Surface modification and functionalization of materials for biomedical applications

BOOK OF ABSTRACTS

Zaragoza (Spain), June 24th, 2010
FOREWORD

The surface of materials plays a major role in their interaction with the biological medium. Processes related to the mechanical stability of articular devices in contact, such as osseointegration, thrombogenicity, corrosion and leaching, or the inflammatory response of rejection of a material are clearly conditioned by the surface properties. Therefore, the modification or functionalisation of surfaces have an important impact on these issues. New techniques for functionalisation by thin film deposition or surface treatments can help improving the superficial properties while understanding the surface-biological medium interaction for applications in new biomedical devices.

The main objective of BIOCOAT-2010 is to gather scientists and national and international experts to create a forum of discussion in the recent advances on the surface functionalisation of biomaterials.
SESSION I:
FUNCTIONALIZATION AND TEXTURES OF SURFACES (FT)
APPLICATION OF PLASMA TECHNOLOGIES TO BIOLOGICAL INTERFACES DESIGN

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1. Bio-Interface engineering
One of the major challenges for the development of bio interfaces relies on the ability to design surfaces with controlled interaction with the biological entities[1]. Surface functionalization techniques provide those bio-interfaces: appropriate surface physico-chemical properties are able to control the conformation and activity of the immobilized biomolecules. The subsequent technological step is the combination of different bio-functions in micro- and nano-patterns on the surfaces. For instance, structuring the surface in adhesive and non adhesive zone in order to preferentially guide the cell growth is one of the most promising tools for the development of cell chips and for tissue engineering[2,3]. The requirement of further integration scales and the study of the special behaviour of the biomolecules interacting with nanostructures have been the two main motivations for the development of submicron patterning techniques[4]. Plasma assisted deposition techniques are interesting methods to produce functionalized surfaces with controlled micro- and nano-patterns: they provide high-level functionality with good stability on different substrates and are compatible with different micro- and nano-patterning techniques.

2. Results
In this work we show some examples of micro- and nano-functional surfaces provided by plasma processes and self assembled monolayers in combination with Electron Beam Lithography and Colloidal lithography, and their application as platforms for cell cultures. In particular, micropatterned surfaces were produced by a spatial arrangement of different functional domains by a combination of plasma polymerisation and electron beam lithography: non-fouling patterns were made of poly(ethylene oxide) (PEO)-like polymers obtained by pulsed plasma polymerization of diethylene glycol dimethyl ether while fouling surfaces were composed of Poly-acrylic acid (PAA) from acrylic acid monomer obtained by plasma polymerization, and stabilized by electron beam. PAA nano pillars of 150nm diameter can be obtained in a PEO non-fouling background. Protein adsorption studies on those surfaces show that the protein adsorbs on the pillars, which results in special interaction with membrane cell receptors. On the other hand, nano-patterns of fouling-antifouling areas have been produced by combining Colloidal Lithography techniques with plasma deposited thin films and SAM’s: in particular carboxylic functionalized nano-spots in a PEO-like anti-fouling matrix have been produced. We show that these chemical nano-patterns are able to immobilize proteins selectively in the carboxylic functional nano-domains, leaving the anti-fouling matrix clear. Moreover Enzyme-Linked Immunosorbent Assay and SPR imaging experiments were set-up showing that nano-patterned surface constrains the immobilization of the antibodies in a biological reactive configuration, thus significantly improving the surface interaction as compared to more conventional non-patterned or disordered patterned surfaces. We show with different methods (SPR, QCM, ELISA) that the protein protein activity increases as the size of the patterns decreases.

THE ROLE OF THE AMINE GROUPS IN THE BIOCOMPATIBILITY OF POLYMERS AND DLC FUNCTIONALIZED WITH PLASMAS

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Abstract: Plasma activation of polymers is a classical technology used to increase their surface reactivity by the incorporation of new functional groups. Nitrogen functional groups, specially amine groups are particularly indicated to improve cellular adhesion. In this context, we have recently proved that diamond-like carbon (DLC) coatings can be functionalized by nitrogen plasma activation in a similar way than polymers. In the present work we have studied the plasma surface activation of polymers like polyethylene tereftalate (PET) and low density polyethylene (LDPE) and diamond-like coatings by XPS, water contact angle measurements and atomic force microscopy (AFM). Low pressure microwave plasmas generated with a surfatron device and atmospheric pressure DBD plasmas of Ar, N2, NH3 and mixtures of these gases have been used for the surface activation of these materials. For comparison, the effect of a beam of neutral species has been also studied. Depending on the materials and the type of plasmas, differences have been found in the concentration and type of functional groups and in the topography and hydrophilicity of the surface of the treated materials. Fibroblast growth studies were performed to determine the influence of the nitrogen functional groups, particularly amine groups, and the effect of the new surface properties on the bioactivity of these plasma activated materials. The role of the amine groups and that of these other surface changes on the growth of cells is critically discussed.

HONEYCOMB STRUCTURED POROUS INTERFACES AS TEMPLATES FOR PROTEIN ADHESION

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Abstract: We prepared breath figure patterns on functional surfaces by surface segregation of a statistical glycopolymer, (styrene-co-2-(D-glucopyranosyl) aminocarbonyloxyethyl methacrylate, S-HEMAGl). The preparation of the glycopolymer occurs in one single step by using styrene and an unprotected glycomonomer. Blends of this copolymer and high molecular weight polystyrene were spin coated from THF solutions leading to the formation of surfaces with both controlled functionality and topography. AFM studies revealed that both the composition of the blend and the relative humidity play a key role on the size and distribution of the pores at the interface. Thus, the topographical features obtained on the polymer surfaces during the film preparation by the breath figures methodology varied from 200 nm to 700 nm. Moreover, this approach leads to porous films in which the hydrophilic glycomonomer units are oriented towards the pore interface since upon soft annealing in water, the holes are partially swelled. The self-organization of the glycopolymer within the pores was additionally confirmed by reaction of carbohydrate hydroxyl groups with rhodamine-isocyanate. Equally, we demonstrate the bioactivity of the anchored glycopolymers by means of the Lectin binding test using Concanavalin A (Con A).

SYNTHESIS AND PHOTOCROSSLINKING OF A BIODEGRADABLE POLYESTER FOR TISSUE ENGINEERING APPLICATIONS

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Radical thiol-ene reaction is being widely used recently since it has been identified as an efficient and orthogonal reaction rather suitable for click chemistry. The homologous radical thiol-yne reaction has been described [1] but only very recently this reaction has been applied to photopolymers [2]. In this work, we describe a biodegradable polymer which can be used as polymeric scaffolds for tissue engineering prepared by a photoinduced thiol-yne reaction. The photopolymer is based in a biodegradable hyperbranched polyester functionalized at the periphery with alkyne groups, a pentaerythritol derivative functionalized with thiol groups and a UV photoinitiator.

Hyperbranched 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) was functionalized with 4-pentynoic acid. A mixture of this alkyne functionalized hyperbranched polymer, pentaerythritol tetra(3-mercaptopropionate) (PETMP) and Irgacure 369 as UV photoinitiator was prepared. Thin films were processed by casting from a solution of this mixture. These films were irradiated with UV light and the reaction was followed by IR spectroscopy. Alkyne and thiol bands on IR spectrum disappeared after irradiation with UV light giving rise to a crosslinked material.

Citotoxicity and cells viability essays had been carried out in thin film of these materials. We have created 2-D structures with controlled geometries using a laser writing techniques followed by an etching step. Cells have been cultured in these bidimensional relief structures and the influence of the geometry in the cell growth and proliferation has been studied. (Fig.1)

Fig.1. HeLa cells growing onto the lines of the scaffold generated by direct laser writing.


Acknowledgements This work was supported by the Spanish MEC project MAT2008-06522-C02, DGA project PI018/08 and FEDER founding (EU). M.Lomba thanks the Gobierno de Aragón (Spain) for his grant.
Abstract: Several medical devices (both implantable and for in vitro diagnosis) benefit greatly from having microtextured surfaces, what helps to improve and promote phenomena such as osteointegration and cell / tissue growth, on the surface of the device. Normally for obtaining such textures post-processes based on the use of abrasives or chemical attacks are involved, with which it is sometimes difficult to precisely control the final surface characteristics (porosity, roughness, among others) as well as the related biological aspects.

