# Publications Ana C. Marques



## PAPERS

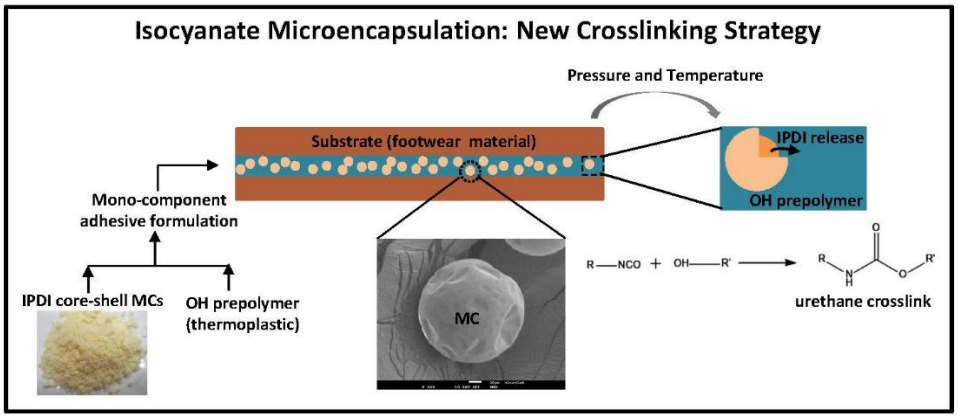
A37 - Mário Vale, Maria Margarida Mateus, Rui Galhano dos Santos, Carlos Nieto de Castro, Aster de Schrijver, João C. Bordado and Ana C. Marques, “Replacement of petroleum-derived diols by sustainable biopolyols in one component polyurethane foams”, Journal of Cleaner Production, 212 (2019) 1036-1043; doi: https://doi.org/10.1016/j.jclepro.2018.12.088

This work reports on the development of eco-innovative and high performance one component polyurethane foams, originated from biopolyols, which were obtained from liquefaction of biomass, industry by-products, namely cork powder and eucalyptus bark. This effort consists of a cleaner production methodto enable more sustainable materials and industry by-products valorisation, but also a reduction of the dependency on fossil oil derivatives. Low-value industrial cork powder and eucalyptus bark shreds were successfully liquefied into polyols, by a process based on acid-catalysed liquefaction, at atmospheric pressure, with conversion ratios up to 79%. The obtained biopolyols exhibited low acid values (1 mg KOH/g) and relatively high hydroxyl numbers (197–272 mg KOH/g) and were introduced into one component polyurethane formulations, fully replacing the petroleum-derived polyether and polyester diols in the formulation. The resultant rigid polyurethane foams exhibited a high output (16 g/s) and acceptable physical quality, assessed by optical and scanning electron microscopy. Their chemical structure, mechanical and thermal properties were evaluated through Fourier Transformed infrared spectroscopy, compression mechanical testing and thermogravimetric analysis, respectively.


A36 - Mahboobeh Attaei, Mónica V. Loureiro, Mário Vale, José A. D. Condeço, Isabel Pinho, João C. Bordado and Ana C. Marques, “Isophorone Diisocyanate (IPDI) Microencapsulation for Mono-

Component Adhesives: Effect of the Active H and NCO Sources", Polymers, 10(8) (2018) 825-841; doi:10.3390/polym10080825

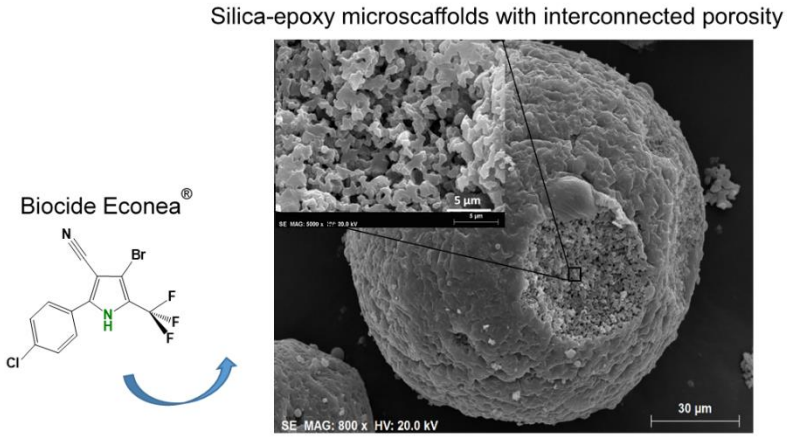
Polyurea/polyurethane (PUa/PU) shell microcapsules (MCs), containing high loadings of isophorone diisocyanate (IPDI) in the core, were developed to enable the production of mono-component, eco-friendly and safer adhesive formulations for the footwear industry. IPDI microencapsulation was obtained via oil–in–water (O/W) microemulsion combined with interfacial polymerization. A methylene diphenyl diisocyanate (MDI) compound (a commercial blend of monomeric and polymeric species), with higher reactivity than IPDI and low viscosity, was added to the O phase to competitively contribute to the shell formation, improving its quality. Four different active H sources were tested, aimed at achieving a high encapsulation yield. The successful encapsulation of IPDI was confirmed by Fourier transformed infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA), while the MCs' morphology and size distribution were assessed by scanning electron microscopy (SEM). The incorporation of a multifunctional isocyanate silane in the O phase, as "latent" active H source, led to the formation of impermeable PUa/PU-silica hybrid shell MCs with more than 60 wt.% of pure encapsulated IPDI. A proof-of-concept study shows high peeling strength and a structural type of failure of the adhesive joint, revealing an effective IPDI release. These new engineered MCs are found to be promising crosslinkers for mono-component adhesives for high demanding applications.




A35 - Mónica V. Loureiro, Mário Vale, Aster De Schrijver, João C. Bordado, Elisabete Silva, Ana C. Marques, "Hybrid custom-tailored sol-gel derived microscaffold for biocides immobilization", Microporous and Mesoporous Materials, 261 (2018) 252 - 258. DOI: https://doi.org/10.1016/j.micromeso.2017.10.056
https://www.sciencedirect.com/science/article/pii/S1387181117307199?via%3Dihub

The present paper regards the development of silica-epoxy matrices, in the form of functional spherical microscaffolds with controlled morphology, comprising an immobilized biocide, for antifouling purposes. The microscaffolds herein presented were obtained from sol–gel processing combined with a microemulsion technique, using as Si precursors, tetraethylorthosilicate (TEOS) and 3-glycidyloxy propyl trimethoxysilane (GPTMS) to be further loaded with biocide Econea®, which has been approved in 2014 by EU Regulator (BPR) as a safe biocide. Biocide immobilization is proposed to be carried out by chemical grafting mainly between the microscaffolds' oxirane ring and the secondary amino groups of the biocide

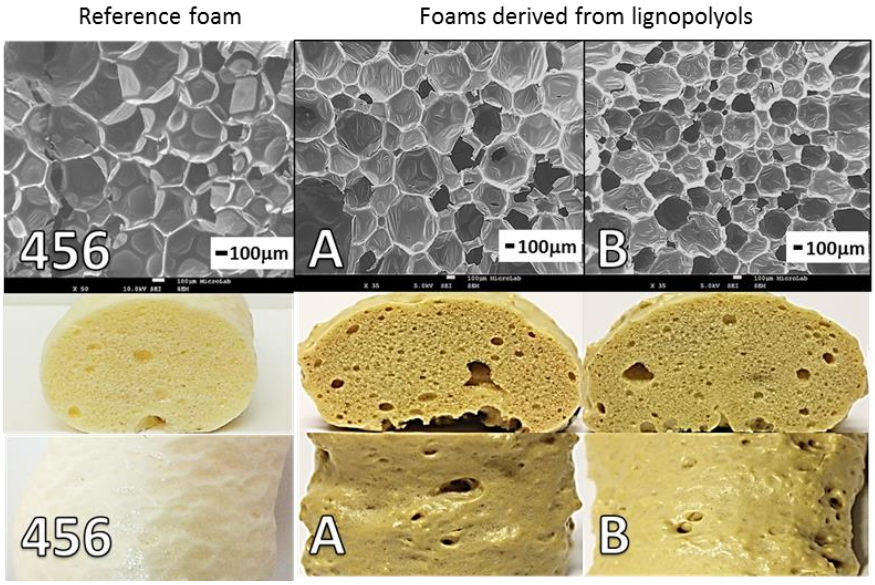
Econea®, as well as by physical entrapment within the “worm-like” morphology and multimodal pore size distribution of the microscaffolds. The presence of Econea® within the microscaffolds was confirmed by Fourier transformed infrared spectroscopy (FTIR), thermogravimetric analyses and scanning electron microscopy (SEM-EDX) and it was found to be nearly constant over the time when those are immersed in artificial seawater, while under mild agitation. The biocidal effect of the Econea® loaded silica-epoxy spherical microscaffolds was assessed by microbiological tests, exhibiting an effective activity against Staphylococcus aureus bacteria, by contact mode, even after exposure to turbulent saline water. These microscaffolds were designed for enabling a more environmental friendly anti-fouling strategy, able to combine a more efficient, long-lasting antifouling performance for water-immersed applications, together with non-toxic properties, being, therefore, a promising and attractive alternative to the actual conventional releasing strategies.



