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PhD Yearbook | 2025

Chair:
Prof. Chiara Bertarelli

DOCTORAL PROGRAM IN MATERIALS ENGINEERING

The Ph.D. Programme in Materials Engineering provides high educational opportunities to young talents and executives who intend to become proactive professionals and researchers skilled in the design, production and application of both traditional and innovative materials, their optimization for specific applications, the prediction and assessment of their performance, and in developing new concepts and technologies in any materials-related fields.

Highlights of the Ph.D. Programme in Materials Engineering are:

- a rigorous scientific approach to address outstanding research
- an effective interdisciplinary approach
- connection with international leading scientific and technical communities
- a strong integration with the Doctorate School of Politecnico di Milano to increase knowledge with transversal courses, to gain soft skill and to join stimulating activities.

PHD CONTENTS AND PROGRAM STRUCTURE

Materials Engineering involves the investigation of correlation among materials structure, processing and functional and structural properties, and the knowledge management from materials design to final applications.

The Programme includes advanced research and training on:

- Research and development in traditional materials (*polymers, metals, ceramics, concretes, composites*) and related technologies.
- Specific application areas: *materials for energy, materials for environment, materials for electronics, optoelectronics and photonics, materials for cultural heritage, materials for product design, materials for packaging, biomaterials.*
- *Smart, responsive and self-healing materials, nanostructured materials.*
- *Materials corrosion and durability, life cycle assessment, coating and surface functionalization*

The achievement of the Ph.D. title in Materials Engineering requires a full-time study and research activity of at least three years which is completed by the development and defense of the Ph.D. thesis.

The PhD. students give an original contribution to increase knowledge in a material-related research field, and they acquire a problem-solving capability in complex contexts, including the ability of performing deep problem analysis, identifying original solutions, and evaluating their applicability in practical contexts. Students can use modern facilities for materials synthesis, processing and characterization available at the Politecnico di Milano or in other research laboratories.

The Ph.D. Programmes and the Ph.D. School offer courses, seminars, project workshops and laboratories. Teaching activities cover both basic research topics (problems, theories, methods) and specialistic topics related to the subjects developed in the theses. Ph.D. students are also encouraged to attend national and international Conferences Workshops and Schools and to plan a research period abroad.

PROFESSIONAL OPPORTUNITIES AND THE JOB MARKET

The Ph.D. Programme in Materials Engineering aims at training graduates with a common background and specialized qualifications in advanced research areas. The knowledge and skillsaquired during the Ph.D. Programme in Materials Engineering enable graduates to pursue their career in the Manufacturing industry, particularly in areas related to innovation in the production, processing, application, and preservation of traditional materials, as well as the development of innovative materials that can enable radically new and currently unforeseeable applications.
Moreover, the experience gained from full-time research and educational activities also qualifies Ph.D. graduates for academic careers. Many alumni of the Materials Engineering Ph.D. Program have secured post-doctoral research positions at prestigious Universities and research Institutes.

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SOLUTION ELECTROWRITING OF NATURAL POLYMERS FOR SKELETAL MUSCLE TISSUE ENGINEERING

Laura Armenio - Supervisors: Lorenza Draghi, Silvia Farè

Tissue engineering main objective consists in creating constructs able to restore partially or totally a tissue or organ of interest, relying on cells, scaffolds, and signalling components. This discipline is gradually evolving towards a higher complexity degree in reproducing tissue architectures, and towards a higher scalability for high-throughput, to unlock its potential as an alternative therapeutic strategy to conventional existing ones, for a more patient-specific approach. Control in shapes and material disposition, as obtained is direct-writing mode, is essential to replicate with high fidelity extracellular matrix, and one determinant requirement is to reach strut dimensions in the typical extracellular matrix scale, which can boost cell viability and proliferation.
Direct-writing electrospinning – performed in form of either solution electrowriting or melt electrowriting – can be regarded as a way to meet both conditions: thanks to electric field application combined to XY axis motion assigned to the fiber collector, both guidance over filament deposition and extracellular matrix-like filament caliber are attained.
Particularly solution electrowriting can bring to thinner fibers than melt electrowriting and other extrusion-based techniques such as wet spinning or fused deposition modeling, and opens the possibility to process even natural polymers, well-known for their cell-adhesive properties and biocompatibility given by their similar macromolecular structure to tissues, offering the convenience of recognition from the biological system compared to synthetic polymers when implanted. Despite this advantageous field of application, solution electrowriting is still far from being a standard in tissue engineering, with still few studies delving into this technique for natural polymers. Additionally, solution electrowriters are often in-house built, without shared protocols or standardized commercial platforms and data comparability amongst laboratories is halted for this reason, which consequently limits solution electrowriting spreading. Proposing a system for solution electrowriting user friendly, easy to be set up, and versatile in terms of admitted motions, would help break barriers towards a more extended use of this technique, allowing to replicate even different intricate tissue morphologies.

In this work, firstly, a setup suitable for solution electrowriting was designed and developed, demonstrating control over process parameters in terms of fiber morphology and an easy placement of fibers even along curved and intricate paths. Both synthetic and natural polymer processing was possible, in form of submicrometric fibers with diameters hardly achieved with natural polymers before with solution electrowriting, and with a higher alignment degree than other common methods to obtain oriented fibers, e.g. electrospinning with parallel plates.
Using a solution made by methacrylated gelatin and bovine serum albumin, multi-layered oriented scaffolds were iteratively fabricated for skeletal muscle regeneration purpose. This tissue is the ideal candidate to biologically test efficiency of solution electrowritten scaffolds, thanks to the highly aligned fibers that can be obtained with controlled fiber deposition which can provide an essential cue towards myotube maturation and complete tissue restoration.
The SEW system developed proved guidance over seeded C2C12 cells and human myoblasts, which were viable and proliferated on samples. More work needs to be done to encourage cell differentiation into myotubes or reserve cells, which is not supported in the long term, despite being ameliorated if compared to plain substrates with no fiber patterns on top. Nevertheless, the overall setup is a promising, cost-effective and easy-to-use tool to fabricate extracellular matrix-like structures with any desired orientation and shape, all features that meet the needs towards more personalized and reliable approaches in regenerative medicine and tissue engineering

STRUCTURE, INTERACTIONS AND PROPERTIES OF FUNCTIONAL POLYMER FIBRES: ELECTROSPINNING OF POLYMER BLENDS AND SPECTROSCOPIC CHARACTERIZATION

Alessia Arrigoni - Supervisor: Chiara Castiglioni

The thesis project is focused on the design, preparation and characterization of innovative polymeric materials. Electrospinning is used to obtain micro- and nanofibers of functional polymers. The blending or doping of the polymer fibers with small organic molecules is explored, with the aim of imparting them new functionalities or improved performances. The use of molecular blends introduces a new level of complexity and possible control over the properties of the resulting material: due to the novelty of these materials, before being tested for potential applications, a comprehensive structural characterization is essential.

In this framework, molecular spectroscopy has been applied as a tool to gain a comprehensive understanding of the molecular structure, interactions, and composition in terms of amorphous and crystalline phases.

The blends studied include optically active molecules mixed with a piezoelectric polymer (polyvinylidene fluoride-co-trifluoroethylene (P(VDFTrFE)) and a semi-conductive polymer (poly-3-hexylthiophene (P3HT)) to which dopant molecules are added. P(VDF-TrFE) fibers have been produced in blend with two different photochromic molecules (namely 4-(4-Nitrophenylazo)aniline and 4-Amino-4′ (dimethylamino) azobenzene) to explore the possibility of triggering the piezoelectric response of the polymer in an unconventional way with light. In the case of P3HT fibers, to increase the polymer conductivity, two different chemical dopants (I2 and F4TCNQ) have been used to produce doped P3HT with raised and potentially modulable conductivity. The preparation of these complex materials required to develop specific strategies, e.g. the addition of a scaffold polymer in the feed solution to improve the spinnability of P3HT, as well as the optimization of electrospinning parameters. The spinning process allows the production of macroscopically oriented fibers, resulting - for piezoelectric fibers - in a highly anisotropic material with oriented crystalline domains which can potentially enhance the piezoelectric response. A material made by semiconducting polymer fibers, on the other hand, takes advantage of peculiar morphological features, which can impact on its physical properties, particularly on the performance of the charge transport which is sensitive to molecular packing and orientation.

Electrospun fibers have been successfully produced with reproducible protocols to obtain high-quality fibers with uniform diameters, no beads, and excellent macroscopic alignment. Electron microscopy techniques such as SEM and TEM have been used to analyze the morphology of the fibers. In particular, SEM microscopy played a vital role in leading the optimization of the electrospinning parameters for P3HT fibers and in the selection of the appropriate molecular weight of P3HT for e-spinning.

In the investigation of P(VDF-TrFE)/dye fibers, by using a combination of SEM and TEM microscopies and EDX analysis, along with the support of IR spectroscopy, we identified unique features like the presence of an electrospinning-induced metastable phase when the polymer is in blend with 4-(4-Nitrophenylazo)aniline molecule. Moreover, a dye concentration gradient across the fibers diameter has been demonstrated: it is characterized by a blend phase rich of the guest molecules on the surface of the fibers.

Vibrational spectroscopy allowed a noninvasive study of molecular and supramolecular architecture in electrospun fibers. The interpretation of the spectra was supported by correlative analysis and by comparison with the spectra of the individual components of the blend. IR measurements on macroscopically aligned fibers in polarized light were particularly crucial as they provided information regarding molecular orientation within the fibers. The analysis of the IR spectra proved that the fibers we prepared from the P(VDF-TrFE)/dye blends preserve the β crystalline phase and the orientation properties of the piezoelectric polymer. This ensures that the blend retains the piezoelectric property and the characteristic anisotropy imparted by the fibrous morphology.

The method of preparation and characterization of phothocromic/piezoelectric fibers is now mature for subsequent research steps, namely the assessment of the efficiency of the photoisomerization reaction within the fiber and the set-up of suitable tests highlighting the activation of the piezoelectric response of the polymer upon photoexcitation of the guest molecules.

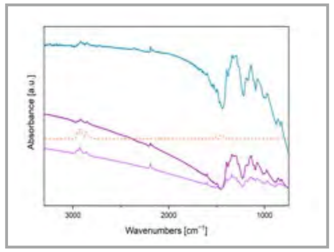

Fig. 1 - IR spectra of P3HT fibers, macroscopically aligned, and doped with F4TCNQ. Blue: spectrum in natural light; purple: spectra recorded in polarized light parallel (dark) and perpendicular (light) to the fiber axis. Dashed: spectrum of pristine fibers in non polarized light.

Concerning semiconducting P3HT fibers, evidence of successful doping in P3HT fibers confirms the creation of charge carriers (i.e., the polarons) in the polymeric material, showing that it is possible to obtain highly anisotropic organic conducting material through the production of doped electrospun P3HT fibers. The arrangement of the crystalline domains and the morphology of P3HT have a significant impact on the mobility of carriers. This is because they influence both interchain charge hopping processes and intrachain transport. The anisotropic structure of P3HT fibers may enhance transport processes in the direction of the fiber axis by taking full advantage of intrachain processes.