In this work we propose an alternative process based on the use of fractal surface models for designing special surfaces, which help with controlling the desired contact properties (from the design stage), with several applications in Biomedical Engineering. Manufacture can be directly accomplished with help of additive rapid prototyping technologies, what supposes a focus change, from a more conventional “top-down”, to a more versatile “bottom-up” approach.

The fractal characterization of “scaffolds” will be made through SEM images. The “Scaffolds” images are imported to the Image J software and transformed in order to eliminate possible noise. The number of pixels on the image contour is determined and the area-Perimeter method is used to obtain the fractal dimension of the designed surfaces. A Dektak 150 profilometer will be used to investigate the roughness parameters of the fractal surfaces.

Finally, in order to improve the biological response, the surfaces of the devices were coated with various hydrogen-free amorphous carbon (a-C) thin films, known to be highly biocompatible materials. The films were deposited at room temperature using the vacuum filter cathodic arc technique.
Resumen: La actividad de un biomaterial específico viene definida por la interfase formada entre la superficie del material y el sistema biológico [1]. Este trabajo está enfocado en la interacción de la poli-L-lisina (PLL), una molécula de adhesión común en cultivos celulares [2], con tres tipos de materiales que están siendo probados para crecimiento celular y aplicaciones eléctricas en el sistema nervioso: PEDOT, PPy y IrOx. Para ello, se han utilizado técnicas experimentales de superficie que evalúan la naturaleza de las especies adheridas, la “mojabilidad” de las muestras y las propiedades electroquímicas. Como resultado, se ha encontrado que la PLL se encuentra adherida a todas las superficies, en diferente cantidad y conformación. Además, se ha encontrado que la adhesión del polipéptido no modifica las propiedades eléctricas del material, ni disminuye la ventana de potencial, lo que es importante para futuras aplicaciones eléctricas de los materiales.


IMPROVEMENT OF THE WETTING PROPERTIES OF POLYPROPYLENE SUBSTRATES BY PHOTOPOLYMERIZATION OF VINYL ACETATE.

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Abstract: Polypropylene is a material widely used at industrial level because it has a good balance of properties together with good processability and low cost. Despite these characteristics, has low surface energy, due to the apolar nature of the molecule. This makes it difficult to be used in technological applications that require surface activity, such as painting or adhesive applications. Therefore it is necessary to modify the surface activity of polypropylene. In this study we used a photopolymerization process by which a highly polar monomer is grafted onto the polypropylene surface. In this case, we used vinyl acetate[1] as grating monomer. To carry out this process, we used ultraviolet (UV)[2] radiation and presence of a photoinitiator. It has been used benzophenone (BP)[3] for this purpose.

The aim of this work was to evaluate changes in surface energy of polypropylene substrate after photopolymerization process. Surface changes have been analyzed by measuring contact angle values with four different test liquids (water, formamide, diiodomethane and glycerol). Then we calculated the corresponding surface energy by the Owens-Wendt method. This analysis was performed for different exposure times to UV radiation, resulting an optimum exposure time of 120 seconds. To check the chemical changes on PP surface we used Fourier transformed infrared spectroscopy with attenuated total reflectance accessory (FTIR-ATR). This analysis confirmed the presence of polar groups which have been grafted during the photopolymerization process.

IMMOBILIZATION OF ANTIBODIES ON LIPID NANOCAPSULES FOR DIRECTED DRUG DELIVERY. PHYSICO-CHEMICAL CHARACTERIZATION

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Abstract: Lipid nanocapsules are recently developed as nanocarriers for lipophilic drugs delivery. The surface characteristics of these colloidal particles are determinant in order to provide a controlled and directed delivery on target tissues with specific markers. We report the development of immuno-nanocapsules, in which antibodies are conjugated to nanocapsules offering the promise of selective drug delivery to specific cells.

Several nanocapsule systems were prepared by the solvent displacement technique obtaining an oily core surrounded by a functional shell with surface carboxylic groups. Antibodies were conjugated with nanoparticles by the carbodiimide method that allows it the covalent immobilization of protein molecules through these carboxylic surface groups. A complete physico-chemical characterization of the immuno-nanocapsules was developed confirming the immobilization of protein molecules on the colloidal nanoparticles via electrophoretic and colloidal stability experiments. The immunoreactivity of the protein-nanocapsules complexes was studied, showing an adequate surface disposition of the covalent bound antibodies in order to a specific immunological recognize.
Abstract: Folic acid plays an essential role in cell division and DNA synthesis. Hence it’s not surprising that many types of cancer cells over-express the folate receptor. This small molecule can be used as a tumor-specific targeting ligand, allowing nanoparticle endocytosis via receptor.

Chitosan is a cationic polymer widely used in nanoparticle coating due to its biocompatibility and mucoadhesivity. The primary amine groups of this polymer have been used to the covalent binding of folate via carbodiimide.

In order to analyze differences in physicochemical properties of nanoparticles with or without folate as a ligand, different folate/chitosan molar ratios were compared.

Using an emulsification/solvent evaporation technique we have prepared nanoparticles with an oily core surrounded by a surfactant shell. The surface of these nanoparticles has also been coated with the polymer chitosan and its modifications.

Nanoparticle size, zeta potential and stability in PBS and DMEM (Dulbecco’s Modified Eagle Medium) were measured. Effects of salt concentrations on stability were also considered.

The results show that folic acid has been efficiently attached to chitosan, obtaining a system suitable for selective delivery of anticancer hydrophobic drugs.
ENZYME IMMOBILIZATION ON PLASMA-GRAFTING MODIFIED POLYMERIC SURFACES

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Abstract: Immobilization of biological active species is crucial for the fabrication of smart bioactive surfaces. For this purpose, plasma enhanced chemical vapour deposition (PECVD) method have frequently been used to modify the surface properties without affecting the bulk properties of the material. Thus, it is possible to create materials with surface functional groups that can promote the anchoring of all kind of biomolecules. In this work, we have developed a novel method to covalently attach the enzyme 1,3-1,4-â- Glucanase, which is highly well known by our group, on polystyrene (PS) surfaces of flat and spherical shapes. The aim of this approach is to quantify the amount of active sites generated with the PECVD technique by measuring the activity of the attached enzyme. The polymeric substrates were previously activated by argon plasma-grafting. Due to the presence of the inert gas, regular reactive sites are created by mechanical work, with no specific chemical groups. After surface activation and under vacuum conditions, the polystyrene substrates were exposed to the monomer pentafluorophenyl methacrylate (PFM) during a defined period of time that leads to both the desired structure and thickness of the film polymerization. The grafted surface with the PFM offers a labile ester group which is of a great interest owing to its high reactivity towards amino-terminated molecules. The functionalized surfaces were analyzed by water contact angle measurements and Atomic Force Microscopy (AFM), showing an extremely homogeneous morphology of the active sites. Moreover, to demonstrate the retention of the PFM group on the surface and its reactivity towards primary amines, a fluorescence assay was performed by using a fluorescent molecule with a free amine on its structure. The fluorescein-5-thiosemicarbazide (FTSC) dye used reacts with the pentafluorophenyl ester and allows the characterization of the coated surfaces by fluorescence microscopy. Subsequently, the synthesis and purification of 1,3-1,4-â-Glucanase was carried out for its following immobilization on both types of the activated surfaces (spherical and flat shapes). The enzyme absorption on the bioactive surface was monitored by the Quartz Crystal Microbalance with Dissipation (QCM-D) technology, by using a quartz sensor crystal of gold and coated with a homogeneous and thin film of PS. Afterwards the sensor was modified with PFM at the same conditions as the PS substrates to ensure equal surface characteristics. This technique also enables a real time study of the interactions between the polymerized PFM film and the enzyme, and measures the thickness of the protein film covalently attached on the surface. After enzyme immobilization was assessed, the activity of the anchored enzyme was tested. 1,3-1,4-â- Glucanase hydrolyzes its substrate, â-Glucan, leading to an increase of the amount of reducing ends, which were quantified by using the dinitrosalicylic acid (DNS) method. The enzyme retains its activity after immobilization demonstrating the suitability of the technique and providing a novel method of enzyme immobilization under mild and controllable conditions.
SESSION II:
TRIBOLOGY AND CORROSION (TC)
STATE OF THE ART AND FAILURE MECHANISMS OF DLC COATED ARTICULATING JOINT REPLACEMENTS

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Abstract: Coatings such as Diamond Like Carbon (DLC) are very promising materials to improve biomechanical properties of articulating implants due to their extreme hardness, chemical inertness, wear resistance and biocompatibility. Implants such as hip and toe joints, compromising of DLC coatings on their articulating surfaces, were used in vivo. However, many of these implanted medical devices have failed due to coating delamination after a few years; slow delamination, in the order of a few m/year, is very difficult to detect but can lead to a complete failure of the coating after a sufficient time in vivo.