Impregnation and grafting for antifouling performance by contact

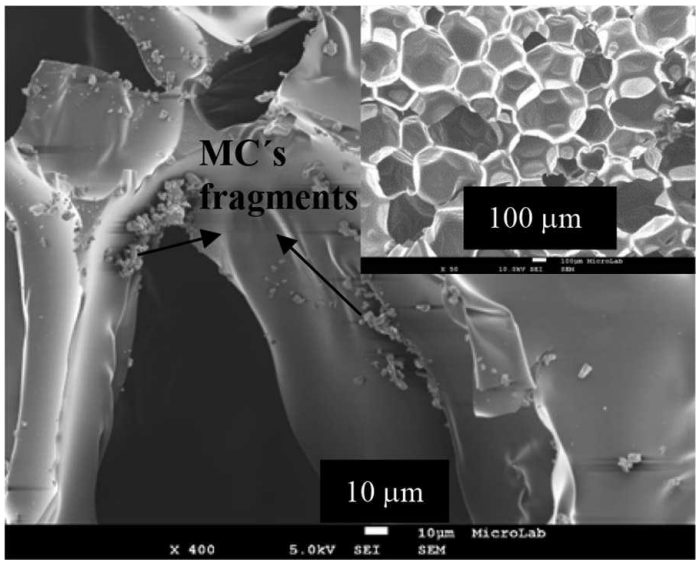
A34 - Rui G. dos Santos, Noemi F. Acero, Sandro Matos, Ricardo Carvalho, Mário do Vale, Ana C. Marques, João C. Bordado, Maria Margarida Mateus, Pursuing Eco-Friendly Materials”, Journal of Polymers and the Environment, 26 (2018) 91-100. DOI: 10.1007/s10924-016-0931-z https://link.springer.com/article/10.1007/s10924-016-0931-z?no-access=true

The use of petroleum-derived products should be avoided regarding the principles of green and sustainable chemistry. The work reported herein, is aimed at the liquefaction of pine shavings for the production of an environmentally-friendly polyol suitable to be used in the formulations of sprayable polyurethane foams. The biopolyols were obtained in high yield and were used to replace those derived from fossil sources, to produce more “greener” polyurethane foams and therefore, less dependent on petroleum sources, since the polyol component was substituted by products resulting from biomass liquefaction. The partial and fully exchange of the polyols was accomplished, and the results compared with a reference foam. The foams were afterward, chemical, physical, morphological, and mechanically characterized. The complete replacement of polyether polyol and polyol polyester has presented some similar characteristics as that used as a reference, validating that the path chosen for the development of more sustainable materials is on the right track for the contribution to a cleaner world.



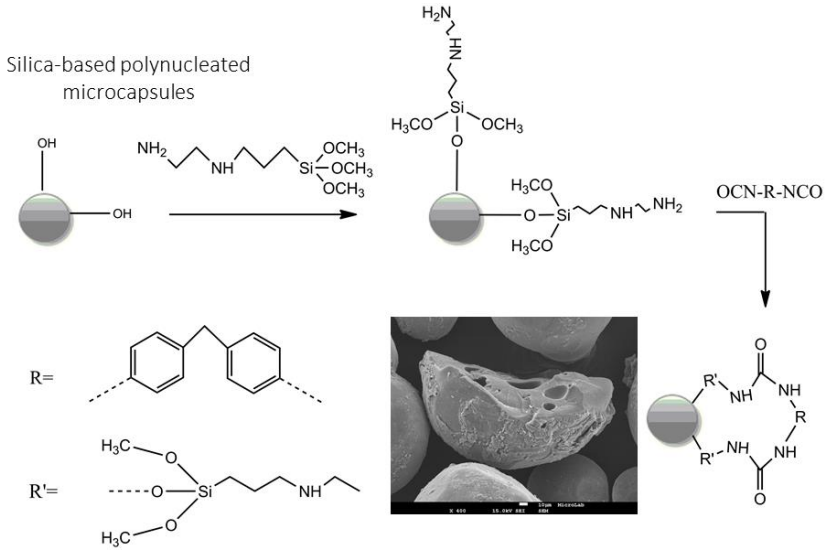

A33 - Ana C. Marques, Mónica V. Loureiro, Maria José Lourenço, Aster De Schrijver, João C. Bordado, “Amino Surface Functionalized Microcapsules as Curing Agents for Polyurethane Foams”, Materials and Manufacturing Processes 32 (11) (2017) 1304-1309 DOI: 10.1080/10426914.2017.1291950. (Q1)
http://www.tandfonline.com/doi/abs/10.1080/10426914.2017.1291950

This work regards the manufacturing process and assessment of amino surface functionalized microcapsules (MCs) containing glycerol in their core, for application in one-component polyurethane (PU) foams to act as a sustainable curing catalyst. Microemulsion techniques combined with sol–gel processing, involving the development of specific steps during the synthesis, were found to enable this type of functional active microparticles. The MCs should only burst and release their content at the spraying stage, in order to assist and promote an accelerated curing of the foam. It has been found that the surface treatment employed in the last step of inorganic silica MCs synthesis procedure, using an amino silane, led to the best curing performance for PU foams. In fact, the amino functionalized MCs exhibited a more perfect spherical format and less aggregation than the inorganic MCs, did not exhibit significant leaching, and led to a significant increase in the curing rate of the PU foam. The study involved characterization techniques, such as scanning electron microscopy, Fourier transformed infrared spectroscopy, thermal gravimetric analyses, leaching, and curing speed evaluation.



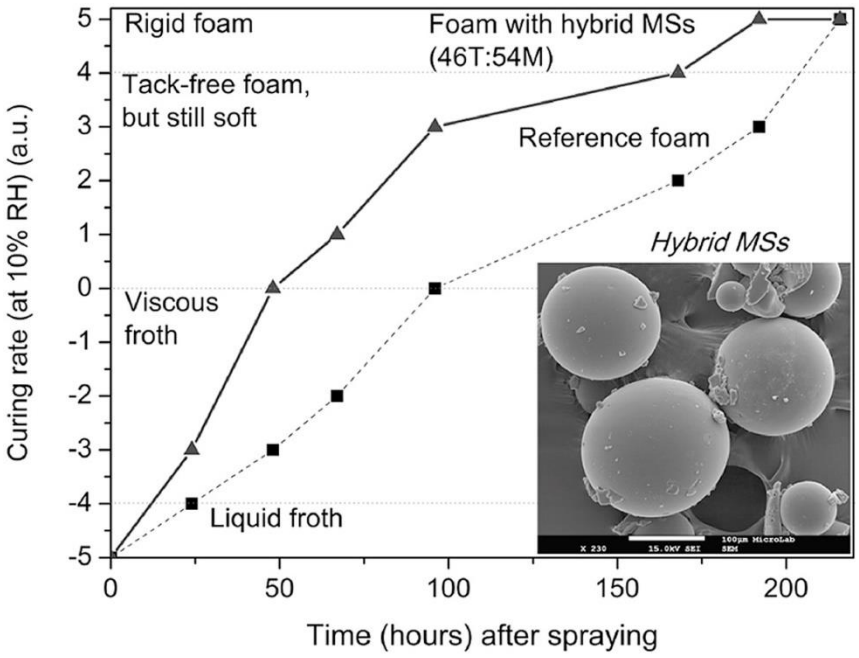

A32 - Mónica V. Loureiro, Maria José Lourenço, Aster De Schrijver, Luís F. Santos, João C. Bordado, Ana C. Marques, "Amino-silica microcapsules as effective curing agents for polyurethane foams", Journal of Materials Science, 52 (9) (2017) 5380–5389. DOI: 10.1007/s10853-017-0782-6.
https://link.springer.com/article/10.1007/s10853-017-0782-6

The present paper regards the development of functional microcapsules (MCs), containing encapsulated glycerol, to act as sustainable solid curing agents for one-component polyurethane (PU) foams. They consist of silica-based MCs with an aminosilane surface treatment, obtained through sol–gel processing technique. These MCs are intended to burst and release their content only at the spraying process, in order to promote an accelerated curing of the PU foam. The superficial amino groups react with the isocyanate groups present in the PU pre-polymer, producing polyurea moieties on the MCs' surface, which prevents the leaching of encapsulated glycerol inside the PU aerosol can. This enables the long shelf life of the product, required for commercial application. The amino-silica MCs exhibit a perfect spherical shape, without significant leaching, in opposition to silica-based MCs and led to a significant increase in the curing rate of the PU foam. The study involved various characterization techniques, such as scanning electron microscopy, Fourier transformed infrared spectroscopy, thermogravimetric analyses, leaching and curing speed evaluation.




A31 - Mónica V. Loureiro, Rosaria Ciriminna, Maria José Lourenço, Luis F. Santos, Aster De Schrijver, João C. Bordado, Mario Pagliaro, Ana C. Marques, “Organically-modified silica based microspheres for self-curing polyurethane one component foams”, Microporous and Mesoporous Materials, 244 (2017) 244 - 250.
DOI: http://dx.doi.org/10.1016/j.micromeso.2016.10.039.
http://www.sciencedirect.com/science/article/pii/S1387181116305042

Hybrid organosilica microspheres (MSs) doped with aqueous glycerol are tested as enablers for self-curing polyurethane one-component foams (OCF). The MSs have been characterized by Scanning Electron Microscopy, Fourier Transformed Infrared Spectroscopy, Thermal Gravimetric Analyses and leaching test. Shaking rate, of the pre-polymer inside the aerosol can, and curing speed tests of the sprayed foam, in a low moisture environment, were performed in order to evaluate the effect of the MSs on the OCF can's lifespan, as well as their contribution to the PU foam's curing process. The organic functionality of these silica-based MSs (methyl and glycidyloxy groups) was found to be responsible for a reduced leaching and low water absorption tendency, which is critical for a longer shelf life of the product required for commercial applications. In addition, the methyl functional MSs presented a significant increase in the curing rate of the PU foam.