This thesis project has demonstrated that the doping level in P3HT fibers doped sequentially with F4TCNQ remained stable for at least seven days. However, when Iodine vapours are used for sequential doping, issues arise regarding the stability of doping. It has been found that spinning fibers from a solution containing the dopant – i.e., one-step doping – is a viable route to make the Iodine-doped phase more stable. However, a protocol still needs to be developed to ensure a good yield of doped fibers and to reduce the presence of defects in the material. When adopting the one-step doping, it is mandatory to keep the scaffold polymer inside the fibers. Indeed, when removing the scaffold PEO polymer, also the dopant is extracted.

In this complex and puzzling context, we believe that the effort to develop effective and reproducible production protocols and characterization tools suitable for electrospun functional polymer can smooth the process toward innovative and technologically relevant materials.

BEYOND NAFION®: INVESTIGATION OF SELF-STANDING SULFONATED GRAPHENE OXIDE MEMBRANES AS ALTERNATIVE PROTON CONDUCTORS FOR PEM FUEL CELLS

Andrea Stefano Basso Peressut - Supervisor: Giovanni Dotelli

Proton exchange membrane fuel cells (PEMFCs) stand out for their ability to generate electrical power with a high throughput and near zero emissions. Hence, they are expected to play a crucial role in the coming energy transition, involving the complete withdrawal from fossil fuels and the replacement of internal combustion engine vehicles with ones based on alternative technologies.

The proton exchange membrane is the core of the device and one of the areas where PEMFCs have extensive room for improvement. Nowadays, Nafion® is the state-of-the-art electrolyte of PEMFCs and enabled their rise as the most widespread fuel cell technology at the commercial scale. However, it is strictly bound to operate between 60 °C and 80 °C with fully humidified fuel and oxidant gases. Moreover, its production and disposal may cause the release of toxic and environmentally persistent per- and polyfluoroalkyl substances (PFASs).

In addition to being PFASs-free, suitable alternative proton exchange membranes should be able to outperform Nafion® above 60 °C and at relative humidity (RH) lower than 60%, i.e., in conditions which would enhance both efficiency and kinetics of the redox reaction, simplify cell design and water management, as well as increase the tolerance to fuel impurities.

Among the most attractive candidates, graphene oxide (GO) acquired significant consideration due to its remarkable self-assembling properties. However, pure GO membranes exhibit a poor performance in the PEMFC environment, due to limited proton conductivity, large hydrogen crossover losses, and unsatisfactory durability.

On these grounds, this work focused on the development of innovative proton exchange membranes via the functionalization of graphene oxide according to three different research paths, with the aim to improve both its ability to carry protons and its structural stability.

The first research line exploited a direct reaction between graphene oxide and sulfuric acid to allow the covalent insertion of sulfonic acid (-SO3H) moieties, analogous to those of Nafion®, on the flakes of GO. Thus, sulfonated graphene oxide membranes (SGO-X) were produced with six different acid-to-GO molar ratios (X between 1 and 20). The successful functionalization of GO was verified via energy-dispersive X-ray, attenuated total reflection Fourier-transform infrared, and X-ray photoelectron spectroscopies. They detected the presence of -SO3H groups and suggested a correlation between the alterations of the original features of graphene oxide and its sulfonation degree. These also include the partial graphitization and amorphization of GO layers, as confirmed by Raman spectroscopy and X-ray diffraction. A leaching action by sulfuric acid residues and thermal reduction effects were identified as the main cause, proving to be more severe in SGO-15 and SGO-20 specimens, prepared with the highest acid-to-GO ratios and showing an unsatisfactory thermomechanical stability. However, these changes did not compromise the electrically insulating ability of the material and the increase in water uptake, ion exchange capacity, and proton conductivity compared to both Nafion® 212 and virgin graphene oxide. At 42% RH and above 60 °C, SGO-10 exhibited a water uptake more than 40% greater than that of GO and roughly one order of magnitude higher than the one of Nafion® 212. Similarly, its ionic conductivity increased by up to 30% in the same conditions with respect to Nafion® 212, and an even greater rise of both properties was measured at 95% RH. Sulfonation also enabled SGO-X membranes to become slightly more flexible than GO ones, with at least a 20%-improved strain at break in SGO-10.

The second path tried to enhance the structural stability of SGO-X samples by using sodium tetraborate decahydrate (SBD) as a possible crosslinker to prepare SGO-BY membranes with two different GO-to-SBD molar ratios (Y = 40, 80), while the acid-to-GO ratio was kept constant to 10. Their characterization demonstrated that a mutual interference exists between -SO3H groups and SBD molecules, which seems to limit up to a certain threshold the integration of the latter into GO and to alter the expected crosslinking mechanism upon heat treatment. The annealing process appeared to amplify this detrimental effect, causing a more severe graphitization and amorphization than those suffered by as-prepared SGO-10. Eventually, this led its proton conductivity at 95% RH to drop by nearly one order of magnitude after the modification with SBD, which also failed to enhance the structural integrity of the material, whose tensile strength and elongation decreased as well. Nonetheless, SGO-B80 A still showed values of ion exchange capacity and mechanical resistance comparable to those of SGO-10, as well as a promising ionic conductivity above 60 °C with respect to other crosslinked membranes reported in the literature.

The third research route developed a composite membrane by combining graphene oxide with naphthalene sulfonate (NS) molecules and exploiting their similar structures to achieve a non-covalent functionalization via π-π interactions. This allowed -SO3H moieties to be inserted within GO sheets while limiting the detrimental effects caused by the previous two functionalizations. Six GONS-Z-TW membranes were produced by evaluating the effect of three GO-to-NS molar ratios (Z = 1, 5, 10) and two alternative temperature profiles (TW = T25, T100) during the mixing stage. Spectroscopic analyses and X-ray diffraction verified the successful integration of NS moieties into GO and the minimal changes to its framework. However, the highest naphthalene sulfonate quantity (Z = 1) seemed to excessively perturb the basal plane of graphene oxide flakes, reducing the interaction between the two components, the structural stability, and the ion exchange capacity with respect to those exhibited by higher GO-to-NS ratios. The GONS-5-T100 membrane showed greater water uptake and proton conductivity than pure GO at 53% RH, proving the strong acid nature of NS species, but it overcame the results of Nafion® 212 only at 95% RH, suggesting a predominance of hydrophobic and steric hindrance effects of naphthalene sulfonate rings at reduced humidity. The insertion of NS into GO also caused its significant embrittlement, even worse than in the case of the modification with SBD, probably due to the interference between these species and the deformation mechanism of graphene oxide, involving the reciprocal sliding of its layers and a local rearrangement of hydrogen bonds.

The investigation of the previous three membrane types led to identifying SGO-10, SGO-B80 A, and GONS-5-T100 as the candidates showing the best compromise among an effective functionalization, a reduced impact on the original features of GO, and a successful increase of most of their functional properties. Thus, they were subjected to a preliminary analysis of their environmental impacts via the life cycle assessment method, with the aim to detect possible environmental hotspots to be faced. This analysis highlighted that the proposed membranes exhibit higher impacts than Nafion® 212, concerning their manufacturing process, due to a greater consumption of electricity. Nonetheless, they show at least one-order-of-magnitude better results than Nafion® 212 in the ozone depletion impact category, since they do not contain fluorine-based species.

In conclusion, this study developed a reliable functionalization process to raise the ionic conductivity of graphene oxide in the desired temperature and relative humidity conditions, while preserving its self-assembling ability and enabling the production of self-standing membranes. Out of the entire set of the investigated materials, SGO-10 eventually demonstrated the most promising trade-off among all properties, due to its superior proton transport at high temperature and reduced humidification, coupled with the best structural stability and carbon footprint.

POLYMERS STRUCTURE AND MORPHOLOGY OF HOT-MELT ADHESIVES: RELATIONSHIPS WITH REHOLOGICAL, THERMAL, MECHANICAL PROPERTIES AND PROCESS PERFORMANCES

Alberto Bugana - Supervisor: Stefania Assoni

Known in industrial practice by the English term "hot-melts", hot-melt adhesive formulations are polymer-based, solvent-free thermoplastic compounds. Hot-melt adhesive technology has become widely used for several reasons compared with other types of adhesives. Firstly because of their low cost, but also at the technological level because of the reduction of VOCs (Volatile Organic Compounds), the elimination of solvent removal steps (organic or aqueous) during application, which makes them particularly popular in high-speed production processes, such as the sanitary-ware market.

Recently, some polymer Companies have abandoned classical Ziegler-Natta type catalytic systems in favor of new metallocene type catalysts that allow the synthesis of new generation polybutenes-1 with new and much improved characteristics, such as significantly lower and much more controlled average Molecular Weights (and thus much lower viscosities); much smaller Polydispersity Indices (much narrower molecular weight distribution), properties all of which are reflected in improved characteristics of these polymers (good processability, good mechanical properties even at relatively low viscosities, lower Volatile Organic Compounds).

Savaré I.C. and LyondellBasell in 2016 designed and patented a new PB-1 polymer, Koattro PBM1500M (Fig.1), with the scope to create a strong innovation in hygiene market, thanks to the low viscosity of this polymer that allows a high percentage of polymer in the hot-melt adhesive formulation, enhancing the mechanical properties and the thermal stability of the adhesive, beside its overall low VOC content and low odor and color.

Unfortunately, during the industrial application of the new adhesive formulation containing this new Koattro PBM1500M, a severe "die build-up" appears on the line, stopping the possibility to commercialize the hot-melt adhesive in Companies using slot die coating technology.

The die build-up is a phenomenon well known in literature that occurs during the slot extrusion coating process of polyolefins, when the coating polymer sticks on the extrusion head rather than to deposit on the substrate (Fig.2).

In this work, starting from a structural characterization of the materials and a rheological characterization, we arrive to define a correlation between the high shear stress in the head of coating and the die build-up. We applied a rheological test that show how metallocenic poly-1-butene polymers have a kinetic of crystallization influenced by the overimposed shear. In detail, we show that PB-1 systems which are more prone to shear induced crystallization in a purposely designed rheological experiment are also more prone to build-up. The shear induced crystallization proneness seems to be correlated to the molecular weight distribution, because increasing the Mw and widening the polydispersity of the PB1 mixtures seem to reduce the tendency to shear induced crystallization reducing or eliminating the occurrence of die build-up. We investigated so the correlation between the molecular weight distribution, the Shear Induced Crystallization (SIC) and the die build-up intensity testing polymers or mix of polymers with the shear induced crystallization test on the rheometer and proposing new hot-melt adhesive formulations to be tested on a pilot line present in Savaré I.C., equipped with slot die coating head. The pilot line runs proves the goodness of our predictive approach using techniques available in laboratory (GPC and rheometers only need), replacing the old trial and error approach used and so producing saving in time and costs of the project for Savaré I.C.. In fact, thanks to the test methods developed in this project work, we are now able to predict if a material has a good processability (no build-up).