To give a reliable adhesion lifetime prediction for DLC coated implants, a thorough estimation of all potential failure mechanisms is of particular importance. Beside mechanical failure, other delayed interface crack growth mechanisms also have to be considered, especially hydrogen embrittlement, galvanic, crevice, and pitting corrosion as well as stress corrosion cracking (SCC). In the case of SCC it will be shown that SCC may occur in a few nanometer thin reactively formed layer at the interface between the DLC coating and the substrate. Here we present new methods to determine three pertinent failure mechanisms, in detail stress corrosion cracking, crevice corrosion (CC) and mechanical failure of coated implants, especially in respect to long term delamination. In addition to hip joint simulator testing, analytical and imaging methods were used to determine the failure mechanisms of the DLC coated implants. The correlations of the three mechanisms are discussed. We found testing in saline solutions to be insufficient, as proteins play an important role, especially as they may provide CC-conditions. Simulator testing shows that mechanical failure is mainly caused by third body wear involving wear particles.
TRIBOLOGICAL PROPERTIES OF SILVER CONTAINING AMORPHOUS CARBON FILMS

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Abstract: Amorphous carbon (a-C) films are materials of interest to many applications due to their favorable mechanical and tribological properties. This family of films has generated interest in the biomedical field because of their high biocompatibility and potentialities to support appropriate cellular activity. Amorphous carbon films are capable of embedding metallic elements as silver, which can add antibacterial properties to their functionality without jeopardizing their biocompatibility.

We have deposited a set of silver containing a-C films using a dual-cathode pulsed filter cathodic arc source onto TiAlV substrates. The arc pulse frequency of the silver and graphite cathodes was controlled in order to obtain samples with various silver contents (0 to 15 at.%).

In this study, we analyze the advantages of incorporating silver into a-C by studying the tribological properties of the deposited films in simulated body fluid against both UHMWPE pins and balls. The silver atomic content of the deposited samples was analyzed using glow discharge optical spectroscopy (GDOES). The deposited films were characterized by X-ray diffraction (XRD) and Raman spectroscopy.
TRIBOLOGICAL BEHAVIOUR OF TI-CONTAINING DLC NANOCOMPOSITE COATINGS IN BIOLOGICAL ENVIRONMENT

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Abstract: The aim of this work was to study the interaction of DLC coating in biological environment, for future biomedical applications. DLC films with and without small additions of Ti were deposited by dc unbalanced magnetron sputtering in Ar atmosphere (H-free) and with methane (hydrogenated). The power in the Ti-target was varied to obtain different Ti contents, in the range [7-15 at.%]. A Ti interlayer (300 nm) was applied to enhance the adhesion between the films and the substrate. Superimposed to the Ti crystalline peaks of the interlayer, broad bands were detected in the coatings with increasing Ti contents, confirming the presence of a nanocrystalline TiC phase, suggesting that a nanocomposite structure was being deposited consisting of TiC nanocrystals dispersed in an amorphous C-based matrix. With increasing Ti content, improvements of the adhesion, as well as of the hardness (from 5 to 9 GPa and from 7 to 9 GPa for H-free and hydrogenated ones, respectively), were observed.

The tribological tests were performed using a pin-on-disc CSM Tribometer at room temperature under dry and lubricated (0.9% NaCl water solution, PS, and 10% fetal bovine serum dissolved in Ringer’s saline solution, FBS) conditions, using 100Cr6 steel balls (diameter of 6mm). The best wear performance was obtained for the hydrogenated samples under lubrication, while the best friction behaviour was achieved under dry condition. The tribological results were supported by Raman analysis of the wear tracks and correlation with wettability results was studied.
IMPROVED WEAR PERFORMANCE OF ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE COATED WITH HYDROGENATED DIAMOND LIKE CARBON

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Abstract: Hydrogenated diamond like carbon (DLCH) thin films were deposited on medical grade ultra high molecular weight polyethylene (UHMWPE) by radio frequency plasma enhanced chemical vapour deposition.

The DLCH-coating thicknesses ranged from 250 to 700 nm. The substrates were discs made of UHMWPEs typically used for soft components in artificial joints, namely virgin GUR 1050 and highly crosslinked (gamma irradiated in air to 100 kGy) UHMWPEs.

Mechanical and tribological properties under bovine serum lubrication at body temperature were assessed on coated and uncoated polyethylenes by means of nanohardness and ball-on-disk tests, respectively. Morphological features of the worn surfaces were obtained by confocal microscopy and scanning electron microscopy (Fig.1).

This study confirm an increase in surface hardness and good wear resistance for coated materials after 24 hours of sliding test compared to uncoated polyethylene (Table 1). These results point out that to coat UHMWPE with DLCH films could be a potential method to reduce backside wear in total hip and knee arthroplasties.

Fig.1

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<th>WEAR RATE, k x 10^-6 (mm^3/ N/m)</th>
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TRIBOCORROSION RESPONSE OF PVD-TiCn COATINGS ON Ti6Al4V FOR ARTIFICIAL JOINTS

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Abstract: Ti6Al4V biomedical alloy is commonly used to manufacture implants and artificial joints, but metallic implants degrade in human fluids due to the synergistic effect of wear and corrosion phenomena. The interaction between these electrochemical and mechanical processes cause premature structural failure and accelerated metal cations release that can be absorbed by the peri-implant tissues. A possible solution to this fact is the application of biocompatible and protective coatings on the metallic joint components.

The actual trends involve the application of DLC (diamond-like carbon) coatings with remarkable tribological properties due mainly to their good frictional behavior [1,2]. These coatings can be applied in many industrial and biomedical applications where sliding can generate wear and frictional forces on the components, such as orthopedic metal implants.

This work describes the structural, corrosion, wear and tribocorrosion behaviour of novel Ti-DLC PVD coatings with different carbon and nitrogen contents on Ti6Al4V substrates for knee joint systems. Thickness, hardness and roughness were estimated as well as structural, tribological and tribocorrosion properties in simulated body fluids.

SOL-GEL DERIVED NANOCRYSTALLINE HYDROXYAPATITE COATINGS – PREPARATION, CHARACTERIZATION, EVALUATION OF THE BIOACTIVITY AND CORROSION PROTECTION BEHAVIOUR

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Abstract: The aim of this work was to prepare bioactive hydroxyapatite coatings by sol-gel method and to study the effect of thermal treatment temperature upon the bioactivity and corrosion protection of these coatings on Titanium alloy Ti6Al4V. The application of DTA/TGA and XRD has provided valuable information about the phase transformation, mass loss, identification of the phases developed, crystallite size, degree of crystallinity, lattice parameters, and unit cell volume. ICP has been used to analyze the evolution of ion release from hydroxyapatite tablets versus the immersion time in SBF. SEM/EDX has been applied to study the surface morphology of HA tablets before and after immersion in SBF to detect the biomimetic precipitation of secondary hydroxyapatite. FTIR has been also applied for studying the structure changes of the samples after being immersed in SBF. The obtained results show that all the prepared samples are ceramic nanopowders with crystal structure and composition like hydroxyapatite, with small deviations from that present in the human bone. The bioactivity of the studied samples is found to be closely related to the thermal treatments applied. That is, the bioactivity decreases as the temperature of the thermal treatment increase. Coatings from such prepared hydroxyapatite sol have been accomplished by dip-coating technique on non-toxic Ti6Al4V alloy for biomedical applications. The corrosion behaviour of the resulting hydroxyapatite coatings in a simulated body fluid (SBF) has been studied by electrochemical impedance spectroscopy. The hydroxyapatite coated Ti6Al4V alloy displayed excellent bioactivity when soaked in the SBF and acceptable corrosion protection behaviour.
TRIBOLOGICAL PERFORMANCE OF DLC COATINGS DEPOSITED BY
PHYSICAL AND CHEMICAL TECHNIQUES ON UHMWPE