A30 - Ana C. Marques, H. Dias, S. Matos, B. Sargaço, R. Simões, A. De Schrijver, J.C. Bordado. "Polyurethane OCF Formulation Optimization for Low Free Isocianate Monomer Content". Journal of Cellular Plastics, 53 (2) (2017) 167–179 DOI: 10.1177/0021955X16639230
http://journals.sagepub.com/doi/abs/10.1177/0021955X16639230

Recent changes in legislation have forced one-component foam producers to drop the amount of free monomeric isocyanate in their polyurethane systems. Also, it is required that commercial polyurethane aerosol cans exhibit at least one year of shelf life and polyurethane foams must be classified as B2 on the fire testing following DIN 4102. This paper reports on a systematic optimization study of polyurethane formulations dedicated to address these current industry requirements. A one-component foam system exhibiting simultaneously all of these parameters was achieved by reacting conventional diols, a relatively low-molecular weight monol (2-ethylhexanol), a flame retardant high-molecular weight monol (tris(bromoneopentyl)alcohol), a methylene diphenyl diisocyanate-based prepolymer (GreenAdduct 13), and a small amount of 2,4'-toluene diisocyanate. The use of monols allows producing prepolymers with low free methylene diphenyl diisocyanate by preventing chain extension and, therefore, avoiding extreme viscosity build-up. Toluene diisocyanate also promotes a lower viscosity inside the aerosol can, which enables the use of high enough quantities of high-molecular weight flame retardant monol to achieve a B2 fire test

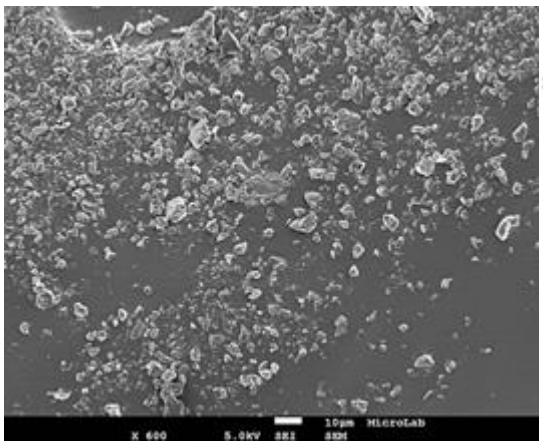
classification.

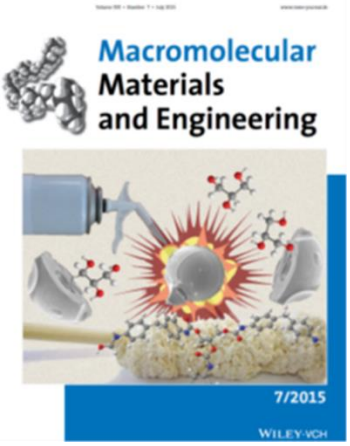
| Aerosol can sample | Output (g/s) | Flame resistance | fmMDI + fmTDI ±0.05 (%) | Foam quality |
|---|---|---|---|---|
| E (4% 2,4′-TDI and 3.8% 2-EH + 7.5% TBNPA + TCPP) | 11.0 | B2 (12 cm) | 0.73 (0.57 + 0.16) | Good |

TBNPA: tribromoneopentyl alcohol; TCPP: tris(2-chloro-1-methylethyl)phosphate; TDI: toluene diisocyanate; 2-EH: 2-ethyl hexanol.

A29 - Rosaria Ciriminna, Marzia Sciortino, Ana C. Marques, Aster De Schrijver, Joao C. Bordado, Mario Pagliaro, "Solid Curing Agents for Polyurethane Foams: Proof of Concept of the Release Mechanism", Macromolecular Materials and Engineering 300-7 (2015) 674-678 DOI: 10.1002/mame.201500072. (Q1) IF: 2.834
http://onlinelibrary.wiley.com/doi/10.1002/mame.201500072/abstract

We show the first evidence that the microporous GreenCaps organosilica microspheres, functionalized with glycerol and sprayed from a pressurized one component polyurethane foam completely break and release their functional payload, thereby noticeably increasing the rate and the extent of the foam's curing. Further positive results concerning the main froth parameters used by urethane foam manufacturers in the presence of the GreenCaps confirm the potential of these materials to cure better and greener spray polyurethane foams.

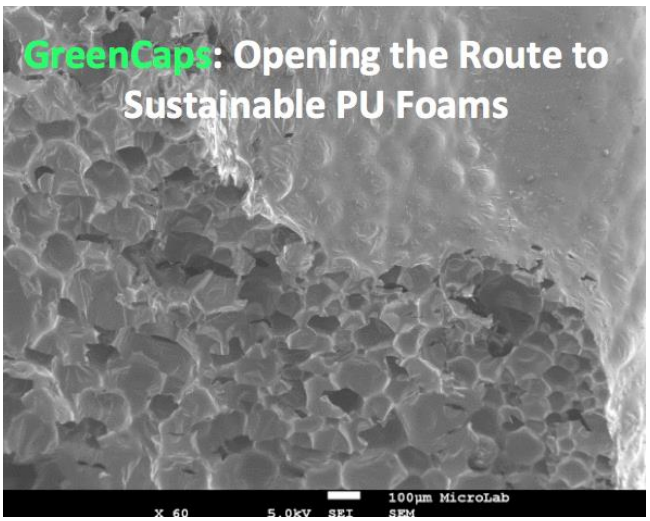





A28 - Rosaria Ciriminna, Ana C. Marques, João C. Bordado, Aster de Schrijver, Mario Pagliaro, "GreenCaps: Towards Solid Curing Agents for Sustainable Polyurethane Foams", Sustainable Chemical Processes 2 (2014) 24. (*open access*)
https://link.springer.com/article/10.1186/s40508-014-0024-z

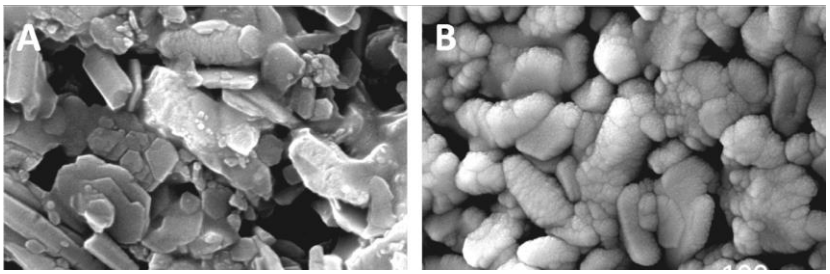
Testing and further investigation of organosilica microspheres functionalized with aqueous glycerol as solid curing agents for polyurethane (PU) foams confirms the potential of these materials to cure better and greener PU foams. The developed microspheres were found to be stable in the foam precursor mixture, allowing handling and mixing of the foam cans, and were shown to provide a slight improvement of the

curing speed. The foams obtained from the froth containing the microspheres were found to maintain the level of quality of reference foam samples. Termed “GreenCaps”, these microspheres will subsequently be tested in pre-commercial applications.



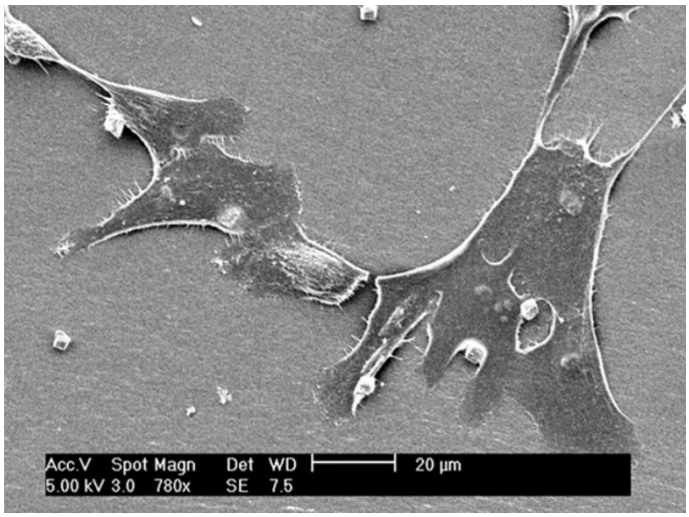

A27 - L. Gomes, A. Marques, A. Branco, J. Araújo, M. Simões, S. Cardoso, F. Silva, I. Henriques, C.A.T. Laia, C. Costa; “*IZO deposition by RF and DC sputtering on paper and application on flexible electrochromic devices*”, Displays 34 (2013) 326–333. DOI: 10.1016/j.displa.2013.06.004.
http://www.sciencedirect.com/science/article/pii/S0141938213000486

The present work describes indium-zinc oxide (IZO) sputtering depositions onto several types of papers, using radio-frequency (RF) and direct current (DC) sputtering with a ceramic IZO target. The electrical and optical properties of the resulting materials were optimized; by studying the argon and oxygen gas flow rates and the sputtering power effects. At optimal deposition conditions, thin films of IZO were achieved with a low sheet resistance (about 20 Ω/sq) and an optical transmittance of ca. 80% in the visible spectrum range. These materials retained these properties for more than 8 months. Electrochromic devices (ECDs) with several configurations were built with those conductive papers and life cycling and contrast were measured for the ECDs. These devices exhibited a very good color contrast (as defined using $L^*a^*b^*$ color coordinates, = 32) and electrochromic cyclability up to 30,000 redox cycles.