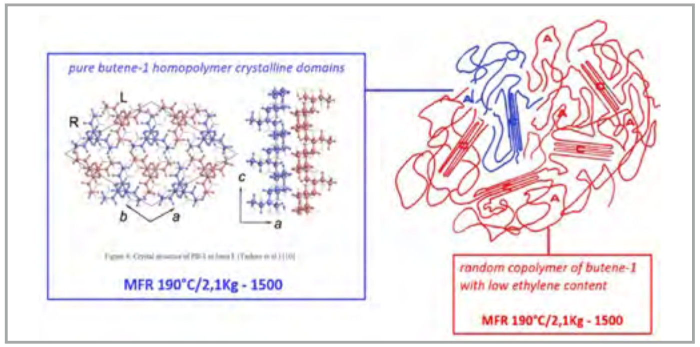

Fig.1 - Qualitative description of Koattro PBM1500M from LyondellBasell

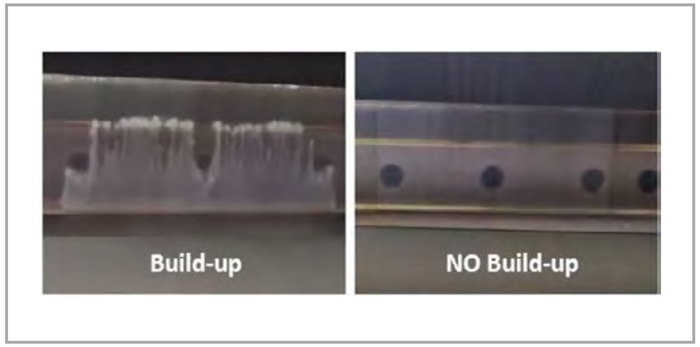

Fig.2 - Die build-up phenomenon

DEVELOPMENT OF HIGH GAS BARRIER BIOPOLYMER-BASED NANOCOMPOSITE COATINGS FOR PACKAGING APPLICATIONS

Alessia Cabrini - Supervisor: Pierfrancesco Cerruti

High gas and water barrier materials for packaging and protective applications are of great interest to improve the shelf life of pharmaceuticals, reduce food waste, and protect flexible electronics. Polymers have been the primary materials employed in these sectors due to their several advantages. However, their elevated consumption, problems with their end-of-life management, and the need to often combine them with less permeable or impermeable materials developing even less sustainable systems, have generated growing concern about the resulting environmental consequences. Thus, recent research has shifted towards using biodegradable and/or bio-based materials.

Nevertheless, even more than synthetic polymers, bio-based polymers' gas and water barrier performance is often inadequate for the mentioned applications. Thus, the use of natural polymers is still restricted because of their low chemical resistance due to their hydrophilicity and poor processing repeatability.

In this context, the work of the PhD thesis was focused on investigating new strategies to develop sustainable and high gas and water barrier nanocomposite coatings based on chitosan, a renewable and biodegradable polymer. In particular, the research activities focused on verifying the potential of some high aspect ratio nanomaterials in developing barrier bionanocomposite coatings, as well as on clarifying the effect of different processing technologies, including ultrasonic spraying and Layer-by-Layer (LbL) assembly, on their chemical-physical and structural characteristics, and functional properties. The goal was to form highly structured thin films with elevated loading of highly aligned and homogeneously dispersed nanoplatelets. This kind of microstructure, shown in Figure 1, significantly extended the gas penetration paths and reduced the available area parallel to the surface, developing the so-called "torturous path effect" and further improving the gas barrier properties.

Homogenous and compact micrometric chitosan-based nanocomposite coatings, containing graphene oxide and crosslinked with PEGDE, were deposited using Ultrasonic Spray. The study of coating thickness and GO loading allowed to observe a minimum point in terms of oxygen and carbon dioxide permeability, with an improvement in CO_2 barrier properties significantly higher than that related to oxygen, suggesting the use of these coatings when permselectivity is needed. The improvement in gas permeability was correlated to the formation of highly oriented morphology of GO nanoplates and compact, densely packed coating layers. Furthermore, the mechanical characterization revealed an effective adhesion of the coatings to the polybutylene succinate films and improved mechanical and scratch resistance thanks to the addition of GO nanofillers.

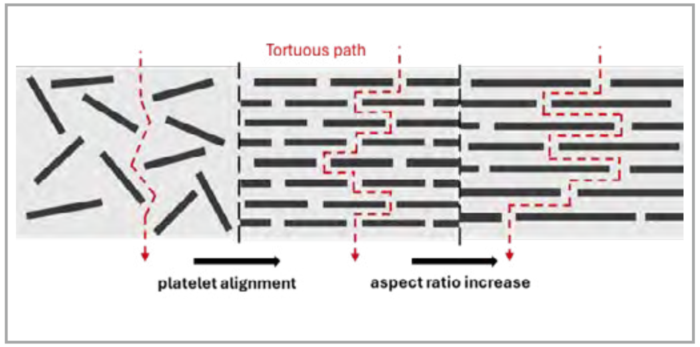

Fig.1 - Effect of nanoplatelets orientation and aspect ratio on gas diffusion path through nanocomposite materials.

To decrease the gas barrier even under high humidity (as high as 50%) and improve the water barrier of sustainable substrates, three approaches were assessed for modifying the chitosan/GO nanocomposite were compared such as i) combining GO with cellulose nanocrystals (CNC), ii) generating a borate-crosslinking network, and iii) functionalizing the coating surface. The borate crosslinking mechanism involved the boric ions' reaction with hydroxyl groups of chitosan, CNC, and GO, increasing the water resistance of the coating formulation.

By exploiting the synergistic effect of CNC nanofibers and the GO nanoplatelets via their dispersion in the chitosan matrix or combining them in a surface barrier layer, the oxygen permeability was reduced by almost 3 orders of magnitude at 0% RH, and by one order of magnitude at 50% RH. Moreover, chemical vapor deposition of triethoxymethyl silane was used as a post-deposition treatment to functionalize cellulose nanocrystals Despite the hydrophilic nature of the materials used, the realized coating systems provided also good water barrier properties to the substrate.

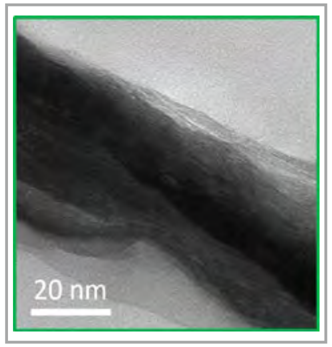

Fig.2 - TEM image of produced chitosan/clay platelets LbL coatings.

Chitosan nanocoatings were realized via the Layer-by-Layer technique to further improve gas barrier properties at high humidity. Furthermore, the selected coating design, in which chitosan layers are alternated with highly oriented graphene oxide and montmorillonite layers, allowed a greater nanoplatelet loading and density if compared to directly embedding the nanoplatelets in the polymer matrix, as well as with systems where only one kind of platelet is alternated with chitosan.

The obtained 123 nm thick nanocomposite coating reduces the oxygen permeability by two orders of magnitude, both in dry and high humidity conditions. The high oxygen permeability and its low variation with increasing were related to the higher content of highly oriented and tightly packed nanoplatelets in the multilayer assembly observed by TEM analysis (Fig. 2). These properties are particularly important for chitosan-based coatings, as one of the key issues limiting their use is high moisture sensitivity.

Lastly, an ionically crosslinked polyelectrolyte complex of chitosan and poly(acrylic acid) was developed to fabricate in two simple steps a high gas barrier coating under different humidity regimes. The pH manipulation allowed to obtain a homogeneous solution of the two polymers, and their complexation through the buffer-curing step after the solution deposition. Cohesive energy density was maximized by studying the chemical structure with different polymer ratio and by boosting interpolymer ionic interactions. The 1.9 μm thick polymer complex coating significantly decreases the oxygen permeability of the PET film, both in dry conditions and high humidity (90% RH), without affecting the PET film transparency.

This study provides important insight to understand better the interaction of chitosan with 2D nanomaterials and their effect on gas and water properties, as well as the potentialities of different manufacturing processes, which could be beneficial for various packaging applications.

RUBBER COMPOUNDS FOR HYDROGEN APPLICATIONS: STRUCTURE-PROPERTIES CORRELATION IN THE STUDY OF THEIR FRACTURE BEHAVIOUR

Isabella Denora - Supervisor: Claudia Marano

Hydrogen is currently considered a promising energy vector to be used in order to reduce carbon emissions and slow down climate change. This PhD thesis was developed in the context of the COMET module Polymers4Hydrogen, which was a project related to the study of polymeric materials to be used in the hydrogen infrastructure. In this project, an interdisciplinary consortium of scientific and company partners was involved, among which there is Polytechnic of Milan. The PhD research was focused on the study of fracture behaviour of filled elastomers, since within the gas infrastructure these materials are used in products such as O-rings, seals, gaskets and hoses. These components could be subjected to harsh conditions of temperature and pressure. Moreover, in the case of high-pressure cycles, they could fail due to the so-called rapid gas decompression (RGD), which is responsible of the formation of irreversible damages in the material.

In this research project, the study of the mechanical behaviour of 13 rubber compounds, which differ in the chemical composition (type of rubber matrix, nature and content of filler, curing system and plasticizing additives) and have been designed by project partners for the application in the hydrogen infrastructure, was conducted. The tensile response and the fracture behaviour of the materials have been analysed focusing on structure-properties correlations. The dissipative behaviour of the materials as a function of the applied strain has also been investigated. As regards the study of material fracture behaviour, a fracture mechanics approach in quasi-static conditions and in mode I has been adopted. Fracture tests on notched specimens have been conducted in pure shear deformation conditions for all the materials. Both the crack initiation and the onset of unstable crack propagation were investigated. The fracture toughness of the materials was compared with high-rate fracture tests performed by project partners. Moreover, the obtained material fracture toughness was also compared with the RGD resistance, obtained from technological tests performed on O-rings by project partners. This type of tests is widely adopted in the industries to rank the materials according to their suitability to be used in high-pressure gas applications. However, the comparison between RGD and fracture tests is a discussed topic between the academia and the companies. Nowadays, a standard procedure for quasi-static fracture tests has not been defined yet: different testing procedures and several energy-based fracture mechanics parameters to express the material fracture toughness are reported in literature. For this purpose, a large part of this thesis concerns an in-depth study on the evaluation of fracture toughness for filled rubber compounds. Fracture tests in different loading conditions (besides the pure shear one) were performed and the energy-based parameters J-integral and tearing energy, T, were evaluated at crack onset by using analytical formulas proposed in literature or by exploiting the finite element analysis. Global and local approaches have been used in the evaluation of fracture toughness. More in details, as regards the adopted testing conditions, quasi-static fracture tests also in uniaxial (on single edge notched in tension, SENT, specimens) and equibiaxial tension mode have been considered. For pure shear tests, J-integral and tearing energy have been analytically obtained for some of the investigated filled elastomers. A more in-depth study of the evaluation of fracture toughness was limited to just two materials that differ in the type and amount of filler and in their mechanical response (one is significantly less stiff and reaches higher deformations at break than the other one). For SENT specimens, the tearing energy has been obtained through an analytical formula. Finite elements analysis has been used to calculate J-integral at crack onset in equibiaxial tensile conditions, since an analytical solution is not available for this loading condition. Finite elements analysis has been used also for J-integral evaluation in SENT specimens (which would have required a multi-specimen testing) and for pure shear specimens (in order to validate the procedure). Mechanical tests in three different loading conditions (uniaxial and equibiaxial tension and pure shear deformation conditions) have been also performed, with the aim to define constitutive equations to be used in finite elements simulations. Validation of material constitutive equations has been also performed.