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Abstract: Diamond like carbon coatings of varying thickness and surface roughness were deposited onto medical grade ultra-high-molecular weight polyethylene (UHMWPE) discs by physical (radio-frequency assisted sputtering, filter cathodic arc, and evaporation) and chemical (chemical vapor deposition) methods (Table 1). The structure and surface mechanical properties of the DLC coatings were characterized by means of Raman spectroscopy and nanoindentation, respectively. Tribological tests were also conducted at body temperature (37 °C) and under bovine serum lubrication for 6 days. In these tests, alumina balls (6mm in diameter and R\textsubscript{a} 20-40 nm) articulated against the DLC coated UHMWPEs describing a circular trajectory while applying a load of 5.23 N (contact pressure 37 MPa). After testing, wear tracks were both visually inspected and documented by confocal microscopy. Friction coefficients of DLC coatings ranged from 0.1 to 0.3 at the beginning of the test. Typically, DLC coated UHMWPE discs exhibited a decrease in friction coefficient up to the usual values of raw UHMWPE (0.1-0.2). However, the thickest DLC coating deposited by sputtering technique displayed a higher friction coefficient (0.25) throughout the test (Figure 1). Visual inspection of the wear tracks confirmed that DLC coated were completely removed in all cases, the only exception being the thickest sputtered DLC coating. Furthermore, volume changes associated to the creation of the wear track pointed out that the sputtered DLC coating suffered the least change, consistent with the preservation of the DLC layer. The promising results found for radio-frequency assisted sputtering DLC deposition warrants further research as a potential coating for orthopedic applications.
WEAR-CORROSION RESISTANCE OF DLC COATINGS FOR HARD/HARD JOINTS

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Abstract: CoCrMo and AISI 316 alloys are commonly materials employed in orthopaedic implants, especially in hip joint applications due to its good corrosion resistance in biological media. But mechanical loads presents in this type of systems can affect drastically the properties of these alloys provoking the alteration or breaking down of its protective passive film and as consequence, corrosion process may occur diminishing the life of the implant and causing health problems if human tissue absorbs excessive quantities of metallic ions. One alternative for improving the corrosion and wear resistance of these biomaterials is the application of protective coatings. DLC coatings are one of the most attractive proposals of the last years for biomedical applications due to its hardness, biocompatibility, and wear - corrosion resistance.

In this work, a type of metallic Ti-DLC coating deposited by PVD cathodic arc method on AISI 316 and CoCrMo substrates is proposed. Corrosion, wear and tribocorrosion properties of this film were analyzed and compared with the substrates ones. For simulating biological media an electrolyte composed by NaCl and albumin was chosen. The DLC coating strongly improved wear and corrosion-wear behaviour of AISI 316 and CoCrMo substrates.
SESSION III:
SURFACE MODIFICATION OF BIOMATERIALS (SM)
LASER PRODUCED COATINGS AND SURFACE MODIFICATIONS FOR MEDICAL IMPLANTS

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Abstract: The final success and lifetime of bone replacing devices is determined by the quality of the bone-implant interface, which depends on the bone tissue reaction to the implant surface topography and chemistry, as well as on the mechanical properties of the implant material. The best commercial materials for bone implants are titanium and calcium phosphate ceramics, although composites and polymers are being introduced lately in the market with great élan.

While titanium and its alloys are biocompatible and provide load bearing capability to a dental or orthopedic implant, calcium phosphates stimulate an unrivaled rapid biological response, improving bone adhesion to the implant, although mechanically they are weak and brittle. Therefore, a suitable solution has been to produce a calcium phosphate coating on a titanium implant. Several methods have been studied to optimize these ceramic bio-coatings onto titanium [1]. This presentation will concentrate on the pulsed laser deposition of bioactive coatings of calcium phosphates and glasses, but will summarize other topographical and chemical modifications induced by laser processing on the surface of a wide variety of materials other than Ti and its alloy, such as biomorphic silicon carbide and biodegradable polymers.

In-vitro and in-vivo testing for the assessment of the biological response of the modified surfaces have been extensively performed, apart from the previous physico-chemical characterization and optimization of the properties of the modified surfaces.

NUEVOS RECUBRIMIENTOS BIFÁSICOS Y BIOACTIVOS DE WOLLASTONITA-DIOPSIDO SOBRE IMPLANTES METÁLICOS MEDIANTE PROYECCIÓN TÉRMICA.

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Resumen: Una de las prioridades actuales es obtener implantes biocompatibles de formas complejas, de mayor durabilidad y elevada fiabilidad. Una vía, es el desarrollo de recubrimientos cerámicos sobre implantes metálicos que faciliten la unión directa al hueso, evitándose así los graves problemas asociados al desgaste del hueso y del metal y al desajuste entre ambos.
Este trabajo plantea la obtención de nuevos recubrimientos cerámicos bioactivos a partir de wollastonita y mezclas eutécticas de wollastonita (CaSiO₃) y diópsido (CaMgSi₂O₆), mediante proyección térmica de llama oxiacetalénica, sobre acero inoxidable y aleaciones de titanio. El objetivo es obtener diferentes microestructuras (W-D), con diferente porosidad y grado de interpenetración entre las diferentes fases cristalinas y/o vítreas que compitan en propiedades y coste con los recubrimientos de HA [1-2], el más desarrollado actualmente. Así mismo, se analiza el efecto de la granulometría de los polvos de partida y de los parámetros de proyección sobre las características del recubrimiento.

BIOFUNCIONALIZACIÓN DE SUPERFICIES DE TITANIO PARA LA MEJORA DEL PROCESO DE OSTEOINTEGRACIÓN

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Resumen: Este estudio pretende mejorar la osteointegración de implantes de titanio por medio de la inmovilización de péptidos en superficie que induzcan una respuesta biológica beneficiosa. Para ello se ha llevado a cabo la biofuncionalización de superficies de titanio mediante silanización y posterior unión covalente de un péptido con una secuencia de adhesión celular [1].

Objetivo: El desarrollo de una nueva técnica de inmovilización de oligopéptidos en la superficie del titanio mediante la utilización de 3-cloropropiltrietoxisilano (CPTES) como agente de unión entre la superficie de titanio y el péptido.

Materiales y métodos: Se ha realizado una caracterización fisicoquímica de las superficies mediante las técnicas de microscopía óptica de fluorescencia, XPS, ToF SIMS [2] y ángulo de contacto. También se han realizado ensayos de adhesión celular para evaluar la respuesta biológica in vitro.

Resultados: Mediante el proceso de silanización la superficie de titanio queda totalmente recubierta de CPTES, que permite la posterior adhesión de oligopéptidos. Los resultados de adhesión celular muestran una mayor adhesión y extensión celular en las muestras biofuncionalizadas.

Conclusiones: Se ha desarrollado un sistema de unión covalente de oligopéptidos en superficies de titanio que permite incidir en la respuesta biológica de las células en contacto.

Los nanotubos de carbono (NTC) son estructuras de tamaño nanométrico visualizables como una lámina de grafeno autoenrollada, formando estructuras de una capa (SWNT) o multicapas concéntricas (MWNT). Su tamaño, propiedades y estructura los hacen apropiados para integrarlos en transistores\(^1\), sensores electroquímicos\(^2\) o utilizarlos como transportadores de fármacos hasta el interior de la célula\(^3\). La cuantificación de la molécula o fármaco unida al NTC es crítica cuando estos se utilizan para aplicaciones como terapias génicas o transporte de fármacos.

El presente trabajo aborda la funcionalización de SWNT y MWNT con ADN y cuantificación de la cantidad unida al nanotubo en cada caso. El ADN puede unirse a las paredes del NTC de forma covalente y/o no covalente, siendo difícil diferenciar entre ambas interacciones y determinar cuál de ellas predomina. El estudio se llevó a cabo a través de mediciones de UV-Visible y el tratamiento de datos se realizó por isotermas de adsorción.

CULTIVO Y DIFERENCIACIÓN A CARTÍLAGO DE CÉLULAS MADRE MESENQUIMALES SOBRE ALEACIONES DE MAGNESIO

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Resumen: La medicina regenerativa es la rama de la medicina que aplica los principios de la ingeniería de los materiales y de las ciencias de la vida a la fabricación de sustitutos biológicos. Uno de los materiales más incipientes en este ámbito debido a su biocompatibilidad, a su bioabsorbilidad y especialmente, a sus propiedades mecánicas, son las aleaciones de magnesio [1]. Estas propiedades hacen del magnesio un material prometedor en la regeneración de tejidos, especialmente del tejido óseo y del tejido cartilaginoso [1, 2, 3]. En este trabajo se analizan dos aleaciones comerciales de magnesio en este tipo de aplicaciones. Se evalúa tanto la influencia de las características superficiales del material en la adhesión y proliferación celular, así como la diferenciación a cartílago de las células madre mesenquimales cultivadas. Para ello se realiza el cultivo de células madre mesenquimales sobre scaffolds 2D en las aleaciones comerciales de magnesio AZ31B y ZM21.