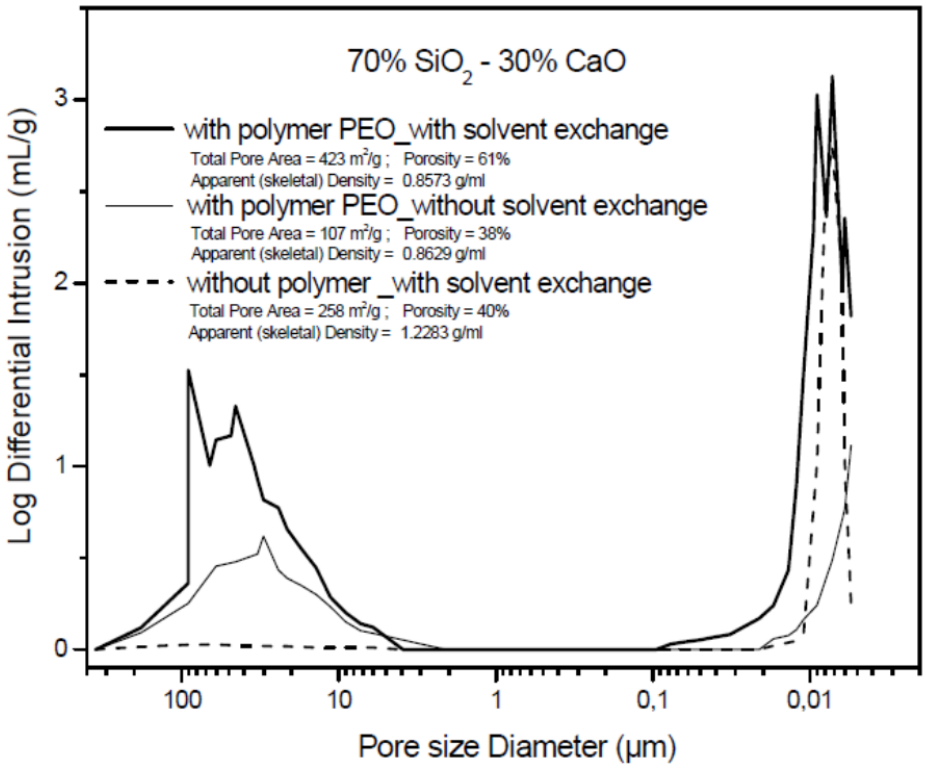
A26 - S. Wang, M. M. Falk, A. Rashad, M. M. Saad, A. C. Marques, R. M. Almeida, M. K. Marei and H. Jain, “Evaluation of 3D nano–macro porous bioactive glass scaffold for hard tissue engineering”, J Mater Sci: Mater Med 22 (2011) 1195–1203. DOI: 10.1007/s10856-011-4297-4
https://link.springer.com/article/10.1007/s10856-011-4297-4

Recently, nano–macro dual-porous, three-dimensional (3D) glass structures were developed for use as bioscaffolds for hard tissue regeneration, but there have been concerns regarding the interconnectivity and homogeneity of nanopores in the scaffolds, as well as the cytotoxicity of the environment deep inside due to limited fluid access. Therefore, mercury porosimetry, nitrogen absorption, and TEM have been used to characterize nanopore network of the scaffolds. In parallel, viability of MG 63 human osteosarcoma cells seeded on scaffold surface was investigated by fluorescence, confocal and electron microscopy methods. The results show that cells attach, migrate and penetrate inside the glass scaffold with high proliferation and viability rate. Additionally, scaffolds were implanted under the skin of a male New Zealand rabbit for in vivo animal test. Initial observations show the formation of new tissue with blood vessels and collagen fibers deep inside the implanted scaffolds with no obvious inflammatory reaction. Thus, the new nano–macro dual-porous glass structure could be a promising bioscaffold for use in regenerative medicine and tissue engineering for bone regeneration.



A25 - Ana C. Marques, Rui M. Almeida, Amath Thiema, Himanshu Jain, “Sol-gel derived glass scaffold with high pore interconnectivity and enhanced bioactivity”, J. Mater. Res. 24, No. 12 (2009) 3495-3502. DOI: 10.1557/jmr.2009.0440
https://www.cambridge.org/core/journals/journal-of-materials-research/article/solgelderived-glass-scaffold-with-high-pore-interconnectivity-and-enhanced-bioactivity/CC9EBEE3C0FA4D373D4D2AA4213BB9CF

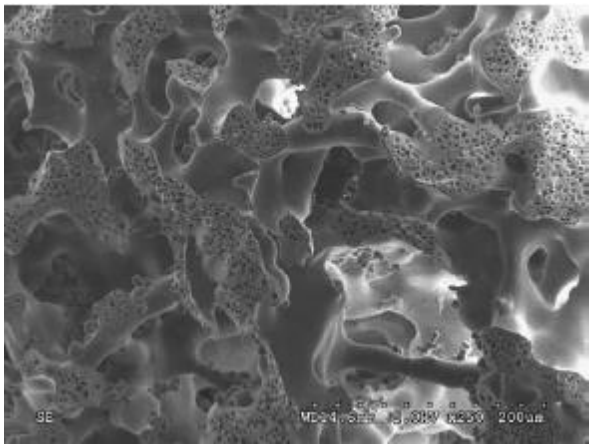
We report on the preparation of a bioactive CaO–SiO2 monolithic scaffold with interconnected bimodal nanomacro porosity, which simulates the morphology of a natural trabecular bone, by a newly developed modified sol-gel process. This method inherently creates nanopores, whose average diameter can be tailored to approximately 5–20 nm by solvent exchange. To achieve interconnected macroporosity (pores ~5–300 μm in size), a polymer [poly(ethylene oxide)] is added, which causes phase separation simultaneously with the sol-gel transition. High-resolution scanning electron microscopy and mercury intrusion porosimetry demonstrate a high degree of three-dimensional interconnectivity and sharp distributions of pore size. In vitro bioactivity tests in simulated body fluid (SBF) show bioactivity of the material after soaking for approximately 5 h, as verified by the formation of a hydroxyapatite layer deep into the scaffold structure. Analysis of the SBF after the reaction indicates the dissolution of the samples, another desired feature of temporary scaffolds for bone regeneration. MG63 osteoblast-like cells seeded on our sol-gel glass samples responded better to samples with nanopores enlarged by a solvent exchange process than to the one with normal nanopores. Thus, the benefits of the high surface area achieved by sol-gel and solvent exchange procedures are most clearly demonstrated for the first time.

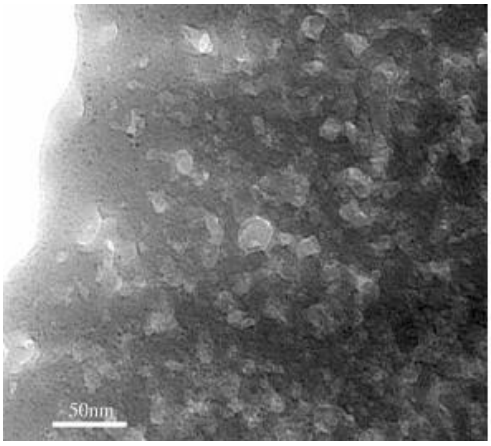



A24 - Ana C. Marques, Himanshu Jain, Carol Kiely, Kai Song, Christopher J. Kiely and Rui M. Almeida, "Nano/macroporous monolithic scaffolds prepared by the sol-gel method", Journal of Sol-Gel Science and Technology 51 (2009) 42–47. DOI: 10.1007/s10971-009-1960-z *(Q2)* 8 citações IF: 1.473
https://link.springer.com/article/10.1007/s10971-009-1960-z

Development of optimal scaffolds for bone tissue engineering and regeneration is still a challenge, since many materials and structures have been proposed but few have reached clinical expectations. This work reports on the preparation and characterization of $SiO_2$-CaO and $SiO_2$-CaO-$P_2O_5$ sol–gel derived monoliths, with potential application as glass scaffolds for bone regeneration, exhibiting a nano/macro trimodal pore size distribution, including pores of ~100's of micrometers (µm), several microns and just a few nanometers (nm) in size. Interconnected macropores (~20–200 µm) have been obtained in the present work by polymerization-induced spinodal phase separation along with the sol–gel transition, when a water soluble polymer [poly(ethylene oxide)] was added to the sol–gel solution; the several-micron pores are spherical and isolated and might be the result of secondary phase separation by nucleation-growth mechanism; the interconnected nanopore (~5–25 nm) structure of the macroporous gel skeleton, on the other hand, was tailored by solvent exchange procedures. The morphological and textural characterization of these materials was performed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray ultra microscopy (XuM), nitrogen adsorption and mercury intrusion

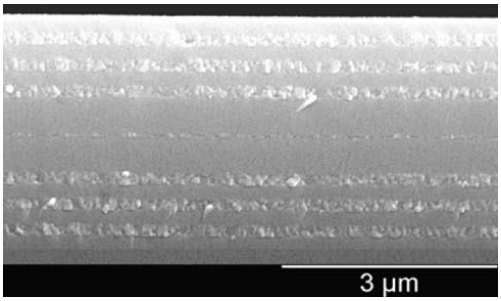
porosimetry. The factors affecting the porosity exhibited by the scaffolds, such as glass composition and solvent exchange conditions, have been assessed.