With the purpose of using these materials in components of the hydrogen infrastructure, the effects on the material mechanical behaviour of temperature, gas pressure and hydrogen exposure were analysed. For this purpose, the effect of temperature has been evaluated on the stress-strain and fracture behaviour of two rubber compounds, by performing tests at different temperatures. Moreover, in order to evaluate the effects of pressurized hydrogen on the material fracture behaviour, tests both in air after hydrogen exposure and under pressurized hydrogen were performed on other two rubber compounds. The fracture tests were performed by using a mechanical testing machine assembled with an autoclave for gas exposure, available at Pprime Institut in Poitiers (FR). Before performing tests, the gas saturation of the specimens was assured. With the aim to decouple the effects of gas pressure and hydrogen permeation within the material, also tests under pressurized nitrogen were conducted, since nitrogen permeability is expected to be significantly lower than the hydrogen one. Moreover, tests performed in air were used for comparison.

The elastomers used in real applications are composed by a rubber matrix and reinforcing nanometric filler particles, which improve their mechanical behaviour and are also responsible of their dissipative behaviour and of a stretch-induced softening. It is well-known that, if stretched, filled elastomers result to soften and this effect is usually recalled to as "Mullins effect". Moreover, it is reported in literature that the softened material can recover the original material response after applying a proper thermal treatment. Since rubber products in real applications are usually subjected to cyclic loading, also for the materials studied in this thesis, to be used in hydrogen infrastructure, the effect of mechanical softening was evaluated. In literature works, this phenomenon is usually evaluated just in uniaxial tensile conditions. In this thesis, how the mechanical softening affects also the fracture response has been evaluated. The fracture behaviour of softened material was also compared before and after an applied thermal treatment.

The research work was performed within the COMET-project "Polymers4Hydrogen" (project-no.: 21647053) at Politecnico di Milano within the framework of the COMET-program of the Federal Ministry for Climate, Action, Environment, Energy, Mobility, Innovation and Technology and the Federal Ministry for Digital and Economic Affairs, Austria with contributions by Polymer Competence Center Leoben (PCCL), Montanuniversität Leoben (Department Polymer Engineering and Science, Chair of Chemistry of Polymeric Materials, Chair of Materials Science and Testing of Polymers), Technical University of Munich, Tampere University of Technology, Bundesanstalt für Materialforschung und -prüfung (BAM) and Arlanxeo Deutschland GmbH, ContiTech Rubber Industrial Kft., Peak Technology GmbH, SKF Sealing Solutions Austria GmbH, Faurecia.

PRODUCTION OF NEW MATERIALS FOR THE VALORIZATION OF THE AGRO-RESIDUAL BIOMASS OF THE CHESTNUT PRODUCTION CHAIN (CHESTMAT)

Marianna Guagliano - Supervisor: Cinzia Cristiani

This PhD thesis aims to valorize agro-residual waste, in particular of the chestnut production chain. The study has been focused on the application of biochar, i.e., the by-product of the thermochemical gasification or pyrolysis of the mentioned waste, in different fields of application. Indeed, the valorisation of the agro-residual biomass of the chestnut processing industry, is in accordance with the policies of the European Commission "more value, less impact, better alternatives" and meet some of the 17 Sustainable Development Goals (SDGs), namely SDG13 (Climate action), SDG7 (Affordable and clean energy), SDG6 (Clean Water and Sanitization), SDG3 (Good Health and well-being), SDG12 (Responsible consumption and production), adopted by all United Nations Member States.
For this purpose, different types of biochar were considered: biochar generated by pyrolysis or gasification of the chestnut's residual biomass, produced at the BEELab, (Università di Modena e Reggio Emilia, Italy), as well as commercial biochar, obtained by other agro-residual biomasses. All the materials were extensively characterized by several techniques, and in view of their textural, morphological and chemico-physical characteristics, were tested in different fields of application, namely: 1) as carriers of bioactive molecules for improved feed for animal nutrition, 2) as sorbents for capture of inorganic and organic pollutants, and 3) as supports for the development of biochar-based photocatalysts.
In feed application, chestnut biochar and vine pruning biochar have been tested as carriers of lysozyme, this last chosen as representative of the bioactive molecules' category. This approach, may protect the biomolecule both by the action of the typical low pH of the stomach, as well as by the action of the hydrolytic enzymes, ensuring an efficient biomolecule release in the intestine.
The loading of lysozyme on the carrier was performed by a simple, green and cost-effective solid/liquid adsorption process performed at room temperature and atmospheric pressure. In the adopted experimental conditions, the lysozyme-biochar interaction occurs via the electrostatic attraction between the negatively charged surface of the carriers, and the positively charged lysozyme. Simulating the pH condition of the gastrointestinal environment, a larger lysozyme release in the intestinal conditions was observed, thus suggesting a potential application of these biochar in controlled release and delivery of bioactive molecules within the animal intestinal environment.
Moreover, a comparison with sorbent materials used in the common practice, such as clays or clay-based materials, conventionally added to feed for many different purposes, has been performed. Therefore, an approach similar to that applied for the biochar has been pursued. Accordingly, clay-based materials, commercial bentonite, sepiolite and zeolite (Phil 75®), and a mixture of them, commercially known as Adsorbo®, already used in the market as feed additive, were studied as potential carriers of lysozyme, by applying the same experimental condition adopted for biochar's experiments. Also in this case, the lysozyme-clays/zeolite interaction occurs via the electrostatic attraction as observed for the biochar-based systems. Differently to biochar, clays materials showed better adsorption yields, but worst release capability, being release only slightly dependent on pH. Considering that biochar is more efficient in the lysozyme release, and that it also possesses peculiar and demonstrated antioxidant and antimicrobial properties, not present in clay-based materials, it can be concluded that biochar should be the additive of choice in the development of new optimized feed formulations for the targeted delivery of natural compound alternatives to, for example, antibiotics.
Regarding wastewater treatment, six different chestnut biochar, obtained both by both gasification and by pyrolysis, were studied as sorbents for copper (Cu) and zinc (Zn), chosen as model pollutants in piglets' slurry. Specifically, the metal adsorption capacity was tested at different metals concentration, two of these corresponding to Cu and Zn found in faeces of weaned pigs, in a rearing system in northern Italy. By applying a simple and environmentally-friendly solid/liquid approach a maximum capture efficiency of 99% and 76% was reached by the chestnut biochar obtained via gasification, that emerged as the most effective sorbent for the metal's removal. Apparently, comparing the adsorption results with the other chestnut biochar, a correlation between the surface area and the adsorption capability is present.
Moreover, in the industrial wastewater treatment, the use of biochar in powder form poses several limitations, and still the use of powders appears to be one of the most problematic point in the implementation of this material. The use of powders, in fact, requires working in batches, which is detrimental when dealing with large quantities of wastewater, as common in real practice, as well as making the recovery of the sorbent material a difficult process. In order to enable the biochar use in the above in-field applications, the possibility of immobilizing the biochar powders in 3-D structured materials has been investigated in cooperation with Opigeo S.r.l. Biochar cannot be easily formed in 3-D structures, and even if the material is obtained, its mechanical strength is limited and too low to be used in this form. Therefore, on the bases of Opigeo Srl. proprietary procedure, biochar has been successfully incorporated in 3-D structured materials, using geopolymer as additives to form a granulated material. A mixed geopolymer-biochar based foam, solid material characterized by a low-density structure of 3-D network of interconnected pores, was obtained. By Micro-Computed X-ray Tomography (Micro-CT) analysis it appeared that the obtained material was characterized by biochar powders quite well incorporated into the bulk of the solid, showing both fibrous and porous features.
A geopolymer-vine pruning-biochar composite was tested in an in-column experiment for the removal of Copper, reaching a removal efficiency of about 70%. This study poses the basis for the production of a monolithic cartridge as viable alternative to packed columns for continuously decontaminating liquid effluents.
In the field of wastewater treatment, both chestnut and commercial biochar were investigated as potential support for the development of biochar-based catalysts for the removal of organic pollutants, in this case Diclofenac. The textural, morphological and physico-chemical properties of the biochar play a pivotal role in determining the performance of the system when applied in the reactions of interest.
Via a combined adsorption-photocatalysis process it was reached almost the total removal of Diclofenac in 120 minutes. The pore filling, in addition to the π–π interactions, seem to govern the adsorption of Diclofenac onto biochar, while during the photocatalytic reaction, two processes are active, adsorption and photodegradation, with the photodegradation process always more efficient in Diclofenac removal than adsorption.

GREEN LIME-BASED MORTARS FOR THE RESTORATION AND REPAIR OF BUILDINGS

Paulina Guzmàn Garcìa Lascurain - Supervisor: Sara Goidanich

Co-Supervisor: Lucia Toniolo

Lime-based mortars have been used in construction since ancient times; evidence of lime production can be traced back to 10,400 – 10,000 B.C. Its use continued uninterrupted until the invention of Portland cement, which now is the main construction material.

Recently architects and restorers are revalorizing the use of lime-based mortars due to their low environmental impact and, particularly for restoration, their compatibility with the original masonry. Nonetheless, lime-based materials still present some limitations to their widespread use, such as limited thermal isolation, long hardening times and relatively low mechanical performance.

A possible solution to overcome these challenges is the inclusion of additives in the mortar, materials that, when included in small amounts (< 1% w/w), modify/improve the physico-mechanical properties of mortars and their durability. In this context, the main objective of this research project was to develop simple and sustainable solutions to improve both the performance and testing methods of lime-based materials, thereby promoting their application in sustainable architecture and built heritage restoration. Specifically, this study focused on two types of additives: PCM and nano- & micro-cellulose.

Assessing the mechanical properties of mortars and binders is crucial for guaranteeing their performance, applicability and durability. However, most testing procedures are adaptations from the mechanical testing of cement materials, thus not fully appropriated for lime-based mortars, and requiring a significant volume of material, complicating research with limited resources. Some alternative methodologies have been developed to overcome these issues, however, none of these techniques allows to evaluate the macro-mechanical performance of pure air-lime binders, which is of particular interest when studying additives.

