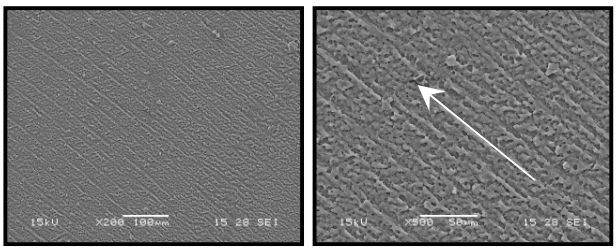

**Figure 3.** SEM surface images showing the film orientation along freezing direction.

- Lead-free piezoelectric ceramics

The effect of sintering temperatures on the microstructure, secondary phase formation and electric properties of $Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5}TiO_3$ (BNKT)-based ceramics obtained by the conventional mixed oxide method was studied. Ceramic powders were prepared by the solid state reaction method using a previous mecanochemical activation

step of reagents. The formation of main perovskite type structure and a secondary phase with a composition close to $K_{2-x}Na_xTi_6O_{13}$ were detected. It was observed that when the sintering temperature was increased, the secondary phase content increased. Interestingly, this secondary phase improved the piezoelectric properties and the remnant polarization of these ceramics.

**III. Working Plan until September 2014**

III.1. Biocide sol-gel coatings

- To develop silver doped sol-gel coatings introducing montmorillonite-like silicate (Laponite) inside the hybrid matrix in order to achieve an optimal release rate of the biocide agent through the coating.

III.2. Preparation and characterization of hydroxyapatite and polycaprolactone nano and micro composites for tissue engineering

- To study the angiogenic effects of the actives (growth factors VEGF and / or bFGF) released from nanostructured composite materials. (Zebrafish embryos -*Danio rerio*- will be used for these tests because of their advantage as an experimental alternative model *in vivo* compared to current models).
- To study and improve the processing of foamed ceramic-polymer systems by supercritical fluids solvents is key to progress in the mass production of these materials, avoiding the use of organic solvents.

III.3. Nanostructured electroceramics

- To determine the structural change that gives rise to the electrical transition in $Bi_xLa_{1-x}FeO_3$ using refinements of diffraction data.
- To determine the relationship between dielectric, structural and microstructural properties of lead-free piezoelectric ceramics corresponding to the $Bi_{0.5}(Na_{0.78}K_{0.22})_{0.5}TiO_3$ system.
- Doped $BaTiO_3$ fiber will be prepared in order to improve the electrical response of BT-epoxy composites.
- The electrical properties of freeze dried low resistivity $TiO_2$-based films will be characterized along and perpendicularly to the grooves, and compared with those of non-patterned films (not freeze dried), in order to establish the influence of the microstructural anisotropy on such properties.