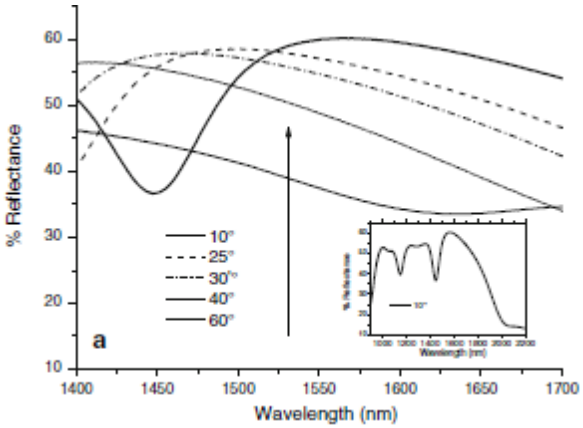





A23 - Rui M. Almeida and Ana C. Marques, "Rare-earth doped photonic crystals via sol-gel", Journal of Materials Science: Materials in Electronics, 20 (2009) 307 – 311. DOI: 10.1007/s10854-008-9596-2
https://link.springer.com/article/10.1007/s10854-008-9596-2

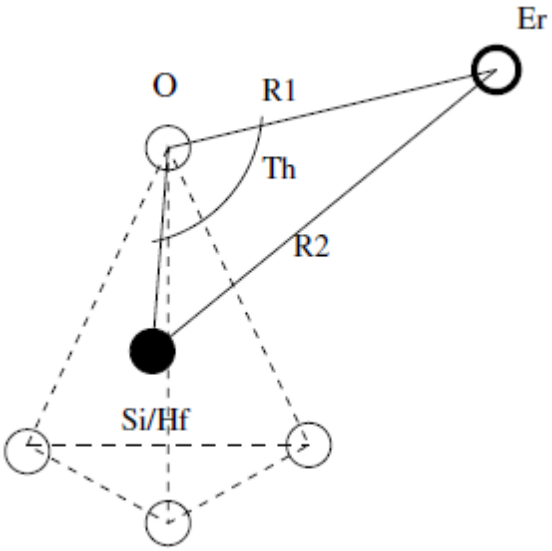
Erbium/ytterbium-doped photonic bandgap materials and structures have been prepared by sol–gel processing, in the form of 1-D structures of the single (Fabry–Perot) and coupled (double) microcavity types, consisting of multilayer stacks of silica and titania. Such multilayers were deposited by spin-coating on silica glass substrates and their reflection spectra were measured in the near infrared range. It was found that, by varying the detection angle, it is possible to broaden the $Er^{3+}$ emission at 1.5 µm, irrespective of the excitation wavelength (514.5 or 980 nm), which is important for applications where broadband emission is necessary, for example for all-optical amplification in dense wavelength division multiplexing (WDM) systems. A remarkable full width at half maximum (FWHM) of 52 nm was achieved for the $Er^{3+}$ emission peak at 1.5 µm, when this rare-earth (RE) dopant was incorporated in a pure silica glass cavity layer. Other described phenomena include $Er^{3+}$ photoluminescence enhancement from microcavities, compared with doped Bragg mirrors and films and enhanced $Yb^{3+} \rightarrow Er^{3+}$ energy transfer in co-doped photonic crystal structures.



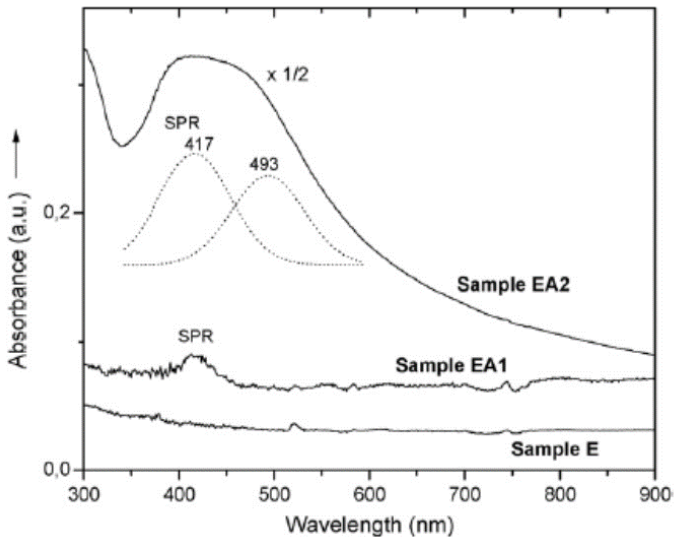

A22- Francesco d´Acapito, Ana C. Marques, Luis F. Santos, Rui M Almeida, "EXAFS study of the $Er^{3+}$ ion coordination in $SiO_2$-$TiO_2$-$HfO_2$ sol-gel films", Journal of Non-Crystalline Solids 354 (2008) 4940–4943. DOI: 10.1016/j.jnoncrysol.2008.07.008
http://www.sciencedirect.com/science/article/pii/S0022309308004808

The local order around ion-implanted $Er^{3+}$ ions in $SiO_2$–$TiO_2$–$HfO_2$ thin films prepared by sol–gel, was studied by extended X-ray absorption fine structure at the Er-$L_{III}$ edge. Both the first and second coordination shells of $Er^{3+}$ were analyzed for different heat-treatments. While the first coordination shell always consisted of ~6–7 oxygen atoms at distances varying between 2.23 and 2.27 Å, the structure of the second shell was found to vary with the film composition and heat-treatment. Namely, whereas Si was found to be the only second neighbor of erbium in binary $SiO_2$–$TiO_2$ films, the addition of $HfO_2$ caused a preferential replacement of Si by Hf. The post-implantation thermal treatments also played a fundamental role in determining the final environment of the erbium ions.



A21- Rui M. Almeida and Ana C. Marques, "The potential of ion-exchange in sol-gel derived photonic materials and structures", Materials Science and Engineering B 149 (2008) 118. DOI: 10.1016/j.mseb.2007.11.026
http://www.sciencedirect.com/science/article/pii/S0921510707006666

Sol–gel is a very convenient technique for the fabrication of high quality thin glass films, optical planar waveguides and photonic bandgap structures. Ion exchange, on the other hand, is a well-established technique to fabricate high quality waveguides in glass and integrated optical amplifiers made by this technique are commercially available. The possible integration of the sol–gel and ion-exchange techniques for the fabrication of passive and active (rare-earth doped) channel waveguides in integrated optic devices has recently gained interest. A general overview of the fabrication of passive and active films and planar waveguides by sol–gel is followed by a brief description of waveguide fabrication by ion exchange and the possible integration between the two processing technologies.



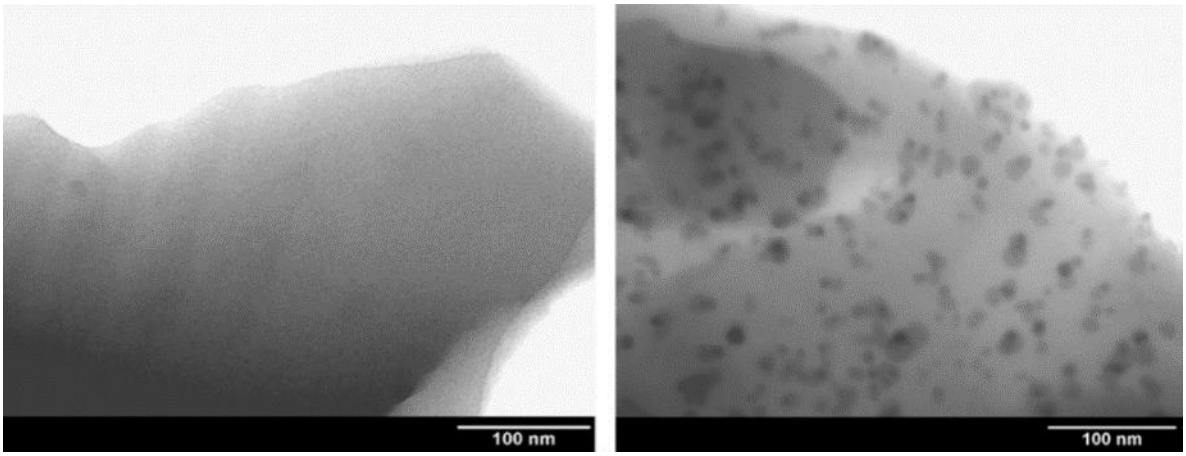

A20- Ana C. Marques, Himanshu Jain and Rui M. Almeida, "Sol-gel derived nano/macroporous monolithic scaffolds", European Journal of Glass Science & Technology Part B - Physics and Chemistry of Glasses 48 (2007) 65 – 68. EID: 2-s2.0-34250880773
https://link.springer.com/article/10.1007/s10971-009-1960-z

Development of optimal scaffolds for bone tissue engineering and regeneration is still a challenge, since many materials and structures have been proposed but few have reached clinical expectations. This work reports on the preparation and characterization of $SiO_2$-CaO and $SiO_2$-CaO-$P_2O_5$ sol–gel derived monoliths, with potential application as glass scaffolds for bone regeneration, exhibiting a nano/macro

trimodal pore size distribution, including pores of ~100's of micrometers (µm), several microns and just a few nanometers (nm) in size. Interconnected macropores (~20–200 µm) have been obtained in the present work by polymerization-induced spinodal phase separation along with the sol–gel transition, when a water soluble polymer [poly(ethylene oxide)] was added to the sol–gel solution; the several-micron pores are spherical and isolated and might be the result of secondary phase separation by nucleation-growth mechanism; the interconnected nanopore (~5–25 nm) structure of the macroporous gel skeleton, on the other hand, was tailored by solvent exchange procedures. The morphological and textural characterization of these materials was performed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray ultra microscopy (XuM), nitrogen adsorption and mercury intrusion porosimetry. The factors affecting the porosity exhibited by the scaffolds, such as glass composition and solvent exchange conditions, have been assessed.