This thesis presents a novel methodology to assess macro-mechanical properties of pure air lime binders in a reliable and consistent manner. The method can help to determine compressive and flexural strength, providing results consistent with literature.

Furthermore, the absence of aggregates in the pure-binder specimens enables micro-scratch resistance testing with an optimal signal to noise ratio (Figure 1).

These results can be correlated also with compressive strength and can be used to evaluate both superficial and bulk properties.

Additionally, the small specimens used in this method reduce material use and waste, thus improving sustainability.

Heating/cooling systems are the principal source of environmental emissions during a building's use phase. Thus, increasing thermal efficiency of buildings is a critical challenge of today's architecture. This task is particularly complicated for historical buildings, where conventional insulation methods often pose risks to heritage structures, potentially damaging original masonries or being unfeasible altogether. As an alternative, Form Stable Phase Change Material (FS-PCM) aggregates, made of a polymeric PCM impregnated inside an inorganic porous matrix can be used in lime-mortars for building restoration, enhancing the thermal performance of the building's envelope. Yet, these FS-PCM aggregates frequently weaken the mortar's mechanical properties.

This thesis explores the use of sustainable FS-PCM aggregates in air lime mortars, aiming to i) understand the underlying reasons behind the mortar's weakening, and ii) improving the confining capacity of the FS-PCM aggregates to mitigate the problems related to their use.

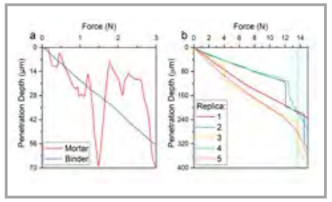

Fig.1 - a) Comparison of the scratch resistance of air lime mortar and binder, and b) average force at fracture for pure air lime binder specimens.

The performed investigation revealed that the poor confinement capacity of the polymeric PCM within the inorganic matrix provokes its dispersion into the binder phase and consequent weakening. Upon hardening of the binder, the PCM hinders crystalline interlocking between calcite crystals and, under compressive stress, acts as a *lubricant*, facilitating the crystalline *gliding* (Figure 2).

To mitigate this issue, a cost-effective coating methodology using fine powders was developed. Five coating materials were tested—calcium hydroxide, milk of lime, NHL, cocciopesto, and pozzolana. Most coatings successfully retained PCM within FS-PCM aggregates, reducing cracks and fissures in the mortar and potentially improving its overall cohesiveness.

Finally, carbonation of air lime is a slow process influenced by different factors. It has been reported that full carbonation of air-lime can take up to years to be completed. This limitation is one of the main factors hindering the current use of air lime mortars. Often, additives are employed to accelerate this process. Some examples are additives that act as external sources of CO2 or bicarbonate in the bulk to accelerate the hydroxide – carbonate conversion. On the other hand, biomimetic-inspired solutions, for instance, use organic molecules like carbohydrates to enhance both carbonation and mechanical performance. So far, despite its abundance, cellulose has yet to be explored to this purpose. Cellulose is one of the most important carbohydrate macro-molecules, present both as a natural resource or from industrial waste. Particularly, nano- and micro-cellulose fibers can be obtained from the waste upcycling of the textile, food, or agricultural industries.

Thus, the final section of this thesis investigates the potential use of nano- and micro-cellulose fibers as sustainable additives to accelerate air lime binder carbonation. Their impact was analyzed during both $Ca(OH)_2$ mineral formation and the carbonation process.

The findings revealed that fiber crystallinity significantly affects mineral morphology during $Ca(OH)_2$ formation (Figure 3), resulting in structures that carbonate more rapidly. The use of nano-cellulose revealed to form mainly smaller plate-like crystals, whereas micro-cellulose allowed to promote the formation of amorphous calcium hydroxide. Lastly, when incorporated into hydrated lime paste, these fibers also accelerate the carbonation process.

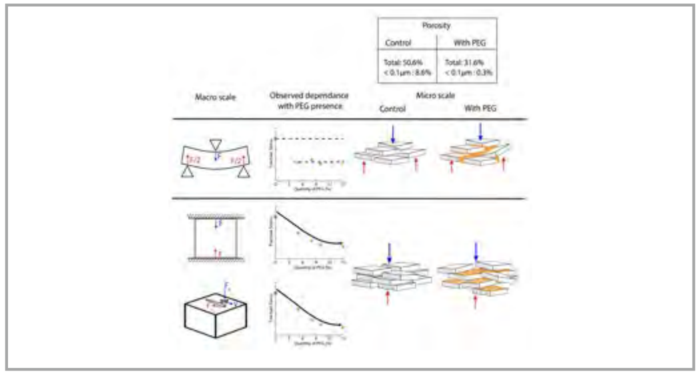

Fig.2 - Summary diagram of the proposed effect of PEG-1000 on lime-based binders and the weakening mechanism. The blue arrows represent the applied forces in the mechanical testing, whereas the red arrows indicate the material's reaction forces. Calcite crystals are represented as white rhombohedra while PEG-1000 is drawn in pale-orange. This figure is obtained from P. Guzmán García Lascurain et al. Construction and Building Materials 456 (2024) 139307.

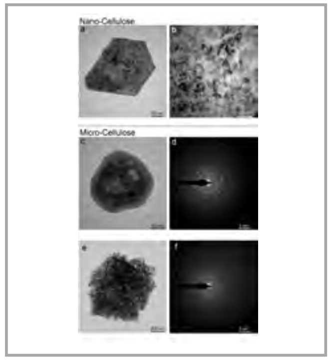

Fig.3 - Representative TEM micrographs of products obtained after slaking quicklime in the presence of (a) nano- cellulose where a hexagonal plate of portlandite is observed, and (b) high-resolution of portlandite crystal showing lattice fringes; and micro-cellulose where a single (c) and a porous aggregates (e) of amorphous calcium hydroxide (ACH) nanoparticles are observed. The SAED (d,f) correspond to the single and the aggregate ACH respectively. The SAED in (d) shows Debye rings corresponding to CaO formed after e-beam decomposition of ACH (d-spacing are indicated). The SAED in (f) shows faint haloes corresponding to ACH and arced spots corresponding to poorly crystalline portlandite (mesocrystal). This figure is obtained from P. Guzmán García Lascurain et al. Submitted to Cement and Concrete Research.

DEVELOPMENT AND CHARACTERIZATION OF GRAPHENE-BASED NANOPARTICLES FOR BIOMEDICAL APPLICATIONS

Hu Kaiyue - Supervisors: Chiara Bertarelli, Chiara Castiglioni

Graphene-based nanoparticles (GNPs) have been proposed as promising materials in drug and gene delivery. The π-conjugated network of condensed six carbon atoms rings is a unique structure that can offer a large loading capability to a variety of fluorescent probes and drugs. Currently, the majority of studies have focused on graphene oxide (GO) and reduced graphene oxide (rGO). However, since strong acids and oxidizing components are needed for the preparation of GO, the processes for GNPs synthesis from GO can be harsh and hazardous, and it requires purification procedures. An environment-friendly method for production of GNPs with lowest toxicity needs to be explored. Moreover, the chemical modification of graphene can allow the conjugation with targeting cells and achieve the targeted delivery of the drug. Therefore, the goal requires a careful control over GNPs size and defects and a suitable functionalization of the particles, in the perspective of their use as drug carriers in a biological environment. These nanosheets could act as "rafts", featuring the anti-cancer drug attached on the basal plane and functional groups grafted around the edges, that would allow the whole structure to travel in the biological environment (Fig. 1).

We developed a safe and reliable protocol for preparing graphene nanoparticles (GNPs) from pure graphite, with a good control over size and defects, by means of ball-milling and liquid-phase exfoliation methods. Two specific GNP samples in form of stable aqueous dispersions, referred to as TOP60 and BOTTOM60, were focused on for detail study. A thorough characterization showed that we can obtain GNPs with small size (average lateral sizes <L> in the range 100 – 200 nm, formed by few, <N> = 1-10 stacked layers), carrying carboxyl functional groups on the edges. The observed UV-vis spectra present a strong absorption feature peaking at about 264 nm, which is assigned to a strong intra-band transition, characteristic of well-exfoliated graphene NPs (Fig. 2). Studies concerning GNPs preparation by means of physical procedures showed that oxidation of GNPs can occur spontaneously during milling. As shown by the spectra displayed, a weak but detectable band at about 1700 cm^{-1}, which can be assigned to C=O stretching appears in the IR spectrum. BOTTOM60 shows bands overall stronger and a higher intensity than TOP60. The presence of these functional groups is of interest in the perspective of further functionalization aimed at improving their targeting ability and their compatibility with a biological environment. Very importantly, the Raman pattern indicates that the small graphene layers mainly maintain their integrity, thus suggesting that such functional groups are grafted on the edges of the graphene sheets.

In Fig. 2, the spectrum of the ROD graphite sample is dominated by the G band. The D band has a very low intensity. The appearance of a strong D band in the TOP60/BOTTOM60 spectrum, with a peak intensity clearly exceeding the G line, indicates a remarkable increase of the disorder (edges formation) due to the breaks of graphite crystals into smaller fragments. TOP60 and BOTTOM60 nanoparticles show quasi-superimposable Raman spectra, with strong D and D' lines as expected for small size (small <L>) particles. Moreover, we observe several transitions involving two vibrational quanta in addition to the 2D line, in particular of the strong G+D combination band, which is a typical molecular feature observed in the Raman spectra of polycyclic aromatic hydrocarbons, PAHs. It can be taken as the evidence that we are approaching the molecular regime. A more detailed description can be reached only by means of a quantitative analysis, based on curve fitting of Raman spectra. Figure 2 shows the graphical result of the curve fitting for two representative examples, namely the Raman spectra (λ_{exc} = 633 nm) of the ROD sample, which maintains the features of crystalline graphite, and the TOP60, which shows remarkable changes in the spectrum, because of the reduced sizes of the GNPs and of their peculiar morphology.