Resumen: Un método para mejorar la osteointegración, fijación y estabilidad de los implantes es crear superficies rugosas para aumentar el área de contacto. Para ello se pueden utilizar arenados con SiO$_2$, ZrO$_2$ o Al$_2$O$_3$, que presentan el inconveniente de dejar partículas incrustadas que favorecen la nucleación de grietas. La tecnología del chorro de agua pura a alta presión eliminaría este problema. A su vez, variar los parámetros de proceso (presión, distancia, velocidad de avance y geometría de boquilla) permite optimizar la rugosidad resultante. En este trabajo se chorrearón con agua dos materiales de interés biomédico, Ti6Al4V y AISI316, utilizando dos velocidades de avance del chorro. Los resultados preliminares indican que la rugosidad prácticamente no varía al disminuir la velocidad a la mitad, pero sí la profundidad del surco, que se duplica. En el caso del Ti6Al4V, la fase que se elimina primero es la $\beta$, debido a que es más blanda.
SILICONIZATION OF METALLIC BIOMATERIALS: A NOVEL COATING APPROACH TO ENHANCE THEIR BIOCOMPATIBILITY?

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Abstract: Conventional biomaterials used for bone replacement become spontaneously encapsulated by fibrous tissue after implantation into the living body, without direct contact to bone, which has been related often to clinical complications. Therefore, the search of biomaterials that facilitate the osseointegration is one of the key objectives in the development of the new generation of dental and orthopaedic implants. Formulations based on some ceramic materials or enriched in silicon oxide, so called bioactive have been shown to be very promising.

The presentation will report on the surface modification of metallic biomaterials by hot dipping in liquid Al-Si alloys, which is a low-cost technique successfully used to increase the Si content at the surface without compromise mechanical properties of the bulk, i.e. thus is so-called siliconisation. The metallurgical procedure is innovative for its potential application in the field of the metallic biomaterials. The developed coatings have an ultrafine grain size (~200 nm) and depending of the processing conditions may have a thickness in the range of 4 to 80 μm, being in all cases dense and very well adhered to the substrate.

Micromechanical characterization reveals that they are harder than the substrate and exhibit a high index of plasticity, which would full fill the trend in the development of hard and tough coatings.

Preliminary in vitro biocompatibility tests using primary cultures of human osteoblasts have shown that adhesion and proliferation is significantly enhanced with regards to the bare substrate when increasing the Si content of the coating.
CHARACTERIZATION BORIDE BIOMEDICAL GRADE STEEL

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Abstract: This paper studies the characterization of the surface in biomedical grade steel exposed at the treatment of boronizing by powder-pack. Moreover, the formation of hard layers type $\text{Fe}_2\text{B}$ were obtained in a temperature range from 1173 to 1273 K with exposure times of 6, 7 and 8 h. The characterization consisted of evaluating the growth kinetics of borides on the surface layer on biomedical grade steel. The borides layers were verified by x-ray diffraction (XRD) analysis, The distribution of alloying elements was detected by means of energy dispersive Spectroscopy (EDS) from the surface to the interior EDS. It also evaluates the fracture toughness, by the technique microindentation Vickers, using loads of 1.9 and 2.9 N, at different distances from microindentation on surface of, using two standard biomedical grade steel models Palmqvist. The determination of the adhesion of the substrate; qualitatively through the technique of indentation Rockwell-C. Finally obtain the diffusion coefficient and the mass gain, with ranges of temperature and time treatment.

MULTI-SUBSTITUTED HYDROXYAPATITE COATINGS OBTAINED BY EXCIMER LASER ABLATION

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Abstract: Hydroxyapatite (HA) is the main component to be found in the mineral part of the bone. The mineral phase of the bone cannot be described only as HA but as a multi-substituted calcium phosphate, being the type and amount of these ionic substitutions crucial in the biochemistry of the bone. Synthetic HA commercially available can be improved by addition of several ionic species (Si, Na, K, CO₃⁻², Sr, etc.), thus achieving production of multi-substituted hydroxyapatite coatings.

Several methods have been used to produce different bioactive coatings for improving the functional connection between living bone and implants. In particular, Pulsed Laser Deposition (PLD) allows to produce coatings with excellent adhesion, stoichiometry and crystallinity.

In the present work, PLD has been used to obtain multi-substituted HA coatings from targets mixtures of HA with different proportions of diatomaceous earth and strontium carbonate. The diatomaceous earth can provide diverse elements such as Si, Fe, Mg, etc. The characterization of the samples in terms of morphology, structure and chemical composition was performed by SEM, EDS, FTIR, XRD and XPS. The results revealed that Si and Sr ions are successfully incorporated into the HA structure, as well as traces of other elements. The dependence of the crystallinity grade and the film growth rate with the silicon and strontium content of the coatings is presented. In order to assess the biocompatibility of the samples, several in vitro analyses are currently being carried out.
SURFACE MODIFICATION OF POLYPROPYLENE (PP) USING ATMOSPHERIC PLASMA TREATMENT

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Abstract: Surface modification by atmospheric plasma treatment is one of the most interesting industrial applications for surface modification compared with other technologies which require vacuum conditions. Many polymeric surfaces offer very low surface energy values; typically there are lower than 30 mJ\textperiodcentered m\textsuperscript{-2}, to solve this problem, a range of surface treatments including chemical, thermal and electrical methods have been devised in recent decades. One of the most interesting treatments is that based on plasma technology because it is environmental friendly whilst promoting high surface energy values and, consequently, improves adhesive properties. In this work, we have used atmospheric plasma technique to modify the wettability properties of polypropylene (PP). The effects of this treatment on the surface of PP sheet have been quantified by contact angle measurements, X-ray photoelectron spectroscopy and atomic force microscopy. With these methods, we have determined how the treatment modifies, activates and functionalises the surface of PP, increasing its hydrophilic behavior, and how the process parameters influence the uniformity and homogeneity of the treated surface.

At the industrial level, atmospheric plasma technology finds many important applications because it promotes surface activation, and allows working in a continuous way. Following the plasma treatment, the polymeric surface undergoes a functionalization phenomenon which includes the formation of various polar groups containing oxygen, such as hydroperoxides, peroxides, hydroxiles, carbonyl, carboxylic acids and esters. Free radicals formed during the surface modification of the polymer can react with reactive species present in the atmosphere, chemically modifying the surface and therefore its initial hydrophobic behavior.
A MATHEMATICAL MODEL TO STUDY THE EFFECT OF DIFFERENT VARIABLES ON THE POTENTIAL DISTRIBUTION IN DAMAGED SOL-GEL COATINGS USED IN BIOMEDICAL APPLICATIONS

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Abstract: The aim of this work was to obtain the potential distribution on damaged organic-inorganic coatings used in biomedical applications after an accelerated delamination test. A computer program was developed to solve the numerical system obtained from the application of the finite element method (FEM) to the variational formulation of the Laplace bidimensional equation with the proper boundary conditions. The main deviation between the experimental and the calculated data appears in the most affected area. The number of elements in the numerical system affects considerably the calculated potential distribution. However, this relevant influence ended when the number of elements is bigger than 2000. There is no guarantee of a solution for a problem that only uses boundary conditions of Neumann type, but the fixed potential condition, obtained in the laboratory, used in both views has resolved this difficulty.
SESSION IV:
SURFACE-BIOLOGICAL ENVIRONMENT INTERACTION (INT)
BACTERIAL ADHERENCE TO ANODIZED TITANIUM ALLOY

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Background: Evaluation of Staphylococcus sp adhesion to modified surfaces of anodized titanium alloy (Ti₆Al₄V). Surface modification involved generation of fluoride-containing titanium oxide nanotube films.

Materials and Methods: Specimens of Ti-6Al-4V alloy 6-4 ELI-grade 23- (*) were anodized in a mixture of sulphuric/hydrofluoric acid at 20 V for 5 and 60 min to form a 100 nm-thick porous film of 20 nm pore diameter and 230 nm-thick nanotube films of 100 nm in diameter. The amount of fluorine in the oxide films was 6 at.% and 4 at%, respectively.

Collection strains and six clinical strains each of S.aureus and S.epidermidis were studied. The adherence study was performed using the protocol by Kinnari et al. (J Biomed Mat Res Part A. 2008. 86:760-8). The experiments were performed in triplicates. Photographs obtained were studied by ImageJ software. Statistical analysis was performed by EPI-INFO software.