A19- Ana C. Marques and Rui M. Almeida, "Er photoluminescence enhancement in Ag-doped sol-gel planar waveguides", Journal of Non-Crystalline Solids, 353 (2007) 2613–2618. DOI:10.1016/j.jnoncrysol.2007.05.010
http://www.sciencedirect.com/science/article/pii/S0022309307004784

This paper reports on the study of the effects of silver ($Ag^o$) nanoparticles on the optical and spectroscopic properties of $Er^{3+}$-doped silica-based gels and glasses, including active bulk materials and planar waveguides for integrated optics. Two different procedures for silver and erbium ion incorporation into the glassy matrices have been investigated: the direct incorporation of a metal salt ($AgNO_3$ and/or $Er(NO_3)_3$) into the sol–gel solution, as well as a modified sol–gel process, based on pore-doping of a precursor gel with $AgNO_3$ and/or $Er(NO_3)_3$ solutions. The study of the parameters determining the average size and size distribution of the nanoparticles, together with their influence on the sol–gel material densification and $Er^{3+}$ photoluminescence at 1.5 µm, has been performed by means of transmission electron microscopy, plus ultra-violet/visible and photoluminescence spectroscopies. The $Ag^o$ colloidal nanoparticles, obtained by thermal precipitation, were approximately spherical, homogeneously distributed and they exhibited an average size between ~2 and 15 nm, depending on the silver content and heat treatment performed. They are shown to be responsible for a remarkable enhancement of the $Er^{3+}$ photoluminescence intensity, which is mainly due to the increase of the local electric field around the $Er^{3+}$ ions, due to the surface plasmon resonance of the $Ag^o$ nanoparticles.




A18- Rui M. Almeida, Ana C. Marques, Alessandro Chiasera, Andrea Chiappini, Maurizio Ferrari, "Rare-earth doped photonic crystal microcavities prepared by sol-gel", Journal of Non-Crystalline Solids, 353 (2007) 490-493. DOI: 10.1016/j.jnoncrysol.2006.10.015 http://www.sciencedirect.com/science/article/pii/S0022309306013688

Rare-earth doped photonic materials and structures have been prepared by sol–gel processing, in the form of 1D photonic bandgap multilayer stacks of silica and titania. A significant enhancement of the $Er^{3+}$ emission at ca. 1530 nm occurred when these ions were inserted into Bragg mirrors and microcavities. In $Er^{3+}/Yb^{3+}$ co-doped structures, an efficient energy transfer at 980 nm was observed from $Yb^{3+}$ to $Er^{3+}$ when these ions were in close proximity and especially when they were simultaneously present, in the same defect layer, with a 1530 nm photoluminescence enhancement of up to ~25 times being observed for excitation at 980 nm, compared to the excitation of the same microcavities samples at 514.5 nm.

A17- Ana C. Marques and Rui M. Almeida, "Raman spectra and structure of multicomponent oxide planar waveguides prepared by sol-gel", Journal of Sol-Gel Science and Technology, 40 (2006) 371-378. DOI 10.1007/s10971-006-9320-8 https://link.springer.com/article/10.1007/s10971-006-9320-8

This work was aimed at understanding the structure of $SiO_2$–$MO_2$ (M = Ti, Zr, Hf) and $SiO_2$–$HfO_2$–$MO_2$ (M = Ti, Zr) materials, used as mixed oxide glass hosts for $Er^{3+}$ ions in the fabrication of optical planar waveguides by sol-gel processing. This structural study was performed by Waveguide Raman Spectroscopy (WRS), complemented with X-ray diffraction (XRD). The admixture of $TiO_2$ to $HfO_2$, $SiO_2$–$HfO_2$ and $HfO_2$–$ZrO_2$ compositions was found to cause precipitation of nanocrystals of tetragonal $HfO_2$ or $ZrO_2$, or the formation of hafnia-titania mixed crystals, depending on the $HfO_2/TiO_2$ molar ratio.

A16- N. R. Nené, A. Vieira, A. C. Marques, R. M. Almeida, A. R. Ramos , E. Alves, N.P. Barradas, “Analysis of sol-gel silica-titania films doped with Ag and Er using artificial neural networks”, Nuclear Instruments and Methods in Physics Research B249 (2006) 804-807. DOI: 10.1016/j.nimb.2006.03.144
http://www.sciencedirect.com/science/article/pii/S0168583X06004101

Sol–gel processing is a cheap and versatile method of producing silica on silicon films for planar integrated optics. It leads to high Er incorporation and to easy incorporation of Ag, that can intensify the rare-earth photoluminescence. Different heat treatments and compositions must be tested to optimise the properties of the films grown, and the annealing may lead to redistribution of the elements into different layers, including of H present in the films. We have analysed sol–gel silica films doped with Er and Ag and subject to different annealing procedures with Rutherford backscattering (RBS) and elastic recoil detection (ERDA), leading to a large quantity of complex spectra. We developed an artificial neural network (ANN) able to analyse simultaneously the RBS and ERDA spectra collected from one sample. Non-standard network architecture was necessary due to the complexity of the problem. The optimised ANN is applied to experimental data leading to results that are practically as accurate as those obtained with a conventional data analysis code.

A15- Rui M. Almeida and Ana C. Marques, “Rare-earth photoluminescence in sol-gel derived confined glass structures”, Journal of Non-Crystalline Solids 352 (2006) 475-482. DOI: 10.1016/j.jnoncrysol.2005.11.059
http://www.sciencedirect.com/science/article/pii/S002230930600007X

The characteristics of rare-earth luminescence in selected sol–gel derived confined structures have been examined. Erbium and erbium/ytterbium doped photonic materials and structures have been prepared by sol–gel processing, in the form of silicate optical planar waveguides, modified with titania and hafnia, and 1-D photonic bandgap structures consisting of multilayer stacks of silica and titania. The $Er^{3+}$ ions were found to be sensitive probes of the waveguide glass matrix structure, especially when hafnia-containing nanocrystallites were present, which narrowed and resolved different Stark components of the photoluminescence peaks. In 1-D Fabry–Perot coupled microcavities, efficient energy transfer was observed from $Yb^{3+}$ to $Er^{3+}$ ions when these were present simultaneously in the same defect layer, but not when the two types of ions were isolated in separate defect layers.

A14- Luca Zampedri, Cristiana Tosello, Hervé Portales, Maurizio Montagna, Maurizio Mattarelli, Andrea Chiappini, Giancarlo C. Righini, Stefano Pelli, Gualtiero Nunzi Conti, Maurizio Martino, Sabine Portal, Ana C. Marques, Rui M. Almeida, Yoann Jestin, Maurizio Ferrari, Alessandro Chiasera, "Spectroscopic assessment of rare-earth activated planar waveguides and microcavities", Applied Surface Science 248, 1-4 (2005) 3-7. DOI: 10.1016/j.apsusc.2005.03.022
http://www.sciencedirect.com/science/article/pii/S016943320500351X

This paper deals with glass-based photonic structures, used to control and modify the optical and spectroscopic properties of rare earth ions. The spectroscopic assessment of sol–gel-derived planar waveguides and 1D photonic band gap structures is reported. The spectroscopic, optical, and structural properties of planar waveguides with $(100 - x)SiO_2–xHfO_2–yErO_{1.5}$ with $y = 0.3$, 0.01; and $x = 10$, 20, 30, 40 have been investigated by photoluminescence and Raman spectroscopy. The radiative quantum efficiency of the $^4I_{13/2}$ metastable state of $Er^{3+}$ ions is between 84 and 88% depending on the Si/Hf molar ratio. The sol–gel-derived one-dimensional cavity was realized by a $Eu^{3+}$-activated dielectric layer placed between distributed Bragg reflectors (DBRs).

A13- A.R. Ramos, C.P. Marques, E. Alves, A.C. Marques, R.M. Almeida, "Stability of erbium and silver implanted in silica-titania sol-gel films", Nuclear Instruments and Methods in Physics Research B, 240 (2005) 415. DOI: 10.1016/j.nimb.2005.06.138 http://www.sciencedirect.com/science/article/pii/S0168583X05011080

We implanted silica–titania sol–gel films with $3 \times 10^{15}$ at./cm$^2$, 180 keV $Er^+$ and $6 \times 10^{16}$ at./cm$^2$, 140 keV $Ag^+$ ions. The energies were chosen so that the profiles of Ag and Er overlap. RBS and ERDA were used to study the behaviour of Ag, Er and H during the heat treatments used to densify the films. Implantation causes H depletion at the film surface and an increase in H concentration just beneath the implanted Ag and Er profiles. The total H content decreases by 27% to 75% during implantation. During annealing the H content decreases, with an almost complete H loss after annealing for 35 min at 800 °C. The Ag profile remains stable up to 600 °C. Above 700 °C Ag becomes increasingly mobile. Annealing at 800 °C for 35 min results in a nearly constant Ag distribution in the film. The Er profile remains unchanged with heat treatment up to the maximum temperature used (800 °C).