Two different kind of GNP-molecule conjugates have been prepared to explore covalent and non-covalent functionalization of our GNPs: the covalent bonding with a peptide aiming at targeting cancerous cells and the non-covalent bonding via π-π interaction with a small molecule, mimicking the interaction between GNP and a drug which should be loaded and reversibly released. The research entails: i) Selection the cell permeable peptide (CPP) poly-arginine-11 (R11) to covalently graft onto GNPs. Target disease: bladder cancer. ii) The study of GNPs loading and release of drugs by using a simplified model of 1-pyrenecarboxylic acid (PyCA). After a thorough structural characterization, stable water dispersions of GNPs featuring COOH groups have been subjected to covalent functionalization with the cell permeable peptide (CPP) poly-arginine-11 (R11). R11@GNPs conjugates are characterized with IR spectroscopy which prove the effectiveness of the coupling (Fig. 3). The difference spectrum (Figure 3a) clearly shows all the main absorption features of R11, thus proving that the peptide is present in the conjugate. To better highlight PyCA contributions in the IR spectrum of the conjugated, we carried out the subtraction between the spectrum of PyCA@B60 and that of B60 (Fig. 3b). Three new peaks, at 846, 757 and 709 cm^{-1} in the spectra of PyCA@B60 (Figure 3b) can be immediately recognized as due to characteristic IR transitions of PyCA, and prove that PyCA is loaded on GNPs. The evidences of the formation of π-π complexes between GNPs and 1-pyrene-carboxylic acid (PyCA@GNP) provide a first test of the drug loading capability of GNPs and of its thermal reversibility. The study of the fluorescence response of PyCA@GNPs conjugates allowed proving the upload of PyCA, which is revealed by fluorescence quenching because of π-π interactions: the fluorescence intensity of PyCA@B60 sample in water is remarkably lower than in the case of PyCA in water. Moreover, by monitoring over time the fluorescence signal of PyCA@GNPs samples heated at 40 °C for 55 min, we demonstrated that it is possible to trigger the drug release with a thermal input at a rather low temperature.

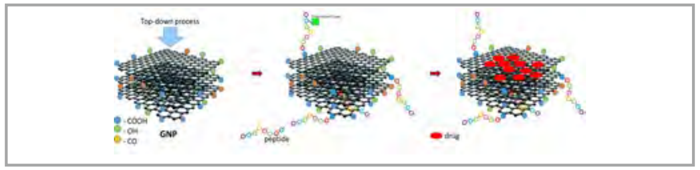

Fig.1 - Designing graphene nanoparticles as platforms for drug-delivery systems. The flexibility of the design enables researchers to tailor nanoparticle specifically to increase their biocompatibility and/or to impart targeting properties, e.g. by grafting a peptide.

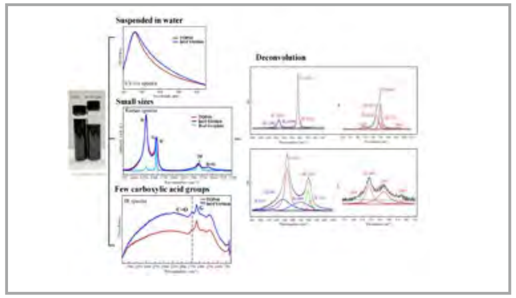

Fig.2 - Structure assessment of tailored TOP60 and BOTTOM60 GNPs by complementary spectroscopic techniques (UV-vis absorption, Raman scattering and FTIR absorption). The results of curve fitting (deconvolution) of the Raman spectra (excitation at 633 nm) of pristine synthetic graphite rod sample and of TOP60. As the particle size decreases, the second order combination peaks D+(G,D') appear.

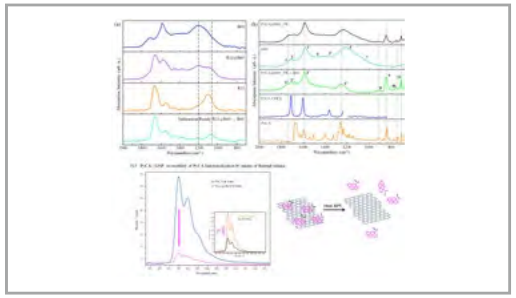

Fig.3 - The spectra of the functionalized GNPs. (a) FTIR spectra of BOTTOM60 (B60), R11@B60, R11 and the difference spectrum obtained by subtraction of the spectrum of B60 from that of the conjugate R11@B60. (b) From the top to the bottom: FTIR spectrum of PyCA@B60 conjugates, FTIR spectrum of B60 GNPs, and the subtraction result (PyCA@B60 – B60); FTIR spectrum of PyCA in CHCl3 solution (CHCl3 non compensated bands have been removed for clarity) and as microcrystalline powder. (c) Fluorescence spectra of water dispersions of PyCA@B60 (red line) and PyCA in water solution (dark blue line). The PyCA concentration is the same for the two samples. In the inset fluorescence spectra of PyCA@B60 conjugates before heating and after local heating at T = 40 °C for 55 min.

PRINTING OF DIELECTRIC AND CONDUCTIVE POLYMERS FOR ELECTRONIC APPLICATIONS

Filippo Iervolino - Supervisor: Marinella Levi

This thesis delves into the investigation of substituting conventional polymeric material deposition methods, such as spin-coating, with Additive Manufacturing (AM) techniques.

The inherent advantages of AM over traditional methods, including reduced material wastage, the ability to fabricate intricate patterns in a single step, and the flexibility to adjust process parameters for tailored geometrical features, are meticulously elucidated and demonstrated.

Two primary applications are meticulously explored: the Inkjet (IJP) and Aerosol Jet (AJP) printing of Benzocyclobutene (BCB), and the development, printing, and characterization of conductive polymer-based materials incorporating Carbon Nanotubes (CNTs).

In the case of BCB, both IJP and AJP techniques are successfully employed. With IJP, the study on the printability of the inks showed that an appropriate choice of the ejection speed is fundamental to achieve good printing quality. A too low speed might result in incomplete ejection, while a too high speed led to the formation of satellite drops. The interaction with the substrate was evaluated to understand when the formation of coffee ring effect occurred. A real bonding pattern was printed with the BCB ink to show the feasibility of printing complex shapes. The results showed that it was possible to print features with dimensions down to 130 µm (Figure 1).

The roman numbers represent the numbering of the measured distances. It is possible to observe how the printed patterns respect the dimensions of the design.

AJP, instead, showcased a superior versatility and printing speed despite encountering certain defects such as poor edge definition and overspray. The effect of the printing parameters was thoroughly characterized to select the ideal processing parameter to print at relatively high speed, i.e., 10 mm s-1 while keeping a homogenous line morphology. The print of complex patterns proved the possibilities of using AJP when complex geometries are present, such as interdigitated lines and cavities. Furthermore, it was shown that complex geometry with features of ~60 µm are printable. However, in all the prints overspray was always present even though its extent was limited. The in-depth analysis of the printing parameters allowed the identification of the conditions that minimized the printing time while maintaining a good print quality, allowing us to cover relatively large substrates (3 cm x 3 cm). The morphological characterization showed the good quality of the bonding process, since no defects were visible. Moreover, the die shear test highlighted that the shear strength of BCB deposited with AJP is comparable with BCB deposited by spin-coating (Figure 2).

The investigation further extends to the development and printing of conductive polymer-based materials containing CNTs, with Stereolithography (SL) technology being employed due to the material's relatively high viscosity and UV-curable behavior. Rheological analyses as well as photo calorimetric (UV-DSC) and photosensitivity tests.

Rheological and UV-DSC analyses showed that the increase of MWCNTs concentration led to a rise in the resin viscosity and a decrease in the resin conversion degree, due to the contribution of MWCNTs in the UV-vis light absorption. Rheological tests also indicated the presence of an optimal concentration of MWCNTs in the free radical resin system (0.25% wt.) that should ensure a higher flowability and a more homogeneous recoating of the resin inside the tank during printing. A 3D printing strategy was defined for these photo-curable resins on the basis of photo-DSC and photosensitivity analyses, thus overcoming the detrimental effect of UV-vis light absorption induced by MWCNTs.

Resistivity tests showed that the free radical system provided a higher electrical conductivity than the cationic system. Moreover, the introduction of 0.25% wt. of MWCNTs resulted in an average conductivity value of 10-4 S cm-1 and a higher value of 4.2 x 10-3 S cm-1 was attained by further increasing filler concentrations to 0.75% wt., as expected according to the percolation theory. The 3D printing of the nanocomposite based on the free radical system and loaded with 0.25% wt. of MWCNTs was successfully demonstrated and the electrical conductivity of the printed MWCNTs samples was equal to 6 x 10-4 S cm-1, which is seven orders of magnitude than that of unfilled ones. The results of this study show that MWCNTs-based photo-resins have enormous potential as 3D printable materials via SL, providing good dimensional accuracy of complex 3D printed geometries and high electrical conductivity straightforwardly without requiring time-consuming and complicated processes or costly equipment (Figure 3).

However, while the feasibility and potential of employing AM in polymeric electronic applications are evident, numerous challenges and limitations persist.

Scaling up to industrial levels necessitates advancements in hardware infrastructure, including the development of multiple printhead systems to rival current industrial machines. Moreover, stringent material restrictions inherent in certain AM technologies constrain material options, posing challenges in adapting to specific applications. Additionally, the scarcity of literature on AM of dielectric polymers for electronic applications presents hurdles in ink development, with limited information necessitating a trial-and-error approach, which can be both time-consuming and inefficient.

Addressing these challenges requires a concerted effort to expand the body of literature on AM techniques and materials, facilitating faster and more effective material and application development. By fostering a deeper understanding of the intricacies of AM processes and materials, researchers can unlock the full potential of AM in polymeric electronic applications, paving the way for transformative advancements in the field.

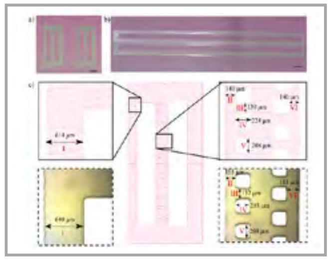

Fig.1 - a-b) Microscopic images of the bonding pattern measuring a) 5.6 mm x 11.5 mm and b) 5.6 mm x 45.5 mm printed with BCB/MES ink. Scale bars measure 2 mm. c) Schematics of the boding pattern and two details and comparison with the actual pattern printed with BCB/MES ink.

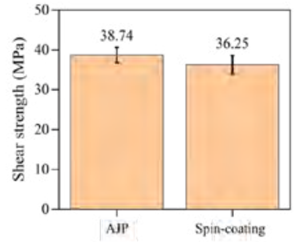

Fig.2 - Shear strength values obtained for bonded Si wafer using AJP and spin-coating to deposit BCB.

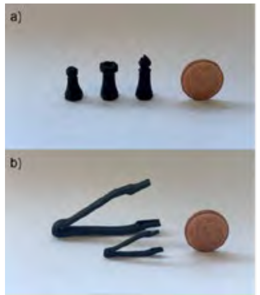

Fig.3 - (a) Optical photograph of SL 3D printed chess pieces and (b) tweezers with different dimensions.

FIBRE-BASED PACKAGING AND DISPERSION COATINGS: INVESTIGATION ON THE BARRIER, CONVERTING, RECYCLABILITY, AND SENSORIAL PROPERTIES

Andrea Marinelli - Supervisor: Barbara Del Curto

Conventional coating technologies for fibre-based food packaging are extrusion coating and lamination.

Recently, packaging converters raised their interest towards dispersion coatings (DCs). DCs are waterborne colloidal dispersions of polymer particles, pigments, and additives such as co-binders, defoamers, and dispersants.

DCs were recently rediscovered to reduce the non-cellulosic content of fibre-based packaging.

As against extrusion coating and lamination films, DCs allow lower dry coat grammages and broader application technologies, including conventional industrial printing technologies due to their rheology, making them similar to inks from the processing perspective.