Results: Lower adherence was detected for collection strains in modified materials than unmodified control. S. epidermidis strains showed lower adherence than S. aureus to all materials. Differences between clinical strains were detected for both species (p<0.01), although global data showed results similar to that of collection strains (p<0.0001).

Conclusions: Adherence of bacteria to modified surfaces was lowered for both species. The results also reflect a difference in the adherence between S.aureus and S.epidermidis to the modified material. Intraspecies differences showed the need to test these kind of isolates in order to obtain more realistic.

*Meets the requirements of ASTM F136 2002A (AMS 2631B class A1).
ADVANCED STRUCTURAL CHARACTERIZATION OF BIOCOMPATIBLE Ag-TiCN COATINGS

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Abstract: One of the main reasons for biomedical implants failure is the generation of wear debris together with microbial infection. To overcome this problem it has been proposed the use of very low wear coatings as diamond-like carbon (DLC), transition-metal carbides (MeCx) or nitrides (MeNₓ) in combination with antibacterial elements such silver, gold or copper. The present work explores the potentialities of silver-containing carbon/nitride (Ag-TiCN) based coatings to be used as protective thin films for biomedical implants. Samples were prepared by DC unbalanced reactive magnetron sputtering with contents of Ag ranging from 0 to 20 at.% and Ti from 35 to 15 at.% while keeping C, N and O content constant. The coatings were fully characterized in terms of structure (XRD, Raman) and depth profiling composition by GDOES and RBS (using the nitrogen resonance at 3.70 MeV He⁺ ions). In particular, we have selected three samples with different Ag contents (0, 6 and 20%) and carried out advanced surface characterization using XPS, ARXPS and HR-SEM to study the segregation of silver towards the surface. We have correlated the structure and composition of the films with their biological properties. Microbial adhesion was assessed for both bacteria (*Staphylococcus epidermidis*) and yeast (*Candida albicans*).
ELECTROCHEMICAL AND BIOMIMETIC CALCIUM-PHOSPHATE COATINGS ON METAL IMPLANTS: HOW DO THEY AFFECT MESENCHYMAL STEM CELLS PROLIFERATION AND DIFFERENTIATION?

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Introduction: Bone regeneration is essential in revision joint surgery. Osseointegration into tantalum and titanium alloys is necessary to achieve good fixation of the revision implant. Studies suggest biomimetic or electrochemical calcium-phosphate coatings on the implants will encourage more bone formation.

The aim of this study was to investigate the effect of these coatings on mesenchymal stem cells (MSCs) proliferation and differentiation; and the hypothesis was that there is no differences in MSCs proliferation and differentiation between biomimetic and electrochemical coatings on Tantalum (Ta) and Ti6Al4V (Ti) discs with polished (P) or sand-blasted surface (SB).

Materials and Methods: Discs were coated using 1) biomimetic (BioM) 2) electrochemical at 20mA/cm2 (E20) and 3) at 6.5mA/cm2 (E6.5) methods and characterised. Ovine MSCs were characterised, seeded on the discs and cultured for 4, 7 and 14 days in standard medium, when proliferation and differentiation were measured. Four coating groups were tested: uncoated (control), BioM, E20 and E6.5. Each group comprises PTa, SBTa, PTi and SBTi surfaces (n=3). Controls for differentiation were MSCs on Thermanox discs in standard or osteogenic medium.

Results: Proliferation, measured by Alamar Blue and DNA, was significantly increased on BioM (p≤0.013) and P surfaces (p≤0.037). Differentiation, measured by ALP, was significantly increased on coated groups (p<0.001), SB surfaces (p≤0.01) and E20-E6.5 (p<0.001). No difference was found between Ti and Ta for either proliferation or differentiation.

Conclusions: The nano-crystals produced by BioM coating enhance MSCs proliferation while MSCs differentiation is favored by complex topographies like those of SB discs and E20-E6.5 coatings.
CHEMICAL AND MORPHOLOGICAL MODIFICATION OF TiO$_2$(110) SURFACES AND ITS RELATIONSHIP TO PROTEIN ADSORPTION

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Abstract: TiO$_2$ surfaces are being largely studied for many different scientific and technological reasons. For example, a thin titanium oxide layer is usually formed in titanium medical implants in aqueous environments. In this respect, it should be desirable to attain a good atomic control of the oxide surfaces at different levels, which would permit the modification of their properties. The biological response of biomaterials is strongly related to the morphological and chemical state of their surface. The work presented here has the aim of i) modifying and characterizing TiO$_2$ surfaces with variable physico-chemical parameters and ii) studying correlations/interactions between the protein adsorption response and the previously studied properties.

TiO$_2$(110) single crystals were modified by controlled Ar$^+$ beam sputtering at low ion energy, locally reducing the surface of the oxide due to preferential sputtering. The reduction was confirmed by Auger Electron Spectroscopy (AES).

Atomic Force Microscopy (AFM) images showed a drastic change in the morphology, obtaining a higher surface roughness and structural disorder at the atomic scale after ion bombardment. Mild annealing in air recovers the stoichiometry of the surface, while roughness is retained, allowing the differentiation between chemical and morphological contributions. Characterization also includes static contact angle (SCA), surface free energy (SFE) and zeta potential (ZP) analysis, to determine surface wettability, energetic and charge properties, respectively. Our preliminary results show changes on the protein (FN) absorption due to the morphological changes as well as different conformations.
THE ROLE OF OXIDE LAYER OF TITANIUM SURFACES ON OSTEOBLAST-LIKE CELL ADHESION

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Abstract: Wettability of biomaterials can become determining for protein adsorption and consequently, cell adhesion. It is well-known that oxide surfaces dramatically evolve in oxygen-rich ambient. This is the case of titanium for implant devices, which fast develops a thin film of titanium dioxide [1]. The previous history of this protective film (storage in water/air, surface treatments…) can be critical in the implant functionality. Advancing and receding contact angles are very sensitive to kinetic processes, such as surface oxidation. Further, since biomaterials are long exposed to physiological fluids, the captive bubble method arises as a suitable approach.

We studied finely-polished commercially-pure titanium surfaces (grade IV) upon different conditions. As-received samples were chosen as control sample. During the contact angle measurement, kinetic contact angle hysteresis was found. In order to guarantee the measure of meaningful contact angles, we stored the titanium surfaces in distilled water overnight (over-hydrated samples). Otherwise, the oxidation effects were mitigated using Ar plasma treatment (Emitech K1050X) [2]. No-hysteresis behavior was readily recovered with this treatment (“memory” removal). In order to control the oxidation process, we treated the freshly-cleaned titanium surfaces with O2 plasma at different power values. Plasma oxidation at 50 W produced similar value of contact angle hysteresis than hydration. Instead, EDX analysis revealed different ratios TiO2/Ti onto the surface as the treatment likely due to the different thickness of oxide layer (thermal oxides vs. plasma oxides). We found that as greater plasma power, greater hysteresis and cell adhesion.

IMPACT OF DLC/DLC-F COATING IN THE BACTERIAL ADHESION ON POLYETHYLENE SURFACES

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Abstract: Development of intrinsically antibacterial surfaces is of key importance in the context of prostheses used in orthopedic surgery. Bacterial adhesion on implant surfaces is the first step in the infection process and can eventually lead to implant removal. Septic failure of prostheses represents severe consequence not only because morbidity and mortality of patients, but also for the society, which faces high economical burdens.

Diamond like carbon (DLC) coatings and other plasma based coatings (as, for example, fluorinated DLC, F-DLC) have been proposed to improve the antibacterial performance of biomaterials [2]. In this work we present a thorough study that correlates the surface chemistry and hydrophobicity of this kind of coatings with their antibacterial performance. DLC and fluorinated DLC (F-DLC) films where deposited by RF-plasma assisted deposition at room temperature on UHMWPE samples. The coatings thickness was about 0.1 micron. Chemistry of the deposited films was characterised by X-ray photoelectron spectroscopy and their hydrophobic character by water contact angles measurements. Fluorine content and relative amount of C-C, CF, CF2, and CF3 groups can be controlled from DLC films to samples with 60 atomic % of F atoms. The film chemistry and hydrophobicity have been correlated to studies of bacterial adherence. Adherence of \textit{Staphylococcus aureus} and \textit{Staphylococcus epidermidis} to non-coated, DLC and F-DLC coated UHMWPE were evaluated according to the protocol described by Kinnari et al.[1]. Bacteria-covered surface was analysed by the \textit{Image J} software. Comparisons were performed using an unpaired \textit{t} test (two materials) and a Kruskall Wallis test (all the materials).