A12- Rui M. Almeida, Ana C. Marques and Sabine Portal, "Glassy and nanocrystalline photonic materials and structures by sol-gel", Optical Materials, 27 (2005) 1718. DOI: 10.1016/j.optmat.2004.11.042 http://www.sciencedirect.com/science/article/pii/S0925346705000844

Erbium-doped photonic materials and structures have been prepared by sol–gel, in the form of silica–hafnia based optical planar waveguides and 1-D photonic bandgap structures consisting of alternating silica and titania layers. The $Er^{3+}$ ions were found to be sensitive probes of the waveguide glass matrix structure, especially when hafnium-containing nanocrystallites were present, which narrowed and resolved different Stark components in the photoluminescence peaks. In 1-D Fabry–Perot microcavities, on the other hand, efficient energy transfer was observed from $Yb^{3+}$ to $Er^{3+}$ ions when these were present simultaneously in the same defect layer, but not when the two types of ions were isolated in separate defect layers of coupled microcavities.

A11- A.C. Marques, R. Cabeça, R.M. Almeida, L. Zampedri, A. Chiasera, M. Ferrari, "The effects of $TiO_2$ on the structure and spectroscopic properties of silica-hafnia based sol-gel waveguides", Glass Technology, 46, 2 (2005) 50. EID: 2-s2.0-23144450549 http://www.ingentaconnect.com/content/sgt/gt/2005/00000046/00000002/art00003

The effects of titania additions on $Er^{3+}$ doped silica–hafnia based optical planar waveguides, prepared by solgel processing have been studied. Structural changes, including crystallisation induced by the presence of $TiO_2$, were assessed by x-ray diffraction, waveguide Raman spectroscopy and Fourier transform infrared spectroscopy. The $Er^{3+}$ photoluminescence spectra at ∼1·5 μm, the corresponding lifetimes and the $Er^{3+}$ relative luminescence yields have been determined as a function of the matrix composition, the densification heat treatments and the $Er^{3+}$ ion concentration. The $Er^{3+}$ quenching concentration and its lifetime at the limit of zero rare earth concentration have also been determined. Typical values for the fluorescence lifetimes varied between 6·5–1·5 ms, for $Er^{3+}$ concentrations ranging from 0·15–2%, in a 75% $SiO_2$–5% $TiO_2$–20% $HfO_2$ matrix. The presence of $TiO_2$ appears to promote the formation of hafnia–titania mixed crystals. Although the $Er^{3+}$ quenching concentration was similar for all the systems studied, at ∼0·6–1·0% Er, even small additions of $TiO^2$ (∼5 mol%) were found to increase the $Er^{3+}$ fluorescence lifetimes of silica–hafnia waveguides by as much as 100%, depending on the actual compositions.

A10- A.C. Marques, R.M. Almeida, A.R. Ramos, E. Alves, "Compositional profiles in silica-based sol-gel films doped with erbium and silver, by RBS and ERDA", Journal of Sol-Gel Science and Technology, 31 (2004) 287. DOI: 10.1023/B:JSST.0000048005.33044.8b https://link.springer.com/article/10.1023/B:JSST.0000048005.33044.8b

The photoluminescence efficiency of Er-doped silica-titania planar waveguides, prepared by sol-gel processing, may in principle be enhanced through the incorporation of silver metal particles. On the other hand, the presence of residual OH groups limits the optical activity of the $Er^{3+}$ ions. In this work, we have used Rutherford Backscattering Spectrometry (RBS), combined with Elastic Recoil Detection Analysis (ERDA), in order to study the incorporation of Ag and H species as a function of the heat treatments used to densify the sol-gel films. Ultraviolet–visible spectroscopy and Fourier transform infrared (FTIR) spectroscopy were used to support and expand the interpretation of the RBS and ERDA data. The RBS results indicate a homogeneous distribution of Er in the as-deposited films. On the contrary, Ag displays a bimodal in-depth profile, centred at the air/film and film/Si substrate interfaces. Heat treatments at up to 700°C eventually lead to in-diffusion and segregation of most of the Ag species at the latter interface. The hydrogen concentration reaches minimum values after heat treatments at 500 and 900°C, with apparently larger values for temperatures in between. During these heat treatments, the Er profile remains stable.

A9- R.M. Almeida, A.C. Marques, R. Cabeça, L. Zampedri, A. Chiasera, M. Ferrari, "Photoluminescence of erbium-doped silicate sol-gel planar waveguides", Journal of Sol-Gel Science and Technology, 31 (2004) 317. DOI: 10.1023/B:JSST.0000048010.74400.f0
https://link.springer.com/article/10.1023/B:JSST.0000048010.74400.f0

$Er^{3+}$-doped silica-titania planar waveguides, prepared by sol-gel processing, have a tendency to exhibit a reversible photoluminescence (PL) quenching phenomenon at 1.5 µm, when they are not fully densified. In the present paper, the presence of porosity and OH species associated with a simultaneous decrease in the $Er^{3+}$ PL intensity and lifetime are followed in detail by infrared and m-line spectroscopies. Different chemical compositions and EtOH/precursor ratios, as well as optimized heat treatments, have been used in order to ensure the preparation of fully densified waveguides with enhanced spectroscopic properties. Both the $Er^{3+}$ PL spectra and the fluorescence lifetimes at 1.5 µm have been determined in the $SiO_2$-$TiO_2$-$AlO_{1.5}$-$ErO_{1.5}$, $SiO_2$-$HfO_2$-$AlO_{1.5}$-$ErO_{1.5}$ and $SiO_2$-$HfO_2$-$TiO_2$-$AlO_{1.5}$-$ErO_{1.5}$ systems, as a function of the matrix composition and $Er^{3+}$ ion concentration. These waveguides, densified at 900°C, appear to offer the best performance in terms of stability and strength of the PL signal.

A8- A.C. Marques, R.M. Almeida, A.R. Ramos, E. Alves, "Study of silica-titania films co-doped with erbium and silver by RBS and ERDA", Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 219-220 (2004) 923. DOI: 10.1016/j.nimb.2004.01.189

A7- R.M. Almeida, A.C. Marques, S. Pelli, G.C. Righini, A. Chiasera, M. Mattarelli, M. Montagna, C. Tosello, R.R. Gonçalves, H. Portales, S. Chaussedent, M. Ferrari, L. Zampedri, "Spectroscopic assessment of silica-titania and silica-hafnia planar waveguides", Philosophical Magazine 84, 13-16 (2004) 1659. EID: 2-s2.0-2442581542
http://www.tandfonline.com/doi/abs/10.1080/14786430310001644459

Silicate glasses remain the most investigated systems for optical planar waveguides, since they offer a reasonable solubility for rare-earth ions, they are transparent in the near-infrared–visible region and they are compatible with integrated optics (IO) technology. In the last decade, various technologies have been employed for the fabrication of silica ($SiO_2$)-based IO components and a broad variety of silicate glass systems have been investigated. Besides the $SiO_2$–titania ($TiO_2$) system, which has been widely studied, it has recently been shown that $SiO_2$–hafnia ($HfO_2$) could be a further viable system for 1.5 µm applications. This paper compares spectroscopic results, in particular infrared and Raman spectra, in order to assess the structural and optical properties of erbium-activated $SiO_2$–$TiO_2$ and $SiO_2$–$HfO_2$ planar waveguides, prepared by two different techniques: rf sputtering and the sol–gel method. Particular attention is devoted to the homogeneity of the material structures obtained in each case.

A6- A. Chiasera, M. Montagna, C. Tosello, R.R. Gonçalves, A. Chiappini, M. Ferrari, L. Zampedri, S. Pelli, G.C. Righini, A. Monteil, V. Foglietti, A. Minotti, R.M. Almeida, A.C. Marques, V. Soares, "Erbium/Ytterbium activated silica-titania planar and channel waveguides prepared by rf-sputtering", Proceedings of SPIE 4990 (2003) 38-46. DOI: 10.1117/12.474774
https://www.spiedigitallibrary.org/conference-proceedings-of-spie/4990/1/Erbium-ytterbium-activated-silica-titania-planar-and-channel-waveguides-prepared/10.1117/12.474774.short

$SiO_2$-$TiO_2$:$Er^{3+}$-$Yb^{3+}$ waveguides were prepared by rf-sputtering technique. The active films were deposited on silica-on-silicon and v-$SiO_2$ substrates. The parameters of preparation were chosen in order to optimize the waveguides for operation in the NIR region with particular attention to the minimization of losses. The thickness of the waveguides and the refractive index at 632.8 and 543.5 nm were measured by an m-line apparatus. The losses, for the TE0 mode, were evaluated at 632.8 and 1300 nm. Roughness measurements were carried out by means of a stylus profilometer. The structural properties were investigated with several techniques such as Energy Dispersive Spectroscopy and Raman Spectroscopy. All waveguides were single-mode at 1550 nm. An attenuation coefficient equal or lower than 0.2 dB/cm was measured both at 632.8 nm and 1300 nm. The emission $^4I_{13/2} \rightarrow {}^4I_{15/2}$ of $Er^{3+}$ ion transition with a 40 nm bandwidth was observed upon excitation in the TE0 mode at 981 and 514.5 nm. Back energy transfer from $Er^{3+}$ to $Yb^{3+}$ was demonstrated by measurement of $Yb^{3+}$ emission upon $Er^{3+}$ excitation at 514.5 nm. Photoluminescence excitation spectroscopy was used to obtain information about the effective excitation efficiency of $Er^{3+}$ ions by co-doping with $Yb^{3+}$ ions. Channel waveguides in rib configuration were obtained by etching the active film by a wet etching process. Scanning Electron Microscopy was used to analyze the morphology of the waveguides.