Recent research focused on developing biobased formulations; however, such solutions usually come at a higher cost, feature lower barrier properties, and are characterised by limited market availability.

Aiming to easy industry adoption, this study tested highly crosslinked experimental styrene-butadiene formulations filled with platy kaolin and talc, along with commercially available products to represent the current state-of-the-art. Aiming to a broad investigation, the study assessed barrier, converting, and recyclability performance, also including the role of the end consumer. Multiple latex-filler ratios (20 % to 60 % on a dry weight basis) formulations were investigated to address the effect of filler content. Coatings were single- or double-layer rod-coated on fibre-based substrates, i.e., both paper and paperboard (Fig. 1). The dry coating grammage ranged ~10–15 g/m^2, whereas the grammage of the substrates ranged from 125–350 g/m^2 (the substrates were calendared, top-coated, or sized).

Barrier properties included water, moisture, and grease barriers. Due to the nature of kaolin, water barrier properties were limited, yet moisture and grease barrier properties were remarkable.

Formulations filled with 40 % on a weight basis of kaolin, i.e., H39K 60, achieved optimal results, especially considering moisture and grease barrier. Among the parameters that affected the results, the substrate had a great impact, having smoother substrates showing lower absorption and permeation; this is typically associated with coating thickness homogeneity and continuity. The commercial grade showing the highest performance achieved <1 g/m^2 and ~20 $g/(m^2 \bullet day)$ for water and moisture barrier, respectively, similar to PET extrusion-coated substrates.

Achieving good barrier properties is, however, a part of the solution to a more complex problem. Indeed, the packaging needs to be converted to achieve its final shape. Therefore, the processing properties explored in this study included heat-sealing, fold cracking, creasing, and tray forming. The heat-seal processing window was proportional to the latex glass transition temperature (T_g).

Increasing filler content reduced the heat-seal ability of experimental coating. Additionally, seal time and temperature seemed to have a significant effect compared to pressure in ensuring maximum seal forces. Typical minimum seal temperatures were around 90 °C higher than the latex Tg. DCs heat-sealed at temperatures as low as 80 °C, as compared to 160 °C for PET extrusion-coated substrates.

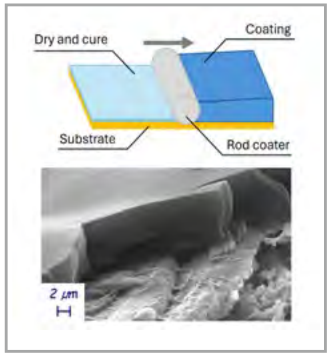

Fig.1 - Rod coating method and SEM micrograph of a coated substrate cross-section.

Substrate anisotropy made fold cracking more difficult along the machine direction - producing a cracked area up to 60 % lower than along the cross-direction.

The outside orientation of the coating does the opposite due to the tensile stresses involved, further eased by increasing kaolin content; however, the latex softness reduced the damage extent. Paperboard creasing at 0.08–0.12 mm residual crease depths provided intact coatings except for the highest latex Tg grade ($Tg>T_{amb}$). The latex Tg ≅ 0 °C used in the experimental coatings resisted despite the high kaolin content. Tray forming (Fig. 2) at industrial parameters required low (4.5–5.0 %) blank humidity content. Decreased speed and reduced blank holding force processing parameters diminished coating defects yet negatively impacted the production rate and flank smoothness.

Fig.2 - Press-forming process and paperboard trays.

The visual and tactile sensorial properties of multiple coated paper samples reinforced the crucial role of aesthetic properties in influencing end consumers' sorting actions.

Matte and rough coatings helped paper-like material perception.

The results suggest broader industry aesthetic-properties consideration in the development phase, as well as further investigation within the topic.

Recycling tests for both UNI 11743:2019 and Cepi v2 showed different results.

Macrostickies represented the main limitation according to the Italian recyclability evaluation system, whereas the samples obtained among the highest achievable scores for the European evaluation method. Such behaviour was somehow expected: the tested coatings were heat-sealable at low temperatures. Despite higher fragmentation, a higher kaolin content reduced the macrostickies' equivalent area.

The fibre-based packaging industry may currently exploit dispersion coatings for short-term food-contact applications, aiming to reduce the non-cellulosic content of the packaging. Their use should not require high-barrier performance. In addition to the distinctive barrier properties, the experimentation returned promising results on converting properties. Dispersion-coated substrates withstood moderate stresses induced by folding and creasing; however, the severe stresses involved in paperboard tray forming showed that DCs may not currently compete against more than two-fold thick extrusion-coated counterparts.

Besides, heat-sealing of DCs ensures energy savings at the converter. For the whole food packaging sector, regardless of the coating technology, the main threats and opportunities are currently represented by the evolution of national and international regulations.

REAL-TIME MONITORING OF MICROBIAL INDUCED CORROSION PROCESSES IN SOIL AND WATER

Luca Murachelli - Supervisor: Antonello Vicenzo

Microbial induced corrosion (MIC) is of critical concern for the integrity and longevity of both underground and submerged structures, as well as for facilities involved in the transportation of microbiologically rich fluids. Proper monitoring of microbial-related processes is essential for predicting and mitigating the onset of microbially related corrosion processes. This thesis highlights and emphasizes the significance of accurate and timely monitoring of microbial correlated electrode processes in order to prevent possible detrimental effects. A novel setup for the targeted detection of microbial activity in soil is proposed and validated for six different materials (iron, copper, brass, iron, carbon steel and stainless steel), specifically in a real clayey matrix (Il Bosco del Molino, Parma - Italy). The proposed innovative sensor configuration (Figure 1) embeds a three electrodes setup, with Titanium counter electrode, Zinc reference electrode and interchangeable working electrode, temperature probe and watering system. The biofilm probe, set between the titanium and the zinc electrodes, functions as a galvanic sensor for microbial cathodic activity and the obtained values are compared to common soil parameters including conductivity, redox potential and material-specific parameters like free corrosion potential and polarization resistance. This setup has demonstrated the capability to independently identify the onset of microbial corrosion without the need for additional monitoring of other parameters (Figure 2). Furthermore, a second sensor is designed as spectroelectrochemical flow cell, is introduced for real-time laboratory-scale monitoring of microbial corrosion processes. Design is supported by computational fluid dynamics simulations in order to ensure optimal laminar flow at electrodes surface and in spectroscopic path region. This advanced cell configuration allows for multiple simultaneous measurements, including biofilm galvanic probe metrics, redox potential, conductivity, and diffused reflectance spectroscopy. In-lab testing using effluent water allows for comparative confirmation of the ability of Biox potential metrics to anticipate the onset of microbial correlated corrosion processes, with respect to the other monitored metrics: diffused reflectance intensity and polarization resistance values (Figure 3). Both sensor systems are validated through corrosion assessments based on polarization resistance measurements and effective biofilm formation via diffused reflectance measurements (when applicable). The proposed sensors open the possibility to more extensive understanding of microbial correlated electrodes processes paving the way to more reliable metrics for corrosion prediction and mitigation. As appendix, the proposed flow cell is also adapted for concentration measurements of dissolved ozone in water and real time monitoring of produced ozone via electrochemical ozone generation process on doped tin oxide electrode. A suitable process for single process deposition and doping of tin oxide layers onto titanium is proposed and based on low frequency unipolar pulsed Plasma Electrolytic Oxidation in low concentration alkaline electrolyte using a catholyte-anolyte separated cell. An optical sensor for dissolved ozone measurement is also proposed, designed and validated using low flux UV-C radiation from light emitting diodes at 275nm.

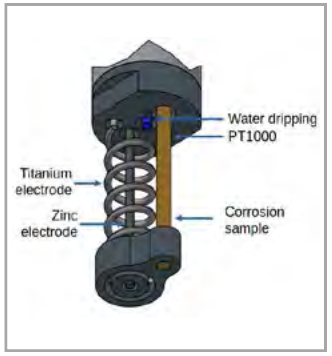

Fig.1 - Proposed probe head design for Microbial Induced Corrosion monitoring, embedding temperature sensor, three electrodes setup and watering system.

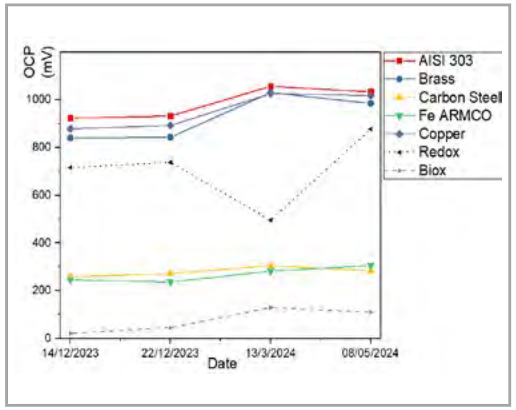

Fig.2 - Trends for Polarization Resistance, Redox and Biox potentials. Measurements are taken in 6 months span in clayey soil at Il Bosco del Molino (Parma - Italy). The correlation of Biox potential with corrosion assessment is strict: any increase in Biox potential reflects the ongoing corrosion process increase, highlighted by a decrease of polarization resistance values. The trend applies to the tested materials which are in accordance with the expected behavior. Redox potential trend alone cannot be correctly correlated to corrosion process.

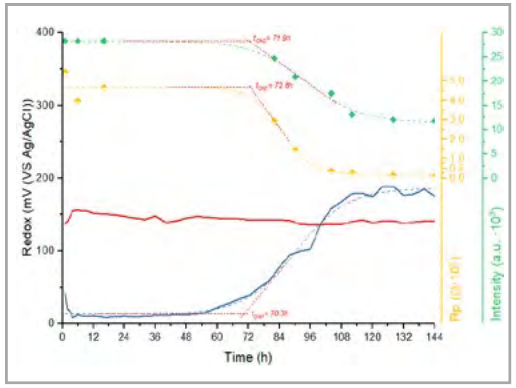

Fig.3 - Trends for polarization resistance, BIOX potential and redox potential. Parameters are measured during in-lab testing of spectroelectrochemical flow cell using effluent water recirculating system, to assess quantity's ability to anticipate corrosion process onset. BIOX potential is in accordance to corrosion assessment by polarization resistance measurements: this highlights the ability of this probe to detect microbial activity at polarizable metallic surfaces, which anticipate microbial corrosion processes occurrence. Diffuse reflectance spectra are in accordance with the other parameters. Diffuse reflectance intensities are taken at 450nm.

DEVELOPMENT OF INNOVATIVE PHOTOANODES AND PHOTOELECTROCATALYTIC TREATMENT OF PFAS-CONTAINING GROUNDWATERS/LIQUID WASTES

Alessandro Pietro Tucci - Supervisor: Silvia Franz

Tutor: Massimiliano Bestetti

This Ph.D. thesis presents and discusses with a multidisciplinary approach the results of a 3 years research activity on photoelectrocatalysis, ranging from Materials Science to Materials and Chemical Engineering. The aim of the thesis is to synthesize and characterize new TiO_2-based photoanodes for photoelectrocatalytic (PEC) applications, and at the same time to demonstrate the potential of photoelectrocatalysis in the water treatment field.