\textit{S. aureus} was statistically significant (p≤0.001) less adherent to DLC and DLC-F surfaces than \textit{S. epidermidis}. Both bacteria showed reduction of adherence on UHMWPE-DLC. For \textit{S. aureus}, reduction of bacterial adherence on UHMWPE-DLC-F was statistically significant respect to all other materials.

BACTERIAL ADHERENCE ON UHMWPE DOPED WITH VITAMIN E:
AN IN VITRO STUDY

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Background: Evaluation of S. aureus (SA) and S. epidermidis (SE) adhesion to UHMWPE versus UHMWPE doped with vitamin E (UHMWPEVE).

Methods: GUR 1050 UHMWPE with 3 % and 0.4 % vitamin E was used for the first set of experiments. Commercial GUR 1020 UHMWPE with 1000 ppm vitamin E was used for all other experiments. Collection strains of biofilm-producing SA and SE and 9 clinical strains (5 SA and 4 SE) isolated by using the protocol previously described [1] were used. Samples were incubated during 90 min. with a 0.5 McFarland bacterial suspension and quantified by 1:10 serial dilutions. Biofilm development was measured using Stepanovic method [2] and used as covariable. Statistical analysis was performed by SPSS 17.0 software.

Results: Comparing adherence data of experimental UHMWPEVE and UHMWPE in the collection strains, significant differences were only found in SE. The results obtained using commercial UHMWPEVE were opposite to these data. All the clinical strains showed no significant differences between both commercial UHMWPEVE and non-treated UHMWPE. However, these results were strain-dependent, being different for 2 SE strains, which showed less adherence to UHMWPEVE. Higher Stepanovic grades showed significantly less adherence to UHMWPE but more to UHMWPEVE.

Conclusions: Although commercial UHMWPEVE seems to reduce adherence in collection strains and some clinical strains, the results showed a great variability. More clinical samples and further studies in future should be done to corroborate the properties of UHMWPEVE.

ENHANCED ANTIBACTERIAL PROPERTIES OF BIOMEDICAL SURFACES THROUGH MICROMETRIC SILVER ISLANDS


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Abstract: A set of Ag2CuMnO4 and CuMnO films were sputter deposited onto polished titanium aluminum vanadium coupons in order to study the adherence of Staphylococcus sp to biomedical surfaces modified using advanced ternary and quaternary oxides incorporating micrometric silver islands. The deposited Ag2CuMnO4 compound crystallizes in a delafossite structure and it is the first example of Ag and Cu maintaining this kind of structure. Upon air annealing, silver-oxygen bonds in the compound destabilize, resulting in the segregation of metallic silver in the form of micrometric layered silver islands with high specific area dispersed at the surface of a copper-manganese-based oxide. Silver is well known to have a natural biocidal character and its presence in the surface forming large micrometric escalonated islands is, in principle, predicted to enhance the antimicrobial properties of biomedical surfaces.

Microbial adhesion tests using collection strains of Staphylococcus aureus and Staphylococcus epidermidis were performed in triplicates using Kinnari et al. protocol. (J Biomed Mat Res Part A. 2008. 86:760-8) Photographs were analysed by Image J software and statistical analysis was performed using EPI-INFO software. Preliminary results indicate that both strains showed lowered adherence to modified materials. S. epidermidis showed higher adherence for all materials than S. aureus, and there were also differences between CuMnO and AgCuMnO containing silver islands due to the higher exposed surface area of the silver-containing compounds and the biocidal efficacy of silver islands. The current modifications could have a potential role in the prevention of implant-related infections.
EVALUATION OF THE EFFECT OF VITAMIN E DOPED UHMWPE ON BIOFILM DEVELOPMENT AND INFECTION USING AN IN VIVO EXPERIMENTAL MODEL

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Background: Evaluation of an in vivo experimental model of implant-related septic arthritis.

Methods: Collection strains S. aureus and S. epidermidis were used. 5 x 10 mm strips out of a polyethylene sheet 500 microns thick were incubated during 90 min. with a 0.5 McFarland bacterial suspension. A surgical experimental model was prepared, implanting the samples in the subquadricipital articular space of the rabbit’s knee. Under general anesthesia with IM Ketolar, a medial proximal parapatellar approach was performed, incising up to the quadriceps tendon. A blunt instrument was introduced from distal to proximal and, while maintaining the instrument as a guide, the sample was introduced and the joint was closed. After 7 days the rabbits were slaughtered by pentobarbital overdose. Following the previous approach, the knee joint was opened wide and the polyethylene sample was retrieved with sterile forceps, and then introduced into the culture tube. Samples were processed following a sonication and quantification protocol. Ten rabbits for each species were studied, five with each material. Negative controls (UHMWPE strips without attached bacteria) were also used.

Results: S. aureus colonies were detected only in three rabbits with non-treated UHMWPE and in two with vitamin E-doped UHMWPE. No differences in colony counts were observed for S. aureus. No growth was detected for S. epidermidis, although clinical signs of infection were detected in all animals with inoculated samples.

Conclusions: The model was useful to evaluate the effect of modifications in biomaterials, although highly pathogenic bacteria are needed to obtain quantifiable data.
Si+ ION IMPLANTATION REDUCES THE BACTERIAL ACCUMULATION ON THE Ti6Al4V SURFACE UNDER FLOW

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Abstract: Ti6Al4V is one of the most commonly used biomaterials in orthopedic applications due to its interesting mechanical properties and reasonable biocompatibility. Nevertheless, after the implantation, microbial adhesion to its surface can provoke severe health problems associated to the development of biofilms and subsequent infectious processes. This work shows a modification of the Ti6Al4V surface by Si+ ion implantation which reduces the bacterial accumulation under in vitro flow conditions. Three Staphylococcus strains were used, S. aureus ATCC29213 (S. aureus), S. epidermidis ATCC35984 (S. epidermidis4) and S. epidermidis HAM892 (S. epidermidis2). Ion implantation was made by using a F4Si precursor on the surface of 25 mm diameter disks of Ti6Al4V. Experiments were carried out at 37 ºC in a parallel plate flow chamber and the results were analysed in terms of flow or static conditions by selecting a constant flow rate or stopping the bacterial flow. In addition, microbial retention to the surface was analysed by passing air-liquid interfaces after the adhesion process. Results have shown that the number of bacteria remaining on the surface at the end of the flow experiments decreased for silicon-treated surface. The new surface also presented a lower ability to retain adhered bacteria.
7-AMINOHEPTANOIC-ACID COATED COBALT NANOWIRES FOR BIOMEDICAL APPLICATIONS

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Abstract: Due to their small dimensions, nanomaterials can interact with living cells allowing their use in medicine both in diagnosis (Medical Imaging) and therapy (hyperthermia and drug delivery). The use of nanowires instead of the commonly used nanoparticles in these applications allow exploring new effects such new geometry which larger active surface and multilayered structures adapted for specific applications. Metallic nanowires can be easily electrodeposited using porous membranes as templates. However, a biocompatible coating is needed to functionalize them and use them in bio-applications. We have electrodeposited Co nanowires, material with high magnetic polarization, which ensures larger magnetic contrast in medical imaging techniques. After electrodeposition, the polycarbonate template used for growth has been removed and the wires have been coated with 7-aminoheptanoic acid and transferred to water. SEM and TEM characterization show that nanowires are well dispersed in the solution. The cytotoxicity and cellular uptake of the Co nanowires have been studied using HeLa cells. The influence of concentration and exposure times on the cytotoxicity of Co nanowires in HeLa cells have been evaluated by MTT assay combined with direct morphology observations by TEM and phase contrast microscopy. The results showed that the presence of Co nanowires had no significant effect on cell viability even at the highest concentrations studied, demonstrating that Co nanowires have a very good biocompatibility. Therefore, we have established a protocol, which allows to synthesize nanowires with large magnetic signal and low cytotoxicity that can be functionalized for bio-applications.
SURFACE-ATRP OF PEGMA ONTO POLYDIMETHYL SILOXANE
FOR BIOMEDICAL APPLICATIONS