A5- Ana C. Marques, Rui M. Almeida, Alessandro Chiasera, Maurizio Ferrari, "Reversible photoluminescence quenching in $Er^{3+}$-doped silica-titania planar waveguides prepared by sol-gel", Journal of Non-Crystalline Solids 322 (2003) 272-277. DOI: 10.1016/S0022-3093(03)00214-X
http://www.sciencedirect.com/science/article/pii/S002230930300214X

$Er^{3+}$-doped silicate planar waveguides are important for the fabrication of integrated optics amplifiers. This paper presents a study of reversible photoluminescence (PL) quenching in $Er^{3+}$-doped silica–titania planar waveguides, prepared by sol–gel processing. The infrared absorption and PL spectra of these waveguides at 1.5 μm are reported as a function of different heat treatments and time of exposure to various atmospheres. The corresponding emission lifetimes have also been measured in selected cases. Several samples have shown a decrease in the 1.5 μm PL peak intensity, after a few days in air at RT and a longer decrease when kept in an ultrasonic water bath. This change is found to be reversible, however, as long as a subsequent heat treatment at temperatures as low as 200 °C is performed on the same samples. In

addition, when these are kept under a controlled atmosphere with low moisture contents (such as in liquid nitrogen, or in a controlled atmosphere glove-box), there is a decrease in the rate at which the PL decreases. A heat treatment in a vacuum furnace, at a relatively high temperature (~700–900 °C), is shown to prevent most of the PL quenching. We examine the possible mechanisms involved, including the effects of residual OH groups and atmospheric $H_2O$, studied by infrared spectroscopy, plus the role of film porosity in the PL quenching phenomenon.

A4- Rui M. Almeida, Ana C. Marques, Maurizio Ferrari, "Optical nanocomposite planar waveguides doped with rare-earth and noble metal elements", Journal of Sol-Gel Science and Technology, 26 (2003) 891. DOI: 10.1023/A:1020776405909
https://link.springer.com/article/10.1023/A:1020776405909

The present paper is focused on multilayer $Er^{3+}$-doped silica-titania planar waveguides, co-doped with silver, which were prepared by spin-coating on silica glass, or buffered single crystal silicon substrates. The single layer thickness (~0.4 μm) and refractive index (~1.60–1.63) were measured by spectroscopic ellipsometry at 715 nm. The thickness of the waveguides (measured by mechanical profilometry) was ~1 μm and their optical propagation losses were measured at different laser wavelengths (488 nm, 514 nm and 633 nm), exhibiting an approximately Rayleigh-like behavior. The thermal precipitation of silver nanocrystallites was achieved, both in air and under a controlled atmosphere (dry nitrogen) and these were characterized by visible absorption spectroscopy, which clearly showed the development of a plasmon absorption band near 415 nm, by X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM). The $Er^{3+}$ metastable level lifetimes for the emission at ca. 1.54 μm were found to be ca. 4–6 ms, for $Er^{3+}$ concentrations varying between 0.2–2.0 mol% (or ~(0.4–4.4) × $10^{20}$ ions/$cm^3$), but no significant variation was observed with the Ag concentration added (up to 2.5 mol%).

A3- Rui M. Almeida, Paulo J. Morais e Ana C. Marques, "Planar waveguides for integrated optics prepared by sol-gel methods", Philosophical Magazine B, 82, 6 (2002) 707. DOI: 10.1080/13642810110084498
http://www.tandfonline.com/doi/abs/10.1080/13642810208224361?journalCode=tphb20

Sol-gel processing is becoming one of the cheapest and most versatile methods for the fabrication of passive and active planar waveguides for integrated optics, in particular for the silica-on-silicon type. The present paper focuses on some recent work in our group on both passive and active ($Er^{3+}$-doped) silica–titania inorganic and hybrid waveguides, considering in detail their densification behaviour, structure and optical properties. Recent advanced topics, such as nanocrystalline active waveguides prepared by by sol–gel method, are also addressed. The main results to be presented will deal first with the structural evolution during the densification of inorganic and hybrid silica-titania waveguides. Then, the fluorescence behaviour of active

waveguides, doped with $Er^{3+}$ ions, will also be described. And finally silver co-doped nanocrystalline waveguides, will be considered in detail, with particular emphasis on, firstly, the influence of preparation conditions on optical properties such as the visible and infrared absorption spectra, including the characterization of the surface plasmon resonances of the silver nanoparticles by visible spectroscopy as well as the 1.5 µm fluorescence lifetime and, secondly, the nature of the chemical environment of the erbium and silver ions, before the thermally induced nanocrystallite precipitation and during the course of film densification.

A2- Daniela di Martino, Luis F. Santos, Ana C. Marques e Rui M. Almeida, "Vibrational spectra and structure of alkali germanate glasses", Journal of Non-Crystalline Solids, 394 (2001) 293-295. DOI: 10.1016/S0022-3093(01)00690-1
http://www.sciencedirect.com/science/article/pii/S0022309301006901

Numerous structural studies have been carried out so far to elucidate the nature of the so-called *germanate anomaly*, but the correct structural model is still unknown. The objective of the present paper is to shed further light on the structure of alkali germanate glasses, namely those containing sodium and cesium oxides. Two series of glass samples were prepared, having molar compositions $(100-x)GeO_2 \cdot xM_2O$ (M=Na and $0 \leqslant x \leqslant 35$, or M=Cs and $0 \leqslant x \leqslant 25$). Polarized Raman and infrared absorption spectra were recorded for these glasses, as a function of the alkali content; infrared reflectivity measurements were also carried out and Kramers–Kronig analysis of the near-normal incidence spectra were compared with the polarized Raman spectra of the glasses. An overall structural picture has emerged, which is compatible with the presence of a fraction of higher coordinated Ge atoms, either five-fold or six-fold.

A1- Ana C. Marques, Janet Gallardo, Alicia Durán, "Síntesis y estructura de recubrimientos híbridos de $ZrO_2$-$SiO_2$ obtenidos por sol-gel", Boletín de la Sociedad Española de Cerámica y Vidrio, 40, 6 (2001) 429.
http://digital.csic.es/handle/10261/4717

Corrosion resistance of stainless steel can be enhanced through the application of $SiO_2$ coatings. However, these coatings are sensitive to alkaline attack, that produces the partial dissolution of the $SiO_2$ network. An homogeneous structure incorporating $ZrO_2$ to the $SiO_2$ coatings would increase their resistance in basic media. In this work, hybrid $ZrO_2/SiO_2$ coatings were prepared and the effect of processing conditions was analysed, including the variation of sol synthesis, coating deposition and sintering treatments. Sols were prepared by hydrolysis and polycondensation of complexed zirconium tetrabuthoxide and pre-hydrolysed methyltriethoxisilane (MTES). For the higher MTES content, critical thickness around 0.5µm were measured.
High concentrations of Si-O-Zr bonds were revealed for sintering temperatures lower than 700ºC from FT-IR and DRX studies, and crystallisation of $ZrO_2$(t) from T=700ºC. The electrochemical resistance and coating stability were evaluated from cyclic polarisation tests, performed on coated AISI304 stainless steel. The coatings revealed

a high resistance against alkaline media preserving an excellent electrochemical behaviour in Cl- rich solutions.

## PATENTS

P8 - Ana C. Marques, Elisabete R. Silva, João C. Bordado, “Biocidal Microcapsules for biofouling control”, PCT application number: PCT/EP2017/074085, (2017) EP3298895A1 (Publication date: 28/3/2018).

P7 - Ana C. Marques, Mónica Loureiro, Elisabete R. Silva, João C. Bordado, “Custom-tailored sol-gel derived matrices for chemical immobilization”, PCT application number: PCT/EP2017/074114 (2017), EP3299083A1 (Publication date: 28/3/2018).

P6 - C. Costa, L. Gomes, Ana C. Marques, A. Branco, J. Araújo, M. Simões, YD Ynvisible S.A., “Method of depositing transparent conductive oxide on paper by radio-frequency or direct current cathodic sputtering and using the method in electrochromic devices”, WO/2013/169133 (Published in 14/11/2013).

P5 - Ana C. Marques, C. Pinheiro, J. Araújo, YD Ynvisible, S.A., “Electrolyte solution, printing method thereof and resulting solid electrolyte”, WO/2013/095170A1, US/2014/0361211 A1 (Published in 11/12/2014).

P4 - Ana C. Marques, P. Chevalier, M. Backer, V. Rerat, Z. Liu, S. Onodera, “POLYMER COMPOSITIONS CONTAINING ALKOXYSILANES“, EP2593496A1, CA2798043A1, US20130065993, WO2011143930A1, WO2011143930A8 (Published in 14/03/2013).

P3 - Ana C. Marques, P. Chevalier, M. Backer, V. Rerat, Z. Liu, S. Onodera, “SILICONE RESINS AND THEIR USE IN POLYMER COMPOSITIONS“, US20130066009 A1, CA2797432A1, EP2593497A1, WO2011143931A1, US 9,006,372 B2 (Published in 14/04/2015).

P2 - Ana C. Marques, P. Chevalier, M. Backer, “POLYMER COMPOSITIONS CONTAINING OXAZINE-BASED ALKOXYSILANES“, International Application Number: US20130065992 A1, CA2796803A1, CN102906194A, EP2571937A2, WO2011144575A2, WO2011144575A3 (Publicada em 14/03/2013).

P1 - Himanshu Jain, Ana C. Marques and Rui M. Almeida, “NANO/MACROPOROUS BONE TISSUE SCAFFOLDS FOR REGENERATIVE MEDICINE”, US Patent WO2008028036 (A1), US8,277,829 B2 (Publicada em 02/10/2012).