A simple and scalable synthesis method was prioritized, leading to the selection of Plasma Electrolytic Oxidation (PEO), an industrial surface treatment technique recently proposed for producing large area photoelectrodes. Novel TiO_2 based photoanodes were synthesized by PEO under various experimental conditions and a comprehensive morphological, compositional, optical and photoelectrochemical characterization was conducted. Specifically, to tailor TiO_2 photoelectrocatalytic activity three different strategies were explored: (a) synthesis of TiO_2 by pulsed unipolar polarization; (b) doping with transition metals (Zn, Cu and Fe); (c) surface decoration with photoactive metal oxide nanoparticles (Anatase, Rutile and WO_3).

TiO_2 synthesis via pulsed unipolar PEO was conducted in 1.5 M H_2SO_4 at 150 V and 10 A, by tuning pulse frequency (100-400 Hz) and pulse duration (30-1000 ms). All TiO_2 films showed a porous and homogeneous sponge-like surface morphology, typical of PEO-produced oxides, and a crystalline phase structure consisting of a mixture of anatase and rutile phases. Morphology, thickness and crystalline composition were affected by pulse frequency and duration. The photoelectrochemical response increased by ≈ 85% under both Vis and UV irradiation with respect to TiO_2 synthetized in DC mode. Correspondingly, decolorization tests using Methylene Blue (MB) as target molecule assessed the improvement of the photocatalytic properties (+60%).

Zn-, Cu- and Fe-doped TiO_2 photoanodes were synthesized via DC PEO (150 V) in H_2SO_4 aqueous solutions containing $ZnSO_4$, $CuSO_4$ and $FeSO_4$ precursors (0.2 – 100 mM), respectively. Morphology and crystalline composition were only slightly affected by doping. The band gap energy was in the 2.85–3.07 eV range. EDS and XPS analysis confirmed Zn, Cu and Fe incorporation in TiO_2 films. Doped oxides prepared with a low concentration of the metal precursors showed monochromatic IPCE values exceeding those obtained with undoped TiO_2 by up to 24 %, best performing in the order Zn- > Cu- > Fe-doped TiO_2. Improvements in the photoelectrochemical properties were achieved under both UV (+11% for Zn-doped samples) and Vis (+13% for Cu-doped samples) irradiation. MB decolorization tests assessed the enhancement of the photocatalytic properties of the photoelectrode in Zn-doping (+100%). On the contrary, PEC degradation of 4-chlorophenol (4-CP) did not reflect the effect of doping, thus remarking the need of testing new photoelectrodes with different water contaminants in order to fully assess their catalytic activity.

TiO_2 surface decoration was performed by adding Anatase, Rutile or WO_3 nanoparticles (NPs) (0.2 – 5 g L^{-1}) to the H_2SO_4 electrolyte. Based on SEM images, nanoparticles were distributed on the TiO_2 surface and penetrated into the pores. Anatase, rutile and WO_3 crystalline phases were observed by XRD analysis, the rutile weight percentage generally increasing in presence of NPs. The photocurrent of decorated TiO_2 increased with respect to pristine material under both Vis (+7% and +20% for Rutile and WO_3 NPs, respectively) and UV (+21%, +26% and +115% for Anatase, Rutile and WO_3 NPs, respectively) irradiation. WO_3-decorated TiO_2 films showed improved photoelectrochemical properties in different media (+ 12%, + 20% and +26% under Vis irradiation in Na_2SO_4, NaOH and H_2SO_4, respectively). Degradation tests under simulated sunlight showed that the best 4-CP removal rate was achieved by using the WO_3-decorated photoelectrodes (+ 15 % with respect to Np-free TiO_2 photoelectrode).

The aim of this thesis was also to validate photoelectrocatalysis in the field of water treatment. To test the potential of this approach as Advanced Oxidation Process, a very recalcitrant class of pollutants was targeted, namely per- and polyfluoroalkyl substances (PFASs).

PFASs are a group manmade organofluoride compounds (> 10000) characterized by persistency, bioaccumulation, high mobility and toxicity. PFAS remediation by conventional strategies (biological, chemical and physico-chemical processes) has proven to be unviable. In this perspective, photoelectrocatalysis represents a very promising approach for the degradation of fluorinated derivatives and long/short-chain PFASs. PEC exploits the synergistic combination of heterogeneous photocatalysis and electrochemistry, allowing to minimize the electron-hole recombination, which usually hampers conventional photocatalysis. PEC tests were carried out using a TiO_2 mesh synthesized by PEO. The mesh was integrated into a bench-scale stainless steel reactor equipped with a tubular UV lamp working at different nominal power values ($P_1 > P_2 > P_3$). The system operated in semi-batch mode, at flow rate of 400 L h^{-1} and 4V (cell voltage). Degradation tests lasted up to 800 min (contact time) and were repeated twice.

PEC was applied to the treatment of PFASs containing groundwater collected from two wells located in the Veneto Region (Italy), where a massive contamination of the aquifer was discovered. Out of 48 monitored PFASs, 9 were detected. PEC treatment effectively oxidized both short and long chain PFASs, the degradation rate following the order: PFOA (C8)>PFHpA (C7)>PFHxA (C6)≈PFPeA (C5)>PFBA (C4) and PFOS (C8)>PFHpS (C7); the concentration of PFHxS (C6) and PFBS (C4) did not change during the tests. Overall PFAS concentration decreased by 63% (well 1) and 65% (well 2). PEC tests of PFOA solutions ([PFOA] = 1 µg L^{-1} in ultrapure water) induced the transient formation of PFHpA, followed by PFHxA, PFPeA and PFBA, confirming the reaction pathway consisting of decarboxylation followed by a stepwise losing of CF_2 units, transiently forming shorter chain intermediates.

The effect of the following parameters was evaluated: H_2O_2 or NaCl (100 ppm) additives, cell voltage (4, 6, 8 V), lamp power ($P_1 < P_2 < P_3$), flow rate (100, 400, 800 L h^{-1}), polarization mode (DC, non-faradaic periodical polarity reversal). Neither the presence of H_2O_2 nor the application of voltages above 4 V significantly affected the process efficiency. Similarly, flow rate and polarization mode had minor effects on the reaction kinetics, whereas NaCl addition strongly reduced it, suggesting that the photocatalytic sites were preferentially involved in Cl_2 evolution. Working at P_2 resulted in an increase in the overall PFAS removal with respect to P_1 (from 65% to 72%). However, the further lowering of the power (P_3) significantly decreased the overall reaction rate. Photolysis (PL), H_2O_2 assisted photolysis and photocatalysis tests were performed for comparison, but a lower performance was observed. The energy consumption of PEC and PL tests was evaluated on the basis of the Electrical Energy for Order of Magnitude (E_{EO}). E_{EO} values concerning PFOA ideal solution demonstrated that photoelectrocatalysis (E_{EO} = 36 kWh m^{-3}) outperforms most of the other advanced oxidation processes described in literature and is comparable to plasma process (E_{EO} = 28 kWh m^{-3}) and advanced reduction processes (E_{EO} = 24 kWh m^{-3}).

PEC experiments were also carried out on wastewater spiked with an aqueous film forming foam (AFFF, 5 – 10 mL/L), which mostly contains PFASs. Large quantities of PFASs were formed over time (in particular 6:2 FTS, PFHpA and PFHxA), regardless of the power of the lamp. This is most probably caused by the oxidation of untargeted PFASs to form target compounds, highlighting the need for different analytical approaches (e.g. non-target analysis, EOF or AOF detection) to fully evaluate this AOP.

ASSESSING THE LIMITS FOR OCEAN ALKALINITY ENHANCEMENT AND CO_2 REMOVAL: FROM LABORATORY TO MODELLING APPROACHES

Selene Varliero - Supervisor: Guido Raos

Research on carbon dioxide removal (CDR) technology has risen in interest within the scientific community. One promising approach for removing CO_2 from the atmosphere and store it is Ocean Alkalinity Enhancement (OAE), a set of processes designed to sequester atmospheric CO_2 while increasing ocean alkalinity to counteract ocean acidification. OAE has the potential to remove between 1 and 100 $GtCO_2$ per year and store it on the order of 10,000 years, providing long-term stability.

This thesis investigates the limitations and feasibility of OAE applications, focusing on two primary processes: Ocean Liming (OL) and Buffered Accelerated Weathering of Limestone (BAWL). The research explores general constraints applicable to all OAE techniques, as well as specific challenges associated with each process.

OL involves the direct addition of slaked lime [$Ca(OH)_2$, SL] into seawater, increasing pH and facilitating the absorption of atmospheric CO_2, ultimately converting it into stable bicarbonate ions, the stable form of inorganic carbon at seawater pH. BAWL, in contrast, is a CO_2 storage technology that utilizes an external CO_2 source combined with alkaline materials [$CaCO_3$ or $Ca(OH)_2$] to produce a solution with high alkalinity, which is then discharged in sea.

This work presents findings from four research studies—–two of which are published—– examining both experimental and modeling aspects of OL and BAWL. The primary objectives include identifying the optimal $Ca(OH)_2$ dosage in OL to investigate the short-term chemical processes following pH and alkalinity increases, as well as assessing the long-term stability of CO_2 storage in BAWL.

Experimental OL studies demonstrated its effectiveness in enhancing seawater alkalinity and sequestering atmospheric CO2. The rapid dissolution of slaked lime, followed by CO2 absorption, confirmed the efficiency of the process. However, the associated pH increase could be potentially harmful to marine ecosystems and may also trigger the precipitation of CaCO3 minerals, such as aragonite, which could reduce the process efficiency. Our research identified a safe dosage range of 120 to 135 µmol/L of TA for Mediterranean seawater, effectively minimizing harmful pH spikes and preventing significant mineral precipitation. Additionally, a kinetic model for aragonite precipitation was developed, providing an initial framework for a predictive tool to manage total alkalinity levels and control mineral formation.

The research on BAWL confirmed its capability to permanently store CO_2, with experiments on a pilot plant validating the chemical stability of alkaline solutions in seawater. The results demonstrated minimal risk of precipitation or CO_2 degassing under optimal conditions with an alkalinity addition of 1000 µmol/L.

Beyond this core work, additional studies are presented that contribute to the broader development of OAE. This includes a techno-economic evaluation of BAWL, as well as a conference contribution discussing the integration of ocean acidification impacts into Life Cycle Assessment (LCA) methodologies.

Both BAWL and OL emerged as adaptable and scalable solutions for carbon removal in marine environments. Their reliance on abundant raw materials and modular infrastructure makes them viable alternatives to geological storage, when this impractical or too expensive.

These findings reinforce the potential for OAE technologies within the portfolio of climate change mitigation strategies.