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Abstract: Silicone rubber (poly(dimethyl siloxane; PDMS)), is extensively used for
biomedical implants due to its low toxicity, flexible processing techniques, long-term
endurance and good blood compatibility. However, the presence of low molecular weight
organic molecules and catalyst residues that cause host systemic inflammatory reactions.
The hydrophobic nature of PDMS also allows microbial adhesion followed by infection.
Hydrophilic PDMS surfaces would be of great value in inhibiting biofilm formation thus
prolonging the lifetime of the implants. This could be obtained by surface-initiated atom
transfer radical polymerization (ATRP). The robustness and versatility of ATRP allow the
preparation of functional bioactive surfaces, including antifouling, antibacterial, stimuli-
responsive, biomolecule-coupled and micropatterned surfaces.[1-3] We aim at establishing the experimental conditions allowing the surface-grafting of
polyethylene glycol methacrylate (PEGMA) by surface attaching an initiator (1-
trichlorosilyl-2-(chloromethylphenyl)ethane) onto PDMS (Sylgard ® 184). Here, cooper is
being used as a metal catalyst and 2,2'-Bipyridine as a ligant. Polymerizations are being
assayed in aqueous media.
The native smooth and transparent surface of the PDMS could be preserved following
polymerization (as confirmed by SEM). FTIR-ATR also showed the presence of PEGMA
polymer chains. By contact angle measurement, a change in the surface hydrophobicity
was observed, the values changing from 114° to 60°, following 30h polymerization.
Work is in progress to optimize the modification of PDMS by PEGMA surface-ATRP.
This implies following up the polymer chain growth kinetics, surface characterization by
XPS, FTIR-ATR, SEM and contact angle measurements. Static and dynamic microbial
adhesion, as well as biocompatibility studies are also envisaged.


Acknowledgments:
Project BIOSURFA, ref. PTDC/SAU-BEB/73498/2006, funded by FCT.
TAILORING SURFACE CHARGE OF TIN THIN FILMS FOR BIOMEDICAL APPLICATIONS

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Abstract: Titanium Nitride (TiN) is a reputed conductive material very often applied in biomedical applications [1,2]. In this work we will describe the tailored modification of TiN to tune the surface conductivity of this material by ion implantation of O²⁺. Implantations onto magnetron sputtered TiN were carried out at energies ranging from 10 to 40 KeV and fluencies ranging from 5.10¹³ to 5.10¹⁶.

Structural (x-ray diffraction), optical (reflectance UV-vis spectroscopy) and electric characterizations (four probe measurements) have been carried out to confirm the possibility of controlling the degree of O integration in the TiN structure, which is hardly feasible by alternative techniques such as thermal processing due to diffusive effects of O. Preliminary influence of surface charge modification on TiN has been assayed by studying the adhesion of human mesenchymal stem cells.


FAILURE ANALYSIS OF A BIOMEDICAL GRADE COMPONENT

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Abstract: The spacer failed to service its fracture producing approximately half the biomedical component. The aim of this study is to characterize the failure of that component and establish the probable causes of the failure of the same from the analysis of the results of various tests performed. Phases present were determined and microstructural characterization of the material. On the other hand also conducted a fractographic analysis of fracture surface by optical microscopy. Also stopped metallographic samples of each piece of the component to evaluate the microstructural phase of each piece of the spacer and hardness. The material is an austenitic stainless steel 316 LVM. Moreover, it was found that the failure was caused by fatigue, caused by overloading of the implant above its voltage, resulting in the decrease in the number of cycles to failure.

COMPUTER SIMULATION OF SCAFFOLD’S DEGRADATION

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Abstract: Aim of the present work is to parametrically generate valid 3D models for scaffold architectures, and to simulate degradation processes occurring on these structures. Such an achievement would result in more effective scaffold design, taking advantage of extended in-silico optimisation in place of time-consuming empirical experiments.

A specific algorithm was developed for the generation of initial 3D scaffold microstructure by randomly arranging fibres in a predefined volume, each fibre trajectory being defined as a polyline. The obtained 3D microstructure was then discretised into small homogeneous cubic elements (voxels).

The second algorithm was devoted to simulating the degradation process, starting from the above described microstructures. The model is based on a Monte Carlo method, according to which the degradation probability of a given voxel is related to the number of solid surrounding neighbours, thus relating fibre degradation with surface curvature.

Geometrical characteristics for the generation of the initial microstructures were obtained from real SEM images of poly-L-lactide (PLLA) scaffolds synthesized by electrospinning, starting from a solution of PLLA in dichloromethane. Evolution of the fibres’ volume fraction was recorded during the simulation and converted into mass loss values. Such data were compared with empirical measurements, obtained by incubating given amounts of PLLA fibres in suitable medium and timely evaluating mass loss. At each certain time, samples also underwent SEM characterization, for a comparison with modelled morphology.

Good agreement with empirical data suggests that the proposed model has great potential for application in the optimisation of scaffold’s design for specific tissue engineering applications.
CHITOSAN NANOCAPSULES: EFFECT OF CHITOSAN MOLECULAR WEIGHT AND ACETYLCATION DEGREE

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Abstract: In the last years, chitosan nanocapsules have shown very promising results as carriers for oral drug or peptide delivery. The success in its applicability strongly depends on the stability of these colloidal systems along the digestive tract. In gastric fluids, a clear stability is found due to the high surface charge density shown by the chitosan shell, which is completely charged at acidic pH. However, in the intestinal fluid – where the pH is almost neutral – the effective charge of these nanocapsules is practically zero, and no stabilization provided by electrostatic forces can occur. Despite the lack of surface charge, chitosan nanocapsules are stable in intestinal simulated fluids. We have recently demonstrated [1] that this anomalous stability (at zero charge) is given by short-range repulsive forces that appear between hydrophilic particles when they are immersed in saline media [2]. The present work aims to study the influence of the chitosan hydrophobicity, as well as it molecular weight, in the stability of different chitosan nanocapsules. The size, polydispersity, electrophoretic mobility and colloidal stability of eight core-shell nanocapsule systems, in which the chitosan shell properties have been modified by using low molecular weight (LMW) and high molecular weight (HMW) chitosan chains containing different degrees of acetylation (DA), have been studied. With regard to the stability mediated by repulsive hydration forces, the LMW chitosan provided the best results. In addition, and contrary to that initially expected, a higher stability (also mediated by hydration forces) was obtained in those samples formed with chitosan chains of high DA values (that is, with less hydrophilic chitosan). Finally, a theoretical treatment was also performed to quantify the hydrophilicity of the chitosan shells.

El Ca₃(PO₄)₂ (TCP) tiene tres formas polimórficas, β, α y α´. La última transforma durante el enfriamiento en la forma α careciendo de interés. El β-TCP es estable a temperatura ambiente y transforma a 1125°C en α-TCP, que es retenida metastablemente durante el enfriamiento hasta temperatura ambiente [1]. Nurse y col.[2] y Fix y col.[3], en el estudio del sistema Ca₂SiO₄(C₂S) - TCP, sugieren tentativamente una zona donde la fase α-TCPₚₛₚ, conteniendo Silicio en solución sólida, es estable hasta temperatura ambiente. Sin embargo, Fernández y col.[4] consideran que el C₂S no estabiliza la fase α-TCPₚₛₚ a temperatura ambiente.

Para aclarar dichas contradicciones, se sinterizaron materiales de α-TCP dopado con diferentes proporciones de C₂S, mediante reacción en estado sólido. Los materiales obtenidos se caracterizaron mediante DRX y SEM-EDX, demostrándose que existe una región entre el 0,5 y 3,0 % en peso de C₂S donde el α-TCPₚₛₚ es estable a temperatura ambiente.

RESUMEN: Uno de los principales problemas de las prótesis articulares es el desgaste. Si es muy elevado, puede llegar a producir el fallo mecánico y/o el aflojamiento del implante, siendo entonces necesaria una nueva intervención quirúrgica.

Los metales y polímeros abarcan aproximadamente el 50% de las aplicaciones de los biomateriales. Las familias de aleaciones metálicas más empleadas son las de Co-Cr [1-6], las de Ti [4-6, 7,8], los aceros inoxidable [8,9] y las aleaciones de Zirconio [9,10]. Los polímeros más empleados son los UHMWPE [3-5]. La reducción del desgaste de los implantes se consigue por aplicación de tratamientos superficiales tanto en los metales como en los polímeros.

Este trabajo realiza una revisión profunda en este tema. Se presentan tanto los materiales y recubrimientos utilizados en prótesis de rodilla, como las técnicas de ensayos de desgaste utilizadas y el comportamiento frente al desgaste de las soluciones actuales y de las nuevas tendencias.

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